

STATE-TO-STATE REACTION DYNAMICS: $H + D_2 \rightarrow HD + D$

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Preliminary results are reported for the bimolecular exchange reaction $H + D_2 \rightarrow HD + D$. Fast H atoms generated by photolysis of H_2 at 266 nm, collide with room temperature D_2 ($v=0$) at 1.3 eV CM collision energy. Using multiphoton ionization combined with time-of-flight mass selection both reaction products are separately detected. The $HD(v=1, J=0-6)$ state distribution is derived and compared to simple theoretical predictions.

INTRODUCTION

About three years after the birth of quantum mechanics, P. A. M. Dirac wrote [1]:

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known..."

This often-quoted statement is just as true and as misleading today as when it was written in 1929. It has had the chilling effect of convincing some that collision phenomena and in particular reaction dynamics is a rather sterile pursuit in which all is solved "in principle." Actually, we confront what might be called "the few-body problem" -- a dynamical problem having too few particles to be governed by the laws of statistics, but too many particles for the rigorous application of quantum mechanics to be successful. Thus, as Dirac himself appreciated [2], it is possible to understand something "in principle" and yet to have no predictive power. Such is the fascination of heavy particle collisions and why it beckons some of us to search for those approximations and insights which reveal the true "microscopic" nature of chemical transformations, collision by collision.

Of all the possible neutral bimolecular reactions that of



and its isotopic analogs is the simplest, consisting of only three electrons and three nuclear charge centers. This hydrogen atom exchange reaction has long served as a prototype system in experimental and theoretical studies of reaction dynamics [3]. The potential energy surface of H_3 has been determined with greater accuracy than that of any other neutral triatomic [4] and many semi-classical and quantum investigations of the collision dynamics have been carried out using it [5]. However, the experimental difficulties of generating hydrogen atoms and detecting the resulting hydrogen molecule reaction product have made detailed comparison between theory and experiment extremely limited for this benchmark system. From the point of view of the experimentalist the best that can be accomplished is to specify the initial conditions of the reagents and

determine the final states of the products. From this data it is then necessary to infer the reaction dynamics connecting reagents to products on the adiabatic potential energy surface. While state-to-state reaction dynamics have been investigated for a number of chemically interesting systems [6-8], such studies have not previously been possible for the $\text{H} + \text{H}_2$ system. This is a consequence of a number of factors: the small cross section; the large activation energy required to make this thermoneutral reaction proceed; and the infrared and optical transparency of the H_2 molecule which makes it resistant to detection by spectroscopic means. However, recent advances in laser technology combined with a number of novel (nonlinear) optical techniques are making it possible to detect H_2 in a quantum-state-specific manner with high sensitivity [9-17], and hence to open the way for the state-to-state study of the fundamentally important $\text{H} + \text{H}_2$ reaction system.

The state detection of H_2 , HD, and D_2 can be accomplished using multiphoton ionization (MPI) [9,10], laser-induced fluorescence (LIF) [11,12], and coherent anti-Stokes Raman spectroscopy (CARS) [13-17]. However, the levels of sensitivity of each of these techniques are such as to require careful design of the experiment to achieve sufficient reaction product densities. To overcome the activation energy of ~ 0.33 eV and the small reaction cross section of less than a few square Angstroms, we have chosen a scheme in which HI is photolyzed to produce fast H atoms in the presence of D_2 [17-19], and the resulting nascent HD and D products are detected using the MPI approach [9,10,20].

EXPERIMENTAL

Figure 1 shows an overview of the experimental layout. The photolysis pulse originates from the 4th harmonic of a Nd:YAG laser (Quanta-Ray DCR 2) operating at 10 Hz and providing 10 mJ, 5 ns pulses at 266 nm. The resulting beam is spectrally separated by a Pellin Broca prism and collimated to ~ 2 mm diameter using a telescope, consisting of 35 and 10 cm lenses, before entering the reaction chamber. The HI and D_2 reagents are introduced in the ratio $\sim 3:1$ via a 3 cm long, 0.6 mm diameter fine glass tube placed with its orifice 0.75 mm above the laser beam axis (see Fig. 2) with the aid of an external vertical translator. This source provides local densities ~ 0.1 Torr for the D_2 reagent (as measured in separate MPI experiments) which are sufficiently confined to prevent electrical breakdown across the ion acceleration plates (repeller and extractor) of the time-of-flight mass spectrometer. In addition, this arrangement minimizes the attenuation of ion signals caused by scattering. With the HI/ D_2 source on, the reaction chamber pressure rises to $\sim 5 \times 10^{-4}$ Torr.

