Very Low Temperature Spectroscopy: The Helium Pressure Broadening Coefficients below 4.3 K for the Higher Lying States of CH₃F

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The temperature dependence of the helium pressure broadening cross sections of the $J = 3 \leftarrow 2$ and $J = 4 \leftarrow 3$ transitions of CH_3F have been measured between 4.3 and 1.8 K. These measurements were made with a new technique which uses a collisional cooling method to allow studies of spectroscopically active gases at temperatures far below their nominal freezing points. All of the observed K components of the transitions had cross sections of ~ 33 Å² at 300 K. However, at 4.2 K the cross sections had increased and varied between 64 and 88 Å² before declining and converging once again to ~ 52Å² near 1.9 K. The attributes of spectroscopy in this environment are also described as are opportunities for other kinds of studies, especially in the infrared. © 1989 Academic Press, Inc.

INTRODUCTION

We have shown that a simple collisional cooling technique makes possible a number of interesting gas-phase experiments at temperatures (typically in the region 4.3–1.7 K) far below the nominal freezing points of spectroscopically active gases (*1*). In addition to providing access to the very low temperature regime, important attributes of this method include a variable, yet well-defined temperature and pressure in the sample region and a macroscopic path length in the sample for the probe radiation. This technique has been used recently to obtain the pressure broadening coefficients of the $J = 1 \leftarrow 0$ transition of the CO–He system, the $K = 0$ and $K = 1$ components of the $J = 2 \leftarrow 1$ transition of CH_3F, and the $J = 3/2 \leftarrow 1/2$ transition of NO (*2–4*).

Spectroscopists have long varied the temperature of their samples to investigate highly excited states, to form new species, and to aid in the study of collisional processes. This has led to the development of a variety of techniques including the use of "hot" cells, variable temperature cells for the study of collisional processes as a function of temperature, low temperature equilibrium cells for the formation of van der Waals molecules, clusters, and other weakly bound species, and free expansion jets.

The desire to study gas-phase systems very near equilibrium in the regime where $h\nu_r > kT$ was the general motivation for the development of the collisional cooling technique. Except at the very low temperatures where the above condition is satisfied, molecular systems have many thermally populated rotational levels. As a result, observables that are related to collisional processes are ordinarily averaged over many states, making these observables rather classical and the inversion of them to recover more fundamental information problematical. Furthermore, the most exact theoretical

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calculations are often precluded because of the multitude of energetically available channels at higher temperatures. Another consequence of the use of low temperatures specifically impacts the results of the work reported here. Because the attractive potential between the collision partners is large or comparable to the collision energy, short-lived collision complexes can be formed. Theoretical calculations show that this can make significant contributions to pressure broadening parameters.

In this paper, we report results of a study in the region 4.3 to 1.8 K of the $K = 0$ and $K = 1$ components of the $J = 3 \leftarrow 2$ and $4 \leftarrow 3$ transitions of the CH_3F–He system near 150 and 200 GHz, respectively. In addition, measurements at 300 K on these transitions as well as on the previously studied $J = 2 \leftarrow 1$ transition were made to provide a reference for this work. Since kT at 4 K is about 90 GHz, these transitions represent a variety of states that are connected to their nearest neighbors by up to ~ 5 kT. The qualitative experimental result of this work is that near 4 K the cross sections, although having about a 40% variation among themselves, are significantly higher for all transitions than at either 1.8 or 300 K. In addition, the cross sections for all observed states converge at the lowest attainable temperatures, ~ 1.8 K, and share a common downward slope at that temperature.

Finally, because the collisional cooling method should be generally useful for a number of other spectroscopic studies, its experimental implementation along with some of the attributes of the technique are discussed. Its extension to infrared applications as well as its characteristics at liquid nitrogen temperature (77 K) are also put forth.

