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Pressure broadening coefficients of transitions in the ν_5 band of methyl bromide from fitting to Voigt and Galatry line profiles

K.J. Hoffman, P.B. Davies *

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, England CB2 1EW, United Kingdom

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ABSTRACT

Tuneable diode laser absorption spectroscopy has been used to measure the room temperature pressure broadening coefficients (γ) of rotational transitions in the ν_5 fundamental band of methyl bromide ($^{12}CH_3{}^{79}Br$ and $^{12}CH_3{}^{81}Br$) around 6.9 μm. Nitrogen, oxygen and self-broadening coefficients have been determined for 125 lines in the $^RQ_1$, $^PQ_3$, $^PQ_5$, $^PQ_7$ and $^PQ_8$ branches and 49 *P* and *R* branch transitions. Line profiles within *Q* branches were recorded at incremental pressures of nitrogen and oxygen up to 15 Torr and fitted to a Voigt profile to yield the broadening coefficients. The nitrogen broadened data for 14 lines, chosen from the five *Q* branches, were also fitted with Galatry profiles. The line profiles of the *P* and *R* branch transitions were recorded for total nitrogen and oxygen pressures of up to 300 Torr and fitted to both Voigt and Galatry profiles. Within individual *Q* branches, nitrogen broadening coefficients were found to decrease monotonically with increasing *J* from 0.14 cm^{-1} atm^{-1} at low *J* to 0.09 cm^{-1} atm^{-1} at high *J*. The corresponding values for oxygen were approximately 25% smaller. Self-broadening coefficients were found to vary between 0.48 and 0.16 cm^{-1} atm^{-1} with a similar *J* dependence to the foreign gas broadening for $J > 20$. However, between $J = 2$ and $J \approx 20$ the broadening coefficient was found to increase with *J*. The magnitude of the pressure broadening coefficient for *P* and *R* branch transitions was found to closely follow the *J* dependence measured for the *Q* branch lines.

1. Introduction

Generally, the two experimental parameters of interest from studying the effects of pressure on absorption lines are the pressure broadening coefficients and the pressure dependent shifts of the line centers. The availability of high resolution infrared absorption spectroscopy techniques over the past few decades, like FTIR and tuneable diode laser spectroscopy, has greatly facilitated the quantitative study of the effects of pressure on the vibration–rotation line profiles of small gas molecules [1,2]. The measurement of the analogous pressure effects on pure rotational transitions was accomplished much earlier because of the high intrinsic resolution of microwave spectroscopy, and the smaller Doppler line width in the microwave region which is orders of magnitude less than in the infrared. Consequently, changes in the rotational line profile and in the position of the line center with pressure could be examined in detail, with experimental factors having a minimum influence on the measurements [3–5].

Methyl bromide is a model symmetric top molecule for high resolution spectroscopy and shows both perturbed and unperturbed vibrational bands. Not surprisingly, there is an extensive literature on its infrared spectrum [6–12]. Pressure broadening studies of its vibration rotation transitions have been undertaken previously. The most relevant study with respect to the present work is that of Jacquemart et al. [13], who measured self and nitrogen broadening coefficients of *Q* branch lines of the ν_6 fundamental band using FTIR at a resolution of 0.001 cm^{-1}.

Methyl bromide is the major source of inorganic bromine in the atmosphere and contributes significantly to ozone depletion [14,15]. Measurements of pressure broadening coefficients are therefore of potential use for determining altitude abundances of the molecule in the atmosphere.

In this work, nitrogen, oxygen and self-broadening coefficients of many *Q* branch lines and some *P* and *R* branch lines of the ν_5 fundamental band of methyl bromide have been measured. Measurements of the line profiles of resolved vibration rotation transitions were analyzed assuming the combined effects of Lorentzian (pressure) and Gaussian (kinetic) contributions which can be most conveniently superimposed using the Voigt profile. However, as is well known, the effect of Dicke line narrowing [16] is not included in the Voigt profiles leading to small deviations from the experimental line shape, of up to a few percent, close to the line center [17,18]. These residual discrepancies reduce at higher pressures where speed dependent effects are relatively smaller.

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* Corresponding author. Fax: +44 1223 336362.
E-mail address: pbd2@cam.ac.uk (P.B. Davies).

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Recently, the precision with which infrared line profiles can be recorded experimentally has improved further. This has permitted speed dependent effects on the line profile to be more accurately modeled. In this study, this is achieved by fitting to Galatry line profiles [19]. The measurements on *Q* branch lines made here provide data on the variation of the pressure broadening coefficients with *J*, and to a lesser extent, with the *K* quantum number. However, because of spectral congestion these can only be measured up to about 15 Torr for foreign gas broadening. On the other hand, the well resolved *P* and *R* branch lines can be monitored up to several hundred Torr, which provides a better data set for comparing Voigt and Galatry results over a wide range of foreign gas pressures.

2. Experimental

Measurements were made using the three channel diode laser spectrometer described in an earlier study of pressure broadening of methyl iodide [20]. Methyl bromide, nitrogen and oxygen (BOC) had stated purities of 99.5%, 99.998% and 99.985%, respectively, and were used as supplied. Pressures in the absorption cell were measured using two capacitance gauges (MKS Baratron), with full scale ranges of 15 and 1000 Torr, respectively, and stated accuracies of ±0.5%. Calibration against a primary pressure standard was routinely performed. All measurements took place at room temperature, 295 K. Most of the profiles of *Q* branch lines were recorded for foreign gas pressures up to 15 Torr, while well resolved *P* and *R* branch lines were recorded up to total pressures of 300 Torr. It was found, however, that the accuracy with which the baseline could be determined diminished above approximately 160 Torr and this therefore imposed a practical upper pressure limit for accurate measurements.

