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LETTERS TO THE EDITOR

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COMMUNICATIONS

The H+D$_2$ reaction in the vicinity of the conical intersection

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Scattering measurements performed at an energy slightly higher than that of the lowest crossing between the ground and the first electronically excited state of the H$_3$ system are reported. The essentials of the reactive dynamics are describable in terms of a classical motion of the nuclei on the lowest adiabatic electronic potential. © *1997 American Institute of Physics.*
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The possible contribution of more than one potential energy surface to reaction cross sections or rate constants is a subject of great interest.[1] However, inaccurate potential surfaces and low resolution data preclude, in general, definitive conclusions on that point. The prototypic H+H$_2$ exchange reaction, well characterized from a theoretical viewpoint, might constitute an exception to this situation, but until now the energetic region of the first excited electronic state had been beyond the reach of reactive scattering experiments. An account of the progress made in the knowledge of this reaction can be found in Refs. 2 and 3. The lowest electronic states of the H$_3$ system have been investigated with great detail (see, for instance, Refs. 4 and 5 and references therein). In particular, thorough *ab initio* calculations have provided very detailed information on the two lowest potential energy surfaces (PES).[6–9] These two PESs exhibit a conical intersection for D_{3h} nuclear configurations; that is, the two electronic states are degenerate for geometries in which the nuclei are at the vertices of an equilateral triangle and that their energies split in an approximately linear way for deviations of this geometry. The minimum conical intersection energy is at ≈ 2.7 eV above the bottom of the H$_2$ ($^1\Sigma_g^+$) potential well[7,9] and it has been suggested that ''electronic nonadiabatic collisions may make a significant contribution to any collisional processes at total energies large enough to reach the conical intersection.''[7] Furthermore, in a series of recent works, Kuppermann and Wu[10–13] have pointed out that the geometric phase (GP), associated with the presence of the conical intersection, should induce observable effects in the dynamics even for energies well below that of the actual surface crossing.

A considerable set of experimental data has now been assembled up to total energies of ≈ 2.4 eV. These data include reaction rate constants for the production of individual internal states ($E_{tot}=1.1$–2.2 eV),[14–16] low resolution angular and/or velocity distributions of the nascent products ($E_{tot}=0.73$, 1.48 eV),[17,18] differential cross sections (DCS) into a specific rovibrational product state ($E_{tot}=2.39$ eV)[19] and angular distributions resolved into the final internal states of the scattered molecules ($E_{tot}=1.47$, 2.39 eV).[3,20] For practical convenience, these investigations have used deuterated isotopic variants of the reaction. Existing discrepancies between theoretical calculations and some of the just mentioned experimental results were apparently removed by the explicit consideration of the geometric phase in quantum mechanical calculations of the dynamics.[10,12] This was fortunate since GP effects are oscillatory in energy and seem to depend in a very critical way on the shape of the PES used;[13] in fact, the highest resolution measurements available could be well reproduced with dynamical calculations that did not incorporate GP effects.[3,20] In any case, GP effects are expected to increase in importance as the energy of the system approaches that of the conical intersection and should be more marked for DCS than for total cross sections or rate constants.[10,11]

In this Communication we report a high resolution experimental study of the H+D$_2$($v=j=0$)→HD(v',j')+D reaction at a collision energy (E_{col}) of 2.67 eV, corresponding to a total energy (E_{tot}) of 2.86 eV, slightly above that of the minimum conical intersection. To the best of our knowledge, this is the first time that the conical intersection is accessed in a reactive scattering experiment. The measurements have been simulated with quasiclassical trajectory
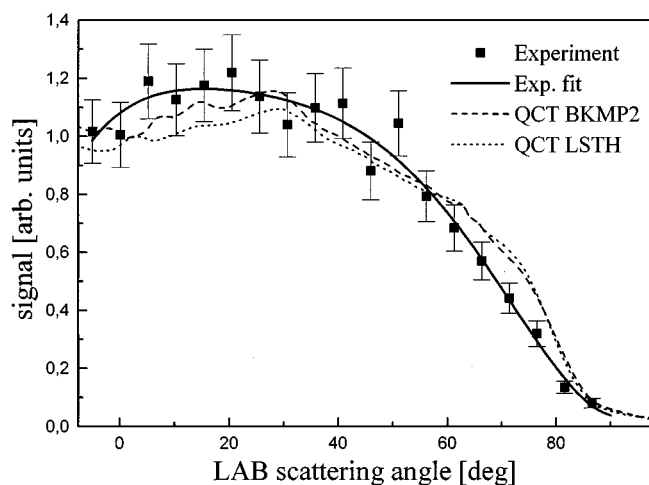
FIG. 1. Laboratory total (including all internal states of the products) angular distribution of the D atoms scattered in the reaction $H+D_2(v = j = 0) \rightarrow HD(v',j')+D$ at a collision energy $E_{col}=2.67$ eV.

