# Rotational and Vibrational Temperatures in a 77 K Collisionally Cooled Cell

THOMAS M. GOYETTE, WILLIAM L. EBENSTEIN, AND FRANK C. DE LUCIA

*Department of Physics, Duke University, Durham, North Carolina 27706*

The rotational and vibrational temperatures of $CH_3F$ and $SO_2$ in a collisionally cooled cell have been investigated. This cell, which uses liquid nitrogen as the cryogen and has an injector whose temperature can be varied between $\sim200$ and 1300 K, is a variant of liquid helium based systems which we have previously described. The work reported in this paper shows that the rotational temperature is equal to that of the buffer gas, which in turn is variable from 77 K up to the trapping temperature of the spectroscopically active gas by adjustment of the wall temperature of the cell. The vibrational temperature is determined by the vibrational temperature with which the gas is injected, the number of collisions with the buffer gas, and the vibrational deactivation probability of these collisions. Thus, it is shown that the vibrational and rotational temperatures of spectroscopic samples can be separately adjusted over a wide range of temperature with a very simple experimental device. Applications are discussed. © 1990 Academic Press, Inc.

## I. INTRODUCTION

We have reported a number of investigations in which a newly developed collisional cooling method was used to investigate collisional processes between gas phase atoms and molecules at temperatures below 5 K. This has included studies of CO, NO, $CH_3F$, $H_2S$, DCl, HDO, OCS, and $CH_2F_2$ (*1–7*). In these studies we noted that this technique can be used for a number of other spectroscopic applications in both the microwave and infrared and that it should prove to be an attractive alternative to free expansion jets for many applications. These include the simplification of complex spectra, studies of weakly bound species and clusters, simulations of the interstellar medium and atmospheres of the outer planets, and studies of reaction dynamics at low temperature. Recently, Barnes *et al.* (*8*) have used this technique (which they refer to as "diffusive trapping") for infrared observations of $CO_2$ at 77 K. They too conclude that it is a "versatile and economical device" and preferable to supersonic jet cooling for some applications.

In this paper we report a millimeter and submillimeter (mm/submm) investigation of rotational and vibrational temperatures in a new implementation of the collisionally cooled cell discussed above. This new system uses a variable temperature injector to produce enhanced populations in excited vibrational states and liquid nitrogen temperature trapping. As we will show below, this makes it possible to separate and control the rotational and vibrational temperatures in a manner which is advantageous for a number of spectroscopic investigations in both the microwave and the infrared spectral regions. In addition, it makes possible the investigation of pressure broadening at temperatures below that obtainable by use of the usual spectroscopic techniques.

In this work we have chosen to study two species, $CH_3F$ and $SO_2$. $CH_3F$ was selected because its collisional properties are well known, which will facilitate the understanding of the results obtained here. $SO_2$ was chosen because it was expected that its lower vibrational energy would provide a system with faster vibrational relaxation to explore.

## II. EXPERIMENTAL DETAILS

Figure 1 shows the 77 K collisionally cooled cell. It consists of a 4-in.-diameter metal pipe 3 ft in length, the center 1-ft section being of copper and the end sections of stainless steel. The windows are $\frac{1}{2}$ in. Teflon, sealed with simple gaskets. One-inch-diameter stainless pipes are attached at each end and provide connections to the gas handling and pumping systems. With the exception of the ends (as indicated by the dashed lines in the drawing) the system is enclosed in a 77 K region. Spectroscopically active gas, which would have a vanishingly small vapor pressure at 77 K, flows into the system via the injector shown in the middle of the system. This injector consists of a 0.040-in.-i.d. copper tube, in a vacuum region separated from the cell by a 0.005-in. stainless diaphragm. It can be maintained at temperatures up to $\sim 1300$ K by an electrically heated oven just above its outlet to the cell. This temperature was measured with a thermocouple.

