

Calculations using the effective-Gaunt-factor estimator formula<sup>20</sup> with a threshold effective Gaunt factor of 0.2 (generally quite good for *singly* charged ions) yields a threshold cross section of only  $2.1 \times 10^{-16}$  cm<sup>2</sup>. This is a factor of 3 less than the threshold value measured here and verifies that, with multiply charged ions, one should estimate using much larger effective Gaunt factors.

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## State-Resolved Rotational Excitation in HD + HD Collisions

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A novel pulsed-molecular-beam technique has been used to measure differential cross sections for state-resolved rotational transitions in HD+HD collisions. Inelastic transition probabilities are reported for the rotation-energy-level transitions  $J_A J_B = 00 \rightarrow J'_A J'_B = (10, 01)$ , 11, and (20, 02) at a center-of-mass scattering angle at 90° and at several collision energies. A brief description of the apparatus is provided.

The processes of vibrational- and rotational-energy transfer in molecular collisions are relevant to virtually all dynamic phenomena in the gas phase. These processes are especially important in some areas of great current interest—most notably in understanding the internal dy-

namics of gas-phase infrared lasers and the chemical and physical effects which the laser radiation induces in gas-phase targets. In recent years, considerable effort has been devoted to using molecular-beam techniques to investigate energy transfer in single bimolecular collisions,

with the goal of measuring differential scattering cross sections for resolved quantum state-to-state transitions.<sup>1</sup> Very recently, Buck *et al.*<sup>2</sup> reported the first measurements of differential cross sections for a well-resolved single-quantum rotational transition, in the system HD+Ne. Soon afterward, we reported similar results for HD+He.<sup>3</sup> In this Letter we describe the first experimental measurements of differential cross sections for state-resolved rotational transitions in a diatom-diatom system, HD+HD. As a prototype example, the HD+HD system has the experimental advantages of widely spaced rotational-energy levels, coupled with rotational-energy transition probabilities which are relatively large because of the strong anisotropy of the intermolecular potential. However, the only previous molecular-beam study of the HD+HD system known to us is a measurement of the integral cross sections for unresolved internal states.<sup>4</sup> From a theoretical point of view, this system is attractive (1) because the potential-energy surface can be derived from that of the much-studied  $H_2+H_2$  system<sup>5,6</sup> by adjusting the coordinates of the molecular centers of mass and adding terms to account for the small dipole moment of HD, and (2) because the small reduced mass and large rotational-energy spacing make the number of states required in the basis set for an accurate quantum-mechanical calculation relatively small. Nevertheless, we are aware of only one calculation dealing with rotational excitation in HD+HD collisions, an early modified-wave-number calculation by Takayanagi.<sup>7</sup> There have been several recent calculations of rotationally inelastic cross sections for  $H_2+H_2$ ,<sup>8</sup> and one for  $H_2+HD$ .<sup>6</sup>

Our apparatus differs substantially from other crossed-molecular-beam instruments in that the beams are produced not by the conventional steady-state nozzle sources, but, instead, by small electromechanical valves which emit pulses of gas, each having a duration of about 15  $\mu$ sec. The apparatus is designed to exploit the special advantages of the pulsed-beam technique, some of which were discussed in our earlier paper.<sup>3</sup> Figure 1 shows a schematic diagram of the apparatus. The pulsed sources are located 8 cm from the beam intersection point. They can be rotated independently in order to scan the laboratory scattering angle  $\theta$  or to vary the beam intersection angle  $\varphi$ , which determines the collision energy in the center-of-mass (c.m.) coordinate system. Each of the HD beams has a velocity spread of about 10% full width at half-maximum

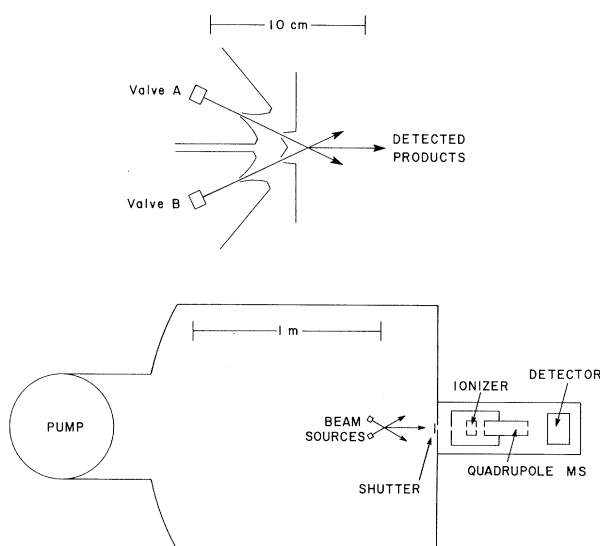


FIG. 1. Schematic diagram of the apparatus, with large features drawn approximately to scale.