FIG. 2. Laboratory kinetic energy spectra of the nascent deuterium atoms from the reaction $H+D_2(v = j = 0) \rightarrow HD(v',j') + D$ at a collision energy $E_{col}=2.67$ eV and for the laboratory scattering angles $\Theta_{LAB}=0°$, $5°$, and $10°$ (solid line) and theoretical simulations (dashed line) using the results of quasiclassical trajectory calculations on the BKMP2 potential energy surface (Ref. 9). The energies corresponding to the various rovibrational levels of the HD molecule are also shown.

(QCT) calculations, which have proven reliable for the simulation of experimental results at lower energies.[3,20]

The experimental arrangement used is described in Refs. 3 and 20, and in more detail in Ref. 21, and only the details relevant to the present measurements are given here. A supersonic beam, of *ortho*-D_2 cooled to the ground rotational level ($j=0$) with virtually no contribution (less than 2%) from other rotational states was crossed with kinematically "hot" H atoms generated by the photolysis of HI with the linearly polarized output of a spectrally narrowed ArF* excimer laser at 193 nm. The laser polarization was chosen so that only the "fast" H atoms (i.e., those corresponding to the formation of $I(^2P_{3/2})$ in the photolysis of the HI molecule) intersect the D_2 beam. The resulting collision energy is 2.67 ± 0.013 eV. Time of arrival distributions of the reactively scattered D atoms were measured at various laboratory (LAB) angles by using the Rydberg atom time-of-flight (TOF) spectroscopy technique, developed at the University of Bielefeld.[22] Kinetic energy spectra (KES) reflecting a partial resolution of the rovibrational states of HD were obtained from the TOF distributions. The total kinetic energy resolution (FWHM) of the KES ranged from 33 meV at $\Theta_{LAB} = 0°$ and low D atom kinetic energy to 88 meV at $\Theta_{LAB}=50°$ and high kinetic energy of the D atoms. The angle of acceptance of the detector is $1°$ in the plane of the molecular beams and $5°$ perpendicular to it.

The details of the QCT method used can be found in previous articles.[23,24] For the present work, 1×10^6 trajectories were run on the new version of the Boothroyd–Keogh–Martin–Peterson (BKMP2) PES[9] at the collision energy of 2.67 eV and for the ground rotational state of the deuterium molecule. The assignment of the vibrational (v') and rotational (j') quantum numbers of the product HD molecules was done as in Refs. 3, 20, and 24 and the rovibrationally resolved DCS are calculated by the method of moments expansion in Legendre polynomials.[23] The simulation of the LAB kinetic energy spectra of the scattered D atoms was performed by transforming the theoretical center-of-mass
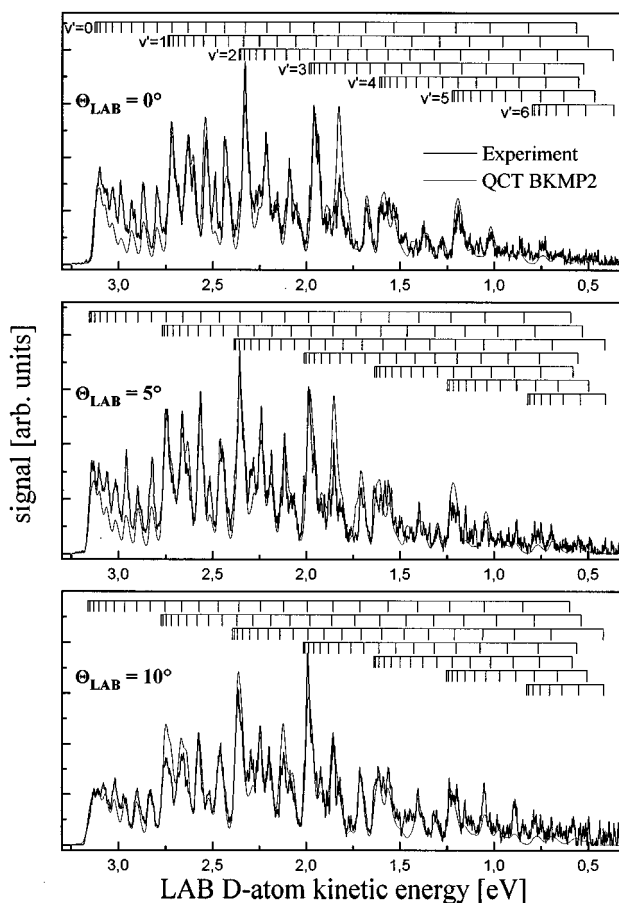
(CM) v', j' state resolved DCSs into the LAB system using the appropriate Jacobian factors and taking into account the experimental broadening and the geometric effects of the apparatus. The scaling between experimental and theoretical total (summed over all products' states) angular distribution (AD), as shown in Fig. 1, has been carried out by a least square procedure. The factor so obtained has been used to scale all the simulated and measured KES. More details of the procedure can be found in Ref. 24. An analogous calculation on the Liu–Siegbahn–Truhlar–Horowitz (LSTH) PES[6] led to similar results.

