PERSPECTIVE

Is the simplest chemical reaction really so simple?

Justin Jankunas[a,1], **Mahima Sneha**[a], **Richard N. Zare**[a,2], **Foudhil Bouakline**[b], **Stuart C. Althorpe**[c], **Diego Herráez-Aguilar**[d], and **F. Javier Aoiz**[d]

[a]*Department of Chemistry, Stanford University, Stanford, CA 94305-5080;* [b]*Max Born Institute, 12489 Berlin, Germany;* [c]*Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom; and* [d]*Departamento de Química Física, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain*

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Modern computational methods have become so powerful for predicting the outcome for the H + $H_2 \rightarrow H_2$ + H bimolecular exchange reaction that it might seem further experiments are not needed. Nevertheless, experiments have led the way to cause theorists to look more deeply into this simplest of all chemical reactions. The findings are less simple.

reaction dynamics | differential cross-sections

H + H_2 Collision Looks Like Playing Molecular Pool on a Warped Table

The reaction in which a hydrogen atom collides with a hydrogen molecule to form a new hydrogen molecule plus a hydrogen atom is often referred to as the simplest neutral bimolecular reaction because this collision system contains only three electrons and three protons. Consequently, the forces acting on the nuclei can be calculated using quantum mechanics from first principles to a very high level of accuracy. It is this reaction system that we believe we can most trust theory to tell us what is happening. Study of this benchmark system and its related isotopic cousins has led to a number of firsts in reaction dynamics: the first potential energy surface with chemical accuracy (less than 1 kcal/mol deviation over the surface), the concept of a transition state, the idea of quantum tunneling in reaction dynamics, the use of transition-state theory to predict reaction rates, the concept of resonances in the reactive scattering cross-section, etc. (1–3). The extension of these concepts to the F + HD and Cl + HD reactions has also been very fruitful (4, 5).

To facilitate a discussion of this reaction, we label the H atoms as if they were distinguishable and examine the reaction:

$$H_a + H_bH_c \rightarrow H_aH_b + H_c.$$

Many studies have taught us that reactions are best described by considering the minimum energy path in going from reactants to products. In the case of H + H_2, the configuration with the lowest energy is for the three H atoms to lie in a straight line (collinear configuration) for which there exists a barrier to reaction of about 0.42 eV (about 9 kcal/mol) which must be surmounted for reaction to proceed at any significant rate (Fig. 1). This can be accomplished by giving the incoming H atom sufficient kinetic energy. The top of the hill is the transition state. Still more insight is obtained by making a contour plot of the potential energy surface (Fig. 2) in which the angle between the forming H_a–H_b bond and the breaking H_b–H_c bond is held fixed at 180° (collinear configuration). The internuclear equilibrium distance of the H_2 molecule is 0.741 Å and the energy needed to pull apart the two hydrogen atoms in H_2 is ∼4.5 eV (104 kcal/mol). A black dot marks the transition state in Fig. 2, which is located at the saddle point of the $H_aH_bH_c$ potential energy surface. Examination of Fig. 2 shows that this reaction is a concerted process in which both H_a–H_b and H_b–H_c bonds are longer at the transition state than the H_2 internuclear equilibrium distance. Instead of requiring the dissociation energy to pull H_bH_c apart, much less energy is needed.

It is common to characterize the reaction by measuring the translational kinetic energy of the recoiling H_c atom, the internal energy of the H_aH_b molecule, and the angles into which these products are scattered, referenced to the direction of the incoming H_a atom (6). The internal energy of the H_aH_b molecule is characterized by its vibrational and rotational energy levels, which are represented by the quantum numbers ν' and j'. The distribution of products as a function of the scattering angle (θ) is called the differential cross-section. Again, past experiments and theory guide our understanding. A great simplification is made by separating the electronic and nuclear motions (Born–Oppenheimer approximation) and treating the nuclei as classical particles. In this picture, elementary chemical reactions of this type might be regarded as molecular billiards (pool). Thus, the expectation is that nearly head-on collisions cause the H_aH_b product to be scattered backward (θ is close to 180°) with little rotational excitation (low j'), whereas more glancing collisions cause the H_aH_b molecule to be scattered sideways ($\theta < 180°$) with more rotational excitation (high j'). Fig. 3 presents a simple cartoon illustrating this behavior.

