

# HIGH RESOLUTION AND HIGH SIGNAL-TO-NOISE MEASUREMENTS IN THE $03^1_0 \leftarrow 01^1_0$ Q-BRANCH OF $N_2O$ AT $1160\text{ CM}^{-1}$

A. Vitcu\*, R. Wehr\*, R. Ciurylo<sup>†</sup>, J.R. Drummond\* and  
A.D. May\*

*\*Dept. of Physics, University of Toronto, Toronto, Canada, M5S 1A7*

*†Inst. Of Physics, Nicholas Copernicus University, Grudziadzka 5/7, 87-100 Torun, Poland*

**Abstract.** High-resolution measurements of the  $\Pi \leftarrow \Pi$  Q-branch of pure  $N_2O$  near  $1160\text{ cm}^{-1}$  were made using a difference-frequency spectrometer with resolution of  $5 \times 10^{-3}\text{ cm}^{-1}$  and a signal-to-noise ratio of 2000:1. Lines Q18F through Q12E have been recorded in a single scan, at room temperature and at pressures ranging from 1 to 130 torr. The spectra are analyzed up to 23 torr on a line-by-line basis using a hard collision profile including Dicke narrowing and line mixing. Since the separation of the central lines of this double-sided Q-branch is of the same order of magnitude with the collisional broadening, line mixing is considered in the analysis even at 1 torr and its dependence with pressure is studied.

## INTRODUCTION

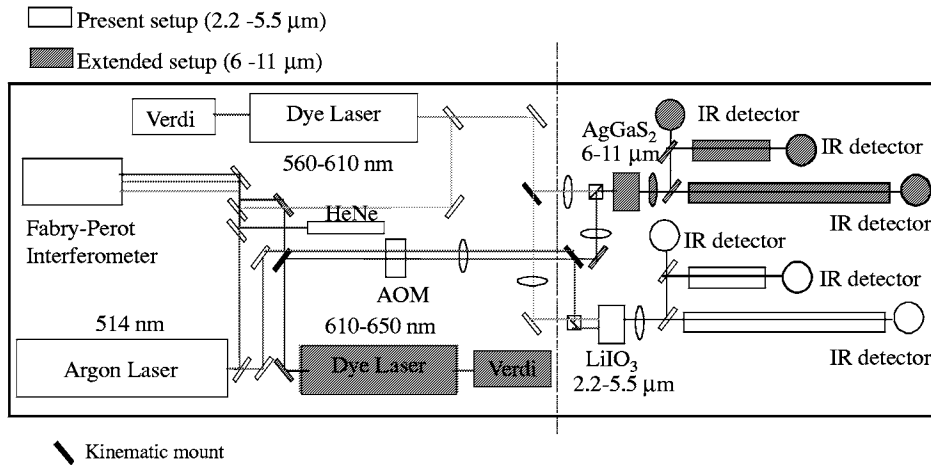
The process of a spectral line shape formation is far from being completely understood. Although Gaussian, Lorentzian and Voigt models have earned their places in the common knowledge about this field, the physics they carry is not enough to explain the details shown by high-resolution experiments. However more recent theories which include line mixing, speed dependent profiles and statistical correlation between the relaxation of the internal motion and the translational motion of the molecules require even better quality spectral information for their validation. Typical values of line mixing effects, for example, are no more than few tenths of a percent of the peak absorption value of a line, so signal-to-noise ratios in excess of 1000:1 are needed if one looks for experimental line-mixing signature in a spectrum with a minimum degree of accuracy.

One of the best ways to experimentally satisfy these demands is the Difference Frequency Spectroscopy technique. It consists of generating IR radiation by mixing

two visible lasers (one of which is modulated) in a nonlinear crystal and extracting the difference frequency. The infrared signals are then detected using a Lock-in amplifier. Using single mode tunable dye lasers as visible radiation creates an important advantage to the technique, in that the single mode signature of the emerging IR beam improves the spectral resolution considerably.

## EXPERIMENTAL

Figure 1 presents the current setup of the Difference-Frequency Spectrometer at the University of Toronto. It consists of two systems (2.2-5.5  $\mu\text{m}$  and 6-11  $\mu\text{m}$ ), each requiring two visible lasers and a nonlinear crystal. The 2.2 to 5.5  $\mu\text{m}$  spectrometer uses the (green) Ar laser and the (yellow) dye laser to generate infrared (IR) in a  $\text{LiIO}_3$  crystal, while two (red and yellow) dye lasers combine into a  $\text{AgGaS}_2$  nonlinear crystal to generate IR in the 6 to 11  $\mu\text{m}$  region for the second spectrometer. The two spectrometers create one versatile unit, and switching from one IR region to the other proves to be rather easy, by removing a couple of kinematic-mounted mirrors.



