Measurement of Pressure-Broadening Parameters for the CO-He System at 4 K

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A technique has been developed to observe collisions in a regime where the rotational energy-level separation is greater than the thermal energy. Pressure-broadening parameters of trace quantities of CO, thermalized by collisions with helium at 4 K, were measured and found to be 10.1 and 11.2 MHz/Torr (half width at half maximum) for the $J=0$-1 and $J=1$-1 transitions, respectively. At 4 K only a small number of collision channels are energetically available and comparisons between experiment and theory are facilitated.

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In this paper we describe the results of a new experiment that makes possible the observation of collisional broadening processes, at or near thermal equilibrium, in a regime where the rotational energy-level separation $h\nu_r$ is greater than the thermal energy kT. This regime is ordinarily not available for experimental studies because most species of interest have vanishingly small vapor pressures at these temperatures. Results for the simple and fundamentally important CO-He system are described.

The experiment uses millimeter and submillimeter spectroscopic techniques to observe trace quantities of condensable gases that have been thermalized by collisions with helium at 4 K. We have previously described the techniques which we have developed for this spectral region.[1-3] For this work the absorption cell, shown in Fig. 1, is immersed in liquid helium. It is a cylinder 5 cm in diameter and 5 cm high which is closed at each end with a Mylar window sealed with an indium gasket. Condensable gases are admitted to this cell via a vacuum-insulated, electrically heated copper capillary tube of 0.25-mm inner diameter. All pressure measurements were made with a MKS capacitance manometer which was located on the same line that was used to evacuate the cell at the end of the experiment. Measurements were made by first admitting the helium to the experimental chamber and allowing the pressure to stabilize. Small amounts of CO were then admitted to the capillary tubing via a needle valve from a reservoir maintained at a pressure substantially higher than that of the sample chamber. As a check against the back diffusion that would occur if this ratio were too low, the pressure in the sample chamber was continuously monitored and no significant changes were observed. Heating of the capillary tube was also held to a minimum, consistent with CO vapor pressure, and it is estimated that CO emerged into the sample chamber at about 75 K. As would be expected, the signal amplitudes varied with flow rates, but even with flow-rate variations of about an order of magnitude, no linewidth variations were detected. It should be emphasized that the method is very general. The spectroscopic technique is widely tunable and very sensitive. This is especially true for samples at low temperatures because of their smaller partition functions, improved absorption/emission ratios, and narrower linewidths. For example, the absorption coefficients for the $J=0$-1 transitions of CO and HCN at 4 K are 25 and 10000 cm^{-1}, respectively.

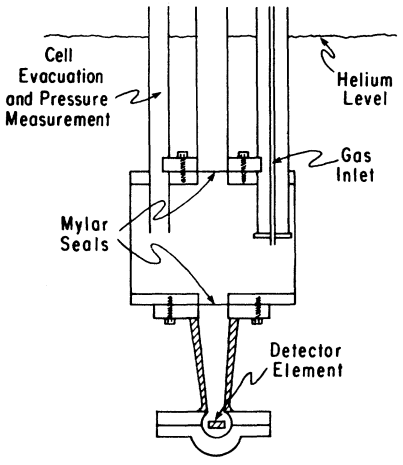

FIG. 1. Experimental chamber and InSb detector.

Much of the work on the CO-He system is summarized in a recent paper by Bel Bruno, Gelfand, and Rabitz[4] which investigates the inversion of experimental data to yield molecular information. The work most closely related to this is the microwave pressure-broadening experiment of Nerf and Sonnenberg,[5] who measured CO-He at 294, 195, and 77 K. More recently, Bassi *et al.*[6] have studied this system in a free jet expansion. Because

