Classical collision complexes in the D+H2(v=0, j=0)→HD(v′, j′)+H reaction

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Classical collision complexes in the $D+H_2(v=0, j=0)\rightarrow HD(v', j')+H$ reaction

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The possibility of detecting scattering resonances in the $H + H_2(v, j) \rightarrow H_2(v', j') + H$ reaction and its isotopic analogs has originated recently a great amount of work both experimental[1–3] and theoretical.[4,5] After a certain controversy it is now generally accepted that the scattering resonances, in accordance with the exact quantum mechanical (QM) predictions, will not show up in the energy dependence of the integral cross section.[3–5] However, Miller, Zhang, and Continetti[5] have demonstrated that a structure is indeed observable in the energy dependence of the state (v', j') resolved differential reaction cross section $d^2\sigma/d\omega$ for the lowest j's. This structure is clearly seen in a three dimensional representation of $d^2\sigma/d\omega$ vs total energy E and c.m. scattering angle θ, where it takes the form of a relative maximum that moves from backward scattering with respect to the incoming atom ($\theta = 180°$) at low energies to forward scattering ($\theta = 0°$) at higher energies building thus a "ridge" along the $E - \theta$ plane. This ridge structure in the differential cross section has a counterpart (via deflection function) in the dependence of the reaction probability on energy and on total angular momentum $P(E, J)$. The authors attribute the ridge structure to the manifestation of a "broad" (i.e., with contributions of several J for each resonant energy) quantum mechanical resonance.

The interest of this finding is further increased by the fact that the ridge structure in the differential cross section could be observed experimentally, providing an experimental scheme is used that allows the simultaneous detection of the scattering angle θ and the internal state (v', j') of the product molecule from the reaction. In fact such a refined experiment has been undertaken by Vrakking, Bracker, and Lee[6] for the $D + H_2 \rightarrow HD + H$ system. They use a cross-beam arrangement and employ resonance enhanced multiphoton ionization (REMPI) and a position sensitive ion detector for the analysis of the HD products.

We have carried out quasiclassical trajectory (QCT) calculations for the $D + H_2$ $(v = 0, j = 0) \rightarrow HD(v', j') + H$ reaction on the LSTH potential energy surface[7] covering the range of collision energies relevant to the quantum mechanical calculations commented on. Figure 1(a) shows a three dimensional representation of the QCT differential cross section vs E and θ for the $v' = 0$, $j' = 2$ case. A ridge structure very similar but somewhat less pronounced than the corresponding quantum mechanical one is also present. Similarly, Fig. 1(b) represents a 3-D plot of the reaction probability $P(J)$ (opacity function) as a function of the (total) angular momentum and

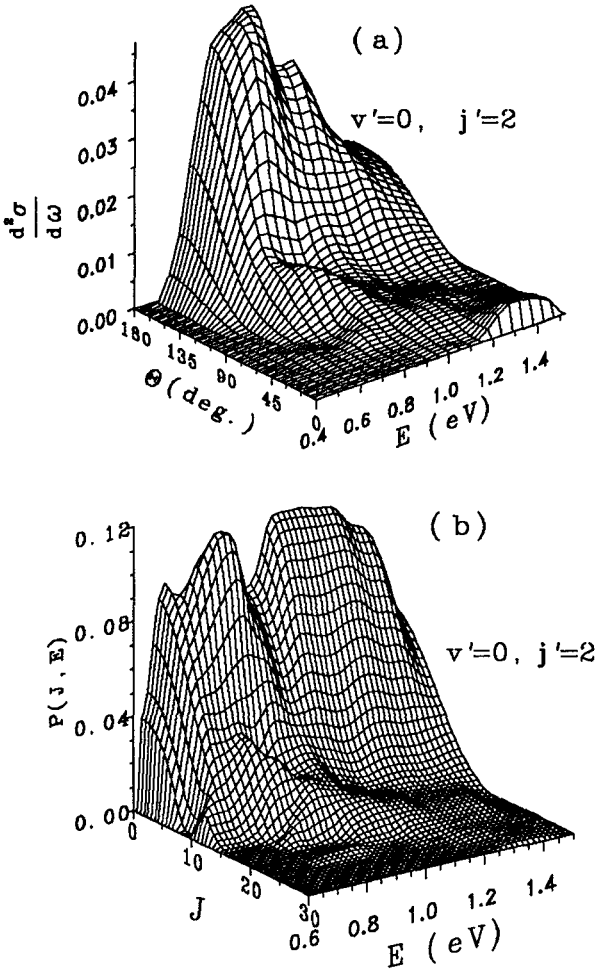

FIG. 1. (a) 3-D plot of the solid angle differential cross section ($Å^2\ sr^{-1}$) as a function of the scattering angle and total energy for the $v = 0$, $j=0\rightarrow v'=0, j'=2$. (b) 3-D plot of the reaction probability (opacity function) as a function of the (total) angular momentum and the total energy. Notice in both cases the ridge moving from low J, high θ towards high J and low θ as E increases.

