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Visible Electronic Emission Spectra of
Diatomic Molecules: Analysis of the AlO (B-X)
and BI(a-X) Systems, and First Observations
of Some 11-Valence Electron Cations, SeO^+ ,
 PCl^+ , PBr^+ , and AsCl^+ .

by

Stavros Naxakis

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

at

Dalhousie University
Halifax, Nova Scotia
August, 1990



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ISBN 0-315-64559-8

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DEDICATION PAGE

To my family

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ABSTRACT

Twenty-five bands of the $B^2\Sigma - X^2\Sigma$ system of AlO with $0 \leq v' \leq 9$ and $0 \leq v'' \leq 6$ have been photographed at high resolution. The measured positions of the assigned lines of each band have been fitted by least-squares to obtain estimates of the constants (B', D', B'', D'') the band origin, and $\Delta\gamma_{v',v''}$, the difference of the upper and lower state spin-doubling constants. The parameters from individual bands have been merged to single-valued estimates, as well as to polynomial representations in $(v + 1/2)$.

New visible systems of red-degraded bands have been observed in emission from reactions of discharged helium with PCl_3 , $AsCl_3$ and $SeOCl_2$, and assigned as $^2\Pi \rightarrow X^2\Pi$ transitions of PCl^+ , $AsCl^+$ and SeO^+ . The same excitation technique with BI_3 substrate was employed for the observation of the $a^3\Pi(0^+,1) \rightarrow X^1\Sigma^+$ band systems of BI; the $a(1) \rightarrow X$ system was observed for the first time. Head positions measured from photoelectrically recorded spectra have been fitted by least-squares to obtain estimates of the vibrational constants of the states involved in the transitions. In addition, eight bands of the $a(0^+) \rightarrow X$ system and two bands of the $a(1) \rightarrow X$ system of ^{11}BI have been rotationally analyzed. Three bands (0-16, 0-17, 0-18) of the $^2\Pi - X^2\Pi$ system of $P^{35}Cl^+$ have been rotationally analyzed. The determined constants include the first estimated spin-orbit coupling constants for both states. The reliability of these estimates is discussed.

Finally, the results of the reactions of discharged helium with PBr_3 , and various other substrate molecules are also discussed.

Definitions of Terms and Symbols

H	Hamiltonian Operator
σ	Standard deviation
f	Degrees of freedom
h	Planck's constant (6.626176×10^{-34} Js)
$\text{\AA}$	Angstrom (1×10^{-10} m)
μ	Reduced mass
$\mathbf{A}^T$	Transpose of matrix $\mathbf{A}$
$\mathbf{A}^{-1}$	Inverse of matrix $\mathbf{A}$
δ_{ij}	Kronecker delta (0, if $i \neq j$)
$\underline{X}$	is a vector

Acknowledgements

I wish to extend my sincerest gratitude to my professor and project supervisor, Dr. J.A. Coxon. His professional expertise and positive support throughout my Ph.D. work has made this undertaking a memorable one.

Thanks goes to Dr. A.B. Yamashita and Dr. U.K. Roychowdhury with whom I collaborated on joint projects.

I extend my thanks to Professor W.E. Jones for access to the 3.5-m spectrograph in his laboratory.

Dr. K. Brabakaran's friendship made student life in Halifax an enjoyable one.

Mr. P. Hajigeorgiou is thanked for proofreading and overlooking final preparations for submission.

Mr. J. Mueller's expertise is appreciated for the construction of the apparatus used in this work.

Thanks is also due to the graduate students, staff and faculty of the Department of Chemistry for their friendship and support.

Ms. D. Cosman, Mrs. C. Slaunwhite, and Mrs. J. Walsh are acknowledged for typing the thesis at such short notice.

A special thanks goes to Anna for her continued enthusiasm and company during those late nights in the lab.

Finally thanks is extended to Dalhousie University and NSERC for the award of Graduate Scholarships.

Chapter 1

Introduction

1.1 General Introduction

The subject matter contained in this thesis deals with the spectroscopic investigation of diatomic molecules and molecular ions. Although, a common factor of this work is that all the diatomic species were observed in emission, the methods of excitation and signal detection broadly divide this thesis into two parts.

In the first part, the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ band system of aluminum monoxide has been recorded and rotationally analyzed using photographic techniques. The excited AlO was produced by flowing trace quantities of oxygen and $AlCl_3$ through an electrodeless discharge. The analysis of the spectrum has either improved or provided the first reliable vibrational dependences of the various molecular constants of the electronic states involved. Details of this work are given in Chapter 3.

In the second part, a flowing afterglow method has been applied to reactions of helium ions and/or metastable atoms with small molecules and established as a powerful tool for observing new emissions from diatomic molecules. All these emissions have been detected photoelectrically, and are discussed in Chapters 5 through 10. Details of the

excitation method used and of the flowing afterglow system are presented in Chapter 4.

In Chapter 5, the vibrational analysis of $a^3\Pi_{0,1} \rightarrow X^1\Sigma^+$ system of BI, a molecule with 10-valence electrons, has been completed with the observation of the $a(1) \rightarrow X^1\Sigma^+$ sub-system for the first time.

In Chapter 7, three isoelectronic ions with 11-valence electrons, PCl^+ , AsCl^+ and SeO^+ , were identified by analyzing vibrationally their corresponding new visible band emission spectra.

In Chapters 6 and 8, rotational analyses of two of the spectra, namely those of BI and PCl^+ , were undertaken with the assistance of a digital electronic interface which allows a laboratory mini-computer to assume complete control of a modern, commercial scanning spectrometer. The dual capability of this interface to generate stepping motor drive pulses for control of grating rotation, and to collect photon-counts before passing these data to the computer for storage and eventual processing, has established the above mentioned analyses as comparable in accuracy as the tedious spectrographic techniques.

Furthermore, in Chapters 9 and 10 unassigned bandheads of a new ion, PBr^+ , are reported and several reactions of discharged helium with various reagents are summarized. Once more, the merit of the flowing afterglow method for generating "clean" spectra is demonstrated.

The correlation of the experimental molecular

parameters to an effective Hamiltonian and some modern fitting procedures, used throughout this work, are reviewed in Chapter 2.

In conclusion, apart from the obvious spectroscopic and kinetic interest, the discovery of new gaseous molecular ions is important in such systems as electrical discharges and flames.

Chapter 2

A Review of Some Spectroscopic Techniques

2.1 Introduction

In this thesis the direct fitting method of Zare et al. (1) has been employed for the reduction of observed line positions to molecular parameters. This method utilizes the complete data set, in contrast with the traditional combination differences method (2), which uses only part of the data and implicitly assumes that all measurement errors are associated with the state under analysis.

Briefly, in the direct fitting method calculated line positions are iteratively compared to the measured line positions in a nonlinear least-squares fit. The calculated line positions are the differences between the eigenvalues of the upper and lower state Hamiltonians, in which the molecular constants appear as adjustable parameters. Algebraic expressions for the roots of secular determinants are not required since this procedure is numerical. Furthermore, the estimated values of the molecular constants are the minimum-variance, unbiased estimates with statistically meaningful errors.

The development of the model Hamiltonians used to represent the molecular states involved in the observed transitions, will be discussed in the next section.

In the remaining sections of this chapter, the following topics will be presented,

- i) the equations and the correlation matrices of the nonlinear and linear band-by-band least-squares fit,
- ii) the method of correlated least-squares fitting (3,4) for reducing multiple estimates of the same parameters to the best single valued estimates, and
- iii) the method used to construct the potential curves of AlO .

2.2 Molecular Hamiltonian

For each of the rotationally analyzed transitions of the present work, namely AlO ($B^2\Sigma^+ - X^2\Sigma^+$), PCl^+ ($^2\Pi - ^2\Pi$), and BI ($a^3\Pi_{0,1} - X^1\Sigma^+$), two effective Hamiltonians are required to describe all the observed line frequencies.

The problem of deriving an effective Hamiltonian for a vibrating rotating molecule has been considered at length by numerous authors. In the present work the methodology of Zare and co-workers (1) has been adopted. In the absence of external fields, the Hamiltonian can be written as:

$$H = H_0 + H_{\text{rot}} + H_{\text{fs}} \quad (2.1)$$

where H_0 represents the nonrelativistic Hamiltonian of the nonrotating molecule, H_{rot} symbolizes the rotational motion of the nuclei, and H_{fs} contains magnetic terms that cause the fine structure. The exact form of H_0 is of little concern in a rotational analysis, because it depends only on

the electronic and vibrational quantum numbers n and v . The rotational part, H_{rot} given by

$$\begin{aligned}
 H_{\text{rot}} &= B(r) \underline{R}^2 \\
 &= B(r) (\underline{J} - \underline{L} - \underline{S})^2 \\
 &= B(r) [(\underline{J}^2 - \underline{J}_z^2) + (\underline{L}^2 - \underline{L}_z^2) + (\underline{S}^2 - \underline{S}_z^2) + (\underline{L}_+ \underline{S}_- + \underline{L}_- \underline{S}_+) \\
 &\quad - (\underline{J}_+ \underline{L}_- + \underline{J}_- \underline{L}_+) - (\underline{J}_+ \underline{S}_- + \underline{J}_- \underline{S}_+)]
 \end{aligned}
 \tag{2.2}$$

plays the major role. In Eq. (2.2)

$$B(r) = h^2 / 8\pi^2 c \mu r^2 \tag{2.3}$$

is the radial part of the rotational operator in wavenumber units, in terms of the internuclear distance r and the reduced mass μ ,

$$\underline{R} = \underline{J} - \underline{L} - \underline{S} \tag{2.4}$$

is the rotational angular momentum operator of the nuclei, in terms of the total angular momentum ($\underline{J}$), electronic orbital angular momentum ($\underline{L}$), and spin angular momentum $\underline{S}$ operators, and

$$\underline{J}_\pm = \underline{J}_x \pm i \underline{J}_y, \quad \underline{S}_\pm = \underline{S}_x \pm i \underline{S}_y, \quad \underline{L}_\pm = \underline{L}_x \pm i \underline{L}_y \tag{2.5}$$

The fine structure Hamiltonian represents the major magnetic interactions by a limited set of parameters; terms that cause shifts rather than splittings of the fine structure components are omitted. The fine structure Hamiltonian is regarded as a sum of three forms,

$$H_{fs} = H_{SO} + H_{SS} + H_{SR} \tag{2.6}$$

where

$$H_{SO} = A(r) \underline{L} \cdot \underline{S} = A(r) [\underline{L}_z \underline{S}_z + 1/2 (\underline{L}_+ \underline{S}_- + \underline{L}_- \underline{S}_+)] \tag{2.7}$$

is the spin-orbit interaction,

$$H_{so} = \epsilon(r) (3\mathbf{S}_z^2 - \mathbf{S}^2) \quad (2.8)$$

is the spin-spin interaction, and

$$H_{sr} = \gamma(r) \mathbf{N} \cdot \mathbf{S} = \gamma(r) (\mathbf{J} - \mathbf{S}) \cdot \mathbf{S} = \gamma(r) [-\mathbf{S}^2 + \mathbf{J}_z \mathbf{S}_z + 1/2 (\mathbf{J}_+ \mathbf{S}_- + \mathbf{J}_- \mathbf{S}_+)] \quad (2.9)$$

is the spin rotation interaction. The z axis lies along the internuclear axis, and in Eq. (2.9), $\mathbf{N} = \mathbf{J} - \mathbf{S}$ is the operator for total orbital angular momentum apart from spin.

The energy levels of a diatomic molecule are given by the solutions to the time-independent Schrödinger equation

$$H\Psi = E\Psi \quad (2.10)$$

In practice, Ψ can be expanded in terms of a convenient finite basis set ϕ_i . Eq. (2.10) can be solved by finding the roots of the secular determinant

$$|H_{ij} - E\delta_{ij}| = 0 \quad (2.11)$$

The basis set can be chosen arbitrarily, but it is convenient to partition the determinant into diagonal blocks that weakly interact with one another. The diagonal blocks refer to Born-Oppenheimer states. Hund's case (a) coupling gives a basis set with good quantum numbers J , S , Λ and Σ . Ω is also good but it is redundant ($\Omega = \Lambda + \Sigma$). For a given electronic state n , $|nJ\Lambda\Sigma\rangle$ are eigenfunctions of the operators $\mathbf{J}^2$, $\mathbf{S}^2$, $\mathbf{J}_z$, $\mathbf{S}_z$, and $\mathbf{L}_z$ with eigenvalues $J(J+1)$, $S(S+1)$, Ω , Σ , and Λ respectively. Matrix elements, off diagonal with respect to Ω and Σ are given according to phase convention (4a) as,

$$\langle J\Omega\pm 1 | \mathbf{J}_\pm | J\Omega \rangle = [J(J+1) - \Omega(\Omega\pm 1)]^{1/2} \quad (2.12)$$

$$\langle S\Sigma\pm 1 | \mathbf{S}_\pm | S\Sigma \rangle = [S(S+1) - \Sigma(\Sigma\pm 1)]^{1/2} \quad (2.13)$$

An advantage of the case (a) basis is that the absence of intermediate angular momenta (N, J_a) and the presence of the maximum number of molecule-fixed z-components (Λ, Σ, Ω) enable H_{rot} and H_{SO} matrix elements to be evaluated using elementary raising and lowering operator techniques.

For a given electronic state and vibration level, the energy levels can be found by diagonalizing a $(2S+1)(2-\delta_{A0})$ by $(2S+1)(2-\delta_{A0})$ submatrix which is called the nvJSA block (Born-Oppenheimer state). If the magnitude of the off-diagonal matrix elements that connect different nvJSA blocks are small, their effect can be included simply by perturbation theory. A convenient way to include these perturbations arising from distant states without the knowledge of the exact energy position, is to transform the original Hamiltonian to a new Hamiltonian in which first-order interactions between the states under consideration and the distant states are eliminated. This transformation is the well-known Van Vleck transformation (5). Therefore, the Van Vleck transformation is an approximate diagonalization procedure which facilitates the factoring of an infinite energy matrix into small submatrices which can be treated individually. The energy matrix can be expanded as:

$$H = H_0 + \lambda H_1 + \lambda^2 H_2 + \dots \quad (2.14)$$

Elements of H_0 lie entirely in diagonal blocks, while H_1 , H_2 are the perturbation terms that may have elements inside and outside these blocks. The transformation is applied to H to

remove the off-diagonal elements of H_1 ; the most important off-diagonal terms which remain are second-order elements that contribute to the energy in the fourth order, and the energy matrix is now diagonal up through third-order.

A further simplification results if the energy separation between the interacting blocks is much larger than the energy separation between the fine structure of the nvJSA block. Then, the second order correction may be written,

$$\sum_n' \frac{\langle m | H_1 | n \rangle \langle n | H_1 | m' \rangle}{E_m - E_n}, \quad (2.15)$$

where $E_m - E_n$ is the energy difference between the unperturbed blocks and m, m' are matrix elements of the nvJSA block of interest. Table 2.1 lists case (a) matrix elements within the same nvJSA block (1), that are used in the present work. The derivation of these matrix elements will not be repeated since this has been considered by various authors, (see for example, Hougen (6), Kovacs (7), Freed (8)). The parameters T_v , B_v , γ_v , A_v appearing in Table 2.1 represent the expectation values of the radial parts of their respective operators,

Table 2.1: Matrix Elements Within The Same $nvJ\Sigma$ Block

$$\langle \Lambda \Sigma | H_o | \Lambda \Sigma \rangle = T_v$$

$$\langle \Lambda \Sigma | H_{\text{rot}} | \Lambda \Sigma \rangle = B_v [J(J+1) - \Omega^2 + S(S+1) - \Sigma^2]$$

$$\langle \Lambda \Sigma | H_{\text{rot}} | \Lambda \Sigma \pm 1 \rangle = -B_v [J(J+1) - \Omega(\Omega \pm 1)]^{1/2} [S(S+1) - \Sigma(\Sigma \pm 1)]^{1/2}$$

$$\langle \Lambda \Sigma | H_{\text{SR}} | \Lambda \Sigma \rangle = \gamma_v [\Sigma \Omega - S(S+1)]$$

$$\langle \Lambda \Sigma | H_{\text{SR}} | \Lambda \Sigma \pm 1 \rangle = \frac{1}{2} \gamma_v [J(J+1) - \Omega(\Omega \pm 1)]^{1/2} [S(S+1) - \Sigma(\Sigma \pm 1)]^{1/2}$$

$$\langle \Lambda \Sigma | H_{\text{SO}} | \Lambda \Sigma \rangle = A_v \Lambda \Sigma$$

$$\begin{aligned}
T_v &= \langle nv | H_0 + B(r) (L_x^2 + L_y^2) | nv \rangle \\
B_v &= \langle nv | B(r) | nv \rangle \\
A_v &= \langle nv | A(r) | nv \rangle \\
\gamma_v &= \langle nv | \gamma(r) | nv \rangle.
\end{aligned} \tag{2.16}$$

The use of the Van Vleck transformation described in the last paragraph becomes necessary because of the radial dependence of the operators of Table 2.1. As the molecule rotates it couples neighbouring vibrational levels within the same electronic state. Probably the most easily observable of the second order terms are the centrifugal distortion effects associated with the off-diagonal matrix elements of $B(r)$, since $B(r)$ has fairly strong dependence on r and also since levels with relatively high values of the quantum number J can be observed. The second order effect of $B(r)$ with itself gives the parameter

$$D_v = -\sum_{v'} \frac{\langle nv | B(r) | nv' \rangle \langle nv' | B(r) | nv \rangle}{E_{nv} - E_{nv'}} \tag{2.17}$$

while the cross-term between $B(r)$ and a function $X(r)$, e.g. spin-orbit function $A(r)$ or the spin-rotation function $\gamma(r)$, gives,

$$X_{Dv} = \sum_{v'} \frac{[\langle nv | B(r) | nv' \rangle \langle nv' | X(r) | nv \rangle + \langle nv | X(r) | nv' \rangle \langle nv' | B(r) | nv \rangle]}{E_{nv} - E_{nv'}} \tag{2.18}$$

Because of the stronger radial dependence of $B(r)$ than other functions, the cross-term needs more extended data in order to be determined experimentally.

To obtain the second-order correction matrix element for H_{rot} , the radial part given in Eq. (2.17) must be multiplied by the angular part of the rotational Hamiltonian, given in Eq. (2.2). It can be seen that centrifugal distortion may be treated as if H_{rot} were replaced by an effective rotational Hamiltonian of the form

$$H_{\text{rot}} = B_v R^2 - D_v R^4 + H_v R^6 + \dots \quad (2.19)$$

The spin-orbit and the spin-rotation interactions may also couple together neighbouring vibrational levels through the weak radial dependence of $A(r)$ and $\gamma(r)$.

So far the nvJSA block separates into two identical diagonal subblocks, one for $+\Lambda$ and one for $-\Lambda$, provided $\Lambda \neq 0$. To remove this degeneracy, perturbations from neighbouring electronic states, must be considered. Different electronic states can be connected by terms of the form $J_+L_- + J_-L_+$ arising from H_{rot} and connecting electronic states differing by one unit in Λ . This interaction is J -dependent and affects the $\pm\Lambda$ components differently. Another type of interaction, that is J -independent is of the form $L_+S_- + L_-S_+$ arising from H_{rot} and H_{SO} . It contributes to the J -independent shifts in the Λ doublets.

A further simplification in the Hamiltonian will result if a transformation is made to a basis set symmetrized with respect to reflection in the plane containing the internuclear axis. These new wavefunctions refer to energy levels which can be labeled as either having e or f parity (9), depending on whether a set of levels transforms as

either a $^1\Sigma^+$ or a $^1\Sigma^-$ state. This parity convention, then, designates the electronic parity of a set of levels according to the following scheme (half-integral spin):

$$\begin{aligned} \text{e levels } \sigma_v \psi &= +(-1)^{J-1/2} \psi \\ \text{f levels } \sigma_v \psi &= -(-1)^{J-1/2} \psi \end{aligned} \quad (2.20)$$

It follows that the resulting wavefunctions necessary to evaluate the Hamiltonian for $^2\Sigma^+$ (AlO) and $^2\Pi$ (PCl $^+$) states are given by,

$$\begin{aligned} ^2\Sigma_{1/2}(\text{e}) &= 1/\sqrt{2} \{ |^2\Sigma_{1/2}^+> \pm |^2\Sigma_{1/2}^-> \} \\ ^2\Pi_{3/2}(\text{e}) &= 1/\sqrt{2} \{ |^2\Pi_{3/2}^+> \pm |^2\Pi_{3/2}^-> \} \\ ^2\Pi_{1/2}(\text{e}) &= 1/\sqrt{2} \{ |^2\Pi_{1/2}^+> \pm |^2\Pi_{1/2}^-> \} \end{aligned} \quad (2.21)$$

As a result of these symmetrized wavefunctions the secular determinants of $^2\Sigma-^2\Sigma$ and $^2\Pi-^2\Pi$ transitions can be factored into two diagonal blocks of order 1 x 1 and 2 x 2 respectively, corresponding to levels with definite parity.

The energy levels of a $^2\Sigma$ electronic state can be represented by analytical expressions. Taking into consideration the matrix elements of Table 2.1 and the rotational centrifugal distortion, the rotational energy levels for a $^2\Sigma^+$ state are given by,

$$F_1(J, \text{e}) = B_v(J-\frac{1}{2})(J+\frac{1}{2}) - D_v[(J-\frac{1}{2})(J+\frac{1}{2})]^2 + \frac{1}{2}\gamma_v(J-\frac{1}{2}) \quad (2.22)$$

and

$$F_2(J, \text{f}) = B_v(J+\frac{1}{2})(J+3/2) - D_v[(J+\frac{1}{2})(J+3/2)]^2 - \frac{1}{2}\gamma_v(J+3/2) \quad (2.23)$$

Equations (2.22) and (2.23) have a more familiar form if $J+\frac{1}{2}$ is replaced by the quantum number N , so that each rotational level (except the $N=0$ level) occurs as a closely spaced pair. Because of the functional form of the $^2\Sigma$

analytical expressions, the molecular constants absorb the effects of any perturbation due to ${}^2\Pi$ electronic states. The result is that there is no simple way to ascertain whether the rotational and spin-rotation coupling constants have the separate mechanical and magnetic meanings usually attributed to them.

${}^2\Pi$ states may be perturbed heterogeneously by ${}^2\Sigma$ and/or ${}^2\Delta$ states. However, the matrix elements $\langle {}^2\Pi_{1/2}(\epsilon_f) | H_{\text{rot}} | {}^2\Sigma_{1/2}(\epsilon_f) \rangle$ are parity dependent because a ${}^2\Sigma_{1/2}$ basis function is involved. This parity dependent matrix element is mainly responsible for the splitting of ${}^2\Pi$ rotational levels that is called Λ -doubling. Therefore, it is reasonable to assume that the Λ -doubling of a ${}^2\Pi$ state is usually accounted for only by consideration of ${}^2\Sigma$ states. It should be noted that the observed splitting of a ${}^2\Pi_{1/2}$ component of a ${}^2\Pi$ state is more significant than for ${}^2\Pi_{3/2}$, since the ${}^2\Pi_{1/2}$ component experiences two types of interactions with a ${}^2\Sigma$ state, namely the spin-orbit, $L_+S_- + L_-S_+$, and the L-uncoupling $J_+L_- + J_-L_+$; however, the ${}^2\Pi_{3/2}$ component experiences only the L-uncoupling.

The weakness of distant ${}^2\Pi$ - ${}^2\Sigma$ interactions permits the use of the Van Vleck transformation to uncouple the interacting states. In Table 2.2 the matrix elements connecting a ${}^2\Pi$ state with perturbing ${}^2\Sigma$ states are given. The derivation of these elements is a direct result of Eq. (2.15) and the matrix elements of Ref. (1) connecting nvJSA blocks with different values of Λ or S .

Table 2.2: Matrix Elements Connecting
 $a^2\Pi$ State with Perturbing $^2\Sigma$ States

$$H_{3/2,3/2}(e) = 1/2q_v(J+3/2)(J-1/2)$$

$$H_{1/2,1/2}(e) = 1/2q_v(J-1/2)^2 - 1/2p_v(J-1/2) + o_v$$

$$H_{1/2,1/2}(f) = 1/2q_v(J+3/2)^2 - 1/2p_v(J+3/2) + o_v$$

$$H_{3/2,1/2}(e) = 1/2q_v(J+3/2)^{1/2}(J-1/2)^{3/2} \\ - 1/4p_v(J+3/2)^{1/2}(J-1/2)^{1/2}$$

$$H_{3/2,1/2}(f) = -1/2q_v(J+3/2)^{3/2}(J-1/2)^{1/2} \\ - 1/4p_v(J+3/2)^{1/2}(J-1/2)^{1/2}$$

The parameters o_v , p_v and q_v introduced in Table (2.2), are defined by,

$$o_v = 1/4 \sum_{n', v'} \frac{|\langle n^2 \Pi v | A L_+ | n'^2 \Sigma v' \rangle|^2}{E_{nv} - E_{n'v'}} \quad (2.24)$$

$$p_v = \sum_{n', v'} \frac{\langle n^2 \Pi v | A L_+ | n'^2 \Sigma v' \rangle \langle n^2 \Pi v | B L_+ | n'^2 \Sigma v' \rangle}{E_{nv} - E_{n'v'}} \quad (2.25)$$

$$q_v = 2 \sum_{n', v'} \frac{|\langle n^2 \Pi v | B L_+ | n'^2 \Sigma v' \rangle|^2}{E_{nv} - E_{n'v'}} \quad (2.26)$$

The centrifugal distortions of the above parameters

($o_{Dv}, o_{Bv}, \dots, p_{Dv}, p_{Bv}, \dots, q_{Dv}, q_{Bv}, \dots$) are not indicated in Table (2.2).

Comparison of the functional forms of Table 2.2 and analytic expressions (2.22) and (2.23) for $^2\Sigma$ states show that $^2\Pi$ perturbations contribute a term o_v to the effective band origin, a term q_v to the effective B_v value and a term $-p_v$ to the effective spin-rotation constant γ_v . This illustrates how the presence of a $^2\Pi$ state impairs the mechanical meaning of the rotational constants of a $^2\Sigma$ state, as mentioned in the previous paragraph. In conclusion, Table 2.3 lists matrix elements of the effective $^2\Pi$ Hamiltonian used in the analysis of the $^2\Pi$ - $^2\Pi$ system of PCl^+ . The matrix elements used in the present nonlinear least-squares fitting routine are essentially identical with those formulated by Brown and co-workers (10). However, the effects of these matrix elements are identical to those obtained by Zare et al (1). The main differences are in the

definitions of B_v , and γ_v and of the parameters used to describe centrifugal distortion of Λ -doubling. However, the latter are not required in the PCl^+ analysis.

Table 2.3: Effective Hamiltonian Matrix

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Elements of ${}^2\Pi$ States^a

	E(1,1)	1		
	(2,2)	1		
B	(1,1)	x^2	D	(1,1) $-x^4-x^2+1$
	(2,2)	x^2-2		(2,2) $-x^4+3x^2-3$
	(1,2)	$-(x^2-1)^{1/2}$		(1,2) $2(x^2-1)^{3/2}$
A	(1,1)	$-\frac{1}{2}$	γ	(1,1) -1
	(2,2)	$\frac{1}{2}$		(1,2) $\frac{1}{2}(x^2-1)^{1/2}$
q	(1,1)	$\pm x$	p	(1,1) $\pm \frac{1}{2}x$
	(1,2)	$\pm \frac{1}{2}x(x^2-1)^{1/2}$		

^a $1 \equiv {}^2\Pi_{1/2}; 2 \equiv {}^2\Pi_{3/2}; (\pm) = \begin{pmatrix} e \\ f \end{pmatrix}$ $x = (J + \frac{1}{2})$

2.3 Band-by-Band Least-Squares Fits

2.3.1 Nonlinear Fitting Procedure ($^2\Pi$ - $^2\Pi$ system)

The nonlinear least-squares fitting routine accepts transitions as input data, together with initial trial values of the spectroscopic constants and their estimated uncertainties. These initial values of the parameters of the band system are used to evaluate the Hamiltonian matrix, which is then diagonalized. The resulting eigenvalues form a set of term energies from which calculated transitions are obtained. These calculated transitions are compared to the experimentally observed frequencies. Corrections to the parameters are computed, and a new set of term energies is constructed using the adjusted parameters.

This procedure is repeated until convergence is achieved. Mention should be made here of the commonly made assumptions that the measured errors of each band are randomly scattered with variance $\hat{\sigma}^2$ and zero covariance.

The final molecular parameters which are obtained by the nonlinear least-squares fitting are minimum-variance, linear unbiased estimated (MVLU); this is in accord with the approximately linear nature of the model in the region about the estimated values of the parameters, as follows.

The molecular parameters ($\beta_1, \beta_2, \dots, \beta_p$) can be derived from the measured line wavenumbers $Y(y_1, y_2, \dots, y_n)$ using the non-linear expression,

$$Y = f(X, \beta) + \epsilon \quad (2.27)$$

where $\mathbf{X}(x_1, x_2, \dots, x_m)$ are the independent variables, and $\epsilon(\epsilon_1, \epsilon_2, \dots, \epsilon_n)$ are the unknown measurement errors. Eq. (2.27) can be expanded by Taylor series with respect to $(\Delta\beta_1, \Delta\beta_2, \dots, \Delta\beta_p)$, the corrections of the molecular parameters. The first term of this expansion for the i^{th} line measurement will yield,

$$\begin{aligned}\Delta y_i &= y_i(\text{observed}) - y_i(\text{calculated}) \\ &= (\partial f / \partial \beta_1)_i \Delta\beta_1 + (\partial f / \partial \beta_2)_i \Delta\beta_2 + \dots + (\partial f / \partial \beta_p)_i \Delta\beta_p\end{aligned}\quad (2.28)$$

where $(\partial f / \partial \beta_1)_i, \dots, (\partial f / \partial \beta_p)_i$ are the partial derivatives of Eq. (2.27), and the initial values of $(\beta_1, \beta_2, \dots, \beta_p)$ are the given trial values. The linearized equation (2.28) can be expressed in matrix form as,

$$\Delta \mathbf{Y} = \mathbf{A} \Delta \boldsymbol{\beta} \quad (2.29)$$

where, $\Delta \mathbf{Y}$ and $\Delta \boldsymbol{\beta}$ are column vectors of order $n \times 1$ and $p \times 1$ respectively, and the first row of $n \times p$ matrix has elements given by,

$$(\partial f / \partial \beta_1)_1, (\partial f / \partial \beta_2)_1, \dots, (\partial f / \partial \beta_p)_1.$$

The linear least-square fitting of Eq. (2.29) is very well documented in a review article (11), and a summary of the derived least-squares equations will be presented. For every iteration the sum of the squared deviations between the measured and the calculated line positions.

$$\Delta \mathbf{Y}^T \mathbf{Y} = \sum_{i=1}^n (\Delta y_i)^2 \quad (2.30)$$

is minimized, and a set of $\Delta \boldsymbol{\beta}$ is given by,

$$\Delta \boldsymbol{\beta} = (\mathbf{A}^T \mathbf{A})^{-1} \mathbf{A}^T \Delta \mathbf{Y}. \quad (2.31)$$

This process is repeated until a preset convergence

criterion is satisfied.

The variance, $\hat{\sigma}^2$, and standard deviation, $\hat{\sigma}$, of a fit are given by,

$$\hat{\sigma}^2 = 1/f(\Delta \mathbf{Y}^T \mathbf{Y}) = 1/f \sum_{i=1}^n (\Delta y_i)^2 \quad (2.32)$$

and

$$\hat{\sigma} = |(\hat{\sigma}^2)^{1/2}|, \quad (2.33)$$

where f represents the number of degrees of freedom of the fit,

$$f = (n-p) \quad (2.34)$$

The variance of the estimated parameters are taken as the corresponding diagonal elements of the square-symmetric variance-covariance matrix, $\hat{\theta}$. Thus, the variance of a parameter β_i is taken as $\hat{\theta}_{ii}$, where

$$\hat{\theta} = \hat{\sigma}^2 \mathbf{V}. \quad (2.35)$$

The dispersion matrix, $\mathbf{V}$, is given by,

$$\mathbf{V} = (\mathbf{A}^T \mathbf{A})^{-1} \quad (2.36)$$

The covariances are the off-diagonal elements of $\hat{\theta}$, denoted by $\hat{\theta}_{ij}$. The normalized variance-covariance matrix is called the correlation-coefficient matrix and given by the symbol $\mathbf{C}$,

$$c_{ij} = \hat{\theta}_{ij} / (\hat{\theta}_{ii} \hat{\theta}_{jj})^{1/2} \quad (2.37)$$

This symmetric matrix, having unity valued diagonal elements and off-diagonal elements in the range -1 to +1, relates the degree of correlation between the estimated parameters of a fit. Thus an off-diagonal element c_{ij} gives a measure of the interdependence of parameter β_i upon

parameter β_j . The correlation is large if $|c_{ij}| \approx 1$ and low²² if $|c_{ij}| \approx 0$.

2.3.2 Linear fitting procedure ($^2\Sigma^+ - ^2\Sigma^+$ system)

The expressions (2.22) and (2.23) for the energy levels of a $^2\Sigma$ state lead to a linear least-squares solution of the equation,

$$\mathbf{Y} = \mathbf{A}\boldsymbol{\beta} + \boldsymbol{\epsilon} \quad (2.38)$$

where $\mathbf{Y}$, $\boldsymbol{\beta}$, and $\boldsymbol{\epsilon}$ are the column vectors containing the n known measured line positions of a band, the p molecular parameters to be determined and the n unknown measurement errors respectively. $\mathbf{A}$ is the known $n \times p$ coefficient matrix with elements given by Eqs. (2.22) and (2.23).

The resulting least-squares values $\hat{\boldsymbol{\beta}}$ of molecular parameters together with expressions for σ^2 , $\hat{\boldsymbol{\theta}}$, and $\mathbf{c}$ are given by Eqs. (2.31), (2.32), (2.35) and (2.37).

2.4 Single-step merging

The band-by-band reduction of the systems analyzed, presently, leads to multiple estimates of various molecular parameters. Simple averaging of these overdetermined constants, weighted or unweighted, does not give satisfactory results. The discrepancy appears due to the fact that no account has been taken of the correlations between the various parameters of each fit. Therefore, the problem is to merge the redundant values from the band-by-

band fits into the "best" nonredundant minimum variance, linear, and unbiased, values.

Albritton and co-workers (3) have developed a satisfactory approach for obtaining MVLU nonredundant values. This method is called merged least-squares fitting and it takes the output of the band-by-band fits, $\hat{\beta}$ and $\hat{\theta}$, to be the input of another least-squares fit that "merges" the redundant values.

Since the variance-covariance matrices $\hat{\theta}$ associated with the $\hat{\beta}$ generally do not have equal diagonal elements and zero off-diagonal elements, the solution of the least-squares fit must employ the weighted, correlated least-squares formalism (11). Using this, the nonredundant molecular constants that minimize their standard errors subject to the interrelations contained in $\hat{\theta}$ are given by

$$\hat{\beta}^M = (X^T \hat{\Phi}^{-1} X)^{-1} X^T \hat{\Phi}^{-1} y \quad (2.39)$$

where matrix X relates the redundant values of the column vector y to the corresponding nonredundant column vector β , matrix $\hat{\Phi}$ is a nondiagonal matrix composed of the individual $\hat{\theta}_i$, $i = 1, 2, \dots$ number of bands merged,

$$\hat{\Phi} = \begin{bmatrix} \hat{\theta}_1 & & 0 \\ & \hat{\theta}_2 & \\ 0 & & \hat{\theta}_k \end{bmatrix}, \quad (2.40)$$

where the circumflex denotes that $\hat{\beta}^M$ values are MVLU estimates, and the superscript M denotes that they are estimates of the merge method.

The precision of the estimates β^M is indicated by their standard errors, which are the square roots of the diagonal elements of the variance-covariance matrix associated with $\hat{\beta}^M$,

$$\hat{\theta}^M = \hat{\sigma}_M^2 \hat{V}^M, \quad (2.41)$$

where the merged dispersion matrix is given by

$$V^M = (X^T \hat{\Sigma}^{-1} X)^{-1}. \quad (2.42)$$

The estimated variance of the merged fit $\hat{\sigma}_M^2$ is given by

$$\hat{\sigma}_M^2 = (y - X\hat{\beta}^M)^T \hat{\Sigma}^{-1} (y - X\hat{\beta}^M) / f_M, \quad (2.44)$$

where the degrees of freedom of the merged fit are denoted by f_M . When the degrees of freedom in the individual band-by-band fits are greater or equal to about 30, the estimated molecular constants and standard errors have their usual statistical meaning. Confidence limits can be constructed by

$$\hat{\beta}_i - t(f, 1 - a/2) \hat{\theta}_{ii}^{1/2} \leq \beta_i^{\text{true}} \leq \hat{\beta}_i + t(f, 1 - a/2) \hat{\theta}_{ii}^{1/2} \quad (2.45)$$

within which one can be 100(1-a)% confident that the unknown "true" value lies. In other words, if the set of measurements could be repeated many times in an identical fashion except for random measurement errors, then the set of $(\hat{\beta}_i - \beta_i^{\text{true}}) / \hat{\theta}_{ii}^{1/2}$ value would be distributed symmetrically about zero in a fashion described by the $t(f)$ function, which is a tabulated function of statistics, for the given degrees of freedom f . Similarly if only random errors in the measurements are considered and the degrees of freedom of band-by-band fits are greater than about 40 then the

estimated variance of the merge $\hat{\sigma}_M^2$ divided by its unknown "true" values has a χ^2/f distribution which again is a commonly tabulated function of statistics for the given degrees of freedom f . Unlike the symmetric t function with range $-\infty \leq t \leq +\infty$ and a mean of zero, the asymmetric χ^2/f function has a range of $0 \leq \chi^2/f \leq \infty$ and mean of unity. The $100(1-a)\%$ confidence limits for $\hat{\sigma}_M^2$ are

$$\hat{\sigma}_M^2/p(f, 1 - a/2) \leq \hat{\sigma}_{Mtrue}^2 \leq \hat{\sigma}_M^2/p(f, a/2), \quad (2.45)$$

and are asymmetric.

If these limits, whose variation about unity is due to random measurement errors, are exceeded, then one can conclude that it is likely that systematic errors are present in some or all of the data sets or Hamiltonians.

2.5 Stepwise Merging

A useful approach for the identification and (if necessary) rejection of data that are likely to contain relative systematic error, is the method of stepwise merging formulated by Coxon (4). In Coxon's work it was established that two or more sets of separately merged parameters can themselves be merged together to a single set of parameters using a least-squares grand merge approach. The output constants and dispersion matrix of such a grand merge are identical with those derived from the equivalent single-step merge. The only difference in the stepwise merge approach is that the weight matrix to be used is derived not from the

variance-covariance matrices of the separately merged input parameters, but from the corresponding dispersion matrices,

$$\hat{\Phi}_M = \begin{bmatrix} (\hat{V}^M)_1 & & & 0 \\ & (\hat{V}^M)_3 & & \\ & & (\hat{V}^M)_3 & \\ & & & \ddots \\ 0 & & & & (\hat{V}^M)_k \end{bmatrix} \quad (2.46)$$

It was also demonstrated that in the absence of systematic errors, confidence limits for a set of merged molecular constants can be derived from the dispersion matrix element, $\hat{V}_{11}$, rather than estimated variance $\hat{\theta}_{11} = \hat{\sigma}_M^2 \hat{V}_{11}$.

Alternatively, if $\hat{\sigma}_M^2$ lies outside of the confidence limits expected from the χ^2/f distribution the standard errors of $\hat{\beta}^M$ derived from $\hat{V}^M$ should be multiplied by $\hat{c}_M$ (4). The estimated variance for a merge performed in a stepwise manner is calculated from:

$$f_{M1} \hat{\sigma}_{M1}^2 + f_{M2} \hat{\sigma}_{M2}^2 + f_{GM} \hat{\sigma}_{GM}^2 = f_M \hat{\sigma}_M^2, \quad (2.47)$$

with

$$f_{M1} + f_{M2} + f_{GM} = f_M, \quad (2.48)$$

where f_{M1} and $\hat{\sigma}_{M1}^2$ and f_{M2} and $\hat{\sigma}_{M2}^2$ are the degrees of freedom and variances of two merges, consolidated as a single set of parameters, in the grand merge, with degrees of freedom and variance f_{GM} and $\hat{\sigma}_{GM}^2$. The degrees of freedom and variance of the single step merge are denoted by f_M , $\hat{\sigma}_M^2$. Finally, the stepwise approach is simpler and less expensive in computer usage.

2.6 RKR Potentials

One of the best methods of obtaining accurate potentials for diatomic molecules is by means of the so-called RKR procedure developed by Rydberg, Klein and Rees (12).

The RKR method is based on the W.K.B. (Wentzel-Kramers-Brillouin) approximation (13). In this approximation, the eigenvalues for the one-dimensional motion of a particle in a potential well are given by the phase integral condition,

$$\oint p(r) dr = h(v + \frac{1}{2}) = I, \quad (2.49)$$

where $p(r)$ is the total radial momentum of the particle, I is the action variable arising from the quantization of the radial momentum, and v is the vibrational quantum number. $\oint$ denotes the integral taken over a complete cycle of the classical motion.

Klein (12) suggested a procedure to solve the integral (2.49), leading to an explicit relationship between the turning points, r_1 and r_2 , and the auxiliary terms f and g . In the case of a rotationless state of the molecule ($J=0$), r_1 and r_2 are given by,

$$f = \frac{1}{2}(r_2 - r_1) \quad (2.50)$$

$$g = \frac{1}{2}(1/r_1 - 1/r_2) \quad (2.51)$$

so that

$$r_{1,2}(U) = (f/g + f^2)^{1/2} \pm f. \quad (2.52)$$

The functions f and g are given by,

$$f(U) = [h/8\pi^2 c\mu]^{1/2} \int_{-\frac{1}{2}}^v \frac{dv'}{\sqrt{U - G(v')}} \quad (2.53)$$

and

$$g(U) = [8\pi^2 c\mu/h]^{1/2} \int_{-\frac{1}{2}}^v \frac{B_v dv'}{\sqrt{U - G(v')}} \quad (2.54)$$

where v' is regarded as a continuous variable, and v is the vibrational quantum number for $E=U=G(v)$. In order to evaluate these integrals it is necessary that the rotational constants (B_v) and energy levels ($G(v)$) be known accurately. The integrals in Eqs. (2.53) and (2.54) may be evaluated by numerical integration except at the upper limits, where the denominators of the integrands become infinite.

This difficulty can be overcome (14) by assuming that the intervals between pairs of energy levels can be adequately represented by local Morse parameters $\tilde{\omega}_e$ and $\tilde{\omega}_e \tilde{x}_e$; the simple Morse polynomial can be integrated to give analytical expressions for f and g . This approach seems a good approximation for most molecules, but is not very adequate for light hydride molecules, especially as the molecule approaches dissociation. However, a new program has been developed recently in this laboratory by Coxon and Foster (15) in which the energy levels are fitted to slowly varying function of the type proposed by Gilmore (16). As a consequence of the weak vibrational dependence, accurate interpolation is achieved with a low-order polynomial. Using the aforementioned program, the available rotational

and vibrational constants have been used to determine potential energy curves for both electronic states of the AlO molecule.

Chapter 3

Rotational Analysis of the B-X

System of AlO

3.1 Introduction

The work presented in this chapter is concerned with rotational analyses of twenty-five bands, specifically 0-1, 0-2, 1-0, 1-2, 1-3, 2-0, 2-1, 2-3, 2-4, 3-1, 3-4, 3-5, 4-1, 4-2, 4-5, 5-2, 5-3, 5-6, 6-3, 6-4, 7-4, 7-5, 8-5, 8-6, and 9-6 bands, of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system of AlO; this system is also well-known as the blue-green system of AlO. Effective molecular parameters are determined by linear least-squares fitting of the measured line frequencies.

The $B \rightarrow X$ system of AlO is readily observed both in emission and absorption. Many different types of sources excite the system in emission. Examples are: [i] an arc running between aluminum electrodes in air or oxygen (17-20); [ii] exploding aluminum wires in an oxidizing atmosphere (21,22); [iii] shock excited Al_2O_3 or $Al+O_2$, (23); [iv] in a high current hollow cathode lamp containing pellets of an Al- Al_2O_3 mixture (24); and [v] from a microwave discharge through gaseous $AlCl_3$ and O_2 (25). Aluminum monoxide is of interest for a number of reasons. In particular, temperatures and densities in the upper

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atmosphere, as well as the differential extinction of solar radiation, have been calculated from observations in AlO (B $\rightarrow$ X) following release of aluminum containing compounds (26-29). It is also known from thermochemical data that AlO is one of the numerous products occurring in the vapour of alumina, the formation and dissociation of which is exceedingly complex (30).

The AlO molecule has already been the subject of a great deal of spectroscopic work. The most complete vibrational analysis published is that of Shimauchi (19) who has extended the observed levels to $v''=12$ for the $X^2\Sigma^+$ state and $v'=16$ for the $B^2\Sigma^+$ state. In the same paper it was reported that the $v''=9$ level of the X state is displaced by a perturbation (due to the low-lying $A^2\Pi$ state).

A rotational analysis of the B $\rightarrow$ X system was first accomplished in 1927 by Pomeroy (20). The 1-0, 0-0, and 0-1 bands were analyzed and the rotational constants, B and D, for both states were reported.

Ten years later Sen (31) using a similar experimental arrangement to that described by Pomeroy, photographed in a high dispersion spectrograph, 1-0, 0-0, 0-1, 2-1, 1-1, and 1-2 bands in emission. The rotational constants obtained by Sen were in good agreement with Pomeroy's values.

Sen initially used a graphical method (2) for determination of the difference of the B and X state spin-rotation constants ($\Delta\gamma$) from the experimentally obtained spectrum. The reported absolute values of the spin-rotation

constants for the $v''=0$, $v''=1$ and $v'=0$ vibrational levels were derived by solving simultaneously the equations involving $\Delta\gamma$.

In 1957, Lagerqvist et al. (18) rotationally analyzed bands involving the vibrational levels $v'=0,1,2$, and 3, $v''=0,1,2,3,4$, and 5, and effective rotational parameters B and D were determined graphically. The differences between the splitting constants γ' and γ'' were determined in a similar way as that of the previously mentioned analysis. The absolute values for γ' and γ'' were obtained from the 0-0 band, where the line positions were most accurately known. However, the reported absolute values were poorly determined.

Finally, in 1975, Mahieu et al. (32) attempted to determine the spin-doubling constants in several vibrational levels of the $X^2\Sigma^+$ and $B^2\Sigma^+$ states from high-resolution spectra obtained from low-temperature discharges. In this paper, eight bands of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system with $v' \leq 2$ and $v'' \leq 3$ were analyzed. The advantage of this excitation source was that it gave "sharp lines" and bands with relatively low rotational quantum number. Therefore, the troublesome band overlapping obtained in the previously mentioned high-temperature sources was avoided. The most interesting consequence of the source used was that the analysis could be performed fairly easily and the correct assignment of the P_1 , R_1 and P_2 , R_2 branches could be deduced. This was accomplished using the Mulliken relation

(33) which indicates that the $P_1(N+\frac{1}{2})$ line is always a little more intense than the $P_2(N-\frac{1}{2})$ line, where N is the nuclear rotation quantum number. The photoelectric trace of the 0-0 band obtained from Mahieu's work suggested that the intense component was always that of lowest wavenumbers. However, this result is just opposite to the conclusions of Sen (31) and Lagerqvist et al. (18), derived from their studies of spectra from an arc discharge, a source which is not favorable for obtaining spectral regions with only one branch present. The spin-rotation constants were approximately two orders of magnitude less than those previously reported and the γ' was negative. However, the lack of smooth vibrational dependence for the γ'_v and γ''_v values and their experimental errors limit the significance of the work by Mahieu et al. (12) for obtaining accurately even the difference of the spin-rotation interactions of the X and B states.

In summary, the high resolution work which has been performed on the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ system of AlO is of less than optimum value given the fact that the evaluated molecular constants from the previous works were determined by analyzing small numbers of bands involving levels $v'' \leq 4$ and $v' \leq 3$ and by using the combination differences method, a method which does not utilize all the available data and which yields overly optimistic error limits.

In the present work, the rotational analysis has been extended to $v'' = 6$ and $v' = 9$. Band origins, effective

rotational parameters and spin-rotation coupling constants³⁴ have been obtained by reducing the line positions of the individuals bands with the method of direct linear least-squares fitting. Multiple determinations of the parameters are merged to obtain single-valued estimates of the same parameters, as well as Dunham coefficients describing their vibrational dependences. However, despite the improved quality of data in the present work, the accuracy of the measured line positions is still not sufficient to provide a determination of the absolute magnitude of the spin-rotation coupling constants of both states. The spin-rotation interaction parameters have been found, nevertheless, to within a common undetermined constant. This constant would be provided from a future microwave spectrum of AlO in the ground electronic state. Furthermore, no interactions between either or both the X and B states with the $A^2\Pi$ state could be detected for the analyzed vibrational levels. Rotational analysis of bands with higher vibrational numbers of the system under study was not possible with the excitation source used. The present work is concluded with calculations of RKR potentials curves for the two states.

Shortly after this work was published (34), a similar analysis was reported (35) in which ten bands of the B-X system of AlO were photographed with $v' \leq 7$ and $v'' \leq 5$. All the bands analyzed overlapped with the Coxon and Naxakis (34) work. Although rotational constants of the B state (B_v , D_v and γ_v) and the bands origins were determined by

simultaneous least-squares fit of the line frequencies, the³⁵ constants B_v and D_v of the ground electronic state were constrained from the work of Lagerqvist et al. (18) and the spin-rotation constants were constrained from the work of Mahieu et al. (32). In conclusion, the recent work of Singh et al. (35) does not contribute anything novel to the analysis of the B-X system of AlO.

3.2 Nature of the Electronic Transition

The ground state of the AlO molecule can be formed from an oxygen and an aluminum atom in their ground atomic states with term symbols 3P_g and 2P_u respectively.

