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Collision-energy dependence of HD($\nu'=1,j'$) product rotational distributions for the H+D_2 reaction

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Product rotational distributions for the reaction $H+D_2 \rightarrow HD(\nu'=1,j')+D$ have been measured for 16 collision energies in the range of $1.43 \leqslant E_{coll} \leqslant 2.55$ eV. Time-dependent quantum-mechanical calculations agree well in general with the experimental results, but they consistently yield slightly colder distributions. In terms of the average energy channeled into rotation, the differences between experiment and theory amount to approximately 10% for all collision energies sampled. No peculiarity is found for $E_{coll}=2.55$ eV at which the system has sufficient energy to access the first HD_2 electronically excited state. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1978871]

I. INTRODUCTION

Interplay between experiment and theory has proven essential for developing a deeper understanding of chemical reactivity.[1] On the one hand, the most subtle details of chemical reactions continue to elude direct observation and thus prevent their complete microscopic description based on experiment alone. On the other hand, the potential wealth of information provided by theory is not meaningful unless its accuracy is proven by comparison with reliable experimental data.

It should be expected that the ability of theory to model successfully experiment increases with the simplicity of the reaction system. As the simplest bimolecular neutral reaction, the hydrogen exchange and its isotopic variants are of special interest and have attracted ongoing attention from theoreticians and experimentalists alike.[2–7] The recently calculated H_3 potential-energy surfaces (PESs) are more accurate than the surfaces for any other neutral triatomic system.[8,9] Therefore, it came as a surprise that both time-dependent and time-independent quantum-mechanical (QM) calculations disagreed with the experimental results for the relative cross sections of the reaction $H+D_2 \rightarrow HD(\nu'=3,j')+D$.[10] For collision energies $E_{coll} \geqslant 1.70$ eV, the rotational distributions derived from the theory were significantly colder than those observed experimentally. A careful check of the experimental methodology did not reveal any substantive systematic errors that could account for this discrepancy.[10] Interestingly, a related study of the reaction $H+D_2 \rightarrow HD(\nu'=2,j')+D$ found a good agreement between experiment and theory for all collision energies investigated.[11]

To understand better the origin of this unexpected behavior, more work on the H+D_2 reaction system is clearly needed. As a systematic extension of previous studies,[10,11] our present contribution reports relative reaction cross sections for the reaction $H+D_2 \rightarrow HD(\nu'=1,j')+D$, obtained from both experiment and time-dependent QM calculations. We have taken care to cover a broad range of collision energies ($1.43 \leqslant E_{coll} \leqslant 2.55$ eV) because interesting effects might depend on the energy provided, as the example of the HD($\nu'=3,j'$) product rotational distributions shows.[10] Note that at the highest collision energy sampled in the present experiments, the overall energy of the system (including the zero-point energy of reactant D_2) lies slightly above the conical intersection at $E_{CI}=2.70$ eV [relative to $E(H+D_2[R_{eq}])=0$],[9] so nonadiabatic effects might influence the dynamics. Even at energies lower than E_{CI}, the electronic wave function changes sign if the nuclei encircle the conical intersection.[12,13] However, the influence of this so-called geometric phase effect on differential or integral reaction cross sections is still under debate[14–20] and has scarcely been tested experimentally at energies actually reaching the conical intersection.[21] The present study serves as an additional experimental probe for the existence or absence of the signature of the geometric phase effect in the hydrogen-exchange reaction.

Previous experimental studies have investigated the $H+D_2 \rightarrow HD(\nu'=1,j')+D$ reaction at selected energies $E_{coll} \approx 1.0$,[22] 1.3,[23–27] 1.6,[28] 2.2,[29,30] and 2.5 eV.[30] Theoretical calculations have been performed for most of these energies as well. Whereas earlier work applied quasiclassical trajectory (QCT) calculations,[21,31,32] more recently fully QM treatments of the title reaction have become feasible.[7,33–36] After outlining how the experiment is carried out and reviewing the theoretical treatment used, we discuss our present results in the light of these previous related studies.

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II. EXPERIMENT

A. Overview

As the apparatus used has been recently described in detail,[10,37] the focus herein lies on aspects specific to the present experiment. A dilute mixture of HX (X=Br or I, respectively) in D_2 is supersonically expanded into a vacuum chamber through a pulsed valve operated at 10 Hz. Synchronized UV laser light intercepting the molecular beam at a right angle photolyzes HX and thus provides fast H atoms. After a time delay of approximately 20 ns during which the H atoms are allowed to react with D_2, a second laser state selectively probes the resultant HD($\nu'=1,j'$) by [2+1] resonantly enhanced multiphoton ionization (REMPI). The HD^+ ions are formed in the ionization region of a Wiley-McLaren time-of-flight (TOF) mass spectrometer, extracted in the direction perpendicular to both the molecular beam and the laser propagation, and guided with an einzel lens to a pair of multichannel plates. The resulting signal is recorded on an oscilloscope and transferred to a computer for data storage and processing. Rotational distributions are inferred on the basis of the assumption that the corrected signal for a specific j' level is proportional to the relative population of that j' state in the nascent HD($\nu'=1,j'$).[10,37]

B. Reagents and photolysis

D_2 (Cambridge Isotope Laboratories, 99.9% isotopic purity) was used without further purification. HBr (Matheson, research grade) and HI (synthesized according to the literature)[38] were purified by a freeze-pump-thaw cycle immediately prior to their use. The HX to D_2 mixing ratios were approximately 10% for HBr and 6% for HI.

Tunable UV photolysis light (1.5–4 mJ) between 201 and 233 nm is generated by tripling the output of a dye laser [Quanta-Ray pulsed dye laser (PDL)] pumped by the second harmonic of a neodymium:yttrium aluminum garnet (Nd:YAG) laser (Quanta-Ray Cobra laser). For the highest sampled collision energy requiring 198-nm light, the energy per pulse was reduced to 0.4 mJ because higher energies were found to disproportionately increase the background noise. As HI has a smaller bond-dissociation energy than HBr, D_0(H–I)=3.05 versus D_0(H–Br)=3.76 eV,[39]photolysis by light of a given wavelength produces faster H atoms in the case of the former precursor. Thus, the use of both reagents is a convenient way to extend the range of collision energies covered in the experiment. At all collision energies, the spread in energy is estimated at approximately 0.05 eV.[40]

Photolysis of HX yields both ground-state $(^2P_{3/2})X$ atoms and spin-orbit excited $(^2P_{1/2})X^*$. As the energy required for this excitation is no longer available for accelerating the H atom, we refer to the photolysis involving spin-orbit excitation as the slow channel, in contrast to the fast channel producing ground-state X. The difference in E_{coll} between the fast and slow channels amounts to 0.36 and 0.75 eV for HBr and HI, respectively.[41] Whereas the branching ratio $[X^*]/([X]+[X^*])$ remains close to 0.17 for all wavelengths probed in the case of HBr,[42] it increases from 0.13 (198 nm) to 0.41 (233 nm) in the case of HI.[43–45] Note that the contribution from the slow channel to the measured signal is smaller than what the branching ratio alone might suggest, because the slower H atoms are less likely to collide with a D_2 molecule and undergo a productive reaction. For the sake of a concise notation, we will only give the collision energy of the fast channel for specifying the photolysis conditions of a particular data subset.

