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State-to-State Dynamics of High-*n* Rydberg H-Atom Scattering with D_2

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Full quantum-state resolved scattering of a highly excited Rydberg H atom with D_2 has been carried out using the Rydberg H-atom time-of-flight method. A detailed analysis of the experimental results shows that both inelastic and reactive scatterings are significant in the H(n)-D_2 collisions, and nuclear spin is conserved in the inelastic scattering process. The differential cross sections for the H(n)-D_2 reaction measured in this work are then compared with the results for the H^+ reaction with D_2 in an ion beam scattering experiment. The remarkable agreement between the two experiments suggests that the Fermi independent-collider model is valid even at the full quantum state-to-state scattering level, providing a promising tool for investigating the state-to-state dynamics of certain elementary ion-molecule reactions.

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Seventy years ago, Amaldi and Segrè made the first measurements probing the collisions of Rydberg atoms (RA) with ground-state atoms by measuring the spectral line shifts of high-*n* potassium RA in the presence of inert gases [1]. To rationalize these observations, Fermi [2] proposed an "independent-collider" model [3–7], in which the (Rydberg) electron + target and ion-core + target scattering events were treated independently in the overall collision of RA with atoms or molecules. This model is physically reasonable in view of the relevant length scales of the problem. The Bohr radius for H($n = 45$), e.g., is $R = 1075$ Å, while the effective range of the scattering potentials is at most tens of angstroms. Fermi's independent-collider model has proven successful in interpreting the results for a number of experiments involving RA collision, and has served as the basis for a number of theoretical models. A particularly notable example was the demonstration that the collision destruction cross sections for H-RA and D-RA with other atoms at high (keV) translational energies was equal to the sum of electronic and core cross sections [8,9]. There have been relatively few quantum-state resolved scattering studies of RA + molecule collisions that were sensitive to the ion-core + molecule scattering event. Most closely related to this work is the elegant study by Davis and co-workers [10] where the vibrational-state resolved inelastic scattering of high-*n* H-RA with N_2 and O_2 were measured for the first time. Pratt *et al.* [11] have also investigated the molecular Rydberg process $H_2^* + H_2 \rightarrow H_3^+ + H + e^-$.

Ion beams have many advantages for ion-molecule scattering studies; for example, the energy and/or direction of ion beams can be easily controlled unlike neutral beams. However, ion beam scattering also has a serious problem that the trajectories of ion products could be affected by the electric field applied to control the ion beam. This problem is especially serious for low energy ion products and thus severely limits the ion time-of-flight (TOF) resolution. Neutral high-*n* RA beams, however, do not suffer this problem. The significance of the validity of the Fermi independent-collider model, should it be found to hold, is rather profound. It states that we can measure the cross section of an ion-molecule interaction using, instead of ions beams, beams of neutral high-*n* RA, and for systems where the high-*n* RA beam may be readily prepared, it could be used to study certain ion-molecule interactions, such as the important proton exchange reactions, at the full quantum state-to-state scattering level.

In this work, we have performed a detailed experimental study of the full quantum-state resolved scattering of high-*n* H-RA with D_2 using the Rydberg H-atom time-of-flight method [12]. The experimental apparatus used in this study is essentially the same as that used previously in the study of the ground-state $H + D_2$ and $H + HD$ reactions [13,14], with the one critical difference that the H atom is pumped to high *n before* the collision occurs. Figure 1 shows the experimental scheme used in this work. A H-RA beam at high-*n* level ($n = 45$) is prepared by pumping the H atom produced from H*I* photodissociation at 266 nm in the molecular beam to a high-*n* Rydberg state via the well-known H-atom Rydberg tagging scheme [15,16]. The resulting H-atom beam velocity is about 11 230 m/s. The H-RA beam then crosses the D_2 beam at 90°. The D_2 beam was generated by expanding an ortho-D_2 sample through a pulsed valve. The D_2 beam density in the cross region was estimated to be about 10^{13} cm^{-3}, while the density of H(n) was estimated to be about 10^{10} cm^{-3} [17]. The valve was

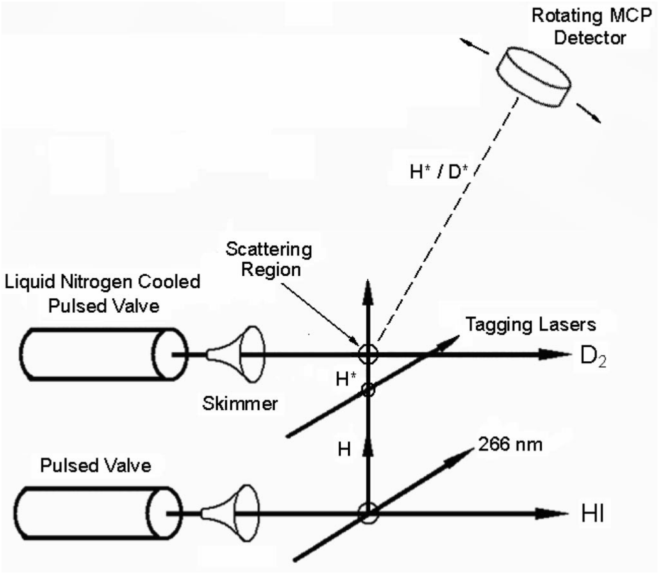

FIG. 1. Experimental scheme for the Rydberg H-atom scattering with D_2.