According to Wigner and Witmer (36), Σ^+ , $\Sigma^+(2)$, $\Pi(2)$, and Δ molecular states can be derived from the lowest states of the separated atoms. Experimental evidence supported by SCF calculations (37) suggests that the ground state configuration of AlO can be written as

$(KKL)(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^1{}^2\Sigma^+$. By promotion of one $y\sigma$ electron to the $x\sigma$ outer orbital, the second excited state (B) can be obtained. Furthermore, because Σ^+ states cannot combine with Σ^- states (2), the B state is also Σ^+ . Therefore, both the X and B states of AlO have zero component of electronic orbital angular momentum in the direction of the internuclear axis ($\Lambda = 0$). The spin vector $S = \frac{1}{2}$ couples with the nuclear rotation vector (R) perpendicular to the internuclear axis, to give the

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resultant total angular momentum (J) of the molecule. This zero coupling of spin to the internuclear axis is the characteristic of Hund's case (b).

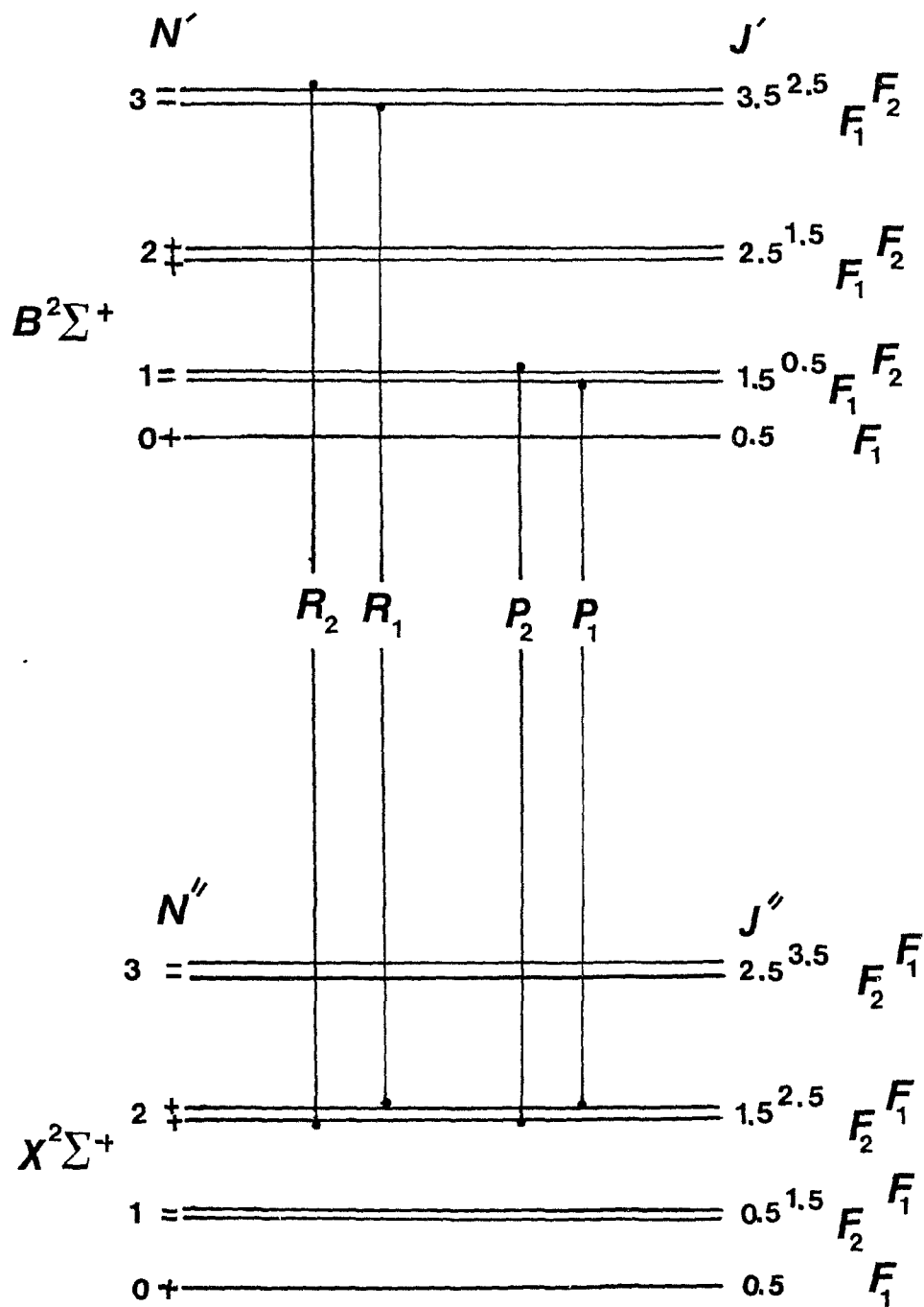
In Hund's case (b) the quantum number N of the total angular momentum apart from spin ($N=R+L$) is defined, and if both states belong to case (b), the following selection rule holds for this quantum number (2), $\Delta N = 0, \pm 1$ with the added restriction of $\Delta N \neq 0$ for $\Sigma - \Sigma$ transitions.

These rules are similar to the selection rules for J and hold to the extent that the interaction of the electron spin S with N can be neglected. It is well-known that transitions with $\Delta J = 1$ (or $\Delta N = 1$) compose the R branch and with $\Delta J = -1$ (or $\Delta N = -1$) the P branch. In branches for which $\Delta J \neq \Delta N$ the intensity falls off very rapidly with increasing N ; these branches are called satellite branches, since their lines lie very close to those of the corresponding main branches with the same ΔN but having $\Delta J = \Delta N$. In the AlO molecule, the satellite branches are completely overlapped by the main R and P branches. Finally, the symmetry selection rules for electric dipole radiation hold quite generally; positive parity terms combine only with negative parity and vice versa. The energy level pattern of a $^2\Sigma^+ \rightarrow ^2\Sigma^+$ electronic transition is shown schematically in Fig. 3.1. The separation of the two rotational sublevels with $J = N + \frac{1}{2}$ (F_1) and $J = N - \frac{1}{2}$ (F_2) for a given N is very small compared to the separation of successive rotational levels. With the instrumental

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resolution of this work, it was normally possible to resolve
the doublet R (R_1 , R_2) and the doublet P (P_1 , P_2) branches
for lines with $N \geq 15$.

Figure 3.1: Energy level diagram for the first lines of a ${}^2\Sigma^+ - {}^2\Sigma^+$ transition. The spin-splitting has been much exaggerated.

Figure 3.1



3.3 Experimental Details and Rotational Assignment

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Electronically excited AlO ($\text{B}^2\Sigma^+$) radicals were produced in the flow system shown in Fig. 3.2. Anhydrous aluminum trichloride (Anachemia) was placed in a side tube connected to the emission cavity and was heated by a nichrome wire. AlCl_3 vapour was produced. Trace quantities of oxygen (Linde, commercial, 99.5%) were flowed through a 2.45 GHz electrodeless discharge (EMS Microtron 200) operated at a power level of ~100 W and the discharged gases were removed by a 20 m^3/hr single-stage pump (Leybold-Heraeus S16A).

The pressure in the system was typically less than ~3 torr. The flow rate of oxygen and the heating temperature of AlCl_3 were adjusted to maintain the blue-green AlO discharge and to optimize the emission.

In order to decide which bands would be rotationally analyzed, a low resolution spectrum in the region 4200-5400 Å was recorded in the first order of a Spex 1704X 1-m spectrometer fitted a 1200 groove/mm (120 x 140 mm) grating blazed at 5000 Å. The reciprocal dispersion in the first order is ~8.0 Å mm^{-1} . The detection system consisted of an RCA-C31014A GaAs photomultiplier (dark count ~4 counts/sec at -20°C and cathode voltage -1500 V) mounted inside an R.F. shielded, water-cooled housing (Products for Research, TE-192-RF) equipped with a heated window assembly and focussing lens. The photomultiplier output was displayed on a

stripchart recorder (Brinkmann 2541), a section of which has⁴¹
been reproduced in Fig. 3.3. The slit width was 50 μm and
slit height was 50 mm. The spectrum was scanned at 1 $\text{\AA}/\text{sec}$.

Figure 3.2: The flow system used for the production of AlO ($B^2\Sigma^+$) molecule.

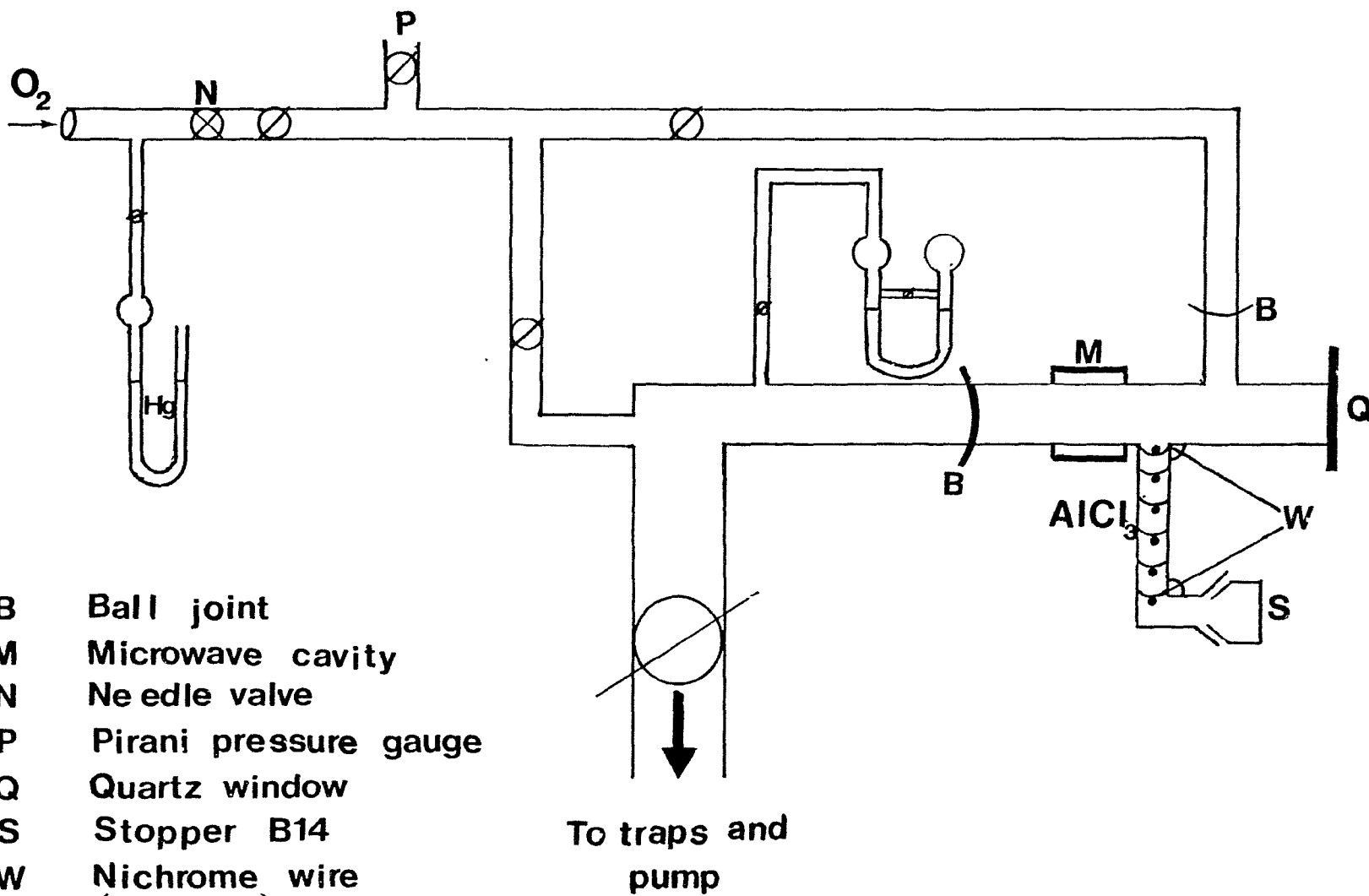


Figure 3.2

- B Ball joint
- M Microwave cavity
- N Needle valve
- P Pirani pressure gauge
- Q Quartz window
- S Stopper B14
- W Nichrome wire
(3.3 Ω/m)

To traps and
pump

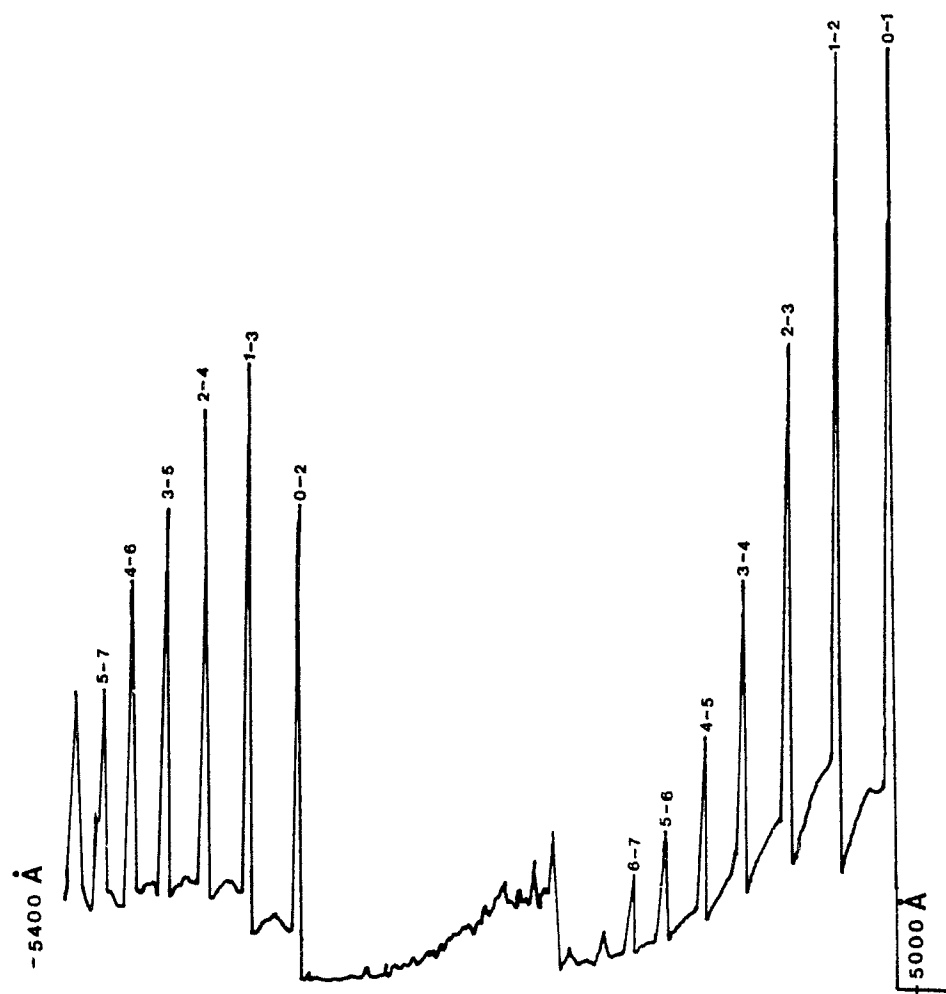
It was decided that high resolution spectra would be recorded photographically in the following regions:

- [i] 4400 Å - 4645 Å ($\Delta v = 3, 2$, sequences),
- [ii] 5080 Å - 5490 Å ($\Delta v = -1, -2$ sequences).

Spectra in these regions were recorded on Kodak 103a0 and 103aD photographic plates. A 3.5-m R.S.V. Ebert spectrograph was used in the 2nd order of a 1200 line/mm grating (reciprocal dispersion of about 1 Å mm^{-1}). The grating was blazed at 10000 Å. Exposure times were 4 hours with a slit width of 15 μm . A quartz filter was inserted for cutting off the third-order wavelengths. Wavelength calibration was made by reference to emission lines in overlapping orders of a commercial hollow cathode iron/neon discharge lamp (Westinghouse WL22810A) operated at 20 mA with exposure time 30 minutes. Spectral and calibration lines were measured on a horizontal, Abbé type comparator (0.5 μm resolution). The dispersion curve of each measured plate was established by fitting the iron and neon standard lines (38) to a second or third-order polynomial in distance; the dispersion curve could be used to generate the wavenumbers of the AlO spectral lines. The standard deviations of these calibration fits were typically 0.004 Å .

Figure 3.3: Photoelectric trace of the $\Delta v = -1$ and $\Delta v = -2$ sequences of the B - X system of AlO.

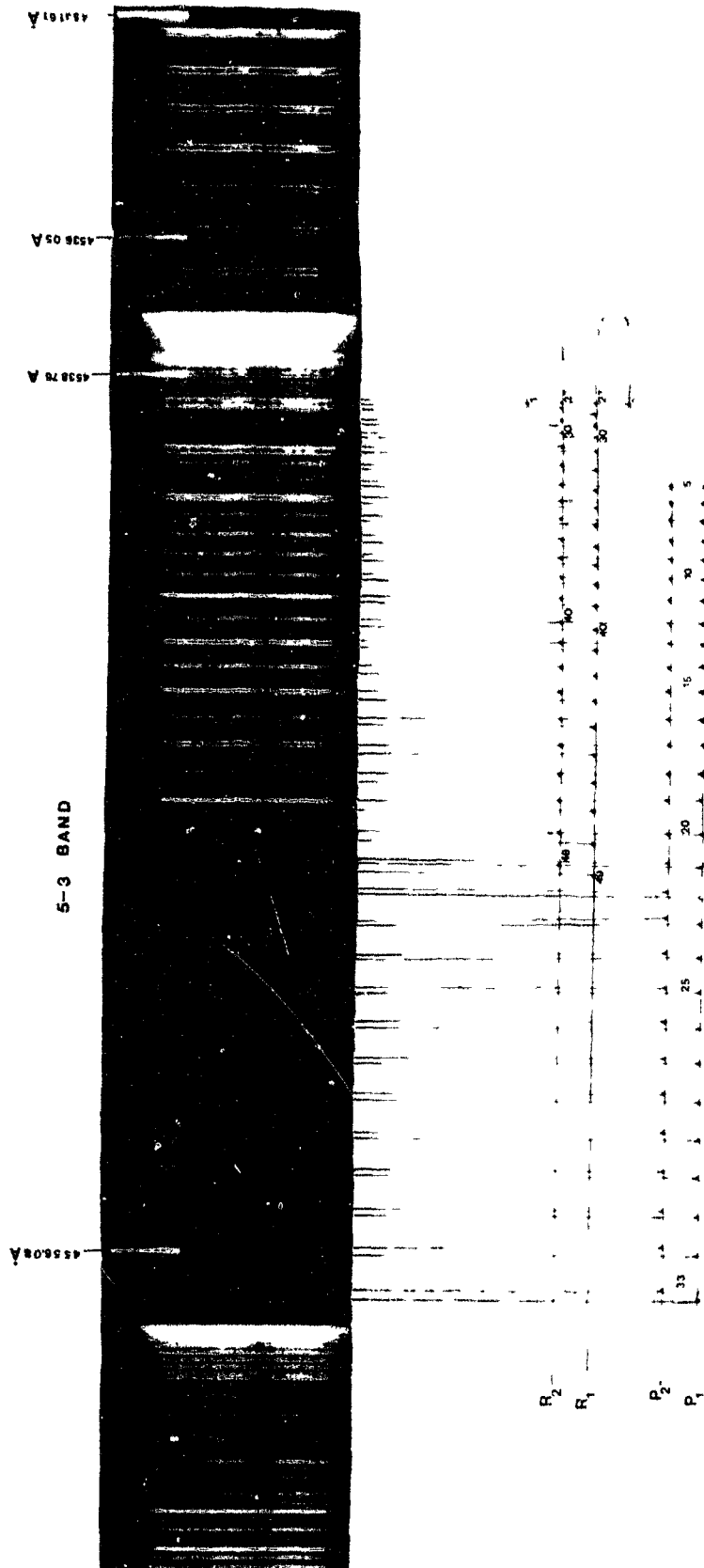
Figure 3.3



For many of the photographed bands with low v' or v'' ,⁴⁷ combination differences agreed with the constants determined by Lagerqvist et al. (18). Preliminary fits of these bands provided approximate constants for higher levels. Thus, the assignments for other bands were obtained progressively. In the case of blended lines, assignments were made in accord with intensity considerations. Because of the similar magnitude of the rotational constants of the X and B states, the observed vibrational sequences are quite compact; this causes considerable and unavoidable blending of lines, particularly within the latter members of the sequences. A portion of the $\Delta v = 2$ sequence is shown in Fig. 3.4. The rotational assignment of the 5-3 band is also indicated. From the spectrum it is obvious that the AlO B-X system is red-degraded with extensive overlapping of R-branch lines of low J near the band heads. As a consequence, it was not possible to make any assignments for the R branch to lines with $N < 27$.

Figure 3.4: A portion of the $\Delta v = 2$ sequence and the rotational assignment of the 5-3 band in the $B^2\Sigma^+ - X^2\Sigma^+$ system of AlO.

Figure 3.4



The problem of unresolved doublets at the beginning of each branch was solved by fitting these doublets to the average of the respective calculated branches. Since the components of each doublet have similar intensities, this procedure is quite satisfactory. It also represents a major improvement over the commonly employed alternatives of either inclusion of each blended line twice in the fit to the experimental data, or exclusion of the blended data.

The high correlation of the spin-rotation coupling constants did not allow determination of the absolute magnitude of γ in both electronic states. Therefore, it was necessary to constrain one of γ_v' or γ_v'' in order to obtain the magnitude of the other or the difference $\gamma_v' - \gamma_v''$ as in the present work. Approximate values for the constrained spin-rotational parameters γ_v'' were obtained from the work Mahieu et al. (32). Finally, the present analysis adopted the negative sign of γ' , first because the experimental method used by Mahieu et al. (32) was better for obtaining the absolute intensity of the spectral lines, as explained in the introduction of this chapter, and second, because the variance of the band-by-band reduction of the system was slightly smaller with γ_v' negative.

3.4 Results and Discussion

A computer program was written for direct least-squares fitting of the measured line positions of individual bands.

The program employs the well-known expressions for a $^2\Sigma^+$ state, as described in Chapter 2,

$$F_v(J,e) = B_v x(x-1) - D_v x^2(x-1)^2 + 1/2 \gamma_v(x-1) \quad (3.1)$$

$$F_v(J,f) = B_v x(x+1) - D_v x^2(x+1)^2 - 1/2 \gamma_v(x+1), \quad (3.2)$$

where $x=(J+1/2)$, and e and f denote the parity labellings, corresponding to the F_1 and F_2 components respectively.

Higher-order parameters ($H_v...$, $\gamma_{Dv}...$) can also be fitted, but these were not required for any of the bands. Several parameters associated with the least-squares fits are given in Table 3.1. For each band, the table gives the band origin, the number of lines fitted, the rotational extent and the standard deviation ($\hat{\sigma}$) of the fit. The values of ($\hat{\sigma}$) range from 0.015 to 0.058 cm^{-1} , a spread which is due to the variation of intensity, and hence measurement precision, of the measured bands and/or the degree of accidental blending of branches. Although the sequence with $\Delta v = -1$ is stronger than the other three measured sequences ($\Delta v = 3, 2, -2$), the vibrational spacings of the B and X electronic states cause considerable overlapping of the latter members of the $\Delta v = -1$ sequence. This effect is in accord with the standard deviations and the number of lines listed in the Table 3.1. Blending of lines was expected to be least troublesome in the sequence with $\Delta v = 3$; accordingly, more bands were analyzed within this sequence, even though it was the weakest one. In order to obtain the parameters given in Table 3.1, several preliminary least-squares fits were performed for each band with the purpose

of identifying and removing any lines with anomalously large⁵² residuals. Such lines were removed from subsequent fits. Systematic error that was not revealed in the individual band fits was identified in preliminary merge fits of the constants. Additional lines were then removed from the data set; the magnitudes of the residuals of such lines were nearly always considerably more than two standard deviations of the final fits.

Table 3.1: Individual Band Fits^a in the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ System of AlO 53

$v' - v''$	ν_0 (cm ⁻¹)	n	$N_{\max}$	$\hat{\sigma}$ (cm ⁻¹)	rms/ $\hat{\sigma}$
0 1	19669.792(6)	124	65	0.016	1.00
0 2	18718.405(8)	49	36	0.028	1.02
1 0 ^b		26	64	0.015	1.02
1 2	19581.512(6)	93	55	0.016	0.99
1 3	18644.137(7)	57	41	0.024	1.00
2 0	22354.059(12)	63	47	0.028	1.08
2 1 ^b		38	64	0.030	1.03
2 3	19499.921(6)	76	53	0.017	1.06
2 4	18576.598(11)	47	38	0.035	0.97
3 1	22237.069(9)	111	54	0.026	0.99
3 4	19425.054(8)	57	42	0.023	1.10
3 5	18515.829(14)	25	30	0.026	1.83
4 1	23078.060(11)	39	33	0.031	1.10
4 2	22126.759(8)	74	32	0.026	1.17
4 5	19357.057(20)	41	42	0.058	1.08
5 2	22960.453(10)	52	38	0.030	0.99
5 3	22023.177(9)	63	49	0.028	1.09
5 6	19295.479(17)	12	22	0.028	2.44
6 3	22849.526(12)	52	34	0.039	1.12
6 4	21926.325(9)	74	46	0.028	1.01
7 4	22745.338(13)	58	40	0.042	1.01
7 5	21836.299(10)	58	42	0.031	1.11
8 5	22647.985(20)	36	36	0.057	1.14
8 6	21752.905(15)	57	40	0.037	1.20
9 6	22557.230(20)	37	31	0.055	1.05

^a For each band fitted, n is the total number of fitted lines, $\hat{\sigma}$ is the standard deviation, and $N_{\max}$ is the maximum value of the quantum number N'' of the fitted lines. The band origins (ν_0) and estimated standard errors (in parentheses) were obtained from a subsequent merge fit (see text); rms/ $\hat{\sigma}$ represents the ratio of the root mean square of the residuals for lines calculated with merged parameters to the estimated standard deviation.

^b For these bands, the measurements were limited to the doublet separations, $R_1(N) - R_2(N)$ and $P_1(N) - P_2(N)$, and the fit led to a single estimated parameter, $\Delta\gamma_{v',v''}$.

As indicated in Table 3.1, special considerations were necessary in the fits for four of the bands. For the 3-5 and 5-6 bands, the rotational development did not permit the determination of all four parameters B' , D' , B'' , and D'' simultaneously. For the 3-5 band, the fit led to estimates of B'_3 , B''_5 , and the difference, $D'_3 - D''_5$; for the 5-6 band, only two effective rotational parameters, $B'_5 - B''_6$ and $D'_5 - D''_6$ were fitted. In the case of the 1-0 and 2-1 bands, the calibration spectrum of the plate was incomplete, and absolute wavenumbers of the lines were obtained necessarily by extrapolation. Despite systematic error in the absolute line positions, the doublet spacings in the P and R branches were obtained reliably, and were fitted as such.

The measured line positions of 25 bands in the $B \rightarrow X$ system of AlO have been employed in a least-squares fitting procedure to give 137 estimated parameters. As mentioned previously, except for the 3-5, 5-6, 1-0 and 2-1 bands, the individual band fits yielded six parameters, ν_0 , B'_v , D'_v , B''_v , D''_v , and $(\gamma'_v - \gamma''_v)$. For the 1-0 and 2-1 bands, only a single estimated parameter, $(\gamma'_v - \gamma''_v)$, is obtained from the spin-rotation splittings, $P_1(N) - P_2(N)$ and $R_1(N) - R_2(N)$. Several merges of the 137 estimated constants from the individual band fits have been performed in a stepwise fashion (4) to obtain the best single-valued estimates of the constants (X_v) for each level, and of "Dunham coefficients" ($X^{(i)}$) in polynomial representation of X_v .

$$X_v = \sum_{i=0}^m X^{(i)} (v + 1/2)^i. \quad (3.3)$$

In the first such merge (A), the reduced set of estimated parameters consists of 23 band origins, 20 parameters for the $B^2\Sigma^+$ state ($B_v, D_v; v = 0 - 9$), 14 parameters for the $X^2\Sigma^+$ state ($B_v, D_v; v = 0, 6$) and 25 unmerged ($\gamma_v' - \gamma_v''$) constants for individual bands.

The estimated variance of the merge (A) with $f = 137 - 82 = 55$ degrees of freedom is given by $(\hat{\sigma}_M)^2 = (1.255)^2$.

The constraints introduced in Merge A improved the vibrational dependence of the estimated values of ($\gamma_v' - \gamma_v''$) over those given by the individual band fits. The estimates of ($\gamma_v' - \gamma_v''$) for the 1-0 and 2-1 bands were unchanged as expected. The estimated values of ($\gamma_v' - \gamma_v''$) output from merge A are listed in the first column of Table 3.2.

It is immediately obvious that γ_v'' changes significantly with v'' , while γ_v' varies slowly with v' . For example, in the $v' = 4$ progression, ($\gamma_4' - \gamma_v''$) changes from -0.01536 to -0.03151 cm^{-1} over the range $v''=1$ to $v''=5$; but in the $v'' = 3$ progression only a small change in ($\gamma_v' - \gamma_3''$) occurs from -0.01809 to -0.01928 cm^{-1} in the range $v'=1$ to $v'=6$.

Unfortunately, the precision of the measured line positions only permitted the determination of the differences ($\gamma_v' - \gamma_v''$) from the individual bands. However, it was possible to determine the spin-rotation constants γ of the B and X states within an undetermined common constant, as follows. The ground state equilibrium parameter, γ_e'' , was

arbitrarily selected as the undetermined constant.

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Expressing γ_v'' as

$$\gamma_v'' = \gamma_{\bullet}'' + \gamma''^{(1)}(v'' + 1/2) + \dots \quad (3.4)$$

then

$$(\gamma_v' - \gamma_v'') = (\gamma_v' - \gamma_{\bullet}') - \gamma''^{(1)}(v'' + 1/2) + \dots \quad (3.5)$$

Table 3.2: Least-Squares Fitting of $(\gamma_v^I - \gamma_v^{II})$ (cm^{-1}), from 57
Individual Bands of AlO ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$)

$v' - v''$	Estimated ^{a)}	Fitted ^{b)}	Residual	Res/ σ	Ref. (32)
0 1	-0.01414	-0.01399	-0.00015	-2.0	-0.0136
0 2	-0.01636	-0.01573	-0.00063	-1.8	-0.0135
1 0	-0.01276	-0.01289	0.00013	2.1	-0.0119
1 2	-0.01569	-0.01587	0.00018	1.8	-0.0129
1 3	-0.01809	-0.01864	0.00055	2.1	-0.0154
2 0	-0.01400	-0.01303	-0.00097	-3.2	-0.0124
2 1	-0.01442	-0.01428	-0.00014	-1.2	-0.0135
2 3	-0.01856	-0.01878	0.00022	1.9	-0.0159
2 4	-0.02379	-0.02314	-0.00065	-1.5	
3 1	-0.01449	-0.01442	-0.00007	-0.5	-0.0137
3 4	-0.02371	-0.02328	-0.00043	-1.8	
3 5	-0.03019	-0.02979	-0.00040	-0.8	
4 1	-0.01536	-0.01456	-0.00080	-1.8	-0.0161
4 2	-0.01599	-0.01629	0.00030	1.6	
4 5	-0.03151	-0.02993	-0.00158	-2.5	
5 2	-0.01658	-0.01644	-0.00014	-0.4	
5 3	-0.01823	-0.01920	0.00097	3.4	
5 6	-0.03999	-0.03928	-0.00071	-0.8	
6 3	-0.01927	-0.01935	0.00008	0.2	
6 4	-0.02406	-0.02371	-0.00035	-1.5	
7 4	-0.02400	-0.02385	-0.00015	-0.3	
7 5	-0.03121	-0.03036	-0.00085	-2.7	
8 5	-0.03198	-0.03050	-0.00148	-1.9	
8 6	-0.03883	-0.03971	0.00088	2.3	
9 6	-0.03799	-0.03985	0.00206	2.1	

^a The estimated values for individual bands were given by the output of a fit (Merge A, see text) in which multiple estimates of B_v and D_v for the two states were reduced to single-valued estimates.

^b The fitted values are those given by the parameters (Table 3.3) of a fit (Merge B) which separates the spin-rotation coupling in the two states to within an undetermined value of γ_v^{II} .

The 25 estimated values of $(\gamma_v^I - \gamma_v^{II})$ can be reduced by least-squares to a fitted set of 10 parameters $(\gamma_v^I - \gamma_v^{II})$, $v' = 0-9$, and a small number of coefficients, $\gamma^{(1)}$, $\gamma^{(2)}$, $\gamma^{(3)}$, representing the vibrational dependence of γ_v^{II} . This fit was performed in merge B, with the fitted parameters given in Table 3.3. The estimated variance of this merge B with $f = 137 - 70 = 67$ degrees of freedom is given by $(\hat{\sigma}_M)^2 = (1.401)^2$. The success of the model used in merge B can be demonstrated by the small residuals between the input values and those given by the fitted parameters, as is also indicated in Table 3.2. It is worth mentioning that the residuals are larger on average by a factor of ~ 1.7 than the standard errors of the input values. The values of B_v and D_v for the two states given in Table 3.3 are considered the best single-valued estimates which the data can provide. A further reduction in the number of parameters was obtained in merge C which was performed by adopting Eq. (3.3) for the rotational constants of both states, as well as of $(\gamma_v^I - \gamma_v^{II})$. The order of the expansion required for each constant was determined by performing fits to increasingly higher-order until the standard deviation of the fitted coefficient $(X^{(1)})$ was larger than its magnitude. The output of merge C consisted of the 16 Dunham parameters listed in Table 3.4 and 23 new estimates of the band origins, listed in Table 3.1. The variance of the equivalent single-step merge from the constants of the individual bands to the parameters of merge C was $(\hat{\sigma}_M)^2 = (1.829)^2$ with

$$f = 137 - 39 = 98 \text{ degrees of freedom.}$$

Table 3.3: Merged Parameters^a (cm⁻¹) for the X²Σ⁺ and B²Σ⁺ States of AlO

v	B ² Σ ⁺			X ² Σ ⁺	
	B _v	10 ⁶ D _v	-10 ² (γ' _v -γ'' _e)	B _v	10 ⁶ D _v
9	0.56267(22)	0.98(20)	1.07(16)		
8	0.567008(115)	1.317(73)	1.211(95)		
7	0.571067(65)	1.174(30)	1.365(52)		
6	0.575437(60)	1.201(25)	1.343(38)	0.603547(130)	1.442(85)
5	0.579662(55)	1.145(19)	1.265(40)	0.609343(55)	1.250(19)
4	0.584132(56)	1.176(18)	1.291(36)	0.615285(56)	1.222(20)
3	0.588482(53)	1.164(14)	1.288(31)	0.621103(56)	1.170(18)
2	0.592953(58)	1.180(20)	1.269(27)	0.626928(53)	1.136(16)
1	0.597389(55)	1.156(17)	1.224(20)	0.632775(54)	1.140(14)
0	0.601936(51)	1.1834(134)	1.248(31)	0.638576(67)	1.133(25)

^a Values in parentheses are estimated standard errors given by $\sigma_M(v_{ii})^{1/2}$, in units of the last significant figure of the corresponding constant. The ground state spin-rotation constant varies with v'' according to $\gamma''_v - \gamma''_e = 1.20(38) \times 10^{-3}(v'' + 1/2) - 2.1(15) \times 10^{-4}(v'' + 1/2)^2 + 1.03(18) \times 10^{-4}(v'' + 1/2)^3$.

Table 3.4: Merged Dunham Coefficients^a (cm⁻¹) for the X²Σ⁺ ⁶¹
and B²Σ⁺ States of AlO

		B	D	$\gamma - \gamma''$
B ² Σ ⁺	X(0)	6.04160(64)x10 ⁻¹	1.1739(162)x10 ⁻⁶	-1.206(24)x10 ⁻²
	X(1)	-4.5338(90)x10 ⁻³	-4.70(140)x10 ⁻⁹	-1.42(51)x10 ⁻⁴
	X(2)	1.11(24)x10 ⁻⁵		
	X(3)	6.1(22)x10 ⁻⁷		
X ² Σ ⁺	X(0)	6.41369(70)x10 ⁻¹	1.099(19)x10 ⁻⁶	
	X(1)	-5.7302(114)x10 ⁻³	1.83(24)x10 ⁻⁸	1.29(34)x10 ⁻³
	X(2)	-1.915(160)x ⁻⁵		-1.73(136)x10 ⁻⁴
	X(3)			9.23(148)x10 ⁻⁵

^a Values in parentheses are estimated standard errors given by $\sigma_M (V_{ii})^{1/2}$ in units of the last significant figure of the corresponding constant.

Table 3.5: Calculated Line Positions and Residuals for the⁶²
B → X System of AlO

All data are in units of wavenumbers (cm^{-1}). Lines flagged with * were excluded from the final least-squares fitting procedure. The columns labelled "Res" are the residuals defined by

$$\text{Res} = \text{observed position} - \text{calculated position}$$

Unresolved $P_1(N)$ and $P_2(N)$ or $R_1(N)$ and $R_2(N)$ blends are listed between the corresponding branches.

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 0 - 1 BAND OF AlO ($\text{B}^2\Sigma - \text{X}^2\Sigma$)

N	P_2		P_1		R_2		R_1	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					19671.008		19670.989	
1		19668.529			19672.157		19672.124	
2		19667.202	-0.039*		19673.244		19673.197	
3		19665.813	-0.039*		19674.270		19674.209	
4		19664.363	-0.029		19675.234		19675.159	
5		19662.851	0.006		19676.136		19676.047	
6		19661.278	0.030		19676.976		19676.873	
7		19659.643	0.001		19677.754		19677.637	
8		19657.946	-0.005		19678.470		19678.339	
9		19656.188	0.006		19679.125		19678.980	
10		19654.369	0.001		19679.717		19679.558	
11		19652.488	0.007		19680.247		19680.074	
12		19650.546	-0.008		19680.716		19680.529	
13	19648.630	0.018	19648.454	0.024	19681.122		19680.921	
14	19646.572	-0.020	19646.381	0.007	19681.466		19681.251	
15	19644.453	0.007	19644.248	-0.026	19681.747		19681.518	
16	19642.272	0.011	19642.053	0.015	19681.967		19681.724	
17	19640.030	0.010	19639.797	-0.009	19682.124		19681.867	
18	19637.726	0.013	19637.479	-0.038	19682.219		19681.948	
19	19635.361	-0.015	19635.100	-0.018	19682.251		19681.966	
20	19632.935	0.016	19632.660	-0.009	19682.221		19681.922	
21	19630.447	0.020	19630.158	-0.020	19682.129		19681.816	
22	19627.898	0.009	19627.595	-0.013	19681.974		19681.647	
23	19625.288	-0.006	19624.971	-0.003	19681.756		19681.415	
24	19622.616	0.012	19622.286	-0.015	19681.476		19681.121	
25	19619.883	0.011	19619.539	-0.005	19681.133		19680.764	
26	19617.089	0.002	19616.730	-0.012	19680.728		19680.345	
27	19614.234	0.011	19613.861	-0.004	19680.259		19679.862	
28	19611.317	0.009	19610.930	-0.000	19679.728		19679.317	
29	19608.339	0.015	19607.938	-0.010	19679.134		19678.709	
30	19605.299	-0.001	19604.884	0.013	19678.476	-0.042*	19678.037	0.004
31	19602.198	-0.002	19601.770	0.003	19677.756	-0.056*	19677.303	-0.017
32	19599.036	0.019	19598.593	-0.002	19676.973	-0.019*	19676.506	0.012
33	19595.813	0.015	19595.356	-0.003	19676.126	-0.030*	19675.645	0.019
34	19592.528	0.118*	19592.057	-0.036	19675.216	0.008*	19674.721	0.022
35	19589.182	0.111*	19588.697	-0.073	19674.243	0.036*	19673.734	0.007
36	19585.774		19585.275		19673.207	0.019*	19672.684	0.017
37	19582.305	-0.006	19581.792	0.001	19672.107	0.009*	19671.570	0.013
38	19578.775	0.025	19578.248	-0.026	19670.944	0.065*	19670.393	0.011
39	19575.183		19574.642		19669.717	-0.019	19669.152	-0.008
40	19571.530	0.001	19570.975	0.028	19668.426	0.036	19667.847	0.008
41	19567.815	0.071*	19567.247	0.016	19667.072	0.091*	19666.479	0.006
42	19564.039	-0.001	19563.457	0.010	19665.654	0.120*	19665.047	-0.013
43	19560.202	-0.021	19559.605	0.010	19664.172	0.162*	19663.551	-0.002
44	19556.303	0.083*	19555.692	0.021	19662.626	0.231*	19661.991	-0.004
45	19552.343	-0.013	19551.718	0.013	19661.017	0.051	19660.368	0.001
46	19548.321	-0.012	19547.682		19659.343	-0.026	19658.680	-0.010
47	19544.237	0.007	19543.585	-0.012	19657.605	-0.028	19656.928	-0.020
48	19540.092		19539.426	-0.013	19655.803	-0.014	19655.112	0.001
49	19535.886	-0.006	19535.205		19653.936	-0.015	19653.231	0.010
50	19531.618	0.007	19530.920	0.024	19652.005	0.003	19651.286	-0.017
51	19527.288		19526.579		19650.010	-0.005	19649.277	-0.039
52	19522.896	0.020	19522.174	-0.014	19647.950	-0.011	19647.203	-0.015
53	19518.443		19517.706		19645.825	-0.008	19645.064	-0.033
54	19513.928	0.016	19513.178		19643.636	0.015	19642.861	0.026
55	19509.352		19508.587		19641.382	-0.004	19640.593	-0.010
56	19504.713		19503.935		19639.063	0.010	19638.260	-0.024
57	19500.013		19499.220		19636.679	0.003	19635.862	0.010
58	19495.251		19494.444		19634.230	0.013	19633.399	-0.011
59	19490.427		19489.606		19631.716	0.013	19630.871	0.044*
60	19485.541		19484.707		19629.136	0.066*	19628.277	
61	19480.593		19479.745		19626.491	0.022	19625.619	
62	19475.584		19474.721		19623.781	0.066*	19622.894	
63	19470.512		19469.635		19621.005	0.027	19620.105	
64	19465.378		19464.488		19618.164	0.105*	19617.249	
65	19460.182		19459.278		19615.257	-0.010	19614.328	
66	19454.924		19454.006		19612.284		19611.341	
67	19449.604		19448.671		19609.245		19608.288	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE O - 2 BAND OF AlO ($B^2\Sigma - X^2\Sigma$)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					18719.622		18719.602	
1		18717.154			18720.784		18720.748	
2		18715.851			18721.895		18721.844	
3		18714.497	-0.003		18722.956		18722.889	
4		18713.093	-0.001		18723.967		18723.885	
5		18711.639	0.032		18724.928		18724.830	
6		18710.135	-0.014		18725.839		18725.725	
7		18708.582	-0.020		18726.700		18726.569	
8		18706.978	-0.035		18727.510		18727.364	
9		18705.325	0.029		18728.269		18728.108	
10		18703.622	-0.007		18728.979		18728.802	
11		18701.869	-0.036		18729.638		18729.445	
12		18700.066	-0.038		18730.246		18730.038	
13		18698.213	0.011		18730.805		18730.580	
14		18696.311	-0.031		18731.312		18731.072	
15		18694.359	-0.006		18731.769		18731.513	
16	18692.481		18692.233		18732.176		18731.904	
17	18690.437	0.069*	18690.174	0.026	18732.532		18732.244	
18	18688.344	-0.013	18688.065	-0.024	18732.837		18732.534	
19	18686.201	0.042	18685.906	0.025	18733.091		18732.772	
20	18684.008	0.038	18683.698	-0.044	18733.295		18732.960	
21	18681.766	0.037	18681.440	-0.042	18733.448		18733.098	
22	18679.474	0.042	18679.133	-0.042	18733.550		18733.184	
23	18677.133	0.037	18676.775	0.002	18733.601		18733.220	
24	18674.742	0.035	18674.369	0.012	18733.602		18733.204	
25	18672.301	-0.016	18671.912	-0.022	18733.551		18733.138	
26	18669.811	-0.001	18669.407	-0.022	18733.450		18733.021	
27	18667.271	0.012	18666.851	0.002	18733.297		18732.852	
28	18664.682	0.009	18664.246	-0.023	18733.093		18732.633	
29	18662.044	-0.035	18661.592	-0.060	18732.839		18732.362	
30	18659.355	0.042	18658.888	0.021	18732.533		18732.041	
31	18656.618		18656.134	0.027	18732.175		18731.668	
32	18653.830	0.022	18653.331	-0.105*	18731.767		18731.244	
33	18650.993	0.048	18650.479		18731.307		18730.768	
34	18648.107	-0.025	18647.577	0.004	18730.796		18730.241	
35	18645.172	-0.016	18644.625	0.014	18730.233		18729.663	
36	18642.186	0.032	18641.624	0.024	18729.619		18729.033	
37	18639.152		18638.574		18728.954		18728.352	
38	18636.068		18635.474		18728.236		18727.619	
39	18632.934		18632.325		18727.468		18726.834	
40	18629.751		18629.126		18726.647		18725.998	
41	18626.518		18625.878		18725.775		18725.110	
42	18623.237		18622.580		18724.851		18724.171	
43	18619.905		18619.233		18723.875		18723.179	
44	18616.524		18615.837		18722.848		18722.136	
45	18613.094		18612.391		18721.768		18721.040	
46	18609.614		18608.895		18720.636		18719.893	
47	18606.085		18605.350		18719.453		18718.694	
48	18602.507		18601.756		18718.217		18717.442	
49	18598.878		18598.112		18716.929		18716.138	
50	18595.201		18594.419		18715.589		18714.782	
51	18591.474		18590.676		18714.196		18713.374	
52	18587.698		18586.884		18712.751		18711.914	
53	18583.872		18583.042		18711.254		18710.400	
54	18579.996		18579.151		18709.704		18708.835	

CALCULATED SPIN SPLITTINGS AND RESIDUALS FOR THE 1 - 0 BAND OF AlO ($B^2\Sigma - X^2\Sigma$)

N	$P_2(N) - P_1(N)$		$R_2(N) - R_1(N)$	
	Calc	Res	Calc	Res
0			0.019	
1	0.007		0.032	
2	0.020		0.044	
3	0.033		0.057	
4	0.046		0.070	
5	0.059		0.083	
6	0.072		0.096	
7	0.084		0.109	
8	0.097		0.122	
9	0.110		0.135	
10	0.123		0.148	
11	0.136		0.160	
12	0.149		0.173	
13	0.162		0.186	
14	0.175		0.199	
15	0.188		0.212	
16	0.200		0.225	
17	0.213		0.238	
18	0.226		0.251	
19	0.239		0.264	
20	0.252		0.277	
21	0.265		0.289	
22	0.278		0.302	
23	0.291	-0.011	0.315	
24	0.304	-0.003	0.328	
25	0.316	-0.005	0.341	
26	0.329	-0.022	0.354	
27	0.342	-0.000	0.367	
28	0.355	-0.018	0.380	
29	0.368	0.031	0.392	
30	0.381	0.020	0.405	
31	0.394	0.001	0.418	
32	0.407	0.011	0.431	
33	0.419	-0.011	0.444	
34	0.432	0.016	0.457	
35	0.445	0.001	0.470	
36	0.458	0.006	0.483	
37	0.471		0.496	
38	0.484		0.509	
39	0.497		0.521	
40	0.510		0.534	
41	0.523		0.547	
42	0.536		0.560	
43	0.548		0.573	
44	0.561		0.586	
45	0.574		0.599	
46	0.587		0.612	
47	0.600		0.625	
48	0.613		0.637	
49	0.626		0.650	
50	0.639		0.663	
51	0.652		0.676	
52	0.665		0.689	0.004
53	0.677		0.702	-0.018
54	0.690		0.715	-0.027
55	0.703		0.728	-0.004
56	0.716		0.741	0.014
57	0.729		0.753	-0.012
58	0.742		0.766	-0.017
59	0.755		0.779	0.043*
60	0.768		0.792	-0.021
61	0.781		0.805	-0.002
62	0.793		0.818	-0.015*
63	0.806		0.831	-0.030*
64	0.819		0.844	-0.040*

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 1 - 2 BAND OF AlO ($\text{B}^2\Sigma - \text{X}^2\Sigma$)

