Observation of the Transition State $HD_2{}^{++}$ in Collisions, $H + D_2$

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(Received 28 September 1987)

We report the observation of the transition state $HD_2{}^{++}$ in the chemical reaction $H + D_2 \rightarrow (HD_2{}^{++} \rightarrow)HD + D$. The $HD_2{}^{++}$ was detected by resonantly enhanced multiphoton ionization. It was identified by velocity-selected time-of-flight mass spectrometry, and by comparison of the time dependence of its concentration with that of reagent H and product D, also studied by resonantly enhanced multiphoton ionization.

There has been considerable discussion of the possibility of probing the transitory intermediate in chemical reactions through what has been called "transition-state spectroscopy" (TSS); the "transition state" in TSS comprises all configurations traversed by the system *en route* from reagents to products.[1,2] There is evidence of success in the detection of transition states in emission[3] and absorption[4-7] and in the femtosecond time domain.[8] The spectrum reflects the relative times that the system spends at successive TS configurations in an electronically excited state[9] or in the electronic ground state.[10-13]

It has been pointed out that the problem of interpretation may be eased if the emission or absorption involves a bound state which can impose quantal structure on the spectrum, and, above all, if TSS is applied initially to the most fundamental of chemical reactions in which only H—H bonds are formed and broken.[10-12] The present communication reports on the detection of the transition state for this reaction.

Substantial information exists regarding H_3; because of space constraints we defer a full review. Recently emission has been observed from $H_3{}^*(2pA'')$ to the repulsive $H_3(2pE')$ state,[14] as also has photoionization of $H_3{}^* \rightarrow H_3{}^+$.[15] The lifetime and ionization potential of the $H_3{}^*(2pA'')$ state has now been measured.[16] (For conformity with the H_3 literature we apply the analogous D_{3h} symmetry labels to the HD_2 states).

The present experiment made use of a pump and probe laser coincident beneath a continuous jet of two mixed reagents,[17] H_2S and excess D_2. This took place in the extraction region of a time-of-flight (TOF) mass spectrometer.[18] Laser L_1 photolyzed H_2S at 248 nm (5 mJ/pulse) to give atomic H. Laser L_2 probed the transition state $HD_2{}^{++}$ by resonantly enhanced multiphoton ionization; a single photon of 193 nm (5 mJ/pulse) excited $HD_2{}^{++}$ to $HD_2{}^*(2pA'')$, and a second photon ionized $HD_2{}^*$ to yield $HD_2{}^+$ which was then mass selected and counted. The delay between L_1 and L_2 was varied systematically. In separate experiments performed under similar conditions a third laser L_3 was used to probe the reagent H or product D by (1+1) resonantly enhanced multiphoton ionization in the vacuum ultravio-

let at ca. 121 nm (obtained by frequency tripling in Kr gas[19]), as a function of time delay between L_1 and L_3. The time dependence of [H], $[HD_2{}^{++}]$, and [D] were found to be as expected for reagent, TS, and product.

Trap-purified reagent gases H_2S and D_2 were mixed in a 2:3 ratio and injected from a total backing pressure of 400 Torr through a 250-μm metal orifice into a reaction vessel at a base pressure of 5×10^{-8} Torr. Two unstable resonator excimer lasers constituted L_1 and L_2. They were collimated, apertured by an iris, focused mildly (L_1 with a 50-cm lens, L_2 with a 100-cm lens), and counterpropagated a few millimeters beneath the nozzle. The pump and probe laser spots were chosen to be of approximately the same diameter (≈ 2 mm) at the nozzle beam axis. To minimize scattered light, the laser beams were introduced via antiparallel laser arms, each with a Brewster-angle window, a Woods horn, and a set of electroformed knife-edge light baffles.[20] Two electron guard rings biased at -150 V prevented electrons generated by photoelectric emission in the laser beam arms from entering the ion-extraction region. All metal surfaces in the extraction region were coated with a graphite layer to reduce scattered light further, to even out surface electric potentials, and to inhibit photoelectric effects on bare metal surfaces. Laser pulse energies were measured on a shot-to-shot basis. Laser pulse energies were controlled and varied by introducing 3-mm-thick quartz attenuation plates pairwise at complementary angles of incidence to avoid laser-beam walkoff. A computer-controlled delay generator provided the timing for the lasers. The zero time-delay setting was determined by our lowering the metal nozzle into the laser beam axis and monitoring the scattered-light peak from each laser. The synchronization of the signal-collection electronics with the probe laser was provided by a subnanosecond-rise-time ultraviolet photodiode.