How well are these expectations fulfilled? To answer this question, we conducted experiments on the related reaction H + $D_2 \rightarrow$ HD + D, in which the deuterium atom D is a heavy isotope of the hydrogen atom having one additional neutron in its nucleus (3). The use of isotopes allows us to distinguish readily the products from the reactants. Briefly, a mixture of HBr and D_2 is coexpanded as

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[1] Present address: Ecole Polytechnique Federale de Lausanne, Institute of Chemical Sciences and Engineering, CH-1015 Lausanne, Switzerland.

[2] To whom correspondence should be addressed. E-mail: zare@stanford.edu.

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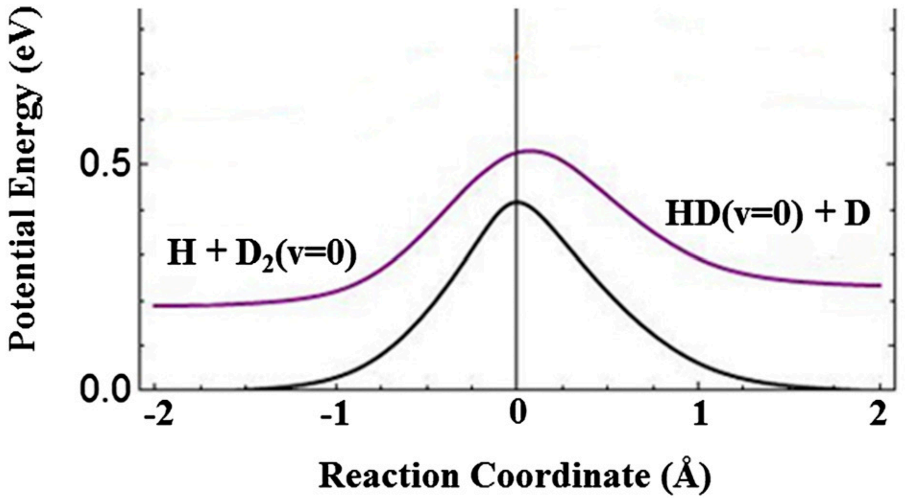

Fig. 1. Plot of the potential energy versus the reaction coordinate for H + D_2 →HD + D. The symmetric black curve is the classical minimum energy path and the purple curve is the vibrationally adiabatic minimum energy path for H + D_2(v = 0) going to HD(v = 0) + H.

a molecular beam into an evacuated chamber and fast H atoms with a controlled translational energy are generated by photolyzing HBr at a variable wavelength (3). Some of these fast H atoms collide with the supersonically cooled D_2 which is in the ground vibrational state ($v = 0$) and the first few rotational levels (j = 0, 1, and 2). The HD(v', j') product is detected state-specifically. In terms of theory, the nuclei move on the same potential energy surface, although we must now introduce an energy-level correction in that D_2 and HD have different vibrational frequencies and different zero-point energies, which is indicated by the purple curve in Fig. 1. In these experiments, we measured the differential cross-sections for HD products in different vibrational and rotational states. The experimental results for four different combinations of v' and j' are compared in Fig. 4 against the best theoretical calculations (which are fully quantum mechanical) (7). Although theory and experiment do not perfectly agree, and some puzzling discrepancies do exist (8), the match is close enough that we have great confidence in both. Likewise, the quasiclassical calculations agree fairly well with the accurate quantum mechanical results (Figs. S1 and S2), lending credence to the classical description of the reaction. Moreover, they both show that our billiard-ball picture for this reaction describes well what is found, although not all reactive collisions proceed only through direct recoil (9). The HD molecules in higher rotational states were found at lower values of θ, meaning they were scattered more sideways. It might seem then that the H + H_2 reaction system is really simple to understand. Indeed, we first thought so (10).

Warped Billiard Table Changes as the Pool Balls Move and Is Weirder than First Imagined

However, then we did one experiment too many; we examined the differential cross-sections of the HD products that were produced with more vibrational excitation (v' = 4) (11). Fig. 5 presents these results. To our initial surprise, we find that with increasing rotational excitation, the HD product is scattered more backward (the distribution moves closer to 180°). Theory agrees with the observations, but what is the explanation? Do we need to abandon our model of billiard-ball collision dynamics? If the last is true, it is a huge setback. What we hope to extract from the study of H + H_2 is not only how this simple reaction system behaves but hopefully generalizations that can be applied to other more complicated chemical reactions that cannot be modeled to the theoretical accuracy achievable for H + H_2.