After a variable delay, typically 10-100 ns, HD products are probed using the third anti-Stokes of a frequency-doubled dye laser (Quanta-Ray DCR1/PDL/WEX system). This beam, with a wavelength of 209-11 nm, selectively ionizes different rotational levels of the first vibrational state ($v''=1$) of HD, via a two-photon transition to the $v'=0, J'$ level of the HD $E_{1\Sigma}^+$ state, followed by absorption of a third photon. The probe beam having $\sim 300 \mu\text{J}$, ~ 3 ns pulses is obtained by Raman shifting the frequency-doubled dye laser (15 mJ/pulse) in a 7 atm H_2 cell. Two back-to-back Pellin Broca prisms isolate the third anti-Stokes and direct it through the reaction chamber via a 15 cm focal length lens which forms a 0.1 mm spot at the center of the reaction zone. The beam exits the reaction chamber through a Brewster-angled window, after which a small fraction is picked off with a 90° prism and imaged onto a pyroelectric joulemeter (Molelectron J-3) to provide a monitor of the anti-Stokes energy.

Similarly, the H atom reagent, from the photolysis of HI, and the D atom product, from the $\text{H} + \text{D}_2$ reaction, are also detected by MPI. This is achieved by changing the probe laser wavelengths to 304.7 and 304.6 nm for H and D, respectively, and using the second anti-Stokes to cause two-photon resonant three photon ionization [20]. By scanning the laser wavelength, Doppler profiles are obtained.

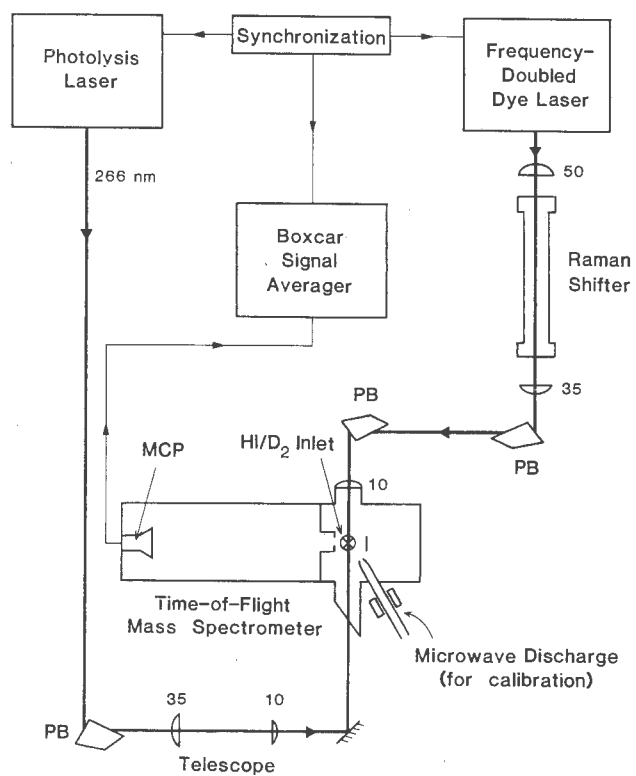


Figure 1
Experimental setup for state-to-state studies of the $H + D_2 \rightarrow HD + D$ reaction. The number by each lens is its focal length in cm; PB = Pellin Broca prism; MCP = multichannel plate.