C. REMPI detection

State-specific detection of HD($\nu'=1,j'$) is achieved by [2+1] REMPI on the Q branch of the $E,F\,^1\Sigma_g^+ - X\,^1\Sigma_g^+(0,1)$ band. Approximately 0.3–1.0 mJ of light in the range of 209–222 nm is generated by tripling the output of a dye laser (Lambda Physik LPD3000) pumped by the second harmonic of a Nd:YAG laser (Quanta-Ray GCR-3). A 40-cm nominal focal length lens is used to focus the probe beam into the reaction chamber. The position of the lens is adjusted to compensate for the change of the refractive index when different j' states are probed, ensuring that the focal point always remains in the center of the molecular beam. For each rotational state, the probe laser then scans the Doppler profile of the HD product, and 30–40 spectra are averaged for each line. The entire rotational distribution is recorded four to eight times for all collision energies. The temporal order in which the different j' states are probed is reversed after each full scan so that the effects of long-term drifts, such as decrease in HX/D_2 backing pressure, tend to cancel.

The experiments employing HBr probe the population in the rotational levels $j'=0-12$. For $j'=13$, the HD^+ signal could not be resolved because of the presence of excessive space charges resulting from an atomic bromine resonance. For some of the other j' states, less pronounced bromine resonances were observed. However, in these cases the line centers of the interfering features were sufficiently far apart such that they overlapped only with one flank of the HD Doppler profile. Thus, the area of the latter could be obtained by integrating its uncontaminated half and doubling it. Note that the population in $j'=14$ cannot be determined because the REMPI transition accidentally overlaps with a transition from the HD($\nu'=2,j'=1$) state.[11] Higher j' levels were not probed either, because their population is expected to be negligible at the collision energies $E_{\mathrm{coll}} \leqslant 1.90$ eV sampled for HBr.

In the HI experiments, the HD rotational states up to $j'=18$ were scanned. Some problems arose for $j'=0$ and 1 where the signal intensity is rather small such that already minor contaminations have substantial effects. Therefore, the relative population in these rotational states could not be determined for all collision energies. As in the case of HBr, the REMPI scheme applied cannot selectively probe the population in $j'=14$.

The efficiency of the REMPI process strongly depends on the power of the probe light. The power is monitored during the entire experiment to correct for variations. To this end, the actual power dependence is measured repeatedly during each scan of the rotational distribution. Moreover, efforts are made to keep the laser power as constant as pos-

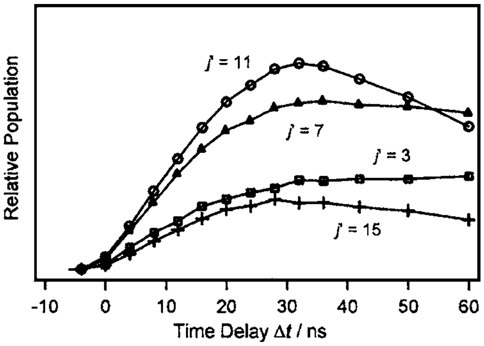

FIG. 1. Dependence of HD $(\nu'=1,j')$ product populations for H+D$_2$ on the time delay between photolysis and probe-laser pulse at $E_{\mathrm{coll}}=2.13$ eV.

sible over the whole range of wavelengths covered. For the HI experiment, we use two different dye mixtures to cover the low and high j' states.

Finally, the relative line strengths for the REMPI transitions must be taken into account. These transition probabilities have been determined experimentally for the Q branch of the $E,F\ ^1\Sigma_g^+ - X\ ^1\Sigma_g^+(0,1)$ band up to $j'=j''=11$; similar measurements have been performed for the (0,0), (0,2), (0,3), and (0,4) bands for HD as well as for H$_2$ and D$_2$.[46,47] In all cases, a good agreement with theoretically predicted line strengths is found, which include all rotational states for the HD (0,1) band relevant to the present work.[47,48] The transition probabilities increase gradually from $j'=j''=0$ to 18 (in total by 36%); an exception is the line strength for $j'=j''=17$, which is a factor of 2 smaller than those for the neighboring rotational states owing to resonant tunneling between the two wells of the $E,F\ ^1\Sigma_g^+$ state.[48]

D. Determination of relative reaction cross sections

Accounting for the rotational line strengths, one can convert the power-corrected Doppler scans to relative concentrations of HD$(\nu'=1,j')$. Because the concentrations of the reactants as well as their relative velocity (for a given collision energy) and the reaction time remain constant for all rotational levels probed, the measured concentrations are directly proportional to relative reaction cross sections $\sigma(\nu'=1,j')$.[10,37] Note that the amount of HD formed increases with reaction time, thus leading to larger signals and enhanced signal-to-noise ratios. However, too long time delays between the photolysis and probe-laser pulses must be avoided because otherwise HD molecules might travel out of the focal volume of the probe laser and thus escape detection. To determine the onset of this product fly-out, the signal dependence on the photolysis-probe time delay is systematically studied at low, medium, and high j' states for every collision energy. For example, deviations from linear product buildup start to become significant for time delays $\Delta t \geqslant 20$ ns at $E_{\mathrm{coll}}=2.13$ eV (Fig. 1). As expected, product fly-out starts earlier for higher and later for lower collision energies. Furthermore, it depends on the j' state. As a close inspection of Fig. 1 reveals, the signal levels off earlier for the higher rotational levels. The reason for this behavior is that HD product molecules with low rotational excitation are mainly backscattered and thus have smaller laboratory-frame velocities.[49,50] In the present experiment, great care was taken to probe the nascent HD molecules in the linear regime of product buildup for all rotational states and thus to exclude any possible systematic errors caused by product fly-out. If nonetheless some bias existed, it should lead to an *underestimation* of the relative rotational population in the high j' states. Note that, unlike the situation in flow-tube studies, collisional relaxation does not occur to an appreciable extent at the lower pressures and shorter delay times of the present experiment.[37]

As the probe laser operates at similar wavelengths as the photolysis laser, the former can photolyze HX as well. To correct the measured signal for this contribution, the profile of every j' state is also recorded at a time delay $\Delta t=5$ ns; the resultant signal area then is subtracted from the signal acquired at the longer reaction time $\Delta t \approx 20$ ns.[10,37] In the case of $j'=9$ at $E_{\mathrm{coll}}=2.55$ eV (HI photolysis at $\lambda=198$ nm), this method proved inappropriate as the signal area exhibits a nonlinear dependence on the reaction delay arising from an interfering resonant two-color process that is sensitive to both the wavelength of the probe and photolysis light. Note that any significant interferences are most likely to occur for $E_{\mathrm{coll}}=2.55$ eV because of the reduced photolysis-laser power and decreased signal intensity at this collision energy (see Sec. II B).