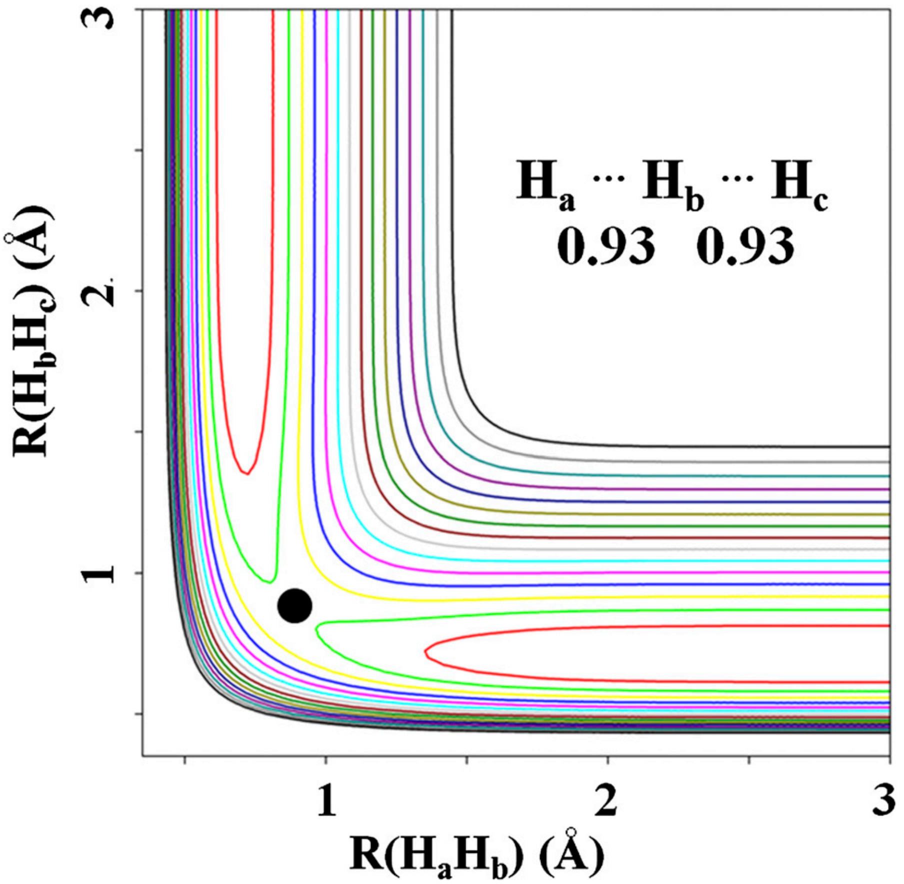

Fig. 2. Plot of the PES for the collinear approach of a hydrogen atom H_a to the hydrogen molecule H_bH_c to break the old H_b–H_c bond and to form the new H_a–H_b bond in a bimolecular exchange reaction. In this diagram, the contours are equally spaced by 0.2 eV. The saddle point region, marked by a black dot, lies in the center about 0.42 eV above the asymptotes. The entrance valley starts at the lower right and the exit valley ends at the upper left of the diagram in the process H_a + H_bH_c → H_aH_b + H_c. This figure is adapted from Bin Jiang and Hua Guo (2013) *J Chem Phys* 138:204104.