The total LAB angular distribution is broader than those found at lower energies. This broad LAB AD corresponds to a CM angular distribution with a significant contribution of sideways scattering. The measured distribution is well reproduced with the QCT data. Kinetic energy spectra of the scattered D atoms at six representative laboratory angles are shown in Figs. 2 and 3. The experimental and theoretical results have been represented together for comparison. The QCT results provide a good global description of the spectra and can account for the observed tendency toward hotter internal states distributions with increasing Θ_{LAB}, but fail to
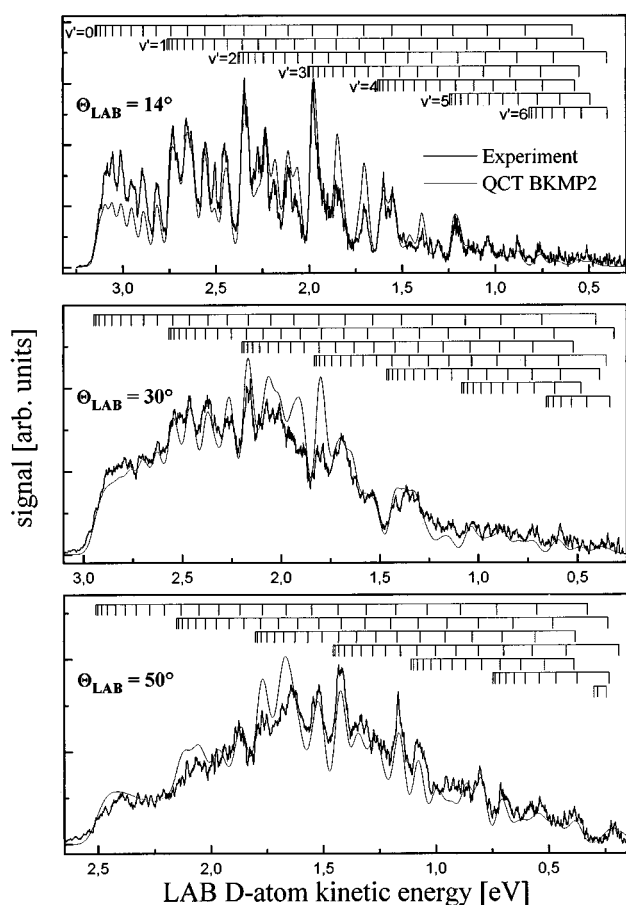
FIG. 3. Same as Fig. 2, but for the laboratory scattering angles $\Theta_{LAB}=14°$, 30°, and 50°.

reproduce the relative intensities in some of the peaks. The measured distributions of rotational levels within each vibrational level of HD are hotter than those obtained at lower energies,[3,20] also in accordance with the theoretical calculations.

The remaining discrepancies between calculations and measurements, within the experimental uncertainty, may have different causes. They can be due to inherent shortcomings of the QCT method, to slight inaccuracies of the PES in this high energy region or to the influence of the upper electronic surface (nonadiabatic transitions or GP effects). In any case they do not blur significantly the picture provided by the classical motion of the nuclei on the lowest adiabatic surface. Except for the eventual contribution of more than one electronic state, the good performance of classical mechanics at high collision energies is not unexpected since in this energetic region the influence of the most typical quantal problems like tunneling or zero-point energy should be negligible. Considering more specifically the possible effects associated with the conical intersection, it is maybe not so surprising that nonadiabatic transitions do not play an important role in this experiment. At the energy of the present work noncollinear collisions, characterized by triangular configurations of the nuclei, make indeed a significant contribution to reactive scattering, but the region of configuration of the three nuclei for which the two electronic states are

nearly degenerate is very small and slight deviations from the D_{3h} symmetry cause a large splitting of the two PESs,[7,9] rendering nonadiabatic transitions unlikely. The possible influence of the geometric phase is more difficult to estimate *a priori* and little can be said until accurate QM calculations taking this effect into account are performed. Such calculations, though cumbersome and computationally very expensive, are becoming feasible. The fact that no dramatic ''nonclassical'' effects are unveiled by the present investigation at the intersection of two electronic states, is in a way reassuring since it strengthens the confidence in the use of quasiclassical trajectories, a method virtually available to everybody, for the design and analysis of high resolution experiments in reaction dynamics.