cooled to liquid nitrogen temperature in an effort to improve the resolution of the scattering experiments by reducing the absolute velocity spread of the D_2 beam. The cold D_2 beam has a velocity of 1036 m/s with a speed ratio ($v/\Delta v$) of about 23. Under these conditions, the center-of-mass collision energy is 0.526 eV with a spread of $\Delta E_C \approx$ 11 meV. The scattered H- (D-) RA is then detected with a rotating multichannel plate (MCP) detector with field ionization in front of the detector. Since field ionization detection is sensitive only to H- (D-) RA with n larger than 20 [10], the scattered RA must remain in high-n Rydberg states in order to be detected. The detector is sensitive only to inelastic [$\mathrm{H}(n) + \mathrm{D}_2(v = 0, j = 0) \rightarrow \mathrm{H}(n') + \mathrm{D}_2(v', j')$] and reactive [$\mathrm{H}(n) + \mathrm{D}_2(v = 0, j = 0) \rightarrow \mathrm{D}(n') + \mathrm{HD}(v', j')$] processes, and does not register ionizing processes since all ion products in the crossing region were pulled away by applying a small dc field ($\sim$ 20 V/cm).

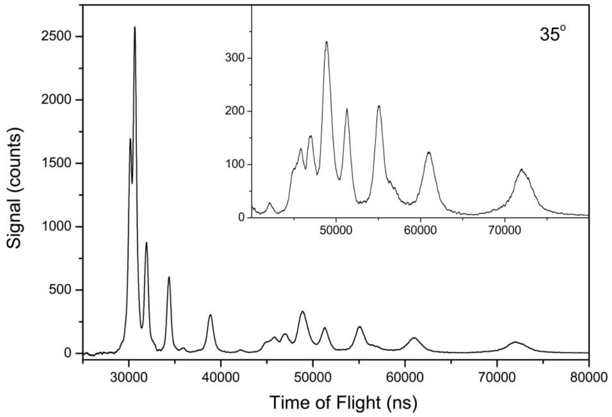

FIG. 2. Time-of-flight spectrum of the scattering products from the $\mathrm{H}(n) + \mathrm{D}_2$ interaction at the laboratory angle of 35° off the H(n) beam or 55° off the D_2 beam.

Figure 2 shows the TOF spectrum of the scattered products from the H(n) scattering with D_2 at the laboratory angle of 35° relative to the H-RA beam direction. The TOF spectrum exhibits many sharp peaks that we expect to correspond to the quantum states of the products but may relate to either the H-RA or D-RA product fragment. In order to make an assignment of all observed peaks, the TOF spectrum was converted into the product translational energy distribution. We first consider the nonreactive inelastic collisions where the translational energy is computed using the reduced mass of the $\mathrm{H}(n) + \mathrm{D}_2$ colliding pair. Figure 3 shows the product translational energy distribution converted from the TOF spectrum in Fig. 2 along with the expected positions of the rovibrational inelastic channels, $\mathrm{H}(n) + \mathrm{D}_2(v', j')$, assuming that n is relatively unchanged during the collision. At high translational energy, $E_T \sim$ 2000–5000 cm^{-1}, the first set of large peaks are seen to agree well with the even-j' rotationally inelastic channels $\mathrm{H}(n) + \mathrm{D}_2(0, 0) \rightarrow \mathrm{H}(n) + \mathrm{D}_2(0, j')$. This result is consistent with our expectation that the cold D_2 beam is dominantly ortho and is in the $j'' = 0$ rotational level. There are some very small extra features in the translational energy spectrum shown in Fig. 3 that are seen to correspond to odd-j' states of the para-para inelastic transitions. From a comparison to the n-D_2 scattering signal (not shown), the p-D_2 impurity in the present (supposed) o-D_2 beam is about 6%, which is consistent with the result of our Raman scattering measurement.

