

Hydrogen and Helium Pressure Broadening of H₂S between 2 and 600 K

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The hydrogen (H₂) and helium (He) pressure-broadening cross sections of the $1_{10} \leftarrow 1_{01}$ transition of H₂S have been measured between 2 and 600 K. This more than two decade range in temperature makes possible the consideration of these collisions as a *spectroscopic* process in which the translational energy plays the role of the spectroscopic variable. Although in the semiclassical region the pressure broadening due to H₂ and He is similar, at low temperature large qualitative differences occur, resulting in almost an order of magnitude larger cross section for collisions with H₂ below 10 K. © 1994 Academic Press, Inc.

I. INTRODUCTION

We have previously described the results of a number of investigations of the collisions between small fundamental molecular species such as CO and CH₃F and helium atoms in the temperature region between 1.5 and 4.3 K (1-7) and above 77 K (8-10). In the former regime, rapidly varying cross sections attributable to resonances associated with quasibound states are observed while at higher temperatures slowly changing cross sections can be described by semiclassical, Anderson-like theories.

This paper reports the first study of the pressure-broadening cross sections of a polyatomic gas in which measurements have been made continuously from temperatures high enough that semiclassical descriptions are appropriate down to a few degrees Kelvin where new phenomena become important. Specifically, we describe a study of hydrogen (H₂) and helium (He) pressure-broadening of hydrogen sulfide (H₂S) in the region between 2 and 600 K. These two decades in temperature include both the low-temperature region where pressure broadening is dominated by resonances associated with quasibound states and other phenomena which require a fully quantum mechanical treatment, and the region at higher temperatures where semiclassical, Anderson-like (11) treatments are appropriate.

II. EXPERIMENTAL DETAILS

We have previously discussed collisional cooling systems in which the spectroscopic cell was either immersed directly in a liquid helium bath (1, 6) or cooled by liquid nitrogen (9, 10). In the former method, by pumping on the liquid helium, it is possible to vary the temperature over the range between about 1.5 and 4.3 K, while the latter method can be used above 77 K. With these systems it was not possible to cover the interesting region in which the quantum mechanical phenomena of the low-temperature region make the transition into the semiclassical phenomena characteristic of the ambient pressure broadening.

For the work described in this paper, a new system and a modification of an earlier system were used to provide a wider range of working temperatures than was previously possible. In the modified system shown in Fig. 1, an external helium reservoir was used to provide continuous coverage through this temperature region. In this system an external 100-liter Dewar was connected via a standard vacuum insulated transfer tube to the helium reservoir which contained the spectroscopic cell. The temperature of the cell was monitored with a calibrated germanium thermometer and controlled by regulation of the pressure in the 100-liter Dewar. In order to have stable operation over this region with a Dewar pressure of ~ 15 – 30 Torr above atmospheric pressure, the input of the transfer tube was restricted with small bore tubing, typically 15 cm in length and of ~ 0.1 – 0.2 mm diameter. By use of computer-controlled valves, it is possible to maintain the cell temperature to better than 0.05 K by means of simple algorithms which make no attempt to correct for the dynamics of the helium transfer process. The remainder of the system, including the mm/submm techniques, is as we have previously described (2).

The second system also made use of a separate helium reservoir and cell, but is of more conventional design. In it a single vacuum enclosure contains an 8-liter helium reservoir and a helium pot, continuously filled from this reservoir via capillary tubing. The temperature of the cell, which is thermally attached to the pot, is controlled by varying the pumping rate on the helium pot. Further details of this system will be provided in a forthcoming publication.

Numerical techniques were used to deconvolute the pressure-broadening contributions to the observed linewidths from the components resulting from Doppler broadening and nuclear hyperfine structure. In our analysis of H_2S , a Voigt lineshape was calculated from the known Doppler contribution and an initial estimate of the pressure broadening for each of the six hyperfine components (12). The resulting lineshape was then compared with the observed lineshape and the contribution of the pressure-broadening component was refined via a nonlinear least-squares procedure. In order to account for baseline effects, contributions from linear and quadratic terms were also allowed to vary in the analysis. If reasonable initial estimates of the parameters were made, we found this procedure to be numerically stable, and the large majority of the ~ 3000 lineshapes in this study were analyzed without operator intervention in batch mode.

