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Dynamics of the $S(^1D_2) + HD(j = 0)$ Reaction at Collision Energies Approaching the Cold Regime: A Stringent Test for Theory

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We report integral cross sections for the $S(^1D_2) + HD(j = 0) \rightarrow DS + H$ and $HS + D$ reaction channels obtained through crossed-beam experiments reaching collision energies as low as 0.46 meV and from adiabatic time-independent quantum-mechanical calculations. While good overall agreement with experiment at energies above 10 meV is observed, neither the product channel branching ratio nor the low-energy resonancelike features in the $HS + D$ channel can be theoretically reproduced. A nonadiabatic treatment employing highly accurate singlet and triplet potential energy surfaces is clearly needed to resolve the complex nature of the reaction dynamics.

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For theory to furnish a good description of elementary gas-phase reaction dynamics requires the use of a highly accurate potential energy surface (PES) describing the passage from reagents to products. Recent progress in the determination of PESs by *ab initio* methods [1] has allowed quantum-mechanical (QM) or quasiclassical trajectory treatments of the reaction dynamics to reproduce the integral and differential cross sections (ICSs and DCSs) obtained in high-resolution crossed-beam experiments for prototypical four-atom $HD + OH \rightarrow H_2O + D$ [2] and six-atom $Cl + CHD_3 \rightarrow HCl + CD_3$ systems [3,4]. This has followed the exquisite agreement between theory and experiment found for the benchmark three-atom $F + HD \rightarrow HF + D$ [5,6] and $F + H_2 \rightarrow HF + H$ [7,8] reactions for which resonance features have been fully rationalized. However, all these studies have been performed at medium to high collision energies to be able to surmount the classical energy barriers, between 70 and 300 meV, which characterize these reactions. The lowest collision energy attained so far is $E_T = 6$ meV in the case of the $F + H_2$ reaction for which substantial tunneling through the barrier occurs [8]. An important question arises: Will the accuracy of electronic structure calculations (currently recognized to be within the 10–40 meV range) be sufficient to reproduce experimental studies of reactive processes occurring at very low collision energies? When only a few partial waves, characterized by a given value of total angular momentum J which is conserved throughout the collision, contribute to the dynamics, individual quantum effects become apparent and the slightest inaccuracy of the PES can lead to dramatic differences in the theoretical results. Multisurface effects arising from the open-shell nature of the reactants may also start to play a dominant role as recently outlined for the $F(^2P_{1/2}) + H_2(j = 0)$ reaction in

which a pronounced resonance peak is predicted in the ICSs around $E_T = 0.2$ – 0.3 meV [9].

Despite the tremendous advances in the generation of cold atomic and molecular species by Stark or Zeeman deceleration, buffer-gas, or laser cooling [10,11], very few experiments are able to approach the cold energy regime at temperatures below $T = 1$ K. One can cite the recent buffer-gas cooling study of the $Li + CaH \rightarrow LiH + Ca$ reaction at $T = 1$ K [12] but experiments of this type provide rate coefficients, not cross sections as a function of E_T , which constitute the most sensitive probes of the underlying PESs. The thermal distribution at $T = 1$ K corresponds to a mean relative translational energy of 0.13 meV ($\langle E_T \rangle = 3/2 k T$, where $k = 8.617 \times 10^{-5} \text{ eV}^{-1} \text{ K}^{-1}$ is the Boltzmann constant). Obtaining such low energies in single collision conditions to yield reactive cross sections is particularly challenging. Indeed, in a collision experiment between two beams of colliding species sharing a reduced mass μ , with laboratory frame velocities v_1 and v_2 and a beam-intersection angle χ defining a relative velocity v_r , the collision energy in the center-of-mass frame (the relative translational energy) is given by the equation $E_T = \frac{1}{2} \mu v_r^2 = \frac{1}{2} \mu (v_1^2 + v_2^2 - 2v_1 v_2 \cos \chi)$. To study a bimolecular reaction fully amenable to time-independent (TI) QM calculations on an accurate PES, i.e., a reaction preferentially involving a H_2 (HD or D_2) molecule which also has the advantage of a favorable reduced mass $\mu \sim 2$ – $4 \times 10^{-3} \text{ kg mol}^{-1}$, a reactant relative velocity of approximately 100 m s^{-1} would have to be achieved, putting substantial constraint on the respective values of v_1 , v_2 , and χ .

