THE H+D_2 REACTION: “PROMPT” HD DISTRIBUTIONS AT HIGH COLLISION ENERGIES

Klaus-Dieter RINNEN, Dahv A.V. KLINER, Richard S. BLAKE [1] and Richard N. ZARE
Department of Chemistry, Stanford University, Stanford, CA 94305, USA

Received 14 November 1988

Probe-laser-induced (“prompt”) reaction of $H+D_2$ was observed in a mixture of HI and D_2 using (2+1) REMPI detection of the HD product. Rotational distributions for HD(v=0–3) of the prompt reaction are reported here, corresponding to center-of-mass collision energies of 1.20–1.65 eV and 1.95–2.40 eV. The measurements of the HD(v=3, J) product probe a previously inaccessible region of the potential energy surface for the title reaction. At these energies, the total reaction cross sections have been both measured and calculated, but quantum state specific theoretical predictions are not yet available.

1. Introduction

The first quantum state specific measurements of the $H+D_2$ reaction were independently performed in 1983 by two research groups [1,2]. Both experiments used laser photolysis of HI at 266 nm to generate H atoms of sufficient translational energy to overcome the reaction barrier [3] of ≈0.42 eV (classical value), but they differed in the method applied for the quantum state selective detection of the HD product. Gerrity and Valentini [1] (GV) used coherent anti-Stokes Raman spectroscopy (CARS), while Marinero, Rettner and Zare [2] (MRZ) employed resonance-enhanced multiphoton ionization (REMPI).

For the latter detection scheme, tunable radiation of ≈200 nm is used. At this wavelength, probe laser photolysis of HI [4] and subsequent reaction are possible; no problem of this kind exists for the CARS detection scheme because the necessary laser light is at wavelengths that do not photolyze HI. In the first REMPI experiment [2], the light was generated by Raman shifting (third or fourth anti-Stokes order) the frequency-doubled output of a pulsed dye laser, yielding pulse energies of 80–200 μJ. This is sufficiently low that the probe-laser-induced reaction is negligible [2]. With the advent of the nonlinear crystal, β-barium borate (BBO), it is possible to generate light at ≈200 nm by sum-frequency mixing with pulse energies of 1.0–1.5 mJ. At these higher pulse energies, probe-laser-induced reaction is observable and contributes to any experiment on the title reaction using (2+1) REMPI for detection.

In performing the measurements reported in the previous Letter [5], probe-laser-induced (“prompt”) product was observed and subtracted on a shot by shot basis. We report here the rotational distributions of the prompt reaction product, HD(v=0–3, J). The experimental details are given in refs. [5–8]

2. Experimental

The setup is identical to that described in the previous communication [5], with the exception of the omission of the photolysis laser. The HI : D_2 mix (ratio 1 : 3.5) is bled into the chamber through a quartz nozzle (orifice ≈0.8 mm; 11–15 Torr). The probe laser (wavelength ≈200 nm, generated with β-barium borate [#1]) is focused into the thermal mix-

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[1] Present address: Battelle Pacific Northwest Laboratory, Molecular Science Research Center, MS K2-44/PSL 1529, Richland, WA 99352, USA.

[#1] The barium borate crystals were supplied by R.S. Feigelson and R.K. Route and grown as part of a research program sponsored in part by the Army Research Office, contract DAAL03-86-K-0129, and in part by the NSF/MRL Program through the Center for Materials Research, Stanford University.

ture of HI and D_2 about 0.5 mm below the orifice. The HI photolysis and detection of the HD product occur during the same laser pulse (≈ 5 ns). The H atoms have two different center-of-mass collision energies caused by the splitting of the iodine spin–orbit states, $I^*(^2P_{1/2})$ and $I(^2P_{3/2})$. Fig. 1 shows the total photoabsorption cross section for HI and the branching ratio for the production of the two spin–orbit channels [4] as a function of excitation energy (the average excitation energies for $v=0$–3 are marked). Both energies are above the reaction barrier. The nascent HD product is detected via (2+1) REMPI by resonant excitation of the HD molecules from the electronic ground state X $^1\Sigma_g^+(v, J)$ to the E,F $^1\Sigma_g^+(v'=0, J'=J)$ state and subsequent ionization of the excited molecules. The HD^+ ions are detected in a shuttered time-of-flight mass spectrometer [6] and the ion signal is processed and recorded by a computer-interfaced, CAMAC-based data acquisition system [7].