In operation, the cell contains a background gas, often helium or nitrogen, which has a significant vapor pressure at 77 K. Because rotational/translational cooling occurs so rapidly, the usable pressure range is very wide, from well below 1 mTorr to a maximum set primarily by spectroscopic considerations such as pressure broadening. The requirements on the spectroscopic gas are primarily that it have a significant vapor pressure at the temperature of the injector and that it can be trapped on the 77 K walls of the cell.

For the experiments described in this paper, we have used a broadband implementation of the millimeter/submillimeter techniques which we have previously described (9–12). Briefly, a computer controlled 10–15 GHz YIG oscillator is tripled to drive
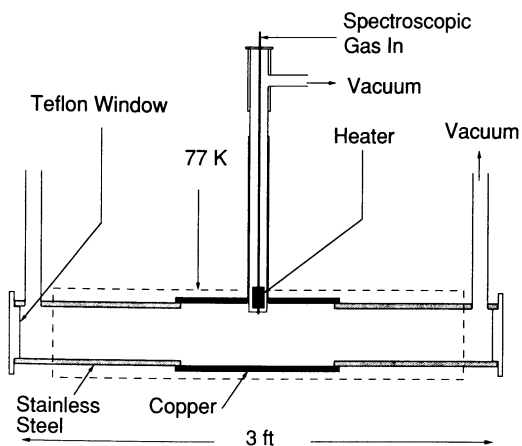


FIG. 1. The 77 K collisionally cooled cell with variable temperature injector.

a 1-W 26–40 GHz TWT amplifier. The output of this amplifier is multiplied into the millimeter/submillimeter by a crossed waveguide harmonic generator, propagated quasioptically through the cell described above, and detected in a 1.5 K InSb detector. For these measurements, FM modulation with lockin detection at $2f$ was used.

### III. COLLISIONAL COOLING

In the collisionally cooled cell described above, the spectroscopic gas is injected at a temperature above its freezing point. This may vary from a relatively low temperature (only high enough to provide the vapor pressure required by the injector) to a very high temperature provided by the oven which surrounds the outlet of the injector. In this latter case, the limit is determined by the construction of the oven and by the decomposition properties of the injected species.

Upon injection into the cell, the spectroscopically active gas begins to undergo a series of collisions with the cold background gas which cool its various degrees of freedom. This cooling gas can be any species with significant vapor pressure ($\geqslant 1$ mTorr) at the temperature selected for the experiment, but helium and nitrogen are typical choices. The number of collisions the spectroscopic gas undergoes before it encounters a cold wall and freezes out depends upon the square of the pressure of this gas, but at a typical pressure for microwave spectroscopy of 10 mTorr, 10 000 is typical. At pressures typical of infrared spectroscopy, this number is much larger. Because the translational temperature is cooled to a value very close to that of the background gas in fewer than 100 collisions, the translational temperature of the spectroscopic gas (except in the near neighborhood of the injector) is essentially that of the collisional cooling gas.

Because of the large cross section for rotational energy transfer, it is well known that except in unusual circumstances the rotational temperature in a system follows closely its translational temperature. Because of the large number of collisions in the system considered here, it would be expected that a single rotational/translational temperature would be established. The vibrational temperature of the spectroscopically active molecules is much more problematic. It clearly depends both upon the widely varying cross section for vibrational relaxation and on the pressure of the cooling gas because the number of collisions depends on the square of this value. Because a molecule which does not vibrationally relax in its first few collisions will spend the remainder of its lifetime with the cooled translational temperature, an additional consideration is the temperature dependence of the vibrational relaxation.