The HD^+ ions are accelerated into a differentially-pumped field-free drift tube through a 1.5 mm wide, 7 mm long slit aligned parallel to the laser beam axes and which can be positioned vertically using an external micrometer. The drift tube is ~ 70 cm long. With the HI/D_2 gases flowing it has a pressure of $\sim 5 \times 10^{-6}$ Torr. Ions are detected by a multichannel plate (Galileo FTD 2002), and the resulting signal is amplified by a $\times 10$ preamplifier which feeds a fast oscilloscope (Tektronix 7104) before being processed by a boxcar signal averager (PAR 162/165).

A microwave discharge has been incorporated into the apparatus to provide a thermal source of H and D, atoms as well as HD molecules in $v = 0-3$. This serves to optimize the detection of these species as well as to calibrate signals against a known Boltzmann distribution. The discharge cavity is placed outside the vacuum and discharge products flow along a 15 cm passivated pyrex tube to emerge through a 1 mm diameter orifice placed 3 cm from the laser axis. Two grids screen the ion optics from the discharge tube (see Fig. 2).

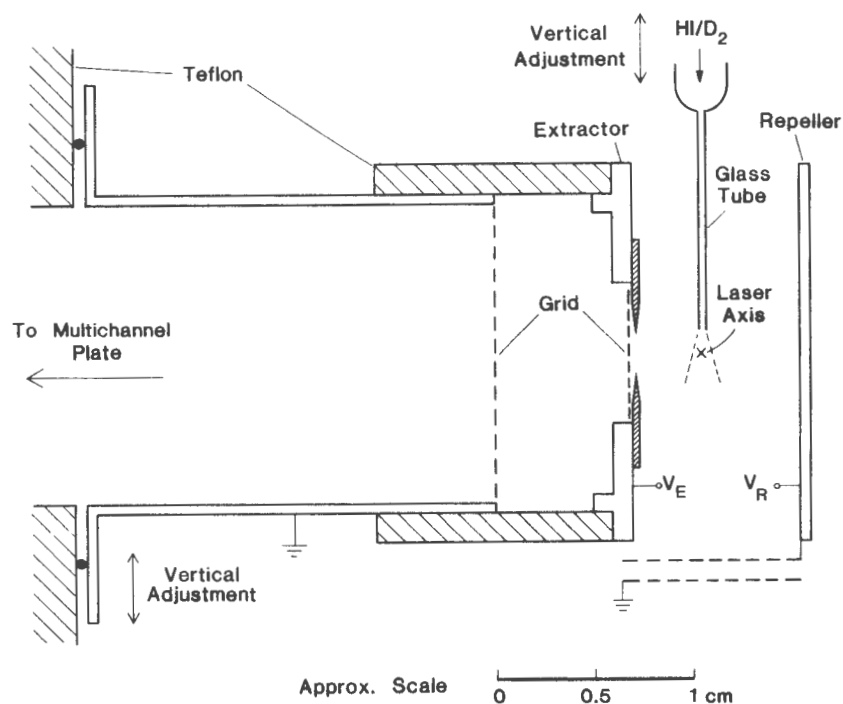


Figure 2
Detailed drawing of the ion optics and reaction zone. Typically, V_R is fixed at 2400 and V_E at 1800 V.

RESULTS AND DISCUSSION

The photolysis of HI at 266 nm has two channels, $H + I(^2P_{3/2})$ and $H + I(^2P_{1/2})$, which result in a ~2:1 ratio of "fast" to "slow" H atoms with CM collision energies with D_2 of 1.30 and 0.55 eV, respectively [21,22]. Because the reaction cross section for production of $HD(v=1)$ is expected to be so much smaller for the "slow" H atoms than the "fast" ones [23], we believe that the following observations on $HD(v=1)$ pertain almost exclusively to a H + D_2 center-of-mass collision energy of 1.30 eV.

Figure 3 illustrates the production of fast H atoms from the photolysis of HI in which we compare the Doppler profile of these atoms to those of a microwave discharge (characteristic of a thermal room temperature source). Here the photolysis wavelength is 243.1 nm and both "fast" and "slow" H atoms contribute to the upper trace with different angular distributions causing a broad Doppler-split profile [24,25]. This photolysis wavelength is also that used in the MPI detection of the H atoms but similar results have been obtained for 266 nm [24].