N	P_2		P_1		R_2		R_1	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					19582.721		19582.700	
1		19580.262			19583.864		19583.828	
2		19578.949			19584.949		19584.897	
3		19577.577	-0.125*		19585.974		19585.906	
4		19576.146	-0.066*		19586.940		19586.856	
5		19574.656	-0.010		19587.847		19587.747	
6		19573.107	-0.004		19588.695		19588.579	
7		19371.500	0.031		19589.483		19589.352	
8		19569.833	0.001		19590.212		19590.065	
9		19568.108	0.012		19590.882		19590.719	
10		19566.323	-0.001		19591.492		19591.313	
11	19564.565	-0.104*	19564.395	-0.357*	19592.043		19591.848	
12	19562.671	-0.013	19562.485	-0.068*	19592.534		19592.324	
13	19560.718	0.008	19560.516	0.020	19592.966		19592.740	
14	19558.707	0.004	19558.489	-0.006	19593.339		19593.096	
15	19556.636	0.006	19556.403	-0.017	19593.652		19593.393	
16	19554.507	-0.003	19554.258	-0.014	19593.905		19593.631	
17	19552.319	0.011	19552.054	0.002	19594.099		19593.809	
18	19550.073	-0.007	19549.792	-0.019	19594.233		19593.927	
19	19547.768	0.016	19547.471	-0.001	19594.307		19593.985	
20	19545.404	0.008	19545.091	0.007	19594.322		19593.984	
21	19542.982	0.011	19542.653	-0.010	19594.276		19593.923	
22	19540.501	-0.017	19540.156	-0.036	19594.171		19593.802	
23	19537.961	-0.014	19537.601	-0.014	19594.007		19593.621	
24	19535.363	-0.017	19534.987	-0.012	19593.782		19593.381	
25	19532.705	-0.011	19532.314	-0.016	19593.497		19593.080	
26	19529.991	-0.004	19529.583	0.000	19593.152		19592.720	
27	19527.217	0.023	19526.793	0.021	19592.748		19592.299	
28	19524.375	-0.008	19523.945	-0.015	19592.283		19591.819	
29	19521.494	0.023	19521.038	0.010	19591.758		19591.278	
30	19518.545	-0.026	19518.073	-0.001	19591.173		19590.677	
31	19515.537	0.015	19515.050	0.005	19590.528		19590.016	
32	19512.471	0.134*	19511.968	-0.015	19589.823		19589.295	
33	19509.346	0.032*	19508.827	-0.010	19589.057		19588.513	
34	19506.163	-0.012	19505.628	0.039	19588.231		19587.671	
35	19502.922	-0.002	19502.371	0.006	19587.345		19586.769	
36	19499.622	-0.016	19499.055	0.058*	19586.398		19585.807	
37	19496.263	-0.006	19495.680	0.020	19585.391		19584.784	
38	19492.846	-0.015	19492.248	0.003	19584.323	0.003	19583.700	0.028
39	19489.371	-0.004	19488.757	0.007	19583.195	-0.018	19582.556	0.030
40	19485.838	0.010	19485.207	-0.161*	19582.006	-0.213*	19581.351	-0.021
41	19482.246	0.001	19481.599	-0.197*	19580.757	0.001	19580.086	0.011
42	19478.595	-0.004	19477.933	0.008	19579.446	-0.013	19578.760	0.040*
43	19474.887	-0.030	19474.209	-0.001	19578.075		19577.373	
44	19471.119	-0.060*	19470.426	0.035	19576.644	0.017	19575.925	
45	19467.294		19466.584	-0.029*	19575.151	0.027	19574.417	
46	19463.410	-0.031	19462.685	0.014	19573.597	0.019	19572.847	
47	19459.468	-0.050*	19458.727	-0.014	19571.983	-0.005	19571.217	
48	19455.468	0.017	19454.710		19570.307	0.018	19569.526	
49	19451.409	-0.006	19450.636	0.013	19568.571	0.007	19567.773	
50	19447.292	-0.004	19446.503	-0.012	19566.773	-0.026	19565.960	
51	19443.116	0.013	19442.311	-0.017	19564.914		19564.085	
52	19438.882		19438.061		19562.994		19562.149	
53	19434.590	0.005	19433.753		19561.013		19560.152	
54	19430.240	0.001	19429.387	0.003	19558.970		19558.093	
55	19425.831		19424.962	-0.039*	19556.866		19555.973	
56	19421.364		19420.479		19554.701		19553.792	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 1 - 3 BAND OF A10 (B2 Σ - X2 Σ)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					18645.347		18645.325	
1		18642.899			18646.504		18646.463	
2		18641.610			18647.613		18647.554	
3		18640.273			18648.675		18648.597	
4		18638.889			18649.689		18649.593	
5		18637.457	-0.003		18650.656		18650.541	
6		18635.979	0.011		18651.575		18651.441	
7		18634.453	-0.008		18652.446		18652.294	
8		18632.880	0.004		18653.270		18653.100	
9		18631.259	0.002		18654.047		18653.857	
10		18629.592	0.048		18654.775		18654.567	
11		18627.878	-0.001		18655.456		18655.230	
12		18626.116	-0.035		18656.090		18655.844	
13		18624.307	-0.030		18656.675		18656.411	
14	18622.581	-0.035	18622.323	-0.004	18657.213		18656.930	
15	18620.687	-0.024	18620.411	0.029	18657.703		18657.401	
16	18618.747	0.002	18618.452	0.002	18658.145		18657.825	
17	18616.760	-0.004	18616.446	-0.023	18658.539		18658.200	
18	18614.725	0.031	18614.393	0.011	18658.885		18658.528	
19	18612.644	0.042	18612.293	0.017	18659.183		18658.808	
20	18610.516	0.008	18610.147	-0.024	18659.434		18659.039	
21	18608.342	-0.007	18607.953	0.006	18659.636		18659.223	
22	18606.120	-0.014	18605.713	-0.012	18659.791		18659.359	
23	18603.852	-0.033	18603.426	-0.026	18659.897		18659.447	
24	18601.536	-0.016	18601.092	0.013	18659.955		18659.486	
25	18599.174	0.007	18598.711	0.044	18659.965		18659.478	
26	18596.766	0.023	18596.284	-0.020	18659.927		18659.421	
27	18594.311	0.057*	18593.810	-0.012	18659.841		18659.316	
28	18591.809	-0.008	18591.290	0.035	18659.707		18659.163	
29	18589.260	0.056*	18588.722	-0.046	18659.524		18658.962	
30	18586.665	-0.033	18586.109	0.043	18659.293		18658.712	
31	18584.023	-0.038	18583.448	0.021	18659.014		18658.414	
32	18581.335	0.020	18580.741	-0.031	18658.686		18658.068	
33	18578.600	-0.002	18577.988	0.001	18658.310		18657.674	
34	18575.818	-0.020	18575.187	-0.010	18657.886		18657.231	
35	18572.990	0.003	18572.341	0.008	18657.414		18656.740	
36	18570.116	-0.024	18569.448	0.030	18656.892		18656.200	
37	18567.195	-0.029	18566.509	0.023	18656.323		18655.612	
38	18564.228		18563.523		18655.705		18654.975	
39	18561.215		18560.491		18655.038		18654.290	
40	18558.155		18557.412		18654.323		18653.556	
41	18555.048		18554.287		18653.559		18652.773	
42	18551.896	0.013	18551.116	0.036	18652.747		18651.942	
43	18548.697		18547.898		18651.886		18651.063	
44	18545.452		18544.635		18650.976		18650.134	
45	18542.160		18541.325		18650.017		18649.157	
46	18538.823		18537.969		18649.010		18648.131	
47	18535.439		18534.566		18647.954		18647.056	
48	18532.009		18531.118		18646.849		18645.933	
49	18528.533		18527.623		18645.695		18644.761	
50	18525.011		18524.032		18644.493		18643.539	
51	18521.443		18520.495		18643.241		18642.269	
52	18517.829		18516.862		18641.941		18640.950	
53	18514.168		18513.184		18640.591		18639.582	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 2 - 0 BAND OF A10 (B2E - X2E)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					22355.257		22355.238	
1		22352.785			22356.358		22356.326	
2		22351.417			22357.368		22357.323	
3		22349.957			22358.287		22358.229	
4		22348.407			22359.114		22359.043	
5		22346.765	0.050*		22359.850		22359.766	
6		22345.033	-0.002		22360.494		22360.397	
7		22343.209	0.057*		22361.047		22360.937	
8		22341.295	0.017		22361.509		22361.386	
9		22339.289	0.024		22361.879		22361.743	
10		22337.192	0.033		22362.158		22362.009	
11		22335.005	0.023		22362.345		22362.183	
12		22332.726	-0.029		22362.441		22362.265	
13		22330.356	0.015		22362.444		22362.256	
14		22327.896	0.010		22362.357		22362.155	
15		22325.344	-0.007		22362.177		22361.963	
16		22322.702	0.007		22361.906		22361.678	
17		22319.969	-0.017		22361.542		22361.302	
18		22317.144	0.027		22361.087		22360.834	
19		22314.229	0.018		22360.540		22360.274	
20		22311.223	0.046		22359.901		22359.621	
21		22308.126	0.046		22359.170		22358.877	
22		22304.939	0.028		22358.347		22358.041	
23		22301.660	0.056		22357.431		22357.113	
24		22298.290	0.023		22356.424		22356.092	
25		22294.830	-0.012		22355.324		22354.979	
26		22291.278	-0.002			22353.953	-0.004	
27		22287.636	0.019			22352.662	0.036	
28	22284.082	-0.016	22283.723	-0.004	22351.470	-0.073*	22351.086	-0.019
29	22280.264	-0.024	22279.892	0.033	22350.000	0.014	22349.604	-0.028
30	22276.356	-0.027	22275.970	-0.015	22348.438	-0.027	22348.028	-0.032
31	22272.356	-0.005	22271.958	-0.043	22346.783	0.032	22346.361	-0.071
32	22268.265	0.023	22267.854	0.013	22345.036	-0.005*	22344.600	-0.019
33	22264.084	0.014	22263.660	-0.037	22343.196	0.070	22342.747	0.004
34	22259.811	0.045	22259.374	-0.003	22341.262	0.050*	22340.800	-0.053
35	22255.448	-0.043*	22254.997	-0.020	22339.236	0.077*	22338.761	-0.032
36	22250.993	-0.051*	22250.530	-0.042	22337.117	0.108*	22336.629	0.017
37	22246.448	0.002	22245.971		22334.905	0.123*	22334.404	-0.020
38	22241.811	0.045	22241.322		22332.600	0.097*	22332.086	-0.008
39	22237.083		22236.581		22330.201	0.170*	22329.674	-0.007
40	22232.264		22231.749		22327.709	0.197*	22327.169	0.078*
41	22227.354		22226.826		22325.124	0.213*	22324.571	-0.017
42	22222.353		22221.812		22322.445	0.264*	22321.879	0.037
43	22217.261		22216.706		22319.673		22319.094	-0.044
44	22212.077		22211.510		22316.807		22316.215	-0.050
45	22206.802		22206.222		22313.847		22313.242	0.029
46	22201.436		22200.843		22310.794		22310.175	0.063*
47	22195.979		22195.373		22307.647		22307.015	-0.037
48	22190.430		22189.811		22304.405		22303.761	
49	22184.790		22184.158		22301.070		22300.412	

CALCULATED SPIN SPLITTINGS AND RESIDUALS FOR THE 2 - 1 BAND OF AlO (B²Σ - X²Σ)

N	$P_2(N) - P_1(N)$		$R_2(N) - R_1(N)$	
	Calc	Res	Calc	Res
0			0.020	
1	0.009		0.034	
2	0.023		0.048	
3	0.038		0.062	
4	0.052		0.077	
5	0.066		0.091	
6	0.080		0.105	
7	0.095		0.119	
8	0.109		0.134	
9	0.123		0.148	
10	0.137		0.162	
11	0.152		0.177	
12	0.166		0.191	
13	0.180		0.205	
14	0.195		0.219	
15	0.209		0.234	
16	0.223		0.248	
17	0.238		0.262	
18	0.252		0.277	
19	0.266		0.291	
20	0.280		0.305	
21	0.295	-0.024	0.319	
22	0.309	-0.007	0.334	
23	0.323		0.348	
24	0.337	0.046	0.362	
25	0.352	0.063	0.376	
26	0.366	-0.009	0.391	
27	0.380	0.083*	0.405	
28	0.394	0.137*	0.419	0.062*
29	0.409	0.027	0.434	0.042
30	0.423	0.035	0.448	0.023
31	0.437	0.007	0.462	0.049
32	0.452	0.022	0.477	0.009
33	0.466	0.017	0.491	-0.020
34	0.480	0.047	0.505	0.156*
35	0.495	0.057	0.519	0.031
36	0.509		0.534	-0.037
37	0.523		0.548	0.020
38	0.537		0.562	-0.012
39	0.552		0.576	-0.043
40	0.566		0.591	0.021
41	0.580		0.605	-0.023
42	0.594		0.619	0.014
43	0.609		0.634	-0.081*
44	0.623		0.648	0.011
45	0.637		0.662	-0.071*
46	0.652		0.676	0.017
47	0.666		0.691	-0.200*
48	0.680		0.705	0.014
49	0.694		0.719	-0.077*
50	0.709		0.734	-0.041
51	0.723		0.748	-0.047
52	0.737		0.762	-0.027
53	0.752		0.776	0.003
54	0.766		0.791	-0.124*
55	0.780		0.805	0.004
56	0.794		0.819	-0.094*
57	0.809		0.833	-0.076*
58	0.823		0.848	0.009
59	0.837		0.862	-0.147*
60	0.851		0.876	-0.052
61	0.866		0.891	-0.003
62	0.880		0.905	-0.169*
63	0.894		0.919	-0.010
64	0.909		0.933	0.036

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 2 - 3 BAND OF A10 (B² Σ - X² Σ)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					19501.123		19501.101	
1		19498.684			19502.262		19502.222	
2		19497.386			19503.348		19503.285	
3		19496.031			19504.370		19504.292	
4		19494.620	-0.009		19505.340		19505.243	
5		19493.153	0.058*		19506.253		19506.137	
6		19491.629	0.012		19507.110		19506.975	
7		19490.050	0.004		19507.909		19507.756	
8		19488.414	-0.012		19508.653		19508.481	
9		19486.722	-0.025		19509.340		19509.149	
10		19484.974	0.072*		19509.970		19509.760	
11		19483.170	0.023		19510.543		19510.315	
12		19481.310	0.092*		19511.060		19510.813	
13		19479.393	-0.009		19511.520		19511.254	
14	19477.551	-0.046*	19477.291	-0.017	19511.924		19511.639	
15	19475.533	-0.005	19475.254	-0.051*	19512.270		19511.967	
16	19473.458	-0.021	19473.160	-0.023	19512.560		19512.238	
17	19471.327	-0.021	19471.011	0.048*	19512.793		19512.452	
18	19469.141	0.014	19468.806	-0.049*	19512.969		19512.609	
19	19466.899	0.005	19466.545	0.010	19513.088		19512.710	
20	19464.601	0.009	19464.228	-0.003	19513.151		19512.753	
21	19462.247	-0.001	19461.855	0.017	19513.156		19512.740	
22	19459.837	0.027	19459.427	-0.009	19513.105		19512.670	
23	19457.372	0.004	19456.943	0.008	19512.996		19512.543	
24	19454.851	-0.042	19454.403	0.014	19512.831		19512.358	
25	19452.274	-0.005	19451.807	0.063*	19512.608		19512.117	
26	19449.642	0.001	19449.156	0.013	19512.329		19511.819	
27	19446.954	-0.007	19446.450	0.041	19511.992		19511.463	
28	19444.210	0.003	19443.687	0.002	19511.598		19511.050	
29	19441.411	-0.010	19440.869	-0.010	19511.147		19510.581	
30	19438.556	0.228*	19437.996	0.128*	19510.639		19510.054	
31	19435.646	0.070*	19435.067	0.062*	19510.074		19509.470	
32	19432.681	0.013	19432.083	-0.066*	19509.451		19508.828	
33	19429.659	0.020	19429.043	-0.011	19508.771		19508.130	
34	19426.583	-0.027	19425.948	0.014	19508.034		19507.374	
35	19423.451	0.005	19422.797	-0.028	19507.240		19506.561	
36	19420.264	0.011	19419.591	0.030	19506.388		19505.690	
37	19417.021	-0.104*	19416.330	0.001	19505.479		19504.762	
38	19413.724	-0.002	19413.013	0.013	19504.512		19503.777	
39	19410.371	0.022	19409.641	-0.001	19503.489		19502.734	
40	19406.962	-0.146*	19406.214	-0.001	19502.407	-0.030	19501.634	0.022
41	19403.499	0.017	19402.732	0.050*	19501.268	-0.051*	19500.477	0.031
42	19399.980	-0.012	19399.194	0.008	19500.072	0.001	19499.262	-0.149*
43	19396.406	0.002	19395.602	-0.019	19498.818		19497.989	0.017
44	19392.777	0.013	19391.954	0.004	19497.507	-0.099*	19496.659	0.018
45	19389.093	0.028	19388.251	0.059*	19496.138	0.119*	19495.271	-0.023
46	19385.354	0.029*	19384.493	-0.012	19494.711		19493.826	-0.022
47	19381.560	-0.033	19380.680	-0.076*	19493.227	-0.016	19492.323	-0.072*
48	19377.711	-0.010	19376.812	0.031	19491.685	-0.044*	19490.762	-0.017
49	19373.807		19372.889		19490.086	-0.032*	19489.144	
50	19369.847	-0.034	19368.911	-0.008	19488.429	-0.027*	19487.468	
51	19365.833	-0.018	19364.879	-0.073*	19486.714	-0.017*	19485.734	
52	19361.765	0.061*	19360.791	-0.012	19484.941	0.105*	19483.943	
53	19357.641	-0.027	19356.648		19483.111		19482.093	
54	19353.462		19352.451		19481.222		19480.186	
55	19349.229		19348.199		19479.276		19478.222	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 2 - 4 BAND OF A10 (B²Σ - X²Σ)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					18577.801		18577.777	
1		18575.373			18578.954		18578.907	
2		18574.098			18580.062		18579.992	
3		18572.779			18581.126		18581.032	
4		18571.415			18582.144		18582.028	
5		18570.006	0.086*		18583.118		18582.979	
6		18568.553	0.027		18584.048		18583.885	
7		18567.056	0.110*		18584.932		18584.746	
8		18565.514	0.005		18585.772		18585.563	
9		18563.928	0.107*		18586.567		18586.335	
10		18562.298	0.019		18587.317		18587.062	
11		18560.624	-0.040		18588.022		18587.744	
12		18558.905	-0.016		18588.683		18588.381	
13		18557.142	0.077		18589.298		18588.973	
14	18555.496	0.013	18555.173	-0.112*	18589.868		18589.520	
15	18553.656	0.028	18553.310	-0.004	18590.394		18590.023	
16	18551.772	0.068	18551.403	0.016	18590.875		18590.480	
17	18549.844	0.024	18549.452	-0.044	18591.310		18590.893	
18	18547.872	-0.005	18547.457	-0.011	18591.701		18591.260	
19	18545.856	-0.003	18545.417	-0.051	18592.046		18591.583	
20	18543.796	0.033	18543.334	-0.054	18592.347		18591.860	
21	18541.692	-0.056	18541.207	0.003	18592.602		18592.092	
22	18539.545	0.105*	18539.036	-0.036	18592.812		18592.279	
23	18537.353	0.008	18536.822	0.018	18592.978		18592.421	
24	18535.118	0.032	18534.563	-0.044	18593.098		18592.518	
25	18532.838		18532.261		18593.173		18592.570	
26	18530.515	-0.030	18529.915	0.038	18593.202		18592.577	
27	18528.149	-0.028	18527.525	0.009	18593.187		18592.538	
28	18525.738	-0.023*	18525.091	-0.052	18593.127		18592.455	
29	18523.285	-0.048*	18522.614	0.009	18593.021		18592.326	
30	18520.787	0.024	18520.094	0.058	18592.870		18592.152	
31	18518.246	0.038	18517.529	0.019	18592.674		18591.932	
32	18515.662	-0.024	18514.922	-0.046	18592.432		18591.668	
33	18513.034	0.006	18512.271	-0.042	18592.145		18591.358	
34	18510.362	0.002	18509.576	-0.056	18591.813		18591.003	
35	18507.648	-0.014	18506.838		18591.436		18590.602	
36	18504.890	0.019	18504.057	0.042	18591.014		18590.157	
37	18502.088		18501.233	-0.027	18590.546		18589.666	
38	18499.244		18498.365	-0.018	18590.033		18589.129	
39	18496.356		18495.454		18589.474		18588.548	
40	18493.425		18492.501		18588.870		18587.921	
41	18490.452		18489.504		18588.221		18587.248	
42	18487.435		18486.463		18587.527		18586.531	
43	18484.375		18483.380		18586.787		18585.768	
44	18481.272		18480.254		18586.002		18584.959	
45	18478.126		18477.086		18585.171		18584.106	
46	18474.938		18473.374		18584.295		18583.207	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 3 - 1 BAND OF AlO ($B^2\Sigma - X^2\Sigma$)

N	P_2		P_1		R_2		R_1	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					22238.261		22238.241	
1		22235.808			22239.356		22239.322	
2		22234.454			22240.363		22240.315	
3		22233.012			22241.281		22241.218	
4		22231.481	0.068*		22242.111		22242.034	
5		22229.862	0.022		22242.852		22242.760	
6		22228.154	0.010		22243.504		22243.398	
7		22226.358	-0.023		22244.068		22243.947	
8		22224.473	-0.016		22244.542		22244.407	
9		22222.500	-0.014		22244.928		22244.778	
10		22220.439	-0.007		22245.225		22245.061	
11		22218.289	-0.022		22245.433		22245.254	
12		22216.051	-0.002		22245.552		22245.359	
13		22213.725	-0.011		22245.582		22245.375	
14		22211.310	0.025		22245.523		22245.301	
15		22208.808	0.032		22245.375		22245.139	
16		22206.217	-0.005		22245.138		22244.888	
17		22203.537	0.032		22244.812		22244.547	
18		22200.770	0.022		22244.397		22244.117	
19		22197.915	-0.006		22243.892		22243.598	
20		22194.971	0.010		22243.298		22242.990	
21		22191.939	-0.011		22242.615		22242.292	
22		22188.819	-0.017		22241.843		22241.506	
23		22185.611	0.002		22240.981		22240.629	
24		22182.315	-0.012		22240.030	-0.040	22239.664	-0.030
25		22178.930	-0.000		22238.989	-0.046	22238.609	-0.021
26	22175.643	-0.089*	22175.273	0.012	22237.859	0.028	22237.464	-0.007
27	22172.089	0.020	22171.705	0.053	22236.639	-0.001	22236.230	0.003
28	22168.448	0.021	22168.049	-0.001	22235.329	0.056	22234.906	-0.049
29	22164.718	-0.003	22164.305	-0.020	22233.930	0.093*	22233.492	0.008
30	22160.901	-0.011	22160.473	0.007	22232.442	-0.082*	22231.989	-0.087*
31	22156.995	0.004	22156.553	-0.011	22230.863	0.018	22230.396	-0.013
32	22153.001	-0.031	22152.545	-0.012	22229.195	-0.006	22228.714	0.022
33	22148.920	-0.011	22148.449	-0.063	22227.437	-0.023	22226.941	-0.032
34	22144.750	-0.015	22144.265	0.001	22225.589	0.016	22225.078	0.002
35	22140.492	0.022	22139.993	-0.020	22223.650	-0.001	22223.126	-0.058
36	22136.146	-0.001	22135.632		22221.622	0.071*	22221.083	0.009
37	22131.712	0.012*	22131.184	-0.181*	22219.504	0.002	22218.951	-0.006
38	22127.190	0.028*	22126.648	0.042*	22217.296	-0.031	22216.728	-0.044
39	22122.580		22122.023		22214.997	0.009	22214.415	0.030
40	22117.882		22117.311	0.027	22212.609	0.029	22212.012	0.036
41	22113.096		22112.510		22210.130	0.004	22209.519	0.020
42	22108.222	-0.016	22107.622	-0.025	22207.560	0.011	22206.935	-0.032
43	22103.260	-0.047	22102.645	-0.005	22204.901	0.025	22204.261	-0.013
44	22098.210	0.011	22097.580	-0.039	22202.150	-0.026	22201.496	-0.030
45	22093.071	0.008	22092.428	0.025	22199.310	-0.001	22196.641	-0.010
46	22087.845		22087.187		22196.378	0.037	22195.695	0.087*
47	22082.530		22081.858		22193.356	-0.000	22192.659	0.034
48	22077.128	0.019	22076.441	0.036	22190.244	0.103*	22189.532	0.069*
49	22071.637	0.060	22070.936	-0.023	22187.040	-0.010	22186.314	0.044
50	22066.059		22065.343		22183.746		22183.005	
51	22060.392	-0.020	22059.662	-0.043	22180.361	-0.029	22179.605	0.055
52	22054.637	0.029	22053.892	0.006	22176.884	0.037	22176.115	-0.002
53	22048.794		22048.035		22173.317	-0.055*	22172.533	-0.001
54	22042.863	-0.042	22042.089	0.047	22169.659	-0.020	22168.860	-0.068*
55	22036.843		22036.056		22165.909		22165.096	
56	22030.736		22029.934		22162.069		22161.241	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 3 - 4 BAND OF A10 (B²Σ - X²Σ)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					19426.250		19426.225	
1	19423.841		19423.819		19427.385		19427.337	
2	19422.569		19422.523		19428.466		19428.395	
3	19421.243		19421.175		19429.494		19429.400	
4	19419.864		19419.772		19430.468		19430.351	
5		19418.374	0.036		19431.389		19431.248	
6		19416.877	0.040		19432.256		19432.092	
7		19415.326	0.031		19433.069		19432.882	
8		19413.722	-0.000		19433.829		19433.619	
9		19412.065	0.033		19434.535		19434.301	
10		19410.355	0.038		19435.187		19434.930	
11		19408.591	0.011		19435.786		19435.506	
12		19406.774	0.042		19436.331		19436.027	
13		19404.905	-0.028		19436.822		19436.495	
14		19402.982	0.003		19437.259		19436.909	
15	19401.180	-0.026	19400.832	0.005	19437.642		19437.269	
16	19399.163	0.039	19398.791	-0.030	19437.971		19437.575	
17	19397.092	-0.001	19396.697	-0.011	19438.247		19437.827	
18	19394.969	-0.016	19394.551	0.007	19438.469		19438.025	
19	19392.793	-0.003	19392.352	-0.021	19438.636		19438.170	
20	19390.564	-0.003	19390.099	-0.029	19438.750		19438.260	
21	19388.283	0.027	19387.794	-0.020	19438.810		19438.297	
22	19385.948	0.014	19385.437	-0.054	19438.816		19438.279	
23	19383.561	-0.039	19383.026	-0.037	19438.768		19438.208	
24	19381.121	-0.042	19380.563	0.041	19438.666		19438.083	
25	19378.628	-0.001	19378.047	-0.012	19438.510		19437.903	
26	19376.083	-0.003	19375.479	0.005	19438.299		19437.670	
27	19373.486	-0.016	19372.858	-0.011	19438.035		19437.382	
28	19370.835		19370.184	-0.016*	19437.717		19437.041	
29	19368.133		19367.458		19437.345		19436.645	
30	19365.378	-0.030	19364.680		19436.919		19436.196	
31	19362.570	-0.001	19361.849	-0.023	19436.438		19435.692	
32	19359.710	0.036	19358.966	0.059*	19435.904		19435.135	
33	19356.798	-0.008	19356.031	0.035	19435.315		19434.523	
34	19353.834	0.027	19353.043	-0.009	19434.673		19433.857	
35	19350.817	0.006	19350.003	-0.003	19433.976		19433.137	
36	19347.749	0.010	19346.911	-0.021	19433.225		19432.363	
37	19344.628	0.004	19343.757	0.033	19432.420		19431.534	
38	19341.455	-0.029	19340.571	-0.043	19431.561		19430.652	
39	19338.230	0.028	19337.323	0.057*	19430.648		19429.715	
40	19334.954	0.073*	19334.023	-0.024	19429.680		19428.725	
41	19331.625	0.033	19330.671	-0.020	19428.659		19427.680	
42	19328.244	0.001	19327.267		19427.583		19426.581	
43	19324.812	0.074*	19323.812		19426.453		19425.428	
44	19321.328		19320.305		19425.269		19424.220	
45	19317.792		19316.746		19424.031		19422.959	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 3 - 5 BAND OF A10 (B2E - X2E)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					18517.026		18516.999	
1	18514.633		18514.601		18518.176		18518.119	
2	18513.388		18513.326		18519.285		18519.198	
3	18512.101		18512.009		18520.351		18520.235	
4	18510.773		18510.651		18521.376		18521.230	
5	18509.403		18509.251		18522.360		18522.183	
6	18507.991		18507.810		18523.301		18523.095	
7	18506.538		18506.328		18524.201		18523.965	
8	18505.044		18504.803		18525.058		18524.793	
9	18503.508		18503.238		18525.874		18525.579	
10	18501.931		18501.631		18526.648		18526.323	
11	18500.313		18499.983		18527.380		18527.025	
12	18498.654		18498.294		18528.071		18527.686	
13	18496.953		18496.563		18528.719		18528.304	
14	18495.211		18494.791		18529.325		18528.881	
15	18493.428	-0.019	18492.978	0.036	18529.890		18529.415	
16	18491.603	0.112*	18491.124	0.011	18530.412		18529.908	
17	18489.738	0.061	18489.229	-0.019	18530.893		18530.359	
18	18487.832	0.016	18487.293	0.058	18531.331		18530.767	
19	18485.885	0.067	18485.316	0.012	18531.728		18531.134	
20	18483.896	0.058	18483.298	0.044	18532.082		18531.459	
21	18481.867	0.002	18481.239	0.033	18532.395		18531.742	
22	18479.797	0.036	18479.140		18532.665		18531.982	
23	18477.687	0.084	18476.999	0.036	18532.894		18532.181	
24	18475.535	0.041	18474.818	0.059	18533.080		18532.338	
25	18473.343	0.051	18472.596	0.045	18533.224		18532.452	
26	18471.111		18470.334		18533.327		18532.525	
27	18468.837	0.058	18468.031		18533.387		18532.555	
28	18466.524	0.077	18465.687	0.075	18533.405		18532.544	
29	18464.170	0.145*	18463.303	0.037	18533.382		18532.490	
30	18461.775	0.013	18460.879	0.161*	18533.316		18532.395	
31	18459.340		18458.414		18533.208		18532.257	
32	18456.865		18455.909		18533.058		18532.077	
33	18454.350		18453.364		18532.866		18531.856	
34	18451.794		18450.779		18532.633		18531.592	
35	18449.198		18448.153		18532.357		18531.287	
36	18446.563		18445.488		18532.039		18530.939	
37	18443.887		18442.782		18531.679		18530.549	
38	18441.172		18440.037		18531.277		18530.118	
39	18438.416		18437.252		18530.833		18529.644	
40	18435.621		18434.427		18530.348		18529.129	
41	18432.786		18431.563		18529.820		18528.571	
42	18429.912		18428.658		18529.250		18527.972	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 4 - 1 BAND OF AlO ($B^2\Sigma - X^2\Sigma$)

N	P_2		P_1		R_2		R_1	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					23079.242		23079.222	
1		23076.799	0.006*		23080.320		23080.285	
2		23075.436	0.116*		23081.301		23081.252	
3		23073.976	0.121*		23082.184		23082.120	
4		23072.418	0.071*		23082.969		23082.891	
5		23070.764	0.079*		23083.657		23083.564	
6		23069.012	0.054*		23084.248		23084.140	
7		23067.162	-0.003		23084.740		23084.619	
8		23065.216	0.003		23085.136		23084.999	
9		23063.172	-0.002		23085.433		23085.282	
10		23061.031	0.009		23085.633		23085.467	
11		23058.794	0.007		23085.735		23085.555	
12		23056.458	-0.053		23085.740		23085.545	
13		23054.026	-0.011		23085.646		23085.437	
14		23051.497	-0.008		23085.455		23085.231	
15		23048.871	-0.060		23085.166		23084.927	
16		23046.147	-0.035		23084.779		23084.526	
17		23043.327	-0.060		23084.294		23084.026	
18		23040.410	-0.003		23083.711		23083.429	
19		23037.395	-0.093*		23083.030		23082.733	
20		23034.284	-0.101*		23082.251		23081.940	
21		23031.075	-0.030		23081.374		23081.048	
22	23027.928	0.057	23027.613	-0.003	23080.395		23080.058	
23	23024.533	-0.088*	23024.203	-0.003	23079.325		23078.970	
24	23021.041	-0.004	23020.697	0.008	23078.153		23077.784	
25		23017.273	0.058		23076.884		23076.499	
26		23013.580	0.102*		23075.515	0.037	23075.117	0.038
27	23009.984	-0.010	23009.596	-0.056	23074.049	0.048	23073.636	0.018
28	23006.104	-0.042	23005.702	-0.025	23072.484	0.005	23072.056	0.055
29	23002.128	0.067	23001.711	0.007	23070.820	0.023	23070.378	
30	22998.055	-0.018	22997.624	-0.053	23069.058	0.008	23068.602	
31	22993.885	0.083*	22993.439	-0.001	23067.198	-0.039*	23066.727	
32	22989.618	0.137*	22989.158	-0.042	23065.239	-0.020*	23064.753	
33	22985.254	0.058	22984.779	-0.014	23063.181	-0.011*	23062.681	
34	22980.794		22980.304		23061.025	0.015*	23060.510	
35	22976.237		22975.732		23058.770	0.031*	23058.240	
36	22971.583		22971.064		23056.416	-0.011*	23055.872	
37	22966.832		22966.298		23053.963	0.052*	23053.405	
38	22961.984		22961.436		23051.412	0.077*	23050.839	
39	22957.040		22956.477		23048.762	0.049*	23048.174	
40	22951.998		22951.421		23046.012		23045.410	
41	22946.860		22946.268		23043.164		23042.547	
42	22941.625		22941.019		23040.216		23039.585	
43	22936.294		22935.673		23037.169		23036.523	
44	22930.865		22930.230		23034.024		23033.363	
45	22925.340		22924.690		23030.779		23030.103	
46	22919.718		22919.053		23027.434		23026.744	
47	22913.999		22913.320		23023.990		23023.286	
48	22908.184		22907.490		23020.447		23019.728	
49	22902.271		22901.563		23016.805		23016.071	
50	22896.262		22895.539		23013.062		23012.314	
51	22890.156		22889.419		23009.221		23008.458	
52	22883.954		22883.202		23005.279		23004.502	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 4 - 2 BAND OF A10 (B2E - X2E)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					22127.940		22127.920	
1		22125.508	-0.033*		22129.031		22128.994	
2		22124.168	-0.046*		22130.035		22129.982	
3		22122.743	-0.106*		22130.954		22130.884	
4		22121.232	-0.007*		22131.787		22131.701	
5		22119.695	-0.006*		22132.534		22132.432	
6		22117.953	-0.038*		22133.195		22133.076	
7		22116.185	-0.038*		22133.770		22133.635	
8		22114.392	-0.038*		22134.259		22134.108	
9		22112.393	-0.010		22134.662		22134.494	
10		22110.368	-0.031		22134.979		22134.795	
11		22108.258	-0.052		22135.210		22135.010	
12		22106.062	-0.054		22135.354		22135.138	
13		22103.781	-0.012		22135.413		22135.180	
14		22101.415	-0.069*		22135.385		22135.136	
15		22098.963	-0.048		22135.272		22135.006	
16		22096.426	-0.064*		22135.072		22134.790	
17		22093.803	-0.026		22134.785		22134.487	
18		22091.095	-0.053		22134.413		22134.098	
19		22088.302	-0.037		22133.954		22133.623	
20		22085.424	-0.033		22133.408		22133.062	
21		22082.460	-0.009		22132.777		22132.414	
22	22079.588	-0.009	22079.234	-0.037	22132.059		22131.679	
23	22076.462	0.015	22076.091	0.037	22131.254		22130.858	
24	22073.250	-0.001	22072.864	-0.069*	22130.363	-0.062*	22129.951	-0.020
25	22069.954	0.055	22069.551	-0.011	22129.385	-0.043	22128.957	-0.005
26	22066.572	-0.001	22066.153	-0.058	22128.321	-0.017	22127.877	0.018
27	22063.106	0.025	22062.670	-0.027	22127.171	0.047	22126.710	-0.020
28	22059.554	0.065*	22059.102	0.020	22125.933	0.019	22125.456	0.019
29	22055.917	0.028	22055.449	-0.035	22124.609	0.033	22124.116	0.006
30	22052.195	0.009	22051.711	0.001	22123.199	0.071*	22122.689	-0.052*
31	22048.388	0.025	22047.888	0.028	22121.701	0.181*	22121.175	0.050
32	22044.496	0.007	22043.979	0.027	22120.117	0.043	22119.575	0.054
33	22040.519	0.023	22039.986	0.030	22118.446	-0.013	22117.888	0.027
34	22036.457	0.010	22035.908	0.005	22116.688	0.028	22116.114	0.033
35	22032.311		22031.745		22114.844	0.043	22114.253	0.041
36	22028.079	0.042*	22027.497	-0.030*	22112.912	0.108*	22112.305	0.078*
37	22023.762	0.103*	22023.164	0.081*	22110.894	0.016	22110.270	0.067*
38	22019.361	-0.009	22018.746	0.013	22108.789	0.020	22108.149	0.057*
39	22014.874		22014.243		22106.596	-0.010	22105.940	0.068*
40	22010.303	0.021	22009.656	0.063	22104.317	-0.021	22103.645	0.124*
41	22005.647	-0.016	22004.984	0.014	22101.951	-0.037	22101.262	0.084*
42	22000.906		22000.227		22099.497	0.005	22098.792	0.123*
43	21996.081		21995.385		22096.957		22096.235	
44	21991.170		21990.458		22094.329		22093.591	
45	21986.175	-0.045	21985.447	-0.013	22091.614		22090.860	
46	21981.096	-0.025	21980.351	0.037	22088.812		22088.041	
47	21975.931	-0.041	21975.170	-0.026	22085.922		22085.136	
48	21970.682		21969.904		22082.946		22082.143	
49	21965.348	-0.022	21964.554		22079.881		22079.062	
50	21959.930		21959.120		22076.730		22075.894	
51	21954.427		21953.600		22073.491		22072.639	
52	21948.839	-0.012	21947.996	0.002	22070.165		22069.297	
53	21943.167		21942.308		22066.751		22065.866	
54	21937.410		21936.534		22063.249		22062.349	

 CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 4 - 5 BAND OF A10 (B2E - X2E)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					19358.246		19358.218	
1	19355.862		19355.829		19359.379		19359.321	
2	19354.608		19354.546		19360.461		19360.373	
3	19353.303		19353.211		19361.492		19361.375	
4	19351.948		19351.826		19362.473		19362.326	
5	19350.543		19350.391		19363.403		19363.226	
6	19349.088		19348.906		19364.283		19364.076	
7		19347.476	-0.141*		19365.112		19364.875	
8	19346.026		19345.784		19365.890		19365.623	
9	19344.420		19344.148		19366.618		19366.321	
10	19342.763		19342.462		19367.295		19366.968	
11	19341.057		19340.725		19367.921		19367.564	
12	19339.300		19338.939		19368.497		19368.110	
13	19337.494		19337.102		19369.021		19368.605	
14	19335.637	-0.050	19335.215	-0.188*	19369.495		19369.049	
15	19333.730	-0.115	19333.279	-0.090	19369.919		19369.442	
16	19331.774	-0.116*	19331.292	-0.134	19370.291		19369.785	
17	19329.767	-0.038	19329.256	-0.095	19370.613		19370.076	
18	19327.711	-0.121	19327.170	-0.005	19370.884		19370.317	
19	19325.605	-0.104	19325.034	-0.148*	19371.104		19370.508	
20	19323.449	-0.064	19322.848	-0.138	19371.273		19370.647	
21	19321.244	0.033	19320.613	-0.201*	19371.392		19370.735	
22	19318.988	-0.012	19318.328	-0.030	19371.459		19370.773	
23	19316.684	0.013	19315.993	-0.093	19371.476		19370.760	
24	19314.330	-0.103	19313.609	-0.033	19371.442		19370.696	
25	19311.926	-0.020	19311.175		19371.357		19370.581	
26	19309.473	-0.008*	19308.692	-0.012*	19371.222		19370.416	
27	19306.970	-0.057*	19306.160	0.006*	19371.035		19370.199	
28	19304.419	0.020*	19303.578	-0.036*	19370.798		19369.932	
29	19301.818	-0.003*	19300.947	-0.066*	19370.510		19369.614	
30	19299.168	0.078*	19298.267	-0.003	19370.171		19369.245	
31	19296.468	-0.022	19295.538	-0.079	19369.781		19368.826	
32	19293.720	-0.020	19292.760	-0.043	19369.341		19368.355	
33	19290.923	-0.016	19289.933	-0.082	19368.849		19367.834	
34	19288.076	0.035	19287.056	-0.080	19368.307		19367.262	
35	19285.181	0.006	19284.131	-0.019	19367.715		19366.639	
36	19282.237	0.063	19281.158	0.019	19367.071		19365.966	
37	19279.245	0.037	19278.135	0.043*	19366.377		19365.241	
38	19276.204	0.044	19275.064	0.012	19365.632		19364.466	
39	19273.114	0.040	19271.944	-0.046	19364.836		19363.641	
40	19269.975	-0.000	19268.776	-0.009	19363.989		19362.764	
41	19266.789		19265.559		19363.092		19361.837	
42	19263.554	0.037	19262.294	-0.056	19362.144		19360.860	
43	19260.270	0.066*	19258.981		19361.146		19359.831	
44	19256.939	0.120*	19255.619		19360.097		19358.752	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 5 - 2 BAND OF A10 (B2E - X2E)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					22961.627		22961.606	
1	22959.209		22959.197		22962.700		22962.663	
2	22957.869		22957.841		22963.678		22963.625	
3		22956.412	0.066*		22964.562		22964.492	
4	22954.906		22954.844		22965.351		22965.265	
5		22953.243	0.017		22966.046		22965.943	
6		22951.517	-0.076*		22966.646		22966.526	
7		22949.697	-0.010		22967.151		22967.015	
8		22947.782	-0.007		22967.561		22967.408	
9		22945.773	-0.012		22967.877		22967.708	
10		22943.670	-0.020		22968.097		22967.912	
11		22941.472	0.009		22968.223		22968.021	
12		22939.180	-0.078*		22968.254		22968.036	
13		22936.794	-0.062*		22968.190		22967.956	
14		22934.314	0.028		22968.032		22967.780	
15		22931.739	-0.018		22967.778		22967.510	
16		22929.071	-0.067*		22967.429		22967.145	
17		22926.308	0.041		22966.985		22966.685	
18		22923.452	0.048		22966.447		22966.130	
19		22920.501	0.022		22965.813		22965.480	
20		22917.456	0.039		22965.084		22964.734	
21		22914.318	-0.042		22964.260		22963.894	
22		22911.085	0.043		22963.341		22962.958	
23		22907.758	-0.104*		22962.327		22961.927	
24		22904.338	0.004		22961.217	0.102*	22960.801	-0.027
25		22900.823	0.051		22960.012	0.020	22959.580	-0.038
26		22897.215	-0.081*		22958.712	-0.039	22958.264	0.005
27	22893.732	-0.071	22893.293	0.004	22957.317	-0.008	22956.852	0.031
28	22889.945	0.051	22889.489	-0.012	22955.826	0.011	22955.345	-0.050
29	22886.063		22885.591		22954.240	-0.031	22953.742	
30	22882.088	0.082*	22881.600	0.004	22952.559	-0.010	22952.045	-0.079*
31	22878.019	0.027	22877.514	-0.013	22950.782	0.031	22950.251	0.029
32	22873.856	0.036	22873.335	-0.046	22948.910	-0.004	22948.363	
33	22869.600	-0.030	22869.062	-0.015	22946.942	0.020	22946.378	0.002
34	22865.250	0.021	22864.696	-0.070*	22944.879	-0.055	22944.299	-0.035
35	22860.806	0.110*	22860.236	0.019	22942.720	-0.017	22942.124	
36	22856.269		22855.682		22940.465	-0.018	22939.853	0.008
37	22851.638		22851.035		22938.116	0.045*	22937.486	-0.036
38	22846.914		22846.294		22935.670	0.048*	22935.024	0.011
39	22842.096		22841.460		22933.129		22932.467	
40	22837.184		22836.532		22930.492		22929.813	
41	22832.180		22831.510		22927.759		22927.064	
42	22827.081		22826.395		22924.931		22924.220	
43	22821.889		22821.187		22922.007		22921.279	
44	22816.604		22815.886		22918.987		22918.243	
45	22811.226		22810.491		22915.871		22915.111	
46	22805.754		22805.002		22912.660		22911.882	
47	22800.188		22799.420		22909.352		22908.559	
48	22794.530		22793.746		22905.949		22905.139	
49	22788.778		22787.977		22902.449		22901.623	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 5 - 3 BAND OF A10 (B²Σ - X²Σ)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					22024.353		22024.331	
1	22021.948		22021.932		22025.439		22025.397	
2	22020.633		22020.598		22026.442		22026.381	
3	22019.235		22019.180		22027.363		22027.282	
4	22017.754		22017.680		22028.200		22028.101	
5		22016.144	0.095*		22028.954		22028.836	
6		22014.488	-0.041		22029.625		22029.488	
7		22012.749	0.056		22030.214		22030.057	
8		22010.928	0.077*		22030.719		22030.543	
9		22009.024	0.037		22031.141		22030.946	
10		22007.038	0.020		22031.480		22031.266	
11		22004.969	0.029		22031.736		22031.503	
12		22002.818	0.022		22031.909		22031.656	
13		22000.584	-0.007		22031.999		22031.727	
14		21998.267	-0.039		22032.005		22031.714	
15		21995.869	0.069*		22031.929		22031.618	
16		21993.387	-0.021		22031.769		22031.439	
17		21990.824	-0.008		22031.525		22031.176	
18		21988.178	-0.038		22031.199		22030.831	
19		21985.450	-0.016		22030.789		22030.402	
20		21982.640	-0.050		22030.296		22029.889	
21	21979.947	0.013	21979.547	0.066	22029.719		22029.294	
22	21976.982	-0.012	21976.563	0.000	22029.060		22028.615	
23	21973.935	-0.033	21973.496	0.028	22028.316		22027.852	
24	21970.806	-0.038	21970.348	0.057	22027.490		22027.066	
25	21967.594	-0.001	21967.117	0.023	22026.580		22026.077	
26	21964.301	0.033	21963.805	-0.054	22025.586		22025.065	
27	21960.925	-0.017	21960.410	-0.031	22024.510		22023.969	
28	21957.468	-0.017	21956.933	0.017	22023.349	-0.104*	22022.789	0.026
29	21953.929	0.009	21953.375	-0.025	22022.105	-0.009	22021.526	0.027
30	21950.307	0.025	21949.734	0.002	22020.778	-0.049	22020.179	0.009
31	21946.604	-0.011	21946.012	0.024	22019.367	-0.015	22018.749	0.010
32	21942.820	-0.049	21942.208	0.016	22017.873	-0.039	22017.236	0.055
33	21938.953	-0.007	21938.322	-0.008	22016.295	-0.056	22015.639	0.028
34	21935.005		21934.355		22014.633	-0.186*	22013.958	
35	21930.975		21930.306		22012.888	-0.083*	22012.194	0.030
36	21926.863	-0.003	21926.175	0.101*	22011.059	-0.054	22010.346	-0.022
37	21922.670		21921.962		22009.147	-0.086*	22008.414	0.028
38	21918.395		21917.669		22007.151	-0.093*	22006.399	0.009
39	21914.039		21913.293		22005.072	-0.074*	22004.300	-0.005
40	21909.601		21908.836		22002.909	-0.069*	22002.118	-0.007
41	21905.082		21904.298		22000.662	-0.085*	21999.852	
42	21900.481		21899.678		21998.331	-0.103*	21997.502	-0.040
43	21895.799		21894.977		21995.917	0.021*	21995.069	
44	21891.036		21890.194		21993.419	-0.053*	21992.551	
45	21886.192		21885.331		21990.837	-0.021*	21989.951	0.001
46	21881.266		21880.386		21988.172	-0.032*	21987.266	
47	21876.259		21875.360		21985.423	0.011*	21984.498	0.046
48	21871.171		21870.252		21982.590	0.000*	21981.646	0.047
49	21866.002		21865.064		21979.673	-0.060*	21978.710	0.026
50	21860.752		21859.795		21976.673		21975.690	
51	21855.421		21854.445		21973.589		21972.587	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 5 - 6 BAND OF A10 (B2C - X2C)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					19296.664		19296.631	
1	19294.305		19294.259		19297.796		19297.724	
2	19293.070		19292.985		19298.880		19298.769	
3	19291.789		19291.664		19299.917		19299.766	
4	19290.460		19290.296		19300.906		19300.717	
5	19289.084		19288.881		19301.848		19301.619	
6	19287.661		19287.419		19302.743		19302.475	
7	19286.191		19285.909		19303.590		19303.282	
8	19284.674		19284.353		19304.390		19304.043	
9	19283.110		19282.749		19305.142		19304.756	
10	19281.458		19281.099		19305.846		19305.421	
11	19279.840		19279.401		19306.504		19306.039	
12	19278.135		19277.657		19307.113		19306.609	
13	19276.383		19275.866		19307.675		19307.132	
14	19274.585		19274.028	0.003	19308.190		19307.607	
15	19272.739	0.067	19272.143		19308.657		19308.035	
16	19270.847	0.069	19270.212		19309.076		19308.415	
17	19268.908		19268.234	0.007	19309.448		19308.748	
18	19266.923	0.033	19266.209	0.065	19309.772		19309.033	
19	19264.891	0.059	19264.138	0.045	19310.049		19309.270	
20	19262.813	0.068	19262.020	0.218*	19310.279		19309.460	
21	19260.688	0.110	19259.856	0.108	19310.460		19309.603	
22	19258.517	0.084	19257.646		19310.594		19309.698	
23	19256.300		19255.389		19310.681		19309.745	
24	19254.036		19253.086		19310.720		19309.745	
25	19251.726		19250.737		19310.712		19309.698	
26	19249.371		19248.342		19310.656		19309.602	
27	19246.969		19245.901		19310.553		19309.460	
28	19244.521		19243.414		19310.402		19309.270	
29	19242.028		19240.882		19310.204		19309.033	
30	19239.488		19238.303		19309.959		19308.748	
31	19236.903		19235.679		19309.666		19308.416	
32	19234.273		19233.009		19309.326		19308.036	
33	19231.597		19230.293		19308.938		19307.609	
34	19228.875		19227.532		19308.504		19307.135	
35	19226.108		19224.726		19308.021		19306.614	
36	19223.296		19221.875		19307.492		19306.045	
37	19220.438		19218.978		19306.916		19305.430	
38	19217.536		19216.036		19306.292		19304.767	
39	19214.588		19213.049		19305.621		19304.056	
40	19211.596		19210.017		19304.903		19303.299	
41	19208.558		19206.941		19304.138		19302.495	
42	19205.476		19203.820		19303.326		19301.644	
43	19202.350		19200.654		19302.467		19300.745	
44	19199.179		19197.443		19301.561		19299.800	
45	19195.963		19194.188		19300.609		19298.808	
46	19192.703		19190.889		19299.609		19297.769	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 6 - 3 BAND OF AlO ($\text{B}^2\Sigma - \text{X}^2\Sigma$)