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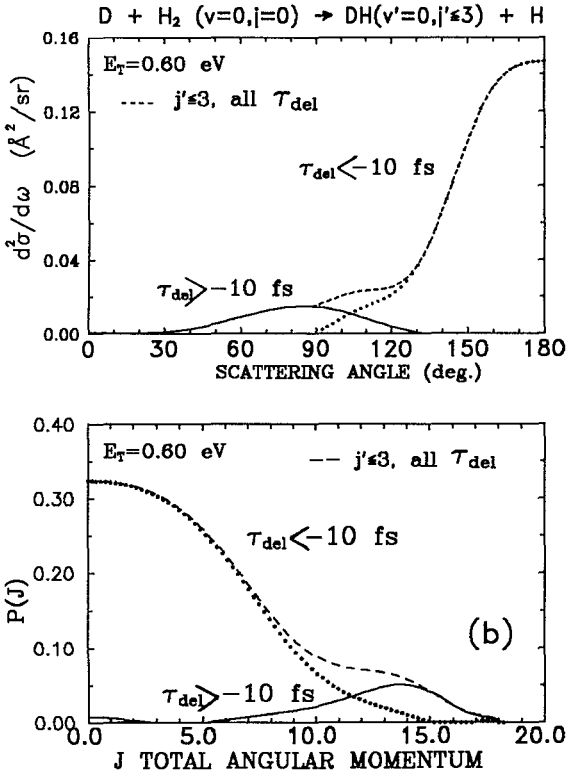

FIG. 2. (a) Solid angle differential cross section and (b) opacity function for the reaction into $v' = 0$ summed on j' from 0 to 3, at 0.60 eV of collision energy. Solid line, trajectories with τ_{del} larger than -10 fs (sideways, high J); dots, trajectories with τ_{del} less than -10 fs (backward, low J); dashed line for all the trajectories. It is clearly seen how the bump centered around 75° (which constitutes the ridge in the $E-\theta$ plane) is due to trajectories with the longest time delays.

total energy where this structure in the J-E plane is also noticeable, also in analogy with QM results.[5] Qualitatively similar results are obtained for $j' \leqslant 3$. In order to clarify the origin of this structure we have investigated the "time delays," τ_{del} of the trajectories leading to scattering angles in the region of the ridge, where τ_{del} is defined, following Ref. 8 as $\tau_{del} = T - R_f/v_{rf} - R_i/v_{ri}$, where T is the total duration of the trajectory initiated in channel i and ended in channel f and R, and v_r are the coordinate and the velocity of the atom diatom relative motion at the initial and final times of the trajectory. The differential reaction cross section for a collision energy (E_T) of 0.60 eV and $j' \leqslant 3$ is shown in Fig. 2(a). This picture shows also the angular distributions for trajectories with τ_{del} longer or shorter than -10 fs. The bimodal character of the angular distribution is clearly seen in this representation, which shows a bump in the angular region corresponding to the ridge. It is also manifest that this bump is caused by the more "delayed" trajectories. The corresponding opacity functions are portrayed in Fig. 2(b) where it is clearly shown that the longest lived trajectories correlate with high values of the angular momentum.

An analysis of individual trajectories shows indeed that those pertaining to the ridge lead typically to a short lived linear collision complex that undergoes one or two oscillations and then dissociates to give the reaction products. The corresponding lifetimes are 15–30 fs. This is less than a rotational period but more than the collision time ($<$6–8 fs) of the most frequent "direct" trajectories. "Trapped" trajectories leading to several oscillations of the collision complex had been found by Muga and Levine[8] for this reaction and are also present in our calculations but they are very rare and have no influence in the shape of the differential cross section.

We conclude from our study that the described structure in the energy dependence of the differential cross section for $D + H_2(v = 0, j = 0) \rightarrow HD(v', j') + H$, which is, in principle, accessible to experimental investigations, can have at least a significant classical contribution.

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[1] H. Buchenau, J. P. Toennies, J. Arnold, and J. Wolfrum, Ber. Bunsenges, Phys. Chem. **94**, 1231 (1990), and references cited therein.
[2] J. J. Valentini and D. L. Phillips, in *Advances in Gas Phase Photochemistry and Kinetics*, Vol. 2, edited by M. N. R. Ashfold and J. E. Baggott (Royal Society of Chemistry, London, 1989), and references cited therein.
[3] D. A. V. Kliner, D. E. Adelman, and R. N. Zare, J. Chem. Phys. **94**, 1069 (1991).
[4] W. H. Miller, Annu. Rev. Phys. Chem. **41**, 245 (1990), and references cited therein.
[5] (a) W. H. Miller and J. Z. H. Zhang, J. Phys. Chem. **95**, 12 (1991); (b) R. E. Continetti, J. Z. H. Zhang, and W. H. Miller, J. Chem. Phys. **93**, 5356 (1990).
[6] M. J. J. Varkking, A. S. Bracker, and Y. T. Lee, XIII International Symposium on Molecular Beams, El Escorial, Madrid, Spain, 2–7 June, 1991. Book of abstracts p. I-4.
[7] (a) P. Siegbahn and B. Liu, J. Chem. Phys. **68**, 2457 (1978); (b) D. G. Truhlar and C. J. Horowitz, *ibid.* **68**, 2466 (1978); **71**, 1514E (1979).
[8] J. G. Muga and R. D. Levine, Chem. Phys. Lett. **162**, 7 (1989); J. Chem. Soc. Faraday Trans. **86**, 1669 (1990).