Complex-forming reactions such as those of $O(^1D_2)$, $C(^1D_2)$, and $S(^1D_2)$ atoms with H_2 , HD , and D_2 isotopomers feature strongly bound intermediates in their

ground-state PES, are barrierless, and possess large cross sections. They are particularly good candidates for testing theoretical methods at very low energies and have stimulated considerable interest [13]. In this Letter, we describe crossed-beam scattering experiments on the $S(^1D_2) + HD(j=0) \rightarrow DS + H$ ($\Delta H_0^\circ = -0.309$ eV) and $HS + D$ ($\Delta H_0^\circ = -0.258$ eV) reaction realized with a setup combining cryogenically cooled fast-pulsed valves [14] and a variable beam-intersection angle. The apparatus was modified during the course of the study to attain a minimum angle $\chi_{\min} = 12.5^\circ$ instead of the initial value of 22.5° [15,16], allowing us to reach $E_T = 0.46$ meV ($T = 3.6$ K). At the same time, we describe TI QM calculations performed on the ground-state $^1A'$ HSD PES. We observe intriguing differences in the behaviors of the DS + H and HS + D channels that cannot be explained by an adiabatic treatment of the reaction dynamics.

$S(^1D_2)$ beams were generated by UV laser photolysis of CS_2 [17] seeded in Ne or He carrier gas just below the nozzle of a first fast-pulsed valve operated at $T = 300$ or 270 K and were characterized by $2 + 1$ resonantly enhanced multiphoton ionization (REMPI) time-of-flight mass spectrometry using the $3s^23p^4\ ^1D_2 \rightarrow 3s^23p^34p\ ^1F_3$ transition at 288.179 nm. Neat HD beams were obtained

from a second fast-pulsed valve cooled down to $T = 60$ or 45 K. Tests performed when recording $HD(C^1\Pi, v=0 \leftarrow X^1\Sigma^+, v=0)R(0)$ and $R(1)$ $3 + 1$ REMPI transitions near 302.18 nm showed that more than 98% of HD molecules were in $j=0$. The recoiling H(D) atoms were detected by $1 + 1'$ REMPI via excitation of the Lyman- α ($^2S_{1/2} \rightarrow ^2P^\circ_j$) transition at 121.567 (121.534) nm followed by threshold ionization with 364.7 nm photons. The branching ratio $\sigma(DS + H)/\sigma(HS + D) = 1.31 \pm 0.31$ (at the 95% confidence interval) was determined from the respective Doppler spectra of the recoiling H and D atoms at $E_T = 13.8$ meV and from 30 back-to-back measurements of the ratio H/D at the respective maxima of the spectra for identical Lyman- α laser intensities. Insofar as the H spectra are significantly broader than the D ones, the density-to-flux conversion [18] was achieved by modeling the experimental spectra, assuming a statistical distribution of rotational levels in DS/HS products and a polar distribution of recoil angles [19].

Excitation functions for the product channels DS + H and HS + D were obtained over the ranges $E_T = 1.63$ – 54.2 meV and $E_T = 0.46$ – 5.63 meV using both 22.5° and 12.5° crossed-beam configurations. They are plotted in Fig. 1 on the same scale with the aid of the