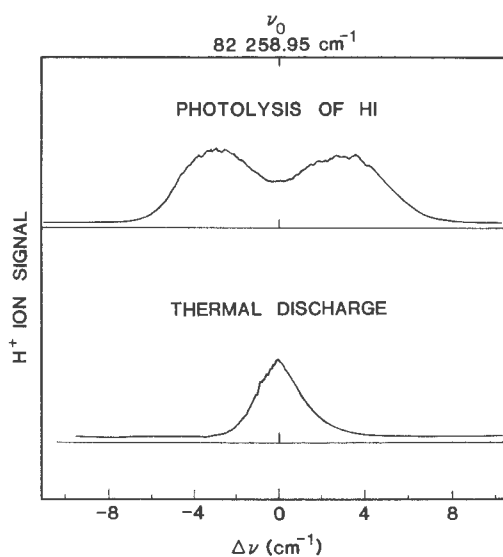


Figure 3
Comparison of H atom Doppler profiles. The upper trace is from the photolysis of HI at 243.1 nm; the lower trace corresponds to room temperature atoms from the microwave discharge.

Figure 4 shows the Doppler profile of the D atom product of the reaction $H + D_2$ at two different probe delay times and compares these to the corresponding D atom Doppler profile from the microwave discharge. It is clear that the nascent D atoms are highly translationally excited, but that after ~ 200 ns the distribution is comparable to the thermal case. This results from both collisional relaxation and from the escape of the fast D atoms from the probed volume. In principle it should be possible to determine the fraction of energy appearing in translation from such Doppler measurements. However, Fig. 4 emphasizes the need to probe at early enough times to capture the nascent translational distribution. Indeed, this applies to all final-state attributes, which are only truly collisionless at "zero" delay.

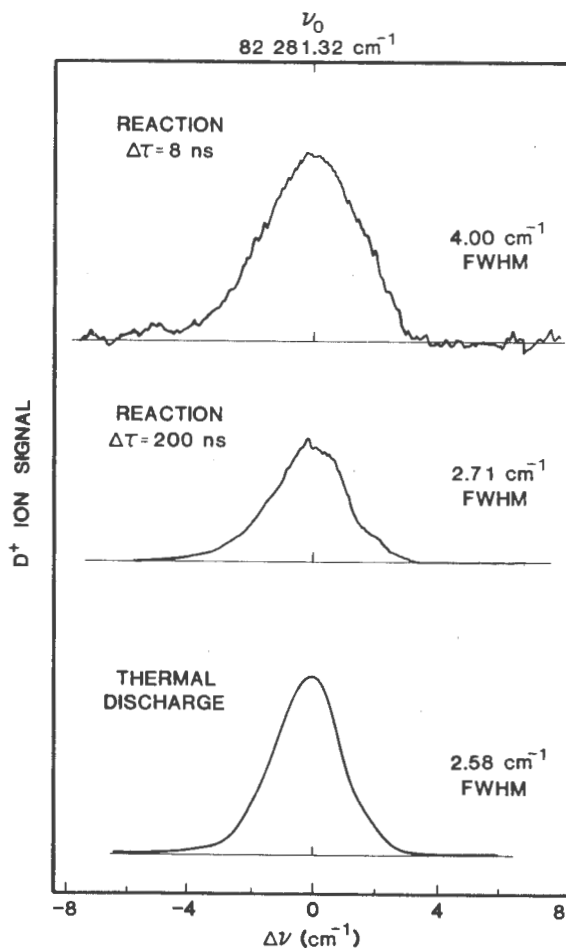


Figure 4
D atom Doppler profiles: the upper and middle traces are for the D atom reaction product from $H + D_2$; the lower trace is for D atoms from the microwave discharge (295 K).