The absorption coefficient for a rotational transition is given by

$$\alpha = \left[\frac{8\pi^2\nu}{3ch}\right]|\langle m|\mu|n\rangle|^2\left[\frac{N}{\Delta\nu}\right][1 - e^{-h\nu/kT}]\left[\frac{1}{Q_r}\right]e^{-E_1/kT}, \tag{1}$$

where $\langle m|\mu|n\rangle$ is the transition moment, $N$ the number density, $\Delta\nu$ the linewidth, $Q_r$ the rotational partition function, and $E_1$ the energy of the lower state of the transition. This equation has been factored in order to separate the temperature-dependent terms according to their physical origins. The rotational partition function, Boltzmann difference between upper and lower states, and linewidth all depend upon the rotational/translational temperature, while (for low lying rotational states) the energy of the

lower state depends primarily upon the energy of the vibrational state which contains it.

Figure 2 shows the temperature variation (relative to an equilibrium sample at 300 K) of the absorption coefficients for rotational transitions in vibrational states at 1000, 2000, and 3000 cm$^{-1}$ with the assumption of rotational/translational/vibrational equilibria. These are approximately the vibrational energies of the $\nu_3$, $2\nu_3$, and $3\nu_3$ states of $CH_3F$. Although there is a significant increase, especially in the more highly excited vibrational states, the gain due to increased vibrational state population is substantially reduced by factors such as linewidth and rotational partition function which depend upon the rotational/translational temperature. This is most obvious for the vibrational state at 1000 cm$^{-1}$ because at the higher temperatures these losses outweigh the gain in vibrational state population. The increase in the number of thermally populated rotational states can be either advantageous or not, but in many experiments the increased spectral complexity associated with a high rotational temperature is undesirable.

Figure 3 shows a similar calculation for a collisionally cooled cell. The differences between this figure and Fig. 2 result from the elimination of the $\sim T^3$ dependence of the absorption coefficient on the rotational/translational temperature and the fixing of this term at $T = 77$ K. At 1000 K, this corresponds to a change in absorption coefficient of about 1000.

In our earlier work on pressure broadening below 5 K, we used very small dilution ratios of the spectroscopically active gas in the background collisional cooling gas. Because of the very large absorption coefficients at low temperature, this was easy to accomplish; dilution ratios between $10^{-4}$ and $10^{-6}$ produced signals that were observable in real time on an oscilloscope. This made it straightforward to satisfy the basic assumption that the warm injected gas did not significantly affect the temperature
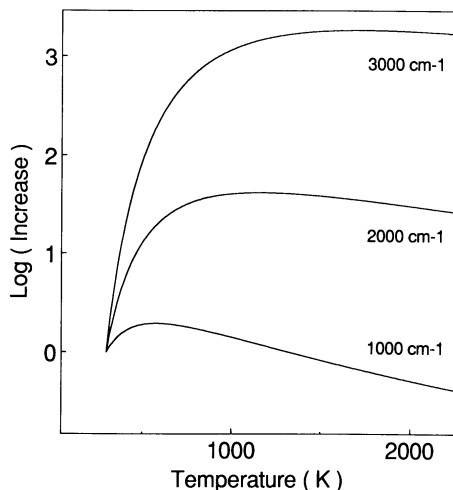


FIG. 2. The log of the fractional increase (relative to an equilibrium cell at 300 K) of the absorption coefficients as a function of temperature for rotational transitions in vibrational states of energy 1000, 2000, and 3000 cm$^{-1}$ with rotational, translational, and vibrational equilibria.
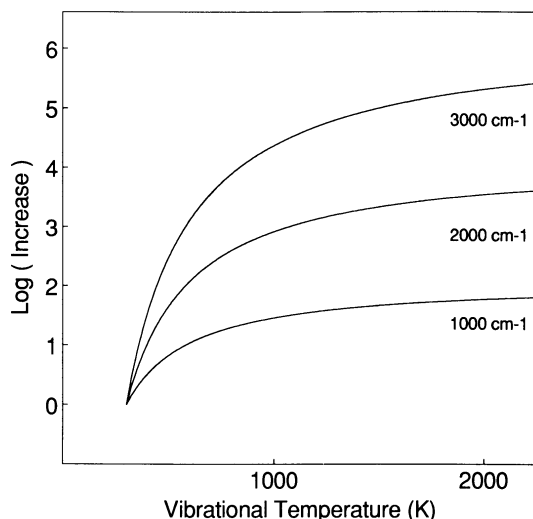
FIG. 3. The log of the fractional increase (relative to an equilibrium cell at 300 K) of the absorption coefficients as a function of vibrational temperature for rotational transitions in vibrational states of energy 1000, 2000, and 3000 cm$^{-1}$ with rotational and translational temperature fixed at 77 K.