**FIGURE 1.** Experimental setup of the difference-frequency spectrometers

All the optics on the table to the right of each crystal are Germanium, which block the visible beams, and are AR coated for the required IR wavelengths. The emerging IR beam is split in two: 2/3 of it goes straight through the main cell to one of the detectors, while 1/3 is reflected towards a second (reference) detector for signal calibration. In the setup in figure 1, there is an extra arm in each spectrometer - created by a second beam splitter. A low pressure cell in this third arm acts as a frequency reference and allows us to include pressure shifts in our measurements.

The characteristics of the two spectrometers are similar:

- S/N ratio in excess of 2000:1
- Resolution: 1.5 MHz ( $5 \times 10^{-5} \text{ cm}^{-1}$ )
- Single mode operation
- Continuous tunability over more than  $1 \text{ cm}^{-1}$

Data recording and processing is computer controlled. The analog infrared signals from each of the Lock-in amplifiers are sampled at 10 Ksamples/sec and fed into a 16 bit analog-to-digital converter. The signal is recorded only if the the frequency of the two visible lasers remains constant relative to a frequency stabilized HeNe laser. The transmission peaks of the three lasers going through a confocal Fabry-Perot interferometer are recorded and the relative position of the peaks determines if the stability condition is met at every IR frequency step measurement.

Figure 2 presents a typical recorded spectrum of the Q-branch of  $\text{N}_2\text{O}$  at  $1160 \text{ cm}^{-1}$  ( $8.6 \mu\text{m}$ ).

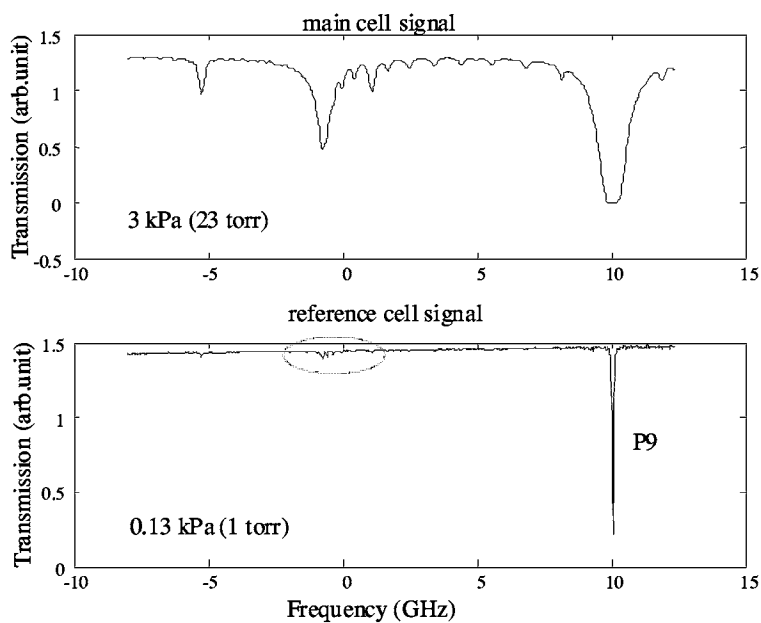


FIGURE 2. Typical experimental transmission spectrum for  $\text{N}_2\text{O}$  around  $1160 \text{ cm}^{-1}$

The upper spectrum represents the main cell at 23 torr; the bottom one shows the reference cell  $\text{N}_2\text{O}$  spectrum at 1.35 torr. The center of the strong P9 line is used as a reference for the pressure shift measurement.