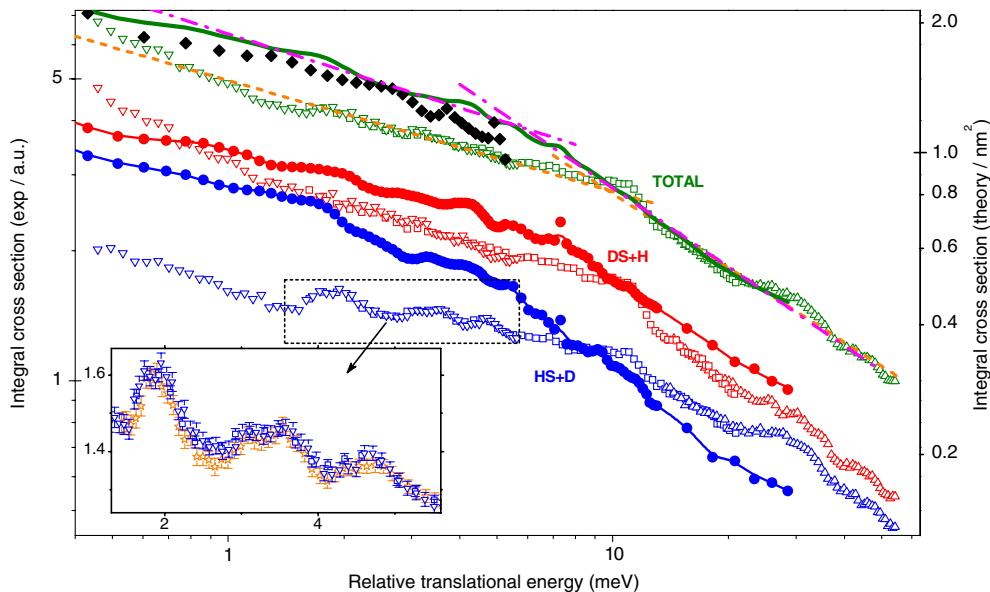


FIG. 1 (color online). Experimental and theoretical integral cross sections (log-log units) for the reaction $S(^1D_2) + HD$ as a function of collision energy for individual DS + H and HS + D channels and for the total reaction flux. Experimental ICSs (left vertical scale in arbitrary units, a.u.) for different crossed-beam conditions: down triangles $v_S = 813$ $m s^{-1}$ with speed ratio (see [31]) $S = 76$, $v_{HD} = 826$ $m s^{-1}$ with $S > 30$, $\chi_{\min} = 12.5^\circ$; squares $v_S = 818$ $m s^{-1}$ with $S = 46$, $v_{HD} = 881$ $m s^{-1}$ with $S > 30$, $\chi_{\min} = 22.5^\circ$; up triangles $v_S = 1736$ $m s^{-1}$ with $S = 27$, $v_{HD} = 881$ $m s^{-1}$ with $S > 30$, $\chi_{\min} = 22.5^\circ$. Inset: details of the HS + D channel (linear scales): same symbols as above with another data set added: stars $v_S = 776$ $m s^{-1}$ with $S = 43$, $v_{HD} = 826$ $m s^{-1}$ with $S > 30$, $\chi_{\min} = 22.5^\circ$. For clarity, the statistical uncertainties at the 95% confidence interval are only shown in the inset. Dashed lines: linear fits of the experimental total ICSs in the low- (1.63–5.63 meV) and high-energy (13.8–54.2 meV) domains. Theoretical ICSs (right vertical scale): filled circles (not shown for total ICSs); the solid curves refer to the theoretical ICSs convoluted over the experimental collision energy spread. Dash-dotted lines: linear fits of the theoretical total ICSs in the low- (0.86–3.45 meV) and high-energy (5.8–28.5 meV) domains. Supplementary theoretical total ICSs (right vertical scale) obtained with the PES of Varandas and coworkers [26]: filled diamonds.

measured branching ratio. The total reaction flux deduced from the DS + H and HS + D excitation functions and the branching ratio is also reported. The figure demonstrates the robustness of the excitation functions since ICSs obtained with different beam conditions display the same behavior in overlapping energy ranges. It can be seen that both reaction channels follow two different regimes marked by a strong change in the slopes. Between $E_T = 54.2$ meV and $E_T \sim 10$ meV, a similar behavior is observed for both channels with only a slight increase of the branching ratio. Around $E_T = 10$ meV, a sudden change in the dynamics is observed. Whereas the DS + H channel continues to grow almost monotonically, the HS + D channel exhibits three peaks of increasing contrast with decreasing E_T , as shown in the inset of Fig. 1 with magnified scales. The branching ratio increases markedly in this range reaching values greater than 2 at the lowest energies.