The collision energy of this reaction is not constant. Because the HI photolysis is effected by the tunable probe laser, the photolysis wavelength and therefore the center-of-mass collision energy is varied as different rovibrational levels are detected. The collision energies as a function of J for $v=0$–3 are shown in fig. 2. For a particular v and spin–orbit channel, the spread in the collision energy is at most 0.15 eV between the lowest and highest J levels. The uncertainty in the collision energy caused by thermal motion at each wavelength is 0.05–0.08 eV. Thus, it is possible to neglect the fact that the collision energy changes by ≈ 0.0005 eV during the scan over a particular rotational transition.

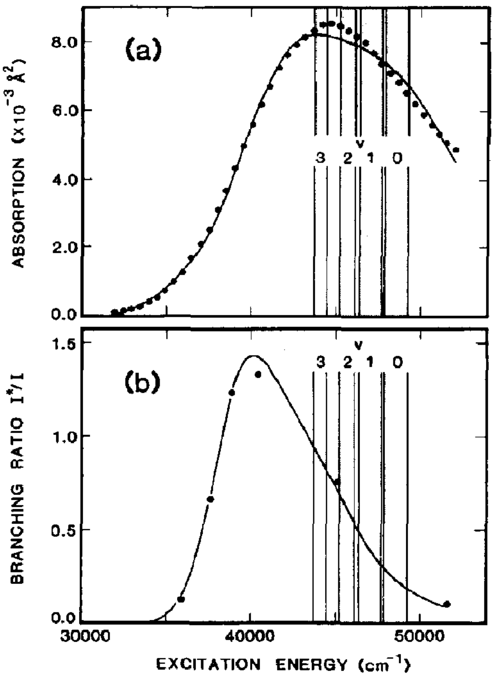

Fig. 1. Plotted against HI photolysis energy are (a) the total photoabsorption cross section and (b) the branching ratio $I^*(^2P_{1/2})/I(^2P_{3/2})$ for the production of the two spin–orbit components of I, taken from the work of Levy and Shapiro [4]. The calculated cross section (solid line) is compared with the experimental results (shown as symbols). The ranges of the excitation energies for $v=0$–3 used in this experiment are marked by the shaded bands.

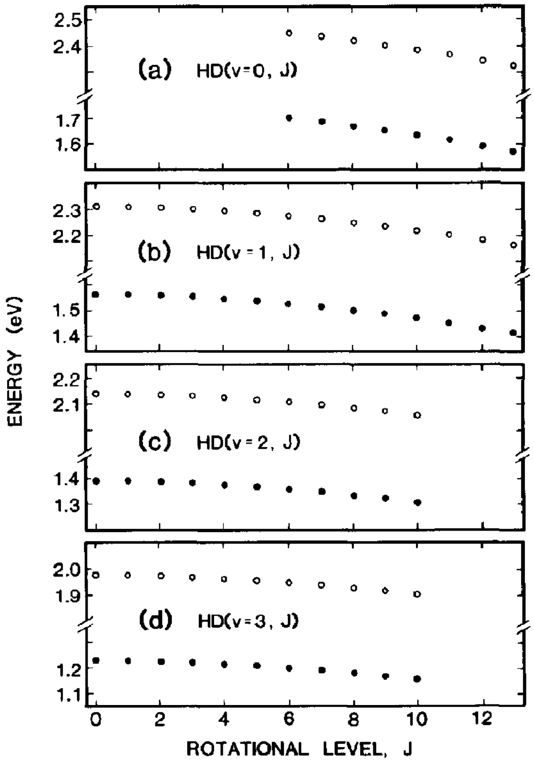

Fig. 2. Center-of-mass collision energy as a function of rotational quantum number for: (a) $v=0$, (b) $v=1$, (c) $v=2$, and (d) $v=3$. The closed circles mark the energies for the H atoms correlated with the production of $I^*(^2P_{1/2})$; the open circles mark the energies for the H atoms correlated with production of $I(^2P_{3/2})$.

The ion signal is processed as described in refs. [5,8,9] to obtain relative populations. A hot oven source ($\leqslant 1800$ K) was used as a calibration standard. It was found that the detection scheme is independent of J for HD($v=0, J=0$–13), ($v=1, J=0$–11), and ($v=2, J=0$, 2–8). The ($v=2, J=1$) transition is blended, as can be seen in an enhanced population in both the calibration spectra and the prompt reaction scans (see fig. 3). The population for $v=2$, $J=1$ is reported, but the degree of contamination could not be determined. This rotational level was therefore omitted in the analysis. No attempt was made to calibrate $v=3$ since the temperature required to populate the HD($v=3, J$) levels observed in the prompt reaction is prohibitively high.