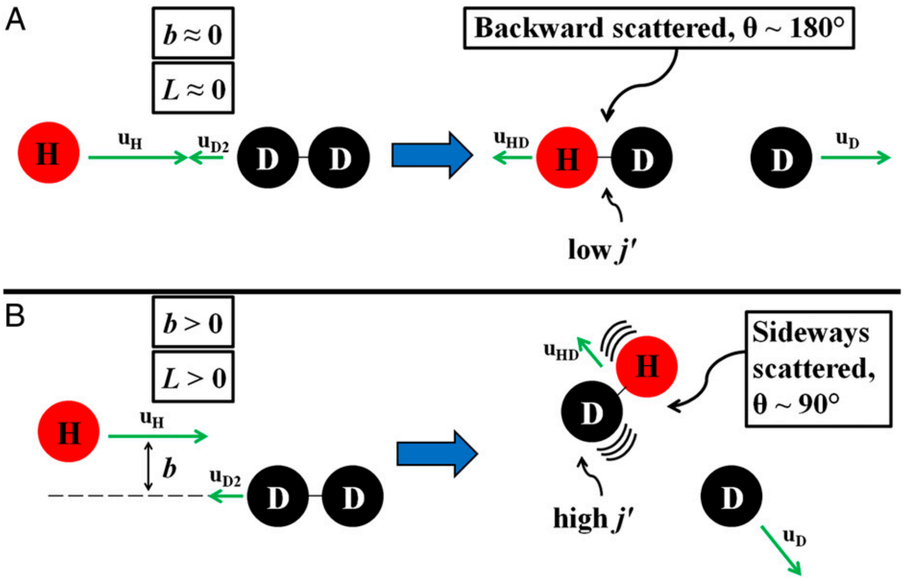

Fig. 3. $H + D_2 \rightarrow HD(v', j') + D$ reactive collision showing typical trajectories in the center-of-mass frame. The symbol u denotes the velocity, j' the rotational quantum number of the HD product, and θ the scattering angle of the HD product measured with respect to the incoming H atom. The b is the impact parameter, defined by the distance of closest approach if the H atom travels in a straight line. The quantity L is the orbital angular momentum of the collision, and is the quantum mechanical analog of the classical quantity b. (*Upper*) Nearly head-on collisions ($b \sim 0$, $L \sim 0$); (*Lower*) More glancing collisions ($b > 0$, $L > 0$).

Happily, we can still keep our billiard-ball model, but we must recognize that the picture we have painted of the H_3 potential energy surface as everywhere purely repulsive needs drastic revision for HD products formed in higher vibrational levels. As shown in Fig. 2, the only minimum in the potential energy surface (PES) occurs when the H atom is infinitely far away from the H_2 molecule. We are only interested in "chemical" wells, and ignore the meager ($\sim 10^{-3}$ eV) van der Waals wells. Within this framework, the $H + H_2$ collision is an archetype of a direct chemical reaction: in the absence of any wells, the reactants approach one another, and promptly recoil away. Such a simple picture of the $H + H_2$ dynamics is incapable of explaining the puzzling scattering behavior exemplified by the differential cross-sections for HD ($v' = 4, j'$) products.

Fig. 6 shows the minimum energy path of the $H + D_2$ reaction for different vibrationally excited HD(v') products. These so-called "vibrationally adiabatic paths" are created by assuming that the D_2 reagent and the HD product have the same vibrational quantum number ($v = v'$). We find for high vibrational excitation that the HD_2 PES develops attractive wells! To illustrate this behavior more dramatically, we present in Fig. 7 a 3D PES for a frozen reactant bond length appropriate for the outer turning point of HD($v = 4$). Wells are readily apparent. The origin of these attractive lakes in the PES is the incipient pairwise bonding among all of the atoms when the D_2 molecule becomes sufficiently stretched in the reaction producing highly vibrationally excited HD. The same type of behavior was observed before in the inelastic scattering process $H + D_2(v = 0) \rightarrow H + D_2(v' = 3) + H$, in which it was found that vibrational excitation of D_2 is not achieved by compressing the D–D bond but rather by stretching it as the D atom closest to the H atom is attracted to it (12). In that sense, we understand the inelastic scattering process leading to highly vibrationally excited D_2 to be an example of a frustrated chemical reaction in which vibrational excitation arises from the D atom snapping back to its original D-atom partner when it is no longer able to catch the H atom to form HD.

Actually, the reaction path for $H + D_2(v = 0) \rightarrow HD(v' = 4) + D$ collision will be even more complicated than the adiabatic potentials shown in Fig. 6, owing to obvious nonadiabatic coupling between the $v = 0$ and $v = 4$ potentials, presumably in the region of close interaction between the three atoms, i.e., in the vicinity of the transition-state configuration. We present in Movies S1–S7 some representative reactive collisions forming HD ($v' = 4, j' = 0$–6), where the impact parameters and the collision times are indicated in each movie file. In some reactive collisions the incoming H atom ends up bound not to the first D atom it encounters but rather its partner via an insertion mechanism [see the second collision trajectory in Movie S6 showing the formation of the HD($v' = 4, j' = 5$) product]. Clearly, the dynamics for the production of HD($v' = 4$) molecules is very different from, say, HD($v' = 0$ or $v' = 1$)