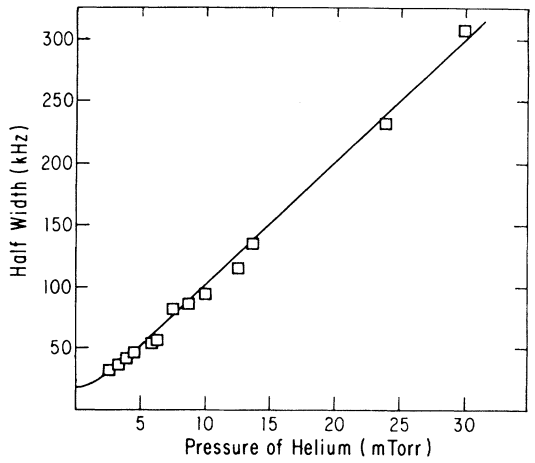

FIG. 2. Pressure broadening of the $J=0$-1 transition. The zero intercept is the Doppler width at 4 K.

the complex nonequilibrum process of the jet did not allow deconvolution of their results, they used the theoretical rate constants calculated by Green and Chapman[7] to compare their experimental results with theory.

Figure 2 shows the half width at half maximum (HWHM) of the CO absorption as a function of the helium pressure for the $J=0$-1 transition of CO at 115 GHz. These data were obtained by fitting a Lorentzian line shape, plus a linear slope to account for baseline effects, to our experimental data. For this transition at 4 K, the Doppler width is ~ 0.015 MHz, a width negligible in comparison to the collisional width at all but the lowest pressures. Similar measurements were carried out on the $J=1$-2 transition of CO at 230 GHz and the experimental results are summarized in Table I. Figure 3 shows the experimental points for the $J=1$-2 transition at a pressure of 33 mTorr. The curve calculated from the derived parameters fits the data so well that it is not plotted in this figure because it would obscure the experimental results. Measurement of the absolute absorption showed that the CO/He ratio was typically less than 10^{-3}. At a pressure of 10 mTorr, a simple random-walk calculation shows that $\sim 10^4$ gas-kinetic collisions are required for the CO to reach the wall, whereas the kinetic energy is effectively thermalized in fewer than 100 collisions. At the very lowest pressures observed, the CO may not be completely thermalized, but these data points do not contribute significantly to our measured pressure-broadening parameters. For the experiments reported here, the mean free path between velocity-changing collisions is much less than a

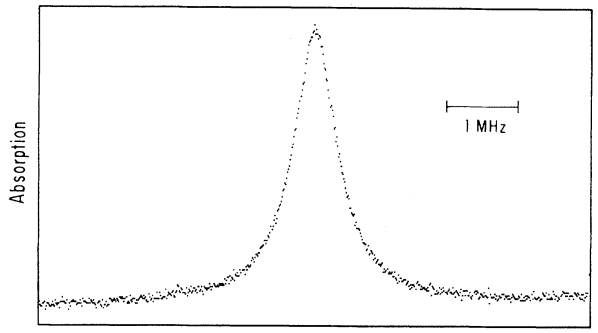

FIG. 3. Experimental data points for the $J=1$-2 transition at a pressure of 33 mTorr.

wavelength. Since our observed pressure-broadening parameters are about a factor of 2 less than those which would correspond to gas-kinetic, it would appear that this experiment approaches a regime in which Dicke narrowing would be observable. It would be very interesting to observe a species such as HCl for which $h\nu >> kT$.

We have done a calculation based on Anderson's theory[8-12] because it provides a straightforward, semiclassical means of demonstrating the effects of lowering the system temperature. The calculation includes the effects of dipole-induced dipole, first-order London dispersion, and quadrupole-induced dipole. Since at 4 K the thermal wavelength of helium is about 7 Å and typical collisions have impact parameters around 3 Å or less, a basic assumption of the Anderson theory is violated. Molecular constants used in the calculations are given in Table II. The results of these calculations are shown in Table I. These calculations show that as the temperature decreases, terms which correspond to adiabatic collisions ($\Delta J=0$) begin to dominate the calculated cross section. This is particularly true at higher J. This is consistent with the simple argument that at 4 K most collisions lack sufficient kinetic energy to cause transitions in the CO.

The CO-He system is computationally simple

TABLE I. Experimental and theoretical linewidth parameters for CO-He at 4.2 K (MHz/Torr).

Transition	Experimental[a]	Anderson theory
1-0	10.1	18.1
2-1	11.2	16.3

[a]Experimental uncertainty estimated at 10%.