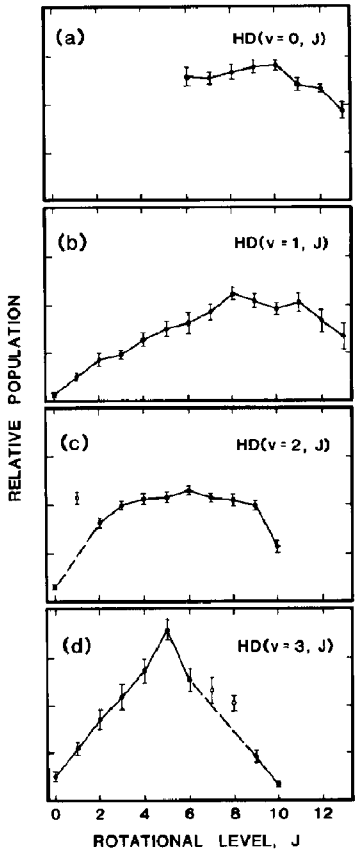

Fig. 3. Rotational distribution of the HD product for the probe-laser-induced reaction $H+D_2$: (a) HD($v=0$, J), (b) HD($v=1$, J), (c) HD($v=2$, J), and (d) HD($v=3$, J). Open symbols represent blended transitions whose populations have not been reliably measured. Error bars represent one standard deviation.

All checks for systematic errors are discussed in ref. [10]. An exception is the delay study. Because the photolysis, the reaction, and the detection occur within the same laser pulse (≈ 5 ns), this study is unnecessary.

3. Discussion

For each vibrational band, 15–18 distributions were taken. The individual scans were normalized to the sum over all J's and then averaged to give the rotational distributions listed in table 1. The data are shown in fig. 3.

3.1. HD($v=0, J$)

The distribution measured for $J=6$–13 is very broad, peaking at $J=10$ (fig. 3a). The populations for $J\leqslant 6$ have a contribution from HD present in the D_2 reagent. A correction on a shot by shot basis, as in the previous Letter [5], is not possible. Therefore, the determination of populations for $J\leqslant 5$ is not feasible; $J=6$ is probably slightly contaminated but is

Table 1
HD product quantum state populations [a,b] for $H+D_2 \rightarrow HD(v, J)+D$

J	$v=0$	$v=1$	$v=2$	$v=3$
0		0.007(02)	0.015(01)	0.025(05)
1		0.025(03)	{0.107(06)}	0.054(06)
2		0.043(07)	0.081(04)	0.086(10)
3		0.048(04)	0.099(04)	0.110(13)
4		0.064(07)	0.106(06)	0.136(13)
5		0.076(08)	0.108(06)	0.179(10)
6	0.129(10)	0.081(11)	0.115(04)	0.127(11)
7	0.127(06)	0.093(08)	0.107(04)	{0.116(13)}
8	0.134(08)	0.112(06)	0.105(07)	{0.103(08)}
9	0.139(07)	0.104(07)	0.099(05)	0.047(06)
10	0.141(05)	0.095(07)	0.057(06)	0.018(03)
11	0.121(07)	0.102(09)		
12	0.116(03)	0.083(12)		
13	0.093(08)	0.067(13)		

[a] Numbers in parentheses represent one standard deviation in the last digits, e.g., 0.129(10) means 0.129±0.010.

[b] The distributions are normalized so that: $\Sigma_{J_{\min}}^{J_{\max}} P(v_i, J)=1$ in each vibrational level, v_i.

reported. The center-of-mass collision energies are ≈ 1.65 and ≈ 2.4 eV.

3.2. HD($v=1$, J)

The populations for $v=1$ (as for $v=2$, 3) are not affected by the HD content of the D_2 reagent because the partial pressures for all rotational levels are below the limit for the detection sensitivity ($\approx 1\times10^6$ molecules/cm^3 per quantum state). The distribution for $J=0$–13 is shown in fig. 3b and has two maxima. The dip at $J=10$ was observed in 13 out of 17 scans. Both collision energies (≈ 1.5 eV and ≈ 2.25 eV) are above the reaction barrier. Thus, the observed distribution is the sum of two distributions, presumably peaking at different values of J. It is reasonable that this sum yields the observed bimodal distribution. Evidence for bimodal rotational distributions was found in the quantum theoretical calculations of Webster and Light [10] for the HD($v=0$, J) product of the title reaction. The calculated distributions are bimodal for collision energies of 0.84–1.3 eV (1.3 eV is the upper limit of the energy range in the calculations).

