PRESSURE BROADENING OF THE LOWEST ROTATIONAL TRANSITION OF OH STUDIED BY LASER MAGNETIC RESONANCE

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Pressure broadening of the $J = 5/2 - 3/2$ rotational transition of OH $X\,^2\Pi_{3/2}$ has been investigated. Line broadening parameters for collisional relaxation of OH by He, Ar and NO_2 are: $a_{OH,X} = 1.77 \pm 0.06$, 3.94 ± 0.03, 3.08 ± 0.07 MHz/Torr.

1. Introduction

The hydroxyl radical plays an important role in atmospheric chemistry and its presence in the interstellar medium has been known for many years. Although widely studied by high-resolution spectroscopy in the laboratory and by radioastronomy detailed knowledge of linewidths and line-broadening parameters of microwave and infrared transitions is relatively sparse; most measurements refer only to specific pressures.

We report here measurement of the collision-induced broadening of the $J = 5/2 \leftarrow 3/2$ ($^2\Pi_{3/2}$) transition in OH $v = 0$ at 118.6 μm over a ten-fold pressure range using far-infrared laser magnetic resonance (LMR) spectroscopy. This technique is well suited for studying the pressure dependence of linewidths because its inherent sensitivity permits investigations over a wide pressure range. In addition the dominant contribution to the linewidth of the transition changes from Doppler to collisional broadening between 1 and 10 Torr and this effect can be clearly detected and investigated. Previous microwave studies [1,2] on pressure broadening were limited to the $F = 4 \leftarrow 4$ and $5 \leftarrow 5$ transitions within the $J = 7/2$ or $J = 9/2$, $^2\Pi_{3/2}$ levels using NO_2 and H_2O as broadening gases at pressures between 10 and 60 mTorr.

2. Experimental

The LMR spectrometer has been described in detail elsewhere [3,4]. The signals were detected using a Golay cell or liquid-helium cooled bolometer and displayed in first-derivative form following phase-sensitive detection. The magnetic field was modulated with a sinusoidal waveform usually at 35 Hz applied through coils mounted on the magnet pole faces. The magnetic field was calibrated (±0.5 G) with an NMR gaussmeter.

OH radicals were produced by a 2450 MHz discharge in water vapour or by the reaction of H atoms with NO_2. Using either source the partial pressure of the source gases was always < 0.1 Torr. For NO_2 broadening studies hydrogen atoms were produced in 2 Torr helium to prevent back diffusion of NO_2 into the microwave discharge. Pressures of added NO_2 were less than 3 Torr and under these conditions the amount of N_2O_4 present was negligible. He and Ar (99.9%) were dried over silica gel and H_2 was removed by passage over copper oxide at 725 K. NO_2 was supplied at 99.5% purity and residual NO removed by addition of excess O_2 followed by trapping and distillation. Pressures in the intracavity LMR sample cell were measured by an oil manometer (accuracy ±0.1 Torr) and/or a capacitance gauge (±0.05 Torr).

In LMR several factors other than Doppler and collisional broadening can contribute to experimental linewidths, namely power saturation, time-constant distortion, modulation broadening and magnetic-field inhomogeneity. The effect of changing these param-

eters was carefully investigated and final results were obtained only after they had been eliminated or assessed quantitatively. Typical scans were 100 G in 5 min using a modulation amplitude of 0.5 G with a 30 ms time constant. The trace was then digitised into about 40 data points and least-squares fitted to a Voigt profile [5,6] which yielded the collision-induced component of the linewidth (full width at half maximum, $^{v}\Delta H_{1/2}$). The calculated Doppler width of 7.6 MHz was assumed in the fit and converted to field units using the g-factors measured by EPR [7]. At low pressures the nuclear hyperfine splitting was almost fully resolved and the least-squares routine accurately fitted the experimental line shape of the hyperfine doublet to yield the hyperfine splitting. However, under experimental conditions where the lines were only partially resolved, time constants of $< 1/60$th the linewidth were necessary to remove distortion.