COLLISIONALLY COOLED SPECTROSCOPY

In general for experiments which require a well defined and characterized temperature and pressure, the low temperature limit has been set by the vapor pressure of the spectroscopically active gas. The collisional cooling technique circumvents this limit. This technique is related to the well-known method of free expansion jets and has many of its attributes. However, its molecular densities and geometry are more favorable for many experiments, including the studies described below which use millimeter and submillimeter (mm/submm) spectroscopic techniques. More importantly, the calculation of molecular parameters from experimental data is greatly simplified because the molecular system is essentially in thermal equilibrium and because the temperature can be easily varied and measured. In this section we will put forth some of the results of cooling gas-phase experiments to the temperature of liquid helium or below.

High-resolution molecular spectroscopy experiments are ordinarily carried out at or near the Doppler limit. This is especially true with the advent of modern infrared experimental techniques. Because Doppler widths are proportional to $T^{1/2}$, spectral lines near 4 K are about an order of magnitude narrower than at 300 K. This provides both greater resolution and measurement accuracy as well as increased peak signal strength. Molecular absorption coefficients are given by

$$\alpha = [8\pi^2 \nu / 3ch] \cdot |\langle m|\mu|n \rangle|^2 \cdot [N/\Delta\nu] \cdot [1 - e^{-h\nu/kT}] \cdot [1/Q_r], \qquad (1)$$

where $\langle m|\mu|n \rangle$ is the transition moment, N the number density, $\Delta\nu$ the linewidth, ν the transition frequency, T the temperature, and Q_r the rotational partition function.

This equation has been factored to show the temperature dependence according to the physical origin of the terms. The exact behavior of the $N/\Delta\nu$ term depends upon the details of the pressure broadening, but simple hard sphere theory gives $N/\Delta\nu$ $\propto T^{-1/2}$. The rotational partition function Q_r approaches 1 in the low temperature limit. For comparison at 300 K for molecules whose $J = 1 \leftarrow 0$ transitions fall at ~ 100 GHz, Q_r is typically ~ 100–1000. For microwave transitions the term $[1 - e^{-h\nu/kT}]$, which represents the difference between induced absorption and emission, is important. It varies between unity in the very low temperature limit to $\sim 1/100$ for transitions of $\nu \sim 100$ GHz at 300 K. Together these factors represent about five orders of magnitude gain in the absorption coefficient in the microwave and perhaps three in the infrared.

Other factors affecting signal strength are more dependent on the details of the experimental system and the chosen operating parameters. For example, the dilution ratio of the spectroscopic gas in the buffer gas will decrease the absorption for stable species, but the smaller pressure broadening parameter of helium will reduce this effect somewhat. The absorption coefficients for the $J = 1 \leftarrow 0$ transitions of CO and HCN at 4 K are 25 and 10000 cm^{-1}, respectively, and are typical of this regime. The expectation of strong signals even with large dilution ratios has been confirmed in all of our work to date. If the flow of CO is adjusted to give $\sim 1\%$ absorption in the 5-cm cell, then the corresponding dilution ratio is $\sim 10^{-4}$. In the work reported below on CH$_3$F, it was possible to produce near 100% absorption in the 5-cm-long cell with moderate flow rates. In practice, much lower flow rates were used to eliminate lineshape distortions associated with large fractional absorption. Because of its larger dipole moment, CH$_3$F is a much stronger absorber than CO, and its dilution ratio was typically $\sim 10^{-5}$.

EXPERIMENTAL DETAILS

Figure 1 shows the experimental layout. The entire apparatus is in a vacuum chamber maintained at a pressure below 10^{-5} Torr by a diffusion pump. Shields at 77 K (maintained by liquid nitrogen) and at ~ 25 K (maintained by a cryocooler), surround a 3-liter liquid helium container, which also contains the collisionally cooled cell. Figure 2 shows this cell in more detail. It is made of oxygen-free high-conductivity copper and has 0.005 Mylar windows. All removable flanges are sealed with indium, a method we have found to be very reliable. The temperature of the cell is varied by pumping on the helium bath through a vacuum regulator valve, which accurately controls the pressure and thus the temperature of the liquid helium. This technique allows the straightforward variation and control of the temperature, which is read directly with a calibrated germanium resistance thermometer.

