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Infrared Laser Spectroscopy of Molecular Beams

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Abstract

A newly constructed crossed molecular beam apparatus and tunable infrared laser system is described. The Doppler effect has been used to measure the narrow velocity distribution in a molecular beam formed from a free jet expansion and to study the translational relaxation which occurs downstream of the nozzle orifice. In addition a laser–crossed molecular beam experiment is described which is designed to measure the rotational and vibrational state dependence of the total scattering cross section of hydrogen fluoride with helium.

1. Introduction

A molecular beam technique provides a method for preparing a stream of atoms or molecules that are widely separated and that are largely in a single internal energy state. Although these methods have recently been applied in a wide variety of fields, they have been best exploited as a tool for studying molecular collision processes. Until fairly recently the low beam intensities from effusive sources largely restricted applications to measurements of total scattering cross sections for inert gas atoms (Amdur and Mason 1954; Amdur and Harkness 1954). The high sensitivity of hot wire detectors enabled the first accurate measurements of elastic differential cross sections to be made by scattering alkali metal atoms from a variety of atoms and molecules (Rothe and Helbing 1968; Barwig et al. 1966). At about the same time major advances in the construction and understanding of supersonic jet sources (Anderson et al. 1965, 1966) permitted scattering techniques to be applied to other systems. The major advantages of these sources compared with effusive sources include substantial increases in beam intensities as well as considerable reduction in the energy distribution. These characteristics are ideal for high resolution differential scattering experiments and have been applied to a wide variety of systems. The quality of the data provided by elastic scattering experiments of this type has continued to improve to the present time.

Among the earlier high resolution differential scattering measurements were those on the Ar/N_2 system by Bickes and Bernstein (1969) who were able to resolve the primary rainbow oscillation. Later, Cavallini *et al.* (1970) resolved the quantum oscillations in He/He scattering and Parson *et al.* (1970) resolved both the primary and supernumary rainbows in the noble gas systems. The following year Siska *et al.* (1971) used the same methods to measure symmetry oscillations in both the He/He and Ne/Ne systems. Recently several molecular beam experiments have been performed which make use of time-of-flight techniques to obtain information concerning rotational energy transfer. Results have been obtained as a function of scattering angle and collision energy for several systems (Buck *et al.* 1977; Gentry and Giese 1977) and provide very stringent tests for non-spherical intermolecular potentials.

The usefulness of molecular beam methods in the above fields relies as much on the development of detection systems as it does on the introduction of improved beam sources. Quadrupole mass spectrometers give a remarkably efficient method for detecting neutral species (Fluendy and Lawley 1973) and have been traditionally used in molecular beam studies. This system has the added advantage that when coupled with time-of-flight techniques it provides a method for studying energy transfer processes. A significant disadvantage is the requirement of ultra-high vacuums in the immediate area of the ionizer. This constraint can be satisfied by introducing two or more stages of differential pumping after the collision region.

Cavallini *et al.* (1967) have developed a sensitive detection system based on the use of an infrared bolometer (Low 1961). Their system can also detect extremely low beam fluxes and has a signal-to-noise level comparable with that of a standard quadrupole system. The bolometer detector does not require an ultra-high vacuum system to achieve this end although cryogenic facilities are needed. As the bolometer is an energy detector it does not give mass discrimination; however, when combined with a tunable infrared laser system it provides a method for the state selective identification of different molecular species (Gough *et al.* 1977).

With the advent of new tunable visible and infrared laser systems it has recently become feasible to combine the advantages of spectroscopy and molecular beam techniques. In the visible region of the spectrum, where dye lasers can be used to obtain laser-induced fluorescence spectra, a large number of experiments have recently been performed. These can be divided into two categories, namely experiments which make use of the internal cooling and collision-free nature of the beam to improve the quality of the spectra obtained (Smalley *et al.* 1974) and experiments which use the laser to probe particular quantum states before or after a collision event (Serri *et al.* 1981). Although these methods have wide applications to the spectroscopy of complex molecules, the number of simple molecules having absorptions within the tuning range of available laser systems is limited. As a result, in the case of collisional studies, the number of systems for which there is an overlap between theory and experiment is rather small.

