Direct Measurement of Rotationally Inelastic Cross Sections at Astrophysical and Quantum Collisional Temperatures

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The first measurements of rotationally inelastic collision cross sections over the 1–40 K temperature range characteristic of much of the interstellar medium are reported. Measurements of the $1_{1,0}$-$1_{0,1}$ transition of H_2S in collision with He are based on a collisional cooling methodology, which allows the direct observation of collision processes at temperatures far below the limits ordinarily imposed by vapor pressure. These cross sections are also of fundamental interest because resonant formation of quasibound complexes mediates rotational energy transfer at low collision energy. [S0031-9007(98)06538-7]

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The physics of collisions between atoms and molecules at low temperature ($\sim$1–20 K) is fundamentally different from that typically observed near ambient. At low temperatures, the collision energies are comparable to the depths of the shallow wells in the intermolecular potentials (IMPs), making resonant formation of quasibound complexes possible. This fundamentally alters the description of the collision from that of "action at a distance," which can be formulated as an interaction between charge distributions, to one in which the quasibound state plays a basic role.

Although this regime is of both astrophysical and fundamental interest, the basic problem of studying collisions at low temperature, where most of the species of interest have insignificant vapor pressure, has severely restricted available experimental data. James *et al.* [1] have recently measured low temperature rotationally resolved inelastic cross sections using molecular beam techniques and optical spectroscopy. We have previously described a collisional cooling method which overcomes vapor pressure limitations, and we reported measurements of both pressure broadening and pressure shifts for neutral species [2,3]. More recently, we have reported the extension of this method to the study of ions at low temperature [4], and Willey *et al.* have demonstrated an ammonia maser in a laboratory collisional cooling cell, where population inversion results from differential relaxation along inelastic scattering channels [5].

In this Letter we report the extension of the collisional cooling technique to make the first direct time resolved measurements of collision induced rotationally inelastic cross sections across a temperature range of 1–40 K. Specifically, we have measured inelastic cross sections involving the $1_{1,0}$-$1_{0,1}$ radiative transition of H_2S in collision with He. H_2S has been identified in a number of interstellar sources [6], and its inelastic cross sections can play a fundamental role in modeling interstellar clouds. In general, low temperature inelastic cross sections are required for the interpretation of data obtained from radio telescopes because molecular species in the interstellar medium are often not in local thermodynamic equilibrium.

We have previously described the details of the collisional cooling technique for the measurement of line broadening and shifts for both neutral [2] and ionic [4] systems. In summary, small amounts of condensable, spectroscopically active sample gas molecules are injected into a region filled with either cold He or H_2 gas at a pressure of $\sim$1–10 mTorr to form a dilute mixture ($\sim 10^{-4}$–10^{-6}). The sample molecules collisionally cool to the temperature of the cold background gas in $\sim$100 collisions, and under the conditions of the experiment take $\sim$10 000 collisions to reach the wall. The result is a quasiequilibrium mixture of the sample gas and its collision partners which has well-defined and measurable temperature and pressure.

We will briefly focus on the extension of the collisional cooling methodology for millimeter wave double resonance measurements of rotationally inelastic cross sections. At room temperature, infrared pumps (typically CO_2 lasers) are convenient for creating nonequilibrium populations in rotational levels of excited vibrational states because $h\nu > kT$. The collision induced rotational relaxation is then monitored by infrared or microwave probes [7]. However, at low temperature, large nonequilibrium populations can be created with millimeter wave pumps, for which $h\nu \geq kT$. Figure 1 shows a schematic diagram of the current experimental apparatus for time resolved experiments. The pump, a backward wave oscillator based synthesizer, is locked to a line center, and its power is square wave amplitude modulated. The weaker probe, a klystron driven harmonic generator system, is locked to a line center in a continuous wave mode. The probe monitors the population difference of the two levels as the system returns to equilibrium following the perturbation of the pump radiation. We use a liquid helium cooled InSb hot electron bolometer ($\sim$1 MHz bandwidth) to detect the probe radiation. The pump and probe sources are

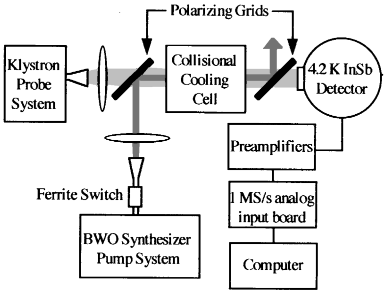


FIG. 1. A block diagram of the millimeter wave pump/probe system integrated with a collisional cooling system for time resolved measurements of inelastic cross sections between 1 and 40 K.

polarized perpendicular to each other, and we reflect most of the pump power away from the detector with a wire polarizer.