The TI QM calculations were performed by applying the hyperspherical quantum reaction scattering methodology, using the *ab initio* ground-state $^1A'$ PES calculated by Ho *et al.* [20], which was complemented with accurate calculations of the long-range interactions [21]. Converged cross sections were obtained on a fine grid up to $E_T = 5$ meV (partial waves $J = 0-16$) and then on a coarser grid up to $E_T = 28.5$ meV (partial waves $J = 0-25$), due to computational time increasing excessively with J . Indeed, the consideration of three nonidentical atoms made the calculations extremely costly. Theoretical ICSs of the individual channels as well as the total reaction flux are shown in Fig. 1 alongside the experimental results. The convolution of the theoretical results over the experimental energy spread is also reported for a direct comparison. The scaling of the experimental excitation functions in arbitrary units is performed by a least-squared method at energies between 10 and 28.5 meV on the total ICSs. With such a scaling, the agreement between experiment and theory appears good for the total flux in the high-energy region, displaying a level of convergence that we obtained in earlier studies of the $S(^1D_2) + H_2 \rightarrow HS + H$ reaction [15,16]. The low- and high-energy slopes of the experimental and theoretical excitation functions are almost identical for the total reaction flux, -0.26 versus -0.28 at low energy and -0.57 versus -0.60 at high energy, although the crossing occurs at slightly different collision energies, $E_T \sim 9.6$ meV for the experiment and $E_T \sim 5.7$ meV for theory. The agreement is less apparent when considering the individual DS + H and HS + D channels. Although the theoretical branching ratio $\sigma(\text{DS} + \text{H})/\sigma(\text{HS} + \text{D}) = 1.72$ at $E_T = 13.8$ meV is only slightly higher than the upper error limit of the experimental one, variations in both theoretical and experimental values are uncorrelated throughout the whole collision energy range. The branching ratio has been the subject of much debate in previous experimental and theoretical papers treating $S(^1D_2) + \text{HD}$ reaction dynamics

[17,19,22–25] while our own experimental values, which attain 1.17 on average between $E_T = 31-54.2$ meV, are noticeably different from the previous crossed-beam determination $\sigma(\text{DS} + \text{H})/\sigma(\text{HS} + \text{D}) = 0.72 \pm 0.07$ between $E_T = 31$ to 570 meV [17]. The present calculations are unable to reproduce the three peaks observed in the experimental HS + D channel. Note that the experiment cannot confirm the peak predicted in the theoretical ICSs in both channels, corresponding to a shape resonance for $J = 19$ at $E_T = 7.3$ meV (see Fig. 2), and still present after partial-wave averaging since the experimental energy spread at this collision energy smooths out this feature.

To determine the extent to which the discrepancies between theory and experiment at low energy are due to inaccuracies in the chosen PES, supplementary TI QM calculations were performed at energies lower than $E_T = 5$ meV, employing a PES calculated by Varandas and coworkers [26]. The results do not differ substantially from those obtained with the PES of Ho *et al.* [20] with differences in the total ICSs not exceeding 10% (see Fig. 1). However, two shape resonances now appear for $J = 15$ and 16 in both channels in the region of the experimental peaks (see Fig. 2). Since the present theory treats the collision dynamics adiabatically on the ground-electronic PES, it is possible that the theory overestimates the total ICSs due to electronic quenching to ground-state reactants $S(^3P_J) + \text{HD}$. In addition, reaction can also occur through intersystem crossing to triplet PESs which results in a