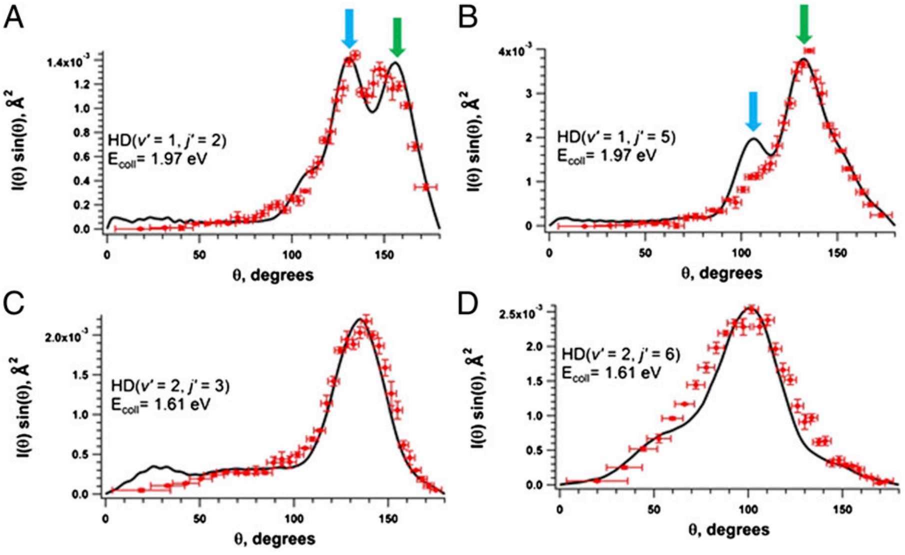

Fig. 4. Comparison of the experimental (red dots) and the blurred time-dependent quantum mechanical (black curve) differential cross-sections for the production of (*A*) HD($v' = 1, j' = 2$) and (*B*) HD($v' = 1, j' = 5$) both at a collision energy E_{coll} of 1.97 eV (46.5 kcal/mol), and (*C*) HD($v' = 2, j' = 3$) and (*D*) HD($v' = 2, j' = 6$) both at a collision energy E_{coll} of 1.61 eV (40.0 kcal/mol). With increasing HD product rotational excitation, the HD is scattered more sideways. To aid visualization of this effect arrows have been added to *A* and *B* because the differential cross-section contains two peaks.

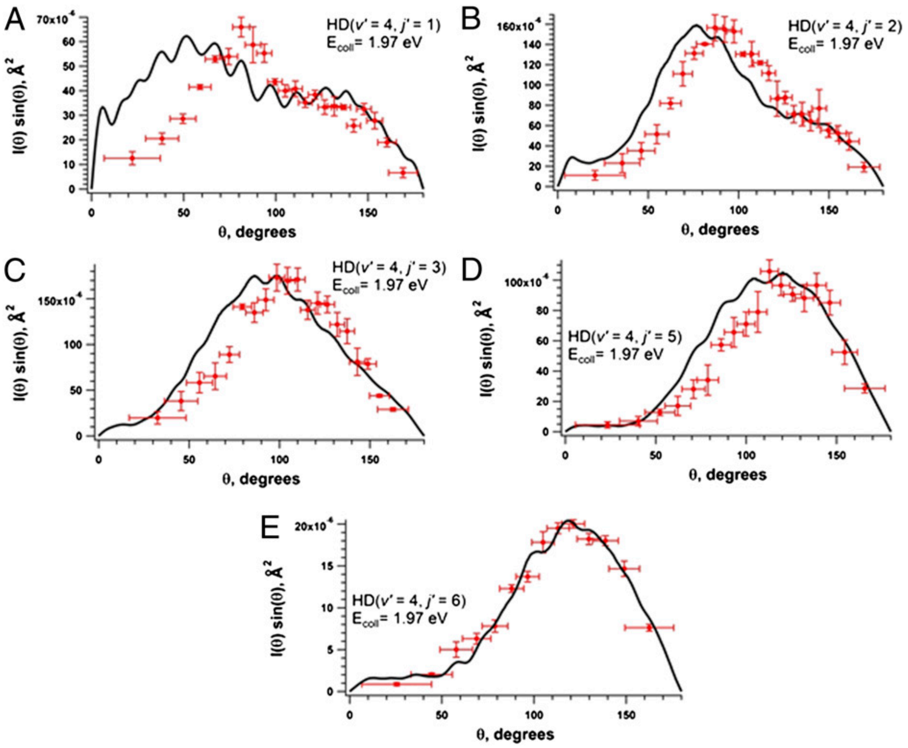

Fig. 5. Comparison of the experimental (red dots) and the blurred time-dependent quantum mechanical (black curve) differential cross-sections at E_{coll} = 1.97 eV (46.5 kcal/mol) for the production of (*A*) HD($v' = 4$, $j' = 1$), (*B*) HD($v' = 4$, $j' = 2$), (*C*) HD($v' = 4$, $j' = 3$), (*D*) HD($v' = 4$, $j' = 5$), and (*E*) HD($v' = 4$, $j' = 6$). With increasing HD product rotational excitation, the HD is scattered more backward.

products! We are only beginning to understand in detail this reaction system.

