

Collisional cooling of the NO-He system

The pressure broadening cross sections between 4.3 and 1.8 K

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We report the results of a very low temperature pressure broadening experiment on the NO-He system. A newly developed collisional cooling technique was used to provide an environment for the study of gas phase collisions below 4 K. In this temperature regime typical rotational energies are greater than available thermal energies. The helium pressure broadening cross section for the $J = 1/2-3/2$ transition of NO in the $^2\Pi_{1/2}$ electronic state was found to drop by ~ 35 per cent from 26 \AA^2 at 4.2 K to 17 \AA^2 at 1.8 K. The 300 K cross section is 22 \AA^2 . The results of this experiment are compared with results from an earlier experiment on the CO-He system in which the cross section rose by ~ 30 per cent over this temperature range. The spectroscopic attributes of the collisional cooling technique are also discussed, some of which are: narrow line widths, large absorption coefficients, and the simplification of otherwise complex spectra. In addition, because, $h\nu_r > kT$, the number of available collisional channels is vastly reduced. This makes exact theoretical calculations possible and allows a more direct comparison between experimental observables and fundamental molecular parameters.

1. Introduction

In an earlier paper we reported the development of a straightforward collisional cooling technique which allows macroscopic samples of spectroscopically active gas to be cooled to a few degrees above absolute zero [1]. This makes possible the study of these samples under essentially equilibrium conditions and with a well defined kinetic temperature. Recently, we have used this method to study gas phase collisions in the CO-He [2] and $\text{CH}_3\text{F-He}$ [3] systems in the 4.3 to 1.8 K temperature region.

The relative size of the energy level spacing compared to kT plays an important role in determining the spectroscopically observable properties of quantum mechanical systems. This is especially true for observables, such as linewidths and energy transfer rates, that are directly associated with collisional rather than resonant processes since available thermal energy plays a first order role in these interactions. These temperature dependent effects are most strongly manifested in interactions associated with the rotational degrees of freedom of molecules since rotational energy spacings are in general smaller than kT , with the exception of a few examples such as H_2 at low temperature and the higher J states of the hydrogen halides under ambient conditions [4]. Consequently, the observables related to collisional processes are in effect averaged over many states obscuring the underlying quantum mechanical processes and making the deconvolution of fundamental information problematical. Furthermore, detailed theoretical calculations are usually precluded

because of the number of energetically available channels. However, at very low temperatures where $h\nu, \sim kT$ the situation is changed: quantum mechanical processes become manifest and the vastly reduced number of thermally accessible states makes exact theoretical calculations possible. Thus, collisionally cooled spectroscopy at temperatures of only a few kelvin provides a unique window on one of the most basic interactions, that between individual atoms and molecules in the gas phase.

The specific goal of our work, thus far, has been to observe systems in which both the attractive intermolecular potential and rotational energy level spacings are larger than or comparable to the collision energy. Theoretical expectations were that several significant differences would occur in this regime, and that these would make new tests of collision theory possible. For states with $h\nu, > kT$, simple theory predicts that insufficient energy is available to cause inelastic collisions. Since, under ordinary conditions, inelastic collisions are the major contributor to pressure broadening, pressure broadening cross sections might be expected to be much smaller in the low temperature limit. On the other hand, at low temperature the shallow attractive wells in the intermolecular potentials allow the formation of short lived collision complexes which also interrupt the wave function, thus contributing to the pressure broadening cross section. These qualitative expectations have been verified by Green [5] and Palma and Green [6] by means of 'exact' close coupled calculations for the CO-He system. Their calculations showed that in the absence of the attractive well the pressure broadening cross section approached zero as $T \rightarrow 0$, but that with inclusion of an attractive potential the cross section increased rapidly (perhaps approaching infinity) in the same limit.

We report here the results of a study of the NO-He system. The most significant difference between NO and the previously studied CO is that the lowest electronic state of NO is $^2\Pi_{1/2}$ which makes $J = 1/2$ the lowest rotational level. Thus, at very low temperatures the rotational energy level spectrum becomes relatively sparse since the lowest allowed transition is now at 150 GHz. The most notable result of the present work is that the cross section for NO-He decreases by ~ 35 per cent between 4.3 and 1.8 K. In contrast, our study of CO-He showed that the cross section increased by ~ 30 per cent, over the same temperature range.