(FWHM) and is collimated to an angular divergence of  $2^\circ$  FWHM by double skimmers. The sources are not differentially pumped. The gas pulses reflected from baffles around the skimmers simply expand into vacuum at the molecular velocity. The large size of the main vacuum chamber (2000 liters) ensures that the collision products which are scattered from the beam-crossing point directly into the detector arrive substantially sooner than do the primary-beam molecules which are reflected into the detector from multiple collisions with various surfaces. Thus the scattered signal of interest is well separated in time from the slower background signal. The stationary detector is relatively conventional. It consists of an electron bombardment ionizer in an inner, differentially pumped chamber, followed by a quadrupole mass spectrometer and an ion counter. Its only unusual feature is that it is isolated from the main chamber by a shutter which opens for only 5 msec during each pulse, when the directly scattered products are passing through. Thus the detector vacuum system never becomes appreciably contaminated with the source gases. The speed distribution of scattered molecules is measured by time of flight (TOF) over a distance of 48 cm from the beam-crossing point to the ionizer. The data acquisition and timing of the experiment is controlled by a microprocessor-based computer system. The normal interval between pulses is about 2 sec, which gives sufficient time for the 0.53-m-

diam main-chamber diffusion pump to reduce the partial pressure of residual background gas from the previous pulse to a negligible value. The small duty factor of the experiment (about  $10^{-5}$ ) is compensated for by the gain in beam intensity made possible because the limitations normally imposed on continuous sources by differential pumping capacity<sup>9</sup> do not exist for pulsed sources. With nozzle diameters of 0.6 mm and an internal pressure of 2 atm, our sources produce beams roughly  $10^2$  times as intense as those normally used in continuous-beam experiments, resulting in a gain of about  $10^4$  in instantaneous product signal.<sup>10</sup> Thus we sacrifice about a factor of 10 in absolute signal per unit of real time, but we gain several orders of magnitude in the signal-to-background ratio relative to what one expects from continuous beams in experiments at similar resolution.

We will denote the initial states of the two HD molecules with the rotational quantum number  $J_A J_B$  and the final states with  $J_A' J_B'$ . After the collision, the  $J_A' J_B'$  states  $mn$  and  $nm$  are, of course, not distinguishable. Because of the internal cooling which accompanies the adiabatic expansion of the supersonic beams,<sup>9</sup> one expects virtually complete quenching of the primary-beam molecules into the initial state 00. In the energy range of the experiments described here, the energetically accessible final states and the corresponding excitation energies are 00 (0 eV), 10 (0.0113 eV), 11 (0.0226 eV), and (at the higher collision energies) 20 (0.0340 eV). Figure 2 shows a velocity vector diagram and the corresponding experimental TOF spectrum for a typical case. The beam intersection angle  $\varphi$  in this example is  $51.0^\circ$ , resulting in an initial c.m. collision energy of 0.0350 eV. The laboratory scattering angle  $\theta$  bisects the intersection angle, so that the scattering angle in the c.m. system is  $\pm 90^\circ$  for all final states. Each final state gives rise to two product laboratory speeds, labeled "fast" and "slow" in the figure. The respective times of flight calculated for each peak are indicated by vertical lines in the TOF spectrum. Although the fast peaks are not resolved, the slow peaks are resolved well for excitations up to  $J_A' J_B' = 11$ . The shoulder in the TOF spectrum between the fast peak and the slow 11 peak is due to a small contribution from the state (20,02), which emerges with a speed very close to that of the system center of mass. This state is well resolved at slightly higher collision energy. The absence of any evidence for rotational deexcita-

