

## COMMUNICATIONS

Rovibrational product state distribution for inelastic H+D<sub>2</sub> collisions

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Experimental measurements of rovibrational product state distributions for the inelastic scattering process  $\text{H} + \text{D}_2(\nu=0, j) \rightarrow \text{H} + \text{D}_2(\nu'=1, 2, j')$  are presented and compared with the results of quasiclassical and quantum mechanical calculations. Agreement between theory and experiment is almost quantitative. Two subtle trends are found: the relative amount of energy in product rotational excitation decreases slightly with increasing collision energy and increases slightly with increasing product vibrational excitation. These trends are the reverse of what has been found for reactive scattering in which the opposite trends are much more pronounced. © 2004 American Institute of Physics. [DOI: 10.1063/1.1804940]

The H+H<sub>2</sub> system has served as the prototypical example of a reaction between two neutrals throughout the history of reaction dynamics.<sup>1–3</sup> Interest in this system derives from its simplicity, the opportunity to compare experiments with what is thought would be the most accurate theoretical calculations, and the richness of dynamical phenomena the reaction presents. The relevance of this system has continued into the era of state-to-state chemistry, with numerous experimental and theoretical studies reported in the past 20 years.<sup>4–14</sup> In contrast to the scrutiny of the reactive channel, the inelastic scattering channel has received considerably less attention.<sup>15–18</sup> The lack of attention paid to this channel does not imply that it is unimportant, as studies of inelastic collisions can provide information complementary to that learned from studies of reactive encounters.<sup>15</sup>

Here we provide a preliminary report of experimental measurements and theoretical simulations of the rovibrational product state distributions for the inelastic scattering process  $\text{H} + \text{D}_2(\nu=0, j) \rightarrow \text{H} + \text{D}_2(\nu'=1, 2, j')$ . Data are presented for several discrete collision energies. Although similar measurements of rotational distributions have been presented before, the current results are of sufficiently high resolution to reveal previously unobserved trends in the distributions.<sup>15–18</sup> The agreement between the experimental observations and both quasiclassical and fully quantum mechanical calculations shows that the origin for these effects should have a classical basis, although a first examination

suggests that the behavior is not explained in terms of a simple impulsive model.

The experimental technique is similar to that described previously.<sup>19,20</sup> Briefly, a mixture of HBr and D<sub>2</sub> expands into a vacuum chamber from a single pulsed valve. H atoms are generated by photodissociating HBr using a pulsed, tunable UV laser. The translational energy of the H-atom photofragment, and therefore the collision energy, can be adjusted by tuning the wavelength of the photodissociation laser. After approximately 20 ns during which collisions occur, the rovibrationally excited D<sub>2</sub> is state-selectively ionized by (2+1) resonant enhanced multiphoton ionization (REMPI). The ionized D<sub>2</sub> is then detected using time-of-flight mass spectrometry, and the ion current at  $m/z=4$  is converted into a relative collisional cross section for forming the D<sub>2</sub>( $\nu', j'$ ) under investigation. Care is taken to adjust the time between photolysis and detection as described previously,<sup>20</sup> and the signal levels are corrected using known REMPI line strengths.<sup>21</sup> Figure 1 presents the experimental results.

Three different full dimensionality theoretical methodologies have been applied to extract the rotationally resolved integral cross sections to be compared with the experimental results: time-dependent quantum mechanical (TDQM), time-independent quantum mechanical (TIQM), and quasiclassical trajectory (QCT). All calculations have been performed on the *ab initio* BKMP2 PES, which has proved to reproduce many experimental findings very accurately.<sup>22</sup> The TDQM calculations used the wave packet method of Ref. 23, which has been modified to yield state-to-state inelastic cross sections by representing the packet on a grid of Jacobi coordi-