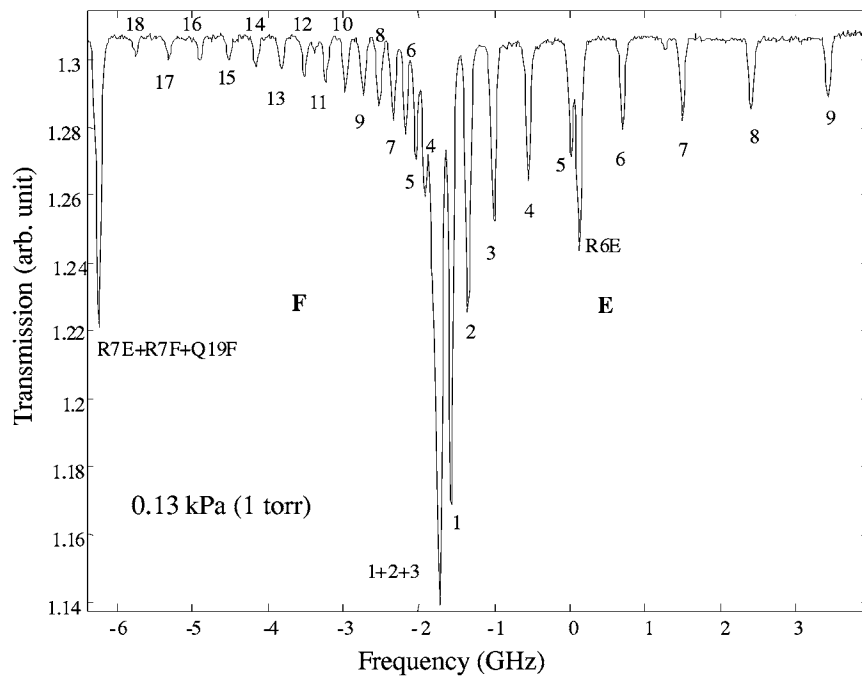


FIGURE 3. N<sub>2</sub>O Q-branch at 1160 cm<sup>-1</sup>: detail

Figure 3 provides a detailed look at the double-sided Q-branch at 1.35 torr (the circled area in the bottom spectrum of figure 2) and shows the signal-to-noise and spectral resolution capabilities of the spectrometer.

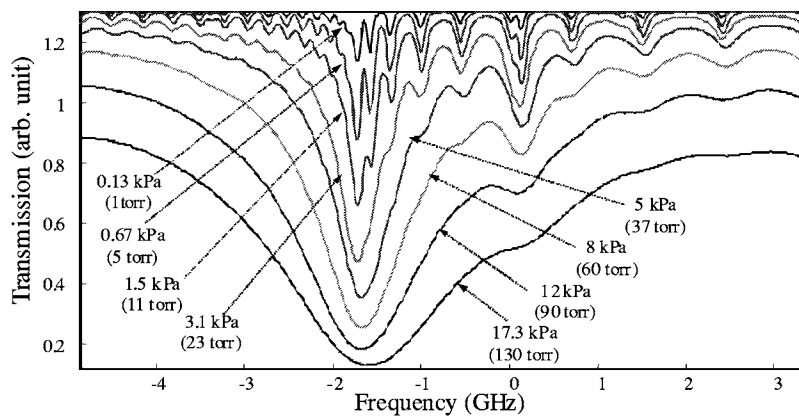


FIGURE 4. Q-branch collapsing as the pressure increases from 1 to 130 torr.

In figure 4, the experimental transmission spectrum for 8 different pressures are presented. The collapse of the Q-branch at high pressures is easily seen.

## ANALYSIS AND RESULTS

In the absorption spectra of linear molecules, Q branches are obtained for  $\Delta l = \pm 1$ , where  $l$  is the vibrational angular momentum. Because the value of  $l$  is not zero, the upper or lower or both levels are split due to  $l$ -type doubling. In our case, the  $03^1_0 \leftarrow 01^1_0$  band of  $N_2O$  is a  $\Pi \leftarrow \Pi$  band ( $l = 1$ ) and two close levels – labeled  $e$  and  $f$ , denoting the parity – are associated with each  $J$  value in both upper and lower vibrational states. Since the Q lines are of the  $f \leftarrow e$  type or  $e \leftarrow f$  type, the Q branch is composed of two subbands denoted as E and F according to the lower level of the transition. For the  $1160\text{ cm}^{-1}$  Q branch of  $N_2O$ , the  $e$  levels are always below the  $f$  ones, so the E subband is positioned at the higher frequency end of the spectrum (figure 3).

The lines Q18F through Q10E have been recorded in a single scan, at room temperature and pressures ranging from 1 to 130 torr. The results presented in figures 5 to 7 are based on a preliminary analysis of the spectra recorded at the first four lowest pressures: 1, 5, 11 and 23 torr. Since the separation of the central lines in this Q-branch is of the same order of magnitude as the collisional width, line mixing is considered in the analysis even at the lowest pressures. In each of the figures, the negative values of the line numbers correspond to the F subband, while the positive ones belong to the E subband. The value zero has no line correspondent in the spectrum of the Q branch.

The spectra are analyzed on a line-by-line basis using a hard collision (HC) profile including Dicke narrowing and line mixing[1]. For each line, four parameters are fitted: the strength, the center, the collisional broadening and the profile asymmetry. The narrowing parameter is fitted as a common parameter to all lines.

Lines on either side of the branch (E or F) having the same  $J$  number should have equal strengths. This is verified at 1 and 5 torr. However at higher pressures, it is more difficult to fit lines near the band centre and more assumptions must be made. In each figure, the 1 torr and 5 torr spectra are fitted allowing the strengths to float independently; the 11 torr spectrum is fitted using two different assumptions: with and without the constraint that equal  $J$  number lines must have equal strength.