The positive ions were extracted perpendicular to the laser-beam axis in an electric field of 1250 V/cm and passed through an orifice into a second differentially pumped region where they were steered, focused, and selected by a unit-transmission Wien filter ($E \times B$ velocity filter).[21] The Wien filter provided mass filtering with

a maximum resolution of $m/\Delta m = 200$; it did not change the arrival times in the subsequent 60-cm drift-length TOF spectrometer. The single ions were detected at a 10^6 gain dual microchannel plate detector. The ions were counted at 100 MHz by an amplifier and discriminator combination. The discriminator had a fast gate capability that was used to set a 50-ns "counting gate" at the TOF arrival time of the mass of interest. A microcomputer controlled the signal-collection electronics. To minimize background counts, the signal from the probe laser alone was subtracted on a shot-to-shot basis from the pump-plus-probe signal. This was done by our accumulating counts at a short time delay, e.g., 40 ns, where neutral-neutral chemical reaction was expected, and subtracting from this (on a shot-to-shot basis) the counts accumulated at a long time delay, e.g., 900 ns, where chemical reaction was expected to be over. Since the pump laser produced a negligible number of ions, this technique was equivalent to subtraction of the effect of the probe laser alone.

Mass calibration of the Wien filter current and the TOF arrival times was provided by ions with $m/e = 1$, 2, 3, 4, and 12, giving excellent linear fits. In the TSS mode the Wien filter was set to transmit $m/e = 5$ and the counting gate was set at the arrival time of an ion with $m/e = 5$. The pump laser photodissociated H_2S and yielded an H atom with a well defined kinetic energy.[22] This defined the center-of-mass collision energy in the jet as 0.81 eV. As a result of the unpolarized nature of the pump laser and the perpendicular transition in H_2S,[22] the H-atom velocity vectors were isotropically distributed. We estimate that approximately 10% of the H atoms collided with D_2 molecules.

Typical experimental ion counting rates at $m/e = 5$ i.e., HD_2^+) are presented in Fig. 1. Variation of the forepressure in the nozzle indicated that the $m/e = 5$ sig-

nal was approximately linear in both H_2S and D_2 backing pressure. Preliminary laser power studies showed the $m/e = 5$ signal to be linear in pump-laser power. Figure 1 shows clearly that the mass-5 ions depended upon the presence of both reagents and both lasers, i.e., they behaved as expected for the $H + D_2 \rightarrow HD_2^{++} \rightarrow HD_2^*$ $\rightarrow HD_2^+$ in which the H comes from single-photon photolysis of H_2S, D_2 is the second reagent, and the probe laser is responsible for the two-photon ionization of $HD_2^{++} \rightarrow HD_2^+$.

The interpretation of the mass-5 species as being the TS HD_2^{++} was confirmed by a study of the time dependence of the signal at 5 u. Studies of the chemical reaction $H + D_2 \rightarrow HD + D$ under similar conditions yielded the time dependence of the H-atom reactant and D-atom product as shown in Fig. 2. Pump and probe laser beam spots were again chosen to be of approximately the same diameter (≈ 2 mm) at the nozzle axis. The H-atom signal, $[H(t)]$, decayed as a result of the escape from the viewing region of the probe laser. The D-atom signal was governed by a chemical rate of formation, R_f, and a rate of decay, R_d, due to the D-atom product leaving the viewing region. The falling portion of the D-atom signal was well approximated by an exponential decay. The first derivative of the rising section of the curve is related to the instantaneous rate of reaction by the equation $d[D(t)]/dt = R_f - R_d$, where $R_f = k[H(t)][D_2]$ and $R_d = (1/\tau)[D(t)]$. The quantity R_f is proportional to the instantaneous concentration of transition states, $[HD_2^{++}]$; $R_f \approx [HD_2^{++}]v$, where v is the frequency with which transition states fall apart into reaction products. The measured time dependence of the $m/e = 5$ signal is shown in Fig. 3 along with the quantity R_f as derived from Fig. 2. These should vary with respect to time delay in the same way if the $m/e = 5$ signal is the transition state. The agreement is good.

A conceivable alternative source of the $m/e = 5$ signal would require an H atom generated by the pump laser to
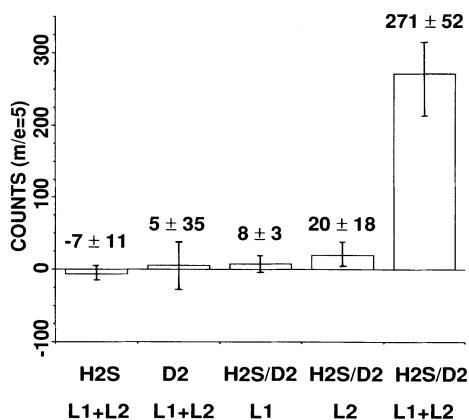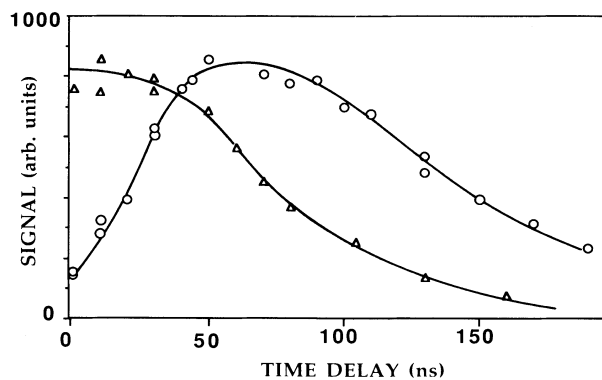