N	P_2		P_1		R_2		R_1	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					22850.694		22850.671	
1	22848.298		22848.282		22851.763		22851.721	
2	22846.974		22846.939		22852.740		22852.679	
3	22845.559		22845.504		22853.626		22853.545	
4	22844.052		22843.978		22854.420		22854.320	
5	22842.454		22842.360		22855.122		22855.003	
6		22840.708	-0.060*		22855.733		22855.594	
7		22838.917	-0.109*		22856.252		22856.094	
8		22837.035	0.131*		22856.679		22856.502	
9		22835.062	-0.063		22857.015		22856.818	
10		22832.998	-0.028		22857.259		22857.043	
11		22830.842	0.009		22857.411		22857.175	
12		22828.595	-0.054		22857.471		22857.216	
13		22826.257	-0.056		22857.439		22857.165	
14		22823.828	-0.046		22857.316		22857.022	
15		22821.308	-0.083		22857.101		22856.788	
16		22818.697	0.062		22856.793		22856.461	
17		22815.995	-0.098		22856.394		22856.043	
18		22813.202	-0.018		22855.903		22855.532	
19	22810.500	-0.039	22810.136	-0.061	22855.320		22854.930	
20	22807.535	-0.044	22807.151	-0.004		22854.441	-0.040	
21	22804.479	0.111*	22804.076	0.022		22853.664	-0.019	
22	22801.332	0.035	22800.909	0.051		22852.795	0.025	
23	22798.094	0.084	22797.652	0.071		22851.835	-0.016	
24	22794.765	0.024	22794.304	0.184*	22851.026	0.026	22850.539	0.077*
25	22791.346	0.061	22790.866	0.065	22849.891	0.038	22849.384	-0.051
26	22787.836	0.068	22787.337	-0.003	22848.664	0.105*	22848.138	0.030
27	22784.236	0.157*	22783.717	0.027	22847.344	-0.017	22846.799	0.102*
28	22780.545	0.006	22780.007	-0.016	22845.933	-0.021	22845.369	0.080
29	22776.763	0.016	22776.206	-0.034	22844.430	0.046	22843.846	0.162*
30	22772.891	-0.019	22772.314	0.041	22842.834	-0.113*	22842.231	0.017
31	22768.929	-0.031	22768.332	0.012	22841.147		22840.524	
32	22764.876	-0.034	22764.260	0.023	22839.367		22838.725	
33	22760.733	-0.019	22760.097	-0.036	22837.495		22836.834	
34	22756.499	0.005	22755.844	-0.045	22835.531		22834.851	
35	22752.175		22751.501		22833.475		22832.775	
36	22747.761		22747.068		22831.326		22830.607	
37	22743.256		22742.544		22829.086		22828.347	
38	22738.662		22737.930		22826.753		22825.995	
39	22733.977		22733.226		22824.328		22823.551	
40	22729.203		22728.432		22821.810		22821.014	
41	22724.338		22723.548		22819.201		22818.385	
42	22719.383		22718.574		22816.499		22815.664	
43	22714.339		22713.510		22813.705		22812.850	
44	22709.204		22708.356		22810.819		22809.945	
45	22703.980		22703.113		22807.840		22806.947	
46	22698.666		22697.779		22804.769		22803.857	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 6 - 4 BAND OF AlO (B²Σ - X²Σ)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					21927.495		21927.470	
1	21925.113		21925.090		21928.578		21928.529	
2	21923.815		21923.768		21929.581		21929.509	
3		21922.402		0.110*	21930.504		21930.408	
4		21920.932		0.052*	21931.347		21931.228	
5		21919.383		0.006	21932.111		21931.967	
6		21917.755		-0.021	21932.794		21932.627	
7		21916.047		0.005	21933.398		21933.207	
8		21914.259		-0.044	21933.921		21933.707	
9		21912.392		0.022	21934.365		21934.127	
10		21910.445		0.011	21934.729		21934.467	
11		21908.419		-0.048	21935.013		21934.727	
12		21906.313		-0.002	21935.216		21934.907	
13		21904.129		0.041	21935.340		21935.007	
14		21901.865		-0.024	21935.384		21935.027	
15		21899.521		-0.009	21935.347		21934.967	
16	21897.288	-0.009	21896.909	0.025	21935.231		21934.827	
17	21894.798	0.064	21894.396	0.002	21935.034		21934.607	
18	21892.229	0.013	21891.803	0.042	21934.758		21934.306	
19	21889.581	0.014	21889.131	0.044	21934.401		21933.926	
20	21886.854	0.019	21886.380	-0.045	21933.964		21933.465	
21	21884.047	0.016	21883.551	-0.003	21933.447		21932.925	
22	21881.162	0.044	21880.642	-0.026	21932.850		21932.304	
23	21878.198	0.025	21877.654	-0.002	21932.173		21931.603	
24	21875.155	0.084*	21874.588	-0.028	21931.416		21930.822	
25	21872.034	-0.014	21871.442	-0.059	21930.578		21929.961	
26	21868.833	0.033	21868.218	-0.007	21929.660		21929.019	
27	21865.554	-0.006	21864.915	0.012	21928.663		21927.998	
28	21862.196	0.032	21861.534	0.011	21927.585		21926.896	
29	21858.760	-0.012	21858.074	-0.027	21926.427		21925.714	0.035
30	21855.245	0.049	21854.535	-0.046	21925.188	-0.023	21924.452	0.006
31	21851.652	-0.015	21850.918	0.025	21923.870	-0.036	21923.110	-0.014
32	21847.980	-0.013	21847.222	-0.021	21922.471	0.041	21921.688	0.164*
33	21844.230		21843.448		21920.992	-0.008	21920.185	0.001
34	21840.401		21839.596		21919.433	-0.044*	21918.602	-0.095*
35	21836.494	0.031	21835.666	0.000	21917.794	-0.060*	21916.940	0.002
36	21832.509	-0.010	21831.657	-0.045	21916.075	-0.023*	21915.197	0.023
37	21828.446	0.048	21827.570	0.023	21914.276	-0.061*	21913.374	0.002
38	21824.305		21823.405	0.005	21912.396	0.018*	21911.470	0.005
39	21820.086	0.010	21819.162		21910.436	0.020*	21909.487	0.050*
40	21815.789	-0.052	21814.842	-0.069	21908.397	-0.026*	21907.423	-0.028*
41	21811.414	-0.001	21810.443	-0.129*	21906.277	0.034*	21905.280	-0.186*
42	21806.961	-0.033	21805.966	-0.015	21904.077		21903.056	0.049*
43	21802.430	-0.003	21801.412	-0.050	21901.797		21900.752	-0.168*
44	21797.822		21796.780		21899.437		21898.369	-0.082*
45	21793.136	0.008	21792.070		21896.996		21895.905	-0.088*
46	21788.373	-0.016	21787.283	0.006	21894.476		21893.361	
47	21783.532		21782.418		21891.876		21890.737	
48	21778.613		21777.476		21889.196		21888.033	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 7 - 4 BAND OF AlO ($B^2\Sigma - X^2\Sigma$)

N	P_2		P_1		R_2		R_1	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					22746.498		22746.473	
1	22744.125		22744.102		22747.564		22747.515	
2	22742.818		22742.772		22748.541		22748.469	
3	22741.423		22741.353		22749.430		22749.334	
4	22739.940		22739.846		22750.231		22750.110	
5		22738.309	0.104*		22750.943		22750.798	
6		22736.638	0.056		22751.566		22751.398	
7		22734.878	0.043		22752.101		22751.309	
8		22733.030	0.023		22752.548		22752.332	
9		22731.095	0.012		22752.906		22752.666	
10		22729.071	0.017		22753.175		22752.912	
11		22726.959	-0.020		22753.356		22753.069	
12		22724.759	-0.000		22753.449		22753.137	
13		22722.471	0.027		22753.452		22753.117	
14		22720.096	-0.002		22753.368		22753.009	
15		22717.632	-0.007		22753.194		22752.811	
16		22715.081	0.015		22752.932		22752.525	
17		22712.442	0.017		22752.581		22752.151	
18	22709.930	0.028	22709.502	-0.004	22752.142		22751.687	
19	22707.127	0.028	22706.676	0.029	22751.614		22751.136	
20	22704.238	-0.115*	22703.762	0.089	22750.997		22750.495	
21	22701.260	-0.032	22700.760	-0.060	22750.292		22749.766	
22	22698.195	0.045	22697.672	0.040	22749.498		22748.948	
23	22695.043	0.142*	22694.495	0.032	22748.615		22748.041	
24	22691.803	-0.074	22691.232	-0.009	22747.643	0.064	22747.046	-0.027
25	22688.476	-0.065	22687.881	0.003	22746.583	-0.069*	22745.962	0.016
26	22685.061	-0.030	22684.442	-0.026	22745.434	-0.007	22744.789	
27	22681.559	-0.000	22680.917	0.131*	22744.197	-0.057	22743.528	-0.061
28	22677.970	-0.054	22677.304	0.071	22742.871	-0.076	22742.178	-0.050
29	22674.294	-0.013	22673.604	-0.010	22741.456	-0.011	22740.739	-0.050
30	22670.531	0.059	22669.817	-0.055	22739.952	-0.014	22739.212	0.075
31	22666.681	0.058	22665.943	0.114*	22738.360	0.053	22737.595	0.133*
32	22662.744	0.032	22661.982	0.008	22736.679	0.015*	22735.891	-0.036
33	22658.720	0.068	22657.934	-0.019	22734.909	0.012*	22734.097	-0.079
34	22654.609		22653.799		22733.051	0.002*	22732.215	0.046
35	22650.412		22649.578		22731.104	0.003*	22730.244	-0.049
36	22646.127		22645.270		22729.068	0.020*	22728.185	
37	22641.756		22640.875		22726.944	-0.005*	22726.037	
38	22637.299		22636.394		22724.731	0.028*	22723.800	-0.026
39	22632.751		22631.826		22722.430	0.068*	22721.475	
40	22628.121		22627.171		22720.040	0.054*	22719.061	
41	22623.407		22622.431		22717.561	0.064*	22716.558	
42	22618.604		22617.603		22714.994	0.102*	22713.967	
43	22613.715		22612.690		22712.338	0.121*	22711.287	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 7 - 5 BAND OF A10 (B²Σ - X²Σ)

N	F ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0								
1	21835.104		21835.072		21837.463		21837.434	
2	21833.824		21833.761		21838.543		21838.485	
3		21832.421	0.078*		21839.548		21839.459	
4		21830.974	0.132*		21840.475		21840.356	
5		21829.450	0.113*		21841.326		21841.177	
6		21827.849	0.101*		21842.101		21841.921	
7		21826.172	0.062		21842.799		21842.588	
8		21824.419	-0.003		21843.420		21843.179	
9		21822.590	0.064		21843.965		21843.693	
10		21820.685	0.057		21844.433		21844.131	
11		21818.703	0.131*		21844.824		21844.492	
12		21816.646	0.032		21845.138		21844.776	
13	21814.711	0.062*	21814.314	0.234*	21845.376		21844.984	
14	21812.516	-0.013	21812.089	0.049	21845.537		21845.114	
15	21810.246	0.068	21809.789	0.025	21845.622		21845.168	
16	21807.900	-0.023	21807.412	-0.063	21845.629		21845.146	
17	21805.478	-0.015	21804.960	0.000	21845.560		21845.046	
18	21802.980	0.008	21802.431	-0.004	21845.415		21844.870	
19	21800.406	0.022	21799.827	-0.002	21845.192		21844.617	
20	21797.757	0.006	21797.148	0.008	21844.893		21844.288	
21	21795.032	-0.016	21794.393	-0.003	21844.517		21843.881	
22	21792.232	-0.096*	21791.562	0.000	21844.064		21843.398	
23	21789.356	-0.024	21788.656	-0.024	21843.534		21842.838	
24	21786.405	0.050	21785.674	-0.007	21842.928		21842.202	
25	21783.378	0.046	21782.617	-0.059	21842.245		21841.488	
26	21780.276	0.017	21779.485	0.030	21841.486		21840.698	
27	21777.099	-0.034	21776.277	-0.004	21840.649		21839.832	
28	21773.846	-0.152*	21772.994	-0.012	21839.736		21838.888	
29	21770.519	0.001	21769.636	-0.009	21838.746		21837.868	
30	21767.116	0.046	21766.203	-0.013	21837.680		21836.771	
31	21763.638		21762.695		21836.537	-0.012	21835.598	0.068*
32	21760.086	-0.004	21759.112	-0.034	21835.317	0.020	21834.348	-0.075*
33	21756.459	-0.005	21755.455	0.061	21834.021	-0.101*	21833.021	
34	21752.757	0.036	21751.722	-0.073	21832.648	-0.149*	21831.618	
35	21748.980	-0.013	21747.915	-0.039	21831.199	-0.093*	21830.138	-0.003
36	21745.129		21744.034		21829.672		21828.582	
37	21741.203	-0.017*	21740.077	0.047	21828.070		21826.949	-0.040
38	21737.203		21736.047	0.019	21826.391		21825.239	-0.060
39	21733.128		21731.942		21824.635		21823.453	-0.043
40	21728.979	-0.010	21727.763		21822.803		21821.591	-0.066
41	21724.756	0.027	21723.509	-0.035	21820.895		21819.652	
42	21720.459		21719.182	0.007	21818.910		21817.637	
43	21716.088		21714.780		21816.849		21815.545	
					21814.711		21813.378	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 6 - 5 BAND OF A10 (82C - X2C)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					22649.140		22649.111	
1	22646.790		22646.757		22650.204		22650.145	
2	22645.501		22645.438		22651.183		22651.093	
3		22644.082		0.027*	22652.076		22651.956	
4		22642.608		0.162*	22652.885		22652.735	
5		22641.050		-0.110*	22653.609		22653.428	
6		22639.408		0.028	22654.247		22654.036	
7		22637.680		-0.121	22654.801		22654.559	
8		22635.868		-0.102	22655.269		22654.997	
9		22633.971		0.100*	22655.653		22655.350	
10		22631.989		-0.145*	22655.951		22655.617	
11		22629.923		-0.068	22656.164		22655.800	
12		22627.772		0.255*	22656.291		22655.897	
13		22625.537		-0.233*	22656.334		22655.909	
14		22623.217		0.100*	22656.291		22655.836	
15		22620.813		-0.285*	22656.163		22655.677	
16	22618.569		22618.079		22655.950		22655.434	
17	22616.012	0.064	22615.491	-0.133*	22655.652		22655.105	
18	22613.370	0.261*	22612.819	-0.154*	22655.269		22654.691	
19	22610.644	0.006	22610.062	0.009	22654.800		22654.192	
20	22607.834	0.011	22607.222	-0.038	22654.246		22653.608	
21	22604.940	0.060	22604.297	0.079	22653.607		22652.938	
22	22601.961	-0.042	22601.288	0.135*	22652.883		22652.183	
23	22598.899	0.058	22598.196	0.163*	22652.074		22651.344	
24	22595.753	-0.024	22595.019	0.029	22651.179		22650.418	
25	22592.523	0.066	22591.759	0.031	22650.199	0.117	22649.408	-0.068
26	22589.210	-0.074	22588.415	0.057	22649.134		22648.313	
27	22585.812	-0.014	22584.987	-0.100	22647.985	0.125	22647.132	
28	22582.331	0.053	22581.475	-0.053	22646.749	0.079	22645.867	
29	22578.767	-0.021	22577.880	0.032	22645.429	-0.101*	22644.516	
30	22575.119	-0.031	22574.202	-0.132*	22644.024	0.085	22643.080	
31	22571.388	-0.017	22570.440	-0.128*	22642.534		22641.560	
32	22567.573	-0.031	22566.595	-0.132*	22640.958	-0.018	22639.954	
33	22563.675		22562.656		22639.298	0.138*	22638.253	
34	22559.694		22558.655		22637.552	0.007*	22636.487	-0.120
35	22555.630		22554.560		22635.722	0.044*	22634.626	
36	22551.483		22550.383		22633.807		22632.680	-0.039
37	22547.252		22546.122		22631.807	0.037*	22630.650	
38	22542.940		22541.778		22629.722	0.133*	22628.534	
39	22538.544		22537.352		22627.552		22626.334	
40	22534.066		22532.844		22625.297	0.007*	22624.049	
41	22529.505		22528.252		22622.958		22621.679	
42	22524.861		22523.578		22620.533	-0.005*	22619.224	
43	22520.136		22518.822		22618.025		22616.685	

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 8 - 6 BAND OF A10 (B²Σ - X²Σ)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					21754.064		21754.031	
1	21751.731		21751.684		21755.145		21755.072	
2	21750.471		21750.385		21756.152		21756.040	
3	21749.138		21749.013		21757.086		21756.934	
4	21747.733		21747.567		21757.947		21757.755	
5		21746.151	-0.012		21758.735		21758.504	
6	21744.703		21744.458		21759.450		21759.179	
7		21742.936	-0.035		21760.092		21759.780	
8		21741.219	-0.033		21760.660		21760.309	
9		21739.429	-0.078*		21761.155		21760.765	
10	21737.769		21737.365	-0.030	21761.577		21761.147	
11	21735.854		21735.410		21761.926		21761.456	
12	21733.866	-0.032	21733.383	-0.156*	21762.201		21761.692	
13	21731.806	0.023	21731.283	0.060	21762.404		21761.854	
14	21729.673	-0.148*	21729.110	-0.141*	21762.533		21761.944	
15	21727.468	0.030	21726.865	-0.047	21762.588		21761.960	
16	21725.190		21724.548		21762.571		21761.903	
17	21722.840	-0.082	21722.158	0.026	21762.480		21761.772	
18	21720.418	-0.032	21719.696	-0.003	21762.317		21761.569	
19	21717.923	-0.060	21717.162	0.004	21762.079		21761.292	
20	21715.357	-0.016	21714.556	0.079	21761.769		21760.942	
21	21712.718	-0.023	21711.878	-0.120*	21761.386		21760.519	
22	21710.008	-0.004	21709.127	0.014	21760.929		21760.022	
23	21707.225	-0.119*	21706.305	-0.034	21760.400		21759.453	
24	21704.371	-0.042	21703.411	-0.050	21759.797		21758.810	
25	21701.445	-0.007	21700.445	-0.002	21759.121		21758.095	
26	21698.447	-0.009	21697.408	0.030	21758.372		21757.306	
27	21695.377	-0.031	21694.299	0.053	21757.550		21756.444	
28	21692.236	-0.086	21691.118	-0.008	21756.654		21755.509	
29	21689.024	-0.031	21687.866	0.022	21755.686		21754.502	
30	21685.740		21684.542	0.061*	21754.645		21753.421	
31	21682.385	-0.017*	21681.148	-0.069*	21753.531	-0.042	21752.267	0.004
32	21678.959	0.035	21677.682	0.071	21752.344	-0.073	21751.040	0.019
33	21675.462		21674.145	-0.026	21751.084	-0.025	21749.741	-0.023
34	21671.893	0.038	21670.537	0.074	21749.752	-0.034	21748.369	-0.005
35	21668.254		21666.858		21748.346	0.018	21746.923	0.026
36	21664.544	0.079*	21663.108	0.065	21746.868	0.081	21745.406	
37	21660.763	0.109*	21659.287	0.095	21745.317	-0.029	21743.815	0.048
38	21656.912	0.115*	21655.396	0.086	21743.694		21742.152	-0.053
39	21652.990		21651.435		21741.998	0.101*	21740.416	0.125*
40	21648.998	0.160*	21647.403	0.144*	21740.229	-0.105*	21738.608	0.010
41	21644.935		21643.301	0.074*	21738.388		21736.727	0.071
42	21640.803		21639.128	0.063*	21736.475		21734.774	-0.037*
43	21636.600		21634.886	0.142*	21734.489		21732.748	-0.053*
44	21632.327		21630.573		21732.431		21730.650	0.041*
45	21627.985		21626.191		21730.300		21728.480	-0.057*

CALCULATED LINE POSITIONS AND RESIDUALS FOR THE 9 - 6 BAND OF A10 (B2C - X2C)

N	P ₂		P ₁		R ₂		R ₁	
	Calc	Res	Calc	Res	Calc	Res	Calc	Res
0					22558.382		22558.349	
1	22556.057		22556.011		22559.446		22559.373	
2	22554.789		22554.703		22560.428		22560.315	
3	22553.440		22553.313		22561.329		22561.176	
4		22551.926		0.026	22562.148		22561.956	
5		22550.394		-0.006	22562.886		22562.653	
6		22548.781		-0.018	22563.542		22563.270	
7		22547.086		0.027	22564.117		22563.805	
8		22545.311		0.095	22564.610		22564.258	
9		22543.454		-0.118	22565.022		22564.630	
10		22541.516		0.053	22565.352		22564.920	
11		22539.498		0.023	22565.600		22565.128	
12		22537.398		-0.140*	22565.767		22565.277	
13		22535.218		0.019	22565.852		22565.300	
14	22533.238	-0.028	22532.674	0.030	22565.856		22565.264	
15	22530.916	-0.059	22530.312	0.111	22565.778		22565.146	
16		22528.191		0.043	22565.618		22564.947	
17	22526.029	-0.008	22525.345	-0.004	22565.377		22564.666	
18	22523.465	0.021	22522.741		22565.054		22564.303	
19	22520.820	-0.057	22520.056	-0.044	22564.650		22563.859	
20	22518.094	0.263*	22517.291	0.076	22564.164		22563.334	
21	22515.289	-0.062	22514.445		22563.597		22562.726	
22	22512.402	-0.084	22511.519	-0.022	22562.948		22562.038	
23	22509.436	-0.097	22508.513	0.076	22562.218		22561.268	
24	22506.389	-0.125	22505.426	-0.018	22561.406		22560.416	
25	22503.263	-0.159*	22502.260	-0.013	22560.513		22559.483	
26	22500.056	0.005	22499.013	-0.174*	22559.538		22558.468	
27	22496.769	-0.105	22495.687	0.009	22558.482		22557.372	
28	22493.403	0.084	22492.280	0.041	22557.344		22556.195	
29	22489.956	0.004	22488.794	-0.019	22556.126		22554.937	
30	22486.430	-0.021	22485.228	0.124*	22554.826		22553.597	
31	22482.825	-0.026	22481.583		22553.444		22552.176	
32	22479.139		22477.858		22551.982		22550.673	
33	22475.375		22474.053		22550.438		22549.090	

This estimate lies, however, outside the limits $(0.8828)^2 \leq (\hat{\sigma})^2 \leq (1.11)^2$ given by the $\chi^2/98$ distribution at the 95% confidence level for random measurement error. Such a result is not unusual; in nearly all applications of the merge method to date, estimated variances of merges have been found to be well outside the limits set by the χ^2/f_m distribution. The values of the present work are, in fact, unusually small. It could be concluded, therefore, that the systematic error in the present work is also unusually small, and that the effect on merged parameters ($\hat{X}_i$) can be accommodated satisfactorily by calculating standard errors ($\hat{\sigma}_i$) for each constant from (4)

$$\hat{\sigma}_i = (\hat{\sigma}_M) (V_{ii})^{1/2} \quad (3.6)$$

In Eq. (3.6), V is the dispersion matrix of the merged constants. All estimated standard errors reported in the present work were obtained from Eq. (3.6). The parameters output in merge C, in fact, reproduce the measured line positions very satisfactorily. This is shown in Table 3.5 which lists line positions and residuals calculated from the parameters of Table 3.1 and 3.4.

The ratio of the root mean square of the residuals (rms), $\{\Sigma(v_i^{\text{obs}} - v_i^{\text{cal}})^2 n^{-1}\}^{1/2}$, for lines calculated with parameters from merge C to the estimated standard deviation, is given in the right-hand column of Table 3.1. The ratios are in general very satisfactory, except the very weak 3-5 and 5-6 bands with few lines fitted.

The presence of significant, but not unusually large,

systematic error was revealed in merge D, in which the band⁸⁹ origins were reduced to a set of relative term values. In merge D, the output consisted of the sixteen term values listed in Table 3.6 which are determined relative to $X^2\Sigma^+$, $v = 0$. The variance of the equivalent single-step merge of the individual band-by-band constants (105 degrees of freedom, $f = 137 - 32$) to this output set was $(\hat{\sigma}_M)^2 = (3.70)^2$, significantly larger than those of the merges described earlier; the large value is due to the presence of relative systematic error between different bands.

It is worth noticing, however, that the estimates in merge D of all the Dunham coefficients of Table 3.4 were unchanged to within the estimated one standard errors when these were defined by $\hat{\sigma}_i = 3.70 (V_{ii})^{1/2}$; this is in agreement with the general conclusion that contamination of least-squares parameter estimates due to systematic error is assessed reliably when Eq. (3.6) is used to specify the standard errors. Vibrational Dunham coefficients given by a final fit, merge E, are included in Table 3.6. Merge E has variance $(\hat{\sigma}_M)^2 = (3.84)^2$ and $f = 137 - 25 = 112$ degrees of freedom, for the equivalent single-step merge. It was necessary to determine nine (five for the $B^2\Sigma^+$ state, and four for the $X^2\Sigma^+$ state) vibrational coefficients in order to represent the sixteen relative vibrational term values.

The Dunham coefficients in Tables 3.4 and 3.6 are considered the best available for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of AlO.

Finally, the vibrational dependence of $(\gamma_v'' - \gamma_0'')$ and $(\gamma_v' - \gamma_0')$ are shown in Fig. 3.5. For $(\gamma_v'' - \gamma_0'')$, the curve is calculated from the parameters of Merge B (Table 3.3), and shows that the magnitude of γ_v'' changes rapidly with v'' for $v'' \leq 6$. The conclusion is valid on the assumption that the magnitude of γ_0'' is small. Approximate estimates of γ_0'' of 0.01 and 0.005 cm^{-1} obtained in references (18) and (32) respectively, would support this assumption. For $(\gamma_v' - \gamma_0')$ the points in Fig. 3.5 are the estimates listed in Table 3.3 and the straight line is from merge C (Table 3.4). The different vibrational behavior of $(\gamma_v' - \gamma_0')$ is in accord with the expectation that the major contribution to the spin-rotational constants comes from the low-lying $A^2\Pi$ state. The potential minimum of this state lies at $\sim 5400 \text{ cm}^{-1}$, between the $v'' = 5$ and 6 levels of the $X^2\Sigma^+$ state.

It would be of much interest to examine spin-doubling in levels above $v'' = 6$ since the levels of the A and X states overlap and large varying spin-doubling would be expected.

The observed v'' -dependence within the individual v' -progressions from the present analysis is not reproduced in the work of Mahieu et al. (32), as it can be seen from the comparison made between the first and the last column of Table 3.2 for the $v' = 0, 1$ and 2 progressions. It is clear though that reasonable agreement exists in terms of the absolute $(\gamma' - \gamma'')$ values.

As a conclusion to this analysis, the effective rotational and vibrational constants were used to calculate the RKR turning points for each state (Table 3.7). These results were obtained using the method described in section 2.6; the data used were the term values of Table 3.6 and the rotational constants (B_v) of Table 3.3. The reduced mass of 10.041951 amu was based on the atomic masses of ^{16}O and ^{27}Al . The RKR curves have been plotted in Fig. 3.6.

Table 3.6: Term Values and Vibrational Parameters^a (cm^{-1})
for the $X^2\Sigma^+$ and $B^2\Sigma^+$ States of AlO.

v	Merge (D)			Merge (E)	
	$T_v(B^2\Sigma^+)$	$G_v(X^2\Sigma^+)$		$B^2\Sigma^+$	$X^2\Sigma^+$
9	28133.989(55)		T_e	20688.726(49)	0.0
8	27334.618(45)		ω_e	870 535(32)	978.266(58)
7	26522.831(37)		$\omega_e x_e$	3.7206(131)	6.9182(102)
6	25703.715(32)	5581.729(37)	$10^2 \omega_e y_e$	0.870(207)	-1.93(64)
5	24877.260(30)	4686.570(35)	$10^3 \omega_e z_e$	-0.443(109)	1.10(46)
4	24043.508(30)	3777.418(31)			
3	23202.452(30)	2854.120(27)			
2	22354.034(24)	1916.762(26)			
1	21498.278(25)	965.399(23)			
0	20635.181(26)	0.000			

^a Values in parentheses are estimated standard errors given by $\sigma_M(V_{ii})^{1/2}$, in units of the last significant figure of the corresponding constant.

Figure 3.5: Plots of $(\gamma_v - \gamma''_0)$ for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of AlO. The points shown for the B state and the smooth curve for X state were obtained from Merge B (Table 3.3). The straight line for the B state is from the fit of Merge C (Table 3.4). Error bars are two standard deviations.

Figure 3.5

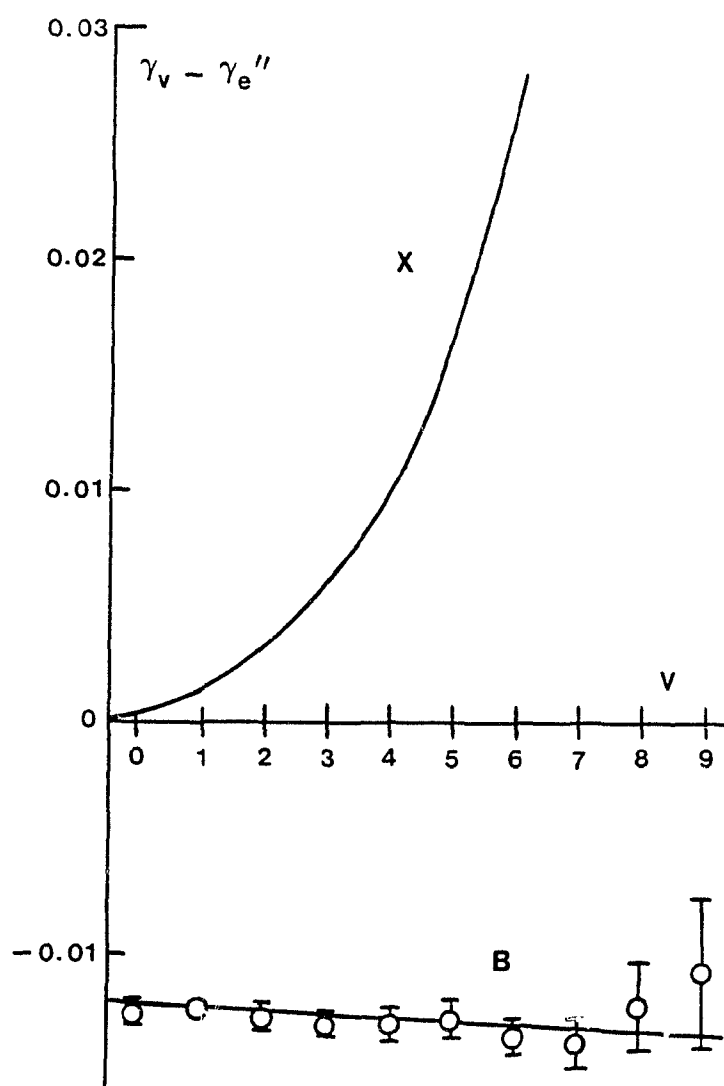


Table 3.7: RKR Turning Points (Å) for the $X^2\Sigma^+$ and $B^2\Sigma^+$ States of AlO^a

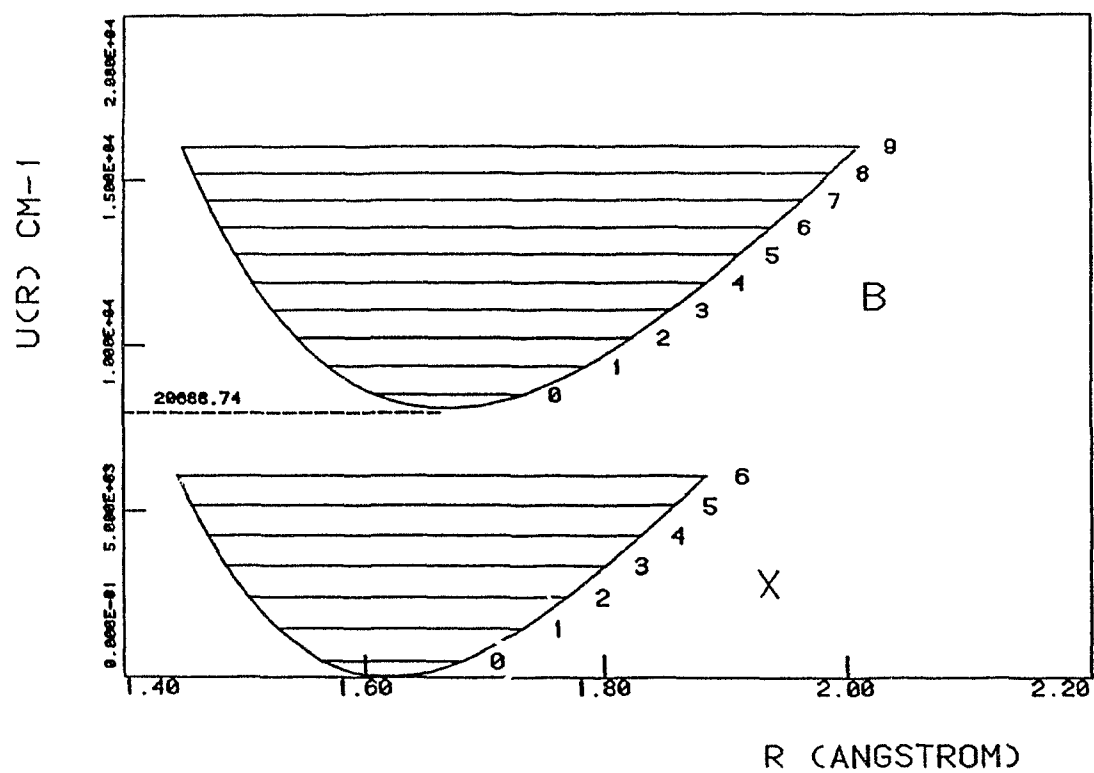
95

$B^2\Sigma^+$				$X^2\Sigma^+$		
v	G_v	$r_{\min}$	$r_{\max}$	G_v	$r_{\min}$	$r_{\max}$
0	434.592	1.60780	1.73227	487.998	1.56251	1.67995
1	1297.689	1.56850	1.78480	1453.397	1.52596	1.73062
2	2153.445	1.54306	1.82330	2404.760	1.50257	1.76840
3	3001.863	1.52337	1.85614	3342.118	1.48452	1.80102
4	3842.919	1.50701	1.88570	4265.416	1.46956	1.83071
5	4676.671	1.49289	1.91307	5174.568	1.45672	1.85855
6	5503.126	1.48043	1.93889	6069.727	1.44542	1.88507
7	6322.242	1.46915	1.96344			
8	7134.029	1.45892	1.98709			
9	7938.400	1.44942	2.00992			

^a $Y_{00}(B) = 0.2558 \text{ cm}^{-1}$; $Y_{00}(X) = -0.0113 \text{ cm}^{-1}$.

Figure 3.6: RKR potential curves for the $B^2\Sigma^+$ and $X^2\Sigma^+$ states of aluminum monoxide; vibrational energy levels are shown.

Figure 3.6



Chapter 4

Excitation of Spectra by Species of a Helium Discharge and Details of the Flowing Afterglow System.

For the second part of this work a fast-flow system was constructed in which a discharge could be excited in helium with the long-lived energetic species then being removed from the active discharge and later mixed downstream with a second gas. Collins and Robertson (39) have experimentally established that in a similar afterglow system the helium active species present were $\text{He}(2^3\text{S})$, $\text{He}_2(\text{a}^3\Sigma_u^+)$, the molecular ion (He_2^+) and the atomic ion He^+ .

Interaction of these active helium species with various substrate gas molecules is responsible for the presently observed luminescence.

In the following chapters spectral analysis of these luminescence reactions gives direct information on the electronic states of the products. The mechanism of the reactions leading to the excited products is beyond the purpose of the present thesis. However, energy conservation requirements together with the Franck resonance rule (40), are generally useful in suggesting reactions and the reasons for predominance of certain reactions, established by other considerations, but they are not specific in themselves. The maximum available energy from the active helium species

are given in Ref. (39) as, $\text{He}^+(24.58 \text{ eV})$, $\text{He}(2^3\text{S } 19.82 \text{ eV})$,⁹⁹
 $\text{He}_2^+(18.80\text{--}21.80 \text{ eV})$ and $\text{He}_2(a^3\Sigma_u^+ 14.60\text{--}17.40 \text{ eV})$.

Three independent investigations (39, 41, 42) on the intensity of various band systems observed from flowing afterglow systems suggest that the intensity is strongly dependent upon the helium pressure. Three characteristic classes of reactions may be distinguished, namely those that show an intensity peak at ~1 Torr, ~2 Torr and ~3 Torr, with metastable He (2^3S), He^+ and He_2^+ being dominant active species, respectively. In the following paragraphs the flowing afterglow apparatus used in the present work will be discussed in detail together with the dispersion, the detection and the data acquisition systems. More experimental details of the reactions of discharged helium with BI_3 , PCl_3 , AsCl_3 and SeOCl_2 will be given in the final part of this chapter.

The experimental arrangement, shown in Figure 4.1, was similar to that used for production of the $\text{A}^2\Pi_1$ state of SO^+ (43). Prepurified helium (Linde 99.996%) was purified further by passage through two traps containing molecular sieve (Davison, 4-8 mesh; 0.5 nm pore size), maintained in liquid nitrogen baths. The helium was passed through a dc-discharge maintained between tantalum foil electrodes 4 cm apart. A ballast resistor (18 k Ω) was included in series with the power supply to reduce power fluctuations. Typical current flows were 15 mA for a supply voltage of ~600 V.

Figure 4.1: The flowing afterglow apparatus.

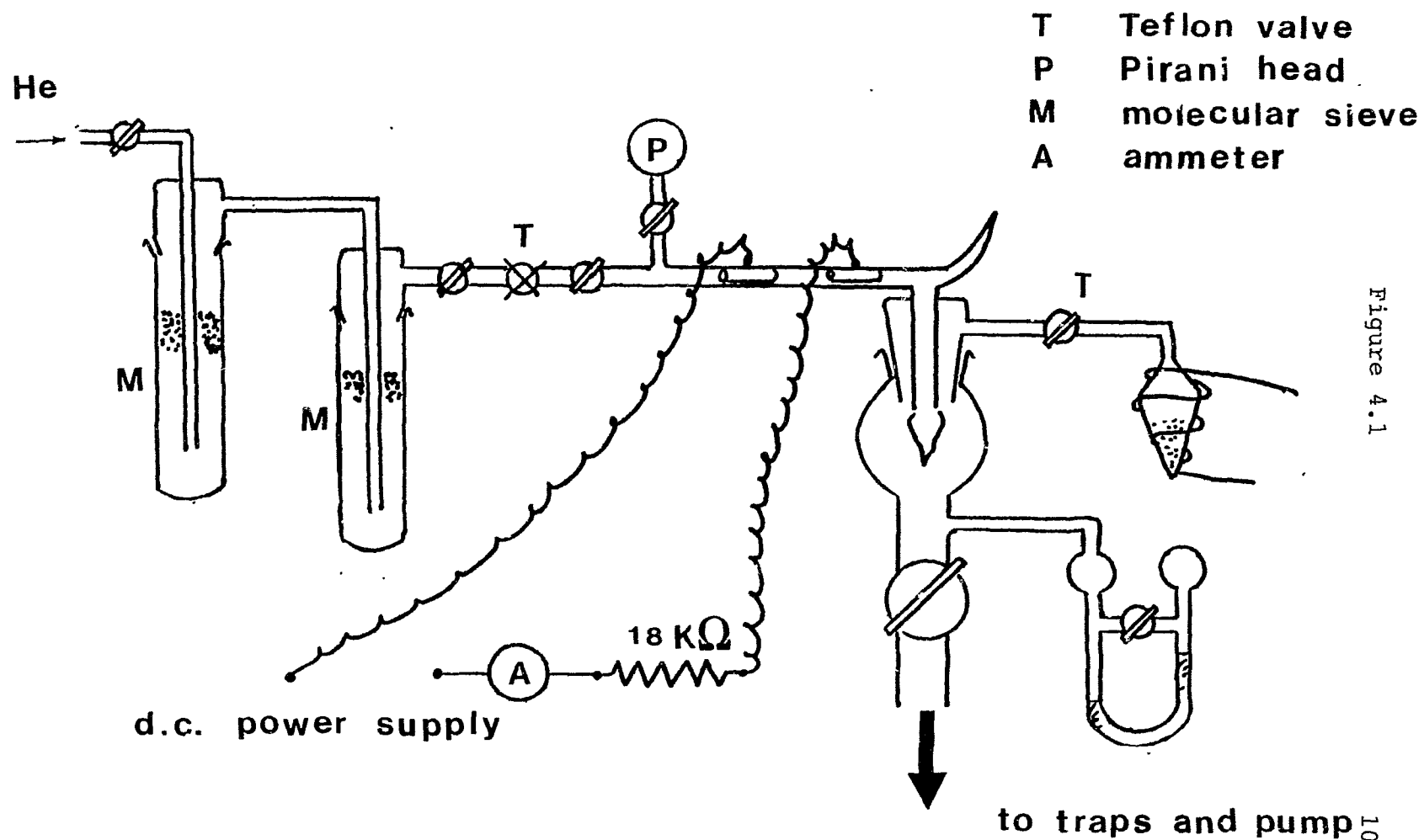


Figure 4.1

Small flows of various substrate molecules were admitted from a resistively heated side tube positioned a few centimeters downstream of the discharge. The system was pumped by a $170 \text{ m}^3\text{h}^{-1}$ pump (Leybold Heraeus E 150) at total pressures between 1.5 and 4 Torr. The emissions could be observed visually.

Spectra were recorded in the first-order of 1.26-m scanning monochromator (Spex 1269) fitted with a 2400-groove mm^{-1} grating (Bausch and Lomb) blazed at 5000 Å. The slit width was 200 μm , corresponding to a spectral width of 0.6 Å. Signals were detected by a GaAs photomultiplier (RCA C31014A) maintained at -20°C in a RF-shielded, water-cooled housing (Products for Research TE-192-RF); the dark current was $\sim 8 \text{ counts s}^{-1}$. The photomultiplier signal was processed with an SSR 1120 Amplifier/Discriminator and a PAR 1105 photon counter, the count rate being displayed on a strip chart recorder (BBC Goerz, Servogor 210).

In the following sections, the automation of the spectrometer and the data acquisition system, which were employed for higher resolution analysis of the spectra of BI and PCl^+ , will be discussed.

The monochromator was operated under full computer control (Digital MINC MNC11-AA, PDP 11/23). The computer is equipped with two 16-bit parallel digital input modules and a 16-bit parallel digital output module which are used to receive data from and send instructions to an interface (44) which contains logic circuits for operations.

The spectrometer is scanned in a stepwise fashion. Depending on the desired resolution interval, a train of pulses is supplied to the spectrometer stepper motor. Signals from the photomultiplier are counted by the interface for a given time interval. After the signal count has been passed to the computer, the above procedure is repeated enabling a spectrum to be recorded digitally as a set of measured counts at a large number of equally spaced wavelengths. In the present work, the resolution interval was 0.02 Å in accord with the spectral slit width of ~0.1 Å which corresponds to a mechanical slit width of 20 μm. With counting times ~4 s, the total count for the more intense lines was typically a few hundred counts, giving good signal-to-noise ratio for all the bands analyzed presently.

Spectra were calibrated by reference to emission lines of either Fe/Ne or U/Ar hollow cathode discharge lamps operated at ~15 mA. The calibration lines were recorded simultaneously with the recorded spectra using the electronic shutter described in detail in Ref. (44). Several calibration lines were obtained both before and after, as well as within, the band being recorded, and were spaced as evenly as possible. Measured (drum) calibration line positions (λ_d) were fitted by a nonlinear least-squares routine according to

$$\Delta\lambda(\text{\AA}) = \sum_{i=0}^2 a_i \lambda_d^i + \alpha \sin[2\pi(\lambda_d - \delta)/50] \quad (4.1)$$

where $\Delta\lambda$ are the residuals ($\lambda_d - \lambda_t$) between the measured (λ_d)

and true wavelengths (λ_t). Eq. (4.1) takes account of a small periodic (50 Å) error in the grating rotation lead screw.

The parameters α and δ were fitted for each calibration along with the set of a_i . The spectra were displayed on a graphics terminal (Digital VT105) and measured manually. A computer program was then employed to obtain vacuum wavenumbers from the calibration parameters. The rotationally analyzed bands of BI and PCl^+ and portions of the low resolution spectra of PCl^+ and AsCl^+ were drawn with a digital plotter (Tektronics 4662) through the interface with the MINC computer.

Boron Iodide

The $a^3\Pi_{0,1}$ state of BI was populated by the reaction of discharged helium with boron triiodide (Alpha products 95%). Small flows of BI_3 were admitted from the resistively heated side tube and the emission could be observed as a red diffuse flame. The helium pressure was kept at 1.5 Torr in order to maximize the intensity of the band systems.

The wavelengths of neon atomic emission lines, which were recorded simultaneously, from a light pen source (Oriel) were used to calibrate the low-resolution spectrum. These neon lines were fitted by least-squares to a quadratic in "d", the distance along the trace (38). The standard deviation of this fit was 0.32 Å. The band head positions were determined at half-maximum intensity above the baseline, and are accurate to ~1 Å.

For the higher resolution analysis the spectra were calibrated by reference to emission lines of either Fe/Ne or U/Ar hollow cathode lamps. The standard deviations of the calibration lines fits were typically 0.01 Å.

Phosphorous chloride cation

Electronically excited PCl^+ was produced by the reaction of PCl_3 vapour with discharged helium at total pressures near 4 Torr. The PCl_3 flow was introduced into the reaction cell from the liquid (BDH chemicals, 98%) contained in a side tube 5 cm downstream fitted with a Teflon needle valve to maximize the brightness of the conical bluish flame. Prepurified helium (Linde, 99.996%) was purified further by passing the gas through the two traps containing molecular sieve cooled by liquid nitrogen.

It was found that the pore size and the physical state of the molecular sieve are more critical factors for obtaining PCl^+ and AsCl^+ emission spectrum than any other emission spectra studied. Experimental trials with either different pore size (4 nm) or traps only partially free from impurities (i.e. water) did not give the optimum intensity of the PCl^+ or AsCl^+ .

The calibration of the low resolution PCl^+ spectrum was obtained by emission lines of atomic Cl and He (45) which were fitted by least-squares to a linear function in "d".

The standard deviation of this fit was 0.27 Å. The PCl^+ bandhead positions were determined at half maximum intensity above the baseline and have an estimated

uncertainty of $\sim 0.6 \text{ \AA}$ (based on a 0.4 mm uncertainty in the distance along the trace).

For the higher resolution work on PCl^+ , a uranium hollow cathode lamp was used for wavelength calibration. Usually, 25-30 uranium lines were fitted for each sub-band with a standard deviation of about $0.008 \text{ \AA}$.

Arsenic chloride cation

Electronically excited AsCl^+ was produced by the reaction of AsCl_3 vapour with discharged helium at total pressures approximately 4 torr. AsCl_3 (BDH chemicals, 99%) was kept in the side tube which was not heated since the room temperature vapour pressure of liquid AsCl_3 was sufficient to maintain a constant flow of AsCl_3 for the production of excited AsCl^+ .

The band head positions were measured manually and were determined with an estimated uncertainty of $\sim 0.6 \text{ \AA}$. Emission lines of atomic Cl(45), He (45) and As (46) were fitted by least-squares to provide wavelength calibration of the spectrum. The quality of this fit was similar to the corresponding fit of PCl^+ .

Selenium oxide cation

SeO^+ was formed in the reaction of selenium dichloride oxide vapour with discharged helium at total pressures of ~ 3 torr. Liquid SeOCl_2 (Alpha, 97%) was heated ($\sim 50^\circ\text{C}$) in order to maintain a constant flow of SeOCl_2 . The band head positions were obtained with an internal calibration provided by emission lines of atomic helium and selenium

(45,46). Estimated uncertainties in the bandhead
measurements are $\sim 2 \text{ cm}^{-1}$.

Chapter 5

Vibrational Analysis of the $a \rightarrow X$ System of the BI

5.1 Introduction

In the present chapter, an investigation of the reaction of BI_3 with discharged helium is described. It was found that the reaction was chemiluminescent, the emission spectrum consisting of systems of violet degraded bands in the 5400-6800 Å region. These bands have been assigned to the $a^3\Pi_0^+ \rightarrow X^1\Sigma^+$ and $a^3\Pi_1 \rightarrow X^1\Sigma^+$ systems of BI. The $a^3\Pi_{0,1}^+ \rightarrow X^1\Sigma^+$ Cameron bands of the boron monohalides have been studied principally by Lebreton and coworkers (47-51); the spectra were excited using a Schuler-type discharge. These investigations comprise rotational analyses of the 0-0 band of the $a^3\Pi$ -X system of BF (47), the 0-0 and 1-1 bands of the $a^3\Pi_1$ -X system of BCl (48) and of selected bands of the many bands identified in the spectra of BBr (49,50) and BI (51). In the case of BBr, rotational constants were derived from an analysis (50) of three bands in the $\Delta v = 0$ sequence (0-0, 1-1 and 2-2). The work of Lebreton et al. (51) on BI is the first observation of this molecule and the bands were obtained from a discharge of a mixture of argon and BI_3 vapour. Twelve head positions ($v' \leq 9$, $v'' \leq 7$) of the $a^3\Pi_0^+ \rightarrow X^1\Sigma^+$ system were reported in the range 5680-6210 Å, together

with a rotational analysis of the 0-0 and 1-0 bands. However, the observation of additional bands was precluded by strong interfering emission due to I_2 . In addition, Lebreton et al. (51) tentatively assigned two bands in the ultraviolet region, obtained by flash photolysis, as due to the $A^1\Pi \leftarrow X^1\Sigma^+$ system of BI. Briggs and Piercy (52) observed the same UV bands near 3490 Å but they also observed several other bands in the range 2660-2790 Å which were assigned to the $\Delta v = -1, 0, 1$ sequences of BI ($A^1\Pi \leftarrow X^1\Sigma^+$). However, the latter bands should be attributed to BCl from BCl_3 impurity, as discussed by Lebreton et al. (51) and Huber and Herzberg (53). In the more recent work by Briggs and Simmons (54), there was no discussion of the possibility that BCl_3 impurity was responsible for their incorrect interpretation (52) of the flash photolysis experiments.