The same considerations apply to the H atom translational energy distribution. This has particular importance because the reaction cross sections for the formation of $HD(v=1, J)$ fall rapidly with decreasing CM collision energy. Consequently, there is another reason to prefer the shortest probe delay time consistent with high signal-to-noise measurements. Finally, we point out that $HD(v=1, J)$ can also arise from the reaction $D + HI$ where the D atoms are the products of $H + D_2$. This highly exothermic reaction is expected to contribute at later times.

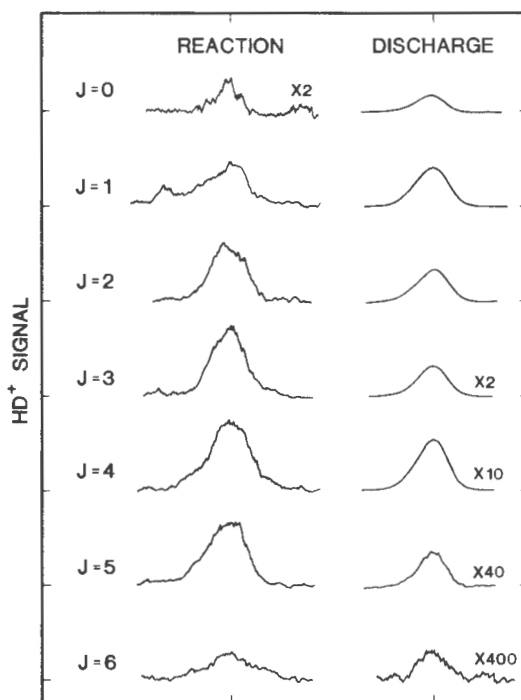


Figure 5

$HD(v=1, J=0-6)$ MPI signals from the $H + D_2$ reaction and from a microwave discharge. These correspond to the Q-branch members of the (0,1) band of the $E \Sigma^+ - X \Sigma_g^+$ system of HD. The gains are unity except where indicated. The small spectral feature on the J=1 trace from the reaction is unidentified but is reproducible.

Figure 5 presents typical ion signals for HD($v=1, J=0-6$) from both the H + D₂ reaction and from the microwave discharge source. The former were obtained for a probe delay time of 14 ± 2 ns at a total pressure in the reaction zone of $\lesssim 1$ Torr. Careful inspection shows that the HD reaction products have a substantially broader Doppler profile than their thermal counterparts. The reaction products have been recorded at the same gain except for HD($v=1, J=0$); however, as much as a gain factor of 400 has been applied to detect HD($v=1, J=6$) arising from the thermal source.

In order to extract populations from the HD MPI signals it is necessary to know relative ionization efficiencies under our experimental conditions for the different transitions. These have been obtained by measuring the HD($v=1, J$) distribution from the microwave discharge which is assumed to follow a Boltzmann distribution at 295 K, the measured temperature at the tip of the discharge tube. The reaction distribution is thus obtained by applying the same corrections which scale the discharge data to a 295 K Boltzmann distribution. These correction factors are not expected to be large [9,10] and never exceed a factor of two. This simple procedure simultaneously corrects for variations in rotational line strengths and laser power. Figure 6 presents the HD($v=1, J$) populations for the H + D₂ reaction at 1.30 eV CM collision energy. For comparison, the 295 K thermal distribution is also displayed.

Inspection of Fig. 6 shows at once that the HD($v=1$) product from H + D₂ is rotationally hot and its shape is suggestive of a Boltzmann distribution. To test this hypothesis, we have plotted in Fig. 7 the logarithm of the normalized populations versus the rotational energy. We find a straight line with a slope characteristic of a rotational temperature $T_R \approx 1100$ K. This slope is obtained from an unweighted least squares fit to our data. The error bars arise largely from the uncertainties introduced in the calibration procedure; this explains why the highest J value is most uncertain.