In the infrared region of the spectrum, where the number of simple systems that can be studied is considerably larger, the technique of laser-induced fluorescence becomes ineffective. This is a result of the long fluorescence lifetimes and the lower sensitivity of detectors in this spectral region. The use of liquid helium cooled bolometer detectors provides a very sensitive method for observing laser-induced rovibrational excitation in molecular beams (Gough *et al.* 1977, 1978, 1981). This is done by using the bolometer to detect directly the increase in molecular energy resulting from laser-induced vibrational excitation. As the bolometer is operated at 2 K essentially all of the molecules reaching its surface will condense, releasing their translational energy, any internal energy, and the adsorption energy. This process increases the temperature of the detector and the resulting change in its resistance is proportional to the energy released. In the case of a molecule, where the laser can be used to excite vibrational states, the spectrum can be obtained from the corresponding change in bolometer signal.



Fig. 1. Schematic diagram of the crossed molecular beam apparatus. In the elevation view, A and B represent cryostat positions, C is the chopper, F a flag, N the nozzle, S the skimmer and A.T. the alignment telescope. In the plan view, B is the bolometer, PBC the primary beam chamber and SBC the secondary beam chamber.

In this paper we describe a new apparatus that allows the infrared laser/bolometer technique to be used to study a variety of collision phenomena. It consists of two supersonic molecular beam sources, a tunable infrared laser and a variety of detection systems, including a quadrupole mass spectrometer and a cryogenic bolometer. The flexibility of the system is demonstrated by describing applications to the study of relaxation processes in a supersonic expansion as well as to the measurement of the internal state dependence of the total scattering cross section for HF–He.

2. Experimental Apparatus

Fig. 1 shows a schematic diagram of the in-plane crossed molecular beam apparatus used in the present study. The main vacuum system consists of a stainless steel chamber to which is fitted a rotatable bottom flange. A rotary seal is provided by a conventional O-ring and a ball-bearing track located outside the vacuum system. Two $1600 \ 1. \ s^{-1}$ diffusion pumps are used to maintain a background pressure in the chamber of less than 1×10^{-6} Torr (1 Torr = 133 Pa). Inside the main chamber, and mounted on the base plate, are two molecular beam source chambers. The primary and secondary beam chambers are pumped by 5300 and 2400 $1. \ s^{-1}$ diffusion pumps respectively. Typical operating pressures in these chambers are in the range 10^{-3} – 10^{-4} Torr. Two conical skimmers ($26^{\circ}/30^{\circ}$), having 500 μ m diameter holes machined at their apex, are used to sample the beam expansions. In the experiments discussed here the primary (secondary) beam was formed by expanding gases through a 40 μ m (45 μ m) diameter room temperature nozzle. This configuration allows the nozzle sources to be rotated relative to various fixed detection systems.



Fig. 2. Spectrum for the R(0) transition of hydrogen fluoride measured in the beam, demonstrating a method for measuring stream velocities and energy distribution (see Section 3).

A liquid helium cooled cryostat, housing the bolometer detector, can be mounted in one of the two positions A or B, shown in Fig. 1. In position A the bolometer is used to monitor the primary beam. This geometry is used either to characterize the initial beam conditions or for high resolution spectroscopic studies. For differential scattering measurements, the cryostat is moved to position B to increase the solid angle subtended by the detection system. The bolometer itself is an antimony-doped silicon chip (2 by 6 by 0.5 mm) onto which are spot welded two gold wires. These leads are indium-soldered to copper wires that are in good thermal contact with, but electrically insulated from, the copper bottom of the liquid helium cryostat. The temperature of the detector is maintained near 2 K by continuous pumping on the helium. Under these conditions the bolometer has a response time of approximately 20 ms and an N.E.P. of 2×10^{-12} W Hz^{-‡}. A second thermal detector is used to monitor the secondary molecular beam. This device is a commercially available room temperature pyroelectric detector (Molectron P1-71) and has an N.E.P. of 3×10^{-10} W Hz^{- $\frac{1}{2}$}. Its use as a detector in molecular beam experiments, particularly to study relaxation processes during a supersonic expansion, is described in detail elsewhere (Miller 1982).

