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Angle-velocity contour maps for the $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ reaction from quasiclassical trajectory calculations

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In a very recent article, Kitsopoulos *et al.*¹ have reported the results of a “reaction product imaging” experiment carried out on the $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ reaction. This novel technique, developed in the late 1980s² is based upon the ionization of the species of interest and subsequent detection by means of a position sensitive ion detector. By choosing the adequate kinematic arrangement and after the appropriate data treatment, one can recover from the recorded images simultaneously angle and velocity distributions in scattering experiments. The application of this technique to one of the isotopic variants of the $\text{H} + \text{H}_2$ reaction is of great interest since it offers the possibility of a sound comparison with theory and with high resolution measurements.

The most resolutive experiment to date on the dynamics of the $\text{H} + \text{D}_2$ (and also of any variant of the H_3 reactive system) has been performed by Schnieder *et al.*^{3,4} In this experiment, differential cross sections have been determined for individual rotational states of the HD product.⁴ The H atoms generated by photolysis of HI were crossed with a cold D_2 molecular beam. The main difference with other experiments lies on the detection of the D atoms, which are promoted to a metastable Rydberg state by resonant two photon absorption, then field ionized in the detector region allowing the measurement of their time-of-flight distribution.

A similar scheme (photolysis of HI and detection of D atoms) has been used by Kitsopoulos *et al.*¹ in their product imaging experiment. Their experimental arrangement has a smaller energy resolution and does not allow the identification of individual internal states of the products. The method provides, however, in a nearly straightforward manner an angle-velocity contour map and hence a global picture of the dynamics.

In the present note angle-velocity contour plots from QCT calculations are reported in order to compare with those from the ion imaging measurements.¹ The QCT calculations are carried out on the LSTH potential energy surface⁵ at collision energies of 0.54 and 1.29 eV corresponding to the mean collision energies of the experiment and include the D_2 initial rotational states $j=0, 1$, and 2

present in the experiment. The resulting contour plots depicted in Figs. 1 and 2 are weighted in D_2 rotational states in the ratio reported for the experiment (0.5:0.25:0.25). The figures include also as a reference the kinematic circles corresponding to the maximum recoil velocities classically allowed for a given vibrotational state of the HD molecule. Note that these “classical circles,” which correspond to vibrational energies $E_v \approx h\nu v'$, are shifted by the amount of about half of the vibrational quantum to higher velocities than those obtained from the energies of the actual quantum states.

A first glance at the measured and calculated contour plots shows a noteworthy qualitative similitude between them. In both cases the preponderance of forward scattering of the D atoms in the center-of-mass (c.m.) frame (corresponding to backscattering of the HD product) is evident as well as the fact that a broader angular distribution is obtained for the higher collision energy. The good agreement between the measured angular distributions integrated on final D velocities and those from QCT calculations⁶ is already commented on in Ref. 1. The present contour plots show that the classical trajectories reproduce also the observed tendency towards lower D atom recoil velocities with increasing scattering angle, which according to previous QCT data⁶ is due to a higher rotational excitation of the sideways scattered products. In fact, in both cases at 1.29 eV is noticeable that sideways scattering lies within the kinematic limits of $v'=1$ and $v'=2$. Also at this energy QCT calculations predict some D atom backscattering, which seems to be in accord with the experiment.

A closer inspection reveals, however, important differences between the calculated and measured velocity distributions. From the kinematic circles of Fig. 4 of Ref. 1, it is easily inferred that the maxima of the measured velocity distributions of the nascent D atoms are located at velocity values smaller than those from the QCT results. Although the maximal velocities classically allowed are higher than the real ones due to the fact that collisions leading to products with a vibrational energy content less than the zero point ($E \sim \frac{1}{2}h\nu$) are possible, this is not enough to justify the differences observed. In addition, experimental velocity

FIG. 1. Bottom: Angle-velocity contour map for the $\text{H} + \text{D}_2(v=0) \rightarrow \text{HD} + \text{D}$ reaction for the collision energy $E_T = 0.54$ eV. The calculations include the D_2 rotational distribution (0.5:0.25:0.25 for $j=0,1,2$) reported in Ref. 1. The crossed circles correspond to the maximum D atom recoil velocity classically allowed for a given HD vibrational state. The separation between the ticks of the axis is 1000 ms^{-1} . Top: Three dimensional representation.

distributions are sensibly broader than the calculated ones at all the angles. The discrepancy is particularly appealing in the $E_T = 1.29$ eV case, where the maximum in the experimental velocity is obtained inside the $v' = 1$ circle, which would imply either a predominance of the $\text{HD}(v' = 1)$ state or a very high rotational excitation of the $\text{HD}(v' = 0)$ even at angles close to 0 deg (c.m.). This is clearly at variance with the results of QCT calculations⁶ as well as with the high resolution experiments of Schnieder *et al.*⁴ that yield for this collision energy a much higher population for the $\text{HD } v' = 0$ than for the $\text{HD } v' = 1$ channel, and at forward D atom scattering angles a low rotational excitation.

In view of the above discussed discrepancies it seems that a more detailed study, both experimental and theoretical, of this prototypic reaction would be very timely.

Note added in proof. After the submission of this letter for publication, we have received additional information on the experimental results reported in Ref. 1 [T. Kitsopoulos (private communication)]. According to this information, the Newton circles corresponding to the nominal collision energies of 0.54 and 1.29 eV do not coincide with the yellow circles depicted in Fig. 4 of Ref. 1 but should rather pass through the center of the full red circles labeling the

FIG. 2. Same as Fig. 1 but for the collision energy $E_T = 1.29$ eV.

internal states of HD. As a consequence, the maximum in the D forward scattering for $E_T = 1.29$ eV lies approximately on the $v' = 1$ circle. In addition, the experimental energy resolution is estimated to be roughly 30% of the total energy of the fragment.

Considering these two facts, the comparison of experimental results and those obtained by convoluting the QCT triple differential cross section with the above mentioned energy resolution still shows differences. The calculated distributions become broader but not so much as the experimental ones, and although the discrepancy in the location of the maxima becomes smaller, it remains noticeable.

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