Each collision of H with D_2 is characterized by an impact parameter b and an angular momentum L, whose magnitude is classically proportional to b and to the velocity of the H atom with respect to the D_2 molecule (in the center-of-mass frame). The potential experienced by H contains an extra repulsive term, the centrifugal barrier, whose magnitude grows with increasing L (actually, proportional to L^2). We suggest (11) that the centrifugal barrier in the exit channel of the $H + D_2 \rightarrow HD + D$ reaction is responsible for “choking off” higher values of L with increasing product rotational quantum number j'. A qualitative (pictorial) illustration of the choking off idea is given in Fig. 8, which shows how the effective potential changes with increasing L. Loosely speaking, certain highly internally excited HD products do not have enough recoil kinetic energy to overcome the centrifugal barrier in the exit channel of the reaction, when the H and D_2 reactants collide with an $L = 26$ amount of orbital angular momentum (Fig. 8). Such trajectories are nonreactive. Thus, such a highly internally excited HD product is a result of a collision between a hydrogen atom and a deuterium molecule with a smaller orbital angular momentum, such as $L = 20$: the centrifugal barrier is lower for such a collision (Fig. 8), and the HD and D products in question have sufficient energy to pass over this obstacle. This explains why, for example, HD($v' = 4$, $j' = 6$) product is more backscattered than HD($v' = 4$, $j' = 3$): the former has even less kinetic energy, and thus the maximum centrifugal barrier that can be overcome is even lower. Correspondingly, lower values of L will contribute to the production of HD($v' = 4$, $j' = 6$), compared with faster HD($v' = 4$, $j' = 3$) products; the $j' = 6$ product will therefore be more backscattered than $j' = 3$. Stated another way, among the high-energy products, the products with high j' must come from collisions that are closer to collinear (b closer to 0) because otherwise there would not be enough kinetic energy for the HD product to escape and the reaction to occur. These arguments are general, that is, not restricted to HD($v' = 4$). They are expected to hold for all other final vibrational states at different collision energies provided the product kinetic energy is not enough to overcome the centrifugal barrier.

Another factor also contributes to favoring increased backward scattering with increasing j'. The differential cross-section for $H + D_2 \rightarrow HD(v' = 4, j' = 0,1,2)$ actually has two peaks, one of which arises from direct scattering and the other is a time-delayed reaction path whose origin has been well-documented as a quantum bottleneck state (13, 14). The time-delayed pathway enhances forward scattered features in the differential cross-section. For $j' = 2$ product state, the magnitude of the two peaks is comparable, but with increasing