At the top of the experimental chamber, warm spectroscopically active gas is injected via a vacuum-insulated tube. Provisions exist for electrically heating this tube, but under normal conditions this has not been necessary. The collisionally cooled cell is first filled with a static pressure of helium in equilibrium with the wall temperature. The spectroscopically active gas then cools as it collides with the cold helium. The quantitative relations that make this a useful and general technique are (1) the injected gas cools very rapidly as it collides with the helium, requiring many fewer than 100

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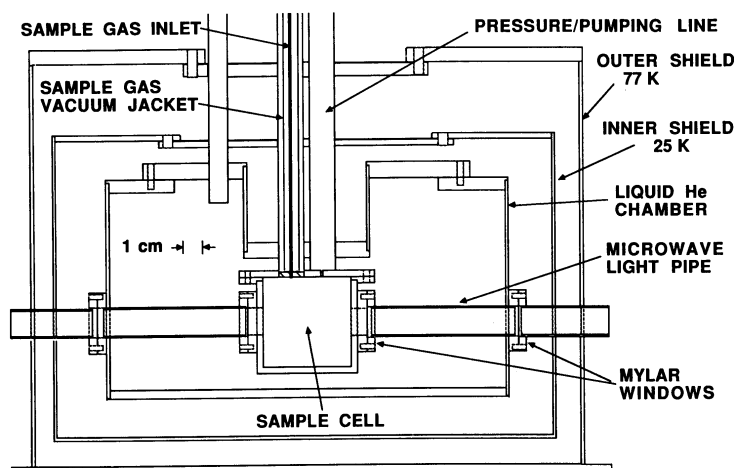
FIG. 1. Experimental apparatus showing radiation shields, cryogen reservoirs, and spectroscopic gas injector.

collisions to closely approach the temperature of the helium background; (2) at typical pressures, about 10 000 collisions are required for the gas to reach the walls and to condense; and (3) the very large absorption coefficients discussed above make possible large dilution ratios, ensuring that the spectroscopic gas does not perturb the temperature of the buffer gas.

A check of several of the approximations inherent in the collisional cooling technique can be made by measuring an observable as a function of the flow rate of the spectroscopic gas. We have previously reported a series of measurements of the pressure broadening parameter as a function of CO flow rate for the He–CO system (2). No observable flow-rate effects were detected, the only variation being the strength of the observed line. Similar measurements have been made for CH₃F. The null results demonstrate that (1) the flow of the warm gases does not significantly alter the temperature of the cold helium, (2) the dilution ratio of the spectroscopic molecules in the background helium is very large and collisions among them do not make a sig-
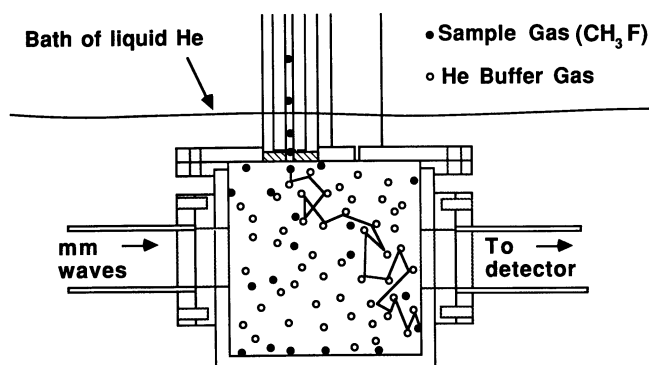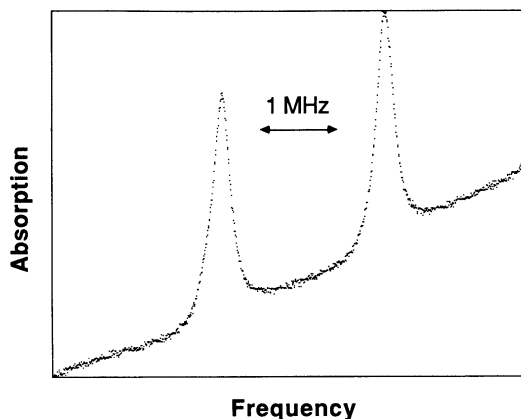

FIG. 2. The collisionally cooled cell.

FIG. 3. $K = 0$ and $K = 1$ components of the $J = 3 \leftarrow 2$ transition at 2.55 mTorr and 4.2 K.

nificant contribution to the measured parameters, and (3) there are no unanticipated flow dependent effects.