2. Experimental

Our earlier work describes in detail the experimental realization of the collisional cooling technique [2] used in the present study. Figure 1 shows a cross section through the fundamental component of the experiment, the collisionally cooled cell. The cell itself is a copper cylinder 5 cm in diameter and 5 cm high with indium sealed mylar windows on either side, immersed in a bath of liquid helium. After filling the cell with a suitable background pressure of helium gas, trace amounts of the spectroscopic sample are injected via the vacuum insulated needle tubing at the top. Cooling of the sample occurs as warm molecules collide with the 4 K background helium gas. A gas kinetic calculation shows that it takes less than 100 collisions to cool the sample gas to the temperature of the helium background, yet at 10 mTorr of helium pressure about 10 000 collisions occur before a molecule reaches the wall. Thus, as long as gas enters through the injector, there will be a quasi-equilibrium spectroscopic sample in the cell. Since absorption coefficients are very large at liquid helium temperatures, the spectroscopic sample need make up

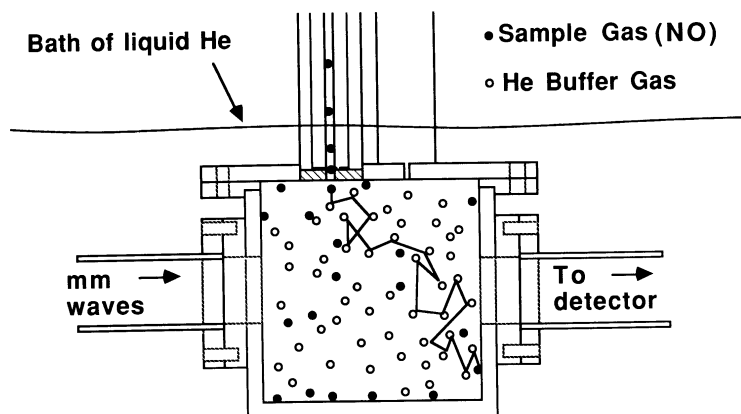


Figure 1. The collisionally cooled cell.

only a very small fraction of the gas present in the cell, thus avoiding any possible problems associated with the warming of the background gas. This expectation was verified quantitatively in our earlier work with the CO-He system by investigating linewidth as a function of CO concentration in the cell. In that study no variation in linewidth was found as the concentration of CO was varied by a factor of five or more. For the present study similar, but less extensive, tests were performed with NO.

Temperatures below 4 K were reached by pumping on the liquid helium bath through a vacuum regulator valve. The temperature of the cell was measured by a calibrated germanium resistance thermometer attached directly to the cell while the pressure of the helium background gas in the cell was monitored with a capacitance manometer. The results of Roberts and Sydoriak [7] were used to correct observed pressures for the effects of thermal transpiration.

The millimeter and submillimeter techniques used in this experiment have been described in detail in earlier works [8]. Briefly, for this experiment a 50 GHz klystron was phase locked to a reference synthesizer and its power matched onto a harmonic generator [9]. The output of this harmonic generator was propagated through the collisionally cooled cell shown in figure 1 and detected with an InSb detector operating at 1.6 K. The frequency of the probe radiation was swept by the synthesizer at a rate of 20 Hz and the output of the detector was digitized synchronously with this sweep. The bandwidth of the system was adequate to reproduce the true lineshape. Figure 2 shows a typical observed line.

Spectroscopically there are a number of advantages to working at very low temperatures. Typically, millimeter and submillimeter experiments are done at temperatures where Doppler broadening is significant compared to other broadening mechanisms. However, since Doppler width is proportional to $T^{1/2}$, linewidths at 4 K are typically reduced by more than an order of magnitude. This results in greater resolution, peak line strength, and measurement accuracy. Absorption coefficients are also strongly enhanced at very low temperatures due to several factors, such as the increased ratio of absorption to emission and a very large reduction in the rotational partition function. As an example, the absorption coefficients of gas phase CO and HCN at 4 K are 25 cm^{-1} and $10\,000 \text{ cm}^{-1}$, respectively, for transitions near 100 GHz. These factors together result in very large signal strengths at

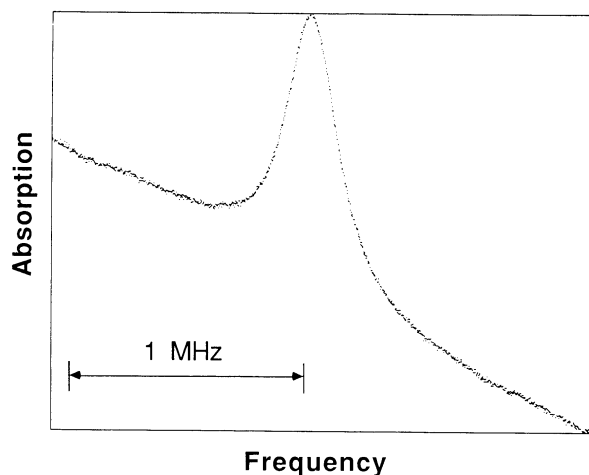


Figure 2. A typical line, the $J = 1/2-3/2$ transition of NO broadened by 7.51 mTorr of He at 2.74 K.

millimeter and submillimeter wavelengths, in spite of the very small fraction of spectroscopic sample present in the cell. For these measurements, the fractional concentration of NO in the sample cell was 10^{-3} – 10^{-4} .

