

RECENT HIGH RESOLUTION LABORATORY DETERMINATIONS
OF LINE BROADENING AND INTENSITY PARAMETERS: PH₃,
CH₃D AND CO₂

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ABSTRACT

We review our recent unpublished laboratory work on rovibrational line strengths and broadening coefficients which is of interest in the study of planetary atmospheres. The molecules discussed are PH₃, CH₃D and CO₂.

Introduction

High spectral resolution infrared rovibrational observational astronomy is a powerful tool for understanding the compositional and dynamical structures of planetary atmospheres. At NASA Ames we are engaged in the measurement of line intensity and broadening coefficients (and their temperature dependence) which are required for the proper interpretation of such astronomical observations.

Line broadening coefficients are dependent on the dynamics of molecular collisions and therefore are temperature dependent. Accordingly we have made some of our measurements down to temperatures as low as 80K with specially constructed absorption cells. On the other hand line intensities, aside from the Boltzmann factor, are independent of temperature. Nevertheless we have measured line intensities at low temperatures because in some cases the very complex structure of the spectra of overlapping lines at room temperature is greatly simplified at the lower temperatures and becomes, therefore, more amenable to analysis. To date we have made broadening measurements with self-, He-, and N₂- collision partners.

The spectra we analyze are recorded with a BOMEM Model DA3.002 Fourier transform spectrometer, and the absorption cell we used was internally coated with evaporated gold and cooled with an Air Products Cryotip. The spectral intensity and broadening parameters were obtained via non-linear least-squares fits (of the spectra) wherein small corrections were applied to the theoretical instrumental resolution.

PH₃

In the 5 μm spectral region PH₃ and CH₃D spectra overlap and accurate line intensities and broadening coefficients are needed to obtain column densities for either species. PH₃ spectra have been obtained between 137 and 294 K in the 2000-2500 cm^{-1} spectral region. Fig. 1 shows a portion of a strongly absorbing region of PH₃'s spectrum under self-broadening conditions with a path length of 0.21 cm. So far self- and He-broadening coefficients have been measured. Fig. 2. shows a typical result where the line broadening parameter for a particular phosphine line at 2250.107 cm^{-1} is plotted versus pressure. To date, 212 line intensities recorded at room temperature have been analyzed with programs (G. Tarrago, paper in preparation) worked out for the frequency and intensity treatment of the pentad, $2\nu_2$, $\nu_2 + \nu_4$, $2\nu_4$, ν_1 , ν_3 . The two dipole moment derivatives relative to the normal co-ordinates, Q_1 and Q_3 , plus three Herman-Wallis type elements of the dipole moment matrix contribute significantly to the fit, and allow the measured intensities to be reproduced to about 5%. Preliminary values, derived for the band strengths S_1 and S_3 , confirm the ratio of 0.28 previously determined¹ for S_1/S_3 , but lead to an overall strength $S_1 + S_3$ about 10 per-cent higher than the value measured by van Straten.² The transition moments for the ν_1 and ν_3 bands are respectively, $\langle\mu_1\rangle = 0.0712(23)$ D and $\langle\mu_3\rangle = 0.1351(14)$ D.

CH₃D

The ν_2 rovibrational band of CH₃D, which is observed in the outer planets is important for understanding the formation of the solar system as well as determining the D to H ratio important in cosmological theories.

At room temperature the Q branch of this band is complicated enough so that even Doppler limited resolution is not sufficient to provide a definitive analysis of the intensities. To circumvent this problem we have made intensity measurements at temperatures down to 80 K with an unapodized instrumental resolution of about 0.0045 cm^{-1} . Figs. 3. and 4. show the evolution of the Q branch with temperature. The resulting rotationless transition moment obtained from the Q branch is compared to that obtained from the P and R branches and work is in progress to understand a global interaction with the ν_6 band. In addition we have determined the low

temperature broadening parameters with N₂ for this band as well as He- and self-broadening coefficients at room temperature.

CO₂

A careful study has been made of the temperature dependence of the self-broadening coefficient,³ γ , of CO₂ in the parallel band centered at 4978 cm⁻¹. In the temperature range 165 to 300 K the average value of the temperature exponent (for J in the range 6 to 32) is $n = 0.745 \pm 7\%$. Here n is defined via the equation $\gamma(T) = \gamma(T_0)(T_0/T)^n$, where T_0 is some reference temperature.

