

Corroboration of Theory for $\text{H} + \text{D}_2 \rightarrow \text{D} + \text{HD}$ ($v' = 3, j' = 0$) Reactive Scattering Dynamics[†]

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The differential cross section (DCS) for the reaction $\text{H} + \text{D}_2 \rightarrow \text{D} + \text{HD}$ ($v' = 3, j' = 0$) exhibits particularly rich dynamics; in addition to the expected direct recoil backscattering feature, a surprising time-delayed forward scattering feature appears that has been attributed to glory scattering arising from nearside and farside interference. This fact leads to a complex DCS that depends strongly on the collision energy. Its accurate calculation requires a fully quantum mechanical (QM) treatment. We report improved measurements of this DCS over the collision energy range $1.55 \leq E_{\text{coll}} \leq 1.82$ eV. Previous measurements using the core extraction method, while generally in agreement with theory, lacked sufficient resolution to capture all of the noteworthy behavior of the system; in the present work, we use ion imaging to observe many previously unresolved features of the DCS, particularly in the forward-scattered region. Agreement with QM calculations is found at all collision energies, reconciling an earlier discrepancy between experiment and theory near $E_{\text{coll}} = 1.54$ eV.

Introduction

The reaction $\text{H} + \text{D}_2 \rightarrow \text{D} + \text{HD}$ (v', j') has long been known to proceed mainly via a direct recoil mechanism, with the lowest barrier appearing at collinear geometry.^{1–3} The generally observed trend over a broad range of collision energies is that (1) HD products with low j' are scattered backward and (2) the angular distribution gradually shifts toward side scattering for higher j' as the angular momentum of the reactants at larger impact parameters is converted into rotation of the HD product.^{4–6} Fernández-Alonso et al.⁷ measured the differential cross section (DCS) for the formation of HD ($v' = 3, j' = 0–3$) at a collision energy of $E_{\text{coll}} = 1.64$ eV. They found, in addition to the expected back scattering, a strong forward-scattered peak for $j' = 0$, which rapidly vanished with increasing rotational excitation of HD. This forward-scattered peak was correlated with a time delay relative to the back-scattered peak in their quasiclassical trajectory (QCT) calculations, but QCT methods proved to underestimate the amount of forward scattering, and thus, the conclusions of Fernández-Alonso et al.⁷ were tentative.

Later experiments and fully converged quantum mechanical (QM) calculations on the BKMP2 potential energy surface (PES) confirmed the time-delayed mechanism and found that the HD ($v' = 3, j' = 0$) DCS depends strongly on the collision energy over the range $1.39 \leq E_{\text{coll}} \leq 1.85$ eV.^{8–10} At lower collision energies, the distribution is mainly side scattered; as the collision energy increases, this peak shifts toward forward scattering, creating a so-called “ E – θ ridge”, while side- and back-scattered E – θ ridges grow in concurrently. Oscillations in these ridges in the forward¹¹ and backward¹² regions of the DCS have been attributed to quantized bottleneck states. Monks, Connor, and Althorpe^{13,14} carried out plane wave packet calculations and decomposed the resulting DCS into contributions from nearside and farside partial waves.¹⁵ They found that the backward peak is dominated by nearside scattering, as expected for a direct

mechanism, while the time-delayed forward-scattered ridge was interpreted as glory scattering arising from interference between nearside and farside pathways.

The agreement between QM calculations and previous experiments using the core extraction method was excellent at most collision energies after accounting for the instrumental blurring function, but these experiments were limited to measuring four to eight distinct angles, whereas the calculations predict as many as four peaks in the DCS (often with narrow quantum oscillations superposed), whose widths and centers vary rapidly with collision energy. In the present work, we use ion imaging with a three-dimensional delay line^{6,16} to repeat these experiments with a higher resolution. We observe most of the major peaks predicted by the QM calculations of Althorpe et al.⁸ The good agreement with theory at all collision energies resolves a discrepancy¹⁰ in which the previous experiment had significantly underestimated the amount of side scattering at one collision energy ($E_{\text{coll}} = 1.54$ eV) for unknown reasons. Our results are also of interest because the forward-scattered hemisphere of the DCS ($\theta < 90^\circ$) contains unusual dynamical features that depend sensitively on quantum interference. The improved resolution of the present experiment (~ 7 vs ~ 2 angles for $\theta < 90^\circ$) allows us to observe the shapes of these forward-scattered peaks. The comparison of these features with theory shows close agreement.