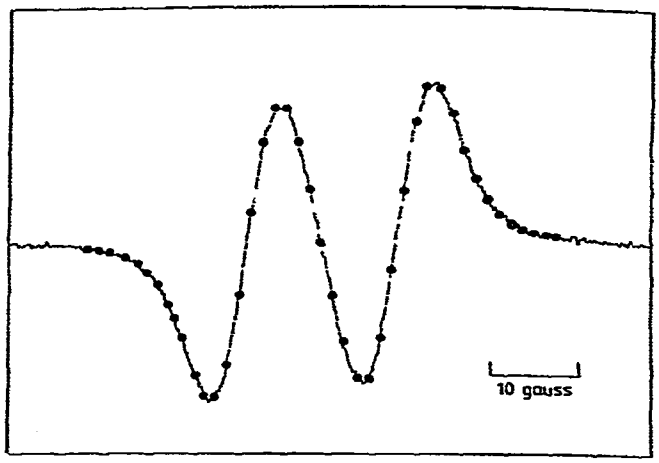

Fig. 1. Experimental line shape of the LMR transition at 13610 G and the fit of the Voigt profile to it (•). Pressure of He 2.6 Torr; detector time constant 30 ms, 100 G sweep in 5 min with field modulation of 0.5 G.

3. Results

The two transitions studied were:

$^2\Pi_{3/2}|J, M_J, \pm\rangle$

$$\begin{cases} 5/2, -1/2(-) \leftarrow 3/2, -3/2(+). & 8420\ \text{G} \\ 5/2, \ \ 1/2(-) \leftarrow 3/2. -1/2(+). & 13610\ \text{G} \end{cases}$$

Fig. 1 shows a typical experimental trace and the fit of the Voigt profile to it. All profiles fitted to better than 3% RMS of the peak-to-peak height. The variation of $^{v}\Delta H_{1/2}$ with pressure of added argon is shown in fig. 2 (combination of data of both lines). A non-zero intercept of 3.0 G was obtained for the data from the 13610 G line. This was attributed to magnetic-field inhomogeneity over the finite sample volume defined by the region of field modulation.

The pressure-broadening parameters $\alpha_{OH,X}$ were identical within experimental error for both lines and with either source of OH, and are listed in table 1 with values obtained by other workers.

The measured hyperfine splittings and those calculated from published hyperfine constants [7] for $J = 3/2$ and $5/2$ OH X $^2\Pi_{3/2}$ are listed in table 2. Good agreement is obtained for the low-field line but the deviation of experimental and theoretical values for the 13610 G transition cannot be attributed to experimental uncertainty which is $< 1\%$ of the hyperfine splitting.

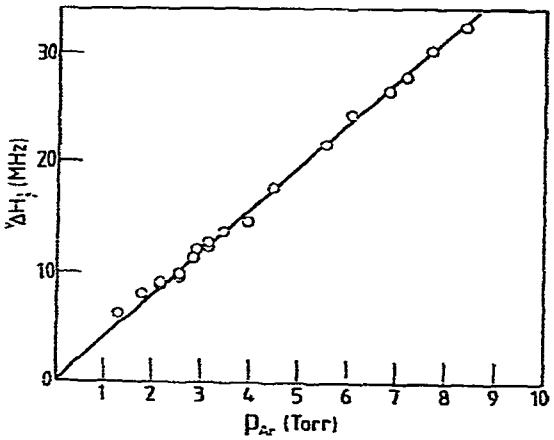

Fig. 2. Variation of Voigt full width at half intensity $^{v}\Delta H_{1/2}$, as a function of argon pressure. Data points are a combination of both transitions.

4. Discussion

There have been no previous measurements of the line broadening parameters of rotational transitions of

Table 1
Line broadening parameter $a_{OH,X}$(MHz Torr^{-1}) for relaxation of OH $X\,^2\Pi_{3/2}$

Foreign gas		He	Ar	NO_2
this work [a]		1.77 ± 0.06	3.94 ± 0.03	3.08 ± 0.07
microwave (J = 9/2)	ref. [2]			3.1 ± 0.4
microwave (J = 7/2)	ref. [1]			(3.6)

[a] Uncertainties quoted are two standard deviations for the LMR results.

