Differential Cross Sections for the Excitation of Single Rotational Quantum Transitions: HD + Ne

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Differential cross sections for the rotational exciation from $j=0$ to $j=1$ of HD molecules in collisions with Ne atoms have been measured in a crossed molecular beam experiment. The inelasticity is obtained by time-of-flight analysis of the scattered particles using the pseudorandom chopper method. The measured cross sections of 0.31 to 0.45 $\text{Å}^2/\text{sr}$ at energies of about 30 meV and angles between 40° and 80° prove very sensitive to the angle-dependent part of the interaction potential as shown by a comparison with calculated data.

In atom-molecule collisions the most important energy transfer process at low energies occurs between translational and rotational degrees of freedom. The cross sections for this energy transfer depend on the angular part of the interaction potential. The direct measurement of the differential cross section for single rotational quantum transitions in a crossed molecular beam experiment provides the most detailed information on this anisotropic part of the potential.[1] Up to now, such detailed cross sections have only been observed in the scattering of molecules on ions,[2] mainly because ions are easy to detect and easy to select for energy. For neutral particles all experiments performed on rotational excitation, with the exception of an early attempt on D_2 + K,[3] display unresolved transitions[4] so that part of the advantage of such experiments is lost.

We have carried out a molecular beam experiment with a universal detection system in which we succeed in resolving single rotational transitions, measuring the differential cross section of HD molecules scattered by Ne. The inelasticity is detected by time-of-flight (TOF) analysis of the scattered particles. The choice of this system was guided by the desire (1) to use a simple molecule in order to compare the results with *ab initio* calculations of the potential and in order to test quantum mechanical procedures for the calculation of the cross section; (2) to take advantage of the large energy-level spacings of hydrogen. The intensity loss compared to an elastic scattering experiment involved in such a high-resolution TOF experiment was compensated for (1) by using intense nozzle-beam sources with small angular and energy spreads, (2) by working at a very low background pressure in the detection region ($\sim 10^{-10}$ Torr), and (3) by applying the pseudorandom chopper method in the TOF part which provides high resolution with small

loss of intensity.

The apparatus[5] is shown schematically in Fig. 1. A supersonic nozzle beam of HD (speed ratio $S = 23$) is crossed by a nozzle beam of Ne ($S = 16$) at an intersection angle of 90°. The two beams are formed in two different differentially pumped chambers by expansions at 2000 Torr stagnation pressure from 0.04-mm-diam nozzles. The two skimmers have openings of 0.7 mm each resulting in an angular divergence of 2.0° for the primary and 8.0° for the secondary beam. The relative velocity has a distribution of 8% full width at half-maximum (FWHM). The temperature of the primary beam can be varied between 77 and 300 K in order to achieve different populations in the low-lying j states. The temperature of the secondary beam is kept at 300 K. The scattered particles are detected on mass $m = 3$ amu by a double
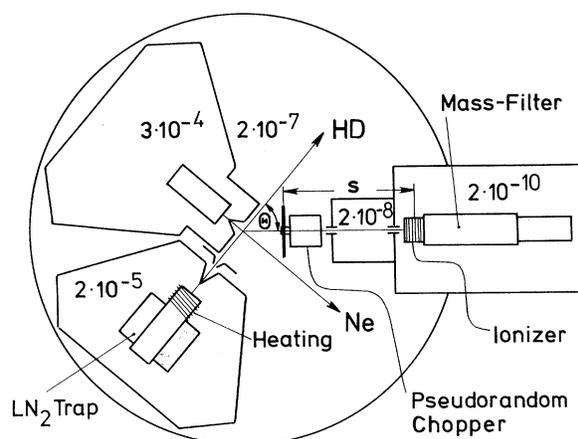

FIG. 1. Schematic of the crossed molecular beam apparatus. The numbers give the pressures in the different chambers in torr. The flight path s is 45 cm. The angular dependence of the differential cross section is measured by rotating the two source chambers with respect to the stationary detector.

differentially pumped quadrupole mass spectrometer utilizing electron-bombardment ionization and ion counting. The angular dependence of the cross section is measured by rotating the two source chambers, which are mounted on a common platform, with respect to the stationary detector assembly. In order to increase the duty cycle (fractional opening time) of the TOF spectrometer without losing resolution, the pseudorandom chopper method is used.[6] The scattered particles are modulated with a pseudorandom binary sequence by chopping the beam with a mechanical disk containing the appropriate pattern of slots and tabs in four sequences each with 127 elements. This arrangement provides a resolution of 4 μs at a cycle frequency of 492 Hz based on the smallest slot of 0.89-mm width with a duty cycle of 0.5. The measured signals are stored in a TOF analyzer with a channel width of 2 μs which is directly interfaced to a minicomputer. The desired TOF spectrum is then obtained by an on-line computation of the cross-correlation of the signal with the pseudorandom pulse train.