The dominant physics of low temperature collisions differs from that of ambient collisions and the resulting cross sections can have a strikingly different functional dependence on temperature. For example, an Anderson-like formulation of the transition probability of near ambient collisions [8] has been pedagogically simplified by Townes and Schawlow [9] to

$$|\langle a|P|b\rangle|^2 \propto \left| \int_{-\infty}^{\infty} \frac{e^{ikx}\,dx}{(1+x^2)^{n/2}} \right|^2, \qquad (1)$$

where $k = (2\pi b/v)\nu_{\mathrm{ab}}$ and $x = vt/b$. In this "action-at-a-distance" picture, the molecule sees a pulsed electric field as the collision partner passes, and the Fourier components of this pulse interact with the multipole moments of order n to induce a transition from state a to state b. As $T \rightarrow 0$ and $k \rightarrow \infty$, the transition probability becomes zero in accordance with the Fourier integral of Eq. (1).

However, at collision energies comparable to the depth of the intermolecular well, the long range tail of the IMP can lead to the capture and the resonant formation of a quasibound state even at very low energy. While it is intuitive that the formation of a quasibound state always leads to broadening because it completely destroys the phase information, it is less clear if the dominant output channels from the quasibound state will represent elastic or inelastic processes. Much of our understanding of the related low energy processes has been obtained theoretically from "exact" quantum scattering techniques [10,11]. These calculations provide a means to test and intercompare the results of *ab initio* calculations of IMPs [12], the spectroscopy of weakly bound complexes and the IMPs calculated from them [13,14], and the results of our measurements of pressure broadening, pressure shift, and inelastic scattering cross sections. It has been found both experimentally and theoretically that, in addition to the depth and shape of the IMP, the availability of energetically accessible rotational states (which can temporarily store energy) plays an important role [15].

The $1_{1,0}$-$1_{0,1}$ transition of H_2S was chosen for the initial experiment because at low temperatures the states are isolated from all of the other states of like symmetry by an energy gap equivalent to 27 K, thereby giving a very close approximation to an ideal two level system. The time resolved data analysis follows Bloch's description of a two level nuclear spin system in a magnteic field [16]. This description has been extended to molecular transient effects by McGurk, Schmalz, and Flygare [17]. In these treatments, the empirical parameter T_1 is ordinarily identified with collision induced changes in the population of rovibrational states. In an ideal two level system, $1/T_1$ is simply the sum of the upward and downward state-to-state rates, the ratio of which is determined by detailed balance. The parameter T_2 is identified with the changes in polarization which lead to pressure broadening. In addition to the state changing transitions associated with T_1, contributions to T_2 can arise from elastic, or purely phase changing, collisions. The use of weak pump and probe power (such that $\mu E/h \ll 1/T_1, 1/T_2$) effectively eliminates coherent effects in the model. We find that an exponential decay model and full Bloch model [18] yield the same results for T_1 to within experimental uncertainty. Figure 2 shows a typical time resolved signal measured at a helium pressure of 2.00 mTorr and a temperature of 2.58 K. While the pump is on ($t < 82$ μsec), we observe heterodyne mixing of the pump and probe signals on the detector, which greatly amplifies the observed noise.

The inelastic rate $(1/2\pi T_1)$, like the pressure broadening linewidth $(1/2\pi T_2)$, exhibit a linear dependence on the He gas pressure in the cell. Inelastic and pressure broadening cross sections were calculated using

$$\sigma(T_{1,2}) = 0.447\sqrt{\mu T}\,\gamma_{1,2}\,, \qquad (2)$$

where $\sigma(T_1)$ and $\sigma(T_2)$ are the inelastic and pressure broadening cross sections in Å^2, μ is the reduced mass in amu, T is the cell temperature in K, and γ_1 and γ_2 are the inelastic and broadening parameters in MHz/Torr. The cross sections $\sigma(T_1)$ and $\sigma(T_2)$ have been plotted,