III. THEORETICAL METHOD

The quantum calculations used the wave-packet method of Ref. 35, which has been applied extensively to various isotopic variants of the hydrogen-exchange reaction.[7,10,11,20,36] The state-to-state integral cross sections were calculated in the energy range $E_{\mathrm{coll}}=1.4-2.6$ eV, including all partial waves in the range $J=0-45$. The initial wave packets were Gaussians, centered about $E_{\mathrm{coll}}=1.8$ eV, with the D$_2$ in the $\nu=0$, $j=0$ initial quantum state. A sufficiently large basis set ($\Delta R=0.07$ a.u., $\Delta r=0.11$ a.u., and $J_{\max}=44$; see Ref. 35) was used to ensure numerical convergence of the computed cross sections to better than 5%. The calculations omitted the geometric phase and the coupling to the excited electronic surface. Recent wave-packet calculations[20] have confirmed earlier predictions[19] that the geometric phase has no discernable effect on the integral cross sections and rovibrational product state distributions of the hydrogen-exchange reaction. A small amount of coupling to the upper surface, however, cannot be ruled out, and indeed one of the purposes of the present work is to investigate whether neglect of this coupling produces significant differences in the comparison with the experiment. If present, such differences would occur at energies close to the lowest point on the conical intersection seam (at $E_{\mathrm{CI}}=2.70$ eV).

IV. RESULTS

Figures 2 and 3 present the HD $(\nu'=1)$ rotational distributions derived from the HBr and HI experiments (assigned with statistical errors based on two standard deviations), respectively, together with the relative integral cross sections predicted by the theory. The theoretical values take into account the contributions of the slow channel (see Sec. II C for

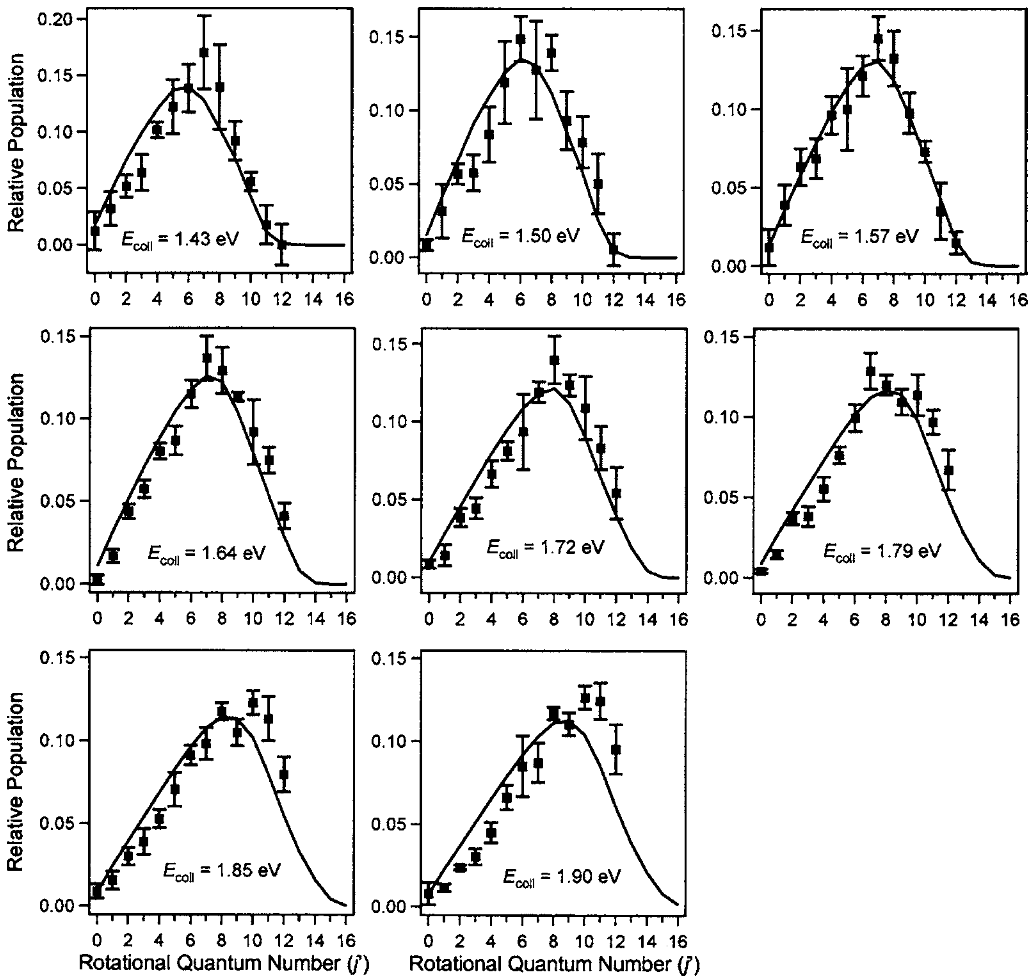

FIG. 2. Experimental (■, with statistical errors based on 2σ) and theoretical (solid line) HD $(\nu'=1,j')$ product rotational distributions for $H+D_2$ at different collision energies. The experiments employ HBr as photolytic precursor; the theory takes into account the slow channel and the experimental spread in E_{coll}.

details) weighted by the branching ratios reported in the literature.[42–45] In addition, the theoretical data are multiplied by the experimental collision-energy broadening profile to facilitate comparison with the measurements; however, this convolution has hardly any effect. Finally, the experimental and theoretical rotational distributions are normalized to equal areas.

The cross sections derived from the HBr experiments (Fig. 2) show at each collision energy a unimodal distribution, and the peaks of these unimodal distributions shift to higher rotational states as a function of E_{coll}. This behavior meets expectations in that the provision of increased amounts of energy leads to the population of higher j' levels in the HD $(\nu'=1)$ product. Analogous energy dependences have been found for nascent HD $(\nu'=2,3,j')$ products.[10,11] The theoretical rotational distributions exhibit a very similar trend but are consistently slightly colder than the experimental ones.