3.3. HD($v=2$, J)

The center-of-mass collision energies are ≈ 1.35 and ≈ 2.15 eV. Fig. 3c shows the HD distribution for $J=0$–10, peaking at $J=6$. As previously discussed, the observed ion signal for the ($v=2$, $J=1$) level must be disregarded.

3.4. HD($v=3$, J)

The center-of-mass collision energies are ≈ 1.2 and ≈ 1.95 eV. The populations for $J=0$–10 are plotted in fig. 3d. The peak of this distribution occurs at $J=5$. The $J=7$ and 8 peaks are asymmetric and significantly broader than the neighboring lines, indicative of blended transitions (as in $v=2$, $J=1$). Thus, the measured populations for $J=7$ and 8 must be disregarded.

As expected, the peak of the rotational distribution shifts to lower J with increasing v. Higher vibrational excitation results from, on average, smaller impact parameter collisions. Also, the center-of-mass collision energy decreases as higher vibrational branches are observed (fig. 2), resulting in lower rotational excitation.

Fig. 4 shows the experimental [11] and theoretical [12] cross section for the $H+D_2$ reaction. The average center-of-mass collision energies for both channels for $v=0$–3 are marked. The reaction cross section varies between 0.9 and 1.2 Å^2. As the figure shows, the cross section associated with the fast channel is almost constant, slightly decreasing for energies above ≈ 2.05 eV, while for the slow channel, it monotonically increases with energy.

The branching ratio I*/I decreases monotonically over the experimental range of center-of-mass collision energies (fig. 2). For $v=0$, I*/I is ≈ 0.2. Therefore, the HD product results mainly from the fast channel with a center-of-mass collision energy of ≈ 2.4 eV. As v increases, the corresponding collision energy decreases and the branching ratio I*/I increases. For $v=3$, I*/I is ≈ 0.9 and the ratio of the reaction cross section for the fast and slow channels is ≈ 0.8; the two channels therefore have similar contributions to the observed rotational distribution. The slow channel contribution to the HD product increases by a factor of ≈ 3.5 between $v=0$ and $v=3$.

The reported distributions constitute the first

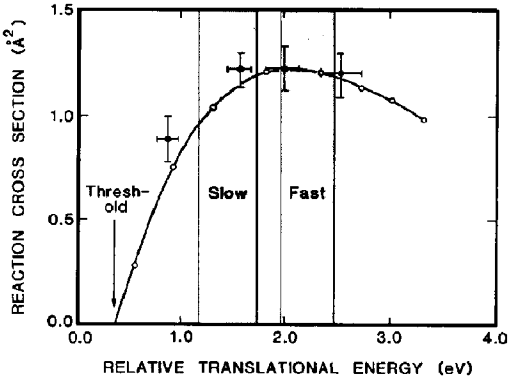

Fig. 4. Reaction cross sections for $H+D_2$ as a function of relative kinetic energy of the reagents. The experimental results of Johnston, Katz, Tsukiyama and Bersohn [11] are represented by full circles, the theoretical results of Schechter and Levine [12] by open circles. The line that connects the theoretical data points is drawn to guide the eye. The ranges of the excitation energies for $v=0$–3 used in this experiment are marked by shaded bands. The labels, slow and fast, refer to the two H atom channels correlated with the production of I*($^2P_{1/2}$) and I($^2P_{3/2}$), respectively.

quantum state specific measurements of the $H+D_2$ reaction at center-of-mass collision energies above 1.3 eV, complementing the total cross section measurements of Johnston et al. [11] at similar energies. The first observation of the $HD(v=3)$ product probes a previously inaccessible region of the potential energy surface. Theoretical distributions are not yet available at these center-of-mass collision energies. While it may be some time before three-dimensional quantum mechanical calculations are feasible, QCT calculations are possible [12]. The complication of the existence of two reactive collision energies contributing to the product distributions is taken into account by running trajectories at both energies (as done at 0.55 and 1.3 eV by Blais and Truhlar [13]). Until these calculations are performed, a comparison with theory is not possible.

Acknowledgement

We thank T.A. Stephenson for early work on this system and are grateful to A.C. Kummel and G.O. Sitz for many useful discussions. We thank L. Wolford for technical assistance with the laser system. Graduate fellowships are gratefully acknowledged by K-DR (Deutscher Akademischer Austauschsdienst, Jahresstipendium 1984/5; Rotary Foundation, 1985/6) and DAVK (National Science Foundation, 1986–89). This project is supported by the National Science Foundation under Grant No. NSF CHE 87-05131.

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