of the cooling gas, thereby leaving unmodified the temperature at which the experiment was being executed. In addition, it assured that collisions between molecules of the spectroscopically active gas were rare. In the context of that work, we described experimental verification of these assumptions (2).

However, in most experiments there will be some weak signals and it is useful to discuss the range of appropriate dilution ratios for these 77 K experiments. First, it must be recognized that different dilution ratios are appropriate for different experiments. The most stringent requirements are placed by collisional experiments in which the temperature of the system as well as the collision partner must be known. An example typical of this class is a pressure broadening experiment. In pressure broadening experiments accuracies are ordinarily a few percent. Thus, concentrations of the spectroscopically active molecules can approach 1% before corrections due to collisions between them need to be considered. It is more difficult to quantify the heating effects on the system which would result from the high flow rates associated with large fractional concentrations because the temperature in the region where the sample interacts with the probe beam is very dependent upon the geometry of the system. As a practical matter, most of the transitions for which pressure broadening measurements might be made are fairly strong and can be observed in very dilute systems. Furthermore, as we have noted (3) at 77 K and above, the cross sections for pressure broadening do not change rapidly with temperature, leaving the relatively weak $T^{1/2}$ relation between pressure broadening and cross section as probably the strongest temperature-dependent effect. Somewhat less stringent requirements are placed by experiments which are designed to aid in the identification and assignment of spectra by providing information about the energy of the states involved in a transition by varying the temperature. Finally, in experiments in which only spectral simplification is desired, only a general cooling is required.

In the final analysis heat energy is very cheap and provides an interesting alternative to vibrational heating via laser pumping or discharges ( $13$ ). By control of the pressure and temperature of the buffer gas and the temperature of the injector, it is possible to separate (and in many cases quantitatively adjust) the rotational/translational and vibrational temperature independently. This will be discussed in more detail in the following section.

## IV. RESULTS

Our first investigations used $CH_3F$ as a means to study rotational and vibrational cooling in the collisionally cooled cell at 77 K. This species is ideal for this task because its vibrational ( $14$, $15$ ) and rotational ( $16–18$ ) relaxation properties have been extensively studied. In addition, the relative amplitudes of the $J + 1 \leftarrow J$ transitions in different $K$ (which are closely spaced in frequency) provide a convenient, stringent test of rotational thermalization. Since the $K$ levels are both widely spaced in energy and not connected by the strong electric dipole allowed selection rules, they are much more difficult to thermalize than states which, for example, differ only in $J$.

Figures 4 and 5 show a comparison between the $K$ structure of the $J = 5 \leftarrow 4$ transition in the ground vibrational state of $CH_3F$ observed in a 300 K cell at equilibrium and in a 77 K collisionally cooled cell. Because of the higher energy of the $K$ components with the larger quantum numbers, they are expected and observed to be relatively weaker in the collisionally cooled cell.

