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Quasiclassical trajectory study of the $H+D_2 \rightarrow HD+D$ reaction at a collision energy of 2.2 eV: A comparison with experimental results

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In a recent article, Zare and co-workers[1] have reported a measurement of the state-specific differential cross section (DCS) for the $H+D_2 \rightarrow HD(v'=4,\ j'=3)+D$ reaction at a collision energy (E_T) of 2.2 eV using a novel photoinitiated reaction technique. The resolution of this technique is at present sensibly lower than that of crossed beam experiments,[2] but it is generally easier to implement and can be applied even to reactions taking place in a bulb. In spite of the moderate resolution of the data, this experiment is of great interest not only from a technical point of view, but also due to the fact that it explores the dynamics of the prototypic H_3 system in a region of the potential energy surface (PES) where the information about the reaction dynamics is scarce. The only studies of reactive collisions between ground state reagents at an energy larger than 2.0 eV correspond to the $H+D_2$ isotopic variant of the reaction and are, to our knowledge, the mentioned measurements of Ref. 1 and the experimental determination of the rovibrational state resolved relative rate constants for the production of $HD(v',j')$ carried out also by Zare and co-workers.[3] From the theoretical point of view, a recent quantum functional sensitivity analysis[4] indicates that the sensitivities of the transition probabilities to small variations in the PES for the $H+D_2$ reaction are different from those for the other isotopomers at energies larger than 1 eV, suggesting that the study of this isotopic variant of the $H+H_2$ system could be of great interest for the assessment of the PES.

Very precise PESs based on *ab initio* calculations[5] are available for this system. The precision is especially high in the vicinity of the minimum energy path for the reaction, but the *ab initio* characterization is not so complete for the higher energy region. In addition, the two lowest electronic surfaces for H_3 exhibit a conical intersection for D_{3h} geometries; this conical intersection should induce geometric phase effects that could be relevant for state resolved dynamical observables at the experimental energy considered in the present work.[6] Accurate quantum mechanical (QM) calculations, though nowadays feasible, are very cumbersome at high collision energies and it is worth trying the more flexible quasiclassical trajectory (QCT) approach, which has performed well for the reaction at lower energies (see Ref. 2, and references therein). On the other hand, the QCT results would also serve as a reference for the identification of possible geometric phase effects in accurate QM calculations.

In this work we present a QCT simulation of the experimental results reported in Refs. 1 and 3. The calculations have been carried out on the Liu–Siegbahn–Truhlar–Horowitz (LSTH) [Ref. 5(a)] and the double-many-body-expansion (DMBE) [Ref. 5(b)] PESs; the latter surface is a modification of the previous LSTH one in which special care was paid to the presence of the conical intersection. 10^6 trajectories were run on each surface for the $H+D_2(v=0,\ j=0)$ reaction at $E_T=2.2$ eV; in addition, 10^5 trajectories were calculated on the LSTH PES at 1.5 eV in order to include in the simulation the contribution of the slower H channel to the state resolved rate constants of Ref. 3. The general procedure for the QCT calculations can be found, for instance, in Ref. 7, and in the references cited therein. The specific details relevant to the present work are given below.

Figure 1 shows the comparison of the QCT results with the experimental rotational distributions obtained by Adelman *et al.*[3] for the $H+D_2 \rightarrow HD(v'=1,\ j')+D$ reaction. In the figure, the measured data have been scaled to the absolute values of the state specific rate constants, $k(\rightarrow v',j')=v_r\sigma_{v',j'}$, where v_r is the reagents' relative velocity, and $\sigma_{v',j'}$ the state resolved cross section, obtained in the present calculations by means of a weighted least-squares fit, taking into account the uncertainties in both experimental and QCT results. In the experiment, the same laser was used to probe the HD product and to initiate the reaction via photolysis of the HI precursor; as a result of that, both the collision energy and the amount of slow and fast H atoms [corresponding to $I^*(^3P_{1/2})$ and $I(^3P_{3/2})$, respectively], are different for each of the rotational states, j', detected. The present simulation takes into account the different ratio of slow to fast H atoms contributing to each j'; this ratio varies from 0.4 to 0.7 along the experimental j' distribution; the collision energy is maintained at 2.2 eV for the faster channel and at 1.5 eV for the slower one (as compared to the 2.1–2.3 eV and 1.4–1.6 eV ranges given in the experimental work). A good agreement is found between the experimental distribution and the QCT simulation, although the calculated distribution is slightly hotter than the experimental one, similarly to the $D+H_2(v=0,1)$ isotopic variant (see Ref. 7, and references therein), where the calculated j' distributions were in general hotter than the measured ones by one or two