We have previously discussed the techniques which we have developed for the millimeter and submillimeter spectral region (5). For this experiment a 50-GHz klystron was phase locked to a multiple of a frequency synthesizer and its power matched onto a crossed waveguide harmonic generator (6). Because of the very narrow lines in the low temperature regime, it was possible and convenient to set the klystron to the fundamental of the molecular harmonic series without interference among the lines in the several harmonics. This made for convenient data acquisition. The output of the harmonic generator was propagated through the system shown in Fig. 1 and detected with a 1.6-K InSb detector. The system was swept in frequency by the microprocessor-controlled synthesizer at 20 Hz and the output of the detector was synchronously digitized. The bandwidth of the detection system was broad enough to reproduce the true lineshape. Figure 3 shows a typical observed line.

At high pressure the collisional contribution to the linewidth is significantly larger than the Doppler, resulting in a Lorentzian lineshape. However, at the lowest pressures observed in these experiments a more complex Voight profile exists. Since the analysis of a Voight lineshape is considerably more complex, we initially calculated all of our linewidths by means of a nonlinear least-squares fit to a Lorentzian lineshape. Adjustable parameters to allow for linear and quadratic variations in the baseline were included. At low pressure, to account for the Doppler contribution to the linewidth, the correction

$$\Delta \nu_p^2 = \Delta \nu_o^2 - \Delta \nu_d^2 \qquad (2)$$

was used, where $\Delta \nu_p^2$ is the contribution of the pressure broadening, $\Delta \nu_o^2$ is the observed line width, and $\Delta \nu_d^2$ is the Doppler width. For a number of low-pressure lines, the linewidths obtained from this procedure were compared with the results obtained from a fit to a Voight profile. No significant differences were observed.

Measurements were restricted to the pressure region that was low enough to avoid overlap between the $K = 0$ and $K = 1$ components of the several rotational transitions.

Measurements at pressures below about 0.5 mTorr were also not included in the analysis because of uncertainties associated with the thermal transpiration correction (7) and the complexities of lineshape effects resulting from Doppler broadening and unresolved hyperfine structure. At the lowest pressures, the linewidth of the $K = 1$ component was significantly larger than that of the $K = 0$ component because of its larger hyperfine structure.

OTHER APPLICATIONS

A number of other applications for the collisional cooling of spectroscopic gases to cryogenic temperatures exist. These include the simplification of complex spectra at low temperature, studies of weakly bound species and clusters, simulations of the interstellar medium and the atmospheres of the outer planets, and studies of reaction dynamics at very low temperature.

Because many of the potential applications of this method use infrared probe radiation, it is worthwhile to consider this regime. The higher frequency of the infrared typically leads to operating pressures that are much higher than in the mm/submm, the pressure scaling approximately as the frequency. First, let us consider the cooling itself in the context of a significantly higher pressure. If the flow rate of the spectroscopic gas is held constant, and only the pressure of the buffer gas is increased, the collisional cooling improves because of the increased number of collisions before the spectroscopically active gas reaches the observation region. As noted above, at 10 mTorr and 4 K, $\sim 10^4$ collisions will occur. Since the number of collisions to travel a given distance scales as the square of the pressure, at 1 Torr the number is $\sim 10^8$. Thus, cooling is assured, however, the time scale for the equilibration is now ~ 1 sec. It should be noted that although it might seem that raising the background pressure alone would lead to a higher dilution ratio and weaker lines, such is not the case. The time that an injected molecule spends in the cell before it condenses is proportional to the background pressure. Thus, at constant flow rate the dilution ratio is independent in first order of the buffer gas pressure. If both the background pressure and flow rate are increased, then the dilution ratio decreases linearly with flow rate. The principal heat load on the cell is the area of the warm injector that is exposed to the cold buffer gas in the cell. Since the pressure of the buffer gas in the cell is so large in comparison to the spectroscopically active gas, the gas flow itself is an insignificant heat load. In our microwave experiments, we have diagnostically investigated the question of cooling as a function of flow rate and have observed no flow-rate-dependent effects other than the trivial increase in signal (2). However, tests should be carried out for possible effects which might result from increasing the number of collisions by four orders of magnitude or having smaller dilution ratios.