In contrast to the HBr data, the cross sections extracted from the HI experiments display bimodal features at collision energies $E_{coll}\leqslant 2.01$ eV. This behavior is not the result of a bimodal distribution of the reaction products, but rather it reflects larger contributions from the slow channel at lower collision energies (Table II). Accounting for the wavelength-dependent branching ratio, the theoretical results qualitatively reproduce the bimodal rotational distributions for $E_{coll}\leqslant 2.01$ eV and allow to separate the contributions of the fast and slow channels (Fig. 4 for $E_{coll}=1.80$ eV). While the general agreement between experiment and theory is fairly good again, the theoretical rotational distributions are slightly colder for all collision energies studied, like in the case of the HBr results. Similar to the HBr data, rotational excitation increases as a function of collision energy.

A straightforward comparison between the different rotational distributions $P(j')$ can be achieved by calculating total amounts of rotational energy E_{rot} defined as

$$E_{rot}=\langle E(j')\rangle=\sum_{j'=0}^{j'_{max}} P(j')E(j'), \tag{1}$$

where $E(j')$ is easily obtained on the basis of the known spectroscopic constants for HD.[51] The HBr experiments measured the relative cross sections only up to $j'=12$ and therefore missed all population in the higher rotational states. Hence, a comparison with the theory has to be limited to $j'\leqslant 12$. In the case of the HI data, the experiments determined relative cross sections up to $j'=18$ and thus missed any rotational population only for the highest collision energies investigated. For $j'=14$ and other j' states whose relative cross sections could not be measured, the rotational

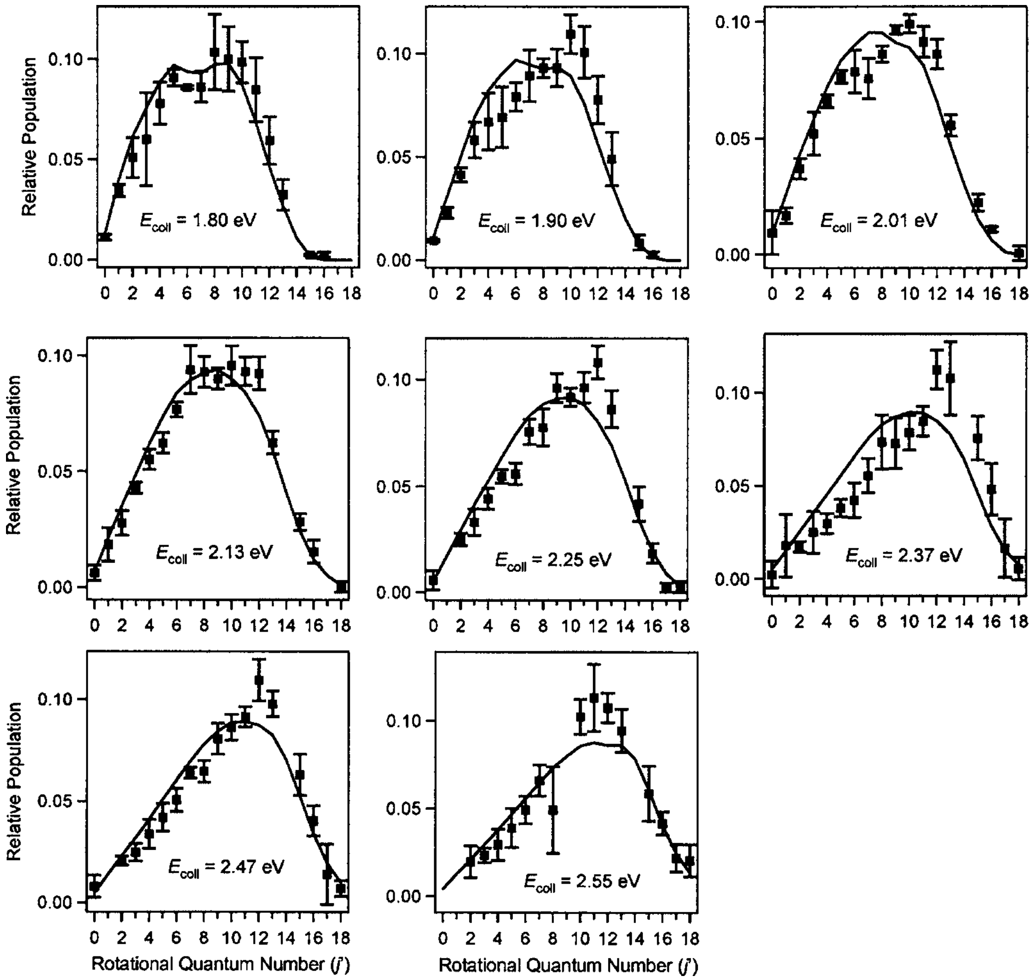

FIG. 3. Experimental (■, with statistical errors based on 2σ) and theoretical (solid line) HD ($\nu'=1,j'$) product rotational distributions for H+D$_2$ at different collision energies. The experiments employ HI as photolytic precursor; the theory takes into account the slow channel and the experimental spread in E_{coll}.

population is approximated as the average of those of the two neighboring j' levels.

A comparison of the resulting rotational energies corroborates the finding that the theoretical j' distributions are consistently colder than the experimental ones and also permits a quantification of this discrepancy (Tables I and II). The relative difference between experimental and theoretical rotational energies is approximately constant over the whole range of collision energies covered and amounts to about 10%. We believe that the similar behavior observed in the HBr and HI measurements serves as an indication of the internal consistency in the experiment. Unfortunately, a more direct comparison between the HBr and HI data at the overlapping collision energies is impossible owing to the significant contribution of the slow channel in the HI experiments.

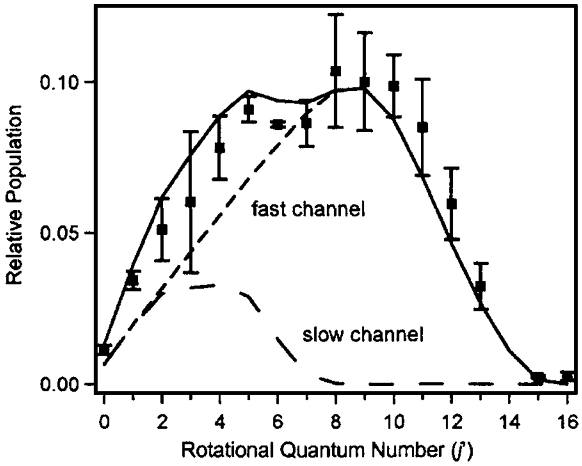

FIG. 4. Experimental (■) and theoretical (solid line) HD ($\nu'=1,j'$) product rotational distributions for H+D$_2$ at E_{coll}=1.80 eV together with the calculated contributions of fast and slow channels (dashed lines) from HI photolysis.