The results vary significantly at 11 torr, depending on which fitting routine is chosen. Most affected are the lines on the F side of the branch, because the line spacing is smaller and mixing is more important. The uncertainty in determining an accurate value of the line strength is a major concern for lines Q5F to Q1E. These 6 lines are confined within a 500 MHz spectral region, while the collisional width (FWHM) is  $\sim 100$  MHz at 11 torr. As shown in figure 5, the mixing causes line Q2F to collapse and redistributes intensity from the central (Q1F, Q2F) lines towards Q5F line. A drop in line strength corresponds in figure 7 to a drop in half width for the central 1F, 2F lines.

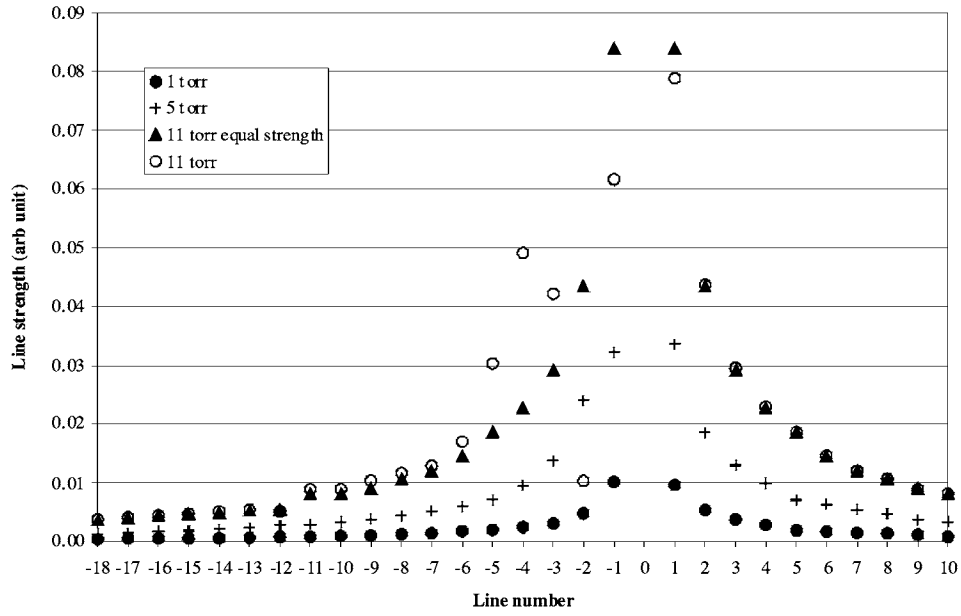


FIGURE 5. Line strength comparison for the three lowest pressures

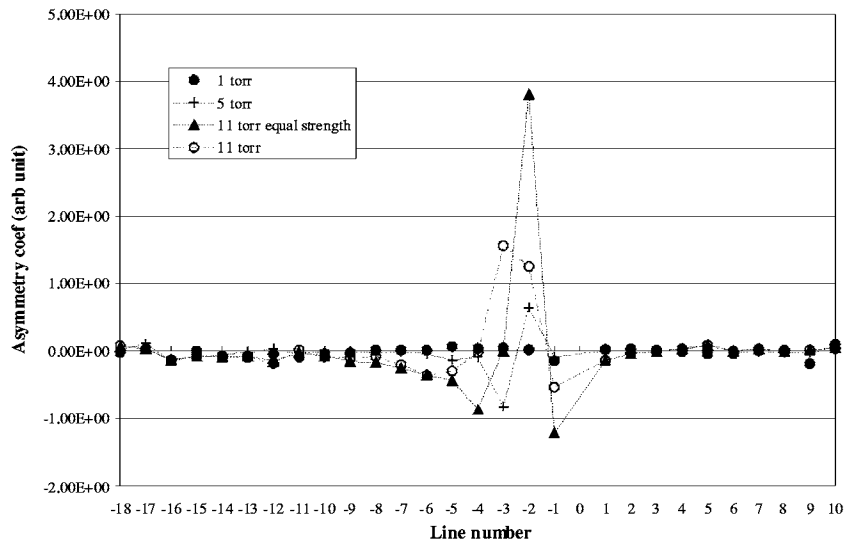


FIGURE 6. Fitted asymmetry coefficients as a function of J

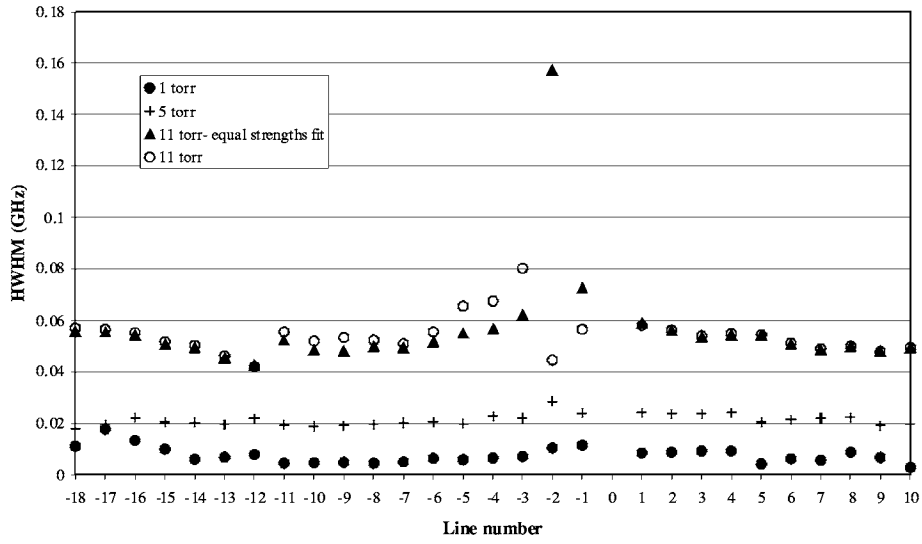


FIGURE 7. Collisional widths (HWHM) for 1, 5 and 11 torr

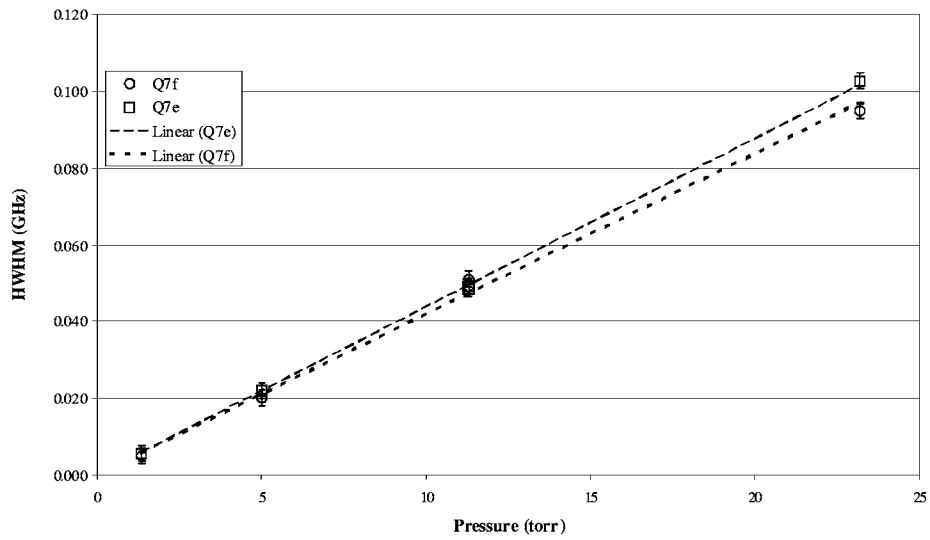


FIGURE 8. Linear pressure dependence of the collisional broadening for Q7F and Q7E lines

In figure 8, the linear pressure dependence of the broadening is presented for Q7E and Q7F lines. Using results from analysis of the spectrum up to 23 torr, the self-broadening coefficients for these lines were calculated and their values are  $0.1115 \text{ cm}^{-1}/\text{atm}$  for Q7E and  $0.1065 \text{ cm}^{-1}/\text{atm}$  for Q7F.

In terms of mixing asymmetry, the results in figure 6 are consistent for higher J values on either side of the branch, where the first order line mixing assumed in the fitting works much better. Although large discrepancies are obvious for the 4F to 1F lines in figure 6, there is a consistent trend that mixing coefficients are positive for low J and negative for higher J, a signature of the band collapse.

### ACKNOWLEDGEMENTS

This work was supported by funding from the Natural Sciences and Engineering Research Council of Canada, COMDEV, ABB BOMEM Inc., Meteorological Service of Canada, University of Toronto Research fund, the Canadian Space Agency and the Industrial Research Chair in Atmospheric Remote Sounding from Space at the University of Toronto.

### REFERENCES

1. Ciurylo, R. *Phys. Rev. A* **58**, p.1029 (2001).





Copyright of AIP Conference Proceedings is the property of American Institute of Physics and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.