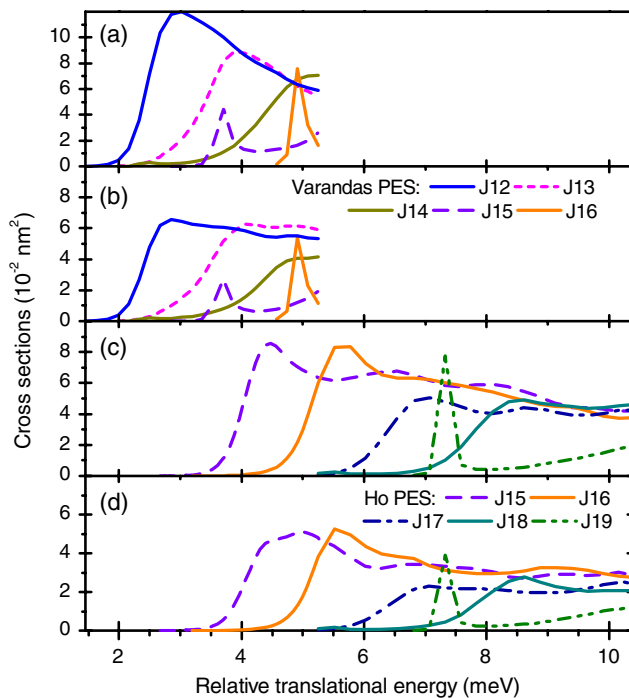


FIG. 2 (color online). Partial-wave cross sections for selected J values. (a) PES by Varandas and coworkers [26] SD + H channel; (b) *idem* SH + D channel; (c) PES by Ho *et al.* [20], SD + H channel; and (d) *idem* SH + D channel.

modification of the branching ratio. Indeed, one $^3A'$ and two degenerate $^3A'$ PESs arising from $S(^3P_J) + HD$ ground-state reactants are expected to play a role in the reaction dynamics due to favorable crossings with the $^1A'$ PES in the entrance channel [27,28]. A complete time-dependent (TD) QM treatment considering the four PESs and their nonadiabatic couplings performed over the range $E_T = 10\text{--}400$ meV has previously demonstrated the importance of intersystem crossing [24]. Although this nonadiabatic treatment in itself does not provide a quantitative explanation for the phenomena observed here, it shows that quenching preferentially affects the flux that would have gone to produce $DS + H$ rather than $HS + D$ hence altering the branching ratio.

The explanation of the change of the reaction dynamics observed around $E_T = 10$ meV in the experiment becomes clear while considering the one-dimensional effective potentials (see Fig. 3) associated with the PES of Ho *et al.* These potentials have been calculated by adiabatically separating the fast coordinates, r and θ , from the collision coordinate R [where (R, r, θ) are the usual reactant Jacobi coordinates]. All the terms in the Hamiltonian, except for the radial collision kinetic energy, were diagonalized in a basis of reactant states for a fixed R [21]. Interestingly, the resulting average over internuclear distances and angles of approach displays in general two barriers as a function of R : the outer barrier is the usual centrifugal one; however, the very sharp inner one seems to be a feature of the system, appearing for many different partial waves and