V. DISCUSSION

The present results demonstrate good agreement between experiment and theory over an extensive range of collision energies. They thus provide strong evidence for the general validity of both approaches. This finding is important because the application of the same methods gave rise to substantial discrepancies between experimental and theoretical rotational distributions for nascent HD ($\nu'=3,j'$) at $E_{coll} \geq 1.70$ eV.[10] Apparently, the system undergoes a significant change at those conditions, with which the experiment or, perhaps more probably, theory cannot cope.

TABLE I. Energy in rotation of product HD ($\nu'=1$) as a function of HBr photolysis conditions.

λ_{photo} (nm)	$[\text{Br}^*]/([\text{Br}]+[\text{Br}^*])$[a]	E_{coll}(fast) (eV)	E_{coll}(slow) (eV)	E_{coll}(eff) (eV)[b]	$E_{\text{rot}}(j'=0-12)$ (eV)		E_{rot}(Expt.)/ E_{rot}(Theo.)[e]	E_{rot} (eV)[f]	$\langle g_{\text{rot}}\rangle$[g]
					Expt.[c]	Theo.[d]			
222.7	0.18	1.43	1.07	1.40	0.25±0.02	0.21	1.17	0.21	0.24
219.5	0.18	1.50	1.14	1.46	0.28±0.02	0.24	1.16	0.24	0.25
215.6	0.17	1.57	1.21	1.54	0.27±0.02	0.27	1.01	0.27	0.25
212.4	0.17	1.64	1.28	1.61	0.32±0.01	0.29	1.12	0.29	0.26
208.7	0.16	1.72	1.36	1.68	0.34±0.02	0.30	1.12	0.32	0.27
205.7	0.16	1.79	1.43	1.75	0.35±0.01	0.31	1.11	0.35	0.28
203.5	0.16	1.85	1.49	1.80	0.36±0.01	0.32	1.13	0.37	0.28
201.4	0.16	1.90	1.54	1.85	0.38±0.02	0.32	1.16	0.39	0.29

[a] Taken from Ref. 42.

[b] Weighted average of E_{coll}(fast) and E_{coll}(slow).

[c] Statistical uncertainties based on 2σ.

[d] Takes into account contributions from slow channel and energy broadening.

[e] $E_{\text{rot}}=\langle E(j')\rangle$, $j'=0-12$.

[f] Theoretical value including all energetically accessible j' states.

[g] $\langle g_{\text{rot}}\rangle = E_{\text{rot}}/E_{\text{avail}}$ with $E_{\text{avail}}=E_{\text{coll}}(\text{eff})+E(\text{D}_2,\nu=0)-E(\text{HD},\nu'=1)$. Theoretical value for E_{rot}.

A. Comparison with previous results

The present experimental and theoretical findings can be compared with previous results reported for the title reaction. Much data available for $E_{\text{coll}}=1.3$ eV suggest that the rotational distribution peaks at $j'=4$ for this energy.[23–27] As expected, the maximum in the rotational population shifts to higher j' states with increasing collision energies and lies near $j'=6$ for $E_{\text{coll}}=1.50$ and 1.43 eV, the lowest energies probed here. Bean *et al.*[28] investigated the title reaction at $E_{\text{coll}}\approx 1.64$ eV, a collision energy we sampled as well. While both data sets show good agreement (Fig. 5), a closer inspection reveals that the rotational distribution reported by Bean *et al.* is slightly colder than the one derived from the current experiments. This difference might result from the fact that Bean *et al.* used a single laser to bring about both HBr photolysis and REMPI detection of the HD product and thus changed the photolysis conditions with j'. As a result, the effective collision energy varied from $E_{\text{coll}}=1.72$ to 1.57 eV for $j'=0-13$ and thereby unduly favored low rotational states compared to the higher j' levels. With respect to theory, Blais and Truhlar performed QCT calculations for $E_{\text{coll}}=1.6$ eV and obtained relative cross sections close to the results of the present study (Fig. 5).[32] Note that their calculations do not account for the slow channel, whose contribution is quite small in the case of HBr photolysis, however.

Other experiments probed the title reaction at $E_{\text{coll}}\approx 2.25$ eV.[29,30] The reported j' distributions are colder than the present one for this collision energy (Fig. 6). These deviations, 15% and 20%, respectively, in terms of $E_{\text{rot}}(j'=0-13)$, appear too large to result only from the use of a single laser for HI photolysis and REMPI detection in the previous experiments. In line with this notion, a comparable disagreement between the current and earlier data arises for a collision energy $E_{\text{coll}}=2.5$ eV, although Adelman *et al.*[30] also used an independent second laser for HI photolysis in that experiment. A possible explanation for these discrepancies could be that the earlier experiments, unlike the present study, did not adjust the focusing conditions of the probe-laser beam while scanning the different j' states.[29,30] Whereas this omission is deemed less problematic at lower collision energies and narrow rotational distributions, it might result in an appreciable discrimination against higher j' states only populated at high collision energies.

The title reaction has also been studied theoretically at $E_{\text{coll}}=2.25$ eV. QCT calculations on the double many-body expansion (DMBE) surface[52] by Blais and Truhlar include

TABLE II. Energy in rotation of product HD ($\nu'=1$) as a function of HI photolysis conditions.

λ_{photo} (nm)	$[\text{I}^*]/([\text{I}]+[\text{I}^*])$[a]	E_{coll}(fast) (eV)	E_{coll}(slow) (eV)	E_{coll}(eff) (eV)[b]	$E_{\text{rot}}(j'=0-18)$ (eV)		E_{rot}(Expt.)/ E_{rot}(Theor.)[e]	$\langle g_{\text{rot}}\rangle$[f]
					Expt.[c]	Theor.[d]		
233.0	0.41	1.80	1.05	1.67	0.36±0.02	0.32	1.12	0.27
227.6	0.37	1.90	1.15	1.76	0.41±0.02	0.36	1.15	0.28
222.0	0.32	2.01	1.26	1.87	0.44±0.01	0.40	1.12	0.29
216.1	0.27	2.13	1.38	1.99	0.48±0.01	0.45	1.06	0.30
210.6	0.22	2.25	1.50	2.12	0.54±0.02	0.50	1.08	0.31
205.3	0.18	2.37	1.62	2.26	0.64±0.04	0.55	1.17	0.31
201.2	0.15	2.47	1.72	2.35	0.61±0.03	0.58	1.04	0.32
198.0	0.13	2.55	1.80	2.45	0.65±0.04	0.61	1.06	0.32

[a] Based on an interpolation of the values reported in Refs. 43–45.

[b] Weighted average of E_{coll}(fast) and E_{coll}(slow).

[c] Statistical uncertainties based on 2σ. For j' states whose population could not be determined, the relative cross section is estimated as the average of those of its neighboring j' levels.

[d] Takes into account contributions from slow channel and energy broadening.

[e] $E_{\text{rot}}=\langle E(j')\rangle$, $j'=0-18$.

