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Pressure Broadening Cross Sections for the H_2S–He System in the Temperature Region between 4.3 and 1.8 K

In this note we report recent results on the helium pressure broadening of the 168 GHz, $1_{10} \leftarrow 1_{01}$ transition of H_2S in the temperature region between 4.3 and 1.8 K. These measurements used millimeterwave spectroscopic techniques (*1*, *2*) to probe cryogenic gaseous mixtures prepared by the collisional cooling technique which we have previously described. This same combination of techniques has been used for studies of CO, CH_3F, and NO broadened by helium in the region below 5 K (*3–6*). Experimental techniques and analysis methods similar to those used in our earlier studies were used for the work reported in this note.

Although the spectroscopic properties of the cryogenic environment tend to produce very strong absorption lines, the $1_{10} \leftarrow 1_{01}$ transition of H_2S is especially favorable. The 1_{01} level is the lowest of its symmetry species, and since at 4 K the next lowest lying state, the 1_{10}, lies at about 2 kT, the lower level contains the majority of the molecules of its symmetry. In addition, the $1_{10} \leftarrow 1_{01}$ transition is strongly allowed, and H_2S has a large (1.0 D) dipole moment. In order to avoid the lineshape problems associated with large fractional absorptions, the H_2S flow rate was adjusted to give fractional absorptions $\leq 10\%$. Under these conditions, the average fractional concentration of H_2S along the 5-cm absorption path length was $\leq 10^{-5}$. This very small fractional concentration helps to ensure that the temperature of the system is determined solely by the background helium gas.

Figure 1 shows a plot of the measured linewidth as a function of cell pressure for a series of measurements at 1.82 K. Table I lists the pressure broadening parameters measured at eight temperatures between 4.3 and 1.8 K as well as the pressure broadening cross sections σ [Å^2] calculated via the relation $\sigma = 0.447\ (\mu T)^{1/2}\gamma$, where μ [a.m.u.] is the reduced mass, T [K] is the temperature, and γ [MHz/Torr] is the pressure broadening cross section. Figure 2 shows a plot of these cross sections as a function of temperature.

The very small size ($\sim$10 Å^2) and monotonic decrease with temperature are the most notable features of the H_2S cross sections. In comparison, the cross sections from our previous work on CO, CH_3F, and NO range from $\sim$80 Å^2 (for CH_3F near 4 K) to $\sim$15 Å^2 (for NO below 2 K) (*3–6*). The small cross sections for H_2S were not unanticipated. The simple physical interpretation is that in the low temperature limit there is not enough translational energy to induce inelastic processes. The energy levels of the $1_{10} \leftarrow 1_{01}$ transition

TABLE I

Pressure Broadening Parameters and Collision Cross Sections for the $1_{10} \leftarrow 1_{01}$ Transition of H_2S

Temperature (K)[a]	Pressure Broadening[b] Parameter (MHz/ Torr)	Cross Section (Å^2)[b]
4.20	6.3	11.0
3.65	6.9	11.2
3.01	7.1	10.4
2.75	7.4	10.4
2.51	7.5	10.0
2.25	7.8	9.9
2.05	7.3	8.9
1.82	7.5	8.5

[a] Experimental uncertainty estimated at ±0.02K.

[b] Absolute uncertainty estimated at ± 10%, relative uncertainty at ± 5%.

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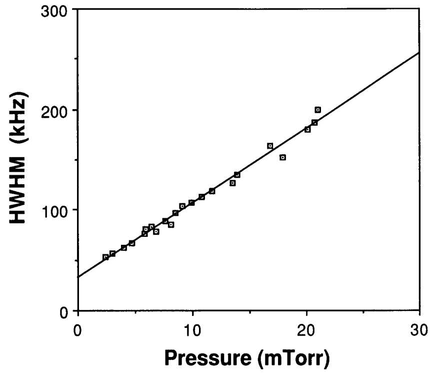

FIG. 1. Linewidth (HWHM) as a function of cell pressure at 1.82 K.

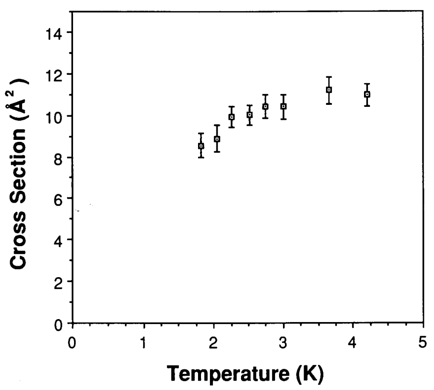

FIG. 2. Measured pressure broadening cross sections as a function of temperature. Error bars are 2σ from the fit.

are isolated from other levels, and the transition frequency itself is high, relative to kT. Since at 4 K, kT/ $\Delta E \sim \frac{1}{2}$ for the observed transition of H_2S, it would be expected that the contribution of inelastic collisions would be small at 4 K and become even smaller at lower temperature. However, it has been shown theoretically for many other systems such as CO–He (*7*, *8*), N_2–He (*9*, *10*), N_2–Ne (*11*), and H_2–Ar (*12*) that the existence of a shallow attractive potential can give rise to resonances which can significantly raise the cross section at low energy. The measured cross sections for H_2S in the 4.3 to 1.8-K range do not show any evidence for this. In previous close coupled calculations on CO–He, Palma and Green (*7*) have shown that in the unusual absence of an attractive well in the potential, the cross sections decline toward zero in the limit of zero translational energy. However, detailed close coupling calculations for H_2S–He will be required before any definitive conclusions can be reached.

REFERENCES

1. W. C. KING AND W. GORDY, *Phys. Rev.* **90,** 319–320 (1953).
2. P. HELMINGER, J. K. MESSER, AND F. C. DE LUCIA, *Appl. Phys. Lett.* **42,** 309–310 (1983).
3. D. R. WILLEY, R. L. CROWNOVER, D. N. BITTNER, AND F. C. DE LUCIA, *J. Chem. Phys.* **89,** 1923–1928 (1988).
4. D. R. WILLEY, D. N. BITTNER, AND F. C. DE LUCIA, *J. Mol. Spectrosc.*, in press.
5. D. R. WILLEY, D. N. BITTNER, AND F. C. DE LUCIA, *J. Chem. Phys.* **89,** 6147–6149 (1988).

6. D. R. Willey, D. N. Bittner, and F. C. De Lucia, *Mol. Phys.*, in press.
7. A. Palma and S. Green, *J. Chem. Phys.* **85**, 1333–1335 (1986).
8. S. Green, *J. Chem. Phys.* **82**, 4548–4550 (1985).
9. W. Erlewein, M. von Seggern, and J. P. Toennies, *Z. Physik* **211**, 35–50 (1968).
10. M. von Seggern and J. P. Toennies, *Z. Physik* **218**, 341–351 (1969).
11. P. G. Burke, D. Scrutton, J. H. Tait, and A. J. Taylor, *J. Phys. B* **2**, 1155–1168 (1969).
12. J. M. Hutson and F. R. McCourt, *J. Chem. Phys.* **80**, 1135–1149 (1984).

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