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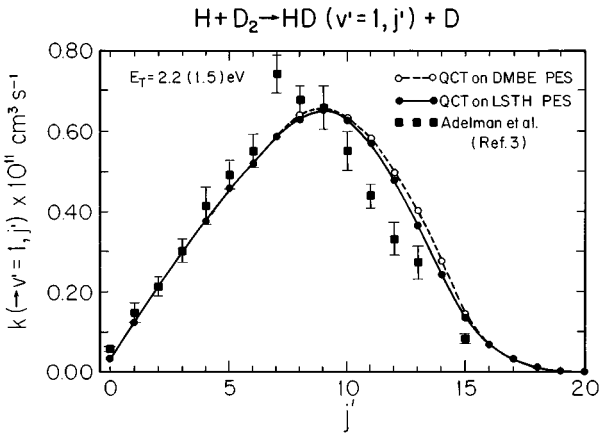

FIG. 1. State specific rate constants for the $H+D_2 \rightarrow HD(v'=1, j')+D$ reaction at $E_T=2.2$ (1.5) eV. The experimental data (solid points and error bars) (Ref. 3) have been scaled to the absolute values of the QCT rate constants (solid line calculations on the LSTH PES; dashed line on the DMBE PES).

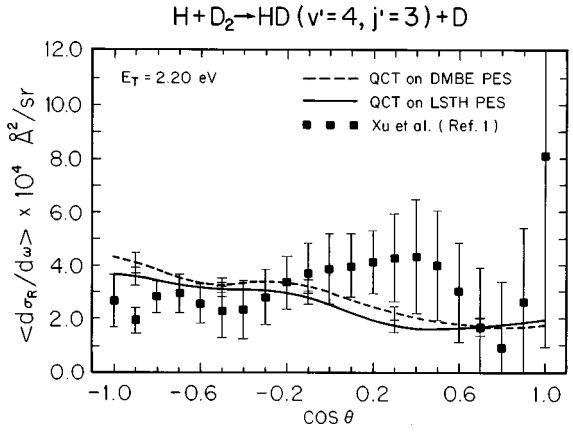

FIG. 2. State specific differential cross section for the $H+D_2 \rightarrow HD(v'=4, j'=3)+D$ reaction at $E_T=2.2$ eV. Solid points with error bars, experimental results of Ref. 1. Solid line calculations on the LSTH PES; dashed line on the DMBE PES. The scattering angle of the calculations corresponds, in accordance with that of Ref. 1, to outgoing HD molecules with respect to the direction of the incoming H atoms. The experimental points have been scaled to the calculated ones on the LSTH by means of a weighted least-square procedure. The theoretical DCS have been blurred by a Gaussian with a FWHM of $\Delta \cos \theta=0.25$.

quanta. The production of j' distributions hotter than those from experiment and QM calculations seems to be a general feature of the QCT method and it has been attributed to inherent defficiencies in the procedures used to assign the final states in QCT calculations (see Ref. 8, and references therein). Additionally, the inclusion of the geometric phase in QM calculations seems to yield colder rotational distributions than those calculations (QM or QCT) carried out without it, and this effect could be important at the collision energy studied in this work. Although at collision energies below 1.6 eV the reactivity on the DMBE PES is found to be somewhat larger than that on the LSTH PES,[4,9] at the energy of the present calculations, the QCT cross sections on both PESs are practically the same within the statistical uncertainty.

In Fig. 2, we compare the state specific DCS reported by Xu *et al.*[1] for the $H+D_2 \rightarrow HD(v'=4, j'=3)+D$ reaction at $E_T=2.2$ eV, with the present QCT calculations. As in the previous figure, the experimental data have been scaled to the theoretical curve by means of a weighted least-squares fit. In this case, the internal state of the HD product probed in the experiment can be accessed only with fast H atoms, i.e., with $E_T=2.2$ eV. In order to make the theoretical results directly comparable to the measurements, the QCT differential cross section has been blurred by a Gaussian with a width (FWHM) of $\Delta \cos \theta=0.25$ which accounts for the reported instrument function.[1] As can be seen, the theoretical results obtained on the two PESs are very similar. Experiment and QCT calculations lead to predominant isotropic scattering for the particular rovibrational state of HD investigated. There is a discrepancy between the measured and calculated DCSs in the region of 60–90 deg c.m. scattering angles, but given the experimental uncertainty, it is not prudent to draw definitive conclusions about possible structures in the DCS. To our knowledge, these QCT data are the only state resolved theoretical DCS reported thus far at this high collision energy for which there is current experimental interest and they can serve as a reference not just for the measurements but also for eventual QM calculations. The present QCT results provide an absolute scale for the experimental data; in this respect, it is interesting to note the very small value of the calculated cross section and, thus, the very high sensitivity of the experimental technique.

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