Figure 2 shows the results of one of these lineshape analyses and Fig. 3 shows the plot of observed pressure broadening as a function of pressure at 11.5 K. Several features of the latter figure are notable. First, at the lowest pressures there is a significant

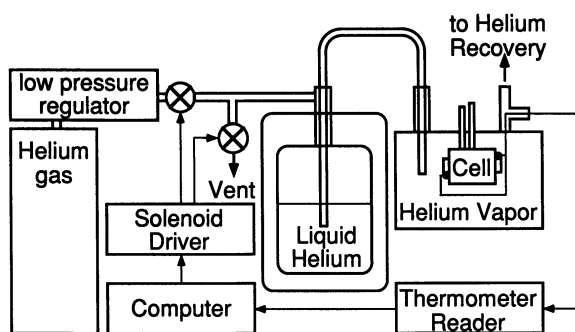


FIG. 1. Collisional cooling system with external reservoir for the temperature region between 1.5 and 77 K.

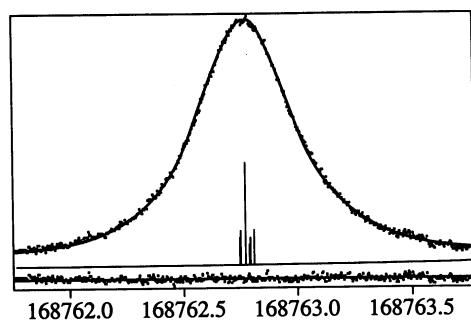


FIG. 2. Comparison of observed lineshape and the resultant fit to the lineshape. The hyperfine spectrum is shown for purpose of comparison.

deviation from the linear relation expected for pressure broadening. However, a simple calculation shows that in this low-pressure regime the basic tenet of collisional cooling is violated; specifically, that enough collisions occur to cool the temperature of the spectroscopic gas to that of the background gas. This effect is somewhat more pronounced with hydrogen than that in our earlier work with helium because collisions with the lighter hydrogen do not deflect or cool the sample gas as much, therefore raising the pressure at which warm sample molecules can reach the interrogation region. Conversely, the linearity of the rest of the curve is good evidence that the basic premise of the collisional cooling method is satisfied. The solid line shown in Fig. 3 is fit to the points above 2 mTorr with both slope and intercept as free variables. The nearness of the intercept to zero is gratifying and evidence that each of the contributions to the lineshape is properly accounted for. Alternatively, it is possible (at great saving in computer time) to analyze the lineshapes without including the contributions of the hyperfine structure. For this simpler procedure, similar broadening parameters result, but the intercept of the graph occurs above zero, reflecting the uncorrected contribution of the hyperfine structure.

Additionally, thermal transpiration must be considered because the pressure is measured at room temperature with a capacitance manometer. In this temperature and pressure regime the correction is quite large and nonlinear (13, 14).

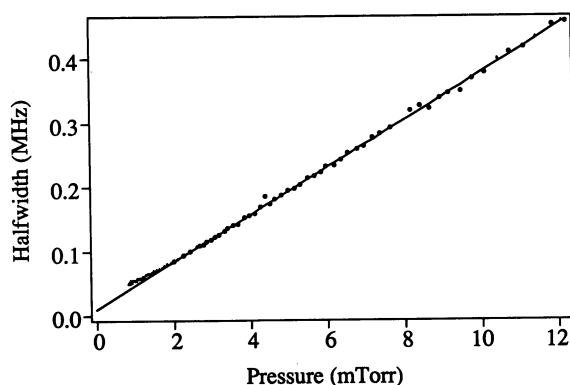


FIG. 3. Observed linewidth for pressure broadening by hydrogen as a function of pressure at 11.5 K.