For purposes of data analysis this experiment is no different from the classic pressure broadening experiment in which linewidths are measured as a function of pressure. Although the Doppler width of the NO transition measured for this work is only 20 kHz at 4 K, this becomes a significant fraction of the total linewidth at the lowest pressures for which we have data. At these low pressures a more complex Voigt profile is expected. Owing to the considerably greater analysis time necessary for the Voigt profile, we initially measured all of our linewidths using a nonlinear least squares fit to a Lorentzian profile in which parameters to allow for linear and quadratic variations in the baseline were included. At pressures where there is a significant Doppler contribution, a correction [10]

$$\Delta\nu_p^2 = \Delta\nu_o^2 - \Delta\nu_d^2 \quad (1)$$

was used, where $\Delta\nu_p$ is the contribution due to pressure broadening, $\Delta\nu_o$ is the observed linewidth, and $\Delta\nu_d$ is the Doppler width. In our work on the CO–He system, a number of linewidths calculated from the above equation were compared with results obtained directly from a fit to a Voigt profile and no significant differences were found. Figure 3 shows a plot of the linewidth, corrected for Doppler width by the above procedure, as a function of pressure at 2.45 K.

Clearly this technique is related to low temperature spectroscopy using free expansion jets and shares many of its attributes. The collisional cooling technique, however, permits a well defined and variable temperature and pressure, a substantial absorption path, and an environment at, or very near, equilibrium. It should be noted that the collisional cooling technique can be favorably used in a number of other applications. For example, at room temperature the complex rotational structure in infrared spectra often precludes assignment of spectral lines. However, dramatic simplifications occur at low temperature due to the large reduction in thermally populated states. In addition, these very low temperatures should significantly enhance the production and lifetime of weakly bound complexes such as van

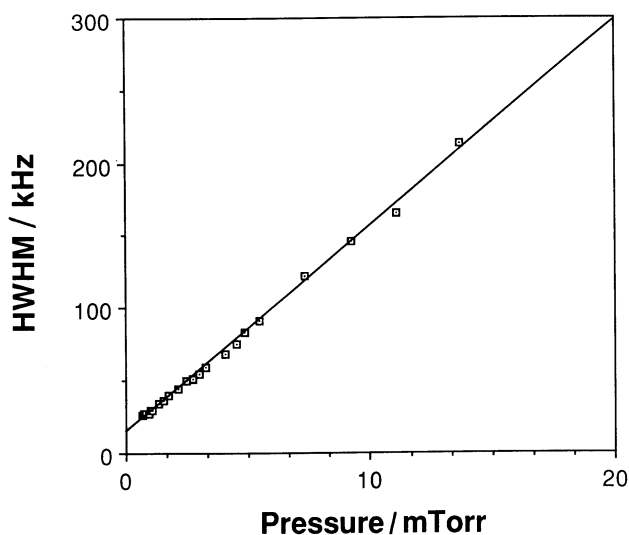


Figure 3. A plot of the measured linewidth of NO as a function of helium pressure at 2.45 K.

der Waals molecules and clusters as well as ions and other transient species. Finally, collisional cooling at very low temperature may help to provide insight into collisional processes in the interstellar medium.

3. Results

For this work the $F = 3/2-5/2$ hyperfine component of the $J = 1/2-3/2$ transition of the lower component of the Λ doublet of NO was studied at 7 different temperatures between 4.21 and 1.79 K. The same transition of the upper component of the Λ doublet was also studied at 4.2 K and found to have the same pressure

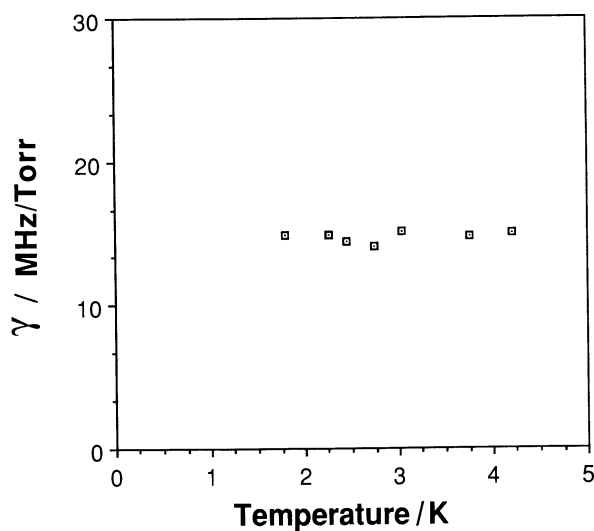


Figure 4. Measured pressure broadening coefficients for NO-He for the region below 5 K.