Although each application of the collisionally cooled cell in the infrared will be different, it is useful to consider here the general spectroscopic implications, especially those related to the resolution and interpretation of complex and crowded spectra. In the infrared many spectral features, especially of the heavier species, are not resolvable into individual lines even with Doppler limited resolution. Since the lower temperature associated with the collisionally cooled cell reduces the Doppler width by about an order of magnitude, this factor alone will separate many previously unresolved spectra. In addition, because of the lower temperature, significantly fewer states will be pop-

ulated. This is a larger factor than the linewidth effect because rotational partition functions decrease very rapidly with temperature. In fact, these two combined will often change a spectroscopic problem from being too difficult to resolve and/or complex to analyze to one which is "uninteresting" because of its simplicity. However, the use of a variable temperature cell should allow a smooth transition from the "uninteresting" problem (which is easy to understand and assign) to the solution at higher temperature of the problem of interest.

Although the effects on spectroscopic parameters of collisional cooling are not nearly so dramatic at 77 K as at 4 K, the ease of experimental implementation at liquid nitrogen temperatures and a different, but complementary set of experimental parameters make this option attractive. The factor of two reduction in Doppler linewidth, combined with about an order of magnitude reduction in partition function will make a dramatic improvement both in marginally resolved situations and in the assignment of complex spectra. In fact, 77 K may be the best *single* temperature for the purpose, a temperature which provides decreased complexity while retaining an "interesting" spectroscopic problem. In addition, it will make possible collisional studies at 77 K. Since most spectroscopically active gases have vanishingly small vapor pressures at this temperature, it will expand considerably the temperature range of such studies. Not only is the factor of four in collision energy large enough to significantly test the temperature dependence of theory, but many gases, including the atmospherically significant O_2 and N_2, can be used as buffer gases and collision partners at this temperature. Finally and more speculatively, this environment may prove to be an interesting alternative to equilibrium cells for the study of dimers, clusters, and other weakly bound species. The collisional cooling method makes possible a very large number of collisions at temperatures far below those usually allowed by the vapor pressure of one of the components.

Finally, it should be pointed out that this is a straightforward technique to implement. To date a 5-cm path length has been used because in all of the experiments good signal-to-noise ratios could be obtained with modest flow rates. Systems that provide single-pass path lengths of 20–30 cm can be installed in commercial dewars without difficulty and multipass cells can be implemented without significant cryogenic engineering problems. None of these are complex on the scale of many modern spectroscopic techniques.

RESULTS

Broadening as a function of helium pressure was measured between 4.3 and 1.8 K for the $J = 3 \leftarrow 2$ and $J = 4 \leftarrow 3$ transitions of CH_3F. This combined with our previously reported study of the temperature dependence of the pressure broadening cross sections of the $J = 2 \leftarrow 1$ transition provides information on the pressure broadening cross sections for transitions whose frequencies correspond to energy differences that range from $\sim kT$ to $\sim 5kT$.

Figure 4 shows the measured linewidths as a function of pressure for the $K = 0$ component of the $J = 3 \leftarrow 2$ transition at 3.01 K. The corresponding pressure broadening parameters, obtained from least-squares fits to the data, and cross sections are listed in Table I for all of the observed transitions. The cross sections are plotted in Fig. 5. The lines, which connect the results for each component, are drawn to aid the
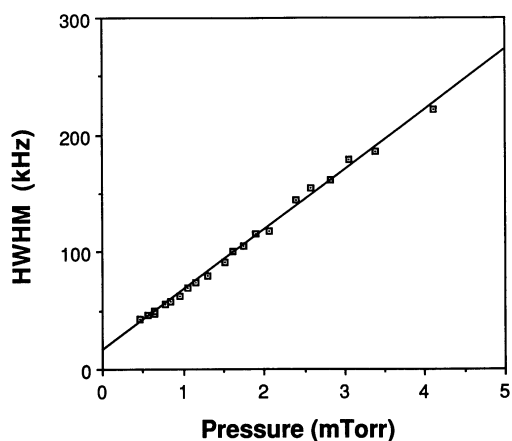
FIG. 4. Measured linewidths (HWHM) for the $K = 0$ component of the $J = 3 \leftarrow 2$ transition of CH_3F at 3.01 K as a function of cell pressure.