A number of checks were made to ensure that the reported distributions refer to the H + D₂ reaction. For example, signals require the presence of HI, D₂, and both lasers. We have also excluded the possibility of energy transfer from fast H atoms to HD impurity in the D₂ sample. The amount of HD in our D₂ sample is of the order of 0.5 percent, as determined by MPI. We replaced the D₂ by "pure" HD which only served to increase the HD($v=1$) signals by less than a factor of 2, indicating that the relevant energy transfer cross section for the process



cannot be much larger than for the reactive cross section for $\text{H} + \text{D}_2 \rightarrow \text{HD}(v=1) + \text{H}$. Moreover, preliminary studies indicate that the HD($v=1, J$) distribution from process (2) yields a distinctly different rotational distribution.

At first it might seem surprising that the H + D₂ reaction yields HD($v=1$) product having a temperature-like rotational distribution when it is known that the reaction does not proceed through a long-lived complex [26-28]. Actually such distributions have been predicted previously [23,29,30]. Schatz and Kuppermann [29,30] have pointed out that this may be a consequence of the restricted bending motion of the transition state where a gaussian wave packet arising from the zero point motion in the bend becomes projected onto the free rotor states of the diatomic product. Here the bending time is much longer than the collision duration and a generalized Franck-Condon argument [31,32] gives a Boltzmann-like rotational distribution. Thus a measure of the rotational temperature of the product provides information on the bending frequency of the H₃ intermediate. It is hoped that the results presented here will stimulate renewed interest in calculating these properties.

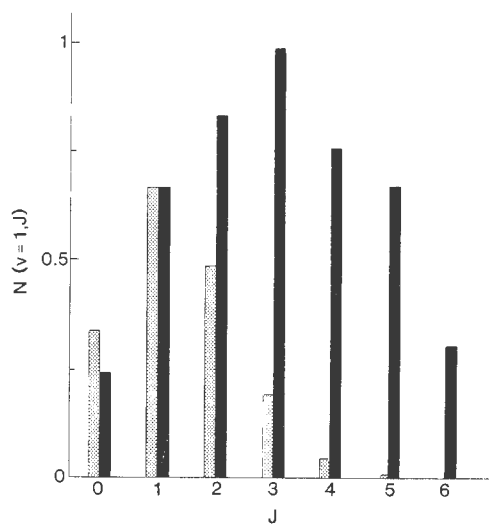


Figure 6
Relative populations of HD($v=1, J=0-6$) from the microwave discharge (shaded bars) and from the $H + D_2$ reaction (solid bars) at 1.30 eV CM collision energy.

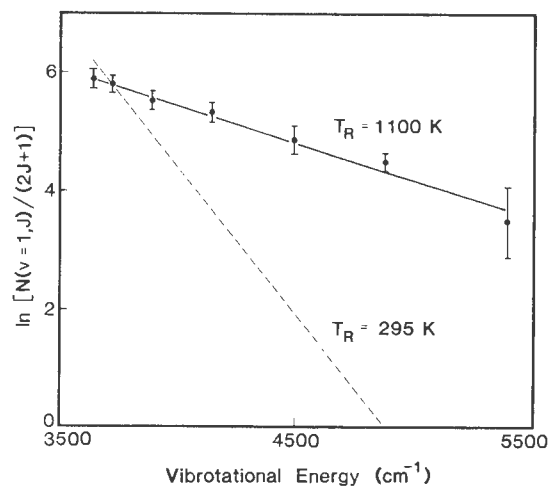


Figure 7
Boltzmann plot of the data given in Figure 6. For comparison purposes the dashed line indicates a room temperature thermal distribution.

Finally, we note that the estimated rotational temperature of 1100 K corresponds to only ~ 0.1 eV. When this energy is added to the ~ 0.45 eV of vibrational energy of HD($v=1$), this leaves ~ 0.75 eV for translational energy of the products. Thus we find that for this system, translational energy of the reagents is largely channeled into product translation, again, in keeping with previous predictions [23,29,30].

In summary, this account has described preliminary results on the translational and rotational state distributions for the H + D₂ reaction. This work has been based on the MPI detection method which we expect will continue to yield data on the H + H₂ reaction family. We also anticipate that other laser techniques as well as advances in time-of-flight beam experiments will contribute to our knowledge of the state-to-state dynamics of this simplest of all neutral reactions, bringing us one step closer to fulfilling Dirac's expectations.

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