For the relative intensities of the different rotational transitions in an equilibrium cell at 300 K, Fig. 6 shows the expected agreement between theory and experiment. Figure 7 shows that in the 77 K collisionally cooled cell the relative rotational intensities are essentially identical in the three vibrational states $v_3$, $2v_3$, and $3v_3$. A nonlinear least-squares fit to the intensities of the rotational transitions in the ground vibrational state yields a rotational temperature of $74 \pm 8$ K. Thus, we conclude that the rotational
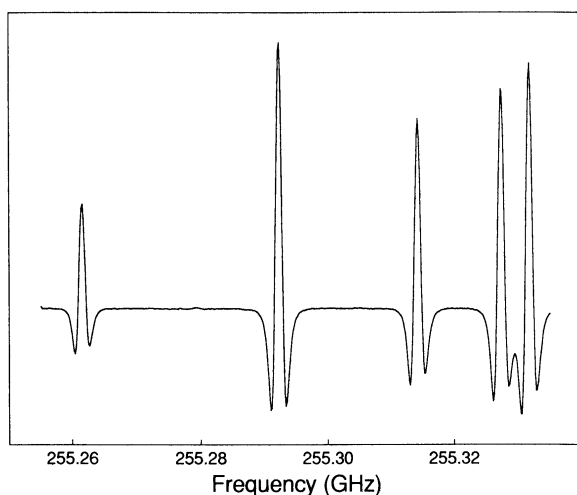


FIG. 4. Relative intensities of the $K$ components (4, 3, 2, 1, 0; left to right) of the $J = 5 \leftarrow 4$ transition at 300 K.
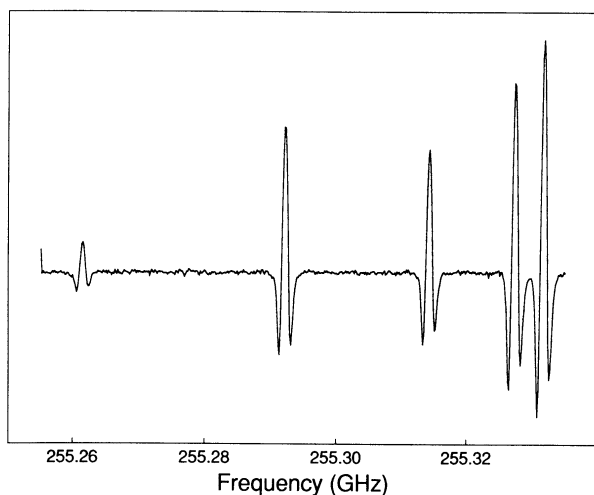
FIG. 5. Relative intensities of the $K$ components (4, 3, 2, 1, 0; left to right) of the $J = 5 \leftarrow 4$ transition in the 77 K collisionally cooled cell.

manifold in all of these vibrational states is in equilibrium with the background buffer gas in the cell. Although this is hardly an unexpected result, the combination of decreasing relaxation efficiency of collisions with reduced collisional energy and the relatively large energy gaps between the $K$ states allowed the possibility of rotational nonequilibrium in the higher $K$ states. Indeed, it seems likely in very highly excited states ($E \gg kT$) that some remnant of the original rotational population distribution would be left behind as the gas cools. This is especially true because the large fraction of kinetic energy that is lost in each collision causes the molecules to approach the buffer gas temperature very rapidly.

Next the vibrational temperatures were investigated. Figure 8 shows a comparison between the observed absorption intensities of transitions in $\nu_3$, $2\nu_3$, and $3\nu_3$ and
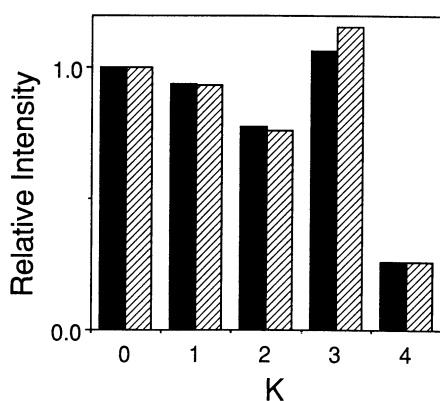