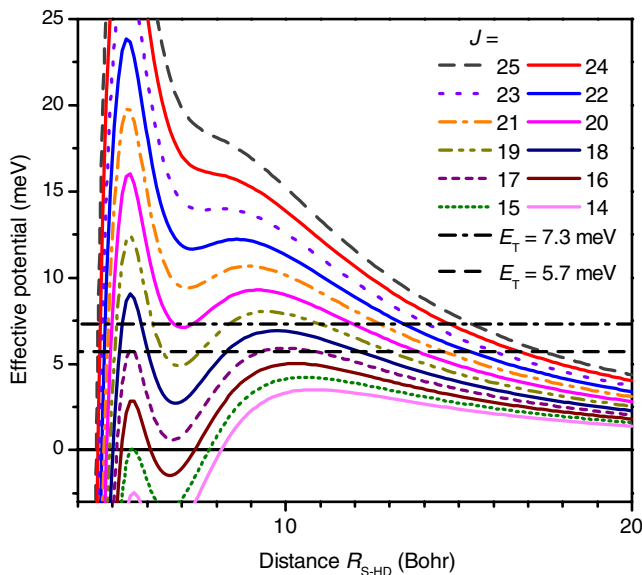


FIG. 3 (color online). Adiabatic effective potentials calculated for selected values of J , using the PES of Ho *et al.* [20]. Horizontal dash-dotted line: position of the shape resonance of the $J = 19$ partial-wave at $E_T = 7.3$ meV. Horizontal dashed line: position of the change in slope of the adiabatic ICSs, with inner and outer barriers for $J = 17$ exhibiting equal heights of *ca.* 5.7 meV.

on both $^1A'$ PESs considered. The inner barrier and the shallow well between maxima, which support shape resonances for particular J values, have a dynamical origin. They result from the balance between the increasing attractions to the insertion well and the collinear repulsive barrier present on the PES at short distances [29]. As J increases, the centrifugal barrier shifts to shorter internuclear distances and progressively merges with the inner repulsive potential, provoking the disappearance of the well. Two different capture mechanisms, associated with the opening of the partial waves being controlled by one of the barriers or the other, can be anticipated. For low J the opening is controlled by the outer barrier, whereas for high J the inner barrier is higher and eventually becomes the only one. The transition, which happens for $J = 17$ in the surface of Ho *et al.*, is identifiable from the pronounced change in slope of the adiabatic total ICSs as shown in Fig. 1.

The nature of the peaks in the experimental ICSs for the $HS + D$ product channel and their connection with the shape resonances obtained in the adiabatic calculations remain open questions. Do they constitute resonances, never previously observed for a reaction without an energy barrier? And, if they are resonances, how can they appear as peaks in the ICSs, features which have never been seen experimentally? Peaks arising from partial-wave resonances have to date only been observed in the state-to-state DCSs corresponding to a particular HF quantum state for a restricted set of scattering angles in the $F + HD \rightarrow FH + D$ reaction [6] while appearing as a steplike feature in the ICSs [5]. It is known that strengths, shapes, and energies of resonance features as calculated by theoretical methods remain very sensitive to the PESs and the QM methods that are utilized. The different theoretical findings for the shape resonances which survive partial-wave averaging predicted by the two different PESs used in this study furnish another example. In our present $S(^1D_2) + HD \rightarrow HS + D$ case, the peaks in the ICSs appear at $E_T = 1.9, 3.4,$ and 4.7 meV, where δE_T (half-width at $1/e$) = 0.17, 0.26, and 0.33 meV, respectively. This is in sharp contrast to the $F + HD \rightarrow HF + D$ reaction where the partial-wave resonances show up at more than 10-fold higher values in E_T and δE_T , rendering them impossible to distinguish as resolved peaks in the ICSs of the crossed-beam experiments [30]. This explains why resonance features could be still discernable in our low-energy ICS measurements. Unfortunately, at these low energies the accuracy of the ground-state $^1A'$ PES employed here, as well as the strict adiabatic treatment, are not sufficient to provide TI QM calculations in agreement with experiment.

In conclusion, a complete nonadiabatic TI QM treatment involving singlet and triplet PESs is needed to elucidate the low energy dynamics of this reaction. The task is extremely challenging and the quality of the reactive PESs may have to reach the spectroscopic accuracy already obtained for

PESs describing van der Waals interactions resulting from neutral species approaching together. Indeed, in a recent study of $\text{CO}(j=0) + \text{H}_2(j=0) \rightarrow \text{CO}(j=1) + \text{H}_2(j=0)$ inelastic collisions, we did detect the shape (orbiting) resonances appearing in the post-threshold region of the $\text{CO}(j=0 \rightarrow j=1)$ transition at $E_T = 0.48$ meV (3.85 cm^{-1}) but we could only find good agreement when the TI QM calculations were performed on an *ab initio* PES rescaled by a factor $f = 1.05$, despite the original PES being capable of reproducing the experimental energies of the infrared transitions of the complex with 0.1 cm^{-1} accuracy [31].

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