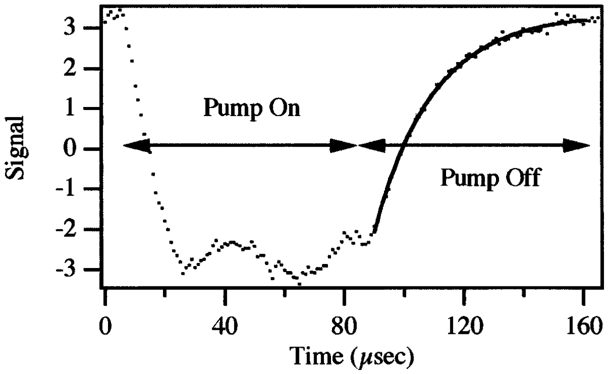


FIG. 2. A typical time resolved H_2S-He probe signal and fit at a helium pressure of 2.00 mTorr and a temperature of 2.58 K. The pump is switched at a 6 kHz rate, and the fit is performed a few microseconds after the pump is switched off.

along with pressure shift cross sections, as a function of temperature in Fig. 3. Pressure broadening cross sections above 20 K were measured by Flatin *et al.* [19] and those below 20 K were remeasured for this study. The remeasured cross sections are about 25% greater than those reported by the previous study.

Figure 3(a) shows that, except at low temperature, the pressure broadening cross sections behave as expected from semiclassical theory. At high temperature ($T > 200$ K), the cross sections are approximately constant, but as the temperature is reduced the collisions do not have sufficient Fourier components to excite rotational transitions, and the cross sections decline. Figure 3(b) shows that, below 40 K, the inelastic and pressure broadening cross sections diverge, with the inelastic cross sections being less than the pressure broadening.

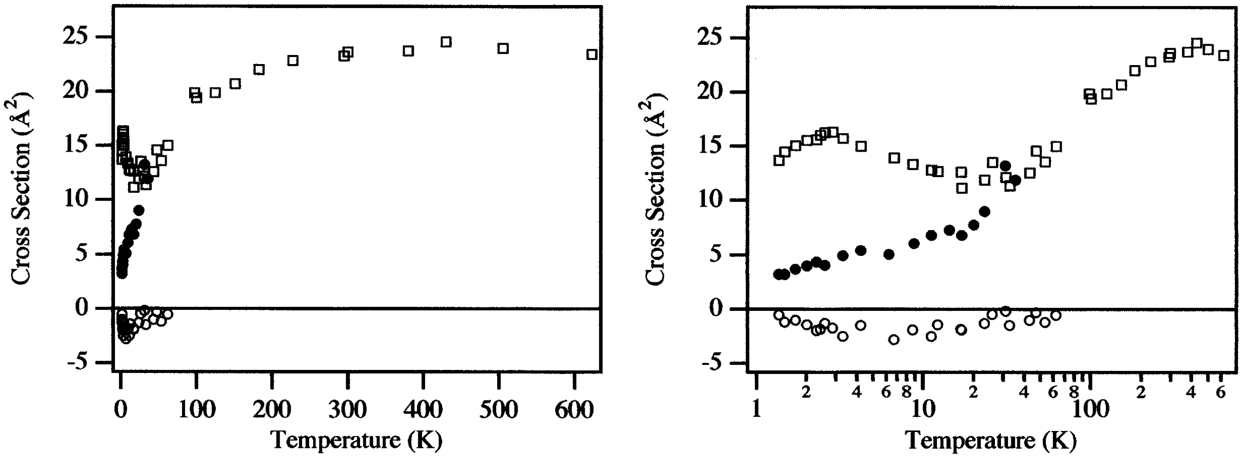
In the absence of elastic collisions, Hoke *et al.* [20] show that, for a two level system in sufficient thermal isolation from other levels, $\sigma(T_1) = 2\sigma(T_2)$ because collisions which deplete one level necessarily populate the other. In contrast, the low temperature data show that $\sigma(T_2)$ are larger by as much as a factor of 3, showing the dominance of elastic collision processes in the low temperature regime. The $\sigma(T_1)$ may become larger than the $\sigma(T_2)$ at temperatures higher than 40 K, but we are currently unable to measure them due to insufficient pump capacity at these higher temperatures.