FIG. 6. Calculated (solid) and observed (cross hatched) intensities for the $K$ components of the $J = 4\text{-}5$ transition in the ground vibrational state of $CH_3F$ in a 300 K equilibrium cell.
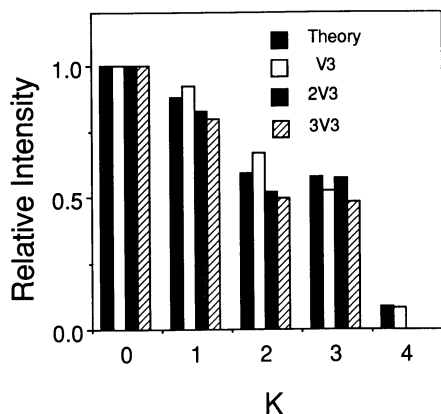
FIG. 7. Calculated and observed intensities for the $K$ components of the $J = 5 \leftarrow 4$ transition in the $\nu_3$, $2\nu_3$, and $3\nu_3$ vibrational states of $CH_3F$ in a 77 K collisionally cooled cell.

intensities calculated on the assumption that the measured injector temperature determines the vibrational temperature. As can be seen, the agreement is very good and the signal enhancement, especially for the highest vibrational state, is very large even for the relatively modest injector temperatures used in these experiments.

It is interesting to note that the efficiency of the rotational relaxation in these experiments was so high that the rotational cooling could be achieved even without the helium buffer gas because the nonunity coefficient of condensation for $CH_3F$ hitting a 77 K wall provided enough cold background gas to accomplish the cooling.

A series of measurements was made on the $\nu_2$ state of $SO_2$ in order to investigate vibrational relaxation in a species with a smaller vibrational energy gap. At 300 K it requires about 10 000 collisions to vibrationally deactivate the 1000 cm$^{-1}$ (5 kT) $\nu_3$ vibrational mode of $CH_3F$ and presumably many more at 77 K. Thus, the result reported above is not surprising. In fact, if the vibrational excitation of $CH_3F$ had
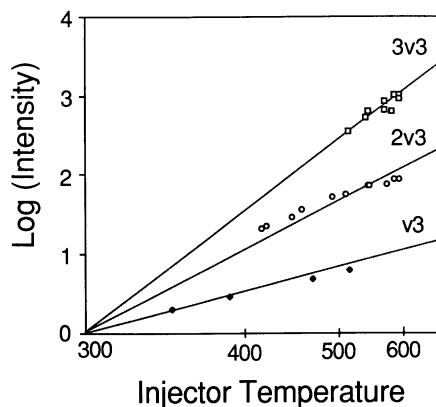


FIG. 8. Calculated (lines) and observed (points) intensities for rotational transitions in the $\nu_3$, $2\nu_3$, and $3\nu_3$ vibrational states of $CH_3F$ in the 77 K collisionally cooled cell as a function of injector temperature.

been observed to be below that defined by the injector temperature, the cause would have been more likely that there were too *few* collisions to establish the vibrational temperature within the injector rather than too *many* to maintain it in the collisionally cooled cell! However, it is well known that as the vibrational energy gap is reduced the probability of collisional relaxation increases rapidly. Since the $\nu_2$ mode of $SO_2$ has an energy of only 519 cm$^{-1}$ ($\sim$2.5 kT), it is to be expected that its deactivation would be much more rapid than that of $CH_3F$.

Figure 9 shows the peak intensity of the $15_{1,15}-14_{0,14}$ transitions in the ground and $\nu_2$ vibrational states of $SO_2$ as a function of the background helium pressure. First consider the ground state observations. The lifetime of the spectroscopically active molecule in the cell is proportional to the pressure of the helium because it must random walk its way through this background on its way from the injector to the cold wall. Thus, at constant injector flow rate the number density in the cell is proportional to the background pressure. This is manifested in the data by the initial linear rise in signal strength. However, as the pressure broadening begins to approach the Doppler width, the peak absorption ceases to increase with increasing number density because both the linewidth and the number density are increasing together. This produces a leveling of the curve. At still higher pressures, because we were using FM modulation with lock-in detection, the modulation efficiency is reduced because the linewidth begins to exceed the deviation of the frequency modulation and the observed peak signal strength begins to fall.