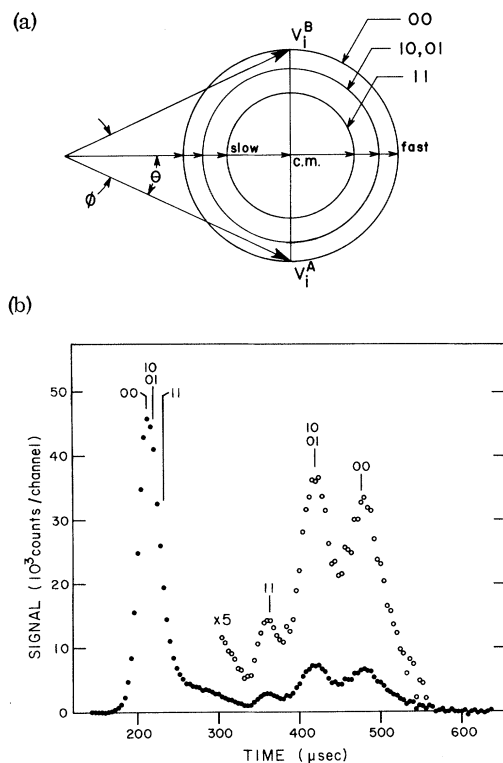


FIG. 2. (a) Velocity vector diagram for HD+HD rotational excitation at a beam intersection angle  $\varphi = 51^\circ$ . The laboratory speeds of the two beams are  $v_i^A = v_i^B = 2.46 \times 10^5$  cm/sec. (b) TOF spectrum for the kinematics shown in (a) has been measured at  $4 \mu\text{sec}/\text{channel}$  and accumulated over 11 000 pulses. The time-dependent background signals, measured separately for each primary beam, have been subtracted. The ratio of the scattered signal to the background signal at the slow 11 peak is about 0.6.

tion verifies that only the 00 state is populated significantly in the primary beams. The relative differential cross sections for the various product quantum states are best determined by fitting the amplitudes of the peaks in the experimental TOF spectra with the theoretical resolution function calculated numerically by averaging over the speed and angle distributions of the beams, the shutter functions of the pulsed sources, and the detector spatial- and speed-resolution functions.<sup>3</sup> The results, expressed as transition probabilities, i.e., as ratios of the differential cross section for the final state  $mn$  to the total differential cross section summed over all final states, are given for three values of collision energy in Table I. Note that the relative amplitudes of the slow inelastic peaks in the TOF spectra are exaggerated compared to the actual transition probabilities given in the table. This is due to the

TABLE I. Rotational transition probabilities for HD+HD collisions at a c.m. scattering angle of  $90^\circ$ .  $p_{mn}$  is the ratio between the differential cross section for the transition  $00 \rightarrow (mn, nm)$  and the total differential cross section summed over all final states. The figures in parentheses are the estimated uncertainties.

$E_i$ (eV)	$p_{00}$	$p_{10}$	$p_{11}$	$p_{20}$
0.0414	0.59 ( $\pm 0.02$ )	0.35 ( $\pm 0.02$ )	0.046 ( $\pm 0.010$ )	0.008 ( $\pm 0.003$ )
0.0350	0.64 ( $\pm 0.02$ )	0.33 ( $\pm 0.02$ )	0.035 ( $\pm 0.010$ )	...
0.0229	0.77 ( $\pm 0.02$ )	0.23 ( $\pm 0.02$ )	...	...

factor  $u^2/v^2$  in the Jacobian for transformation from laboratory to c.m. coordinates, where  $u$  and  $v$  are, respectively, the c.m. and laboratory speeds of the detected molecule.<sup>11</sup> For a given detector laboratory solid angle of acceptance, the c.m. solid angle intercepted becomes larger as the excitation energy is increased. This kinematic advantage results from using an acute beam intersection angle, and can be extremely helpful in extracting a measurable signal for a small-probability process.

The inelastic transition probabilities in Table I show the expected increase with collision energy and are of the order of magnitude anticipated by analogy with the previous experimental studies of HD+Ne<sup>2</sup> and HD+He,<sup>3</sup> and the theoretical calculations on HD+H<sub>2</sub>.<sup>6</sup> A quantitative theoretical analysis will have to await detailed calculations using a realistic potential-energy surface and an accurate dynamical treatment of the diatom-diatom scattering problem, in which approximations are much less well understood than for atom-diatom scattering.<sup>12</sup> The quality of the data appears to be sufficient to provide a rigorous test of theoretical calculations. In a future paper we will report state-resolved differential cross sections for HD+HD collisions at additional c.m. collision energies and over a broad range of c.m. scattering angle. A detailed description of the pulsed-beam source and its performance will be published separately. It is clear that the new pulsed-beam technique will also make possible state-resolved experiments on many other simple molecular collision systems. We note in closing that a pulsed-molecular-beam source lends itself to the use of a pulsed laser for preparation of beam molecules in an initially excited state, since every molecule in the beam pulse can be irradiat-

ed at high laser power. Studies of collisional relaxation and excited-state reactions for well-defined initial excited states should therefore be possible. Experiments of this type are also planned.

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