In the earlier work [20] it was found that Voigt and Galatry fits of lines recorded as first derivatives using source modulation were more accurate than fits of absorption line recordings. Hence, in this work, all the lines were recorded in first derivative mode and subsequently numerically integrated to retrieve the line profiles. During the fitting process, the baseline could be simultaneously modeled by one of several standard functions. Usually a quadratic function was chosen. A Levenberg–Marquardt nonlinear fitting procedure [21] was used to simultaneously optimize the baseline and the line profile to the experimental data. In cases where partial overlap with other less intense lines occurred, the profiles and baseline were simultaneously fitted and thus overlapped-profiles were automatically de-convoluted into their constituent line profiles. Between 100 and 200 points per line were used, thereby ensuring an accurate representation of the line-profile, whist keeping recording and computational times practical.

All the absorption lines were fitted to a Voigt profile:

$$k_V(x,y,z) = A\frac{y}{\pi}\int_{-\infty}^{+\infty}\frac{e^{-t^2}}{y^2+(x-t)^2}dt$$

Where $A \equiv \frac{S\sqrt{\ln 2}}{\gamma_D\sqrt{\pi}}$, $y \equiv \sqrt{\ln 2}\frac{\gamma_C}{\gamma_D}$, $x \equiv \sqrt{\ln 2}\frac{\tilde{v}-\tilde{v}_0}{\gamma_D}$, γ_C is the collision half-width at half maximum (HWHM), γ_D is the Doppler HWHM, S is the line intensity and $\tilde{v}$ is the line center. For comparison with the Voigt fits many of the lines were also fitted to the Galatry profile, which takes into account the effect of Dicke line narrowing.

$$k_G(v,p) = \frac{A}{\sqrt{\pi}}\mathrm{Re}\left[\frac{1}{\frac{1}{2z}+y-ix}M\left(1;1+\frac{1}{2z^2}+\frac{y-ix}{z};\frac{1}{2z^2}\right)\right]$$

where *A*, *x* and *y* are as defined above and *M* is a hypergeometric confluent function and arises through the solution of a second order differential equation [18]. The collisional narrowing coefficient, β_C, is given via $z \equiv \sqrt{\ln 2}\frac{\beta_C}{\gamma_D}$. During the fitting process, the line centers were allowed to vary between fits and no attempt was made to quantify the magnitude of the very small pressure dependent shift of the line centers in this study. The stated line positions therefore refer to the line centers determined here at low pressure (~80 mTorr).

3. Results

Pressure broadening measurements were carried out following the procedure described in the earlier study on methyl iodide [20]. The available diode laser spectral coverage permitted 125 lines from five *Q* branches to be measured along with 49 *P* and *R* branch lines. No difference was detected for data from the two isotopic forms of the same transition and hence no distinction is made here between the results for $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ and only the average values are reported in the results. Foreign gas broadening of *Q* branch lines was possible up to pressures of ~15 Torr before the lines became poorly resolved and merged to such an extent that quantitatively accurate de-convolution became unreliable. On the other hand, well resolved *P* and *R* branch line profiles were measured and fitted at pressures up to 300 Torr.

Typical diode laser scans are presented in Fig. 1. A small section of the $^RQ_1$ branch is shown in part (a) while (b) shows some *P* and *R* branch transitions. Both spectra are recorded in first derivative form and the assignments and line positions were provided by

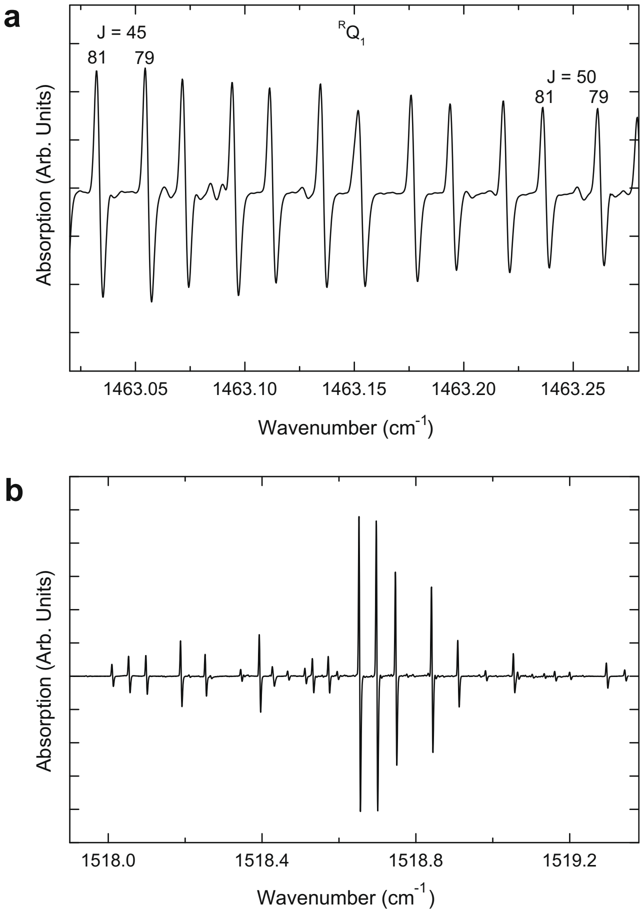

Fig. 1. Diode laser scans, recorded in first derivative form, for sections of the v_5 fundamental band of $^{12}CH_3Br$. Both the ^{79}Br and ^{81}Br isotopes are present at natural abundance. (a) A section of the $^RQ_1$ branch and (b) some well separated *P* and *R* branch lines around 1518 cm^{-1}.