FIG. 1. Typical counting rate at $m/e = 5$ (HD_2^+) per 5000 laser shots. L1 and L2 indicate the presence of the pump (248 nm) and probe (193 nm) laser radiation, respectively.

FIG. 2. H atom reactants (triangles) and D atom products (circles) in the chemical reaction $H + D_2$ as a function of pump-to-probe delay time.
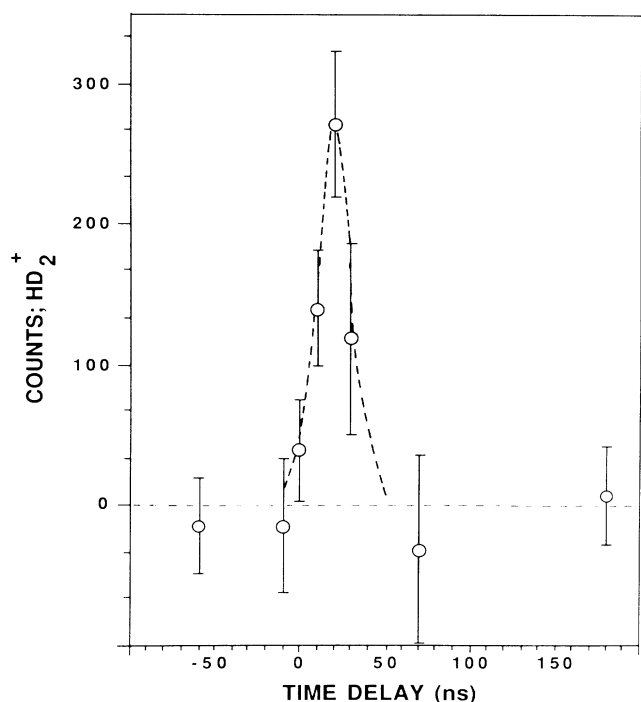
FIG. 3. The signal (counts per 5000 laser shots) at $m/e = 5$ (HD_2^{++}) as a function of pump-to-probe delay time. The dashed line is the quantity $R_f = k[H(t)][D_2]$ obtained from Fig. 2, normalized to the peak counting rate in Fig. 3.

recombine with a D_2^+ ion generated by the probe laser *in the presence of a third body*. The measured rate constant for a comparable atom-plus-ion termolecular association is $k = 1 \times 10^{-31}$ cm^6 s^{-1} ($H_3^+ + Ar + H_2 \rightarrow ArH_3^+ + H_2$ at 300 K [23]). Using this rate constant and estimates of ionic, atomic, and third-body densities ($[D_2^+] \approx 10^4$ cm^{-3}, $[H] \approx 10^{11}$ cm^{-3}, $[M] \approx 10^{15}$ cm^{-3}), we calculate that the termolecular source of $m/e = 5$ would be 7 orders of magnitude smaller than our measured signal. This three-body rate constant is an overestimate in view of the temperature dependence of three-body ion-molecule reaction rates[24]; both H and D_2^+ were at energies much greater than thermal (the latter because of the strong electric field in the extraction region of the spectrometer).

A study of the L_2 power dependence of the $m/e = 5$ signal gave a preliminary figure of $I^{1.4}$ as compared with $I^{2.3}$ for D_2^+ ions; this significant difference serves to rule out D_2^+ as a reagent in the formation of HD_2^+.

We conclude that we have detected transition states HD_2^{++} in the reactive encounter $H + D_2$.

Under our present experimental conditions van der Waals dimers $D_2 \cdot H_2S$ will have a negligible concentration. The use of dimers as a starting point for experiments of the present type would be advantageous. A reduction in averaging over reagent geometries and ranges of impact parameters has been achieved in this fashion[25,26] and also by surface-aligned photochemistry[27] in which the molecule being photolyzed and that under attack are aligned at a crystal surface. Such a reduction in dimensionality would increase the power of the TSS approach by restricting the range of TS configurations.[10]

Studies are presently under way to probe HD_2^{++} as a function of wavelength with a view to the characterization of transition-state internuclear geometries.

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