References

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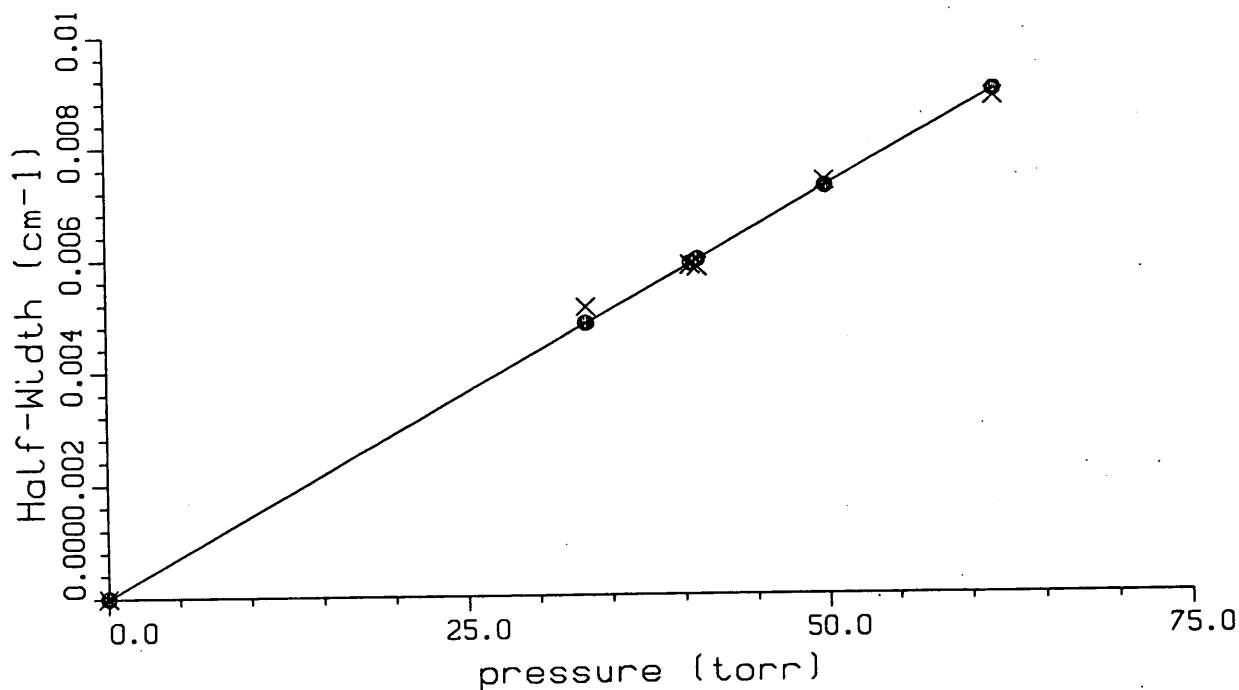


Fig. 1. Retrieved half width (X's) for a PH₃ self-broadened line at T = 293.5 K. •'s represent fitted values. Broadening coefficient determined from slope of the line thru the data.

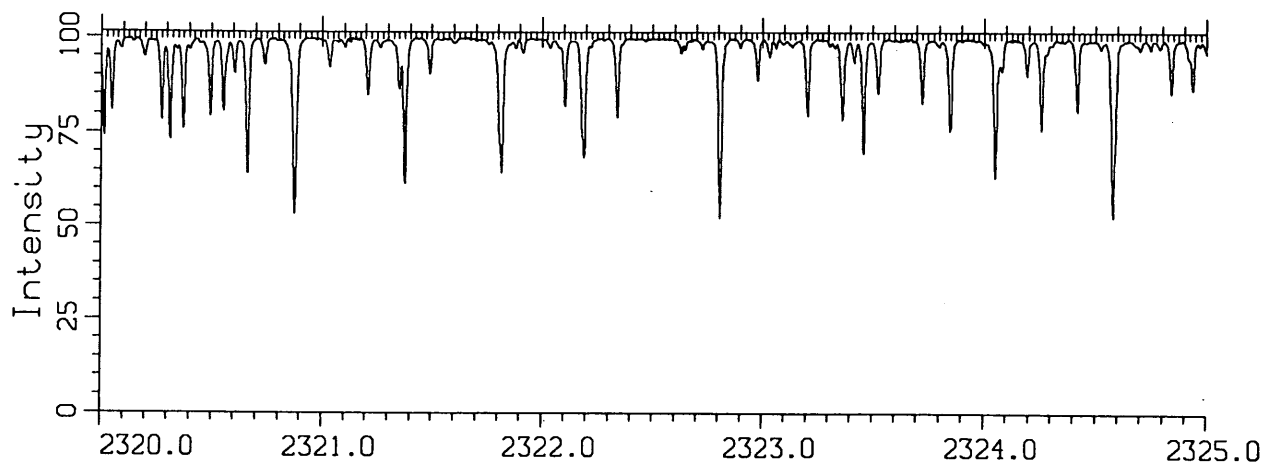


Fig. 2. Portion of the PH₃ rovibrational spectrum between 2320 and 2325 cm⁻¹. T=293.5; L=0.21 cm; P=14.9 torr.