Quantum scattering calculations can, in principle, provide detailed insight into these results. Unfortunately, to the best of our knowledge, an IMP for the H_2S-He collision system does not exist. However, it is possible to use the well-studied CO-He system to illustrate the underlying physics. Figure 4 shows theoretically calculated CO-He pressure broadening cross sections as a function of collision energy as well as all of the significant state-to-state inelastic cross sections. The MOLSCAT routines of Hutson and Green [21] and the IMP of Le Roy *et al.* [14] were used in these calculations. The thermal average observed in experiments has not been done so that a detailed comparison of the underlying resonance structures is possible.

The salient features of Fig. 4 follow. First, some of the resonances associated with the quasibound states in the pressure broadening cross sections can also be observed in the inelastic cross sections. Second, there are significant resonances (e.g., those at 1 and 3 cm^{-1}) in the pressure broadening cross sections which are not associated with inelastic collisions. Third, the upward inelastic rates have low energy thresholds consistent with the conservation of overall energy. Finally, the magnitudes of the cross sections in the pressure broadening resonances are not the exact sum of the inelastic rates and are often less than the sum.

For the H_2S-He system, there is the possibility of a sparse, weak resonance in the cross sections, but this will remain unclear until an H_2S-He IMP is developed and calculations are done with MOLSCAT. The best evidence for an underlying resonance structure can be seen in the pressure broadening cross sections, which show an increase with decreasing temperature between 30 and 2.5 K, and the pressure shift cross sections, which are largest in this region. Calculations show that appreciable pressure shifts are also associated with the resonant formation of quasibound states. H_2S-He cross sections, however, should exhibit fewer and smaller resonances than in the case of CO-He because the H_2S rotational energy levels are more widely spaced and energetically less accessible than in CO.

In conclusion, we have made the first measurements of rotational inelastic cross sections for molecule-atom collisions across the 1–40 K temperature range. The experimental method is general and is applicable to a



(a) (b)

FIG. 3. Rotationally inelastic [$\sigma(T_1)$—solid circles], pressure broadening [$\sigma(T_2)$—open squares], and pressure shift (open circles) cross sections for collisions of H_2S with He. Data are plotted on a linear scale in graph (a) to show the transition between classical and quantum regimes, and on a semilogarithmic scale in graph (b) to more easily view the low temperature phenomena.

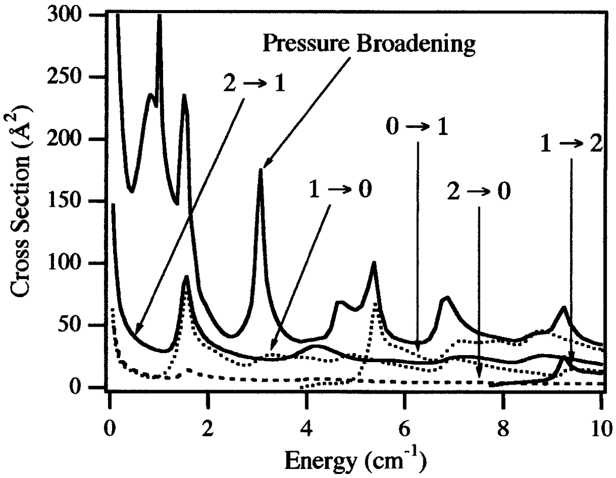


FIG. 4. Calculated inelastic and pressure broadening cross sections of CO in collision with He as a function of collision energy from the IMP of Le Roy *et al.* [14]. Individual state-to-state inelastic cross sections (labeled $i \longrightarrow j$) exhibit resonances which coincide with some of the resonances in the pressure broadening cross sections. Additionally, the pressure broadening cross sections exhibit resonances from elastic processes, which do not coincide with the inelastic resonances.

large number of astrophysically significant systems as well as the systems which are most appropriate for the development of our basic understanding of low energy quantum collisions. The dominant physics and appropriate models are radically different from those which govern collisions near ambient conditions, being the resonant formation of quasibound complexes rather than action at a distance. Based on the results shown in Fig. 3 and the understanding obtained from a number of measurements of the pressure broadening and pressure shifts of other systems, we believe for the H_2S-He system that the paucity of energetically accessible rotational states in H_2S results in a much sparser set of resonances than in the CO-He system and a resulting drop in both the inelastic and broadening cross sections at low temperature. Additionally, the difference between the inelastic and pressure broadening cross sections shows the substantial role of elastic collisions in the broadening of spectral lines at low temperatures.

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