Experimental Methods

The experimental setup has been described previously.^{6,16} A mixture of 5% HBr in D_2 ($P_{\text{back}} \approx 1.3$ bar) is supersonically cooled by expansion into a vacuum chamber through a 10 Hz pulsed valve. Two focused linearly polarized UV laser pulses ($\Delta\tau \approx 5$ ns, $E_{\text{pulse}} \approx 300$ μJ) intersect the molecular beam at right angles. Output from the first pulse ($205.0 \leq \lambda \leq 217.5$ nm) photolyzes HBr, producing fast H atoms with a well-defined spatial anisotropy and collision energy. After a 10 ns delay to allow a single collision between H atoms and D_2 molecules, nascent HD ($v' = 3, j' = 0$) products are probed via $[2 + 1]$ resonance-enhanced multiphoton ionization (REMPI) on the Q branch of the $\text{E, F } ^1\Sigma_g^- - \text{X } ^1\Sigma_g^+$ transition ($\lambda \approx 224.8$ nm). These

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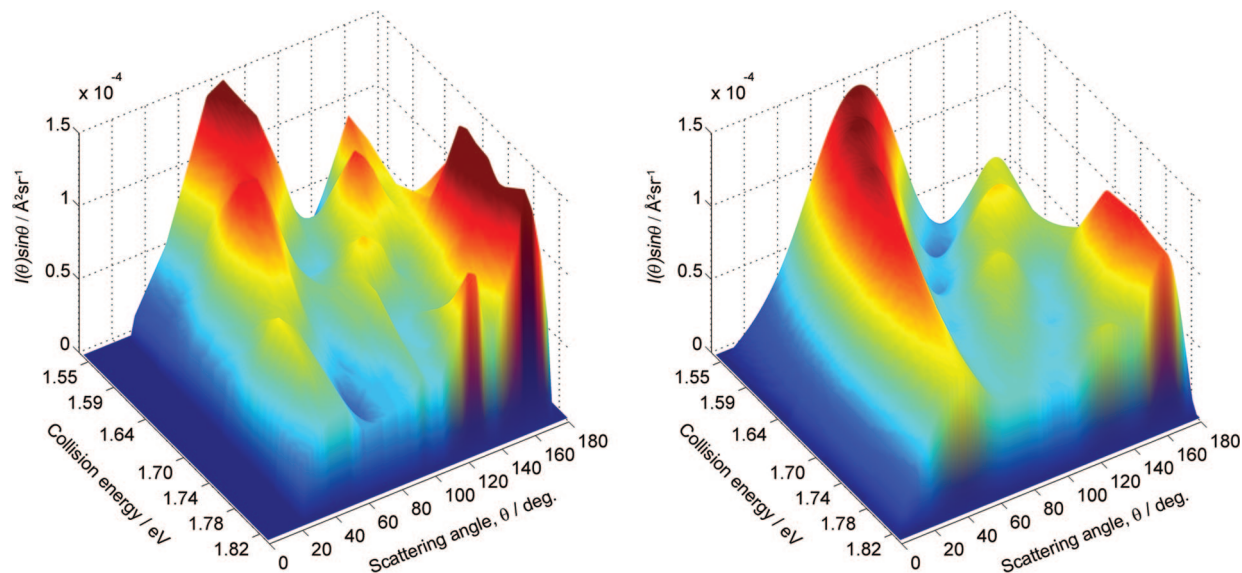


Figure 1. Measured (left) and calculated (right) E - θ plot for HD ($v' = 3, j' = 0$).