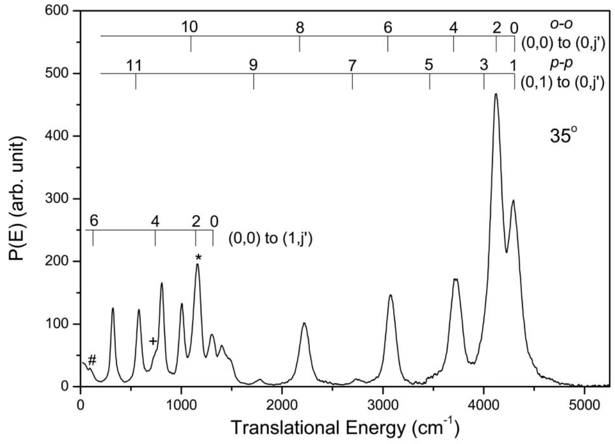

FIG. 3. Total translational energy distribution of the scattering products from the $\mathrm{H}(n) + \mathrm{D}_2$ interaction at the laboratory angle of 35° off the H(n) beam, assuming all signals in Fig. 2 are from the elastic and inelastic scattering processes. The label in the graph is from (v, j) to (v', j'), while the numbers labeled are the final state j' quantum numbers. The shoulder marked with "+" is due to the $\mathrm{D}_2(v' = 1, j' = 4)$ product, while the shoulder marker with "#" is due to the $\mathrm{D}_2(v' = 1, j' = 6)$ product. There are clearly two inelastic components, $\mathrm{D}_2(v' = 0, j' = 10)$ and $\mathrm{D}_2(v' = 1, j' = 2)$, in the peak marked with "*."

The absence of clearly assigned signals for ortho-para conversion in our results strongly suggests that the nuclear symmetry is largely maintained in the process of H-RA collisions with D_2, at least to within the detection limit of this experiment. In principle, the magnetic fields generated during the lifetime of the ion-molecule complex (~ 1 ps) could induce the flipping of nuclear spin. However, the present observation is consistent with simple order of magnitude estimates that indicate that the magnetic fields generated within the collision complex are far too weak to generate significant numbers of transitions over the lifetime of the complex.

At low translational energies, $E_T \sim 0$–$2000\ \mathrm{cm}^{-1}$, we see an additional progression of sharp peaks in Fig. 3. It is clear from this figure that these peaks cannot be readily assigned to the rotationally inelastic scattering process. Furthermore, as also shown in the figure, the peaks are too numerous to be due to an additional progression within the $v' = 1$ product manifold, $H(n) + D_2(0, 0) \rightarrow H(n') + D_2(1, j')$. The other possibility is that these slower structures are high-n D-RA products coming from the $H(n) + D_2(0, 0) \rightarrow D(n') + HD(v', j')$ reactive scattering event. If this is the case, then the peaks should correspond to various product states of HD. In Fig. 4, the TOF spectrum of Fig. 2 is converted into the translational energy distribution using the appropriate mass ratio for this product channel and plotted for the low energy regime. The progression of peaks is observed to be unambiguously assigned to the different rotationally excited $HD(v = 0, j' = 0$–$9)$ products from the H-RA reaction with D_2. Since the HD product is a heteronuclear diatom, both even and odd j' values are appreciably populated. The relative propensity for the collision to yield $H(n) + D_2$ products compared to the $D(n) + HD$ products can be estimated from the areas underneath the high and low energy progressions, respectively. At this scattering angle and collision energy, the ratio is found to be roughly 2:1. This is consistent with the branching ratio for the decay of the H^+-D_2 ion-molecule complex that we have computed using a trajectory simulation. A further intriguing observation in Fig. 4 is the appearance of a small extra shoulder (marked with +), which is shown as a clear peak in Fig. 5. This peak can be assigned only to the $D_2(v' = 1, j' = 4)$ product from inelastic scattering. In addition, the $D_2(v' = 1, j' = 6)$ peak is also present (see peak marked with "#" in Figs. 3 and 4). No products for the $D_2(v' = 1, j' = \mathrm{odd})$ were observed, consistent with the conclusions that the vibrationally inelastic scattering occurs dominantly through collisions with the o-D_2 and that the nuclear-spin symmetry is also conserved in the vibrationally inelastic scattering process. Finally, we note that the peaks of the reactive and inelastic processes in the translational energy distribution have widths of ~15 meV for the lowest translational peaks. The broadening of a scattering peak could have three contributions: (1) the thermal distribution of the collision energy (11 meV), (2) the time-of-flight distance uncertainty (~ 1%–2%), (3) the electronically nonadiabatic processes $n \rightarrow n'$. The second contribution would cause increasing linewidths as the translational energy increases; this is also observed in the experiment. From this analysis, we can conclude that the linewidths come mainly from the first two contributions, implying that the electronically nonadiabatic processes $n \rightarrow n'$ is not very significant.