[f] $\langle g_{\text{rot}}\rangle = E_{\text{rot}}/E_{\text{avail}}$ with $E_{\text{avail}}=E_{\text{coll}}(\text{eff})+E(\text{D}_2,\nu=0)-E(\text{HD},\nu'=1)$. Theoretical value for E_{rot} including contributions from $j'=0-20$.

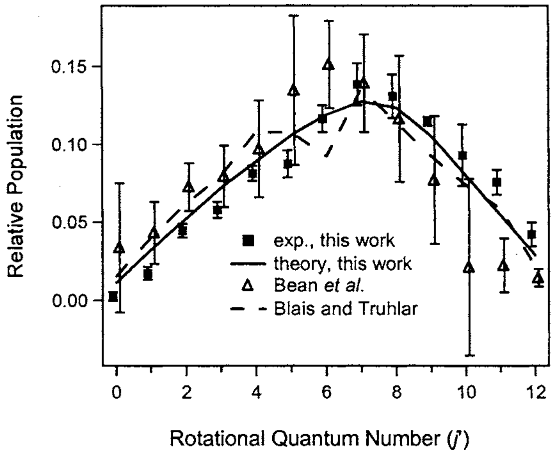

FIG. 5. Comparison of the present experimental and theoretical HD ($\nu'=1,j'$) product rotational distributions for H+D$_2$ at $E_{\text{coll}}=1.64$ eV with previous results by Bean *et al.* (Ref. 28) and Blais and Truhlar (Ref. 32) for similar collision energies.

$E_{\text{coll}}=1.5$ eV and thus allow to account for the slow channel.[32] The resulting rotational distribution agrees well with our experimental observations and is slightly warmer than that predicted by the present QM calculations (Fig. 6). Wrede *et al.*[33,53] used both QCT and QM methods to investigate the hydrogen-exchange reaction at $E_{\text{coll}}=2.20$ eV, and they found results similar to those of the theoretical studies at $E_{\text{coll}}=2.25$ eV. These authors also noticed that the QCT approach yields slightly warmer rotational distributions than the QM calculations.

B. Implications for the dynamics of the hydrogen-exchange reaction

As mentioned above, the absolute energy going into product rotation increases with E_{coll}. Another interesting quantity is the averaged reduced rotational energy $\langle g_{\text{rot}}\rangle$ (Tables I and II). The reduced rotational energy g_{rot} and its average $\langle g_{\text{rot}}\rangle$ are defined as

$$g_{\text{rot}}(\nu',j') \equiv \frac{E(j')}{E_{\text{tot}}-E(\nu')} \tag{2}$$

and

$$\langle g_{\text{rot}}(\nu',j')\rangle \equiv \sum_{j'} P(j')g_{\text{rot}}(\nu',j') = \frac{E_{\text{rot}}}{E_{\text{tot}}-E(\nu')}, \tag{3}$$

with

$$\begin{aligned} E_{\text{tot}} &= E_{\text{coll}}(\text{eff}) + E_{\text{rxn}} \\ &= E_{\text{coll}}(\text{eff}) + E(D_2,v=0) - E(\text{HD},v'=0). \end{aligned} \tag{4}$$

In the present case, $E_{\text{coll}}(\text{eff})$ is the weighted average of collision energies for the fast and slow channels (accounting for the branching ratio, different velocities, and different reactivities of both channels). Thus, $\langle g_{\text{rot}}\rangle$ is a measure of the ratio of the energy actually channeled into rotation E_{rot} to the total energy available for rotational excitation, $E_{\text{avail}}(\text{rot}) \equiv E_{\text{tot}}-E(\nu')$. Note that the remainder of $E_{\text{avail}}(\text{rot})$ not consumed for rotational excitation appears in the product translation. For HD ($\nu'=1$), $\langle g_{\text{rot}}\rangle$ slightly increases as a function of collision energy (Tables I and II, the values given rely on the theory to include contributions from rotational states up to $j'=20$). Similar but more pronounced trends have been observed for product HD ($\nu'=2,3,j'$).[10,11] Such increases of rotational excitation at the expense of translational energy are not necessarily expected, given that the density of translational states grows with energy ($\omega_{\text{trans}} \propto E^{1/2}$), in contrast to the density of rotational states ($\omega_{\text{rot}}=\text{const}$). Obviously, a purely statistical approach does not adequately describe the system.

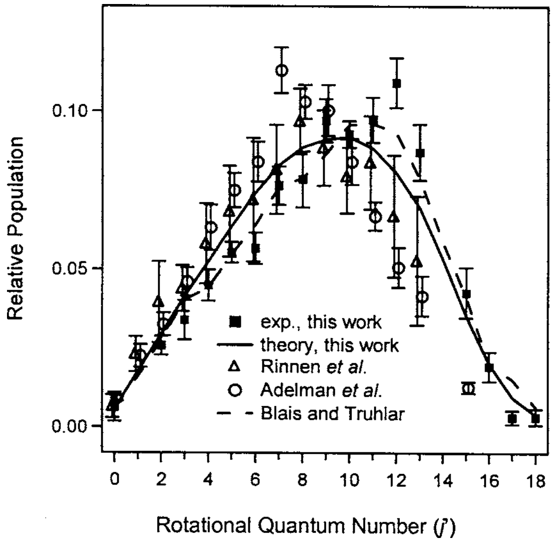

FIG. 6. Comparison of the present experimental and theoretical HD ($\nu'=1,j'$) product rotational distributions for H+D$_2$ at $E_{\text{coll}}=2.25$ eV with previous results by Rinnen *et al.* (Ref. 29) (corrected for REMPI line strengths not accounted for in the original work), Adelman *et al.* (Ref. 30) and Blais and Truhlar (Ref. 32) for similar collision energies.

A comparison between the results obtained for HD ($\nu'=1-3$) is also instructive in another regard. For the highest collision energies sampled in the HD ($\nu'=2,3$) experiments, $1.7 \leqslant E_{\text{coll}} \leqslant 1.9$ eV, $\langle g_{\text{rot}}\rangle \approx 0.3$ was found.[10,11,54] Similar values are derived in the present work for HD ($\nu'=1$) at comparable E_{coll}. Note, however, that equal E_{coll} values do not correspond to equal values of $E_{\text{avail}}(\text{rot})$ for HD in different vibrational states because the energy tied up in vibration is no longer available for rotational excitation [$E_{\text{avail}}(\text{rot})=1.26$, 0.83, and 0.42 eV for $\nu'=1-3$ at $E_{\text{coll}}=1.80$ eV]. Given the positive slopes of $\langle g_{\text{rot}}\rangle$ as a function of E_{coll}, it is not clear whether the $\langle g_{\text{rot}}\rangle$ values for HD ($\nu'=1-3$) would still agree at equal $E_{\text{avail}}(\text{rot})$, which might be a more adequate basis for such a comparison than equal E_{coll}.