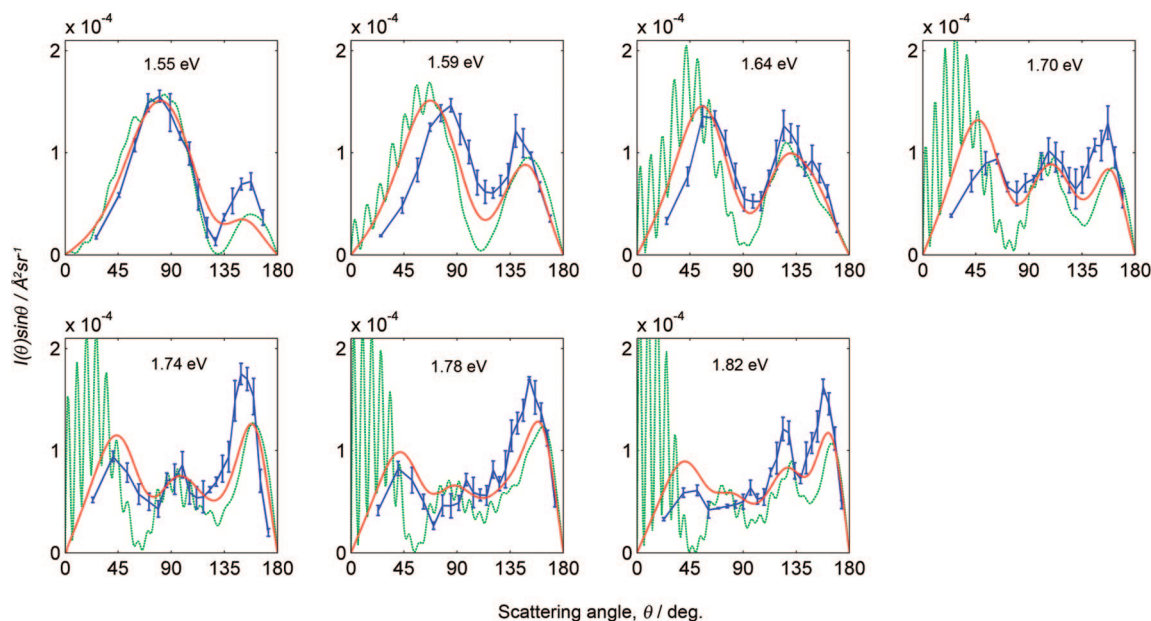


Figure 2. Experimental HD ($v' = 3, j' = 0$) differential cross sections (blue line), normalized to the blurred QM calculations (red line) and exact QM calculations (green line) of Althorpe et al.⁸

HD⁺ ions are formed in a Wiley–McLaren time-of-flight mass spectrometer; extraction and acceleration voltages of $V_{\text{ext}} = -15$ and $V_{\text{acc}} = -60$ V propel the ions toward a microchannel plate/delay line anode detector, whose output is analyzed to determine the three-dimensional velocity of each impinging ion. The DCS is obtained by using the *photoloc* (photoinitiated reaction analyzed by the law of cosines) method¹⁷ to convert the measured velocity distribution into the center-of-mass scattering angle distribution $I(\theta)$.

Results and Discussion

Differential cross sections for the reaction $\text{H} + \text{D}_2 \rightarrow \text{D} + \text{HD}$ ($v' = 3, j' = 0$) were measured at seven collision energies over the range $1.55 \leq E_{\text{coll}} \leq 1.82$ eV and are presented in Figures 1 and 2. Each measured DCS was normalized to the calculated cross section from Althorpe et al.⁸ integrated over the range of observed angles, which is always slightly less than the full range of 0–180° because the conversion of measured