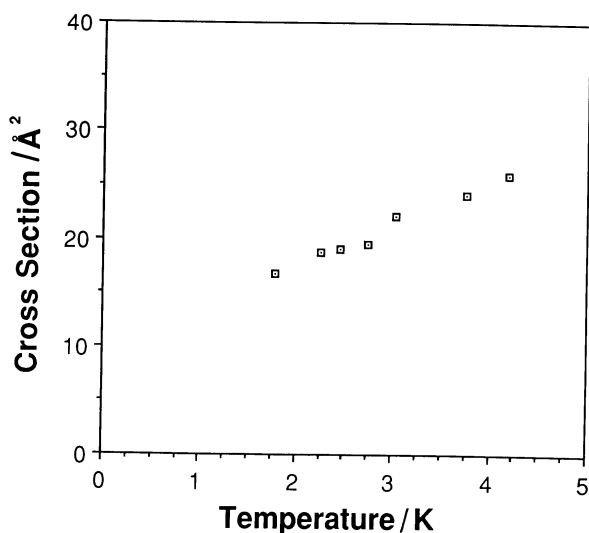


Figure 5. Measured pressure broadening cross sections for NO-He for the region below 5 K.

broadening parameter as the lower component. Figure 4 shows the observed pressure broadening parameters as a function of temperature for the region below 5 K. The relation, $\sigma = 0.447(\mu T)^{1/2}\gamma$, where μ is the reduced mass in AMU, and T the temperature in kelvin, was used to convert pressure broadening parameters, γ , in MHz/Torr to cross sections, σ , in Å². Figure 5 shows the resulting cross sections. If these observed cross sections are to be compared with theoretical calculations, the results of the calculations must be averaged over the thermal velocity distribution. This is especially important in cases where the calculated cross sections show sharp resonances as a function of collision energy. Although NO is one of the most spectroscopically investigated molecules, we are not aware of any previous studies of NO broadened by helium. This is perhaps because much of the research on this species has been driven by atmospheric considerations in which interactions with

Pressure broadening parameters and collision cross sections for the $J = 1/2-3/2$, $F = 3/2-5/2$ transition of NO.

Temperature (K)†	Pressure broadening‡ parameter (MHz/Torr)	Cross section Å ² ‡
Lower component of Λ doublet (150 176.52 MHz)		
1.79	14.9	16.8
2.26	14.9	18.9
2.45	14.5	19.0
2.74	14.0	19.5
3.03	15.1	22.0
3.75	14.8	24.0
4.21	15.0	25.9
300.0	1.81	22.1
Upper component of Λ doublet (150 546.50 MHz)		
4.20	15.0	25.9

† Experimental uncertainty estimated at ± 0.02 K.

‡ Absolute uncertainty estimated at ± 10 per cent, relative uncertainty at ± 5 per cent.

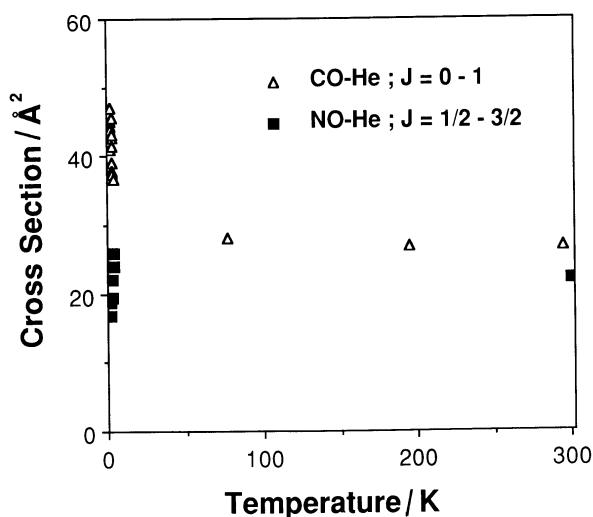


Figure 6. Pressure broadening cross sections for NO-He and CO-He below 300 K.