Finally, Bredohl has very recently reported (55) a complete analysis of the 0-0 band of the $a^3\Pi_r - X^1\Sigma^+$ system of BCl. The spectrum was well-developed and the spin-orbit constant of the $a^3\Pi$ state could be determined. In the present study, on BI, most of the bands observed by Lebreton et al. (51) in the $\Delta v = 1$ sequence of the $a^3\Pi_0 - X^1\Sigma^+$ system were also obtained. In addition, the $\Delta v = 2$ and 3 sequences were recorded together with several bands of the less abundant ^{10}BI isotope. The vibrational parameters of the $a^3\Pi_0 - X^1\Sigma^+$ system were determined with greater reliability and differed significantly from the previous work. Another contribution of the present analysis was the observation of

the $a^3\Pi_1 - X^1\Sigma^+$ system of BI which was completely absent or¹¹⁰
overlapped in Lebreton's work (51). Fifteen bands with
clearly resolved P and Q heads have been assigned and the
molecular parameters of the $a^3\Pi_1$ state of BI were well
determined.

It should be mentioned also that the presently used
source of excitation demonstrates an efficient method of
obtaining weak emission spectra without interferences from
strong extensive systems that can result when a substrate
molecule is introduced into a microwave discharge cavity.

5.2 Results and Discussion

Part of the visible emission spectrum of BI is shown in
Figure 5.1. Sequences of violet-degraded bands are observed
with the strongest bands near 6000 Å. Assignment of bands
to the $a^3\Pi_0^+ - X^1\Sigma^+$ system was straightforward since some
bands have been identified previously (51). Twenty-three
bands were assigned to the $a^3\Pi_0^+ - X^1\Sigma^+$ system and are shown in
a Deslandres array in Table 5.1. For two sequences ($\Delta v = 1$
and 2), additional heads were observed with lower intensity,
and are due to corresponding transitions of the less
abundant (~20%) ^{10}BI isotope; Table 5.2 shows the ten heads
which were assigned to the $a^3\Pi_0^+ - X^1\Sigma^+$ system of ^{10}BI . After
the assignments of the $a(0^+) \rightarrow X$ system had been made, three
sequences remained that did not belong to this system.
These bands have been assigned to the $a(1) \rightarrow X$ system of

¹¹BI. The validity of this assignment¹¹¹ was justified by two principal arguments; i) when the bandheads were arranged in a Deslandres table, Table 5.3, the lower state vibrational intervals were similar to those of the $a(0^+) \rightarrow$ system of ¹¹BI; and ii) all the observed bands in the three sequences were double-headed, as expected for a Hund's case (c) $\Delta\Omega = 1$ transition for which $\Delta J = 0, \pm 1$. (A more detailed description of case (c) coupling case is presented in the following chapter.) The two heads are formed by the P and Q branches, with the P head $\sim 7 \text{ cm}^{-1}$ lower in energy. For $\Delta\Omega = 0$, as in $a(0^+) \rightarrow X^1\Sigma^+$, $\Delta J = 0$ is forbidden, and the corresponding bands of this system show only single heads. It can be noted also that the separations of $\sim 300 \text{ cm}^{-1}$ between the $a(0^+) \rightarrow X^1\Sigma^+$ and $a(1) \rightarrow X^1\Sigma^+$ sub-systems provide an approximate estimate for the spin-orbit coupling constant of the excited state. The corresponding separation of the two sub-systems in BBr (50) is $\sim 180 \text{ cm}^{-1}$, significantly smaller, as expected.

Table 5.1: Deslandres table for the $s^3\Pi_0^+ - X^1\Sigma^+$ system of ^{11}Br

v'	$v'=0$	$v''=1$	$v''=2$	$v''=3$	$v''=4$	$v''=5$	$v''=6$
0	16087.1	569.0	15518.1				
	641.0		641.6				
1	16728.1	568.4	16159.7	562.7	15597.0		
	629.7	629.3					
2	17357.8	568.8	16789.0				
	617.5		619.8				
3	17975.3	566.5	17408.8	563.1	16845.7		
			606.5		608.8		
4		18015.3	560.8	17454.5	558.2	16896.3	
				595.0		596.4	
5			18049.5	556.8	17492.7	549.0	16943.7
					587.3		585.9
6				18080.0	550.4	17529.6	544.7
						574.0	573.0
7					18103.6	545.7	17557.9
							561.0
8						18118.9	537.3
							17581.6

Table 5.2: Deslandres Table for the $a^3\Pi_0^+ - X^1\Sigma^+$ System of ^{10}Br

v'	$v''=0$	$v''=1$	$v''=2$	$v''=3$	$v''=4$
0		15495.2			
1	16758.5		15575.0		
2		16821.3			
		644.2			
3		17465.5	586.4	16879.1	
			631.5		
4			17510.6	582.0	16928.6
				625.1	
5				17553.7	575.3 16978.4

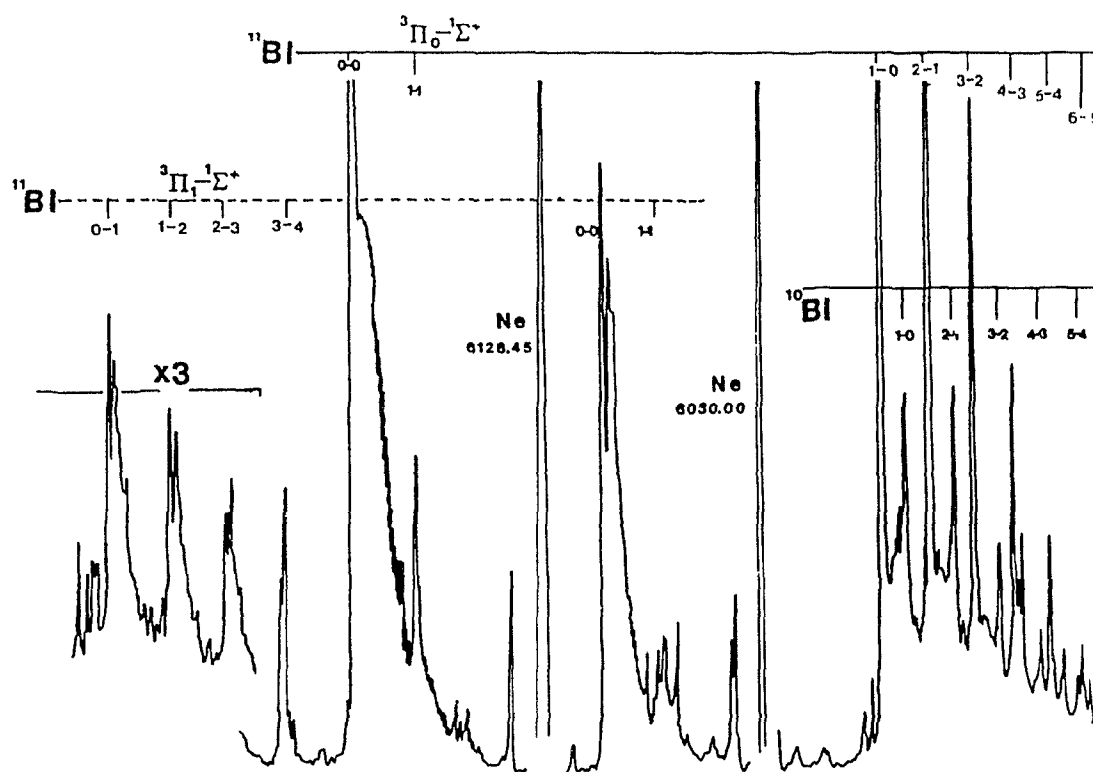
Table 5.3: Deslandres Table^a for the $a^3\Pi_1 - X^1\Sigma^+$ system of ^{11}BI

v'	$v''=0$	$v''=1$	$v''=2$	$v''=3$	$v''=4$	$v''=5$
0	16391.3	570.6	15820.7	564.9	15255.8	
	16384.0	570.1	15813.9	563.4	15250.5	
	630.6		634.8		633.6	
	630.0		634.3		633.5	
1	17021.9	566.4	16455.5	566.1	15889.4	559.5 15329.9
	17014.0	565.8	16448.2	564.2	15884.0	558.7 15325.3
			621.1		623.9	621.8
			621.0		622.7	621.4
2			17076.6	563.3	16513.3	561.6 15951.7 550.9 15400.8
			17069.2	562.5	16506.7	560.0 15946.7 551.9 15394.8
					612.6	617.6
					610.4	617.0
3					17125.9	16018.4
					17117.1	16011.8*
4					*	
					*	
5						17204.9
						17198.7
6						17238.0
						17229.5

a) For each band, the upper and lower entries denote the positions of the Q and P heads, respectively, heads flagged with an asterisk were overlapped by intense atomic lines.

Figure 5.1: A portion of the BI emission spectrum from
~5890 to ~6325 Å.

Figure 5.1



Since the present measurements refer to positions of band heads, rather than origins, it is appropriate to determine the reliability of the derived vibrational intervals in Tables 5.1, 5.2, and 5.3. This can be achieved by calculating head-to-origin separations for P or R branches from the equation (2),

$$\nu_{\text{head}} - \nu_0 = - \frac{(B_v' + B_v'')^2}{4(B_v' - B_v'')}. \quad (5.1)$$

If it is assumed that α_v'' is similar to α_v' $\sim 0.004 \text{ cm}^{-1}$ (51), the calculated head-to-origin spacings increase with $\Delta v = v' - v''$. For example, the spacings are $\sim 4 \text{ cm}^{-1}$ for $\Delta v = -3$, $\sim 5.4 \text{ cm}^{-1}$ for $\Delta v = 0$, and $\sim 10 \text{ cm}^{-1}$ for $\Delta v = 3$. Such separations are of the same order as that of the measurement precision of the present work. It can be expected, therefore, that the head measurements are quite suitable for deriving effective vibrational parameters that differ insignificantly from their true values. For the $a(1) \rightarrow X$ bands, the error introduced with the use of head data is negligible, because the Q-heads are available. It is interesting to note that the P- and Q-head separations, Table 5.3, are in accord with the calculated head-to-origin spacings for the $a(0^+) \rightarrow X$ system. The measured P- and Q-head positions of the $a(0^+) \rightarrow X$ and $a(1) \rightarrow X$ systems respectively can be represented adequately by the difference between the two power series expansions in vibrational quantum number,

$$\nu_{iv'v''} = T_0 + \sum_{k=0} Y_{ik}' (v' + 1/2)^k - \sum_{k=0} Y_{ik}'' (v'' + 1/2)^k, \quad (5.2) \quad 118$$

where i represents a particular isotope. The Y_{ik} coefficients can be related to isotopically invariant parameters, U_k (56), by,

$$Y_{ik} = \mu_i^{(-k/2)} U_k, \quad (5.3)$$

where μ_i is the reduced mass of the isotopic molecule i . The expression (5.2) is valid strictly only for sub-band origins; however, from the earlier discussion, it was not expected, nor found, that such a model introduces any systematic trend in the residuals between the fitted and observed band positions. Instead, the head-to-origin shifts are accommodated by the determination of effective T_0 values of the two excited states ($^3\Pi_0^+$, $^3\Pi_1$). It was found that the accuracy of the measurements and the vibrational extension of the heads permitted the evaluation of only the first two effective isotopically invariant vibrational parameters ($k = 1, 2$). The six parameters (U_{10} and U_{20} for the $^1\Sigma^+$, $^3\Pi_0^+$, and $^3\Pi_1$ electronic states) have been derived using a simultaneous least-squares fit to the model given by equations 5.2, 5.3, and are listed in Table 5.4. The standard deviation of the fit was $\hat{\sigma} = 1.6 \text{ cm}^{-1}$ with 40 degrees of freedom, and is in accord with estimated uncertainties in the data. In Table 5.5, the equilibrium term values, T_0 , and ω_0 , $\omega_0 x_0$, $(U_{10}/(\mu_i)^{1/2}$, $-U_{20}/\mu_i$) are reported and compared with the corresponding constants for the X , $a(0^+)$ and $a(1)$ states of BCl and BBr. From Table 5.5, it is immediately obvious that, i) the $a(1)$ states lie at higher energy than the $a(0^+)$ states and,

ii) the similar magnitudes of the vibrational parameters of the $a(1)$ and $a(0)$ electronic states of BBr and BCl suggest that both states correlate with the same electronic configuration. In accord with Barrow's discussion (57) on the low-lying states of the Group 3B halides, the observed energy ordering of the excited states of BBr and BI can be correlated only with the lowest excited configuration, $(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)(v\pi)$, $^1\Pi$, $^3\Pi_r$. If a bonding $w\pi$ electron is promoted to the $x\sigma$ orbital, the resulting state will be $^3\Pi_i$. Furthermore, Barrow argued that the $a^3\Pi_r$ excited states of the boron monohalides are correlated with $B(^2P_{3/2})$ and $X(^2P_{3/2})$ atomic states.

Table 5.4: Isotopically Invariant Dunham Coefficients^{a)}
 (cm^{-1}) for the $X^1\Sigma^+$ and $a^3\Pi$ States of BI

	U_{10}	U_{20}
$X^1\Sigma^+$	1830.4(21)	-30.1(12)
$a^3\Pi_0^+$	2076.3(17)	-56.0(7)
$a^3\Pi_1$	2050.5(29)	-55.4(13)

^{a)} Values in parentheses are estimated standard errors in units of the last digit of the corresponding parameters. These errors do not include contributions arising from the use of head data, rather than origin data; see text.

Table 5.5: Molecular Constants (cm^{-1}) for the $X^1\Sigma^+$ and $a^3\Pi$ States of the Boron Monohalides^a.

		^{10}BI	^{11}BI		$^{11}\text{B}^{79}\text{Br}$	$^{11}\text{B}^{35}\text{Cl}$
		this work	this work	(51)	(42, 49, 50)	(48, 53, 55)
$X^1\Sigma^+$	ω_e	600.84(69)	575.08(66)	574	684.3	839.12
	$\omega_e x_e$	3.24(13)	2.97(12)	2.4	3.52	5.11
$a^3\Pi_O^+$	T_e	16049.0(10)		16058	18673.80(5)	-
	ω_e	681.55(56)	652.34(53)	645	759.80(10)	-
	$\omega_e x_e$	6.030(76)	5.524(70)	5	4.80(2)	-
$a^3\Pi_1$	T_e	16355.2(13)		-	18851.48(4)	20234.86 ^{b, c}
	ω_e	673.08(85)	644.24(81)	-	757.10(10)	911
	$\omega_e x_e$	5.97(14)	5.47(13)		4.81(3)	5.7

a) Values in parentheses are estimated standard errors in units of the last digit of the corresponding constant. Reduced masses of BI, calculated from the atomic masses of Ref. (58), are ^{10}BI 9.2806796, ^{11}BI 10.130461 amu.

b) T_0 values

c) $A = 49.541$ (22)

It is quite clear that the coupling of the angular momenta changes from Hund's case (b) in BF to an intermediate case (a)-case (c) in the BCl, BBr and BI molecules. With increasing mass, case (c) coupling becomes predominant; as a consequence, the total electronic angular momentum about the internuclear axis is well-defined, the $\Delta S = 0$ selection rule holds less and less rigorously, and larger transition moments for the ${}^3\Pi(0^+,1) \rightarrow X$ transitions are expected. In addition, the case (c) selection rule $\Delta\Omega = 0, \pm 1$ forbids the ${}^3\Pi(2) \rightarrow X$ transition, which is observed in BF (47).

In conclusion, some consideration should be given to the difference in intensity between the two sub-systems of the Cameron bands for the BCl, BBr and BI molecules. The coupling of electronic states which are derived from the same configurations, presently $a{}^3\Pi$ and $A{}^1\Pi$, are of greatest importance in understanding the strong spin-orbit mixing toward the case (c) limit. As the selection rule for the spin-orbit operator is always $\Delta\Omega = 0$, only the states having $\Omega = 1$ can interact. Thus, non-zero spin-orbit matrix elements will occur between the $a(1)$ and $A{}^1\Pi_1$ states.

The factors affecting the intensity of forbidden transitions in diatomic molecules are discussed in the work of James (59). He assumed that the $a \rightarrow X$ transition of the Cameron system is allowed by the spin-orbit perturbation which mixes the ${}^1\Pi_1$ state with ${}^3\Pi_1$. Perturbation theory was followed to derive the first-order correction to the zeroth-

order wavefunctions of the $a(1)$ state. The corrected wavefunction was employed to determine the transition moment matrix element between the $a(1)$ and $X^1\Sigma^+$ states.

The approximate final expression for the effective electronic transition moment, the square of which is proportional to the band emission intensity, is given by

$$(R_e)_{a,X} = A (R_e)_{A,X} \Delta E^{-1} \quad (5.4)$$

where $(R_e)_{a,X}$ and $(R_e)_{A,X}$ are the electronic transition moments between the forbidden and allowed transitions respectively, A is the spin-orbit constant of the $a^3\Pi$ state and ΔE is the energy difference between the $A^1\Pi_1$ and $a(1)$ states. Using Eq. (5.4) with the data of Table 5.5, the spin-orbit mixing of the $a(1)$ and $A^1\Pi$ states becomes more significant with increasing mass, so that the transition probability of the $a(1) \rightarrow X$ system relative to the $a(0^+) \rightarrow X$ system is expected to be largest in BI. However, the $a(0^+) \rightarrow X$ bands of BI have approximately twice the intensity of the $a(1) \rightarrow X$ bands. It can be concluded, therefore, that the reaction of discharged helium with BI_3 favours population of the lower-lying $a(0^+)$ state.

Chapter 6

Rotational Analysis of the $a \rightarrow X$ System of ^{11}BI

6.1 Introduction

Although the present technique for excitation of emission from BI is relatively clean, with only few atomic lines as significant interference, the intensity of the observed bands is weak compared to a discharge source. However, the present work has established that spectra recorded with a scanning spectrometer and photoelectric detection show sufficient resolution for a useful rotational analysis. For the $a(0^+) \rightarrow X$ system of BI, the analysis has been extended considerably to eight bands (2-0, 3-1, 4-2, 1-0, 2-1, 3-2, 0-1, 0-0) with better rotational development than was possible in the work of Lebreton et al. (51).

In addition, two bands (0-0, 0-1) of the $a(1) \rightarrow X$ system have been analyzed, and rotational constants for the $a(1)$ state are obtained for the first time.

For the eight bands of the $a(0) \rightarrow X^1\Sigma^+$ system, the measured line positions have been reduced by direct least squares fitting to four parameters (ν_0 , B_v^I , D_v^I , B_v^{II}). For the two bands of the $a(1) \rightarrow X^1\Sigma^+$ system, five parameters have been determined (ν_0 , B_v^I , D_v^I , B_v^{II} and the Ω -doubling parameter (q) of the excited state). Multiple determinations of the parameters are reduced by the method

of merging to optimum single-valued estimates, as well as Dunham coefficients describing their vibrational dependences. The optical data of the present study are not sufficiently precise and extended to provide reliable estimates of absolute D_v' , D_v'' values simultaneously. Accordingly, values of D_v'' calculated by Hutson's method (60) from a preliminary RKR potential were used as a constraint in the direct least-squares fitting.

6.2 Nature of the Transition, Analysis and Data Fitting

As indicated in Chapter 5, the excited $a(0^+, 1)$ state of BI can be described by a coupling scheme close to Hund's case (c). The interaction between the orbital angular momentum and spin of the electrons (L and S) is stronger than the interaction with the internuclear axis of the molecule. In this case, Λ and Σ (the projections of L and S on the axis) are not defined; rather, L and S first form a resultant J_e which is then coupled to the internuclear axis with a component Ω . The electronic angular momentum Ω and the angular momentum of nuclear rotation (R) then form the resultant total angular momentum J. Therefore, electronic states which are represented by case (c) cannot be classified as $^1\Sigma, ^1\Pi, ^1\Delta$ states, but instead are simply called 0,1,2,, according to the value of Ω .

Since the excited state of BI is formally $a^3\Pi$ in Hund's case (a), three separate states with Ω values of 0, 1 and 2

are obtained in case (c). However, since the ground state is $^1\Sigma^+$, the case (c) selection rule $\Delta\Omega = 0, \pm 1$ restricts the observed transitions to two independent systems, $a(1) \rightarrow X^1\Sigma^+$ and $a(0^+) \rightarrow X^1\Sigma^+$. In addition, the $a(1)$ -X individual bands show $P(\Delta J = -1)$, $Q(\Delta J = 0)$, $R(\Delta J = 1)$ structure with P and Q bandheads; while the $a(0^+) \rightarrow X$ bands only show P and R structure with one P bandhead in accord with the restriction that if both states have $\Omega = 0$, no Q branch occurs.

The criterion in the selection of BI bands for analysis was that they be sufficiently intense to yield good signal-to-noise. For this reason, no attempt was made to analyze bands of the less abundant ($\sim 20\%$) ^{10}BI isotope observed at low resolution.

The line frequencies (ν_i) of individual bands were fitted by least-squares to determine the parameters in the equation

$$\begin{aligned} \nu_i = \nu_0 + \{B'_{vk}J'(J' + 1) - D'_{vk}[J'(J' + 1)]^2\} \\ - \{B''_{v}J''(J'' + 1) - D''_{v}[J''(J'' + 1)]^2\} + \varepsilon_i, \end{aligned} \quad (6.1)$$

where ν_0 is the band origin of the $v' - v''$ band, B''_v , D''_v are the ground state rotational constants, B'_{vk} , D'_{vk} , $k = e$ or f are the effective rotational constants for the two Ω -doubled e and f components of the $a(1)$ state, and ε_i are the unknown measurement errors. For the $a(0^+)$ state, the rotational levels are nondegenerate and hence they can be represented by a single set of rotational constants (B'_v , D'_v), as in the ground state. Furthermore, the sets of e and f levels are

each associated with different branches in the $a(1) \rightarrow X$ system; as indicated in the rotational level energy diagram in Figure 6.1, the P and R branches are associated with e levels, and the Q branch with f levels.

In practice, Eq. (6.1) was modified by introduction of the Ω -doubling parameter $q_v = B_{v_e} - B_{v_f}$, so that the constants employed in the computer fits to describe the excited state $a(1)$ were B_{v_f} , D_{v_f} together with q_v . Higher-order centrifugal distortion terms were not required in the band-by-band fits. In fact, due to the high correlation of the centrifugal distortion constants, D_v^I and D_v^{II} , and the extension of the available data, D_v^{II} always constrained at the value $D_0^{II} = 5.97 \times 10^{-7} \text{ cm}^{-1}$ calculated using Hutson's method (60) with the $X^1\Sigma^+$ potential energy curve. The D_v^{II} parameter did not show any significant variation for $v'' = 0, 1, 2$. In addition, the same parameter at the potential minimum, D_0^{II} as given by the Dunham relationship (2) $D_0^{II} = 4B_0^3/\omega_0^2$, had the same value as D_0^{II} .

Firstly, bands belonging to the $a(0^+) \rightarrow X$ system were analyzed. The numbering of the lines in the P and R branches was by no means obvious. In the vicinity of the bandheads and the origins, the lines appear as closely spaced doublets composed of a P(J) line with an R(J) line of low-J or a P(J) line of high-J. These doublets were not resolved with the present resolution so that the P(1) or R(0) lines could not be identified directly. Although

intensity considerations of the rotational lines in the neighbourhood of the central gap (space between the P(1) and R(0) lines) reduced the possibilities of a correct absolute numbering to two or three different schemes, an unequivocal assignment could not be obtained. However, the problem was resolved as follows. Approximate estimates for B_v'' were calculated from B_v' and α_v' assuming that α_v'' is similar to α_v' , $\sim 0.004 \text{ cm}^{-1}$ (51).

The r_v'' value that defines B_v'' was estimated by using Badger's rule (2), $\mu\omega_v^2 (r_v - \delta)^3 = C$. The parameters δ and C were calculated from the known r_v and ω_v for BCl and BBr (53), and gave $r_v'' = 2.10 \text{ \AA}$ for BI. This estimate is consistent with the estimate calculated from the covalent radii of Cl, Br and I.

For the band-by-band fits of the $a(0^+) \rightarrow X$ system, the rotational constants of the X state were constrained to values less than, close to, and greater than the estimated values. The three absolute trial numberings of the rotational lines led to fits with similar standard deviations. However, for only one case of the absolute numbering were the multiple estimates of the same molecular constant in agreement to within two standard errors. For the other numbering schemes, such multiple estimates differed by many standard errors (typically ~ 15 standard errors). Furthermore, the J numbering found by this approach is in agreement with that used by Lebreton et al.

(51) for the two bands common to both studies. It should be noted that the numbering which was given in Ref. (51) was not assumed at the outset of the present work since no discussion about its validity was presented, and it is not obvious from the published spectrum that an unequivocal absolute numbering had been properly considered. It has been mentioned already that the P(J) and R(J) lines near the origins of the analyzed bands of the $a(0^+) \rightarrow X$ system are blended with P(J) lines of high J-values in the returning limb of this branch. In order to accommodate these blended lines into the least-squares fit and obtain the best possible results, it was decided to fit the blends of lines of similar intensity as the weighted means of the separate transitions; however, blended lines with an intensity ratio greater than four were fitted as single lines in the corresponding strong branch. For the $a(0^+) - X$ bands, the blends were $(P(J)+P(n-J-1))$ and $(R(J) + P(n+J))$. The range of n is broad, from $n = 27$ for 0-1 band to $n = 43$ for the 4-2 band. The weights were taken as the corresponding squares of intensity factors for a $^1\Sigma - ^1\Sigma$ transition given in Ref. (2) by,

$$I \sim S_J \exp(-B_v^\dagger J'(J'+1)/kT) \quad (6.2)$$

where T is the rotational temperature, $k = 0.695 \text{ cm}^{-1}\text{K}^{-1}$ is the Boltzmann constant, and S_J is the line strength given by $S_J = J' + 1$ for the R branch, and $S_J = J'$ for the P branch.

From an intensity analysis of the 0-1 band recorded

under stable conditions, and using Eq. (6.2), it was found that the rotational temperature of BI was close to 300 K. In the 3-1 band, the blending of the PP and RP lines was not so close as in the other bands; therefore, the rotational lines in the region of the band origin appear to be broader and with low signal-to-noise ratio. For this reason, only lines which can be assigned as essentially unblended R(J) were included in the fit.

The blending problem in the bands of the $a(1) - X$ system is similar but more complicated. Figure 6.2 shows that many of R(J) lines are blended not only with P(n+J) lines, as in the $0^+ - X$ bands, but also with much stronger Q(n'+J) lines. In this case, the weights were obtained from the intensity factors for a $^1\Pi - ^1\Sigma$ transition; the line strengths are then (2),

$$S_J = 0.25 (J' + 1) \text{ for the R branch,}$$

$$S_J = 0.25 (2J' + 1) \text{ for the Q branch,}$$

$$\text{and } S_J = 0.25 J' \text{ for the P branch.}$$

The contributions of P(n + J) lines were so much smaller than those of Q(n' + J) that they were neglected entirely. Thus for the $a(1) - X$ bands only blends of P(J) + P(n, J-1) and R(J) + Q(n' + J) were considered.

Figure 6.1: An energy level diagram for the first lines of a ${}^1\Pi - {}^1\Sigma^+$ transition. The Ω -doubling of the $\Omega = 1$ state has been much exaggerated.

Figure 6.1

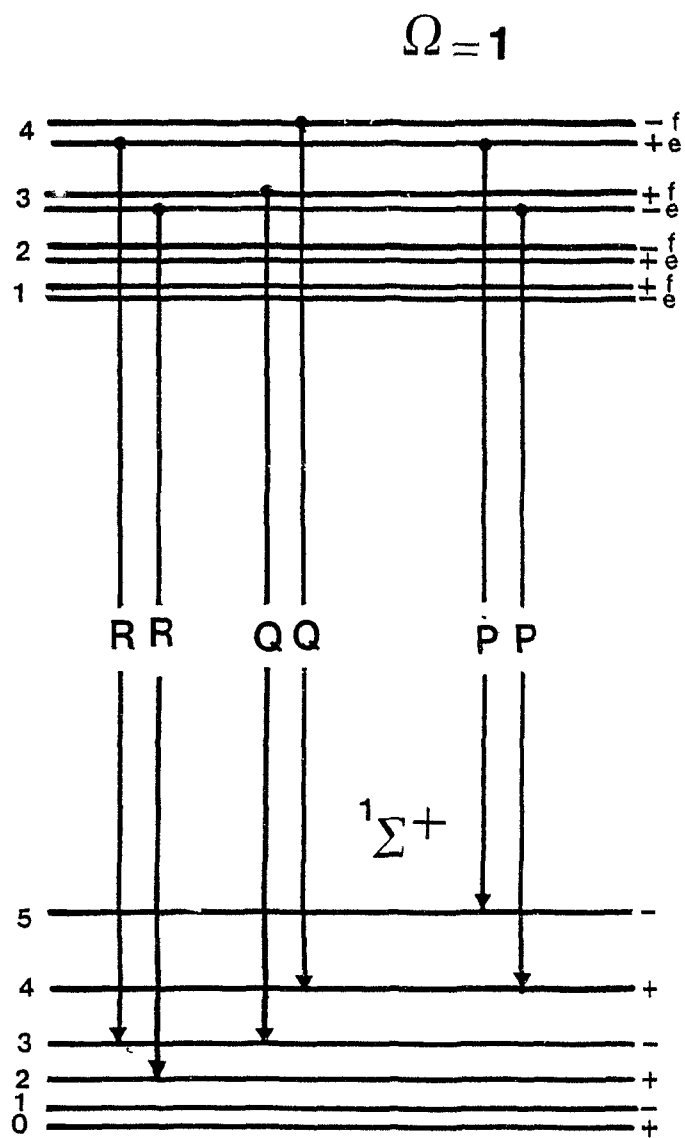
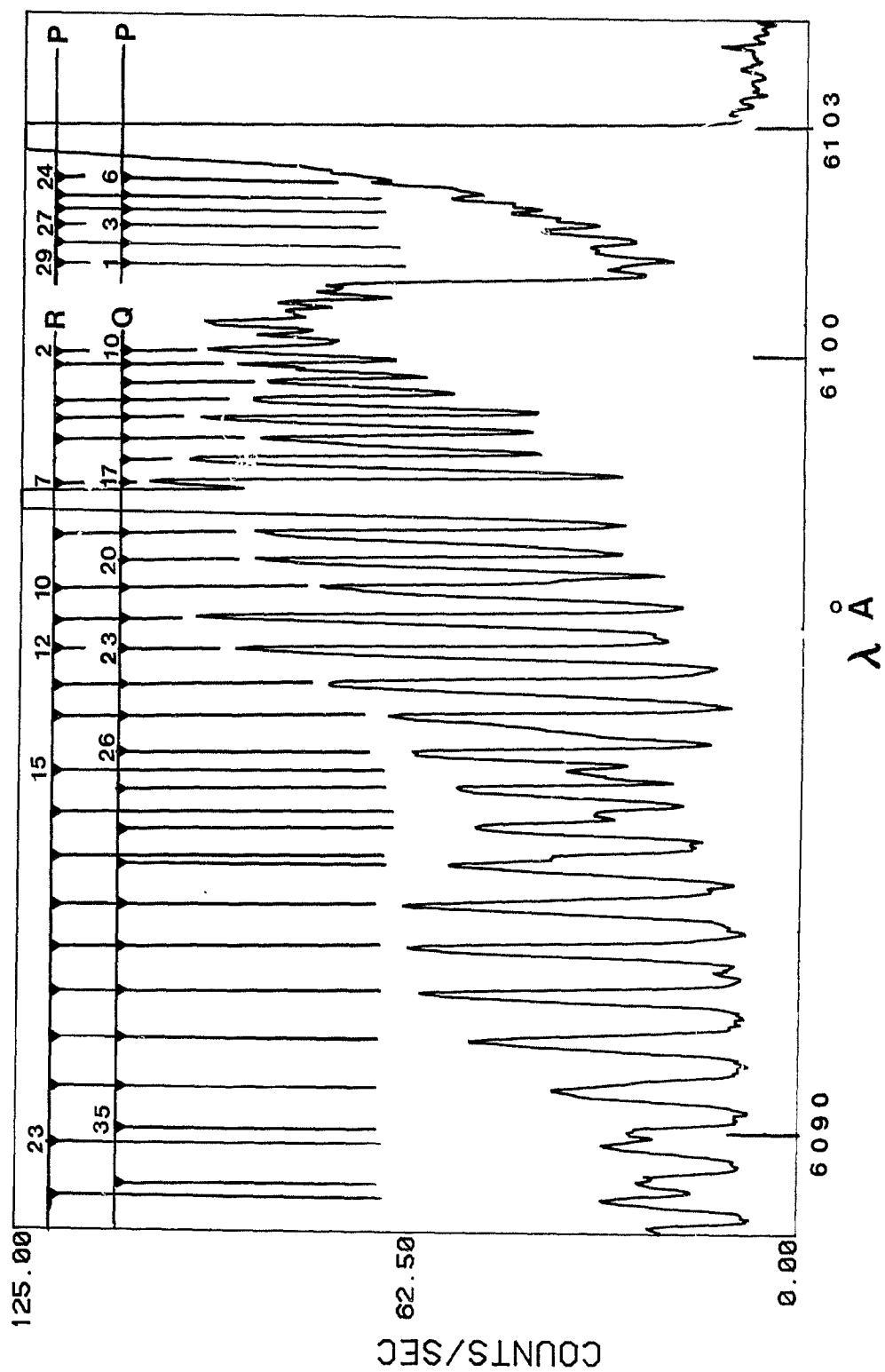


Figure 6.2: Rotational structure of the 0-0 band of the $a(1) \rightarrow X^1\Sigma^+$ system of ^{11}BI . The trace illustrates the extensive blending of the R and Q branches. The intense emission near the R(7) line is an unidentified atomic line.

Figure 6.2

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6.3 Results and Discussion

A summary of the final individual band least-squares fits is given in Table 6.1. Lines were excluded in all bands when the magnitudes of their residuals exceeded ~ 2.5 standard deviations of the fits. The standard deviations of the fits in Table 6.1 range between 0.018 and 0.042 cm^{-1} , and are consistent with the estimated measurement precision for single lines. The measured line positions of the ten individual bands in the $a \rightarrow X$ system of BI thus provided a set of 42 estimated parameters. Each band yielded four constants, ν_0 , B_v' , D_v' , B_v'' , and for the 0-0 and 0-1 bands of the $a(1) \rightarrow X$ system, the Ω -doubling parameter q_0' was obtained. The method of merging, discussed in Chapter 2, was employed subsequently to reduce the 42 parameters to a smaller set of parameters which takes account (in the least-squares sense) of the entire data set simultaneously. Merging was performed in a stepwise fashion. In the first merge (A), account is taken of the fact that many of the 42 parameters are multiple estimates of the same molecular constants. Therefore, the 42 parameters were reduced to a new set of 25 estimated constants (ten origins, ten B_v' and D_v' values for $v' = 0-4$, three B_v'' for $v'' = 0-2$, B_0' for the $a(1)$ state and the Ω -doubling parameter q_0').

The estimated variance of the merge is $\hat{\sigma}^2 = (1.140)^2$, with $f = 17$ degrees of freedom, and the results are given in Table 6.2.

A second step in the fit, merge (B), was performed to

Table 6.1: Individual Band Fits^a in the $a^3\Pi(0^+,1) - X^1\Sigma^+$
System of ^{11}BI

	v'	v''	$\nu_0(\text{cm}^{-1})$	n	$\hat{\sigma}(\text{cm}^{-1})$	$\text{rms}/\hat{\sigma}$
$0^+ - X$	0 - 1		15525.316(16)	38	0.029	1.00
	0 - 0		16095.250(11)	49	0.018	1.00
	1 - 0		16735.902(13)	36	0.032	1.16
	2 - 1		16796.967(13)	35	0.032	1.09
	3 - 2		16853.512(16)	33	0.031	1.07
	2 - 0		17366.931(13)	30	0.026	1.31
	3 - 1		17418.063(19)	13	0.032	0.91
	4 - 2		17464.338(19)	28	0.042	0.98
$1 - X$	0 - 1		15820.780(13)	52	0.029	1.00
	0 - 0		16390.690(15)	49	0.036	1.00

^aFor each band, n is the number of fitted lines and $\hat{\sigma}$ is the standard deviation. The band origins (ν_0) and estimated standard errors were obtained from Merge (B) (see text).

$\text{rms}/\hat{\sigma}$ represents the ratio of the root mean square of the residuals for lines calculated with merged parameters to the estimated standard deviation.

obtain B_v and α_v for the $a(0^+)$ and X states, according to Eq. (6.3),

$$B_v = B_0 - \alpha_v(v + \frac{1}{2}). \quad (6.3)$$

The results of merge (B) are summarized in Tables 6.1 and 6.3, which list the 10 band origins and the coefficients defined by Eq.(6.3) respectively. The centrifugal distortion constant of the $a(0^+)$ state did not show any significant vibrational dependence, so it was kept constant over the range of v' , $0 \leq v' \leq 4$. The estimated variance ($\hat{\sigma}_M^2 = (1.784)^2$ with $f = 25$) indicates the presence of only small systematic error in the data, assuming the model is adequate. However, in this case, the results is very acceptable compared with similar merges for other band systems. The output parameters in merge (B) reproduce the measured line positions very satisfactorily. This is shown in detail by the listing of line positions and residuals calculated from the parameters of Tables 6.1 and 6.3, and listed in Tables 6.4 and 6.5, and in summary by the entries in the last column of Table 6.1.

Table 6.2: Merged Parameters^a (cm^{-1}) for the X and a States of ^{11}BI

	v	B_v	$10^7 D_v$	$10^5 q_v$
$a^3\Pi(0^+)$	4	0.37716(10)	5.68(39)	
	3	0.380649(66)	5.72(39)	
	2	0.384286(56)	6.75(23)	
	1	0.387769(72)	6.22(42)	
	0	0.391093(52)	5.59(12)	
$a^3\Pi(1)$	0	0.390581(56)	b	-4.1(11)
$X^1\Sigma^+$	2	0.359697(71)		
	1	0.362350(55)		
	0	0.365104(54)		

^aParameters are fitted values output from Merge (A) (see text). Values in parentheses are estimated standard errors given by $\hat{\sigma}_M(V_{ii})^{1/2}$ in units of the last significant figure of the corresponding constant.

^bThe merge assumes that D'_0 for $v' = 0$ of $a^3\Pi(1)$ is the same as D'_0 for $v' = 0$ of $a^3\Pi(0^+)$.

Table 6.3: Molecular Constants^a (cm⁻¹) for the X and a States of ¹¹BI

	a ³ Π(1)	a ³ Π(0 ⁺)	X ¹ Σ ⁺
B _e		0.392939(70)	0.366510(80)
B ₀	0.390692(77)		
10 ³ α _e		3.493(11)	2.726(17)
10 ⁷ D		5.89(15)	[5.97]
10 ⁵ q ₀	-4.8(16)		

^aParameters are fitted values output from Merge (B) (see text). Values in parentheses are estimated standard errors given by $\hat{\sigma}_M(V_{ii})^{1/2}$ in units of the last significant figure of the corresponding constant. The fit assumes that D' is independent of v, and has the same for the a(0⁺) and a(1) states. D'' was held fixed at the value listed, see text.

Table 6.4: Line Positions^a (cm⁻¹) for the a³Π(0⁺) - X¹Σ⁺ System of ¹¹Bi

0 - 0				1 - 0			2 - 0		
	P*	Calc	Res	P*	Calc	Res	P*	Calc	Res
P(9)	20	16090.558	0.036						
8	21	16090.872	-0.020	25	16731.267	-0.048	31	17362.130	-0.028
7	22	16091.239	0.003	26	16731.673	-0.051	32	17362.591	-0.021
6	23	16091.658	0.027	27	16732.124	-0.043	33	17363.090	-0.064
5	24	16092.130	0.029	28	16732.619	0.043	34	17363.627	-0.064
4	25	16092.654	0.021	29	16733.157	-0.093*	35	17364.202	-0.110*
3	26	16093.231	-0.002	30	16733.738	-0.009	36	17364.813	0.000
2	27	16093.861	-0.014	31	16734.360	0.077*	37	17365.461	0.023
1	28	16094.545	-0.000	32	16735.020	-0.000	38	17366.144	-0.123*
	29	16095.284	-0.007	33	16735.712	0.044	39	17366.854	-0.042
R(0)	30	16096.068	0.013	34	16736.479		40	17367.624	
1	31	16096.901	-0.007	35	16737.350	0.103*	41	17368.463	-0.031
2	32	16097.787	0.003	36	16738.239	0.060	42	17369.321	-0.002
3	33	16098.724	0.002	37	16739.169	-0.025	43	17370.212	-0.078*
4	34	16099.714	-0.004	38	16740.141	-0.007	44	17371.139	-0.044
5	35	16100.756	-0.004	39	16741.156	0.002	45	17372.102	-0.049
6	36	16101.849	0.013	40	16742.213	-0.031		17373.110	-0.002
7	37	16102.995	0.011	41	16743.313	-0.143*		17374.144	-0.075*
8	38	16104.192	0.005	42	16744.457	0.039		17375.217	0.005
9	39	16105.442	0.001		16745.683	-0.027		17376.328	-0.099*
10	40	16106.744	0.036		16746.909	-0.096*		17377.477	-0.042
11	41	16108.097	-0.014		16748.180	-0.055		17378.664	0.026
12		16109.479	0.066*		16749.495	-0.031		17379.889	0.048
13		16110.937	0.013		16750.856	-0.068		17381.151	0.009
14		16112.448	0.022		16752.261	-0.025		17382.452	0.004
15		16114.010	0.012		16753.712	-0.004		17383.791	0.034
16		16115.624	-0.025		16755.207	-0.030		17385.167	0.027
17		16117.290	0.009		16756.747	-0.042		17386.581	0.005
18		16119.007	-0.021		16758.332			17388.034	-0.007
19		16120.777	-0.022		16759.962	-0.013		17389.524	0.002
20		16122.599	-0.038		16761.637	0.038		17391.052	0.035
21		16124.472	-0.012		16763.356	0.015		17392.618	0.018
22		16126.397	-0.011		16765.121	0.011		17394.222	0.007
23		16128.374	0.014		16766.930	0.042		17395.863	0.090*
24		16130.403	-0.010		16768.784	0.017		17397.543	0.107*
25		16132.483	0.020		16770.683	0.015		17399.260	0.057
26		16134.615	-0.023		16772.627	0.022		17401.015	-0.008
27		16136.800	0.011		16774.615	0.042		17402.808	0.060
28		16139.035	0.029		16776.649	0.030		17404.639	0.279*
29		16141.323	-0.024		16778.727	0.073		17406.507	0.036
30		16143.663	0.011		16780.849	-0.026		17408.413	-0.148*
31		16146.054	-0.025		16783.017	-0.043			
32		16148.497	-0.011		16785.229	0.060			

(cont'd.)

Table 6.4: Line Positions^a (cm⁻¹) for the $a^3\Pi(O^+)$ - $X^1\Sigma^+$ System of ^{11}BI (cont'd)

0 - 0			1 - 0			2 - 0		
P*	Calc	Res	P*	Calc	Res	P*	Calc	Res
33	16150.991	-0.009		16787.486				
34	16153.537	-0.007		16789.788	0.022			
35	16156.135	-0.028						
36	16158.785	0.017						
37	16161.486	0.068*						
38	16164.239	0.013						
39	16167.044	-0.016						
40	16169.901	0.023						

Table 6.4: Line Positions^a (cm⁻¹) for the $a^3\Pi(0^+) - X^1\Sigma^+$ System of ^{11}BI (cont'd)

0 - 1				2 - 1			3 - 1		
	P*	Calc	Res	P*	Calc	Res	P*	Calc	Res
9				25	16791.985	0.063			
8				26	16792.357	-0.021			
7	19	15521.421	-0.157*	27	16792.772	-0.011			
6	20	15521.794	-0.157*	28	16793.231	0.056			
5	21	15522.224	-0.158*	29	16793.733	0.001			
4	22	15522.711	-0.110*	30	16794.278	-0.020			
3	23	15523.254	-0.030	31	16794.866	0.006			
2	24	15523.853	-0.008	32	16795.495	0.047			
1	25	15524.508	-0.023	33	16796.164	-0.019			
	26	15525.217	0.056	34	16796.869	0.168*			
$R(0)$	27	15526.000	0.085*	35	16797.647				
1	28	15526.848	0.013	36	16798.476	0.112*			
2	29	15527.753	0.017	37	16799.345	0.049			
3	30	15528.715	0.011	38	16800.255				
4	31	15529.735	-0.007	39	16801.206	0.028			
5	32	15530.811	-0.021	40	16802.200	-0.091*			
6	33	15531.945	0.032	41	16803.235	-0.065			
7	34	15533.135	0.048	42	16804.313	-0.025			
8	35	15534.383	0.040	43	16805.433	-0.085*			
9	36	15535.687	0.001		16806.609	-0.099*	17427.321	0.010	
10	37	15537.049	-0.030		16807.813	-0.064	17428.428	0.034	
11	38	15538.468	-0.021		16809.060	-0.048	17429.611		
12	39	15539.943	0.037		16810.350	-0.064	17430.810		
13		15541.499	0.033		16811.683	-0.023	17432.046	-0.017	
14		15543.086	-0.008		16813.060	0.022	17433.318	-0.032	
15		15544.730	0.025		16814.481	-0.013	17434.626	-0.035	
16		15546.431	0.012		16815.945	0.045	17435.971	-0.002	
17		15548.190	0.011		16817.452	-0.065	17437.353		
18		15550.006	-0.009		16819.002	-0.051	17438.770		
19		15551.879	-0.060		16820.596	0.034	17440.224	0.047	
20		15553.809	0.025		16822.233	0.075*	17441.715		
21		15555.797	-0.039		16823.913	0.006	17443.241		
22		15557.842	0.027		16825.637	0.004	17444.804	-0.016	
23		15559.945	-0.017		16827.404	-0.004	17446.404	-0.036	
24		15562.104	-0.027		16829.214	0.017	17448.039	0.034	
25		15564.321	0.025		16831.068	0.022	17449.711	-0.021	
26		15566.595	-0.025		16832.965	0.019	17451.419		
27		15568.927	-0.037		16834.905	0.027	17453.164	-0.007	
28		15571.315	-0.020		16836.888	0.028	17454.944	0.039	
29		15573.761	0.009		16838.915	0.030			
30		15576.264	-0.038		16840.985	0.010			
31		15578.824	0.022		16843.098	-0.007			
32		15581.441	-0.043		16845.254	-0.007			
33		15584.116	0.038						
34		15586.847	-0.002						

Table 6.4: Line Positions^a (cm⁻¹) for the a³Π(0⁺) - X¹Σ⁺ System of ¹¹BI (cont'd.)

3 - 2				4 - 2		
	P*	Calc	Res	P*	Calc	Res
P(8)	27	16848.914	-0.026			
7	28	16849.336	-0.043	35	17460.073	0.023
6	29	16849.801	-0.013	36	17460.586	-0.008
5	30	16850.308	0.007	37	17461.135	0.053
4	31	16850.856	-0.000	38	17461.721	0.009
3	32	16851.446	-0.097*	39	17462.345	0.059
2	33	16852.077	-0.053	40	17463.009	-0.010
1	34	16852.748	-0.029	41	17463.720	-0.035
	35	16853.457	-0.096*	42	17464.501	
R(0)	36	16854.226	0.081*	43		
1	37	16855.041	0.007	44	17465.976	-0.044
2	38	16855.895	0.097*	45	17466.776	0.107*
3	39	16856.789	-0.053	46	17467.620	0.153*
4	40	16857.724	0.067	47	17468.504	0.013
5	41	16858.699	0.050		17469.390	0.091*
6	42	16859.716	0.000		17470.354	-0.019
7	43	16860.774	0.081*		17471.354	-0.010
8	44	16861.873	-0.096*		17472.388	0.076
9		16863.015	-0.045		17473.457	0.078
10		16864.197	0.023		17474.561	0.032
11		16865.419	0.029		17475.701	-0.069
12		16866.684	0.026		17476.875	-0.005
13		16867.991	0.036		17478.083	-0.020
14		16869.339	0.043		17479.327	-0.037
15		16870.730	-0.008		17480.606	-0.003
16		16872.162	-0.019		17481.919	-0.100*
17		16873.636	0.020		17483.267	0.044
18		16875.152	-0.009		17484.650	0.022
19		16876.709	0.039		17486.068	-0.036
20		16878.309	0.018		17487.521	-0.064
21		16879.950			17489.008	-0.068
22		16881.633	0.003		17490.531	-0.016
23		16883.357	0.017		17492.088	0.021
24		16885.124	-0.020		17493.679	0.050
25		16886.932	0.048		17495.306	-0.030
26		16888.782	-0.006			
27		16890.674	0.013			
28		16892.607	-0.034			
29		16894.582	-0.028			
30		16896.599	-0.043			

^aThe table lists positions of single lines and intensity-weighted blends calculated from the parameters of Merge (B). Blended positions are those for which P*(J) is listed in addition to P(J) or R(J). The residuals are defined as res = $\nu_{\text{obs}} - \nu_{\text{calc}}$. Data not included in the least-squares fits are indicated by an asterisk.