laboratory speeds to angles is limited by the bin width required to achieve reasonable statistical error. We neglect potential contributions from slower-moving H atoms generated by the minor channel of HBr photolysis in which spin-orbit-excited Br* is produced instead of ground-state Br. For the three lowest collision energies, these slow H atoms lack sufficient energy to react with D₂ to form HD ($v' = 3, j' = 0$), and their contribution is rigorously excluded. At the highest collision energy, where contributions from slow H atoms should have the largest effect, the cross section for forming HD ($v' = 3, j' = 0$) is 50 times smaller than that for fast H atoms. This already small contamination is further reduced by the branching fraction of $\Gamma \approx 0.18$ for forming slow H atoms over the range of photolysis wavelengths used.¹⁶

The calculated DCS from Althorpe et al.⁸ was sampled at each of the experimental collision energies, including a Gaussian-weighted sum of neighboring collision energies to account for the broadening in energy resolution caused by residual

rotational excitation of the HBr and D₂ reactants in the molecular beam (0.016 and 0.023 eV, respectively). These energy-broadened DCSs were inverted using *photoloc* to obtain the speed distributions that would be observed in an ideal experiment and then convoluted with a 500 m s⁻¹ Gaussian to simulate the instrumental blurring function. Finally, the blurred speed distributions were converted to angular distributions. The main effects of this blurring procedure are to dampen the narrowest oscillations in the calculated DCSs and to decrease the apparent forward scattering.

Figure 1 presents the qualitative trends in the HD ($v' = 3, j' = 0$) scattering angle distribution as a function of collision energy. At the lowest collision energy ($E_{\text{coll}} = 1.55$ eV), the distribution is primarily side-scattered into a broad peak centered near 80°. At higher collision energies, the distribution becomes increasingly forward–backward peaked. All three of the major E – θ ridges predicted by the QM calculation are observed, although the relative peak heights vary. In particular, as the collision energy increases, the experiment finds slightly less forward scattering and slightly more backward scattering than the calculation. The small peak near 130° at the highest collision energies is resolved by the experiment more sharply than expected, but overall, the separation between ridges is slightly worse than that in the blurred calculations. Despite these small differences, the qualitative agreement is excellent, thus confirming the QM theory to a much higher level of detail compared with previous experiments.

Figure 2 compares the measured DCSs with blurred and exact theoretical DCSs. Satisfactory agreement between experiment and theory is found at all collision energies. For $E_{\text{coll}} = 1.55$ eV, there is perfect agreement for the main peak near 80°, resolving the discrepancy of Ayers et al.¹⁰ in which they reported asymmetric forward–backward scattering instead of side scattering. For $1.59 \leq E_{\text{coll}} \leq 1.70$ eV, the calculation predicts more intensity in the extreme forward-scattered peak than is found in the experiment, although the shapes of the measured and calculated DCSs are similar. For the highest collision energies, $1.74 \leq E_{\text{coll}} \leq 1.82$ eV, the agreement between the experiment and the blurred calculation is good for the forward-scattered peak, though the resolution is still insufficient to allow observation of the rapid oscillations predicted by the exact calculation. Nonetheless, the close agreement in the shape of this peak, which is dominated by quantum interference effects, provides strong evidence to corroborate the theory.

For all collision energies, the experimental ratio of backward scattering to forward scattering is slightly larger than that predicted by theory. An earlier measurement of HD ($v' = 1, j' = 2, 6, 10$) DCSs using exactly the same method found excellent agreement with theory for all scattering angles,⁶ but we cannot rule out the presence of a small additional speed-dependent blurring function in the present experiment, which preferentially suppresses the signal in the forward-scattered direction. It is unlikely that there are significant errors in the PES or the QM calculation, but dynamical effects arising from rotationally

excited D₂ reactants (beyond the increased total energy, which has already been accounted for) could still contribute to the small remaining differences between experiment and theory.