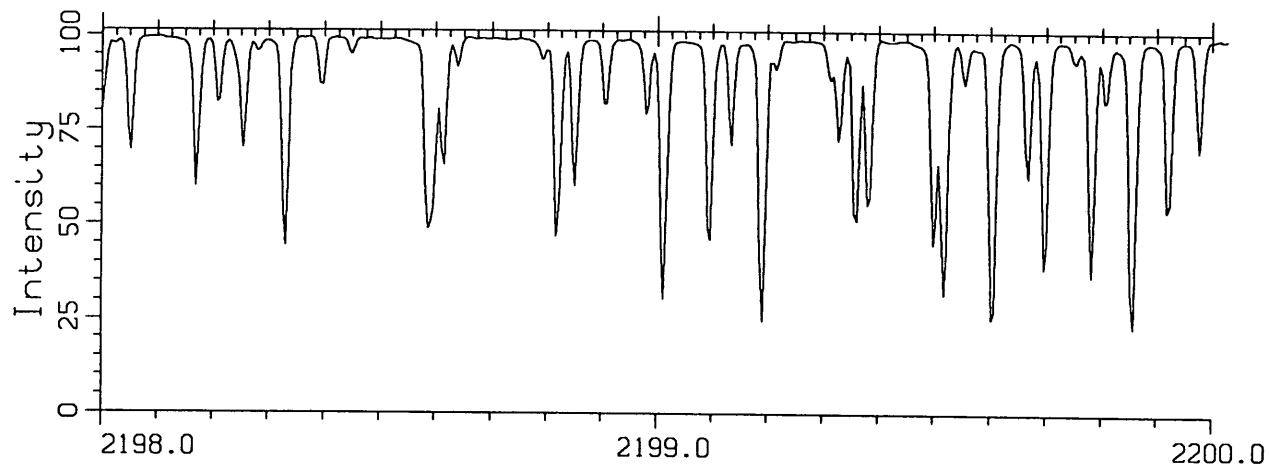


Fig. 3. Q branch of CH₃D ν₂ band. T=296.3 K; L=5.74 cm; P=9.35 torr.

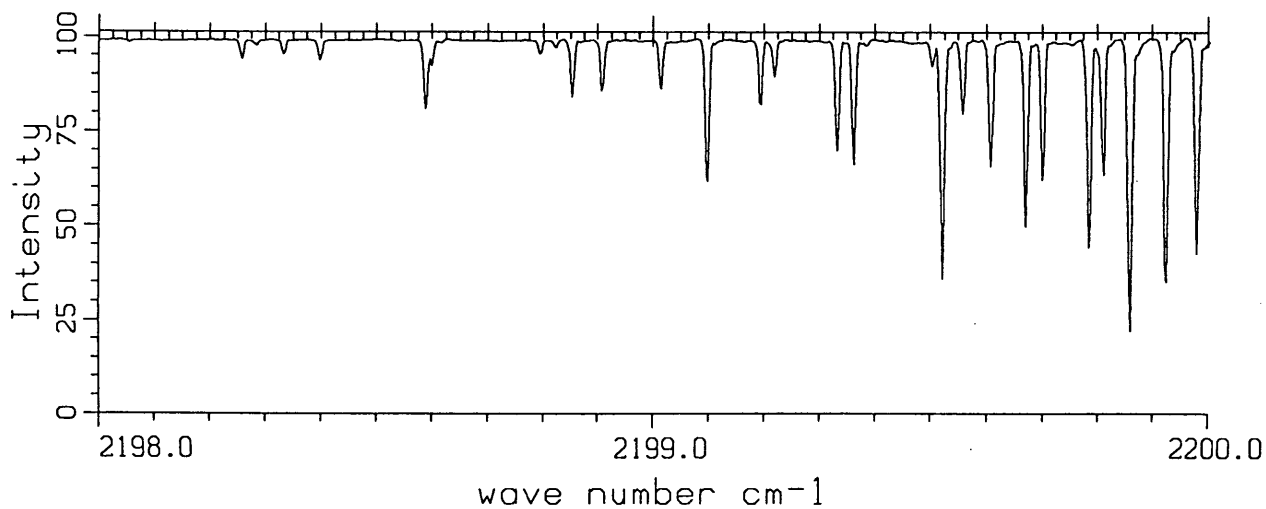


Fig. 4. Q branch of CH₃D ν₂ band. T=81 K; L=5.74 cm; P=0.79 torr.