Table 6.5: Line Positions^a (cm⁻¹) for the a³Π(1) - X¹Σ⁺ System of ¹¹Bi

		Q-Branch		Blends		R-Branch	
0 - 0 Band		Calc	Res	Calc	Res	Calc	Res
P(10)	P(20)			16385.746	0.046		
9	21			16386.031	-0.088*		
8	22			16386.368	0.000*		
7	23			16386.758	0.057		
6	24			16387.202	-0.047		
5	25			16387.700	0.022		
4	26			16388.254	-0.001		
3	27			16388.865	0.050		
2	28			16389.539	-0.028		
1	29			16390.283	-0.017		
Q(0)		16390.690					
1		16390.741					
2		16390.843					
3		16390.997					
4		16391.201					
5	R(0)	16391.456				16391.471	
6		16391.763					
7	1	16392.121				16392.304	
8		16392.529					
9		16392.989	-0.017				
10	2			16393.446	0.058		
11	3			16394.074	-0.007		
12		16394.675	0.029				
13	4			16395.289	0.108*		
14	5			16396.075	0.023		
15	6			16396.925	-0.072		
16		16397.639	0.023				
17	7			16398.469	0.056		
18	8	16399.427				16399.556	
19	9			16400.520	-0.069		
20	10	16401.420	0.028			16402.087	0.011
21		16402.493	-0.034				
22	11			16403.551	0.046		
23	12			16404.803	-0.025		
24	13			16406.112	-0.016		
25	14	16407.297	-0.020			16407.757	0.060
26	15	16408.626	0.044			16409.302	-0.004
27	16	16410.006	0.009			16410.898	-0.042
28	17	16411.437	0.004			16412.544	-0.009
29		16412.919	-0.052				
30	18			16414.353	0.067		
31	19			16416.014	0.010		
32	20			16417.731	0.015		
33	21			16419.503	0.020		
34	22			16421.330	-0.020		

Table 6.5: Line Positions^a (cm⁻¹) for the $a^3\Pi(1) - X^1\Sigma^+$ System of ^{11}BI (cont'd.)

		Q-branch		Blends		R-Branch	
0 - 0 Band		Calc	Res	Calc	Res	Calc	Res
35	23	16422.888	-0.014			16423.489	-0.105*
36	24	16424.729	0.006			16425.490	-0.040
37	25	16426.621	-0.018			16427.543	-0.061
38	26	16428.564	-0.035			16429.645	-0.047
39		16430.558					
40	27	16432.604				16431.799	0.014
41	28	16434.701				16434.004	-0.018
42	29	16436.849				16436.259	
43	30	16439.048				16438.565	-0.103*
44	31	16441.299				16440.921	-0.029
45	32	16443.600				16443.328	
46	33	16445.954				16445.786	-0.005
47	34	16448.358				16448.294	
48	35	16450.814				16450.853	-0.083*
49	36	16453.321				16453.463	-0.053

Table 6.5: Line Positions^a (cm⁻¹) for the $a^3\Pi(0^+) - X^1\Sigma^+$ System of ^{11}BI (cont'd.)

		Q-branch		Blends		R-Branch	
0 - 1 Band		Calc	Res	Calc	Res	Calc	Res
P(8) P(19)				15816.633	0.019		
7	20			15816.979	-0.119*		
6	21			15817.383	-0.057		
5	22			15817.847	0.025		
4	23			15818.371	0.037		
3	24			15818.957	-0.012		
2	25			15819.608	-0.006		
1	26			15820.328	-0.062*		
Q(0)		15820.780					
1		15820.837					
2		15820.950					
3		15821.119					
4		15821.345					
5	R(0)	15821.628				15821.561	
6		15821.967					
7	1	15822.363				15822.399	
8		15822.815	-0.037				
9	2	15823.324				15823.293	
10		15823.890	-0.078*				
11	3			15824.459	0.058		
12	4			15825.204	-0.009		
13		15825.925	-0.095*				
14	5			15826.622	0.032		
15	6			15827.532	0.006		
16	7			15828.508	0.006		
17	8	15829.431	0.018			15829.843	
18	9	15830.449	-0.025			15831.131	-0.019
19		15831.524	-0.006				
20	10			15832.597	0.016		
21	11			15833.854	-0.008		
22	12			15835.175	0.015		
23	13	15836.387	-0.025			15836.850	
24	14	15837.745	0.033			15838.420	0.024
25	15	15839.159	-0.029			15840.047	-0.001
26	16	15840.630	0.026			15841.729	-0.029
27	17	15842.157	-0.031			15843.468	-0.037
28		15843.741	-0.049				
29	18			15845.328	-0.003		
30	19			15847.095	0.013		
31	20			15848.923	-0.001		
32	21			15850.811	0.044		
33	22	15852.509	0.021			15853.007	-0.050
34	23	15854.433	0.013			15855.083	0.003
35	24	15856.413				15857.216	-0.027
36	25	15858.450	0.009			15859.404	-0.027
37	26	15860.543	0.001			15861.649	0.005
38	27	15862.694				15863.950	-0.032

Table 6.5: Line Positions^a (cm⁻¹) for the $a^3\Pi(1) - X^1\Sigma^+$ System of ^{11}Bi (cont'd.)

		Q-branch		Blends		R-Branch	
0 - 1 Band		Calc	Res	Calc	Res	Calc	Res
39	28	15864.901				15866.307	-0.093*
40	29	15867.164	-0.008			15868.720	0.003
41	30	15869.485	0.018			15871.190	-0.008
	31					15873.715	-0.052
	32					15876.297	
	33					15878.934	-0.002
	34					15881.628	
	35					15884.378	
	36					15887.184	0.054
	37					15890.045	0.049

^aThe table lists positions of single lines and intensity-weighted blends calculated from the parameters of Merge (B). The residuals are defined as $\text{res} = \nu_{\text{obs}} - \nu_{\text{calc}}$. Data not included in the least-squares fits are indicated by an asterisk.

These entries are the ratios of the root-mean squares (rms) of the residuals to the standard deviations for the individual bands. The final merges, (C) and (D), employed the output of merge (B) as input to obtain estimates of vibrational term values and vibrational constants respectively for the $a(0^+)$ and X.

The ten estimated band origins were reduced in merge (C) to eight term values relative to $G''(0) = 0.0$, and in merge (D) to T_0' , ω_0' , $\omega_0'x_0'$, $\omega_0'y_0'$ for the $a(0^+)$ state, $T_0' + G'(0)$ for the $a(1)$ state, and ω_0'' , $\omega_0''x_0''$ for the X state. The results are given in Table 6.6. The estimated variances of the equivalent single step merges to the parameters of merges (C) and (D) are $(2.00)^2$ and $(1.97)^2$, indicating the absence of any appreciable systematic error in the absolute wavenumbers.

In conclusion, the following observations can be emphasized:

The estimates in Table 6.2 of B_0' , B_1' , B_0'' , and these reported by Lebreton et al. (51) ($B_0' = 0.389$, $B_1' = 0.385$, $B_0'' = 0.363 \text{ cm}^{-1}$), are in very good agreement.

Since the latter constants were derived from conventional spectrographic data, there is much confidence in the reliability of the present approach for gaining useful fundamental data from weak spectra.

The present work demonstrates, then, the advantages of the photoelectric technique. These are: the very high

sensitivity permitting the use of the weak, but specific emission source, without the problems of spectral interference. The analysis of the $a(0^+) \rightarrow X$ system has thus been extended considerably and the first data on the $a(1)$ state have been obtained.

Table 6.6: Term Values and Vibrational Parameters^a (cm⁻¹)
for the X¹Σ⁺ and a³Π(0⁺,1) States of ¹¹BI

a ³ Π(1)	E ₀ = 16390.707(16)	T ₀ + G'(0) = 16677.695(20)
a ³ Π(0 ⁺)	E ₄ = 18598.828(34)	T ₀ = 16058.399(26)
	E ₃ = 17988.002(26)	ω _e = 649.989(44)
	E ₂ = 17366.922(14)	ω _e x _e = 4.585(22)
	E ₁ = 16735.905(14)	10 ² ω _e y _e = -5.14(30)
	E ₀ = 16095.253(12)	
X ¹ Σ ⁺	E ₂ = 1134.489(30)	ω _e = 575.322(26)
	E ₁ = 569.937(13)	ω _e x _e = 2.693(10)
	E ₀ = 0.0	

^aValues in parentheses are estimated standard errors given by $\hat{\sigma}_M(V_{ii})^{1/2}$, in units of the last significant figure of the corresponding parameter.

Chapter 7

Vibrational Analysis of PCl^+ , AsCl^+ and SeO^+ .

New Visible Emission Spectra

7.1 Introduction

A relatively small number of diatomic molecular ions have been observed spectroscopically. The present chapter describes experiments that have been carried out to produce new emission spectra of 11-valence electron diatomic ions. Specifically, two new ionic emissions were analyzed and attributed to Group 5 halides (PCl^+ , AsCl^+) and one new emission (SeO^+) extended the knowledge of the relatively well characterized diatomic ions of Group 6. Although the homonuclear O_2^+ (61, 62), S_2^+ (63, 64, 65), Se_2^+ (66), Te_2^+ (66) and heteronuclear SO^+ (43, 67, 68) and TeO^+ (69) ions have been the subjects of varying degrees of analysis, only three observations of the isovalent Group 5 monohalides are known.

Douglas and Frackowiak (70) have rotationally analyzed five red-degraded bands of the $\text{A}^2\Sigma^+ - \text{X}^2\Pi$ band system of the PF^+ ion, excited in a discharge through helium mixed with a trace of PF_3 . Dyke and coworkers (71) studied the ground state of NF^+ via the photoelectron spectrum of NF , $\text{NF}(\text{X}^3\Sigma^-, \text{a}^1\Delta) \rightarrow \text{NF}^+(\text{X}^2\Pi) + \text{e}^-$. Finally, in a similar study by the same group (72), the photoelectron spectrum of the products of the $\text{F} + \text{PH}_3$ reaction was observed in the ionization energy region 9.5-10.0 eV. This spectrum has been assigned

as the first ionization band of PF, $\text{PF}(\text{X}^3\Sigma^-) \rightarrow \text{PF}^+(\text{X}^3\Sigma^-) \rightarrow \text{PF}^+(\text{X}^2\Pi) + e^-$.

PCl^+

Earlier experimental work in this laboratory (73) was concerned with the study of the reaction of phosphorous trichloride with metastable $\text{Ar}({}^3\text{P}_{2,0})$ atoms of energy ~ 11.5 eV. Numerous red-degraded emission bands in the 4000-6000 Å region were assigned to the $\text{A}^3\Pi_x - \text{X}^3\Sigma^-$ system of PCl , and weak system in the 8100-8300 Å region was assigned to the $\text{b}^1\Sigma^+ - \text{X}^3\Sigma^-$ system of PCl .

Presently, the reaction of PCl_3 with the products of discharged helium were examined under the experimental conditions described in Chapter 4. Numerous red-degraded bands have been observed in the 4000-6900 Å region and assigned to a ${}^2\Pi \rightarrow \text{X}^2\Pi$ system of the PCl^+ ion.

Although this ion has been detected mass spectrometrically from electron-impact ionization of phosphorous trichloride and phosphoryl chloride (74), there have been no previous spectroscopic observations.

AsCl^+

As was the case with most of the ionic species studied in this laboratory, electronic excitation of AsCl^+ was achieved in the reaction of discharged helium with a suitable substrate, in this case AsCl_3 . An extensive system of red-

degraded bands has been observed in the visible (4800 Å - 7850 Å); the system is similar in appearance to that of PCl^+ and it was assigned as a $^2\Pi - X^2\Pi$ transition of AsCl^+ .

SeO^+

By analogy with the use of S_2Cl_2 as substrate for excitation of S_2^+ ($A \rightarrow X$) (63), the first observation of an emission spectrum of the selenium monoxide cation has been obtained from the reaction of discharged helium with SeOCl_2 . The observed spectrum (3900 Å - 6700 Å) is similar in appearance to the $A \rightarrow X$ system of SO^+ , and is assigned to the same $^2\Pi - ^2\Pi$ transition in SeO^+ . The only previous observation of SeO^+ was by mass spectrometric detection in the vapour above SeO_2 and SeO_3 at high temperature (75).

7.2.1 PCl^+ : Vibrational Assignment

The PCl^+ emission spectrum consists of an extensive series of double-headed, red-degraded bands in the range 14550-25000 cm^{-1} . A small portion of the spectrum is shown in Figure 7.1, which illustrates the intensity difference of the two spin-orbit components. The shorter wavelength spin-orbit sub-bands are approximately three times more intense than the longer wavelength sub-bands. For the less abundant P^{37}Cl^+ ion, only the more intense shorter wavelength sub-bands can be observed.

The absolute vibrational numbering in the ground state

was obtained from the observed isotopic splittings between corresponding bands of $P^{35}Cl^+$ and $P^{37}Cl^+$ in the $v' = 0$ progression, as follows. Letting δG_v denote the difference between the vibrational term values for two isotopically related diatomics,

$$\delta G_v = G(v) - G^i(v), \quad (7.1)$$

δG_v is given to a good approximation (73) by

$$\delta G_v = (1 - \rho)(v + 1/2)\Delta G_v \quad (7.2)$$

where ΔG_v is the vibrational frequency for the v^{th} level and ρ is the square root of the ratio of the reduced masses, $\rho = (\mu/\mu^i)^{1/2}$. If the frequency of the $v' = 0 \rightarrow v''$ transition is denoted by $\nu_{0,v''}$, then the observed isotope shift, $\delta\nu_{0v''}$ is given by

$$\begin{aligned} \delta\nu_{0v''} &= \delta G_{v''} - \delta G_{v'} = 0 \\ &= (1 - \rho)[(v'' + 1/2)\Delta G_{v''} - 1/2\Delta G_{v'} = 0] \end{aligned} \quad (7.3)$$

or

$$\delta\nu_{0v''}/\Delta G_{v''} = (1 - \rho)[(v'' + 1/2) - 1/2\Delta G_{v'} = 0/\Delta G_{v''}] \quad (7.4)$$

$\Delta G_{v''}$ were obtained from the plot of $\Delta G(v'' + 1/2)$ against $(v'' + 1/2)$. The second term of the right-hand side of Eq. (7.4) is small and almost constant. The approximate value used to calculate this term was $\Delta G_0 = 318.5 \text{ cm}^{-1}$. The results are given in Table 7.1 and are plotted according to Eq. (7.4) in Figure 7.2.

It should be noted that only strong sub-band heads with reliable $P^{37}Cl^+$ measurements were used in Table 7.1. The

solid line in Figure 7.2 is drawn with a slope of 0.01277, which is the value of $(1-\rho)$ calculated for $P^{35}\text{Cl}$ and $P^{37}\text{Cl}$ (58). Ruling out the possibility that the spectrum obtained in the present work was actually due to PCl , there is no doubt that the emitter is PCl^+ . Further confirmation about the nature of the emitter will be given in the next section. Finally, the ground state numbering is established unequivocally and is presented in the Deslandres Table, Table 7.2.

Figure 7.1: A portion of the PCl^+ emission spectrum.

Figure 7.1

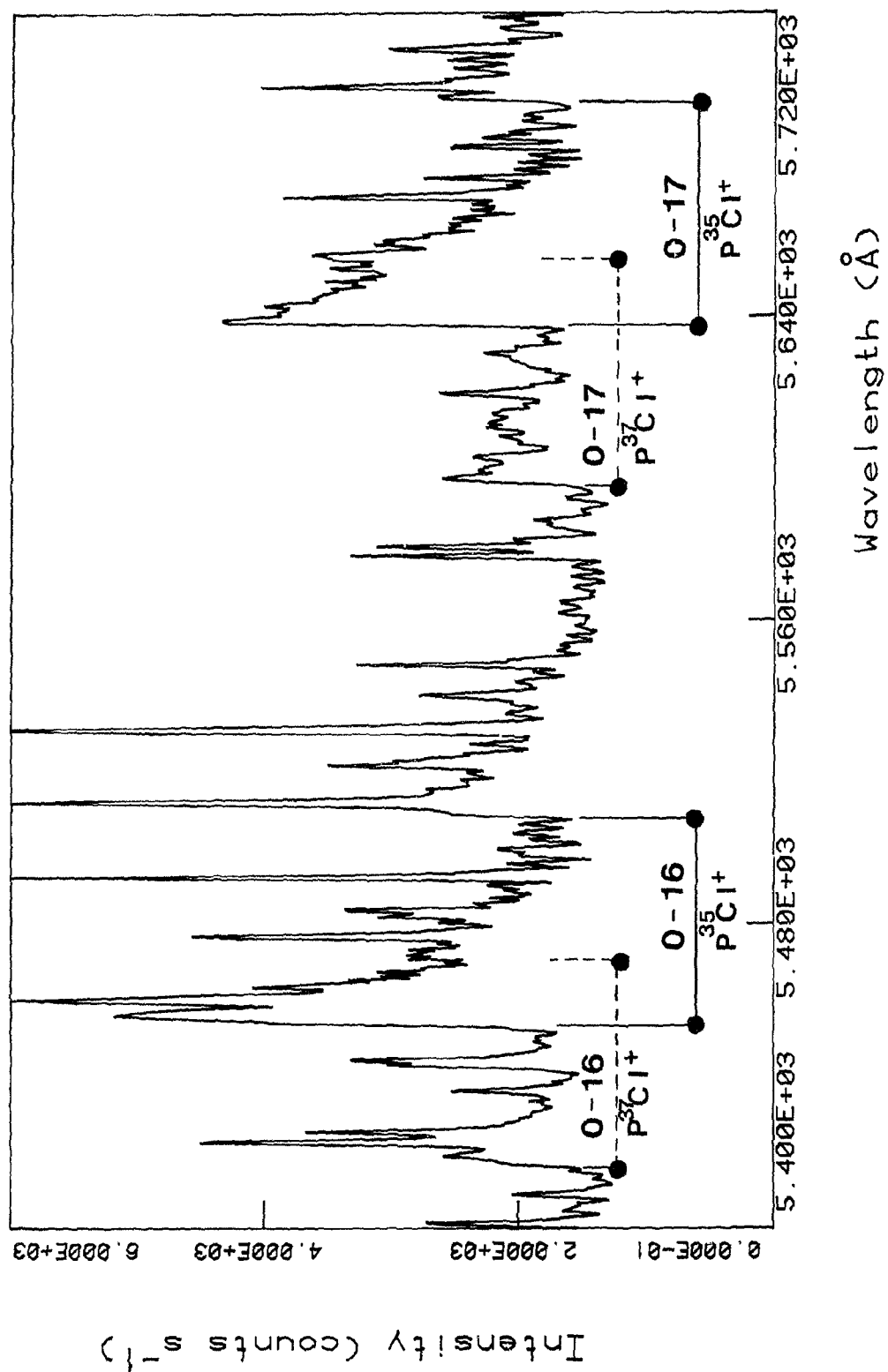


Table 7.1: Vibrational Isotope^a Effect in the $^2\Pi-X^2\Pi$ System of $P^{35}Cl^+$ and $P^{37}Cl^+$

$\delta\nu_{0v''}$	$\Delta G_{v''}$	v''	$(v'' + \frac{1}{2}) - \frac{\Delta G_0'}{2\Delta G_{v''}}$	$\delta\nu_{0v''}/\Delta G_{v''}$
109.8	615.5	14	14.24	0.1784
118.3	610.7	15	15.24	0.1937
127.2	606.0	16	16.24	0.2099
135.2	600.0	17	17.23	0.2253
141.5	593.6	18	18.23	0.2384
148.5	586.2	19	19.23	0.2533

^aSee Eq. (7.4) for definitions of the symbols.

Figure 7.2: Vibrational isotope effect in the $X^2\Pi$ state of PCl^+ . Plot of sub-bandhead differences of P^{35}Cl^+ and P^{37}Cl^+ for the $v' = 0$ progression according to Eq. (7.4); see text. The solid line corresponds to the theoretical slope, $1 - \rho = 0.01277$

Figure 7.2

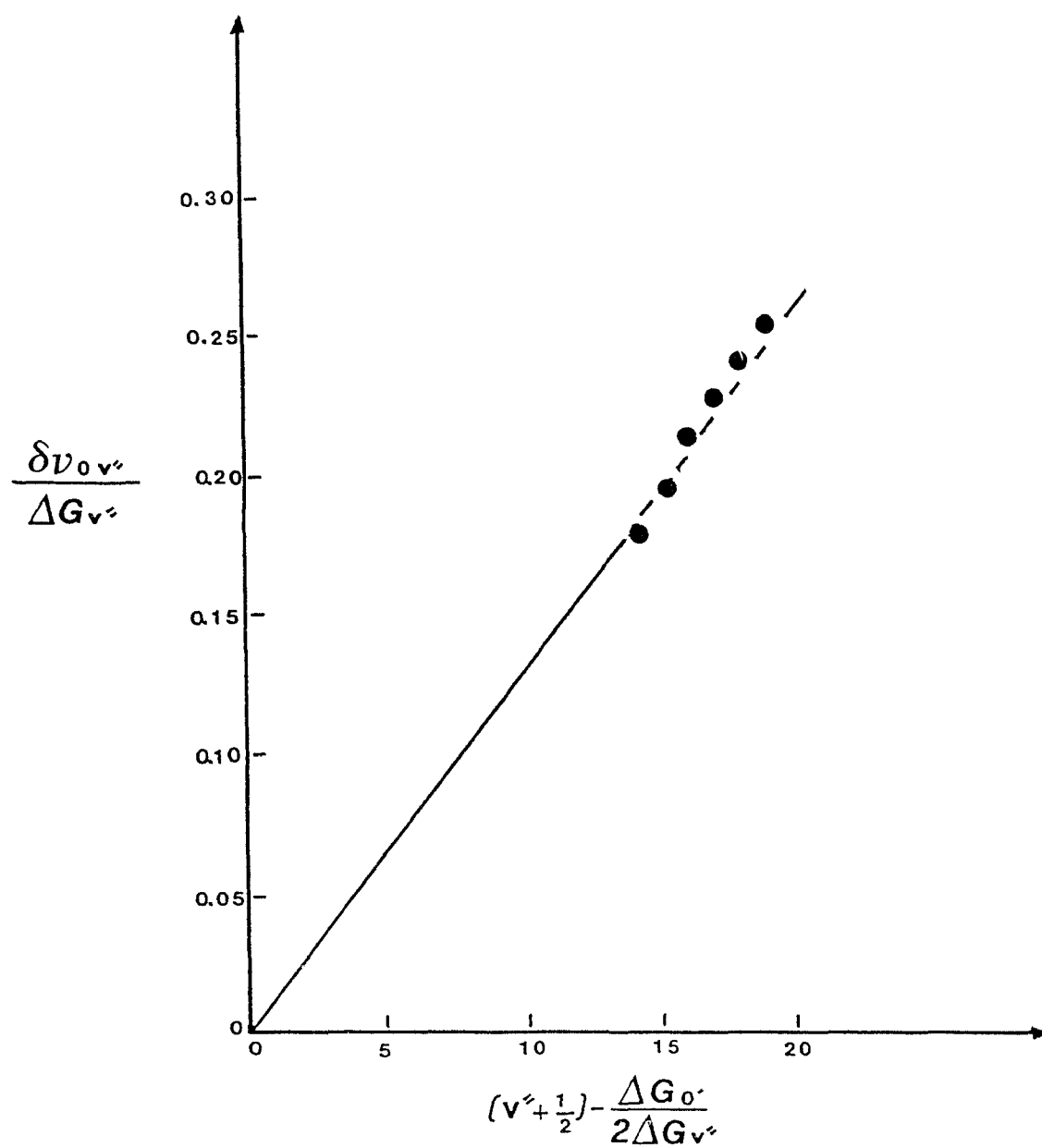


Table 7.2: Deslandres Table^a for the $2\Pi - X^2\Pi$ System of PCl^+

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P^{35}Cl						P^{37}Cl					
v''	$v' = 0$			$v' = 1$			$v' = 0$			$v' = 1$	
6	24623.9	199.8	24424.1*								
	650.6		643.6								
7	23973.3	192.8	23780.5*	317.3	24290.3					24341*	
	644.9		638.0		630						
8	23328.4	185.9	23142.5	331.1	23660*						
	642.2		634.4		655						
9	22686.2	178.1	22508.1	317.8	23004.0*						
	633.4		637.3		632.2						
10	22052.8	182.0	21870.8	314.2	22371.8	191.7	22180.1	22138.7*	316.2	22454.9*	
	627.3		626.6		634.6		626.8			628.6	
11	21425.5	181.3	21244.2*	310.4	21737.2*	183.9	21553.3			21826.3	
	627.7		636.5		622.5		631.2			618.0	
12	20797.8*	190.1	20607.7	315.7	21114.7	192.6	20922.1	20892.5*	315.8	21208.3	
	628.2		625.4		624.5		622.6	620.9		621.0	
13	20169.6	187.3	19982.3	318.9	20490.2	190.7	20299.5	20271.6	315.7	20587.3	
	619.0		614.5		620.1			611.2			
14	19550.6	182.8	19367.8	319.5	19870.1			19660.4			
	612.4		611.2		614.4			603.9			
15	18938.2	181.6	18756.6	317.5	19255.7			19056.5			
	609.1		608.5					600.2			
16	18329.1	181.0	18148.1					18456.3			
	603.3		603.2					595.3			
17	17725.8	180.9	17544.9					17861.0			
	598.0		594.7					591.7			
18	17127.8	177.6	16950.2					17269.3			
	589.8		588.0					582.8			
19	16538.0	175.8	16362.2					16686.5			
	582.1							581.0			
20	15955.9*							16105.5			
	579.2										
21	15376.7	182.6	15194.1*								
	576.5		570								
22	14800.2	175.8	14624.4*	318.1	15118.3						
					565.9						
23					14552.4						

^aBands not included in the least squares fits are flagged by an asterisk, see text.

7.2.2 PCl^+ : Results and Discussion

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It is clear from Table 7.2 that the spectrum consists of a long progression of bands from $v' = 0$ and a shorter progression from $v' = 1$. This intensity distribution is consistent with a considerable difference in the equilibrium internuclear separations and vibrational frequencies of the two states; the single excited state spacing, $\Delta G'(\frac{1}{2}) \sim 320 \text{ cm}^{-1}$, is about half the $\Delta G''(v + \frac{1}{2})$ intervals, indicating a relatively shallow and weakly bound excited state.

The head positions $\nu(i\Omega v'v'')$ of both isotopic bands can be represented adequately by Eq. 5.3, involving a difference of two Dunham power series in $(v' + \frac{1}{2})$ and $(v'' + \frac{1}{2})$:

$$\begin{aligned} \nu(i\Omega v'v'') = T_0^i + \sum_{k=1} U_{k0}^i(x_1^i)^k - \sum_{k=1} U_{k0}^{ii}(x_1^{ii})^k \\ + (\Omega - 1) \left(\sum_{k=0} A_k^i(x_1^i)^k - \sum_{k=0} A_k^{ii}(x_1^{ii})^k \right). \end{aligned} \quad (7.5)$$

U_{k0} and A_{k0} are mass-invariant parameters describing the vibrational terms and spin-orbit splittings of the two states as a function of mass reduced quantum number, $x_1 = (v + \frac{1}{2})/\mu_i^{1/2}$, where i denotes a particular isotope. The isotopically invariant parameters U_{k0} are related (56) to the usually reported Y_{k0} Dunham coefficients by Eq. (5.3) given in Chapter 5.

It should be noted that Eq. (5.3) is correct only when higher-order Dunham and/or Born-Oppenheimer breakdown terms are neglected, as in the present case of a low resolution spectrum. For the present data on PCl^+ , with only two vibrational levels for the excited state being observed, and

with the accuracy of the measurements inadequate for detection of any vibrational dependence of the ground state spin-orbit separation, Eq. (7.5) could be reduced to the 5-parameter expression,

$$\nu(i\Omega v'v'') = T_0' + U_{10}'x_1' - [U_{10}''x_1'' + U_{20}''x_1''^2] + (\Omega - 1)\Delta A \quad (7.6)$$

When the assignment of the sub-bands is $\Pi_0 \leftrightarrow \Pi_0$ with, $\Delta\Omega = 0$ and the designation $\Omega = 1/2$ or $3/2$ unknown, as in the present case, only $|\Delta A| = |A_0' - A_0''|$ can be calculated.

It was found possible to fit simultaneously most of the bandheads of Table 7.2 by weighted least-squares to the model given by Eq. 7.6. In this way, estimates of the vibrational parameters of the two states and ΔA could be obtained. The rejected data from Table 7.2 were mostly weaker heads overlapped by strong atomic lines. The weight of each band was taken as inversely proportional to the square of the estimated wavenumber uncertainty, which corresponds to a constant value of 0.6 Å.

This uncertainty varied from 3.6 cm^{-1} at short wavenumber to 1.2 cm^{-1} at long wavenumber. The results of this fit according to Eq. (7.6) of 35 heads of P^{35}Cl^+ and 10 heads of P^{37}Cl^+ are listed in Table 7.3. The estimated standard deviation of the fit was $\hat{\sigma} = 1.4$ with $f = 40$ degrees of freedom; the difficulty encountered in locating the heads of several of the weaker bands is the principle factor leading to residuals of the fit being somewhat larger than the estimated measurement precision. Confirmation

that the emitting species is PCl^+ can be established from two observations: i) The relative intensity of the isotope bands is in accord with the $^{35}\text{Cl}:^{37}\text{Cl}$ natural abundance. In addition the presence of spin-orbit doublets indicate a chlorine-containing diatomic with an odd number of electrons. ii) An electron-impact study (74) reported that an energy of 16.5 ± 0.5 eV is required for the formation of PCl^+ from dissociative ionization of PCl_3 . Combining this result with the energy required for formation of the excited ($v' = 0$) state of PCl^+ , ~ 20 eV is needed to form PCl^+ from PCl_3 . This is larger than the 19.82 eV available from the metastable $\text{He}(^3\text{S})$ but less than that of He_2^+ (~ 21 eV). In accord with this energy consideration the large helium flow rate and pressure (~ 4 Torr) used experimentally to induce the emission, are conditions known to enhance production of He_2^+ (39,41,42), as mentioned in Chapter 4. Additional evidence for PCl^+ as the carrier of the emission is provided by a comparison of the ground state vibrational frequency with those of isovalent species. Values of $T_0^!$, $|\Delta A|$, $\omega_0^!$, ω_0'' ($U_{10}/\mu_1^{1/2}$), and of $\omega_0''x_0''$ ($-U_{20}/\mu_1$), calculated for P^{35}Cl^+ from the results in Table 7.3 are listed in Table 7.4, and compared with the corresponding constants of selected isovalent molecules having excited states with $\omega_0^! < \omega_0''$. The ratios of ω_0'' (X) of PCl^+ with those of the isoelectronic species SiCl and PS , 1.26 and 0.93, are similar in magnitude to the ratios of ω_0'' (X) of PF^+ with those of the

corresponding isoelectronic molecules, SiF and PO, 1.23 and 0.85. The ratios $\omega''(X)$ to $\omega'(A)$ for the isovalent PF^+ and PCl^+ molecules are 1.70 and 2.15 respectively.

The observed system of PCl^+ can be attributed to either a ${}^2\Pi \rightarrow X^2\Pi$ or to a ${}^2\Sigma \rightarrow X^2\Pi$ system. In the latter case, the spin-orbit splitting is directly correlated with the spin-orbit coupling constant of the ground state. However, there are several indications that the excited state is a ${}^2\Pi$ state, and not ${}^2\Sigma$, as in the observed PF^+ system (70). First, the observed spin-orbit coupling constant in PF^+ ($X^2\Pi$) about 324 cm^{-1} , almost twice the sub-band separation in PCl^+ . However, comparing the spin-orbit constants of the ground state of the isovalent molecules SiF, SiCl and PO, PF^+ , (Table 7.4), a larger magnitude of A for the heavier molecule is observed; second, work at higher resolution indicates the absence of any Q branches ($\Delta J = 0$) which is characteristic for a transition with $\Delta \Lambda = 0$. More details of the nature of a ${}^2\Pi - {}^2\Pi$ transition will be presented in the next chapter. Finally, a considerable intensity difference between the sub-bands is consistent with a ${}^2\Pi$ excited state where the higher energy spin-orbit component has a lower rate of population than the lower one.

Table 7.3: ^aIsotopically Invariant Parameters (cm⁻¹) for the X²Π and A²Π States of PCl⁺

	A	X ² Π
T _e	28753.3(64)	0.00
U ₁₀	1299.2(43)	2795.8(31)
U ₂₀		-42.69(40)
ΔA ^b	183.1(11)	

^aValues in parentheses correspond to one standard deviation in units of the last digit of the corresponding parameters.

$$^b \Delta A = A_e' - A_e''$$

Table 7.4: Molecular Constants^a (cm^{-1}) for the Ground and
Low-lying Excited States of Selected 11-valence
Electron Diatomics.^c

		T_e	ω_e	$\omega_e x_e$	A_e	$ \Delta A $	Ref.
SiF	$A^2\Sigma^+$	22858.3	718.5(8)	10.167			
	$X^2\Pi$	0.0	857.19	4.735	161.88 ^b		(53)
PF ⁺	$A^2\Sigma$	35434.64	619.00	4.62			
	$X^2\Pi$	0.0	1053.25	5.05	323.95		(70)
PO	$B^2\Pi$	33120.7	759.2	3.8(5)	-13.3 ^b		
						237.3	(53)
	$X^2\Pi$	0.0	1233.34	6.56	224.03		
Si ³⁵ Cl	$A^2\Sigma$	23010.4	296.4	0.73			
	$X^2\Pi$	0.0	535.60	2.16 ₈	207.21		(76)
P ³⁵ Cl ⁺	A	28753.3(64)	320.6(11)				
						183(1)	this
	$X^2\Pi$	0.0	689.8(8)	2.60(2)			work
PS	$B^2\Pi$	22573.3	510.80(2)	1.79(2)	91.85		
						230.1	(77)
	$X^2\Pi$	0.0	739.49(2)	2.97(2)	321.93 ^b		

^a Values in parentheses correspond to one standard deviation in
units of the last digit of the corresponding parameters.

^b $v = 0$

^c Reduced masses of $P^{35}Cl^+$ and $P^{37}Cl^+$, calculated from the atomic
masses of ref. [58] are 16.425144 and 16.852792 amu respectively.

The eleven valence electrons of the PCl^+ ion can be correlated with the following electron configuration, ... $(z\sigma)^2(y\sigma)^2(\omega\pi)^4(x\sigma)^2(v\pi)$ leading to a $^2\Pi$ regular ground state. A weakly bound excited $^2\Pi$ state can be obtained only by promotion of a bonding $\omega\pi$ electron to the $v\pi$ orbital, giving the configuration $(z\sigma)^2(y\sigma)^2(\omega\pi)^3(x\sigma)^2(v\pi)^2$, with possible states $^{2,4}\Pi$, $^2\Phi$. The corresponding $^2\Pi$ states of SiF and SiCl have not been observed. It can be noted, however, that Verma (78) tried to correlate the observed higher lying $^2\Pi$ states of SiF and SiCl with strong bonding character to a $(\omega\pi)^3(x\sigma)^2(v\pi)^2$ configuration. Johns and Barrow (79) suggested that the $(\omega\pi)^3(x\sigma)^2(v\pi)^2$ electronic configuration gives rise only to repulsive states in the SiF molecule. A better understanding of the electronic states of the 11-valence electrons molecules can be obtained from the ab initio CI calculations on SiF published recently by Bialski and Grein (80). In this work, a minimal basis set was used and states with $\omega'_e > \omega''_e$ (X) and/or $r'_e < r''_e$ (X) were considered to be Rydberg states. An unobserved stable excited $^2\Pi(3)$ state of SiF with calculated $T_e = 31800 \text{ cm}^{-1}$ was found to have a leading configuration $(\omega\pi)^3(x\sigma)^2(v\pi)^2$ and $r'_e \sim 2.4 \text{ \AA}$ compared to $r''_e = 1.6011 \text{ \AA}$ for the ground $^2\Pi$ state. The spectroscopic constants ω_e and D_e for this state were not given due to its shallow potential curve.

From the preceding discussion, it would be reasonable to assume that the excited $^2\Pi$ state of PCl^+ observed

presently, corresponds to the ${}^2\Pi(3)$ state predicted in SiF, and observed in NS as $H^2\Pi$ (81). Another ${}^2\Pi(2)$ state has the same configuration as the ${}^2\Pi(3)$ state but in the CI calculations was found to be repulsive, in accord with the expected correlation with ground state $Si(^3P) + F(^2P)$ atoms. As in SiF, but not NS, the lower ${}^2\Pi(2)$ state of PCl^+ could be repulsive. In their conclusion, Bialski and Grein reported (80) that the three low-lying ${}^2\Sigma^+$ valence states of CCl, SiF, NS and PO were all repulsive. The observed $A^2\Sigma^+$ states in PO and NS should be almost pure Rydberg states corresponding to $v\pi \rightarrow ns$ transitions. In the case of PF^+ emission observed by Douglas and Frackowiak (70) the $A^2\Sigma^+$ state with $T_e \sim 35\,435\text{ cm}^{-1}$ is probably a higher-lying valence state and not a Rydberg state. Finally, after the present work was complete, Nguyen (82) reported an ab initio investigation, with a split-valence plus diffuse and polarization basis set extended by Moller-Plesset perturbation theory up to fourth-order, of the lower-lying bound electronic states of three diatomic molecules PH, PF, PCl and their cations. In this work the vibrational frequency of the ground state $X^2\Pi$ of PCl^+ was calculated as 696 cm^{-1} . The value of 690 cm^{-1} for the same constant in the present experimental work is further confirmation that the emitting molecule is PCl^+ . It should be noted that within the Moller-Plesset perturbation theory only the lowest state of a given symmetry and multiplicity can be reliably

calculated; hence, the excited $^2\Pi$ state with configuration $(\omega\pi)^3(x\sigma)^2(v\pi)^2$ could not be obtained in the recent ab initio study. Furthermore, Nguyen reports an excited $^2\Sigma$ state derived from $\dots(x\sigma)^1(v\pi)^2$ with an extremely shallow potential and lying $\sim 6696 \text{ cm}^{-1}$ higher than $^2\Pi$ excited state reported in the present work. Therefore, the lack of agreement between the calculated $^2\Sigma \rightarrow X^2\Pi$ and the observed $^2\Pi \rightarrow X^2\Pi$ energies supports the assignment of the latter as the system responsible for the PCl^+ emission spectrum.

7.3.1 AsCl^+ : Vibrational Assignment

The AsCl^+ emission spectrum consist of a large number of red-degraded sub-bands in the range $12800\text{--}21000 \text{ cm}^{-1}$, with the most intense emission around 16000 cm^{-1} . Figure 7.3 shows a portion of the spectrum. As in the case of PCl^+ , the higher energy member of the spin-orbit coupled pairs is more intense than the lower energy member; but since the constant separation of the spin-orbit components is $\sim 1390 \text{ cm}^{-1}$, the weaker sub-band of each (v', v'') transition was either very close to or overlapped by the stronger sub-band of the $(v', v'' + 3)$ transition. For this reason, measurements of the weaker heads were less certain, or impossible. Although complicating the spectrum, the two isotopes of AsCl^+ provided a means for establishing the correct vibrational numbering for the observed transitions using Eq. (7.4) as for the PCl^+ ion. The approximate value

used for ΔG_0 , was 240.3 cm^{-1} . The results are given in Table 7.5 and are plotted according to Eq. (7.4) in Fig. 7.4. The solid line in Figure 7.4 is drawn with a slope of 0.01859, which is the value of $(1 - \rho)$ calculated for As^{35}Cl and $\text{As}^{37}\text{Cl}(58)$. However, since the possibility that the spectrum obtained presently was due to $\text{AsCl}(83)$ is ruled out, there is no doubt that the emitter is AsCl^+ .

Finally, the head positions of both isotopes with unequivocal numbering are arranged in a Deslandres array in Table 7.6.

Figure 7.3: A portion of the AsCl^+ emission spectrum, showing bandheads belonging to the ${}^2\Pi - X^2\Pi$ systems of $\text{As}^{35}\text{Cl}^+$ and $\text{As}^{37}\text{Cl}^+$. The long wavelength member of each of spin-orbit coupled pair (----) is weak, and often overlapped (see text)

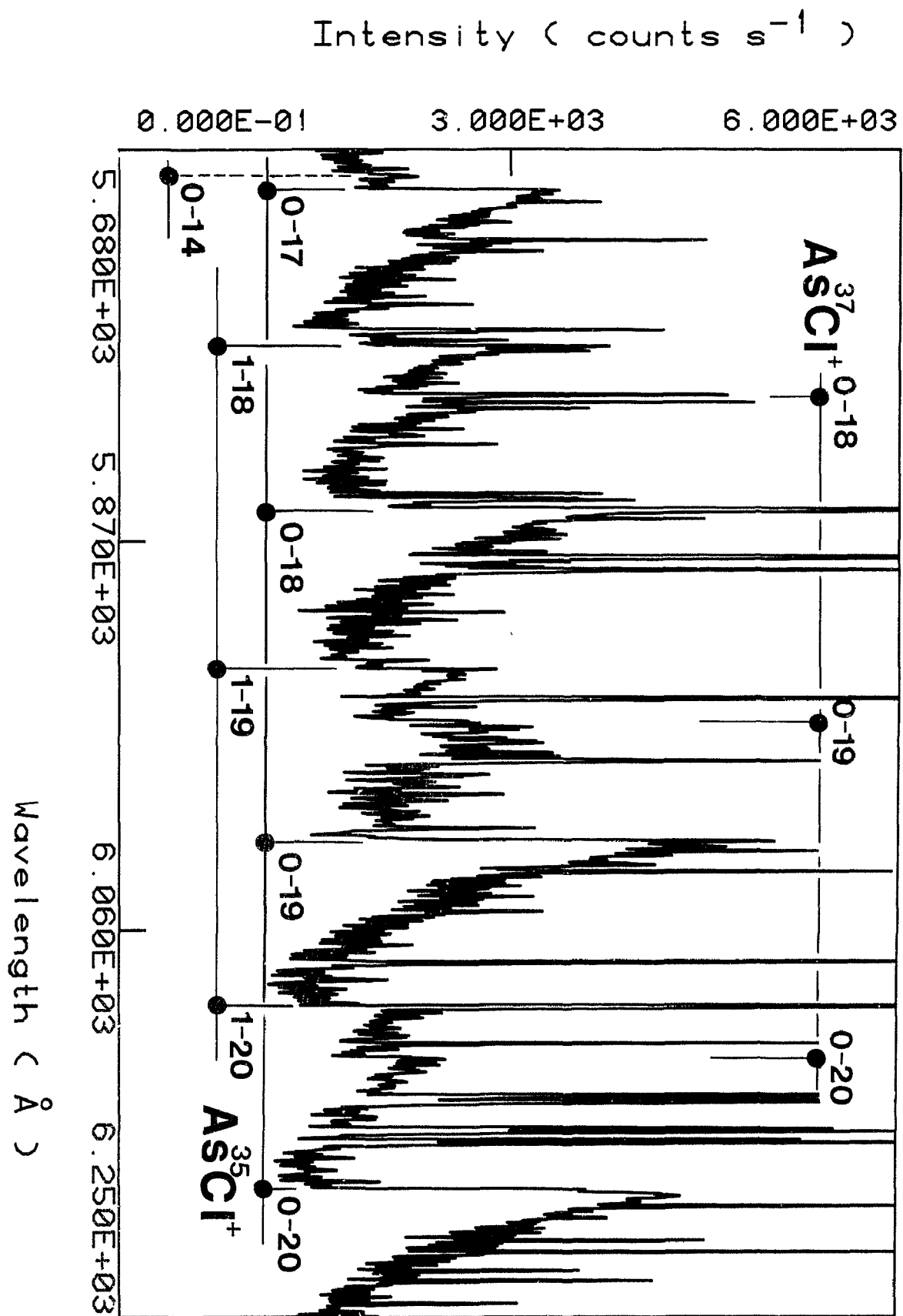


Figure 7.3

Table 7.5: Vibrational isotope^a effect in the $^2\Pi-X^2\Pi$ system of $\text{As}^{35}\text{Cl}^+$ and $\text{As}^{37}\text{Cl}^+$

$\delta\nu_{0v''}$	$\Delta G_{v''}$	v''	$(v'' + \frac{1}{2}) - \frac{\Delta G_0'}{2\Delta G_{v''}}$	$\delta\nu_{0v''}/\Delta G_{v''}$
165.1	463.0	19	19.24	0.3566
172.8	457.3	20	20.24	0.3779
186.9	450.0	22	22.23	0.4153
192.6	444.7	23	23.23	0.4331
206.4	440.0	25	25.22	0.4691
211.6	434.3	26	26.22	0.4872

^aSee Eq. (7.4) for definitions of the symbols.

Figure 7.4: Vibrational isotope effect in the $X^2\Pi$ state of AsCl^+ . Plot of sub-bandhead differences of $\text{As}^{35}\text{Cl}^+$ and $\text{As}^{37}\text{Cl}^+$ for the $v' = 0$ progression according to Eq. (7.4); see text. The solid line corresponds to the theoretical slope $1 - \rho = 0.01859$.

Figure 7.4

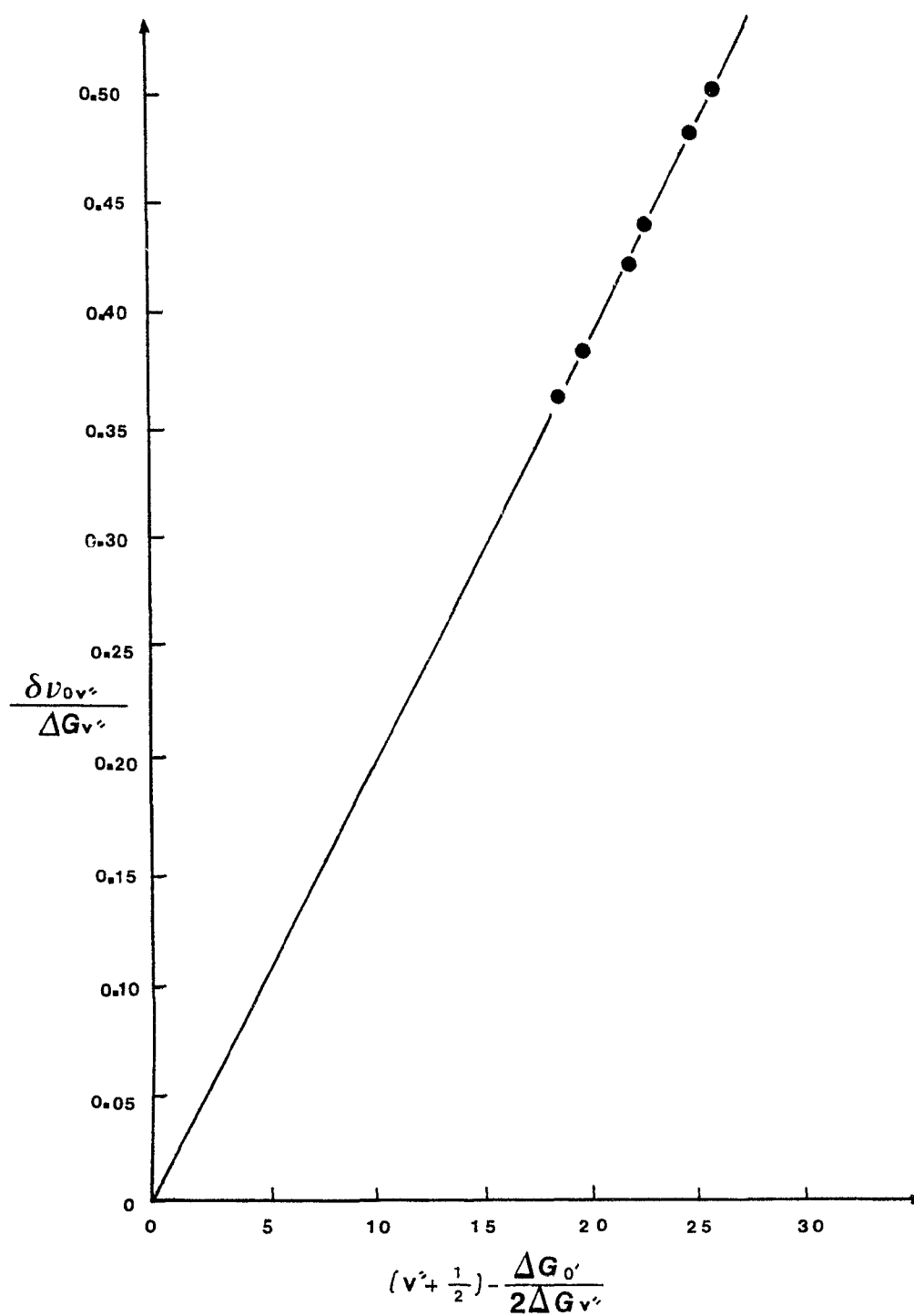


Table 7.6: Deslandres Table for the $^2\Pi - X^2\Pi$ System of AsCl^+

$\text{As}^{35}\text{Cl}^+$					$\text{As}^{37}\text{Cl}^+$				
v''	$v'' = 0$				$v'' = 1$				
9		20004.1	243.9			20247.9			
						489.0			
10	20892.3					19758.9			
	488.9					(485)			
11	20403.4	1375.1	19028.3	250.6	20653.9 (1380)	19274.0*	20510.5		
	483.3		487.0		484.0	(491)	(480)		
12	19920.1	1378.8	18541.3	245.7	20169.9	1386.9	18783.0	20030.0*	
	(471)				483.0			(471)	
13	19449.5*		(237)	19686.9			19558.8		
	(487)			479.8			469.8		
14	18962.1	1386.1	17576.0	245.1	19207.1	1386.0	17821.2	19089.0	241.1 19330.1
	474.9				477.6				470.3
15	18487.2		242.4	18729.5					18859.8
	467.9			474.5					468.3
16	18019.3		235.7	18255.0			18162.2	229.3	18391.5
	466.1			467.7			(457)		457.3
17	17553.2		234.1	17787.3			17705.3*	(229)	17934.2
	(465)			467.5			(454)		
18	17087.8* (1395)	15693.2	246.6	17319.8	1380.0	15939.8	17251.0* (1399)	15851.6	
	(465)	(464)		458.4			(463)	455.6	
19	16623.0 (1394)	15228.8*	238.4	16861.4			16788.1	1392.0	15396.0
	461.0	(455)		458.4			453.3		449.6
20	16162.0	1387.7	14774.3	241.0	16403.0		16334.8	1383.4	14946.4
	453.6		453.2				446.5		447.5
21	15708.4	1387.3	14321.1				15888.3	1389.4	14498.9
	452.7		448.9				445.7		
22	15255.7	1383.5	13872.2				15442.6		
	447.2		(445)				441.5		
23	14808.5 (1381)	13427.3*					15001.1		
	442.2	(442)					438.6		
24	14366.3 (1381)	12985.6*					14562.5		
	443.8						433.6		
25	13922.5						14128.0		
	436.1						430.9		
		*Heads not included in the least-squares fit, see text.							
26	13486.4						13698.0		
	432.5								
27	13053.9								

The head positions of the bands of both sub-systems and of both isotopes were, fitted simultaneously by weighted least-squares to the same model as that employed for PCl⁺, as given by Eq. (7.6). The isotopically invariant parameters of Table 7.7, U_{k0} , are related to the more familiar vibrational Dunham coefficients Y_{k0} by Eq. (5.3).