Conclusions

We have measured the DCS for $\text{H} + \text{D}_2 \rightarrow \text{D} + \text{HD}$ ($v' = 3, j' = 0$) as a function of collision energy for $1.55 \leq E_{\text{coll}} \leq 1.82$ eV, and we observe all of the major E – θ ridges predicted by the QM calculations of Althorpe et al.⁸ The present experiment has a higher angular resolution than previous experiments and thus serves as a stricter test for the theoretical predictions. In particular, Ayers et al.¹⁰ were only able to observe two to three distinct angles in the forward-scattered hemisphere ($\theta < 90^\circ$), whereas the present experiment resolves as many as eight angles in that range. This fact allows us to observe the shapes of the forward-scattered peaks that Monks et al.¹³ attributed to glory scattering arising from the interference of nearside and farside partial waves. We find good agreement with QM calculations for all collision energies, though future experiments with even higher angular and energy resolution may be able to observe the predicted rapid oscillations in the extreme forward-scattered peaks.

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References and Notes

- (1) Hirschfelder, J.; Eyring, H.; Topley, B. *J. Chem. Phys.* **1936**, *4*, 170.
- (2) Truhlar, D. G.; Wyatt, R. E. *Annu. Rev. Phys. Chem.* **1976**, *27*, 1.
- (3) Aoiz, F. J.; Bañares, L.; Herrero, V. J. *Int. Rev. Phys. Chem.* **2005**, *24*, 119.
- (4) Wrede, E.; Schnieder, L. *J. Chem. Phys.* **1997**, *107*, 786.
- (5) Wrede, E.; Schnieder, L.; Welge, K. H.; Aoiz, F. J.; Bañares, L.; Castillo, J. F.; Martínez-Haya, B.; Herrero, V. J. *J. Chem. Phys.* **1997**, *110*, 9971.
- (6) Koszinowski, K.; Goldberg, N. T.; Zhang, J.; Zare, R. N.; Bouakline, F.; Althorpe, S. C. *J. Chem. Phys.* **2007**, *127*, 124315.
- (7) Fernández-Alonso, F.; Bean, B. D.; Ayers, J. D.; Pomerantz, A. E.; Zare, R. N.; Bañares, L.; Aoiz, F. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2748.
- (8) Althorpe, S. C.; Fernández-Alonso, F.; Bean, B. D.; Ayers, J. D.; Pomerantz, A. E.; Zare, R. N.; Wrede, E. *Nature* **2002**, *416*, 67.
- (9) Fernández-Alonso, F.; Zare, R. N. *Annu. Rev. Phys. Chem.* **2002**, *53*, 67.
- (10) Ayers, J. D.; Pomerantz, A. E.; Fernández-Alonso, F.; Ausfelder, F.; Bean, B. D.; Zare, R. N. *J. Chem. Phys.* **2003**, *119*, 4662.
- (11) Allison, T. C.; Friedman, R. S.; Kaufman, D. J.; Truhlar, D. G. *Chem. Phys. Lett.* **2000**, *327*, 439.
- (12) Dai, D.; Wang, C. C.; Harich, S. A.; Wang, X.; Yang, X.; Chao, S. D.; Skodje, R. T. *Science* **2003**, *300*, 1730.
- (13) Monks, P. D. D.; Connor, J. N. L.; Althorpe, S. C. *J. Phys. Chem. A* **2006**, *110*, 741.
- (14) Monks, P. D. D.; Connor, J. N. L.; Althorpe, S. C. *J. Phys. Chem. A* **2007**, *111*, 10302.
- (15) McCabe, P.; Connor, J. N. L. *J. Chem. Phys.* **1996**, *104*, 2297.
- (16) Koszinowski, K.; Goldberg, N. T.; Pomerantz, A. E.; Zare, R. N. *J. Chem. Phys.* **2006**, *125*, 133503.
- (17) Shafer, N. E.; Orr-Ewing, A. J.; Simpson, W. R.; Xu, H.; Zare, R. N. *Chem. Phys. Lett.* **1993**, *212*, 155.

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