TABLE I
The H₂ and He Pressure-Broadening Cross Sections of the 1₁₀ ← 1₀₁
Transition of H₂S

H ₂		He	
Temperature (K)	$\sigma(\text{\AA}^2)$	Temperature (K)	$\sigma(\text{\AA}^2)$
585.0	31.274	623.0	23.447
505.0	33.688	505.0	23.963
430.0	34.923	430.0	24.569
300.0	36.650	300.0	23.600
253.0	37.582	295.0	23.24
200.0	40.132	227.0	22.824
148.0	40.302	182.0	22.035
130.0	44.876	151.0	20.695
100.0	45.034	124.0	19.885
62.701	52.728	100.0	19.380
45.137	58.410	97.13	18.70
30.959	67.016	61.56	15.22
24.137	67.730	52.96	13.73
20.922	73.010	46.96	12.72
16.664	71.452	42.84	12.64
14.905	76.557	32.53	11.94
14.159	77.423	25.72	12.51
13.863	76.582	16.74	12.58
13.789	74.730	12.19	12.71
13.105	77.538	8.59	12.84
12.318	76.688	6.15	12.81
11.759	75.008	4.20	10.92
11.513	77.074	4.10	12.55
11.362	73.148	3.65	11.15
10.376	84.458	3.26	12.10
10.032	81.491	3.01	10.42
8.9926	82.317	2.77	11.68
8.6261	78.546	2.75	10.38
7.5718	77.594	2.51	10.05
		2.25	9.90
		2.05	8.84
		1.82	8.56

III. RESULTS

The results of our work are given in Table I and displayed in Fig. 4. In both, $\sigma = 0.447 (\mu\text{T})^{1/2} \gamma$ was used to convert the observed pressure-broadening parameter γ to

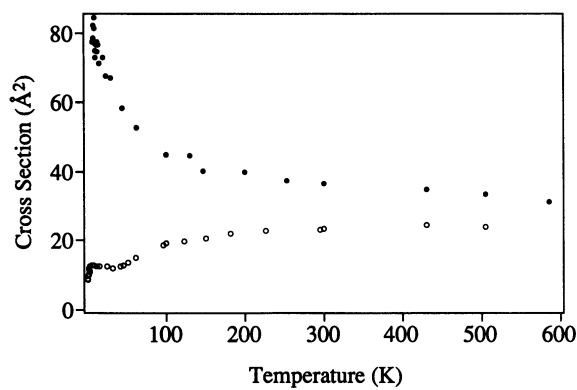


FIG. 4. The H₂ (upper) and He (lower) pressure-broadening cross sections of the 1₁₀ ← 1₀₁ transition of H₂S.

the reported cross section σ . This figure shows the similarity of the broadening efficiencies of H_2 and He in the semiclassical regime above 100 K, the accelerating difference in the transition region, and the rapid variation in cross section, especially for collisions with He, in the quantum regime below about 50 K. Although historically it has been difficult to accurately estimate absolute uncertainties in pressure-broadening experiments, from an intercomparison among both our experiments using different apparatus, experimental techniques, and analysis methods, we estimate an absolute uncertainty of about 5% for the measurements reported here.

IV. DISCUSSION

We have previously discussed experiments of this type in the context of "collisional spectroscopy" (15) and noted that it is conceptually useful to delineate between the low-temperature, quantum regime and the higher temperature, semiclassical regime. In this context Fig. 4 shows two important qualitative features: the clear transition between these regimes and the large difference between the cross sections for He and H_2 collisions at low temperature.

First, let us consider the higher temperature regime where most previous measurements of the pressure broadening of polyatomic molecules have been done because of vapor pressure considerations. In this semiclassical regime it has been found that pressure-broadening cross sections can ordinarily be characterized by the relation

$$\sigma(T) = \sigma(T_0)(T/T_0)^n, \quad (1)$$

where T_0 is a reference temperature (typically 300 K).

Thus, even though in principle the cross sections can exhibit complex behavior as the energy defects of the collision channels change in relation to the temperature, they do not in the temperature regimes ordinarily investigated.