Heads not included in the fit are flagged by an asterisk in the Deslandres Table (7.6), and are mostly weak heads overlapped by atomic lines. Weights were chosen as $1/\sigma^2$ where σ are the uncertainties in the measurements of band-heads, and varied from 0.9 cm⁻¹ at the red end of the spectrum to 2.7 cm⁻¹ at the blue end.

The 39 heads of As³⁵Cl⁺ and the 20 heads As³⁷Cl⁺ were fitted satisfactorily only for the numbering given in Table 7.6. As mentioned earlier, the numbering was established initially from the observed isotope shifts. The standard deviation of the fit was 1.4 with 54 degrees of freedom. This standard deviation increased considerably to ~ 3.0, where the vibrational numbering, was changed up or down by one unit. The spin-orbit coupling separations were represented by a single parameter $|\Delta A|$, which corresponds to the difference between the spin-orbit coupling constants of the upper and lower ²Π states. Additional parameters representing the v'' -dependence could not be obtained from the present experimental data. Although the magnitude of $|\Delta A| \sim 1386$ cm⁻¹ is considerably larger than the

corresponding constant of the isovalent phosphorous cation, $\sim 183 \text{ cm}^{-1}$, it is similar to $|\Delta A|$ of the isovalent arsenic species, AsS and AsO, as shown in Table 7.8. The observed transitions of AsCl^+ from $v' = 0,1$ to the vibrational levels $v'' = 9-27$ of the ground state are consistent with a weakly bound excited state having $r'_e > r''_e(X)$, and can be readily correlated with the similar observed progressions of the isovalent PCl^+ cation. It is reasonable to assume that the configuration and the nature of the electronic states involved in the observed AsCl^+ emission are the same as for PCl^+ . The assignment of the excited state as $^2\Pi$, as opposed to $^2\Sigma$, is also in accord with the difference in intensity between the two sub-systems in AsCl^+ ; this observation implies different rates of population of the F_1 and F_2 components of the excited $^2\Pi$ state. It should also be noted from Table 7.8 that for the isovalent AsO and AsS molecules, an excited $^2\Pi$ state is known at similar energy.

Presently, the problem of whether the AsCl^+ excited state is regular or inverted cannot be resolved unequivocally. However, it is believed that much of the observed spin-orbit separation can be attributed to large spin-orbit coupling in the ground state, as in AsO (84). In addition, an examination of Table 7.8 shows that the ground vibrational frequency of AsCl^+ is similar to that of the AsS molecule but that the $\Delta G'(\frac{1}{2})$ value determined for AsCl^+ is significantly lower than those of the $^2\Pi$ states of AsO and

AsS. This anomalously low vibrational spacing in the excited state is also observed in PCl^+ . Small vibrational intervals in the excited states of other isovalent species have also been found, for example, the $\text{A}^2\Sigma$ states of the silicon halide molecules. In conclusion, Shimauchi (88) has compared the ω_e'' values of the phosphorus and arsenic oxide and sulphide ions with those of the neutral molecules; the magnitude of the ratios, $\omega_e''(\text{ion})/\omega_e''(\text{neutral})$, is 1.14 in all cases. The ratios of the ω_e'' values for AsCl^+ and AsCl (83), and for PCl^+ and PCl (73) are 1.24 and 1.25 respectively.

Table 7.7: Isotopically Invariant Parameters^a (cm⁻¹) for the X²Π and Excited ²Π States of AsCl⁺

	² Π	X ² Π
T ₀	25435(5)	0.0
U ₁₀	1183(4) ^b	2576.6(24)
U ₂₀		-41.5(3)
ΔA ^c	1386.3(7)	

^a Values in parentheses correspond to one standard deviation in units of the last digit of the corresponding parameters.

^b v' = 0,1 only.

^c ΔA = A₀['] - A₀^{''}

Table 7.8: Molecular Constants^a (cm⁻¹) for Selected States
of Some 11-valence Electron Diatomics

		T_e	ω_e	$\omega_e x_e$	A_e	$ \Delta A $	Ref.
AsO	$G^2\Pi_{1/2}$	26485.2	630.30	3.006	-316.8		
						1342.8	(84)
	$X^2\Pi_{1/2}$	0.0	967.08	4.850	1025.97		
SiBr	$A^2\Sigma$	20937.6	250.3	0.5			
	$X^2\Pi_{1/2}$	0.0	424.5	1.5	419.2		(85)
AsS	$A^2\Pi_{1/2}$	~20475	402.26	1.21			
						~1210	(86,87)
	$X^2\Pi_{1/2}$	0.0	567.94	1.97			
As ³⁵ Cl ⁺	$^2\Pi$	25435(5)	242.4(9) ^b				
						1387(1)	this
	$X^2\Pi$	0.0	527.7(5)	1.74(1)			work ^c

^a Values in parentheses correspond to one standard deviation in units of the last digit of the corresponding parameters.

^b $\Delta G(1/2)$

^c Reduced masses of As³⁵Cl⁺ and As³⁷Cl⁺, calculated from the atomic masses of ref. (58) are 23.841219 and 24.752939 amu, respectively.

The numerous red-degraded bands of the SeO^+ emission are in the range $15000\text{--}25500\text{ cm}^{-1}$. Figure 7.5, shows a portion of the SeO^+ spectrum, and its characteristic feature, namely the presence of "double-headed" bands. This closeness of heads cannot be attributed to any selenium isotope effect, and arises instead from the similarity in magnitude of the spin-orbit splittings and the ground state vibrational spacings. More specifically, one head is the first head of a spin-orbit component of a (v', v'') transition, while the other is the second head of the neighbouring $(v' - v'' - 1)$ band. This accidental overlapping causes considerable difficulty in measuring accurately the longer wavelength member of each pair. The measured head positions are arranged in a Deslandres array given in Table 7.9. In this table, which was obtained taking into consideration the similar intensity of the two spin-orbit coupled pairs of the same (v', v'') transition, there is also good agreement between the several estimates of the upper and lower state vibrational intervals, which decrease steadily with increasing v .

In addition, the intensity distribution of the bands is consistent with the larger vibrational frequency of the ground state, and is similar to the observed intensity of the $A \rightarrow X$ system of SO^+ . With this type of distribution, there is little doubt that the absolute vibrational numbering in Table 7.9 is correct.

Figure 7.5: A portion of the SeO^+ emission spectrum from
~19750 to ~22050 cm^{-1}

Figure 7.5

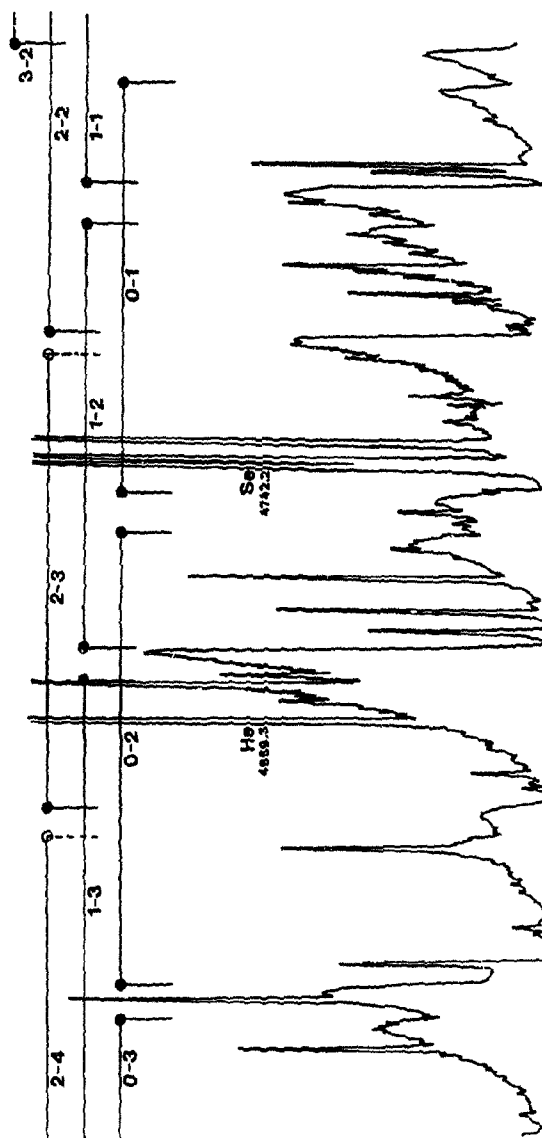


Table 7.9: Deslandres Table for the $A^2\Pi - X^2\Pi$ System of SeO^+

v'	$v'' = 0$	$v'' = 1$	$v'' = 2$	$v'' = 3$	$v'' = 4$	$v'' = 5$	$v'' = 6$	$v'' = 7$	$v'' = 8$
0		21913.5	20943.4	19981.6	19031.4	18104.9 ^a	17179.3 ^a	b	
		972.0	962.6	951.2	937.2	928.1	912.2	15358.1	
		21025.0	20051.0	19087.7	18135.6	17198.4	16270.3		
		659.6	656.5	655.8	658.3				
	23548.3	22571.5	21598.1	20635.9	b				
1	983.1	975.2	936.2	951.2					
	22675.7	21686.3	20709.3	19745.1	18793.9				15111.7
	649.8	649.5	648.1	649.2					
	24194.9	23212.6	b	b	20336.8 ^a	b	b		
2	987.6	978.4	963.1						
	23328.6	22335.8	21357.4	20394.3	19470.6 ^a	18509.5 ^a	17576.3		
	643.2	645.0	641.9						
	24840.9	23846.6 ^a	b						
3	988.3	981.5							
	23969.1	22980.8	21999.3						
	634.7	632.1							
		24485.6 ^a							
4	990.9								
	24603.8	23612.9							
	628.0								
5									
	25231.8								

^a Not included in the least-squares fit

^b Band head overlapped by an adjacent band

The estimates of the vibrational and spin-orbit parameters of the two states were obtained using a least-squares fitting procedure with the head positions given in Table 7.9. It was found that these data are represented adequately by a simple expression involving a difference of two Dunham series in $(v' + \frac{1}{2})$ and $(v'' + \frac{1}{2})$,

$$\begin{aligned} \nu_{v',v''} = & T_0' + \sum_{k=1} Y_k'(v' + \frac{1}{2})^k - \sum_{k=1} Y_k''(v'' + \frac{1}{2})^k \\ & + (\Omega - 1) (A_0' + \alpha_A' (v' + \frac{1}{2}) - A_0'' - \\ & \alpha_A'' (v'' + \frac{1}{2})) \end{aligned} \quad (7.7)$$

However, A_0' and A_0'' are totally correlated, so that only the magnitude of the difference of $\Delta A_0 = A_0' - A_0''$ could be determined. The constants α_A' and α_A'' represent the variation of the unknown individual spin-orbit coupling constants with vibrational quantum number. If ΔA_0 has negative sign, which will be argued in the following sections, α_A' and α_A'' will have positive sign.

In addition, the two vibrational Dunham coefficients obtained for each state are listed in Table 7.10. The least-squares fit had a standard deviation of 2.2 cm^{-1} and 27 degrees of freedom. The molecular constants given in Table 7.10 follow the expected trends of those of a number of isovalent species, as shown in Table 7.11. It is clear that for all the molecules in this table, the nature of the ground and first excited electronic states is well-known, and that definite overall trends in the values of the constants are clearly established. For example, except for

O_2^+ , the ratios of $\omega_e(X)/\omega_e(A)$ are in the range 1.45-1.62. For SeO^+ , this ratio is 1.51. It should be mentioned also that in all of $T_e(A)$, $\omega_e(A)$, $\omega_e X_e(A)$, $\omega_e(X)$ and $\omega_e X_e(X)$, there is a decrease in magnitude with increasing reduced mass.

Although the molecular constants given in Table 7.10 are very similar, as expected, to those of NSe (90,91), the possibility that the spectrum obtained in this work actually belonged to NSe was eliminated by comparing the bandhead positions determined in the present work with those of Refs. (90,91). In a similar way, Se_2 (92) and SeO (93,94) were also eliminated as possible carriers of the bands observed presently.

Finally, the question concerning the sign of $\Delta A_e = A_e' - A_e''$ can be resolved with reasonable certainty by examination of the data of Table 7.11. It can be seen from the isoelectronic pairs NS, SO^+ and NSe, SeO^+ that there is a close similarity in the molecular parameters. The spin-orbit coupling constant of the ground state, A_e'' , for SO^+ is considerably larger than for NS, while the same constants for the excited state, A_e' , are smaller and have opposite signs. Accordingly, A_e' for SeO^+ should be not only positive, but probably of larger magnitude than the value for NSe ($\sim 890 \text{ cm}^{-1}$). Taking into consideration the magnitude of $|\Delta A_e|$ ($\sim 878 \text{ cm}^{-1}$) that has been obtained in the present work, it is reasonable to expect that the excited $A^2\Pi$ state of SeO^+ is also regular. There is also little

doubt then that $\Delta A_0 = A'_0 - A''_0$ is negative for SeO^+ , in accord with all the isovalent molecules in Table 7.11 for which A'_0 and A''_0 are known.

Table 7.10: Molecular Constants^a (cm⁻¹) for the X²Π
and A²Π States of SeO⁺

	A ² Π	X ² Π
T _e	22625.7(17)	0.00
ω _e	663.1(9)	999.7(6)
ω _e X _e	3.65(18)	6.31(8)
α _A ^b	3.0(9)	5.0(7)
ΔA _e ^{b,c}	878.4(28)	

^a Values in parentheses correspond to one standard deviation in units of the last digit of the corresponding parameters.

^b Although the signs of α' and α'' are not known, both parameters have sign opposite to that of ΔA_e, see text.

^c ΔA_e = A_e' - A_e''

Table 7.11: Molecular Constants (cm^{-1}) for the $A^2\Pi$ and $X^2\Pi$ States of Some Diatomic Species with 11-valence Electrons.

	O_2^+ (61,89)	NS (81)	SO^+ (67)	NSe ^d (90)	SeO^+ this work	S_2^+ (65)	Se_2^+ (66)	TeO^+ (65)	Te_2^+ (66)
T_e	40570.7	30296.4 ^b	31432	24205 ^{ba}	22625.7	22344.69	19200	19760	14510
ω_e	898.24	797.31 ^b	805.25	658.9 ^{bf}	663.1	552.72			
$\omega_e x_e$	13.57	3.72 ^b	6.34 ^c		3.65	3.14			
A_e	-3.496 ^a	90.4	-53.91	449 ^a		13.5			
ω_e''	1904.77	1219.14 ^b	1311.4	957.37 ^b	999.7	805.9			
$\omega_e x_e''$	16.26	7.28 ^b	8.36	5.72 ^b	6.31	3.38			
A_e	200.289 ^a	223.15	363.8	890.84		469.7	1935	4840	3790
$ \Delta A_e $	203.785 ^a	132.8	417.7	~440	878.4	456.2			

^a $v = 0$

^b $^2\Pi_{1/2} - ^2\Pi_{1/2}$ sub-system

^c constrained value

^d $^{14}\text{N}^{80}\text{Se}$

^e T_0 value

^f $\Delta G_{1/2}$ value

Chapter 8

Rotational Analysis of the $A \rightarrow X$ System of PCl^+

8.1 Introduction

The only previous work on a rotationally resolved spectrum of a Group 5 monohalide cation is the analysis of five red-degraded bands of PF^+ (70). The present chapter is concerned with the first rotational (spectroscopic) analysis of $A^2\Pi \rightarrow X^2\Pi$ system of PCl^+ . In the low-resolution study (Chapter 7) of this system of PCl^+ , a considerable number of red-degraded bands were observed in the range of 4000-7000 Å. In view of the time available for the completion of the present thesis, it was necessary to limit the present work to the analysis of only three of the most intense bands of P^{35}Cl^+ . No attempt was made to investigate any bands of the less abundant isotope molecule P^{37}Cl^+ . The recorded spectra were clean and free of overlap from any other species. The bands studied belong to the $v' = 0$ progression (0-16, 0-17 and 0-18), and the molecular constants for the two electronic states were fitted directly to the measured line positions of individual bands. The multiple estimates of the constants for $v' = 0$ were reduced to single-valued parameters by the method of merging, and estimates of the spin-orbit coupling constants for both states are reported for first time. It should be noted here that the three bands analyzed by the author represent a

contribution to the more extensive analysis undertaken subsequently by Coxon et al. (95).

8.2 Nature of the Transition, and Rotational Assignments

Since the observed transition of PCl^+ has been assigned as $A^2\Pi \rightarrow X^2\Pi$, the X and A states have a non-zero component of electronic orbital angular momentum in the direction of the internuclear axis ($\Lambda = 1$). This vector couples strongly with the corresponding component ($\Sigma = \frac{1}{2}, -\frac{1}{2}$) of the spin angular momentum, S to form the resultant electronic angular momentum ($\Omega = 3/2, 1/2$). Ω couples with the nuclear rotation vector (R) perpendicular to the internuclear axis, giving the resultant total angular momentum (J) of the molecule. The coupling of Λ and Σ to the internuclear axis is characteristic of Hund's case (a).

If both states belong to case (a), besides the general selection rules ($\Delta J = 0 \pm 1$; $\Delta S = 0$; $++--$), the following additional restrictions hold: $\Delta \Sigma = 0$; $\Delta \Omega = 0, \pm 1$. As a result, a $^2\Pi - ^2\Pi$ band splits into two sub-bands, $^2\Pi_{1/2} - ^2\Pi_{1/2}$ and $^2\Pi_{3/2} - ^2\Pi_{3/2}$, as presently observed. In general, as a result of the selection rules and the fine splitting of each rotational level into two distinct levels of opposite parity (Λ -doubling), each sub-band has six branches which form three close pairs, two P ($\Delta J = -1$), two Q ($\Delta J = 0$), and two R ($\Delta J = 1$) branches, the two Q-branches being very weak.

With the 0.06 Å resolution of the present analysis, there was no evidence for any Λ -doubling splitting. In addition, there was no indication for the presence of Q-branches. The energy level pattern of a ${}^2\Pi \rightarrow {}^2\Pi$ electronic transition, with the four observed branches R_{11} , P_{11} , R_{22} , P_{22} , is shown schematically in Figure 8.1.

As described in Chapter 7, one sub-band is approximately three times more intense than the other. The stronger sub-band always lies at higher energy, and was assigned as the $\Pi_{1/2} - \Pi_{1/2}$ transition. This conclusion was based on the fact that all the isovalent molecules in Table 7.4 have a regular ground state ($\Omega = \frac{1}{2}$ component has lower energy), and the spin-orbit splitting of the ground state is larger in magnitude than the corresponding splitting of the excited state. The difference in intensity arises from the different rates of population of the two spin-orbit components of the excited ${}^2\Pi$ state.

The weak spin-orbit components of the $P^{37}\text{Cl}^+$ isotope were not observed in the present work, since they were overlapped with the intense sub-band of the $P^{35}\text{Cl}^+$ isotope. Both sub-bands of the more abundant isotope $P^{35}\text{Cl}^+$ were recorded for the 0-16, 0-17, and 0-18 bands. These bands are well-separated, free from any overlapping, and showed well-resolved rotational structure even for low J . Therefore, these three bands were selected for preliminary rotational assignment by the method of combination

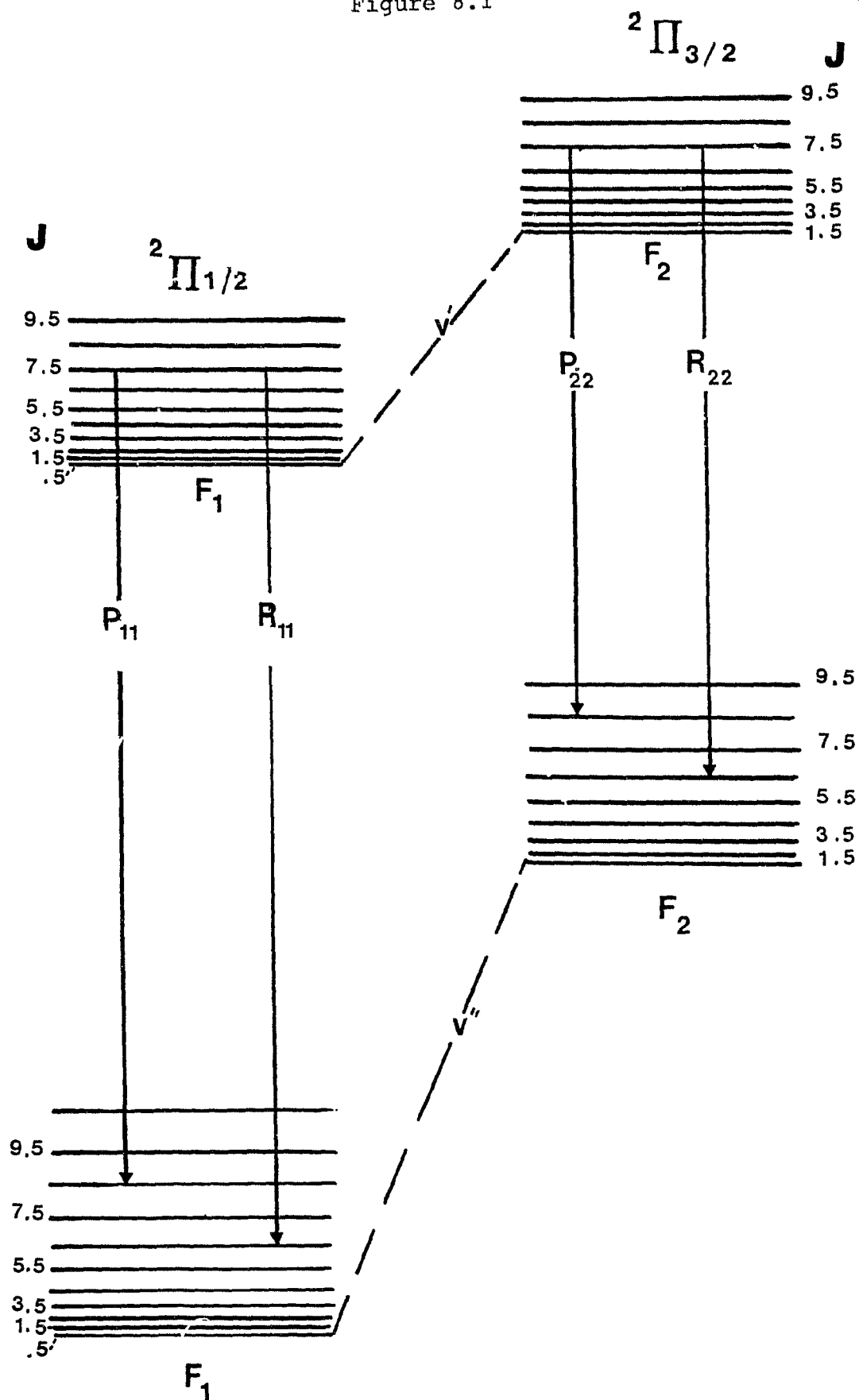
differences. For two bands with same upper state vibrational number, the combination differences,

$$R(J) - P(J) = \Delta_2 F'(J) \approx 4B'_v (J + \frac{1}{2}) \quad (8.1)$$

(neglecting centrifugal distortion, D) must agree exactly for each J value. Thus, in order to find the correct relative numbering, a trial numbering of the lines in the two bands is used. The trial numbering is then varied systematically until the $R(J) - P(J)$ values agree exactly. This can be achieved by changing the numbering in one of the branches of each band by 1,2,3 units.

Figures 8.1: Energy level diagram for the first rotational lines of the $A^2\Pi - X^2\Pi$ transition of the PCl^+ ion.

Figure 8.1



It is obvious that in order to employ this procedure, the rotational lines must be first assigned as R or P branch transitions. In the present work, the red degradation ($B'_v < B''_v$) of the bands and the intensity contours of the branches enabled an unequivocal identification of the lines as P or R branches. Once the correct relative numbering has been established, successive $\Delta_2 F'$ values differ by $4B'_v$, in accord with Eq. (8.1). Consequently, dividing one of the $\Delta_2 F'$ values by $4B'_v$ estimated in this way, the absolute J value can be obtained. Confirmation for the absolute J-numbering was provided by the requirement for D'_0 to be close to the theoretical value of $4B'_0/\omega_s^2$. For the three bands analyzed, estimates of seven constants ($\nu_0, B', D', A', B'', D'', A''$) could be obtained by fitting directly the measured line positions of both sub-bands. Line positions were calculated as the differences of the eigenvalues of a standard ${}^2\Pi$ Hamiltonian containing the molecular constants as variables for the upper and lower states of the transition, as discussed earlier in Chapter 2. Trial values of the constants were then improved iteratively using nonlinear least-squares fitting to yield the final set of estimated molecular parameters.

8.3 Results

A portion of the ${}^2\Pi_{1/2} - {}^2\Pi_{1/2}$ sub-band of the 0-17 band is shown in Fig. 8.2. This is a characteristic trace which

illustrates the quality of the spectra for all the sub-bands recorded presently. The two branches, P_{11} and R_{11} , are easily distinguished, and there is little blending with overlapping weak structure of the other bands. The results of the present investigation are summarized in Table 8.1.

The standard deviations ($\hat{\sigma}$) of the final least-squares fits for individual bands, along with the number and maximum value of J'' of lines fitted, can be obtained from this table. The standard deviations, are in accord with the estimated measurement precision. Band origins of the individual bands are also listed in Table 8.1. These estimates were obtained after merging (4) the parameters from the individual band-fits.

The three individual band-fits yielded 21 estimated constants, with three estimates of the same excited state constants (B_0' , D_0' , A_0'). Single-valued estimates were obtained by merging the individual band constants to a new set of 15 constants (merge (A)). Since the centrifugal distortion constants of the ground state (D_v'') in the output of merge (A) did not show any significant vibrational dependence, it was decided to reduce these 3 constants to a single vibrationally independent parameter D'' (merge (B)). The variance of the equivalent single step merge to the 13 output parameters of merge (B) is $\hat{\sigma}^2 = (1.59)^2$ with $f = 8$ degrees of freedom. This estimate lies just outside the limits $(0.584)^2 \leq \hat{\sigma}^2 \leq (1.40)^2$ given by the $\chi^2/8$ distribution

at the 95% confidence level. This satisfactory merge is considered to indicate the absence of any significant systematic error. The constants from merge (B) are listed in Table 8.2, and the band origins are listed in Table 8.1.

Finally, calculated line positions for the bands analyzed have been obtained with the parameters of merge (B) and are listed in Table 8.3, along with the corresponding residuals (observed-calculated). The merged parameters reproduce the analyzed bands very successfully, as indicated by the similar magnitudes of the standard deviations and root mean-squares (rms) of the residuals for individual bands. The rms of the residuals for the 0-16, 0-17, and 0-18 bands are also listed in Table 8.1.

Figure 8.2: The $A^2\Pi_{1/2} - X^2\Pi_{1/2}$ 0-17 sub-band of $P^{35}Cl^+$.
The trace was recorded photoelectrically from
the flame of the $He_2^+ + PCl_3$ reaction. The
spectral resolution is about 0.06 Å.

Figure 8.2

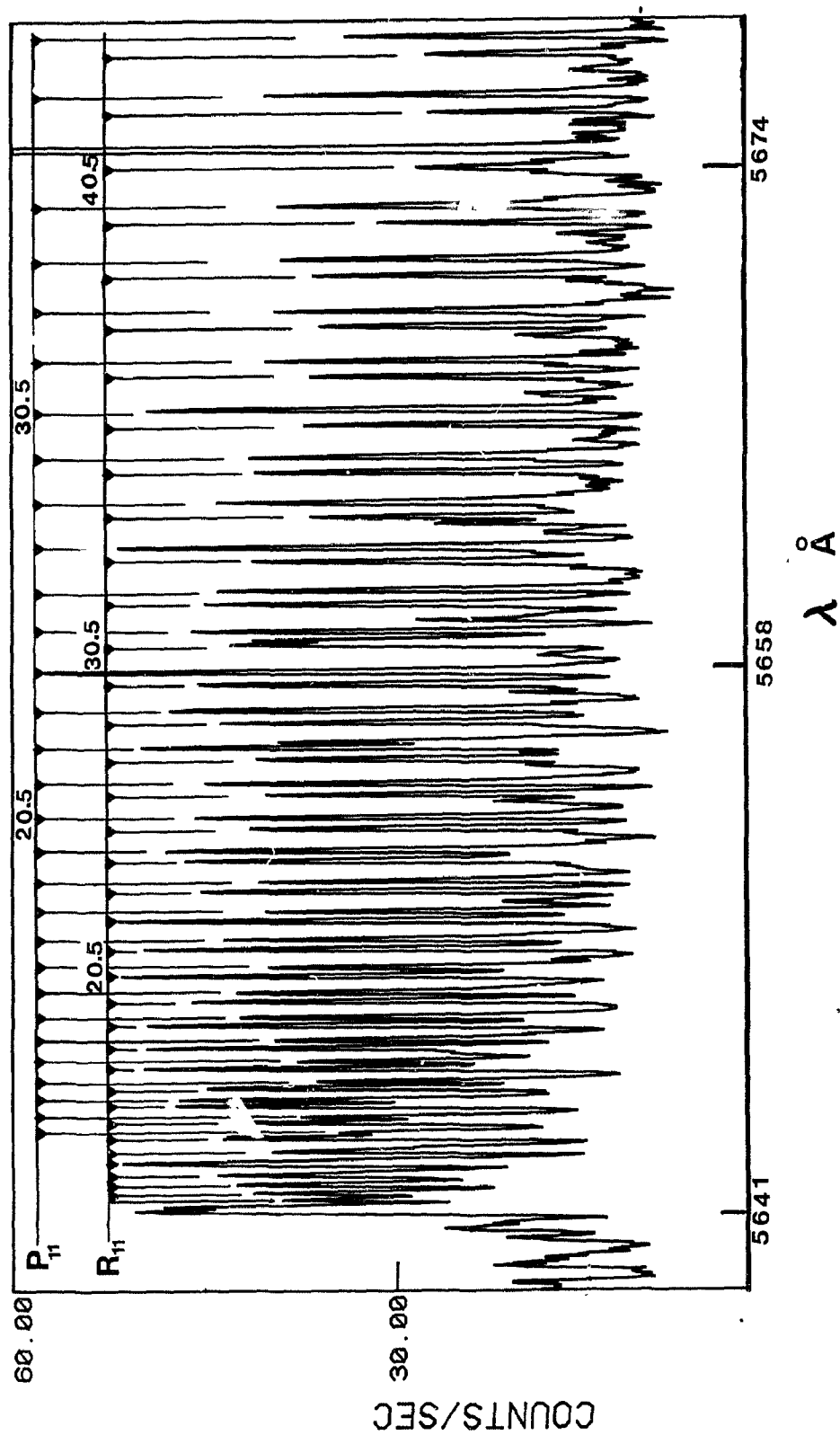


Table 8.1: Least squares fits^a for individual bands of the $A^2\Pi \rightarrow X^2\Pi$ system of $P^{35}Cl^+$

Band	ν_0	N	$\hat{\sigma}$	rms	$J_{\max}$
0-16	18236.635(13)	115	0.0405	0.0398	52.5
0-17	17634.819(11)	131	0.0383	0.0379	58.5
0-18	17038.661(14)	101	0.0477	0.0507	54.5

^a For each band fitted, N is the total number of fitted lines, $\hat{\sigma}$ is the standard deviation, ν_0 is the fitted band origin from merge (B), rms is the root mean square of the residuals between the observed and calculated line positions, and $J_{\max}$ is the maximum value of the quantum number J'' of the fitted lines. All data are in cm^{-1} units. Values in parentheses are estimated standard errors given by $\hat{\sigma}_M(V_{ii})^{1/2}$ in units of the last significant figure of the corresponding constant.

Table 8.2: Fitted Constants^a for the $A^2\Pi$ and $X^2\Pi$ States of $P^{35}Cl^+$

$A^2\Pi$			
v	B_v	$10^7 D_v$	A_v
0	0.18770(12)	2.09(34)	98.52(320)
$X^2\Pi$			
v	B_v	A_v	
16	0.25933(12)	282.56(320)	
17	0.25781(12)	282.19(320)	
18	0.25621(12)	281.43(320)	
$D = 1.52(34) \times 10^{-7}$			

^a The results, in cm^{-1} units, are from merge (B) (see text). Values in parentheses are estimated standard errors given by $\hat{\sigma}_M (V_{ii})^{1/2}$ in units of the last significant figure of the corresponding constant.

Table 8.3: Calculated Line Positions for the 0-16 Band of $P^{35}Cl^+$ (A - X).

J	P1		R1		P2		R2	
	Calc.	Res.	Calc.	Res.	Calc.	Res.	Calc.	Res.
0.5			18329.144				18145.253	
1.5	18426.895		18329.304		18045.383		18145.414	
2.5	18327.072		18329.320		18143.176		18145.433	
3.5	18326.195		18329.192		18142.299		18145.308	
4.5	18325.174		18328.921		18141.280		18145.041	
5.5	18324.011		18328.506		18140.117		18144.630	
6.5	18322.703		18327.948		18138.812		18144.077	
7.5	18321.252		18327.247		18137.363		18143.380	
8.5	18319.658		18326.401		18135.771	-0.106*	18142.540	
9.5	18317.920		18325.412		18134.037		18141.557	
10.5	18316.039		18324.280		18132.159	-0.127*	18140.431	
11.5	18314.014	-0.018	18322.996		18130.138	-0.058	18139.162	
12.5	18311.846	0.036	18321.584		18127.974	0.026	18137.750	
13.5	18309.534	0.021	18320.021		18125.668	-0.071	18136.194	-0.073
14.5	18307.079		18318.314		18123.218	-0.138*	18134.496	
15.5	18304.480	0.037	18316.463		18120.625	0.104*	18132.654	-0.021
16.5	18301.737	-0.016	18314.468	0.088	18117.888	0.024	18130.668	-0.067
17.5	18298.851	0.041	18312.330	0.031	18115.009	0.074	18128.540	-0.059
18.5	18295.821	-0.133**	18310.048	-0.041	18111.987	-0.004	18126.268	0.149*
19.5	18292.648	0.001	18307.622	-0.102*	18108.821	0.024	18123.853	-0.010
20.5	18289.330	-0.051	18305.052	0.007	18105.513	0.016	18121.294	-0.084
21.5	18285.870	-0.026	18302.338	0.013	18102.061		18118.592	-0.006
22.5	18282.265	-0.026	18299.481	0.021	18098.465	0.050	18115.747	0.049
23.5	18278.517	0.002	18296.479	0.048	18094.727	0.105*	18112.758	0.027
24.5	18274.625	0.043	18293.334	-0.049	18090.845	0.121*	18109.325	0.038
25.5	18270.590	0.014	18290.044	0.019	18086.820	0.066	18105.349	-0.016
26.5	18266.410	0.030	18286.611	0.003	18082.652	0.000	18102.929	0.023
27.5	18262.087	-0.026	18283.035	-0.011	18078.340	0.031	18099.366	-0.009
28.5	18257.620	-0.001	18279.311	0.000	18073.885	0.070	18095.659	-0.052
29.5	18253.009	-0.042	18275.445	0.095*	18069.286	-0.000	18091.808	0.091*
30.5	18248.254	0.018	18271.435	-0.013	18064.544	-0.046	18087.813	0.082*
31.5	18243.355	-0.061	18267.281	0.056	18059.658	-0.014	18083.675	0.142*
32.5	18238.312	0.010	18262.982	0.070	18054.629	0.010	18079.393	0.089*
33.5	18233.125	-0.007	18258.539	0.016	18049.456	-0.049	18074.966	0.021
34.5	18227.793	-0.071	18253.951	-0.075	18044.140	0.026	18070.396	
35.5	18222.318	-0.017	18249.219	-0.022	18038.680	-0.035	18065.682	-0.039
36.5	18216.699	-0.041	18244.342	-0.034	18033.076	0.020	18060.823	-0.008
37.5	18210.935	-0.034	18239.321	-0.025	18027.328	0.051	18055.821	0.028
38.5	18205.028	-0.055	18234.155	-0.011	18021.427	0.115*	18050.674	-0.007
39.5	18198.976	0.320**	18228.845	0.018	18015.401		18045.383	-0.021
40.5	18192.779	0.008	18223.390	-0.027	18009.222	0.071	18039.947	-0.045
41.5	18186.438	-0.042	18217.790	-0.001	18002.899		18034.388	-0.029
42.5	18179.953	0.039	18212.045	0.036	17996.431		18028.643	0.034
43.5	18173.323	0.076	18206.155	-0.015	17989.820		18022.775	-0.010
44.5	18166.549	-0.013	18200.121	0.002	17983.064		18016.761	0.082*
45.5	18159.630	-0.041	18193.941	0.054	17976.164		18010.603	-0.103*
46.5	18152.567	-0.043	18187.616		17969.120		18004.300	
47.5	18145.359		18181.146	-0.016	17961.932		17997.853	
48.5	18138.006		18174.531	-0.073	17954.599		17991.260	
49.5	18130.508		18167.771	0.010	17947.122		17984.523	
50.5	18122.865		18160.865	0.031	17939.501		17977.641	
51.5	18115.078		18153.813	0.071	17931.734		17970.613	
52.5	18107.145		18146.617	0.012	17923.823		17963.441	

TABLE 8.3 cont'd...

TABLE 8.3 cont'd ^{a)} Calculated Line Positions for the 0-17 Band of P³⁵Cl⁺ (A - X)

J	P1		R1		P2		R2	
	Calc.	Res.	Calc.	Res.	Calc.	Res.	Calc.	Res.
0.5			17727.146				17543.619	
1.5	17824.901		17727.310		17443.754		17543.785	
2.5	17725.085		17727.333		17541.554		17543.811	
3.5	17724.219		17727.216		17540.688		17543.697	
4.5	17723.212		17726.959		17539.682		17543.443	
5.5	17722.065		17726.561		17538.536		17543.049	
6.5	17720.777	0.007	17726.022	0.071	17537.250		17542.516	
7.5	17719.349	-0.009	17725.343	-0.019	17535.825	0.062	17541.842	
8.5	17717.781	-0.083	17724.524	0.007	17534.259		17541.028	
9.5	17716.072	-0.013	17723.564	-0.009	17532.553		17540.074	
10.5	17714.222	0.010	17722.463	-0.100	17530.707	0.008	17538.979	-0.006
11.5	17712.232	0.024	17721.222	0.009	17528.721	-0.102	17537.745	
12.5	17710.101	-0.009	17719.840	-0.014	17526.595	0.158*	17536.371	-0.033
13.5	17707.830	0.025	17718.317	-0.045	17524.329		17534.856	
14.5	17705.419	0.002	17716.654	0.001	17521.923	0.032	17533.201	0.015
15.5	17702.867	-0.004	17714.850	0.053	17519.377		17531.406	-0.045
16.5	17700.174	-0.075	17712.905	0.010	17516.691		17529.471	-0.023
17.5	17697.341	0.019	17710.820	0.056	17513.865	-0.015	17527.396	-0.068
18.5	17694.367	-0.010	17708.394	0.033	17510.899		17525.180	-0.145*
19.5	17691.252	0.049	17706.227	0.038	17507.792	0.048	17522.824	-0.020
20.5	17687.997	0.003	17703.719	-0.031	17504.546	0.019	17520.327	0.016
21.5	17684.601	-0.002	17701.070	-0.036	17501.159	-0.005	17517.691	-0.036
22.5	17681.065	-0.014	17698.281	-0.052	17497.632	-0.089*	17514.913	0.030
23.5	17677.388	-0.034	17695.350	0.045	17493.965	-0.018	17511.996	0.015
24.5	17673.570	-0.010	17692.279	0.032	17490.158	-0.070	17508.937	0.094
25.5	17669.611	-0.041	17689.066	0.038	17486.210	-0.018	17505.739	-0.051
26.5	17665.512	0.019	17685.713	0.028	17482.122	0.072	17502.399	
27.5	17661.272	-0.038	17682.218	-0.003	17477.893	-0.001	17498.919	
28.5	17656.891	-0.080	17678.582	0.023	17473.525	-0.049	17495.299	0.058
29.5	17652.369	0.018	17674.806	-0.020	17469.016	0.045	17491.537	-0.006
30.5	17647.706	-0.016	17670.888	-0.042	17464.366	-0.079	17487.635	-0.096*
31.5	17642.902	-0.014	17666.828	0.016	17459.576		17483.592	0.006
32.5	17637.958	0.043	17662.628	0.019	17454.645	0.034	17479.408	-0.012
33.5	17632.872	0.025	17658.286	-0.007	17449.574	-0.357*	17475.084	
34.5	17627.645	0.049	17653.803	0.042	17444.362		17470.618	
35.5	17622.277		17649.178	0.022	17439.009		17466.011	
36.5	17616.768	0.018	17644.412	0.031	17433.516		17461.264	
37.5	17611.118	-0.022	17639.504	0.014	17427.882		17456.375	
38.5	17605.327	-0.046	17634.454	0.055	17422.108		17451.345	
39.5	17599.394	-0.013	17629.263	0.095	17416.192		17446.124	
40.5	17593.320	-0.064	17623.931	-0.003	17410.135		17440.861	
41.5	17587.105	-0.020	17618.456	0.062	17403.938		17435.407	
42.5	17580.748	0.156*	17612.840	-0.015	17397.600		17429.812	
43.5	17574.250	-0.045	17607.082	-0.317*	17391.120		17424.075	
44.5	17567.610	0.030	17601.182	-0.011	17384.499		17418.196	
45.5	17560.829	-0.031	17595.139	0.002	17377.738		17412.176	
46.5	17553.906	0.005	17588.955	-0.048	17370.835		17406.015	
47.5	17546.841	-0.020	17582.629	-0.023	17363.790		17399.711	
48.5	17539.635	-0.016	17576.160	-0.062	17356.605		17393.266	
49.5	17532.287		17569.549	-0.014	17349.278		17386.679	
50.5	17524.797	0.043	17562.796	-0.007	17341.809		17379.949	
51.5	17517.165		17555.901	0.028	17334.199		17373.078	
52.5	17509.391	0.041	17548.862	-0.021	17326.447		17366.065	
53.5	17501.475		17541.682	0.000	17318.554		17358.909	
54.5	17493.417	-0.027	17534.358	-0.045	17310.519		17351.611	
55.5	17485.217	-0.055	17526.892		17302.342		17344.171	
56.5	17476.874	0.051	17519.284	0.009	17294.023		17336.588	
57.5	17468.390	0.005	17511.532	-0.067	17285.562		17328.863	

TABLE 8.3 cont'd...

TABLE 8.3 cont'd ^{a)} Calculated Line Positions for the 0-18 Band of P³⁵Cl⁺ (A ~ X)

J	P1		R1		P2		R2	
	Calc.	Res.	Calc.	Res.	Calc.	Res.	Calc.	Res.
0.5			17130.608				16947.841	
1.5	17229.367		17130.776		16847.980		16948.012	
2.5	17128.560		17130.808		16945.789		16948.046	
3.5	17127.705		17130.702		16944.934		16947.943	
4.5	17126.712		17130.459		16943.943		16947.704	
5.5	17125.583		17130.079		16942.815		16947.328	
6.5	17124.316		17129.561		16941.550		16946.815	
7.5	17122.912		17128.906		16940.148		16946.165	0.046
8.5	17121.371		17128.114		16938.609		16945.378	
9.5	17119.692		17127.184		16936.934		16944.455	0.076
10.5	17117.876		17126.117	0.011	16935.122		16943.394	0.066
11.5	17115.923		17124.913	-0.027	16933.173	0.051	16942.197	0.044
12.5	17113.832		17123.571	-0.027	16931.087		16940.863	-0.121
13.5	17111.605	-0.214*	17122.091	0.006	16928.865		16939.392	0.064
14.5	17109.240	-0.013	17120.475	-0.034	16926.506		16937.784	-0.262*
15.5	17106.737		17118.720	0.066	16924.010	-0.153*	16936.039	
16.5	17104.097	-0.152*	17116.829	0.000	16921.377	-0.009	16934.156	0.079
17.5	17101.320	-0.071	17114.799	0.050	16918.607	0.009	16932.137	0.167*
18.5	17098.406		17112.633	-0.016	16915.700	0.030	16929.981	0.014
19.5	17095.354	0.023	17110.328	-0.048	16912.656	-0.039	16927.688	-0.001
20.5	17092.165	0.001	17107.886	-0.010	16909.476	0.143*	16925.257	-0.195*
21.5	17088.838	0.045	17105.306	0.014	16906.158		16922.690	-0.049
22.5	17085.374	-0.003	17102.589	0.037	16902.704	-0.021	16919.985	-0.026
23.5	17081.772		17099.734	0.047	16899.112	-0.151*	16917.143	0.157*
24.5	17078.033	-0.045	17096.741	-0.010	16895.383	0.039	16914.163	-0.046
25.5	17074.156	0.078	17093.611	0.000	16891.518		16911.046	-0.019
26.5	17070.141		17090.342	-0.036	16887.515	-0.083	16907.792	0.046
27.5	17065.989	0.002	17086.936	-0.016	16883.375	0.084	16904.401	-0.072
28.5	17061.700	-0.017	17083.392	0.072	16879.098	0.059	16900.872	-0.108
29.5	17057.273	0.059	17079.709	-0.043	16874.684		16897.205	-0.127
30.5	17052.708	-0.058	17075.889	-0.071	16870.132		16893.401	0.037
31.5	17048.005	0.019	17071.931	-0.027	16865.443		16889.460	-0.136
32.5	17043.165	0.099	17067.835	-0.044	16860.617		16885.381	0.047
33.5	17038.186	0.020	17063.600	0.011	16855.654		16881.164	-0.071
34.5	17033.070	0.014	17059.228	0.020	16850.553		16876.809	
35.5	17027.816	0.010	17054.717	-0.026	16845.315		16872.312	
36.5	17022.424	0.044	17050.068	-0.003	16839.939		16867.686	
37.5	17016.894	0.041	17045.280	-0.058	16834.426		16862.918	
38.5	17011.227	-0.017	17040.354		16828.775		16858.012	
39.5	17005.421	-0.052	17035.290	-0.056	16822.986		16852.968	
40.5	16999.477	0.145*	17030.087	0.072	16817.060		16847.786	
41.5	16993.394	0.090	17024.746	0.090	16810.996		16842.465	
42.5	16987.174	-0.004	17019.266	0.011	16804.794		16837.007	
43.5	16980.815	0.078	17013.647		16798.455		16831.410	
44.5	16974.318	0.056	17007.890	0.031	16791.977		16825.674	
45.5	16967.683	0.185*	17002.994	0.009	16785.362		16819.801	
46.5	16960.909	0.073	16995.953	-0.030	16778.600		16813.785	
47.5	16953.997	0.018	16989.785	0.033	16771.717		16807.638	
48.5	16946.946	0.029	16983.472	0.021	16764.688		16801.349	
49.5	16939.757		16977.020	0.044	16757.520		16794.921	
50.5	16932.429		16970.429	0.034	16750.214		16788.354	
51.5	16924.962		16963.698	0.060	16742.769		16781.648	
52.5	16917.357		16956.829	-0.002	16735.187		16774.804	
53.5	16909.613		16949.820	0.123*	16727.465		16767.820	
54.5	16901.730		16942.671	-0.021	16719.606		16760.698	

* Lines flagged by * were excluded from the least squares fits. All calculated lines positions are obtained from the parameters of merge (B) (see text). Residuals are defined as Res. = $\nu_{\text{observed}} - \nu_{\text{calculated}}$.

The estimated molecular constants of the PCl^+ ion in Table 8.2 merit further discussion. The rotational constants B for both states of the isoelectronic SiCl molecule (76) are similar in magnitude with the corresponding constants of PCl^+ , as indicated by the following numerical values;

$$\text{SiCl: } B_{10}'' = 0.2397 \text{ cm}^{-1} (\text{X}^2\Pi)$$

$$B_0' = 0.1983 \text{ cm}^{-1} (\text{A}^2\Sigma^+)$$

$$\text{PCl}^+: B_{16}'' = 0.25933(12) \text{ cm}^{-1} (\text{X}^2\Pi)$$

$$B_0' = 0.18770(12) \text{ cm}^{-1} (\text{A}^2\Pi)$$

The spin-orbit coupling constant in the ground $^2\Pi$ state of PF^+ is well-determined (70) from a $^2\Sigma - \text{X}^2\Pi$ transition as 323.95 cm^{-1} . For the isovalent species SiF and SiCl , the ground state A'' values are 161.9 (17) and 207.2 (18) cm^{-1} (53) respectively. If a similar halogen dependence holds for PF^+ and PCl^+ , A'' for PCl^+ should be $\sim 370 \text{ cm}^{-1}$, considerably larger than the value in Table 8.2 of $\sim 282 \text{ cm}^{-1}$.

A probable explanation for this anomaly can be obtained by considering the absolute spin-orbit constants obtained recently for a similar $^2\Pi-^2\Pi$ system, namely $\text{SiN } \text{D}^2\Pi-\text{A}^2\Pi$. For the 4-3 band of this system Linton (96) estimated $A_4' = -45.14(97) \text{ cm}^{-1}$ and $A_3'' = -72.18(94) \text{ cm}^{-1}$. Bredohl et al. (97) analyzed the same band with the A_3'' value already determined from the $\text{K}^2\Sigma - \text{A}^2\Pi$ transition as $A_3'' = -88.65 \text{ cm}^{-1}$. Knowing the spin-orbit constant of the $\text{A}^2\Pi$ state a

corresponding estimate of A for the $D^2\Pi$ state could be determined from the term values $F_2(J) - F_1(J)$ using the Hill-Van Vleck expression (2). The calculated value of A' was -61.80 cm^{-1} . Since the reported spin-orbit constants differed significantly between these two analyses, it was decided to reexamine the SiN data from both studies, and if possible to determine the source of disagreement.