A way to assess the deviations from the statistical limit in the product distributions is a surprisal analysis.[1] This method compares the measured rotational distribution $P(j',\nu';E_{\text{tot}})$ with the so-called prior distribution $P^0(j',\nu';E_{\text{tot}})$. The prior distribution corresponds to the statistical limit where all accessible product quantum states are populated with equal probability. It is therefore given by the product of rotational and translational degeneracies for the reaction of an atom with a diatom:

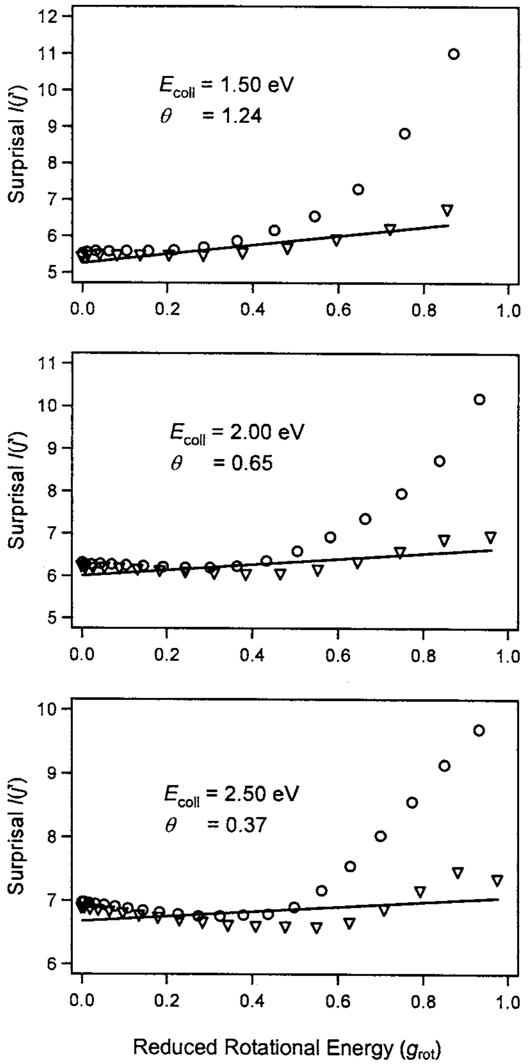

FIG. 7. Linear surprisal analyses of the theoretical HD $(\nu'=1,j')$ product rotational distributions for $H+D_2$ at E_{coll}=1.50, 2.00, and 2.50 eV. Conventional analyses without (○) and modified analyses with inclusion of kinematic constraints (∇) are shown together with linear fits to the latter with slopes θ.

$$P^0(j',v';E_{tot}) = [2j'+1][E_{tot}-E(j')-E(v')]^{1/2}. \tag{5}$$

The negative logarithm of the ratio between the measured and the prior distribution is then called the surprisal $I(j',\nu')$, that is

$$I(j',\nu') \equiv -\ln\left[\frac{P(j',\nu';E_{tot})}{P^0(j',\nu';E_{tot})}\right]. \tag{6}$$

In linear surprisal analysis, $I(j',\nu')$ is plotted against the reduced rotational energy g_{rot} and fitted to a line. The slope of this line is referred to as the surprisal parameter θ, which becomes zero for a purely statistical product distribution.

For the present experimental data, the contributions of the slow channel are likely to complicate the interpretation of the surprisal analysis. Therefore, only the theoretical data excluding the slow channel (as well as the experimental spread in E_{coll}) are subjected to the analysis. This approach appears valid because the generally good agreement with the experiment lends support to the accuracy of the theoretical results. The conventional surprisal analysis (Fig. 7, circles) finds a significant nonlinear behavior and thus we conclude that the data cannot be fitted successfully to a linear surprisal. Similar observations for the $H+D_2$ reactions have been reported previously.[27,55] However, Picconatto *et al.*[56] found that the curvature in the surprisal plots is much reduced if kinematic constraints are taken into account. The model that these authors propose for high collision energies assumes that most reactive trajectories do not follow the minimum-energy path, but are reflected from the repulsive walls of the PES from the reactant into the product valley. As a result, there is a minimum product translational energy, which cannot be channeled into internal degrees of freedom.[56] Hence, the effective energy to be considered in the surprisal analysis must be reduced by this amount. For the $H+D_2$ reaction, only 83% of E_{tot} is available for internal excitation of product HD. If this kinematic constraint is imposed, the surprisal analysis indeed yields an approximately linear dependence between $I(j',\nu')$ and g_{rot} (Fig. 7, triangles). The positive slope of the fit for E_{coll}=1.50 eV indicates that the calculated rotational distribution is colder than the statistical limit. With increasing collision energies, θ decreases and approaches zero. However, for E_{coll}=2.50 eV deviations from linearity become significant again and suggest that dynamic restrictions in addition to the kinematic constraints are important. At that energy, the surprisal plot clearly shows two regions with distinctive slopes, which might point to the operation of two different reaction mechanisms. We also find population in j' states that should not be accessible according to the model of Picconatto *et al.*[56] Similar violations of the model's predictions were observed for the measured and calculated rotational distributions for product HD $(\nu'=2,3,j')$.[10,11]

Another aspect potentially relevant to the dynamics of the title reaction is the influence of nonadiabatic effects. The highest collision energy sampled, E_{coll}=2.55 eV, corresponds to an overall energy of $E=E_{coll}+E(D_2,\nu=0)$ =2.74 eV, which lies just above the conical intersection at E_{CI}=2.70 eV [relative to $E(H+D_2[R_{eq}])=0$].[9] Thus, interactions with the upper PES are energetically feasible. However, the fact that the adiabatic QM calculations apparently do not describe the measured rotational distribution worse than those at lower energies points to the absence of such interactions. Wrede *et al.*[21] came to similar conclusions based on experimental and theoretical works sampling the hydrogen-exchange reaction at an overall energy of E=2.86 eV.

C. Residual differences between experiment and theory

Although the overall agreement between the experimental and theoretical results is good, slight discrepancies remain. As stated above, these deviations are not of random nature, but they are consistent in that the theory yields colder rotational distributions than the experiment. This finding implies the existence of a small yet systematic error in the experimental or theoretical method.