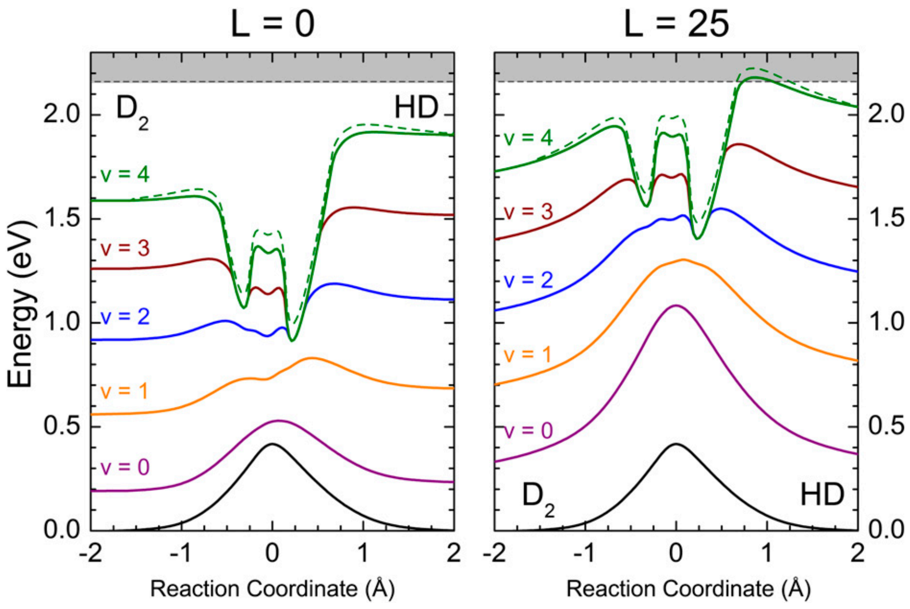

Fig. 6. Vibrationally adiabatic potentials for the $H + D_2(v) \rightarrow HD(v') + D$ reaction showing the formation of wells for $v = v' = 3$ and 4. (*Left*) Orbital angular momentum $L = 0$; (*Right*) $L = 25$. The dotted line is when one quantum of bending motion in the HD_2 triatomic is also included. The horizontal dashed line at the top of the figure represents the total energy of the collision.

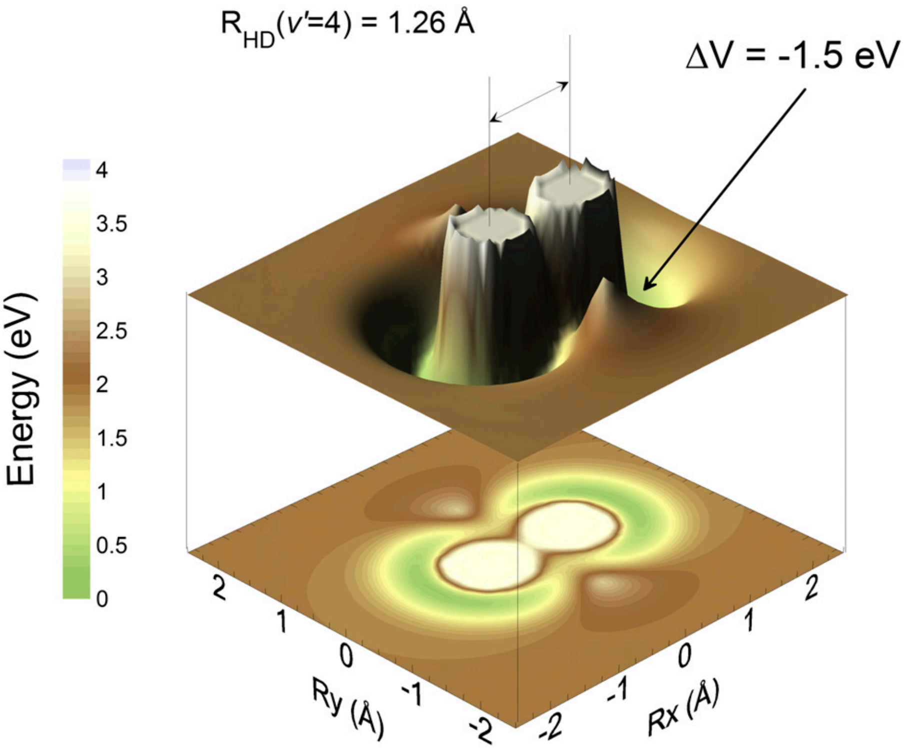

Fig. 7. PES plot for the H + D_2 system and its associated 2D projection, with an internuclear HD separation fixed at $r = 1.26$ Å, corresponding to HD($v' = 4$) vibrational quantum state. It is evident that for compact collinear HD_2 geometries, a deep well is present as H approaches D_2 along the R_x axis for $R_y = 0$. R_x and R_y stand for the Cartesian coordinates of the H atom with respect to the D_2 center of mass.

product rotational excitation the contribution from the time-delayed pathway diminishes so that for $j' = 5$ it is negligible (Fig. 9). Both the choking-off argument and the time-delayed mechanism are subtly intertwined; only through theory and experiment working together is it possible to explain the measured and calculated angular distributions shown in Fig. 5.