[1] E. E. Nikitin and L. Zülicke, in *Selected Topics of the Theory of Chemical Elementary Processes*, edited by de. G. Bertier *et al.* (Springer-Verlag, Berlin, 1978).

[2] H. Buchenau, J. P. Toennies, J. Arnold, and J. Wolfrum, Ber. Bunsenges. Phys. Chem. **94**, 1231 (1990).

[3] L. Schnieder, K. Seekamp-Rahn, J. Borkowski, E. Wrede, K. H. Welge, F. J. Aoiz, L. Bañares, M. J. D'Mello, V. J. Herrero, V. Sáez Rábanos, and R. E. Wyatt, Science **269**, 207 (1995).

[4] R. N. Porter, R. M. Stevens, and M. Karplus, J. Chem. Phys. **49**, 5163 (1968).

[5] A. C. Roach and P. J. Kuntz, J. Chem. Phys. **84**, 822 (1985).

[6] P. Siegbahn and B. Liu, J. Chem. Phys. **68**, 2457 (1978); D. G. Truhar and C. J. Horowitz, *ibid.* **68**, 2466 (1978); **71**, 1514 (1979).

[7] A. J. C. Varandas, F. B. Brown, C. A. Mead, D. G. Truhlar, and N. C. Blais, J. Chem. Phys. **86**, 6258 (1987).

[8] A. I. Boothroyd, W. J. Keogh, P. G. Martin, and M. R. Peterson, J. Chem. Phys. **95**, 4343 (1991).

[9] A. I. Boothroyd, W. J. Keogh, P. G. Martin, and M. R. Peterson, J. Chem. Phys. **104**, 7139 (1996).

[10] Y-S.M. Wu and A. Kuppermann, Chem. Phys. Lett. **201**, 178 (1993).

[11] A. Kuppermann and Y-S.M. Wu, Chem. Phys. Lett. **205**, 577 (1993).

[12] Y-S.M. Wu and A. Kuppermann, Chem. Phys. Lett. **235**, 105 (1995).

[13] A. Kuppermann, A. Wu, and Y-S.M. Wu, Chem. Phys. Lett. **241**, 229 (1995).

[14] D. A. V. Kliner, D. E. Adelman, and R. N. Zare, J. Chem. Phys. **95**, 1648 (1991).

[15] D. E. Adelman, N. E. Shafer, D. A. V. Kliner, and R. N. Zare, J. Chem. Phys. **97**, 7323 (1992).

[16] D. Neuhauser, R. S. Judson, D. J. Kouri, D. E. Adelman, N. E. Shafer, D. A. V. Kliner, and R. N. Zare, Science **257**, 519 (1992).

[17] T. N. Kitsopoulos, M. A. Buntine, D. P. Baldwin, R. N. Zare, and D. W. Chandler, Science **260**,1605 (1993).

[18] N. E. Shafer, H. Xu, R. P. Tuckett, M. Springer, and R. N. Zare, J. Phys. Chem. **98**, 3369 (1994).

[19] H. Xu, N. E. Shafer-Ray, F. Merkt, D. J. Hughes, M. Springer, R. P. Tuckett, and R. N. Zare, J. Chem. Phys. **103**, 5157 (1995).

[20] E. Wrede, L. Schnieder, K. H. Welge, F. J. Aoiz, L. Bañares, and V. J. Herrero, Chem. Phys. Lett. **265**, 129 (1997).

[21] L. Schnieder, K. Seekamp-Rahn, E. Wrede, and K. H. Welge (in preparation).

[22] L. Schnieder, W. Meier, K. H. Welge, N. M. R. Ashfold, and C. M. Western, J. Chem. Phys. **92**, 7027 (1990).

[23] F. J. Aoiz, V. J. Herrero, and V. Sáez Rábanos, J. Chem. Phys. **97**, 7423 (1992).

[24] F. J. Aoiz, L. Bañares, M. J. D'Mello, V. Herrero, V. Sáez Rábanos, L. Schnieder, and R. E. Wyatt, J. Chem. Phys. **101**, 5781 (1994).