TABLE I

Pressure Broadening Parameters and Cross Sections for CH_3F

Temperature (K)[a]	Pressure Broadening[b] Parameter (MHz/Torr)		Cross Section (Å^2)[b]	
	$J = 2 \leftarrow 1$			
	$K = 0$	$K = 1$	$K = 0$	$K = 1$
4.21	43.4	38.4	75.2	66.6
3.90	47.2	42.7	78.9	71.3
3.50	48.3	40.6	76.4	64.3
3.25	47.8	38.9	72.9	59.3
3.00	46.0	41.6	67.4	61.0
2.47	50.0	47.0	66.5	62.5
2.25	45.7	—	58.0	—
2.00	49.2	48.0	58.9	57.4
1.90	47.6	46.7	55.5	54.5
	$J = 3 \leftarrow 2$			
	$K = 0$		$K = 0$	
4.21	45.7		79.2	
3.01	52.6		77.2	
2.14	50.4		62.4	
1.90	43.5		50.7	
	$J = 4 \leftarrow 3$			
	$K = 0$	$K = 1$	$K = 0$	$K = 1$
4.21	40.5	36.6	70.2	63.5
3.01	48.0	43.6	70.5	64.0
2.48	51.0	42.0	67.9	56.0
1.98	47.5	42.7	56.5	50.8

[a]Experimental uncertainty estimated at ±0.02K.
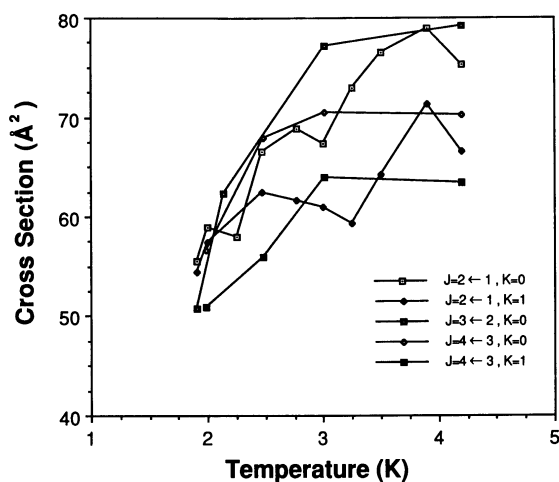[b]Absolute uncertainty estimated at ± 10%, relative uncertainty at ± 5%.

FIG. 5. Pressure broadening cross sections as a function of temperature for a number of transitions of CH_3F.

viewer and have no theoretical significance. Although the relative uncertainties with variation in either quantum number or temperature may approach the statistical uncertainty (~ 1–2%) of the fits, it is well known that pressure broadening experiments can be subject to substantial systematic error. Therefore, a 10% uncertainty in the absolute magnitude of the parameters is probably more appropriate. Figure 6 shows the low temperature data for the $K = 0$ component of the $J = 3 \leftarrow 2$ transition along with a measurement at 300 K of 33 Å^2. The lines which connect these points are discussed in the next section.

DISCUSSION AND SUMMARY

The purpose of this work was to explore the higher lying J states of CH_3F, especially those for which $h\nu_r \gg kT$, and to study the change of the pressure broadening parameter
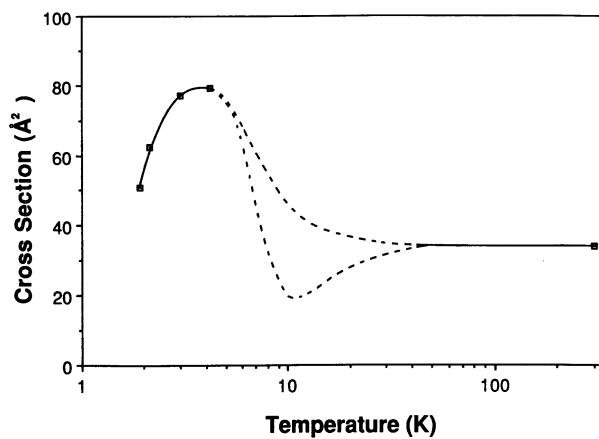