Table 2
Measured and calculated LMR hyperfine splittings

Line position (G)	Hyperfine splitting (G)	
	measured	calculated
8420	24.2 ± 0.3	24.1 ± 0.1
13610	17.2 ± 0.3	16.4 ± 0.1

OH. Nevertheless our results are worth comparing with microwave measurements on individual rotational levels (hyperfine Λ doubling transitions). Our value of $a_{OH,X}$ for X = NO_2 is identical with that for J = 9/2 obtained by Bustreel et al. [2] and both results are similar to the microwave measurement [1] for J = 7/2, although in the latter study the nature of the collisional gas is not specifically stated. Although the microwave measurements were made at considerably lower pressure than the LMR measurements, the combined data suggest that for relaxation by NO_2 there is no detectable dependence of $a_{OH,X}$ on rotational quantum number.

Microwave line-broadening parameters for relaxation of OH by He and Ar have not been reported. The LMR results in table 1 for relaxation by He and Ar yield $\sigma_{OH,He}$ = 12.3 Å^2 and $\sigma_{OH,Ar}$ = 52.5 Å^2 assuming a hard-sphere collision model. There are very few data in the literature on the relaxation of other hydrides by these gases but the values of $a_{OH,X}$ for He and Ar are reasonable compared with the corresponding values for HCl. Working at much higher total pressures Gebbie and Stone [8] found a strong dependence of $a_{HCl,X}$ on rotational quantum number at low J for HCl, Ar. From their data on the far infrared rotational spectrum $a(J = 0 \rightarrow 1)$ = 4.72 MHz/Torr and $a(J = 1 \rightarrow 2)$ = 2.94 MHz/Torr for Ar, and $a(J = 0 \rightarrow 1)$ = 1.70 MHz/Torr for He. These results yield $\sigma_{HCl,Ar}$ = 80 Å^2 and $\sigma_{HCl,He}$ = 12.5 Å^2, and $a_{HCl,Ar}/a_{HCl,He}$ = 2.8 for the lowest rotational transition, compared with $a_{OH,Ar}/a_{OH,He}$ = 2.2.

Although microwave and LMR measurements yield similar information on rotational relaxation the former is restricted to pressures below 1 Torr; this introduces experimental difficulties particularly with regard to the nature of the collisional gas. The problem of self broadening or broadening by reactants and products is essentially absent in LMR where it is possible to employ partial pressures of collision partners up to 30 Torr [9]. At these pressures only pair interactions are significant which is an important advantage over the high pressures needed for techniques where the Doppler or observed width is greater for the unbroadened line. When combined with the large range of rotational levels that can be investigated by using different laser lines it appears that LMR is a promising technique for further studies of collisional broadening.

References

[1] D. Bastard, A. Bretenoux, A. Charru and F. Picherit, Compt. Rend. Acad. Sci. (Paris) 284 (1977) 445.

[2] R. Bustreel, J.L. Destombes and C. Marlière, Chem. Phys. Letters 42 (1976) 154.
[3] P.B. Davies, D.K. Russell, B.A. Thrush and F.D. Wayne, J. Chem. Phys. 62 (1975) 3739.
[4] J.P. Burrows, G.W. Harris and B.A. Thrush, Nature 267 (1977) 233.
[5] T. Sundius, J. Raman Spectry. 1 (1973) 471.
[6] D.I. Cliff and B.A. Thrush, to be published.
[7] H.E. Radford, Phys. Rev. 122 (1961) 114.
[8] H.A. Gebbie and N.W.B. Stone, Proc. Phys. Soc. (London) 82 (1963) 309.
[9] C.J. Howard and K.M. Evenson, J. Chem. Phys. 61 (1974) 1943.