Figure 4 shows for collisions with He that above about 200 K, the cross section is essentially constant. This is a result which we have also observed in studies of a number of other species including H_2O , HDO , and SO_2 (8, 9, 16, 17). It is interesting (but perhaps not too surprising) that the simple physics of these circumstances is well described by the general observation and basic theory of Van Vleck and Weisskopf (18) in which "hard shell" collisions effect pressure broadening of constant cross section. Additionally, because of the lack of internal degrees of freedom in He, the elegantly simple limit of Anderson Theory presented by Townes and Schawlow (19) gives a more microscopic view, which also provides for a transition out of the high-temperature regime. In this view, the measure of the broadening effectiveness of the Fourier components of the collision is given by a dimensionless parameter

$$k = (2\pi b/v)\nu_{ab}, \quad (2)$$

where b is the impact parameter, v the molecular velocity, and ν_{ab} the rotational transition frequency. For He at 300 K, $2\pi b/v \sim 10^{-12}$, thus providing broadening efficiency up to about 1 THz, a frequency which includes all energy levels below $J = 3$. However, for temperatures below ~ 200 K, the reduced extent of this Fourier spectrum begins to lessen the broadening efficiency of the collisions and the cross section begins to drop. This result for H_2S -He can be compared with that of CO -He in which the constant, semiclassical cross section extends to below 50 K due to the more closely spaced energy levels of CO (20). Since for collisions involving H_2 and He well depths are typically tens of wavenumbers, pressure-broadening cross sections in this higher

energy regime are not significantly affected by the existence of the shallow ($\leq 50 \text{ cm}^{-1}$) wells of the intermolecular potential nor by the phenomena associated with them.

However, for collisions with H_2 below about 150 K, independent of the spectroscopic molecule and transition observed, deviations from the simple two-variable relation of Eq. (1) have been observed (8, 16, 17). Again, in the context of semiclassical theory, these deviations are not unexpected, because the rotational energy level spacing in H_2 is comparable to the thermal quanta, and the complete semiclassical theories which include the internal degrees of freedom of both collision partners must be used.

At still lower temperatures, new phenomena associated with resonances involving quasibound states become important and the cross sections for collisions with both H_2 and He vary rapidly. In this regime quantum scattering approaches to pressure broadening become appropriate. In these calculations "exact" numerical methods which use intermolecular potentials (ordinarily obtained by ab initio methods), such as those employed by the MOLSCAT routines of Green and Hutson,¹ become appropriate. An interesting example of such a calculation is the study by Palma and Green (20) of the effect of a variation in well depth on the low-temperature pressure-broadening cross sections of CO broadened by He. In this work they show that a reduction in the well depth by a factor of two produces a dramatic reduction in pressure-broadening cross section at low temperature without significant effect on the cross section at high temperature.

Unfortunately, to the best of our knowledge no intermolecular surfaces have been calculated for collisions between either H_2 or He and H_2S , so it is not possible to make a direct quantitative comparison between our experimental results and theoretical predictions. However, the results of the CO-He and similar calculations lead to a number of interesting conclusions. First, consider the cross sections for collisions of H_2S with He shown in Fig. 4. At about 50 K the decrease in cross section is halted, presumably by the onset of phenomena associated with the attractive well and quasibound states. As for CO-He collisions, this increase in cross section begins around a temperature which corresponds to the well depth of about 60 K (21). At the lowest temperatures, the cross section begins to drop rapidly once more due to the energetic unavailability of collisional channels involving the relatively widely spaced rotational levels of H_2S .

For collisions of H_2S with H_2 , similar considerations lead to quite different results. Because at high temperatures the phenomena associated with the internal degrees of freedom of H_2 which lead to the modest increase in cross section with decreasing temperature are well known, we do not elaborate on them here. However, it should be noted that because of the smaller mass of H_2 the Fourier spectrum of the collision extends to higher energy at a given temperature, and correspondingly, the drop in cross section will begin at a lower temperature. More significantly, the attractive well for collisions with H_2 is about twice as deep (110 K) as that for collisions with He. Thus, for collisions with H_2 the temperature regimes for semiclassical and quantum broadening overlap and provide a monotonically increasing cross section.

V. SUMMARY

In this paper we have presented the first measurements of the pressure broadening of a polyatomic molecule which cover a wide enough temperature range to encompass

¹ S. Green, National Resource for Computation in Chemistry Software Catalogue (Lawrence Berkeley Laboratory, Berkeley, CA, 1980).

both the semiclassical broadening regime and the quantum regime. Although dramatically different pressure-broadening cross sections were observed at low temperature, it was shown that a consideration of the Fourier spectrum of the collision at high temperature and the influence of the depth of the well in the intermolecular potential at low temperature provide a basis for understanding the observed divergent behavior of the two collision systems.

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