To test the hypothesis that the $H(n) + D_2 \rightarrow D(n') + HD$ cross section is essentially equivalent to the cross section for the ion-molecule reaction $H^+ + D_2 \rightarrow D^+ + HD$, it is desirable to directly compare the state-to-state results from different experiments on the two systems. An experiment was previously carried out for the

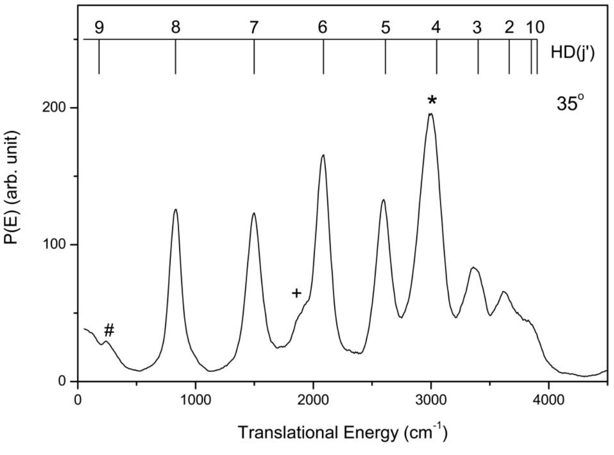

FIG. 4. Translational energy distribution of the $H^* + o$-$D_2 \rightarrow D^* + HD(v = 0, j')$ reaction at the laboratory angle of 5° off the Rydberg H-atom beam. All main structures can be assigned to the different HD rotationally excited products. See the caption in Fig. 3 for the "*," "+," and "#" symbols.

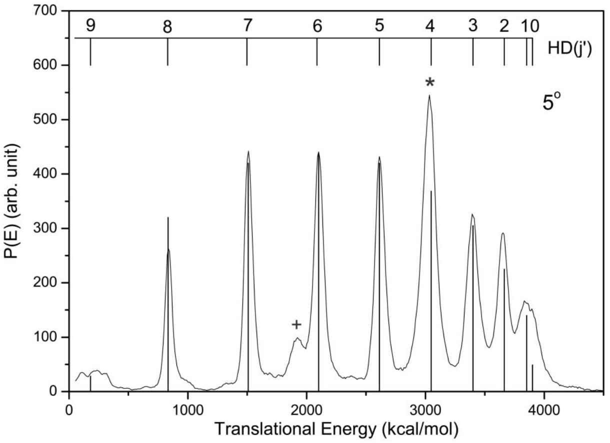

FIG. 5. Translational energy distribution of the $H^* + o$-$D_2 \rightarrow D^* + HD(v = 0, j')$ reaction at the laboratory angle of 5° off the Rydberg H-atom beam. The sticks are the partially rotationally resolved studies on the $H^+ + o$-$D_2 \rightarrow D^+ + HD(v = 0, j')$ reaction at the laboratory scattering angle of 5° off the H^+ beam by Gerlich *et al.* [18].

$H^+ + D_2 \rightarrow D^+ + HD$ reaction by one of us [18] using an H^+-ion beam scattering from a cooled D_2 sample at a collision energy of 0.524 eV. TOF spectrum of the D^+-ion product at the scattering angle of 5° from the H^+ beam has been measured carefully with partial rotational resolution of the HD product. Figure 5 shows the translational energy distribution at the same laboratory angle of 5° (from the H-RA beam) and a similar collision energy (0.52 eV) from the current Rydberg atom scattering experiment along with the earlier ion-beam result. The overall agreement of the state-to-state differential cross sections for the two experiments is remarkably good. The obvious disagreement for the peak $j' = 4$ (marked as "*" in Figs. 4 and 5) is mainly due to the overlapping of the reactive product of $HD(j' = 4)$ with the inelastic products of $D_2(v = 0, j = 10)$ as well as $D_2(v = 1, j = 2)$. It is also necessary to point out that there is some angle averaging effect in the ion beam experiment because the D_2 sample is a cooled gas sample and not a molecular beam. Nevertheless, the remarkable agreement between the differential cross sections of the two experiments at a specific scattering lab angle provides the most stringent quantitative test thus far for the validity of the Fermi independent particle model.

The implications of the present study are quite significant for the development of experimental methods for state-to-state scattering of ion-molecule reactions. The result of this work suggests that Rydberg-tagged atom + molecule scattering could provide a unique way to investigate experimentally the state-to-state dynamics of certain elementary ion-molecule reactions, such as the proton exchange reactions that are important in areas of physics and chemistry, without the problem associated with the effect of the electric field in ion-beam experiments. It also poses a theoretical challenge to establish the range of validity of the Fermi independent-collider model. The influence of vibrational autoionization from the collision complex appears to be a particularly important issue. This study could also provide an experimental benchmark system for the state-to-state dynamics of Rydberg atom reactions with molecules, as well as stimulate the development of quantum and classical theoretical dynamics methods to investigate Rydberg atom (or molecule) reaction dynamics using the first principle methods.

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