The laser system consists of an F-centre laser (Burleigh FCL-20) pumped by the 647 \cdot 1 nm line of a Kr⁺ laser (Spectra Physica 171). This system provides continuously tunable radiation in the wavelength range $2 \cdot 2 - 3 \cdot 1 \mu m$ with an output power of approximately 10 mW (Mollenauer 1975; Beigang *et al.* 1978). The laser has a linewidth of 1–2 MHz and this is well matched to the residual Doppler width determined by the divergence of the molecular beam. This consideration is important since it is the power per unit band width that determines the efficiency of the excitation.

3. Results and Discussion

As indicated in the Introduction, a supersonic nozzle source can be used to produce high intensity monoenergetic molecular beams. Traditionally, the stream velocity and energy distribution in the beam have been measured using time-of-flight techniques. Recently a method for measuring these quantities that is based on the Doppler shift of absorption lines has been developed (Bergmann *et al.* 1975, 1978).

Fig. 2 demonstrates how this technique is applied using the molecular beam-laser system described in the previous section. This spectrum shows the R(0) transition for hydrogen fluoride and was determined for a 10% mixture of hydrogen fluoride in helium expanded from a source pressure of 2 atm (1 atm = 101325 Pa). It was obtained by adjusting the apparatus to provide 90° and 46° crossings of the laser and molecular beams. The narrower transition is a result of the 90° crossing and its width is determined by the residual Doppler broadening due to the finite width of the detector. Some idea of the power of this method as a spectroscopic tool can be obtained by comparing the linewidth of this measurement, 8 MHz, with the value of 330 MHz expected for a gas at room temperature. The broad peak shown is due to the 46° crossing and is representative of the velocity distribution in the beam. Making use of the etalon trace that is also shown, and the frequency difference between the two peaks, we find the stream velocity to be 1.55 km s^{-1} . The width of the 46° crossing transition is proportional to the energy distribution in the beam and corresponds to a translational temperature of 25 K. Although this method can only be applied to systems that absorb within the tuning range of the laser, it does provide the interesting possibility of obtaining state-dependent velocity distributions.

As previously indicated, the idea of using a thermal detector to observe the increase in molecular energy resulting from laser excitation is a very attractive one. We have recently examined the possibility of using a thermal detector operating at room temperature (Miller 1982) in order to remove the need for liquid helium. Although such detectors are less sensitive than the bolometer, they are inexpensive, simple and compact, and can be incorporated into an existing apparatus. In this study the pyroelectric detector described in the previous section was placed 7 cm downstream of the secondary beam skimmer, as shown in Fig. 3. The laser was focused to a $450 \ \mu m$ (FWHM) waist just upstream of the skimmer orifice. The distance between the laser crossing and the secondary nozzle was varied by moving the nozzle on an *xyz* translation stage (see Fig. 1).



Fig. 3. Schematic diagram of the laser system showing how it is interfaced with the molecular beam: S, skimmer; M, mirror; D, detector; BS, beam splitter.



Spectrum A in Fig. 4 shows the R(0) transition for a mixture of 10% hydrogen fluoride in helium obtained at large laser-nozzle crossing distances and demonstrates the sensitivity of this technique. The spectrum obtained in this way is comparable with that given in Fig. 2, showing that the device provides an attractive alternative to the bolometer under circumstances where the reduced sensitivity can be tolerated. One example is in laser-induced chemistry where the device could be used to monitor the amount of vibrational excitation in the beam of reactants. Since the molecules in the beam do not stick to the surface of the room temperature detector, as they do on the bolometer, vibrational accommodation with the surface is not assured. However, the spectra shown in Fig. 4 suggest that the vibrational accommodation coefficient is quite large.