Next consider the measurements made in the $\nu_2$ state. As expected, they too initially rise linearly with the pressure as the number density of the $SO_2$ molecules increases. However, the figure shows that the intensity of the $\nu_2$ state begins to fall at about 30 mTorr due to vibrational deactivation. Since in the figure the observed peak signal strengths for both vibrational states are normalized at low pressure (before any significant vibrational relaxation), the difference between these data is due to the increase in vibrational relaxation with the increase in collision number as a function of pressure.

Figure 10 shows a comparison between the $\nu_2$ data and the function

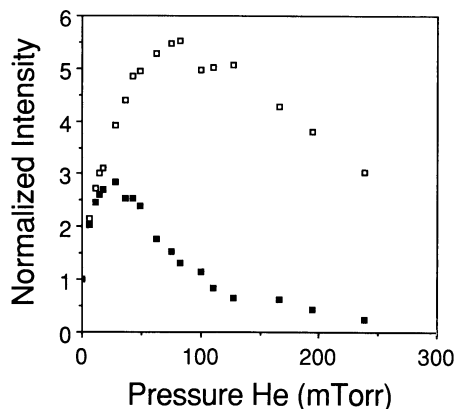$$\alpha = C_1 P e^{-C_2 P^2} + C_3, \tag{2}$$



FIG. 9. Peak intensities of observed rotational transitions in the ground (open boxes) and $\nu_2$ (solid boxes) vibrational states of $SO_2$ as a function of helium pressure.
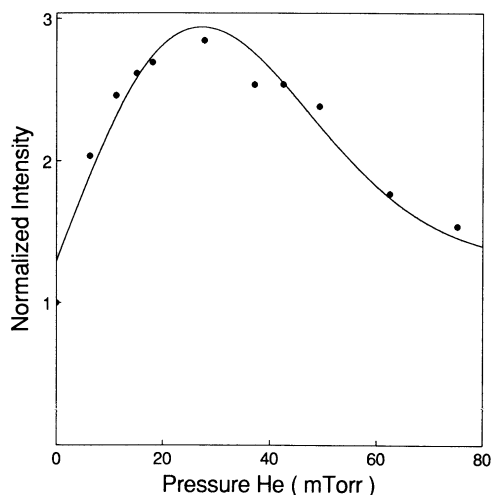
FIG. 10. Calculated (line) and observed (points) intensities of rotational transition in the $\nu_2$ vibrational state of $SO_2$ as a function of helium pressure.

where $P$ is the pressure of the helium buffer gas and $C_1$, $C_2$, and $C_3$ are constants. In this function the leading linear pressure term is a manifestation of the increased number density of molecules in the absorption path with pressure. The quadratic pressure term in the exponent represents the functional dependence of the number of collisions experienced by a molecule on the way to the absorption path. The constants are complicated functions of geometry and collisional relaxation parameters; however, simple assumptions lead to the conclusion that about 5000 collisions between $SO_2$ and He at 77 K are required for vibrational relaxation. Since the number of collisions in the infrared study of Barnes et al. (8) at 100 Torr is much higher and $CO_2$ has fairly efficient vibrational relaxation pathways, the absence of hot bands in their experiment is consistent with these results.

## V. CONCLUSIONS

We have shown that the collisional cooling technique can be implemented using very simple techniques at liquid nitrogen temperature and that it is possible to independently and quantitatively adjust the rotational and vibrational temperatures over a wide range. More specifically, the rotational temperature of the spectroscopically active species is determined by the translational temperature of the collisional cooling gas, and the vibrational temperature by the temperature of the injector, modified by possible vibrational relaxation at higher pressures. It was also suggested that this collisionally cooled system provides an interesting environment for a wide range of other experiments including pressure broadening measurements at low temperature, studies of complex spectra, and investigations of weakly bound species.

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