Figure 2(a) shows the Newton diagram of the scattering process for the laboratory angle of θ = 50°. For source temperatures of 92 and 300 K of the primary and the secondary beam, respectively, the elastically scattered HD molecules have a velocity of 1895 m/s after the collision whereas the particles which are excited from j = 0 to j = 1 are found at 1621 m/s. Thus the resolution provided by the TOF spectrometer (45-cm flight path) is $\Delta t/t = 2.0\%$ which corresponds to 38 m/s, far beyond the desired 274 m/s or 14.5% necessary to resolve this transition. The total velocity resolution of the apparatus is mainly determined by the width of the two nozzle beams of 8% FWHM since other effects like the finite length of the ionization region (17 mm) and the angular acceptances of scattering volume and detector (7 $\times 10^{-3}$ rad) can be neglected compared to this spread.[7] The TOF spectrum for this system is displayed in Fig. 2(b) after a measuring time of 1.5 h. The expected peak locations for the elastically and inelastically scattered particles are marked by arrows and agree well with the measured peak location. The 0 → 1 transition peak is clearly resolved. The number of scattered particles is only 1% of the background, which is suppressed in the figure.

To reduce the TOF spectra to differential cross sections in center-of-mass (c.m.) coordinates three steps are necessary. (1) Relative intensities are extracted from the measured histogram.
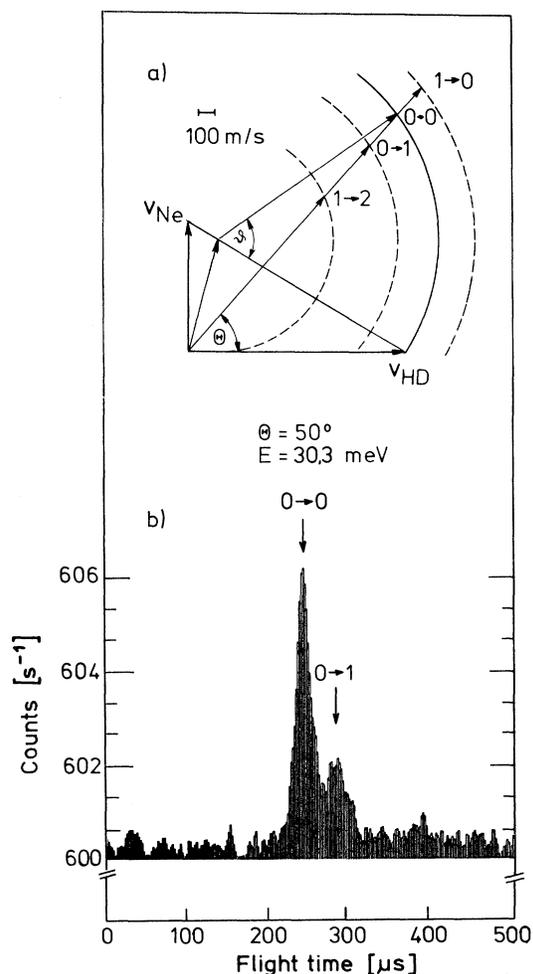

FIG. 2. (a) Newton diagram for elastic and rotationally inelastic collisions of HD (source temperature, T_0 = 92 K) from Ne (T_0 = 300 K). (b) Time-of-flight spectrum for the same process obtained after 1.5 h measuring time. Note that the total background is suppressed.

(2) The relative distribution of rotational states in the nozzle beam is calculated from the measured data of the nozzle beam, accounting for the fact that beam temperature and rotational temperature differ from each other and from the stagnation temperature.[8] (For the operating temperature of the primary beam of 92 K all of the beam particles are in the j = 0 state.) With angles and velocities transformed to the c.m. system, these two numbers give relative differential cross sections. (3) The absolute value is obtained from the measured elastic cross section. The angular dependence of these cross sections displays well-resolved diffraction oscillations which are used to fix the absolute value via a careful determina-

TABLE I. Differential cross sections for $j=0$ to $j=1$ of HD scattered from Ne.

E (meV)	ϑ (deg)	$d\sigma/d\Omega$ (Å^2/sr) a	b	c	d	e	f
28.6	64.0	0.40(5)	0.192	0.347	0.432	0.435	0.385
30.3	40.0	0.31(5)	0.136	0.266	0.316	0.319	0.343
30.3	64.1	0.43(3)	0.216	0.363	0.451	0.457	0.406
30.3	80.6	0.45(8)	0.268	0.417	0.529	0.538	0.450

[a]Experiment; absolute value obtained from experimentally determined isotropic potential V_0.