Fig. 5. Linewidth as a function of nozzle-laser crossing distance X (in units of D_n). The solid curve represents calculated values based on a smooth transition from continuum to free molecular flow. The dotted curve represents calculated values based on the sudden freeze model.

Having demonstrated the usefulness of the pyroelectric detector in spectroscopic beam experiments let us now consider what effect crossing the laser within the collision region, close to the nozzle, has on the observed spectra. As shown in Fig. 4 the linewidth of the transition increases as the nozzle-laser crossing distance (X) is decreased. Fig. 5 gives the experimentally determined linewidths as a function of X (in units of nozzle diameter D_n) together with the results of two theoretical calculations. The linear behaviour at large distances represents the residual line broadening due to the finite detector size and shows that the laser excitation occurs within the free molecular flow regime. Any deviation from this linear behaviour, as seen at small distances, can be attributed to collisions in the expansion. In the absence of collisions, molecules that at the time of excitation have large velocities perpendicular to the beam miss the detector and hence do not contribute to the linewidth. However, if these molecules undergo a number of collisions after excitation, their perpendicular velocities can be altered such that they reach the detector. Consequently the increased Doppler width observed for short distances gives a measure of translational relaxation in the expansion region. If excitation occurs sufficiently far upstream, so that the number of collisions experienced by the excited molecule is sufficient to scramble the molecular velocities, then the observed width is representative of the translational temperature at the point of excitation.

The calculated linewidths shown in Fig. 5 were obtained from an expression for the translational temperature as a function of distance downstream of the nozzle. This expression is based on an empirical equation for the Mach number (Ashkenas and Sherman 1966) and the isentropic equation relating the temperature to the Mach number (Zucrow and Hoffman 1976). A detailed discussion of these calculations is given in the paper by Miller (1982). It is found that the Doppler width resulting from this calculation of the translational temperature is substantially greater than that determined by geometrical factors out to distances beyond the point where collisions cease. Consequently we expect the experimental results to follow the calculated curve to distances where the collision rate is no longer sufficient to scramble the molecular velocities. Beyond this point a transition to the curve determined by geometrical effects must occur. The solid curve shown in Fig. 5 was calculated assuming that this transition occurs smoothly, whereas the dotted curve was obtained assuming that the collision rate falls suddenly to zero (Anderson et al. 1965). Clearly, the experimental results indicate that there is a smooth transition from hydrodynamic to free molecular flow.



In addition to using the apparatus to study relaxation processes we have also used the above techniques to examine collision processes between atoms and state-selected molecules. Fig. 3 shows schematically the experimental geometry used in this work. A primary beam of helium is formed by expanding the gas from a stagnation pressure of 14 \cdot 5 atm. It is attenuated by a secondary beam formed from a mixture of 10% hydrogen fluoride in helium. As discussed above, the laser can be used to modulate the relative populations of the hydrogen fluoride ro-vibrational states. If the HF-He total scattering cross section varies with the internal state of the molecule, then this dependence can be obtained by measuring the corresponding change in the bolometer signal. We present here preliminary results for the variation in cross section resulting from R(0) and P(1) excitations of hydrogen fluoride at a collision energy of 0.09 eV. This energy has been estimated using the hydrogen fluoride stream velocity determined from Fig. 2 and an estimated helium stream velocity of 1.76 km s⁻¹.