We have carefully checked the experimental methodology (see Sec. II) without finding any significant errors that could explain the discrepancy. Note, in particular, that product fly-out as a potential matter of concern would discriminate against the high j' states and thus lead to too cold j' distributions, which is the opposite of what is observed. Apart from the collection of raw data, their conversion to relative cross sections could be fault prone as well. This conversion is based on the line strengths for the REMPI transitions reported in the literature and must rely on their accuracy. Although the calculated values used herein agree well with the available experimental results, the large uncertainty ranges of the latter and the lack of experimental data for $j' \geq 12$ somewhat weaken the significance of this comparison.[46,48] Whereas the theoretically predicted line strengths slightly increase as a function of j',[47,48] the experimental transition probabilities remain approximately constant for $j' = 0-11$ and are thus relatively smaller than the theoretical values for the higher rotational levels.[46] This means that a recalculation of the cross sections on the basis of the available experimental line strengths would yield even warmer rotational distributions. Therefore, it does not appear very likely that the differences between the experimentally and theoretically determined cross sections of the present work are caused by erroneous line strengths, although we cannot rigorously rule out this possibility. We note in passing that the experimental rotational distributions relying on the calculated line strengths do not display any noticeable feature for $j' = 17$. This finding is interesting because the theoretical transition probability for this rotational state is particularly low (see Sec. II C).[47,48] The present results may thus be considered an indirect corroboration of the predicted line strength for the $E,F\, {}^1\Sigma_g^+(v'=0, j'=17) - X\, {}^1\Sigma_g^+(v''=1, j''=17)(2+1)$ REMPI transition in HD.

A further point to be mentioned is the assumption of complete absence of internal energy in the D_2 reactant (in excess of the zero-point vibrational energy) made in the calculations. Whereas vibrational excitation of D_2 indeed can safely be neglected, the estimated rotational temperature of $T_{\mathrm{rot}} \approx 90$ K achieved by the supersonic expansion corresponds to significant population in $j=0$, 1, and 2.[10,11,40] However, previous QCT calculations found the effect of this rotational excitation to be insignificant for product HD $(v'=2,3,j')$ at $E_{\mathrm{coll}}=1.64$ and 1.85 eV.[10,11] No appreciable effect of D_2 rotational excitation is expected in the present case either, particularly because the ratio between the internal energy of the reactant and E_{coll} is even smaller for most of the collision energies sampled here.

Another issue is the contribution of the slow channel. The calculated reaction cross sections weight both the fast and slow channels according to their reactivities, their velocities, and the experimental branching ratios reported in the literature. Thus, errors in these branching ratios could lead to errors in the theoretical predictions. However, the obtained distributions are rather insensitive to the branching ratio; indeed, even complete neglect of the slow channel in the calculated cross sections produces rotational distributions colder than the ones derived from the HBr and part of the HI experiments (those at high collision energies where $[\mathrm{I}^*]/([\mathrm{I}]+[\mathrm{I}^*]) < 20\%$). Therefore, errors in the branching ratios can hardly explain the observed deviations from the experimental rotational distributions.

Finally, the differences between the experimental and theoretical cross sections could result from errors in the QM calculations. These calculations use the BKMP2 PES, which is considered to be very accurate.[8] In particular, previous QM calculations based on this surface succeeded in reproducing experimental results for the hydrogen-exchange reaction.[7,11,33] Nonetheless, there remains the possibility of residual errors in the BKMP2 PES causing small errors in the calculated integral HD $(v'=1, j')$ cross sections. Apart from the PES, the theoretical method itself could be deficient. The present QM calculations do not include the geometric phase effect whose influence on integral cross sections still is controversial, although a growing body of evidence suggests that its effect is negligible.[14–18,20,57] In line with these results, the overall good agreement between the theoretical predictions and experimental findings supports the contention that a particularly pronounced geometric phase effect does not occur for $1.43 \leq E_{\mathrm{coll}} \leq 2.55$ eV. Another potential cause for this discrepancy is the omission of the Born-Oppenheimer diagonal correction in the present QM treatment, but without explicit calculations no conclusion can be reached, and in any case, this effect is likely to be very small.[58] Thus, at present we cannot identify with certainty the origin of the small discrepancy between theory and experiment for these relative integral cross sections.

VI. CONCLUSIONS

Relative integral cross sections for the reaction $\mathrm{H}+\mathrm{D}_2 \rightarrow \mathrm{HD}(v'=1, j')+\mathrm{D}$ have been measured at collision energies 1.43–2.55 eV. The experiments employ HBr and HI as photolytic precursors for the fast hydrogen atoms. Although the complicating effect of spin-orbit excitation does not permit a straightforward comparison between the HBr and HI data, indirect evidence suggests good internal consistency of the experimental results. With increasing collision energy, the peaks in the rotational distributions shift to higher j' values and the average energy in rotation grows slightly more rapidly than linearly. Similar behavior has previously been observed for the HD $(v'=2,3,j')$ product rotational distributions.[10,11]

Time-dependent QM calculations on the BKMP2 PES overall reproduce the experimental results well, but they consistently yield slightly colder rotational distributions. A comparison of the total energy in rotation shows that this difference amounts to approximately 10% over the entire range of collision energies sampled. A careful analysis does not find any significant systematic errors in the experimental method. On the side of the theory, residual errors in the BKMP2 surface or the neglect of nonadiabatic effects in the QM calculations could potentially be problematic. Note, however, that the relative disagreement between experiment and theory stays constant even when the available energy is sufficient to reach the conical intersection. This finding suggests that interactions with the upper surface do not strongly affect the dynamics at $E_{\mathrm{coll}} \leq 2.55$ eV and conversely that the neglect of these interactions in the calculations is unlikely to account for the discrepancies with the experiment. A surprisal analysis of the theoretical rotational distributions yields approximately linear plots only if kinematic constraints according to the model of Picconatto *et al.*[56] are included.

With the present work and related recent studies, an extensive body of experimental data on the collision-energy dependence of the hydrogen-exchange reaction is available.[10,11] It is reassuring to note that state-of-the-art theoretical methods agree reasonably well with experiment in the rotational distributions of nascent HD $(\nu'=1,j')$ and HD $(\nu'=2,j')$. In turn, the substantial discrepancies between experiment and theory observed for product HD $(\nu'=3,j')$ at $E_{\mathrm{coll}}\geqslant 1.7$ eV appear to reflect qualitative changes in the dynamics of the system. To elucidate the nature of these changes, additional measurements of differential cross sections for HD $(\nu'=3,j')$ at high collision energies would be helpful. For the time being, it must remain open why the differences between experiment and theory do not follow a clear trend but are minimal for HD $(\nu'=2,j')$, small yet noticeable for HD $(\nu'=1,j')$, and largest for HD $(\nu'=3,j')$. Other efforts may involve further sophistication of the theoretical methodology, such as the use of the more accurate CCI PES (Ref. 9) or the incorporation of nonadiabatic effects. It would also be interesting to see whether these advances in theory could eliminate the remaining small deviations from the measured rotational distributions for HD $(\nu'=1,j')$ and thus achieve quantitative agreement with the experiment.

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