Firstly, the program for direct fitting of the measured line positions was used to obtain estimates of the spin-orbit coupling constants using first Linton's data then those of Bredohl et al. In these initial fits, trial values of A were taken from Ref. (97) and the spin-rotation constants were constrained to zero. The estimates of A' and A'' obtained from both fits were similar to the values reported by Linton, within the experimental error.

In the second set of fits, the spin-rotational constants of both states were set at approximate trial values calculated using the expression of Brown and Watson (98) relating γ and A_D , and with Veseth's formula (99) for A_D (centrifugal distortion of spin-orbit coupling) and neglecting the first-order effect. The numerical values were calculated to be: $\gamma_4' \approx -1.6 \times 10^{-2} \text{ cm}^{-1}$ and $\gamma_3'' \approx 2.9 \times 10^{-3} \text{ cm}^{-1}$. The precision of the measured line positions from both studies was not sufficient to permit the simultaneous determination of γ_4' and γ_4'' . However, when γ_4' was constrained to its trial value, it was of much interest

to find that the estimated spin-orbit parameters were $A'_4 = -57.7(1) \text{ cm}^{-1}$, $A''_3 = -84.8(1) \text{ cm}^{-1}$; very close to the values reported by Bredohl et al. (97). From this discussion, it can be concluded that the absolute values of A''_v and A'_0 of PCl^+ determined in Table 8.2 are considerably less reliable than is suggested by the quoted standard errors, and it is of some interest to consider this topic in more detail. The two spin-orbit coupling constants A' and A'' of a ${}^2\Pi - {}^2\Pi$ transition are highly correlated. The determination of separate values of A' and A'' with direct fitting program such as that employed presently is made possible only when the $Y = A/B$ values for the two states are significantly different, since the spin-orbit splittings then have different J -dependences for the two states, as follows. In Hund's case (a), the analytical expressions for the rotational term values of the spin-orbit components of a ${}^2\Pi$ state are given quite adequately by expression (2),

$$F(J) = B_{\text{eff}} J(J + 1) - D_v J^2(J + 1)^2 \quad (8.2)$$

where the effective rotational constant B_{eff} is slightly different for each spin-orbit component and where terms independent of J have been omitted. Furthermore, Mulliken (33) showed that B_{eff} can be expanded as a series, with the first two members given by,

$$B_{\text{eff}} = B (1 \pm B/A) \quad (8.3)$$

where B is the mechanical rotational constant and the "+" and "-" are for the F_2 and F_1 components respectively. For

a transition in which both Y values are large, the magnitudes of the J -dependences become small, and can be comparable with higher order effects (centrifugal distortion of spin-orbit coupling and second order spin-rotation, which are strongly correlated (98)). As a result, the absolute magnitude of the fitted spin-orbit coupling constants obtained from a $^2\Pi - ^2\Pi$ transition can depend significantly on the corresponding γ (or A_0) values. The precision of the present data on PCl^+ could not afford determinations of γ_v for either state, so that A' and A'' are then strictly effective parameters that absorb unknown spin-rotational/centrifugal distortion effects. Data of better precision from a future study or from the photoelectron spectrum of PCl might resolve this problem.

Chapter 9

Unassigned Bands of PBr^+

9.1 Introduction

After the observation and analysis of the emission due to the phosphorous monochloride cation, it was of interest to investigate the chemiluminescence reaction of discharged helium with PBr_3 . The emission observed was not known hitherto, and is tentatively attributed to a new ion, PBr^+ .

Although it has not been possible to arrange the numerous bands of PBr^+ in a Deslandres table, and hence to derive the vibrational constants, it is believed that this work will stimulate other spectroscopic investigations on this molecule.

9.2 Results and Discussions

The PBr^+ emission spectrum obtained at low resolution in the present work, under the same conditions as for the other ions, consists of a large number of red-degraded bands in the range $13000\text{--}24500\text{ cm}^{-1}$, with the most intense emission in the range $15300\text{--}17350\text{ cm}^{-1}$. Figure 9.1 shows a portion of the spectrum and illustrates the presence of "quadruple-headed" bands. As discussed later, this characteristic feature is a principal source of difficulty in vibrationally assigning the PBr^+ bands.

The wavelengths ($\text{\AA}$) and vacuum wavenumbers of the

unassigned band-heads are given in Table 9.1. The calibration of the spectrum was obtained by least squares fitting of emission lines of atomic Br, P and He (45) to a linear function in d , the distance along the trace. The standard deviation of this fit was $\sim 0.07 \text{ \AA}$. The PBr^+ single bandhead positions were determined at half maximum intensity above the baseline and have an estimated uncertainty of $\sim 0.6 \text{ \AA}$.

By comparison with the isovalent ions PCl^+ and AsCl^+ , it is reasonable to believe that the two states involved in this emission should have a similar well-bound $^2\Pi$ ground state and a weakly-bound excited state, most probably $^2\Pi$. However, the two factors that complicate the PBr^+ spectrum to a greater degree than for the other reported ions are, i) the similarity in magnitude of the spin-orbit splitting and the ground state vibrational spacings, and ii), the existence of two equally abundant ^{79}Br and ^{81}Br isotopes. The corresponding closeness of heads causes difficulty in obtaining accurate measurements of the heads of the overlapped longer wavelength members of each "quadruple-headed" band, which are very important in determining accurately the isotope shift.

Recently, the vibrational constant $\omega_0^{\text{e}}(X)$, of the PSe molecule, isoelectronic with PBr^+ , was reported in Ref. (100) as 556.8 cm^{-1} . Considering that the ratio of $\omega_0^{\text{e}}(X)$ for the isoelectronic species $\text{PCl}^+ + \text{PS}$, which was reported

0.93, is probably very similar to the corresponding ratio for PBr^+ and PSe , the ground state vibrational constant of PBr^+ is estimated as $\sim 530 \text{ cm}^{-1}$.

This value is in very good agreement with the observed difference of $\sim 490 \text{ cm}^{-1}$ between the shorter wavelength members of the multiple-headed bands assigned to PBr^+ . The expected value of ω_e for the excited state of PBr^+ , should be similar to the estimate of ω_e for the $\text{A}^2\Sigma$ state of the SiBr and the $^2\Pi$ excited state of the AsCl^+ ion. On the other hand, a value for the spin-orbit separation cannot be predicted from the isoelectronic species, since the question of whether the excited state, if $^2\Pi$, is regular or inverted, cannot be addressed at the present time. Nevertheless, there is little doubt that much of the spin-orbit separation is due to spin-orbit coupling in the ground state. Therefore, ΔA is expected to be greater than $\sim 183 \text{ cm}^{-1}$, as for PCl^+ , assuming the halogen dependence for the ground state spin-orbit coupling constants of PCl^+ and PBr^+ is similar to that of their isoelectronic species SiCl ($A'' \sim 207.2 \text{ cm}^{-1}$) and SiBr ($A'' \sim 419.2 \text{ cm}^{-1}$), see Tables 7.4, 7.8.

In conclusion, it seems likely that the use of isotopically pure PBr_3 as the substrate molecule would be of much help in obtaining a simplified spectrum, from which an unequivocal assignment of the bands could be achieved. It should also be mentioned that photoelectron spectroscopy on PBr will be very helpful in determining the spin-orbit

coupling constants of the ground or of both the electronic states of PBr^+ .

Figure 9.1: A portion of the PBr^+ emission spectrum from ~5750 to ~6350 Å.

Figure 9.1

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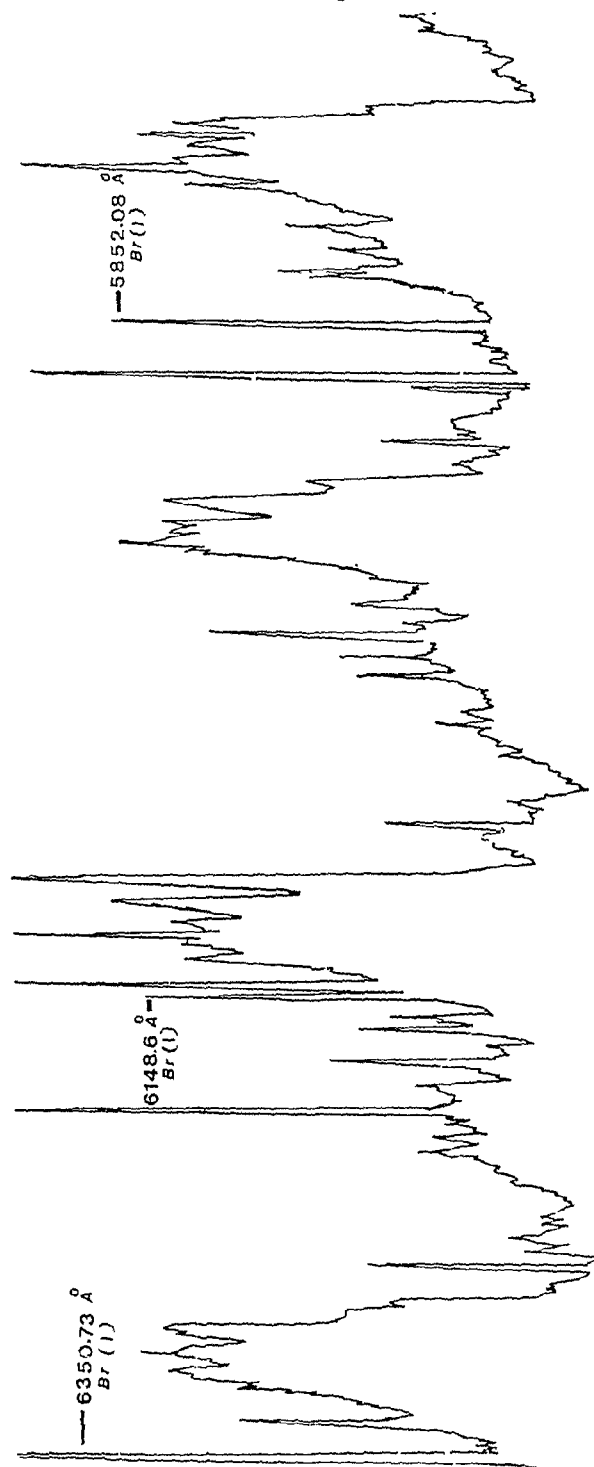


Table 9.1: Wavelengths and Vacuum Wavenumbers for the
Unassigned Band System of PBr^+

λ (Å)	ν_{vac} (cm^{-1})	λ (Å)	ν_{vac} (cm^{-1})
4055.4	24651.2	4817.5	20751.7
4085.4	24470.8	4819.6	20742.6
4087.8	24456.3	4852.1	20603.7
4113.8	24301.8	4884.8	20466.1
4123.7	24243.3	4887.6	20454.2
4178.1	23927.3	4911.7	20353.8
4179.0	23922.1	4941.5	20231.1
4181.2	23910.1	4957.4	20166.0
4220.4	26687.8	4975.9	20091.4
4221.8	23680.0	5009.4	19957.0
4223.4	26670.9	5012.8	19943.3
4270.2	23411.4	5036.5	19849.4
4318.4	23150.4	5040.8	19832.4
4220.1	23141.0	5083.2	19667.3
4361.8	22919.8	5086.6	19654.0
4366.5	22895.2	5100.6	19599.9
4372.5	22864.0	5108.5	19569.9
4418.0	22628.5	5139.6	19451.4
4419.4	22621.1	5143.6	19436.4
4463.1	22399.7	5171.5	19331.4
4466.3	22383.7	5183.2	19287.9
4474.2	22344.3	5217.1	19162.4
4515.1	22141.5	5221.3	19146.9
4532.0	22058.9	5239.4	19080.9
4565.0	21899.5	5243.6	19065.5
4569.9	21876.1	5280.0	18934.0
4580.6	21825.0	5309.2	18829.9
4590.5	21778.1	5315.4	18807.9
4621.7	21631.2		
4639.7	21547.0	5357.4	18660.6
4675.3	21382.8	5362.2	18643.9
4677.6	21372.4	5375.9	18596.3
4680.0	21361.4	5377.8	18589.6
4701.5	21263.8	5385.0	18564.9
4703.5	21254.8		
4733.0	21122.4		
4734.8	21114.3		
4766.0	20976.2		
4766.7	20973.1		
4791.2	28065.6		
4793.2	20857.2		

(cont'd.)

Table 9.1: Wavelengths and Vacuum Wavenumbers for the
Unassigned Band System of PBr^+ (cont'd.)

λ (Å)	ν_{vac} (cm^{-1})	λ (Å)	ν_{vac} (cm^{-1})
5444.7	18361.5	6475.2	15439.2
5459.7	18310.9	6489.8	15404.6
5503.8	18164.3	6497.0	15387.4
5509.7	18144.8	6511.4	15353.5
5527.7	18085.5		
5531.0	18074.7	6618.7	15401.6
		6626.7	15086.3
5600.3	17851.3	6680.7	14964.4
5614.4	17806.4	6715.1	14887.6
5621.0	17785.4	6734.9	14843.9
5639.4	17727.4		
5645.0	17710.0	6836.7	14623.0
5695.2	17553.8	6844.1	14607.1
		6853.4	14587.3
5753.2	17376.9		
5760.3	17355.4	6935.5	14414.7
5771.5	17321.8	6971.3	14340.6
5778.7	17300.2	6979.1	14324.6
5809.1	17209.5		
5819.4	17179.1	7083.8	14112.9
5892.7	16965.5	7094.0	14092.6
5908.7	16919.6	7121.2	14038.8
		7129.1	14023.2
5920.2	16886.7	7223.8	13839.4
5928.0	16864.4	7232.4	13822.8
5939.1	16832.9		
5983.7	16707.3	7238.6	13622.8
6078.5	16447.0	7348.0	13605.4
		7349.8	13602.1
6092.5	16409.0	7384.0	13539.0
6097.3	16396.2	7393.4	13521.8
6105.0	16375.4		
		7492.6	13342.8
6124.0	16324.6	7502.6	13325.0
6170.2	16202.5		
6188.0	16155.9	7610.4	13136.4
		7624.1	13112.7
6280.5	15917.9	7665.0	13042.7
6285.6	15904.9	7676.2	13023.6
6290.9	15891.6		
6300.3	15867.7		
6391.9	15640.4		
6412.5	15590.2		

Chapter 10

Additional Reactions of Discharged Helium

The spectra described in Chapters 5-9 from various reactions of discharged helium have been investigated quite thoroughly. In the present chapter, preliminary observations on reactions with additional substrates will be described. Most of the spectra have been observed previously by other means of excitation and have been analyzed with different degrees of completeness by other workers.

The observations are summarized in Table 10.1. Each entry of this table indicates the reagent used, the excited molecule, the nature of the transition, and the spectral range. The following sections provide further detail on the individual reactions:

Table 10.1: Survey of Some Emission Spectra Arising
from Discharged Helium Impact Reactions

Reagent	Observed Emission	Range (Å)	Ref.
$\text{N}_3\text{S}_3\text{Cl}_3$	$\text{NS}(\text{B}^2\Pi_r-\text{X}^2\Pi_r)$	3150-5500	(81,102)
PSCl_3	$\text{PS}(\text{B}^2\Pi_r-\text{X}^2\Pi_r)$	3400-6300	(77)
	$\text{PS}(\text{C}^2\Sigma-\text{X}^2\Pi_r)$	2700-3400	(102,104)
	$\text{PS}^+(\text{A}^1\Sigma^+-\text{X}^1\Sigma^+)$	2480-2750	(105)
VOCl_3	$\text{VO}(\text{C}^4\Sigma^--\text{X}^4\Sigma^-)$	4300-6200	(106)
POCl_3	$\text{PO}(\text{B}^2\Sigma^+-\text{X}^2\Pi_r)$	3250-3450	(107)
BCl_3	$\text{BCl}(\text{A}^1\Pi-\text{X}^1\Sigma^+)$	2700-2850	(107)
BBr_3	$\text{BBr}(\text{a}^3\Pi_{1,0^+}-\text{X}^1\Sigma^+)$	5100-5600	(50)
SbCl_3	$\text{SbCl}(\text{A}_1-\text{X}^3\Sigma^-)$	4750-7000	(110,111)
NCl_3	--	--	(112)

Trithiazyl chloride ($N_3S_3Cl_3$) was prepared following the procedure of Ref. (101). The NS spectrum obtained from the reaction of discharged helium with $N_3S_3Cl_3$ was free from other interfering species. This can be compared with the method of microwave excitation of NS through a mixture of nitrogen and sulphur (81, 102) in which the high v'' NS bands are overlapped strongly by the $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ system of S_2 . As a consequence, bands of NS with $v'' \geq 2$ could not be analyzed. Presently, the $B \rightarrow X$ system of the NS was extended towards longer wavelengths, and bands were observed with $v'' = 10$. In Figure 10.1 a portion of the NS spectrum is shown. Quite recently, Karna and Grein (103) have performed ab initio CI calculations on NS^+ , using double-zeta basis sets with diffuse and polarization functions. Nine stable excited states of NS^+ were found. Among these excited states, only one $^1\Pi$ state is stable and lies at ~ 6 eV above the $^1\Sigma^+$ ground state. It is possible then that the unsuccessful search for a spectrum of NS^+ emission is due to the lack of response of the present spectrometer/photomultiplier outside the range 2200-7500 Å.

(b) PS ($B, C \rightarrow X$) and PS^+ ($A \rightarrow X$)

The PS and PS^+ emission spectra observed in the present work are among the best examples of the helium afterglow method for providing very specific excitation. The extensive red-degraded band systems of PS and PS^+ were free

from overlap by any other bands, in particular emission due to P_2 or S_2 . In Figures 10.2 and 10.3 portions of the PS and PS^+ spectra are shown. Jenouvrier and Pascal (77) have studied the $B \rightarrow X$ system of PS and rotationally analyzed 50 sub-bands with vibrational quantum numbers $v' \leq 11$ and $v'' \leq 6$. The $C \rightarrow X$ system has been studied vibrationally by Narasimham and Subramanian (102); the 2-0 and 1-0 bands have been rotationally analyzed by Narasimham and Balasubramanian (104). It was not possible to analyze more bands of this system because of P_2 and S_2 interference.

The $A \rightarrow X$ emission spectrum of PS^+ was first observed by Dressler (105). An attempt was made to analyze the present spectrum in order to obtain the first rotational constants of PS^+ . However, the intensity of the observed bands was not sufficient for high-resolution work. Improved techniques to obtain a more intense PS^+ emission spectrum would be advantageous.

Figure 10.1: A portion of the NS emission spectrum, showing bandheads belonging to the $B^2\Pi - X^2\Pi$ system.

Figure 10.1

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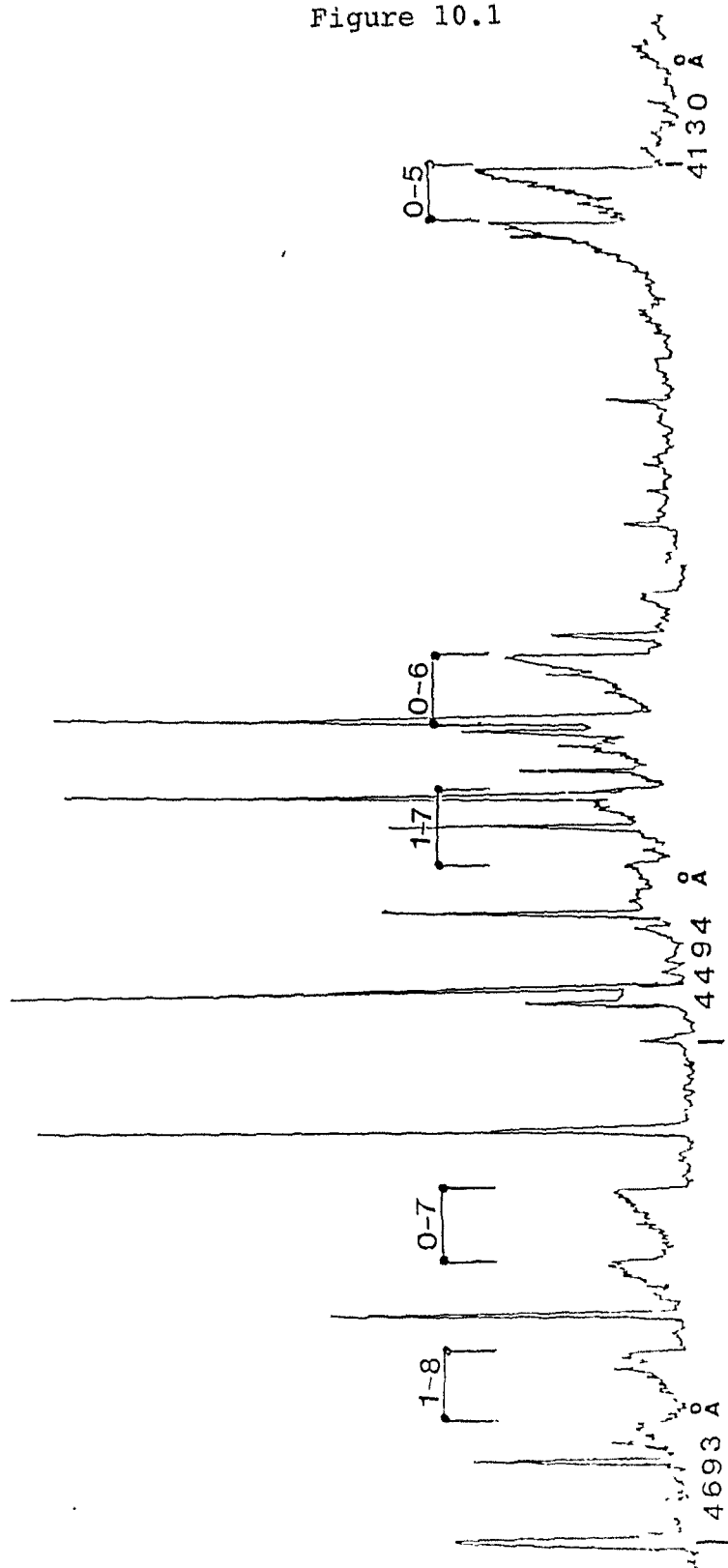


Figure 10.2: A portion of the $B^2\Pi-X^2\Pi$ emission spectrum of PS.

Figure 10.2

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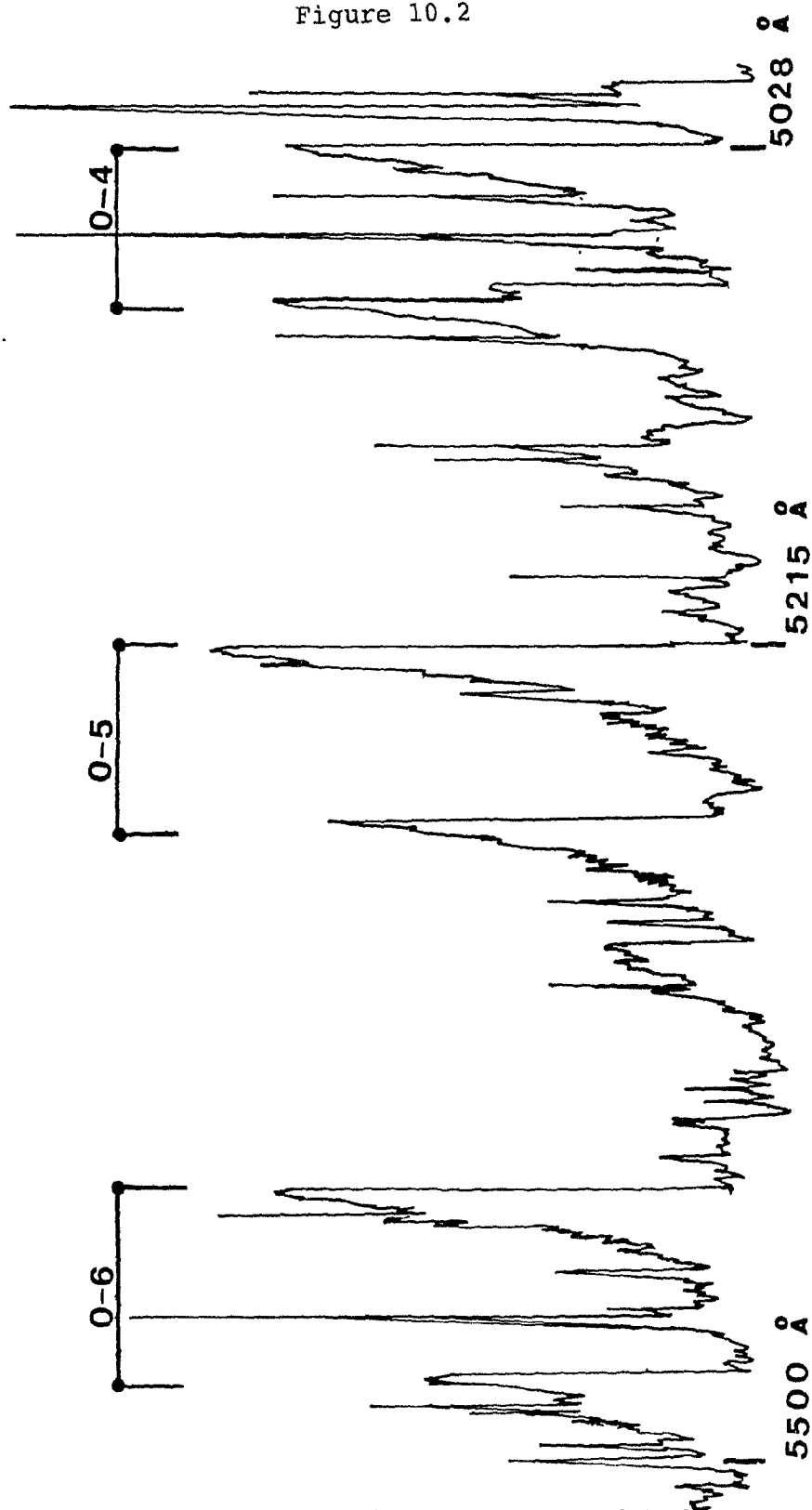
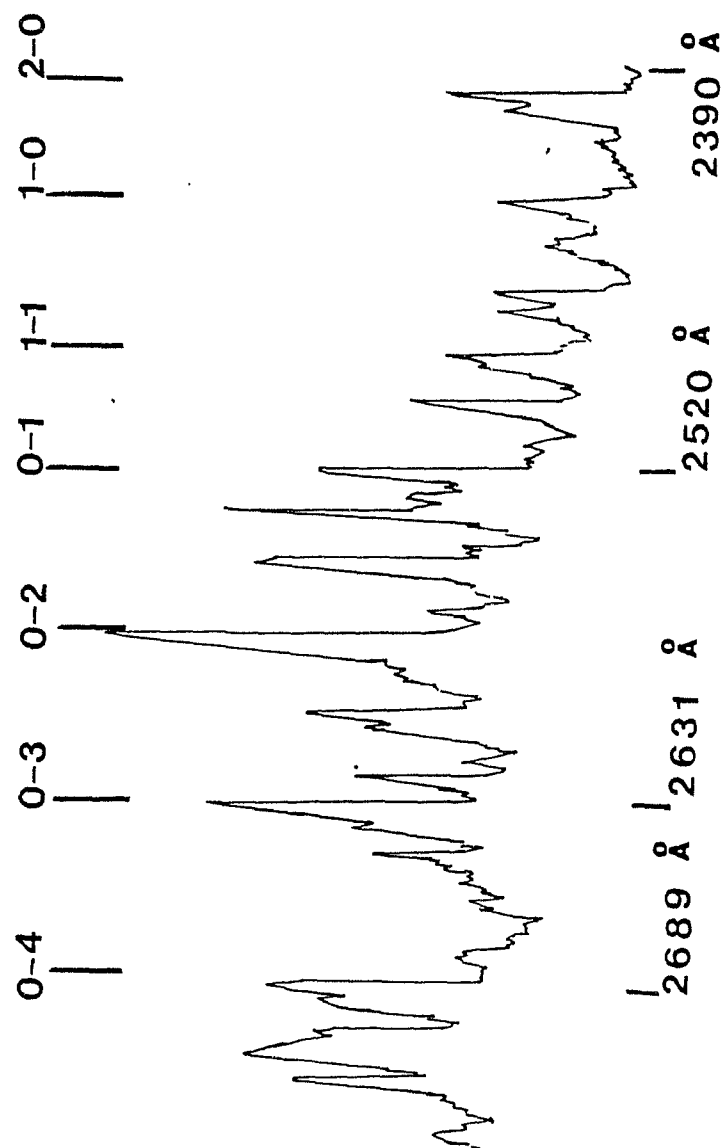


Figure 10.3: A portion of the PS^+ ($A \rightarrow X$) emission spectrum.

Figure 10.3



In the pursuit of identification of new ions through their emission spectra, the Group 3 monohalide cations were the prime target since no optical emissions were known hitherto for these molecules. However, the reactions of BCl_3 and BBr_3 with discharged helium, generated in the fast flow system described previously, only produced emissions assigned to the corresponding neutral diatomics. According to a mass spectrometric study of photoionization of BCl_3 by Dibeler and Walker (108), $\Delta E = 18.37 \pm 0.02$ eV for the formation of BCl^+ in the ground state. It was not surprising then that even at large helium flow rates and pressure (~ 4 Torr), conditions which are known to enhance production of He_2^+ , insufficient energy (~ 21 eV) was available from He_2^+ to form electronically excited BCl^+ .

However, in recent work by Yamaguchi et al. (109), a new emission spectrum was observed in the 4700-5150 Å region from the flowing afterglow reaction of BBr_3 and assigned to the $A^2\Pi_r - X^2\Sigma^+$ transition of BBr^+ . From the vibrational analysis, the vibrational constants of both states of $^{11}\text{BBr}^+$ were determined. Although the afterglow apparatus was similar to the one used during the present study, lower total pressures (~ 0.5 Torr) of the discharged helium were achieved at high flow rates using a fast 600 m³/h mechanical booster pump. This supports the claim of Yamaguchi and co-worker (109) that the active helium species responsible for the BBr^+ emission was He^+ , and that the minimum energy

required for the production of the $A^2\Pi_{1/2}$ state of BBr^+ was 19.2 ± 0.5 eV.

(d) $He_2^* + SbCl_3$.

Most of the red-degraded bands in the range of 17800-20900 cm^{-1} observed from the reaction of discharged helium with $SbCl_3$ have been assigned to the $A_1 - X$ system of $SbCl$. This system has been studied vibrationally by two separate groups. Ferguson and Hudes (110) had first seen this emission and assigned the most intense bands to a $v' = 0$ progression. In the later analysis by Avasthi (111), the spectra were recorded at higher resolution and a larger number of bands were vibrationally assigned. Although the same system seems to have been observed by both groups, the common bands were not assigned to the same quantum numbers. In the present work on $SbCl$, all the bands of the $A_1 \rightarrow X$ system reported previously were also observed.

The relative intensity distribution of the bands was more consistent with the original assignment by Ferguson and Hudes (110). Figure 10.4 shows a portion of $SbCl$ spectrum. In addition, however, several new bands were observed in the longer wavelength region. The wavenumbers of the most intense of these bandheads, which were obtained directly from the wavelength drum reading of the spectrometer with an estimated uncertainty of ~ 4 cm^{-1} , are as follows: 16930, 16576, 16222, 15871, 15519, 15171, 14824 cm^{-1} . It can be

readily seen that the difference between adjacent heads is $\sim 350 \text{ cm}^{-1}$, similar to the corresponding difference of the bands belonging to the $A_1 \rightarrow X$ system. Therefore, it is suggested that either these bands are members of the $v' = 0$ progression with high v'' of the $A_1 \rightarrow X$ system or that they belong to a new system or SbCl having the same ground state or a state with similar vibrational constant.

The work on this molecule was not completed. Further work was precluded because the substrate molecule (SbCl_3), which is a solid compound at room temperature and which boils at 283°C , requires modifications on the existing apparatus in order to increase the amount of vapour reaching the reaction zone; with more intense spectra it would be possible to identify bands of the Sb^{37}Cl isotope. In addition, more intense emission would allow the spectrum to be recorded at higher resolution, as is necessary in obtaining more accurate band head measurements for both chlorine isotopes.

(e) $\text{He}_2^* + \text{NCl}_3$.

Recently, Obase and co-workers (112) observed a new emission system in the 4400-5700 Å region from the reaction of He^+ with NF_3 . This emission is assigned to the $\text{NF}(c^1\Pi - b^1\Sigma^+)$ transition. Prior to this publication a 12% mixture of NCl_3 in CCl_4 was prepared in this laboratory, according to the procedure reported by Noyes (113), and

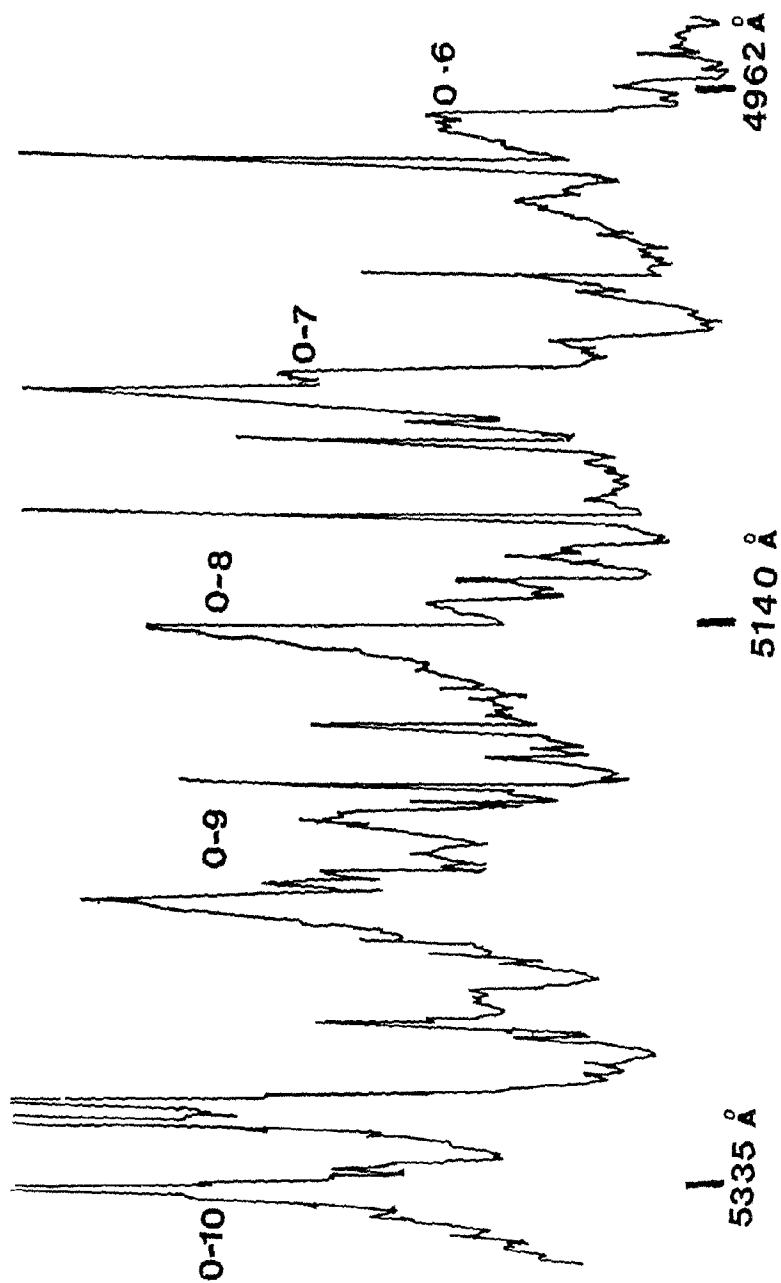
reacted with discharged helium. The recorded spectrum did not indicate the existence of any emitting diatomic species. It is believed, now, that a more concentrated NCl_3 solution might produce a corresponding $c^1\Pi - b^1\Sigma^+$ emission of NCl and/or a $^2\Pi - X^2\Pi$ emission of NCl^+ .

In conclusion, a significant portion of the research presently undertaken and presented in Chapters 5 through 10 of this thesis might encourage research on the kinetic aspects of the reactions reported.

Figure 10.4: A portion of the $A_1 - X$ emission spectrum of $SbCl$.

Figure 10.4

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BIBLIOGRAPHY

1. R.N. Zare, A.L. Schmeltekopf, W.J. Harrop and D.L. Albritton, *J. Mol. Spectrosc.*, **46**, 37 (1973).
2. G. Herzberg, *Spectra of Diatomic Molecules*, 2nd Ed., Van Nostrand Co. Inc., Princeton, NJ (1950).
3. D.L. Albritton, A.L. Schmeltekopf and R.N. Zare, *J. Mol. Spectrosc.*, **67**, 132 (1977).
4. J.A. Coxon, *J. Mol. Spectrosc.*, **72**, 252 (1978).
4a) E.V. Condon and G.H. Shortley, *The Theory of Atomic Spectra*, Cambridge Univ. Press, NY (1953).
5. E.C. Kemble, *Quantum Mechanics*, Dover Publications, New York, NY (1958).
6. J.T. Hougen, *The Calculation of Rotational Energy Levels and Rotational Line Intensities in Diatomic Molecules*. National Bureau of Standards Monograph 115, U.S. Government Printing Office, Washington, DC (1970).
7. J. Kovacs, *Rotational Structure in the Spectra of Diatomic Molecules*, American Elsevier, New York, NY (1969).
8. K.F. Freed, *J. Chem. Phys.*, **45**, 4214 (1966).
9. J.M. Brown, J.J. Hougen, K.P. Huber, J.W.C. Johns, I. Kopp, H. Lefebvre-Brion, A.J. Merer, D.A. Ramsay, J. Rostas and R.N. Zare, *J. Mol. Spectrosc.*, **55**, 500 (1975).
10. J.M. Brown, E.A. Colbourn, J.K.G. Watson and F.D. Wayne, *J. Mol. Spectrosc.*, **74**, 294 (1979).

11. D.L. Albritton, A.L. Schmeltekopf and R.N. Zare, in "Molecular Spectroscopy: Modern Research", Vol. 2, pp. 1-67, Academic Press (1976).
12. R. Rydberg, Z. Physik, **73**, 376 (1931); O. Klein, Z. Physik, **76**, 226 (1932); A.L.G. Rees, Proc. Phys. Soc., **59**, 998 (1947).
13. J.L. Dunham, Phys. Rev., **41**, 713 (1932).
14. J.A. Coxon, J. Quant. Spectrosc. Rad. Transf., **11**, 443 (1971).
15. S.C. Foster, Ph.D. Thesis, Dalhousie University, Halifax, NS (1982).
16. F.R. Gilmore, J. Quant. Spectrosc. Rad Transf., **5**, 369 (1965).
17. A.S. King, Astrophys. J., **62**, 283 (1925).
18. A. Lagerqvist, N.E. Nilsson and R.F. Barrow, Arkiv for Fysik, **12**, 543 (1957).
19. M. Shimauchi, Science of Light, **7**, 101 (1958).
20. W.C. Pomeroy, Phys. Rev., **29**, 59 (1927).
21. B. Rosen, Phys. Rev., **68**, 124 (1945).
22. V.A. Loginov, opt. i spektroskopiya, **6**, 67 (1959).
23. R.W. Nicholls, W. Parkinson and E.M. Reeves, Applied Optics, **2**, 919 (1963).
24. J.K. McDonald and K.K. Innes, Nature, **183**, 243 (1959).
25. V.W. Goodlett and K.K. Innes, Nature, **183**, 243 (1959).
26. B. Authier, J.E. Blamond and G. Carpentier, Ann. Geophys., **20**, 342 (1964).

27. B. Authier, *Ann. Geophys.*, **20**, 353 (1964).
28. O. Harang, *Planet. Space Science*, **12**, 567 (1964).
29. E.R. Johnson, *J. Geophys. Res.*, **70**, 1275 (1965).
30. J. Drowart, G. De Maria, R.P. Burns and M.G. Inghram, *J. Chem. Phys.*, **32**, 1366 (1960).
31. K.M. Sen, *Ind. J. Phys.*, **11**, 251 (1938).
32. M.J. Mahieu, D. Jacquinet, J. Schamps and A.J. Hall, *J. Phys. B*, **8**, 308 (1975).
33. S.R. Mulliken, *Rev. Mod. Phys.*, **3**, 89 (1931).
34. J.A. Coxon and S. Naxakis, *J. Mol. Spectrosc.*, **111**, 102 (1985).
35. M. Singh, G.V. Zope and S.L.N.G. Krishnamachari, *J. Phys. B*, **18**, 1743 (1985).
36. E. Wigner and E.E. Witner, *Z. Physik*, **51**, 859 (1928).
37. J. Schamps, *Chem. Phys.*, **2**, 352 (1973).
38. H.M. Crosshwhite, *J. Res. Nat. Bur. Stand.*, **79A**, 17 (1975).
39. C.B. Collins and W.W. Robertson, *J. Chem. Phys.*, **40**, 701 (1964).
40. J. Franck, *Naturwiss.*, **14**, 211 (1926).
41. L.G. Piper, L. Gundel, J.E. Velazco and D.W. Setser, *J. Chem. Phys.*, **62**, 3883 (1975).
42. M. Tsuji, H. Obase, M. Matsuo, M. Endoh and Y. Nishimura, *Chem. Phys.*, **50**, 195 (1980).
43. J.A. Coxon and S.C. Foster, *J. Mol. Spectrosc.*, **103**, 281 (1984).

44. L. Ramaley, S.C. Foster and J.A. Coxon, Chem. Biomed. Environ. Inst., **12**, 229 (1982/83).
45. A.R. Striganov and N.S. Sventitskii, Tables of Spectral Lines of Neutral and Ionized Atoms, IFI/Plenum Data Corp., New York, NY (1968).
46. J. Reader, C.H. Corliss, W.L. Wiese, and G.A. Martin, Wavelengths and Transition Probabilities for Atoms and Atomic Ions, (NSRDS-NBS68) National Bureau of Standards, Washington, DC (1980).
47. J. Lebreton, J. Ferran and L. Marsigny, J. Phys. B, **8**, L465 (1975).
48. J. Lebreton, L. Marsigny and J. Ferran, C.R. Acad. Sci. (Paris), **272**, 1094 (1971).
49. J. Lebreton, L. Marsigny and G. Bosser, C.R. Acad. Sci. (Paris), **271**, 1113 (1970).
50. J. Lebreton, J. Chim. Phys., **70**, 738 (1973).
51. J. Lebreton, J. Ferran, A. Chatalic, D. Iococca and L. Marsigny, J. Chim. Phys., **71**, 587 (1974).
52. A.G. Briggs and R. Piercy, Spectrochim. Acta, **29A**, 851 (1973).
53. K.P. Huber and G. Herzberg, Molecular Structure and Molecular Spectra, Vol. 4, Constants of Diatomic Molecules, Van Nostrand Co., Inc., Princeton, NJ (1979).
54. A.G. Briggs and R.E. Simmons, Naturwissenschaften, **67**, 402 (1980).

55. H. Bredohl, I. Dubois and F. Mélen, *J. Mol. Spectrosc.*, **121**, 135 (1987).
56. J.K.G. Watson, *J. Mol. Spectrosc.*, **80**, 411 (1980).
57. R.F. Barrow, *Trans. Faraday Soc.*, **56**, 952 (1960).
58. A.H. Wapstra and K. Bos, *At. Data Nucl. Data Tables*, **19**, 185 (1977).
59. T.C. James, *J. Chem. Phys.*, **55**, 4118 (1971).
60. J.M. Hutson, *J. Phys. B*, **14**, 851 (1981).
61. J.A. Coxon and M.P. Haley, *J. Mol. Spectrosc.*, **108**, 119 (1984).
62. P.H. Krupenie, *J. Phys. Chem. Ref. Data* **1**, 423 (1972).
63. J.A. Coxon and K. Brabaharan, *J. Mol. Spectrosc.*, **128**, 540 (1988).
64. M. Tsuji, I. Murakami and Y. Nishimura, *Chem. Phys. Letters*, **75**, 536 (1980).
65. A.J. Capel, J.H.D. Eland and R.F. Barrow, *Chem. Phys. Letters*, **82**, 496 (1981).
66. D.G. Streets and J. Berkowitz, *J. Electron Spectrosc.*, **9**, 269 (1976).
67. J.L. Hardwick, Y. Luo, D.H. Winikur and J.A. Coxon, *Can. J. Phys.*, **62**, 1792 (1984).
68. M. Tsuji, C. Yamagiwa, M. Endoh and Y. Nishimura, *Chem. Phys. Letters*, **73**, 407 (1980).
69. A.W. Potts and T.A. Williams, *Chem. Phys. Letters*, **42**, 550 (1976).

70. A.F. Douglas and M. Frackowiak, *Can. J. Phys.*, **40**, 832 (1962).
71. J.M. Dyke, N. Jonathan, A.E. Lewis and A. Morris, *J. Chem. Soc., Faraday Trans. 2*, **78**, 1445 (1982).
72. Unpublished data, quoted by J.M. Dyke, N. Jonathan and A. Morris, *Intern. Rev. Phys. Chem.*, **2**, 3 (1982).
73. J.A. Coxon and M.A. Wickramaaratchi, *J. Mol. Spectrosc.*, **68**, 372 (1977).
74. M. Halman and Y. Klein, *J. Chem. Soc.*, 4324 (1964).
75. P.J. Ficalora, J.C. Thomson and J.L. Margrave, *J. Inorg. Nucl. Chem.*, **31**, 3771 (1969).
76. S.R. Singhal and R.D. Verma, *Can. J. Phys.*, **49**, 407 (1971).
77. A. Jenouvrier and B. Pascat, *Can. J. Phys.*, **56**, 1088 (1978).
78. R.D. Verma, *Can. J. Phys.*, **40**, 586 (1962); **42**, 2345 (1964).
79. J.W.C. Johns and R.F. Barrow, *Proc. Phys. Soc. London*, **71**, 476 (1958).
80. M. Bialski and F. Grein, *J. Mol. Spectrosc.*, **61**, 321 (1976).
81. A. Jenouvrier and B. Pascat, *Can. J. Phys.*, **51**, 2143 (1973).
82. M.T. Nguyen, *Molec. Phys.*, **59**, 547 (1986).
83. H. Kruse, R. Winter, E.H. Fink, J. Wildt and F. Zabel, *Chem. Phys. Letters*, **111**, 100 (1984).

84. V.M. Anderson and J.H. Callomon, *J. Phys. B*, **6**, 1664 (1973).
85. K. Babu Rao and R.B.V. Haranath, *J. Phys. B*, **2**, 1381 (1969).
86. M. Shimauchi, H. Iwata, T. Matsuno, Y. Sakaba, S.K. Lee and S. Karasawa, *Sci. Light*, **21**, 145 (1972).
87. M. Schimauchi and S. Karasawa, *Sci. Light*, **22**, 127 (1973).
88. M. Shimauchi, *Sci. Light*, **18**, 90 (1969).
89. D.L. Albritton, W.J. Harrop, A.L. Schmeltekopf and R.N. Zare, *J. Mol. Spectrosc*, **46**, 89 (1973).
90. D. Daumont, A. Jevourier and B. Pascat, *Can. J. Phys.*, **54**, 1292 (1976).
91. K.V. Subbaram and D.R. Rao, *J. Mol. Spectrosc.*, **36**, 163 (1970).
92. R.F. Barrow, G.C. Chandler and C.B. Meyer, *Phil. Trans. Roy. Soc. London*, **260A**, 395 (1966).
93. V.S. Kushwaha and C.M. Pathak, *Spectrosc. Lett.*, **5**, 393 (1972).
94. K.K. Verma, M. Azam and S.P. Reddy, *J. Mol. Spectrosc.*, **65**, 289 (1977).
95. J.A. Coxon, S. Naxakis, U.K. Roychowdhury, *Can. J. Chem.*, **65**, 980 (1987).
96. C. Linton, *J. Mol. Spectrosc.*, **55**, 108 (1975).
97. H. Brehohl, I. Dubcis, Y. Houbrechts and M. Singh, *Can. J. Phys.*, **54**, 680 (1976).

98. J.M. Brown and J.K.G. Watson, *J. Mol. Spectrosc.*, **65**, 65 (1977).
99. L. Veseth, *J. Mol. Spectrosc.*, **38**, 228 (1971).
100. S.N. Vempati, J.L. Ma and W.E. Jones, *J. Mol. Spectrosc.*, **110**, 301 (1985).
101. W.L. Jolly and K.D. Maquire, *Inorg. Syntheses*, **9**, 103 (1963).
102. N.A. Narasimham and T.K. Balasubramanian, *J. Mol. Spectrosc.*, **29**, 294 (1969).
103. S.P. Karna and F. Grein, *Chem. Phys.*, **109**, 35 (1986).
104. N.A. Narasimham and T.K. Balasubramanian, *J. Mol. Spectrosc.*, **37**, 371 (1971).
105. K. Dressler, *Helv. Phys. Acta*, **28**, 563 (1955).
106. J.A. Harrington, R.M. Seel, G.R. Hébert and R.W. Nicholls, *Identification Atlas of Molecular Spectra*, York University, **7** (1970).
107. B. Rosen, *Spectroscopic Data Relative to Diatomic Molecules*, Pergamon Press (1970).
108. V.H. Dibeler and J.A. Walker, *Inorg. Chem.*, **1**, 50 (1969).
109. S. Yamaguchi, M. Tsuji and Y. Nishimura, *Chem. Phys. Letters*, **138**, 29 (1987).
110. W.F.C. Ferguson and I. Hudes, *Phys. Rev.*, **57**, 705 (1940).
111. M.N. Avasthi, *Spectrosc. Lett.*, **3**, 291 (1970).

112. H. Obase, M. Tsuji and Y. Nishimura, Chem. Phys. Letters, **126**, 134 (1986).
113. W.A. Noyes, Inorg. Syntheses, **1**, 65 (1955).