Before discussing the experimental data we must consider several factors that complicate the interpretation of the results. These are associated with the fact that the laser-molecular beam crossing occurs upstream from the skimmer. The reason for choosing this geometry was to maximize the efficiency for exciting hydrogen fluoride molecules that subsequently enter the scattering volume. However, as seen earlier, if the laser excitation occurs close to the nozzle it is necessary to take into account the collisions which occur downstream from this point. In this case at least part of the laser-induced change in attenuation of the primary beam can be caused by density fluctuations in the secondary beam. These result from the relaxation of the laser-excited internal energy of the molecules. On the other hand, if the laser excitation occurs sufficiently far downstream so that there is free molecular flow, any laser-induced change in the attenuation must be attributed to the dependence of the scattering cross section on the internal state of hydrogen fluoride. The results reported in Fig. 5 suggest that both the collisional and free molecular flow regimes are covered by scanning X over the range shown.

Fig. 6 shows the laser-induced bolometer signal as a function of X for the R(0)and P(1) transitions of hydrogen fluoride. The bolometer signals plotted here have been normalized by the corresponding signal from the pyroelectric detector to remove effects due to variations of the excited state populations in the secondary beam. A positive bolometer signal represents a decrease in the primary beam attenuation as a result of the laser-induced excitation. The large positive signals observed at small distances can be explained in terms of vibrational relaxation in the collision region. This leads to an increase in the translational temperature and a corresponding decrease in the density. Ellenbroek et al. (1981) have reported measurements on a pure hydrogen fluoride beam which indicate that the major relaxation mechanism in the expansion region is due to vibrational-vibrational energy transfer from HF to (HF)₂. We have examined the possibility of this mechanism being significant for the mixture used here by heating the nozzle to a temperature in excess of 500 K. No changes were observed in the normalized bolometer signals. As this heating will obviously change the (HF)₂ concentration significantly we conclude that the dominant relaxation mechanism is vibrational-translational energy transfer.

As X increases, both signals decrease rapidly, with the R(0) result remaining positive and the P(1) becoming negative. At large distances both signals tend towards zero due to the fact that the nozzle-skimmer separation is increased. This in turn leads to a decrease in the attenuation of the primary beam.

If we assume that laser excitation occurs entirely within the collision-free regime, as is suggested by Fig. 5, these positive and negative effects can be explained in terms of the state dependence of the HF–He total cross sections. For the R(0) transition, the bolometer signal is proportional to the difference between the cross sections for ground and excited state hydrogen fluoride and can be written as

$$S_{\mathbf{R}(0)} = c\{\sigma(J=0, v=0) - \sigma(J=1, v=1)\},\$$

where c is a constant.

Since the observed bolometer signal is positive at large values of X we conclude that

$$\sigma(J=0, v=0) > \sigma(J=1, v=1).$$

Similarly, for the P(1) transition we have

$$S_{R(0)} = c\{\sigma(J=1, v=0) - \sigma(J=0, v=1)\}$$

and, as the bolometer signal is negative, it follows that

$$\sigma(J=1, v=0) < \sigma(J=0, v=1).$$

These conclusions are supported by coupled-states calculations we have performed using an accurate *ab initio* potential surface (Rodwell *et al.* 1981). This approximation has been shown to give accurate cross sections for systems similar to the one considered here (McGuire and Kouri 1974; Bernstein 1979). The calculations were performed under the assumption that the hydrogen fluoride molecule is rigid, giving values for the cross sections of $\sigma(J=0) = 50.9 \text{ Å}^2$ and $\sigma(J=1) = 49.7 \text{ Å}^2$. Clearly these calculations agree in sign with the experimental results. However, before quantitative statements can be made it will be necessary to ensure that contributions to the signal from collisions within the secondary beam are indeed negligible. It is quite clear from the results shown in Fig. 6 that the vibrational relaxation channel vanishes rapidly as X increases. It is possible, however, that some rotational-translational energy transfer processes extend out to large distances and may contribute to the observed signals. Experiments are now being planned in which the laser excitation will occur downstream from the skimmer to ensure that the collision effects are absent. In addition, further coupled-states calculations are in progress which will include the vibrational dependence in the potential surface.

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