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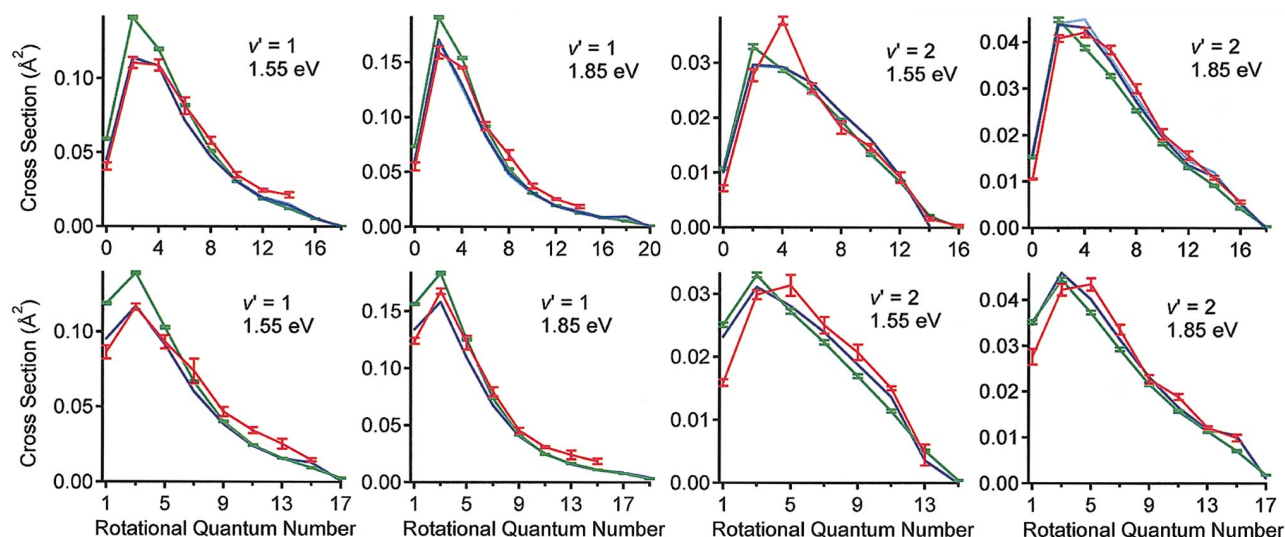


FIG. 1. (Color) Rotational distributions at different collision energies and vibrational manifolds for H+D<sub>2</sub> inelastic scattering. Experimental (red), quasiclassical (green), time-dependent quantum mechanical (dark blue), and time-independent quantum mechanical (light blue) results are shown, but the two quantum mechanical results are virtually indistinguishable. Error bars are statistical and represent one standard deviation.

nates in the H+D<sub>2</sub> arrangement. The density of the grid and the range of total angular momentum quantum numbers included ( $J=0 \rightarrow 50$ ) was sufficient to converge the inelastic cross sections to better than 2%. The TIQM calculations employ a coupled-channel hyperspherical method as implemented in the ABC code of Skouteris *et al.*<sup>24</sup> At the collision energies of the present work, well converged integral and differential cross sections have been obtained using the parameters<sup>24</sup>  $j_{\max}=20$ ,  $E_{\max}=2.85$  eV, and  $k_{\max}=10$  and by including all partial waves up to total angular momentum  $J=48$ . With these parameters the number of channels to be propagated ranges from 198 at  $J=0$  up to 1532 at  $J \geq 10$ . Note that for the reactant D<sub>2</sub> molecule only channels that correlate with even  $j$  have been included in the basis set. A maximum value of the hyperradius  $\rho_{\max}=25 a_0$  and a number of 250 sectors were selected to perform the calculations.

Quasiclassical trajectory calculations were carried out using the same methodology of Ref. 25. Batches of  $2 \times 10^6$  trajectories were run at each collision energy and initial rotational state. The maximum impact parameter was taken as 1.8 Å ensuring that all inelastic transitions were included. Beyond 1.3 Å no reactive trajectories were found. To account for the  $\Delta j$  even parity rule in inelastic collisions, the assignment of final rovibrational D<sub>2</sub> states have been made in the following way. First the (real value) vibrational and rotational quantum numbers were determined in the usual way<sup>25</sup> using the semiclassical quantization of the classical action and the  $[j'(j'+1)]^{1/2}$  quantization rule for the rotational angular momentum of the D<sub>2</sub> molecule. The vibrational quantum number,  $\nu'$ , was then found by rounding to the nearest integer the real value obtained by equating the internal energy of the D<sub>2</sub> molecule to the rovibrational Dunham expansion in  $(\nu'+1/2)$  and  $j'(j'+1)$ , whose coefficients are calculated by fitting the semiclassical rovibrational energies. The final rotational quantum number was assigned by taking the integer part of the classical (real value) rotational quantum number. If this value corresponded to a  $\Delta j = j' - j$  even, the rotational number was taken to be  $j'$ , if the resulting

value corresponded to  $\Delta j$  odd, the final rotational state was taken to be  $j'+1$ . The integral cross sections so calculated were almost indistinguishable from those obtained by neglecting the trajectories with a  $\Delta j$  odd value and multiplying by two the cross sections with a  $\Delta j$  even value.