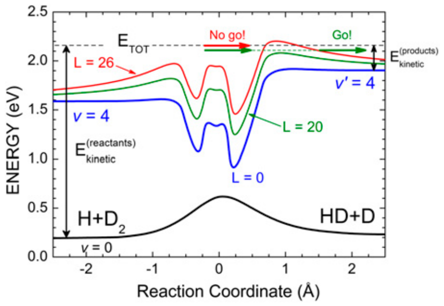

Fig. 8. Cartoon illustration of the "centrifugal barrier" mechanism responsible for the choking off reaction from higher orbital angular momentum L. The production of certain highly internally excited HD(v', j') product states is impossible when a hydrogen atom and a deuterium molecule collide with an $L = 26$ amount of orbital angular momentum (red traces). Such trajectories are nonreactive. The HD(v', j') products with low kinetic energy may be produced when the centrifugal barrier in the exit channel is lower (green trace), corresponding to $L = 20$. Consequently, such HD(v', j') products are more backscattered compared with HD(v', j') products with more recoil kinetic energy.

Future Directions

Clearly, the H + H_2 reaction system is not quite as simple as first imagined. And, we have only begun to familiarize ourselves with its complex nature. Moreover, the situation is about to become markedly more complicated with increasing translational energy of the incoming H atom or with extra energy in the reactant's internal degrees of freedom. So far, we have been fortunate to consider only one PES as governing the motion of the nuclei. However, the H_3 system is a Jahn–Teller system having a second PES connected to the first at a conical intersection seam whose minimum is located about 2.7 eV (64 kcal/mol) above the asymptotes of the ground state (6). Once this is energetically accessed, we can expect electronic nonadiabatic transitions to occur in which we must consider motion of the nuclei on both PESs at the same time (15, 16). This hurts the classical mind. We will need to consider playing molecular pool on interconnected warped billiard tables whose shapes change with the motion of the pool balls. Well, no one ever promised us that chemical reactions would be simple, even for what is called the simplest chemical reaction of them all.

Clearly, one inviting direction for future experiments is to increase the translational energy of the two collision partners to access the region of the conical intersection of the H_3 PES and beyond. It is believed that the theoretical apparatus for calculating the behavior of such high-energy collisions is sufficiently well developed, but experimental tests remain to be made. Past history teaches us that some surprises might be expected, even though we think we understand how to treat fully nonadiabatic couplings for this simple system.

Another inviting direction is to remove the averaging over the $2j + 1$ different magnetic sublevels m of the rotational state j all of the same energy, which presently must be included to describe the molecular reactants and products. Classically, a molecule in the state characterized by the quantum numbers j and m has its rotational angular momentum vector $\mathbf{j}$ making a projection m on the axis of quantization and might be regarded as the $\mathbf{j}$ vector spinning at a uniform rate about the quantization axis. By achieving m-state resolution either of reagents or products we will be able to explore more deeply the quantum nature of the scattering process. However, even more information might be achieved by preparing molecular reagents in a coherent superposition of m states. This feat involving the control of phase of how $\mathbf{j}$ precesses about

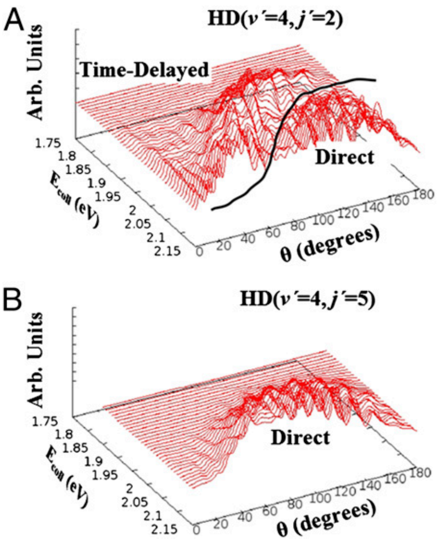

Fig. 9. $E_{coll} - \theta$ plot for (*A*) HD($v' = 4$, $j' = 2$) and (*B*) HD($v' = 4$, $j' = 5$) product states, showing that the HD($v' = 4$, $j' = 2$) product has a substantial contribution from the time-delayed mechanism, which enhances the forward features in a differential cross section. In contrast, the HD($v' = 4$, $j' = 5$) product proceeds only via a direct mechanism. The black curve in *A* shows a clear separation between the direct and time-delayed reaction mechanisms in the H + D_2 → HD($v' = 4$, $j' = 2$) + D reaction.

the quantization axis might allow us to identify reaction paths looping in opposite senses around the conical intersection. Of course, we should not overlook some ultimate experiments that detect in coincidence all of the characteristics of the scattering process and thereby provide many different vector correlations (6), although this dream seems presently beyond what we know how to realize experimentally.

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