O₂ and N₂ are more important. As a result, we have also measured the broadening at 300 K to provide a reference for the very low temperature work reported here. The table collects these results in numerical form. Although the fits to our data yield statistical uncertainties of a few percent, a 10 per cent uncertainty is quoted to account for the well known systematic effects that can plague pressure broadening experiments.

4. Discussion

Figure 6 shows the measured pressure broadening cross sections for temperatures below 300 K for NO-He collisions as well as earlier results for CO-He. Although the majority of the points are compressed at the left of the plot, this graph shows the relation between the cross sections in the classical regime, where inelastic collisions are dominant, and the very low temperature regime, where resonance effects can be important.

Structurally, CO and NO are similar species. They have similar masses, bond lengths, dipole moments, and moments of inertia. Although no specific experimental or theoretical information is available on the NO-He cross section between 300 and 4.3 K, the results for the similar CO-He system [2, 5, 6, 11] lend strong support to an assumption that the cross section of the NO-He system remains essentially constant from 300 K to temperatures well below 77 K. Thus, in this region these collisions can be understood in the context of simple hard collisions. For example, a variety of experimental and theoretical studies of the CO-He system between 300 and 77 K for $J \leq 10$ give a pressure broadening cross section of $\sim 28 \text{ \AA}^2$ [11, 12-14], independent of rotational transition. These essentially invariant results are presumably because: (1) over this temperature range the collision energy is much larger than the energy level spacing, thereby making inelastic collisions probable, and (2) the short range nature of the interaction coupled with the many energetically allowed channels averages out any significant quantum effects. Our measurement at 300 K of the NO-He system yielded essentially the same cross section as that

obtained for the CO–He system. Since CO and NO are geometrically similar this result is consistent with this simple picture.

A detailed calculation by Green and Thomas [15] for the CO–He system is especially illuminating. They calculated cross sections using potentials derived from both electron gas and self-consistent field-configuration interaction (SCF-CI) models for a wide range of collision energies. From room temperature to below the energies corresponding to 77 K, both potentials yielded essentially the same cross sections, but at the lowest collision energies ($\sim 15 \text{ cm}^{-1}$) the calculated cross sections differed by more than a factor of two. This result illustrates the relative insensitivity of pressure broadening measurements at higher temperatures to the details of the intermolecular potentials.

It is interesting to note that the pressure broadening cross sections of CO and NO, although similar above 4.3 K, diverge at lower temperature, with CO having more than twice the cross section at 1.8 K. The only detailed calculations that have been done on collisional processes in the very low temperature regime are for the CO–He system. Fortunately, since this is a fairly similar system it can serve to provide at least a qualitative understanding of the results obtained in this work for the NO–He system. Green showed that at temperatures below 4 K a sharp increase in cross section could occur due to the existence of resonances at very low energy [5]. These resonances resulted from quasi-bound states associated with a shallow attractive well in the CO–He potential. More recently, the calculations of Green and Palma on the CO–He system showed that a decrease in the assumed attractive potential could change the predicted rise in cross section at low temperature into a decline, with the limit of no attractive potential predicting a cross section of zero at zero kelvin [6]. On the other hand, with the attractive potential held constant, the number of energetically accessible collision channels decreases, as the energy gap between adjacent states widens. Because NO is in a $^2\Pi_{1/2}$ electric ground state, its lowest energy rotational transition is $J = 1/2$ to $J = 3/2$, an energy spacing of about one-and-a-half times that of the $J = 0-1$ transition of CO. It is possible that the decline in the cross section in the NO–He cross section is due to the wider level spacing in NO, but until a detailed calculation for the NO–He system is done, it is not possible to rule out the possibility that the drop is due to a smaller attractive potential.

5. Summary

This paper has reported recent results of a very low temperature pressure broadening experiment on the NO–He system in a collisionally cooled cell and compared them with earlier results for the CO–He system. From this, we concluded: (1) in the temperature regime for which $kT \gg hv$, observed pressure broadening cross sections are insensitive to the details of the collision for both the NO–He and CO–He systems and can be viewed as due to simple hard interactions, and (2) for the temperatures below 5 K where $kT \leq hv$, the cross sections can either rise or fall depending upon the effectiveness of the resonances associated with the shallow attractive potential in countering the fall in total cross section that results from a declining inelastic cross section. We have also discussed some of the important attributes of the collisional cooling technique. Among these are: (1) a reduction in Doppler limited linewidths of about an order of magnitude, (2) increases of several orders of magnitude in absorption coefficients, (3) the opportunity to investigate

molecular interactions at or near equilibrium in a regime where $kT \leq hv$, and (4) applications to a wide variety of other scientific problems.

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