[b-f]Calculated by the coupled-states method (basis j = 0, 1, 2, 3) for the potentials published by (b) A. Gelb et al., J. Chem. Phys. 57, 3421 (1972); (c) experimental V_0, V_2 from J. W. Birks et al., J. Chem. Phys. 63, 1741 (1975); (d) K. T. Tang and J. P. Toennies, to be published; (e) L. Zandee et al., Chem. Phys. Lett. 37, 1 (1976); (f) K. R. Forster and J. H. Rugheimer, J. Chem. Phys. 56, 2632 (1971).

tion of the interaction potential from the measured data.[9] The resulting values obtained from the plotted TOF spectrum are given in Table I together with some other results at different angles and energies. The inelastic cross sections increase with increasing angle and, to a much smaller extent, also with increasing energy.

These cross sections for a $\Delta j = 1$ transitions should be very sensitive to the anisotropy of the potential, in particular to the $U_1(R)$ term of the usual expansion of the potential into Legendre polynomials, $U(R,\gamma) = \sum_k U_k(R) P_k(\cos\gamma)$. $U_1(R)$ is given by

$$U_1(R) = (\delta/R)[-RV_0' - \tfrac{6}{5}V_2 - \tfrac{2}{5}RV_2'],$$

in terms of the derivative of the isotropic part, V_0', and the anisotropic part V_2 and its derivative V_2' with respect to the coordinates R' of the homonuclear case.[10] δ is the displacement of the center of mass from the center of the molecule. Test calculations performed by solving the coupled equations utilizing the coupled-states method[11] with a basis of four states indicate that sufficient sensitivity is left for the determination of the V_2 term. A variation of the ratio of V_2/V_0 from 0.6 in the repulsive region to 0.3 in the attractive region changes the ratio of the differential cross section for $j = 0 \rightarrow j = 1$ to the cross section for $j = 0 \rightarrow j = 0$ from 17.4% to 28.6%. We have performed calculation of the measured cross section for some of the recently published potential models for this system obtained from ab initio or

semiempirical calculations, spin-lattice relaxation data, and molecular beam measurements with oriented molecules. The results, also given in Table I, clearly indicate that even our preliminary data are able to discriminate between these potentials. In conclusion we may state that the V_2 potential in the region probed by our measurement (2.8 to 4.0 Å) has a very shallow attractive minimum of -0.2 meV (compared to -2.75 meV of V_0) at about 3.8 Å, starts to become repulsive at about 3.2 Å, and reaches 2 meV at 2.9 Å. Further measurements on other angles and energies will exploit the anisotropic potential to a much larger extent. Since the resolution of the apparatus is good enough to extend the measurements to other light molecules, these experiments mark the starting point for a series of precise determinations of the anisotropic potential for some important atom-molecule and molecule-molecule systems.

[1]J. P. Toennies, Ann. Rev. Phys. Chem. 27, 225 (1976).

[2]H. E. van den Bergh, M. Faubel, and J. P. Toennies, Faraday Discuss. Chem. Soc. 55, 203 (1973); H. Udseth, C. F. Giese, and W. R. Gentry, Phys. Rev. A 8, 2483 (1973); H. Schmidt, V. Hermann, and F. Kinder, Chem. Phys. Lett. 41, 365 (1976).

[3]A. R. Blythe, A. E. Grosser, and R. B. Bernstein, J. Chem. Phys. 41, 1917 (1964).

[4]D. Beck and H. Förster, Z. Phys. 240, 136 (1970); H. J. Loesch and D. R. Herschbach, J. Chem. Phys. 57, 3028 (1972); J. M. Farrar, J. M. Parson, and Y. T. Lee, in Proceedings of the Fourth International Symposium on Molecular Beams, Cannes, France, 1973 (to be published); W. D. Armstrong, R. J. Conley, R. P. Creaser, E. F. Greene, and R. B. Hall, J. Chem. Phys. 63, 3349 (1975).

[5]U. Buck, F. Huisken, H. Pauly, D. Pust, and J. Schleusener, 50 Jahre Max-Planck-Institut für Strömungsforschung, 1975 (unpublished), p. 380.

[6]K. Sköld, Nucl. Instrum. Method 63, 114 (1968).

[7]The measured width of the elastic peak of the TOF spectrum [see Fig. 2(b)] is indeed 8% FWHW in agreement with the expected value.

[8]P. Poulsen and D. R. Miller, in Proceedings of the Tenth International Symposium on Rarefied Gas Dynamics, Aspen, Colorado, 1976 (to be published).

[9]U. Buck, F. Huisken, and J. Schleusener, to be published.

[10]H. Kreek and R. J. LeRoy, J. Chem. Phys. 63, 238 (1975).

[11]P. McGuire and D. J. Kouri, J. Chem. Phys. 60, 2488 (1974). We thank Dr. Paul McGuire for providing us with a copy of his program.