

Shifts of Helium and Argon Broadened CO Lines: Asymmetry in Line Number m

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Abstract. Pressure shifts of CO fundamental lines perturbed by He and Ar have been measured at 296 K with a laser frequency difference spectrometer. The results are compared with close coupling calculations based on recent potential energy surfaces with an analysis on the parts of the shifts that are symmetric and antisymmetric with respect to a change in the sign of the line number m .

INTRODUCTION

Pressure shifts in the fundamental band of CO are quite small and hence difficult to measure. With the increasing level of sophistication of both lineshapes theory and the determination of potential energy surfaces, there is a need for ever more accurate measurements. Mixtures of CO with helium or argon are two of the few heavy rotor-rare gas systems for which accurate potential surfaces are available. As will be shown, with the experimental accuracy now achieved, lineshifts must be considered as one of the quantities theoreticians can use for the test of potential surfaces.

EXPERIMENT

We have used a three beam difference frequency IR spectrometer to measure the broadening and shifting coefficients of many P and R lines of the fundamental band of CO strongly diluted (0.1 % CO) in He or Ar at 296 ± 1 K [1]. The extra IR beam passed through a cell containing pure CO at very low pressure and provided, for each line studied, a reference absorption profile, essentially at the frequency of the free molecule. The center frequency of the absorption profile, for both the reference cell and the regular absorption cell was determined by fitting the profiles to a Lorentzian. The shift is simply the difference between the two centre frequencies. We verified that

the shifts were linear in pressure. Subsequent shifts were measured several times at a single pressure (0.5 atm) with an accuracy of ± 3 MHz. With such an increased precision, rotational structure of the shifts is now clearly apparent, as shown in Fig.1.

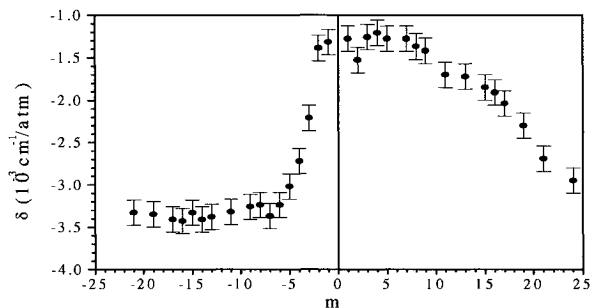


FIGURE 1. Measured line shifts for CO-Ar in the 1-0 band at 296 K.

Unlike the broadening, the shifting differs greatly between P and R branches. For the analysis one can then decompose the values, as a function of $|m|$, into a symmetric (δ_s) and antisymmetric (δ_a) components, according to :

$$\delta_a(m) = \frac{1}{2} [R^{0-1}(J) - P^{0-1}(J+1)] ; \delta_s(m) = \frac{1}{2} [R^{0-1}(J) + P^{0-1}(J+1)] \quad (1)$$

As it is known from Ref. [2], additional information on both the intermolecular potential and the shifting mechanisms may be obtained from that decomposition.

THEORY AND COMPARISON WITH MEASUREMENTS

Calculations have been done, within an essentially exact fully quantum treatment, at the Close Coupling level. The theoretical cross sections presented here have been predicted using the MOLCOL algorithm [3] together with recently proposed energy surfaces which have been shown to give a good overall agreement with measurements for various properties (dimers spectra, transport properties,...). For CO-He, we have used the potential of Ref. [4], which includes a vibrational dependence. For CO-Ar, we have used that of Ref. [5], which does not depend on the vibration of the CO molecule.

CO-He: Figure 2 shows that the calculated results are very satisfactory for the antisymmetric component. In a classical path analysis, such an agreement may be interpreted as a validation of the anisotropic part of the potential [6]. On the contrary, the disagreement observed for the symmetric component suggests that the vibrational dependence of the isotropic part of the potential needs to be improved.

CO-Ar : Since the vibrational dependence of the potential is unknown, the analysis is limited to the antisymmetric component. Indeed, it can be shown [6] that, neglecting vibration-rotation coupling and assuming a weak vibrational dependence of the

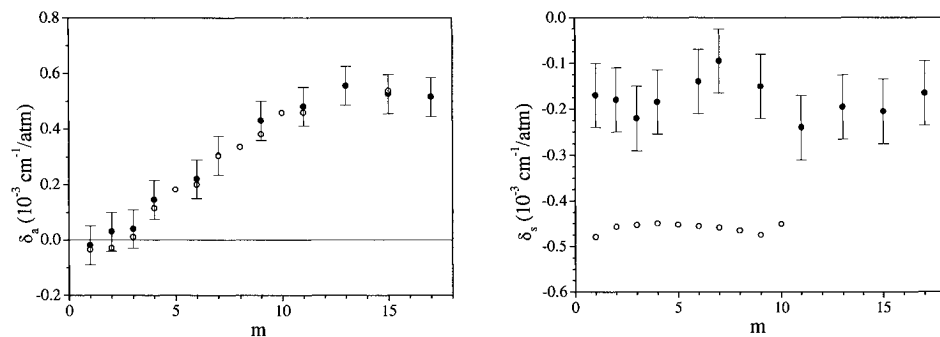


FIGURE 2. Antisymmetric (δ_a) and symmetric (δ_s) components for CO-He. ● and ○ are experimental values and calculated results, respectively.

anisotropic part of the potential, one has $\delta_a(m) \approx R^{0-0}(J)$, where the $R^{0-0}(J)$ lineshifts in the pure rotational band can be calculated from the rigid rotor potential surface of ref. [5]. The results, given in Fig. 3, are rather good for $m > 4$ but the poor predictions below $m=4$ suggest that a refinement of the anisotropic part of the potential is needed. However, note that our measurements need to be confirmed.

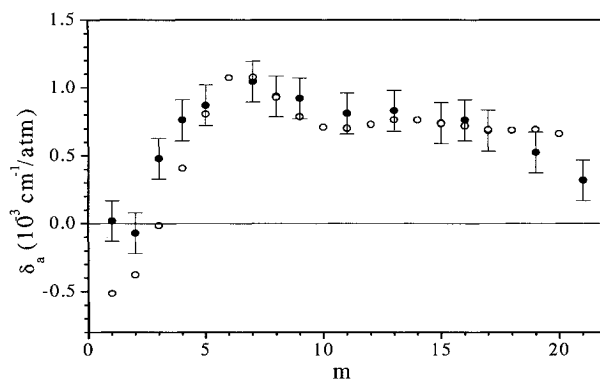


FIGURE 3. Antisymmetric component δ_a for CO-Ar. ● Experimental values. ○ Calculated results

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