TABLE II. Constants used in the calculation of theoretical linewidths.

Constant	CO	He
Dipole moment[a]	0.10 D	...
Ionization potential[b]	2.245×10^{-11} erg	3.915×10^{-11} erg
Anisotropic polarizability[c]	$\alpha_{\parallel}=26.0\times10^{-25}$ cm^3	...
	$\alpha_{\perp}=16.3\times10^{-25}$ cm^3	...
Average polarizability[c,d]	19.5×10^{-25} cm^3	2.03×10^{-25} cm^3[d]
Quadrupole moment[e]	0.80 D Å	...

[a]Ref. 13.
[b]Ref. 14.
[c]Ref. 15.
[d]Ref. 8.
[e]Ref. 16.

enough that a number of detailed calculations have been done. However, the large number of degrees of freedom that are thermally available to the collision partners contributes substantially to the complexity and size of most theoretical calculations and in many cases precludes the most exact calculations. Furthermore, experimental results represent an average over this large number of channels and makes the recovery of fundamental molecular parameters difficult. In a recent review, DePristo and Rabitz[17] point out that experimental techniques based upon line-shape measurements are in effect half state selected because the spectral radiation labels the initial state of the system whereas many output channels are energetically available to the collision pair. However, for the experiments described here, only one or a small number of output channels are available because the translational energy available at 4 K is small ($\sim$80 GHz) or comparable to the widely spaced rotational levels that are observed in the millimeter and submillimeter spectral region.

Perhaps the best quantum mechanical approach is the close-coupling technique of Arthurs and Dalgarno.[18] However, as Green and Thaddeus[19] point out, it is computationally prohibitive except at very low temperatures. They have used this close-coupling technique and an intermolecular potential derived from the electron-gas model of Gordon and Kim[20] to investigate collisions typical of the cold, "dense" molecular clouds of astrophysical interest. As a check of these calculations they compare their results with the experimental pressure-broadening results of Nerf and Sonnenberg with generally good agreement. Although the theoretical results are not in a form which allows a comparison with our experiment, they do closely follow the temperature dependence of simple gas, $(1/T)^{1/2}$. An extrapolation of these results, or the experimental results of Nerf and Sonnenberg, predicts a linewidth parameter at 4 K of about 18 MHz/Torr. This number is substantially higher than our experimental result.

More recently, Green and Thomas[21] have numerically addressed the problem of the relation between pressure-broadening data and CO-He interaction potentials. This study was motivated by the observation that although pressure-broadening parameters calculated by use of either the Gordon-Kim electron-gas model or the more exact intermolecular potentials calculated from self-consistent field and configuration-interaction (SCF-CI) calculations were in general agreement with the existing experimental data, scattering cross sections calculated from these potentials were dramatically different.[22,23] In their work, Green and Thomas calculated, as a function of collision energy, cross sections using the two different potentials. These calculations show dramatic differences at low collision energy. For example, for the $J=1$-0 transition at a collision energy of 15 cm^{-1} ($\sim$25 K), the electron-gas potential predicted a cross section of 63.35 Å^2 whereas the SCF-CI potential predicted 26.34 Å^2. However, at 200 cm^{-1} ($\sim$300 K), the corresponding cross sections were 27.33 Å^2 and 26.91 Å^2, respectively. Thus, we conclude that low-temperature experiments, such as the one described here, provide very important information for the testing of potentials and theoretical techniques.

In summary, we have demonstrated a technique that makes possible the observation of linewidth parameters in the regime where the rotational energy spacing is large or comparable to the kinetic energy of the collision partners and have studied the fundamental CO-He system. In this regime, only a small number of collision channels are open, theoretical calculations become more tractable, and experimental results are more closely related to

fundamental molecular parameters. Finally, we note that the technique is very general and should make possible the experimental study of many molecular species. The most interesting straightforward extension of this technique would be to replace the helium with hydrogen. Although the collision system would be theoretically more complex, it would be of considerable astronomical significance since hydrogen and helium form the overwhelming majority of interstellar collision partners.

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