FIG. 6. Cross section for the $K = 0$ component of the $J = 3 \leftarrow 2$ transition of CH_3F between 300 and 1.8 K.

with changes both in temperature and state. Since the only system for which detailed theoretical calculations have been made which are applicable in this temperature regime is the CO–He system (8, 9), it is instructive to first review the results of those calculations. Palma and Green found two important differences between the "classical" regime for which $kT \gg h\nu_r$ and the very low temperature regime. At the higher temperatures pressure broadening is dominated by inelastic collisions and since the condition $kT \gg h\nu_r$ is satisfied to well below 77 K, little change in cross section is expected or observed (10). However, in the absence of any other mechanism, as $T \rightarrow 0$ the pressure broadening cross section also approaches zero because of the lack of translational energy needed to induce inelastic transitions. But the calculations also showed that the existence of shallow attractive wells in the intermolecular potential can lead to quasibound states. The resonances associated with these states exist only at low energy and can lead to significantly increased collisional cross sections. It was also demonstrated that the resonant structure and its contribution to the pressure broadening cross section is a very strong function of the details of the potential.

Results of a study of the pressure broadening of the $J = 3 \leftarrow 2$ and $J = 4 \leftarrow 3$ transitions of the CH$_3$F–He system were reported in this paper. Comparison of these and our earlier results on the $J = 2 \leftarrow 1$ transition (see figures and table above) shows that the cross sections for $K = 0$ are systematically larger than the cross sections for the higher lying $K = 1$ around 4 K, but that they drop more rapidly with decreasing temperature. The helium broadening cross sections for all of the observed transitions at 4 K are more than twice as large as the 33 Å^2 obtained at 300 K. Although no experimental data between 300 and 4.3 K exists, based on the experimental and theoretical results for the CO–He system, it seems likely that the cross sections remain fairly constant near the 300 K value until the region of our low-temperature observations is approached. Thus, it is likely that the rise in the cross section between 300 and 4 K is primarily in the region immediately above 4 K. Below about 4 K the cross sections of all of the observed transitions in the CH$_3$F–He system begin to decrease. The lines in Figure 6 are drawn to reflect this, with the portion shown as two dashed lines divided to emphasize that in the region immediately above our measurement it is not possible at this time to argue convincingly about the general shape of the curve. Since the size of the contributions of the resonances is a strong function of the intermolecular potential, energy level structure, and collision channels, with the available information it is not possible to say whether the decline in cross section below 4 K is due to a drop in the probability of inelastic transitions or a smaller contribution from the resonant structure or both. However, because the cross section does drop it can be concluded that the resonant structure in CH$_3$F does not make a strong contribution around 2 K. Given the wide range of energy level spacings relative to the thermal energy studied in the work reported here, it is perhaps surprising that larger state-to-state variations are not seen.

At the lowest temperatures the cross sections of all of the observed transitions converge to within about the expected experimental uncertainty. Because of this convergence and relatively steep downward slope, the region below 1.8 K would be especially interesting to investigate. In contrast, the measured CO–He cross sections increase by about 30% in the temperature region between 1.8 and 4.3 K, with the 4.3 K values being near the 300 K values. However, the detailed calculations for CO–He showed

that this is the result of an accidental cancellation of the decrease in inelastic cross section by an increase in broadening due to the formation of collision complexes at lower temperature.

Also, in this paper we have put forth the characteristics of very low temperature spectroscopy in a collisionally cooled cell and have described the experimental system used. The extension of the technique into the infrared was discussed as well as its implementation and characteristics at 77 K. Among the attributes of this method are (1) increases of several orders of magnitude in absorption coefficients as compared to room temperature, (2) macroscopic path lengths, (3) an order of magnitude reduction in Doppler broadening, (4) the opportunity to investigate molecular interactions near equilibrium in a new energy regime, and (5) significant spectral simplification.

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