Figure 1 compares the experimental rotational distributions with different theoretical results. The distributions show the population of rotational states for a given vibrational manifold and collision energy; owing to space limitations, distributions are presented for only  $\nu'=1$  and 2 at the collision energies 1.55 and 1.85 eV. The experiment determines only relative values of the cross sections, but absolute cross sections are available from the calculations. Thus, the experimental cross sections were normalized such that the area under the experimental distributions equals the average of the areas under the theoretical distributions. All distributions are presented separately for D<sub>2</sub> with even  $j'$  (*ortho*-D<sub>2</sub>) or odd  $j'$  (*para*-D<sub>2</sub>). Inelastic collisions have a negligible probability to cause interconversion between *ortho*- and *para*-D<sub>2</sub>, so *ortho* (*para*) product D<sub>2</sub> originates from inelastic scattering of *ortho* (*para*) reagent D<sub>2</sub>. The D<sub>2</sub> reagent is composed of the statistical distribution of 2:1 *ortho*:*para* modifications. If the inelastic scattering cross section is the same for *ortho*- and *para*-D<sub>2</sub>, the product should be composed of twice as much *ortho* as *para* modification. The experimental values of the population of *ortho*- and *para*-D<sub>2</sub> products can be directly compared, and the ratio of inelastic scattering cross sections for the two modifications can be found by dividing that population ratio in half. The result of this analysis is that the two modifications have equal inelastic scattering cross sections within experimental uncertainty (see Table I), and this result is confirmed by the calculations.

The experiment is also sensitive to the vibrational distribution. The relative population of the two vibrational states, summed over the rotational levels, is also presented in Table I. The  $\nu'=1$  state is more populated at every collision energy, although the relative population of  $\nu'=2$  increases with increasing collision energy.

TABLE I. Experimental values of the H+D<sub>2</sub> inelastic cross section ratios for *ortho/para* states of reagent D<sub>2</sub> and for the product vibrational distribution at four different collision energies.

	1.55 eV	1.65 eV	1.75 eV	1.85 eV
$\nu'=1$	0.96±0.05	1.07±0.13	1.00±0.19	1.08±0.06
<i>ortho/para</i>				
$\nu'=2$	0.92±0.08	1.01±0.09	0.91±0.09	0.92±0.12
<i>ortho/para</i>				
$(\nu'=1)/(\nu'=2)$	2.59±0.19	2.37±0.22	2.19±0.38	1.95±0.16

The agreement between quantum mechanical and quasi-classical calculations and experiment is almost quantitative. The minor discrepancy is that the simulated distributions are slightly too cold. The primary cause for this disagreement is the fact that the calculations presented here considered collisions with only the two lowest rotational states of the reagent D<sub>2</sub> (one *ortho* state and one *para* state), whereas higher-lying rotational states were present in the molecular beam. Simulations including a distribution of reagent D<sub>2</sub> rotational states mimicking the experimental distribution show an improved agreement with experiment.

Many experimentally determined rotational distributions for the reactive channel in this system have been reported and can be compared with these data on inelastic scattering.<sup>4,5,7,20,26–34</sup> As pointed out before, rotational distributions for inelastic scattering are much colder than the distributions for the reactive channel at the same collision energy and product vibrational state.<sup>15–18</sup> The average energy in rotation for  $\nu'=2$  at 1.85 eV collision energy is much greater for reactive scattering<sup>33</sup> than for inelastic scattering (2280 to 1590 cm<sup>-1</sup>); those rotational distributions are presented in Fig. 2. The inelastic rotational distributions are also much less sensitive to collision energy or product vibrational quantum number than their reactive counterparts. The average energy in rotation for  $\nu'=2$  lies between 1320 and 1590 cm<sup>-1</sup> for inelastic scattering in the collision energy range 1.55–1.85 eV but ranges from 1490 to 2280 cm<sup>-1</sup> for reactive scattering in the same vibrational manifold and collision energy range.<sup>33</sup> Similarly, the average energy in rotation at 1.55 eV collision energy changes only from 1370 to 1320 cm<sup>-1</sup> between  $\nu'=1$  and 2 for inelastic scattering but

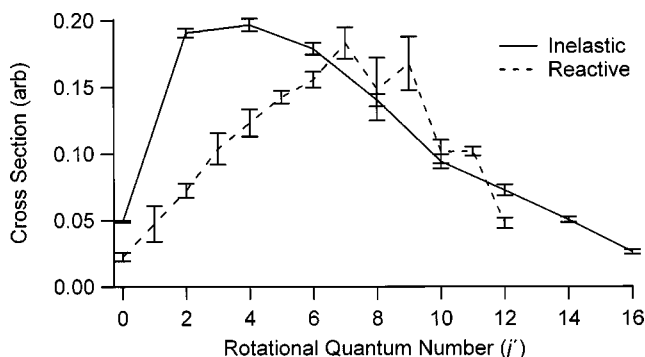


FIG. 2. Rotational distributions for inelastic and reactive (Ref. 33) scattering in H+D<sub>2</sub>. Both distributions are experimental measurements at 1.85 eV collision energy and two quanta of product vibration ( $\nu'=2$ ). Error bars are statistical and represent one standard deviation.

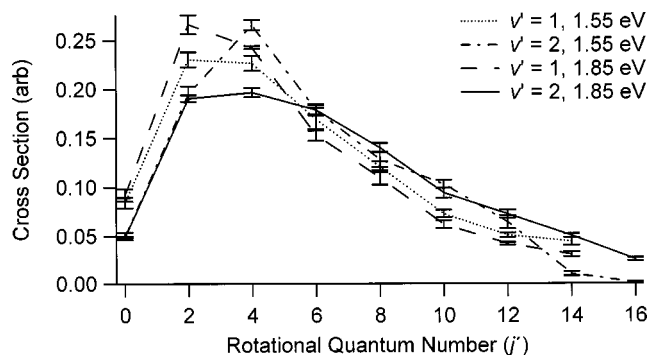


FIG. 3. Experimental rotational distributions for the *ortho* products of H+D<sub>2</sub> inelastic scattering at different collision energies and vibrational manifolds. The data shown are the same as in Fig. 1, here placed on the same graph to allow easy comparison. The slight increase in rotational excitation at lower collision energies and for more vibrationally excited products can be seen.

changes from 1490 to 300 cm<sup>-1</sup> between  $\nu'=2$  and 3 for reactive scattering at the same collision energy.<sup>20,33</sup> This effect might be partially explained by the fact that the vibrational spacing is smaller in D<sub>2</sub> (the product molecule in inelastic scattering) than in HD (the product molecule in reactive scattering), but the small differences in vibrational spacing compared to the dramatic variations in rotational distributions for reactive scattering make that explanation unlikely to be the sole cause of what is observed.

Although these rotational distributions are similar for each vibrational state and collision energy, two subtle trends are apparent (see Fig. 3). First, the fraction of energy going into rotation decreases slightly at higher collision energies; and second, the fraction of energy going into rotation increases slightly for products with more vibrational excitation. These trends may seem counterintuitive: one might expect that providing additional energy in terms of collision energy or removing less energy in terms of vibrational energy would permit more energy to go into rotation. This behavior has indeed been observed in reactive scattering<sup>20,33</sup> in which a line-of-centers hard-sphere model<sup>31,35</sup> seems to account well for the product internal state distributions. Clearly, this same model cannot explain the present observations.

We note that similar trends have been observed for inelastic scattering in other systems. Flynn and co-workers<sup>36–41</sup> have measured rotational distributions for the inelastic collision process H+CO<sub>2</sub> to form vibrational ground state and asymmetric stretch excited CO<sub>2</sub>. They observed that rotational distributions with one or two quanta in the asymmetric stretch look very similar and peak around 40 quanta of rotational excitation, whereas the products in the vibrational ground state would be expected to have rotational state populations that decrease monotonically with increasing rotational quantum number. To explain these results, they proposed a “breathing ellipse” model<sup>41</sup> similar to the one developed by Serri, Bilotta, and Pritchard<sup>42</sup> and based on the traditional hard ellipse model of rotationally inelastic scattering.<sup>43</sup> Their model assumes that a point mass and a rigid ellipse do not interact until a critical configuration is reached in which an impulsive force is felt between the par-



ticle and the infinitely high potential wall of the ellipse.

Quasiclassical trajectories calculations can be used to assess the applicability of such a model to this system. The good agreement between QCT and experiment, as well as the past success of QCTs for this system,<sup>15,18,25,27,33</sup> suggest that these calculations provide a fairly faithful representation of the scattering mechanism. Examination of the QCT calculations suggests that a simple breathing ellipse mechanism may not grasp the complexity behind the inelastic scattering mechanism. In particular, the calculations indicate that a previously discovered recrossing mechanism,<sup>25,44,45</sup> in which trajectories cross the barrier into the product valley and then recross back into the reagent valley, plays an important role. In fact, for inelastically scattered products with high vibrational excitation, the cross section for recrossing is larger than the cross section for direct inelastic scattering. Although the presence of recrossing suggests a level of complexity that may not be captured by an impulsive model, the success of the quasiclassical trajectories in reproducing the experimental data implies that a classical explanation of these dynamics exists. A simple model capable of explaining these results is currently being developed.

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