Product Angular Distribution for the H + CD$_4$ → HD + CD$_3$ Reaction

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Received: May 29, 2006; In Final Form: July 19, 2006

Using an analytical potential energy surface previously developed by our group, namely PES-2002, we analyzed the gas-phase reaction between a hydrogen atom and perdeuterated methane. We studied the effect of quasiclassical trajectory (QCT) and reduced dimensionality quantum-scattering (QM) calculations, with their respective limitations, on CD$_3$ product angular distributions in the collision energy range 16.1–46.1 kcal·mol^{-1}. It was found that at low collision energy, 16.1 kcal·mol^{-1}, both the QCT and QM calculations yielded forward scattered CD$_3$ products, i.e., a rebound mechanism. However, at high energies only the QM calculations on the PES-2002 surface reproduced the angular scattering found experimentally.

1. Introduction

The reaction of methane with hydrogen is the prototype of polyatomic reactions and has been widely studied both theoretically and experimentally with two objectives: first, in itself, to obtain accurate kinetics and dynamics information and, second, as a test to probe the efficiency and accuracy of new experimental techniques and theoretical results (see ref 1 and references therein).

Experimentally, state-to-state dynamics studies are difficult to perform at low energies for the title reaction, because the H atoms, which are produced in a photolysis process, are hot. Furthermore, the cross section is small, even for the case of high collision energies. For example, the reaction cross section is only 0.14 ± 0.03 Å^2 at 34.6 kcal·mol^{-1} (ref 2). Thus, experimental studies of the product angular distributions[3-6] have been scarce, recent, and focused on the high-energy region.

Only recently, Camden et al.[5] reported the first study of the state-to-state dynamics differential cross section at high energies (45.0 kcal·mol^{-1}) for the H + CD$_4$ gas-phase reaction. They found that the CD$_3$ products are sideways/backward scattered with respect to the incident H, suggesting a stripping mechanism. Later, this same laboratory[3,4] reported new experimental studies, also at high energy (27.8 kcal·mol^{-1}), finding the same experimental behavior. To explain the experimental product scattering distribution, these authors[3,4] performed quasiclassical trajectory (QCT) calculations on different potential energy surfaces (PES): (1) a DFT surface at the B3LYP/6-31G(d,p) level; (2) an analytic PES developed by our group,[1] named PES-2002; and (3) two semiempirical surfaces, MSINDO and reparametrized MSINDO. They found that while the DFT surface reproduces the experimental behavior at high energies, the QCT calculations based on the PES-2002 surface give CD$_3$ products strongly forward scattered, suggesting a rebound mechanism, in strong contrast with the experimental evidence.

In 2002, our group developed an analytical potential energy surface (PES-2002) to describe the H + CH$_4$ reaction and its

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isotopic analogues.[1] The PES is wholly symmetric with respect to the permutation of the four hydrogen atoms of methane and was calibrated to reproduce thermal rate constants, i.e., for low collision energies, using canonical variational statistical theory with semiclassical multidimensional tunneling (CVT/MT). From a kinetics point of view, it reproduces the behavior of the experimental measurements of thermal rate constants and kinetic isotope effects. Moreover, recently Zhao et al.[7] applied the quantum instanton approximation for thermal rate constants to this reaction using our PES-2002, finding good agreement with available experimental data over the wide temperature range 200–2000 K and concluded that this result lends support to the accuracy of the present potential energy surface. From a dynamics point of view, the PES-2002 surface qualitatively predicts that excitation of the CH$_4$ symmetric stretching and "umbrella" bend modes might be expected to enhance the forward rates, while only the CH$_3$ "umbrella" bend mode can appear vibrationally excited. This qualitative prediction agrees with other quantum scattering calculations.[8-10]

We emphasize that the PES-2002 surface was calibrated to reproduce thermal rate constants, i.e., low energies, and its ability to reproduce dynamical features was neither sought nor tested. Given that the H atom is very difficult to obtain in thermal conditions, hot H atoms were used in the experiment and QCT calculations.[3-5] Thus, collision energies in the range 16.1–46.1 kcal·mol^{-1} were used, as compared to the barrier height of 12.9 kcal·mol^{-1} obtained with the PES-2002 surface. A priori, these experimental and previous theoretical calculations were performed at energies much higher than those taken into account during the calibration of the PES. As our analytical surface was fitted to reproduce thermal conditions, any calculation based on this PES using these high energies would involve extrapolation to untested regions of the PES. Therefore, agreement between experiment and accurate theoretical calculations on PES-2002 would represent a predictive character of the PES.

In general, when comparing theoretical and experimental dynamics results (in this case the product scattering distributions), many factors are involved. First, of course, the quality and accuracy of the experimental data and, from the theoretical

point of view, the dynamics method used (classically, quasi-classically, or quantum mechanically based), and the accuracy of the potential energy surface. Thus, when theoretical results are compared with accurate experimental measurements, the dynamics method, as well as the PES, is being tested.

To elucidate whether the reasons for the discrepancies found in the angular distribution of the products at high energies are due to deficiencies of the surface or to limitations of the dynamics method used, we decided to compare QCT results to reduced dimensionality quantum scattering (QM) results on the PES-2002 surface, at collision energies ranging from low values, 16.1 kcal·mol^{-1}, to high values, 46.1 kcal·mol^{-1}. This paper is structured as follows: in section 2 we briefly outline the potential energy surface, the computational procedures in the QCT calculations, and the reduced-dimensionality QM scattering calculations. The calculated results are presented and compared with experimental results in section 3. Finally, in section 4 the conclusions are summarized.

2. Potential Energy Surface and Computational Details

2.1. Potential Energy Surface. In 2002, our group developed a new PES[1] for the $H + CH_4 \rightarrow H_2 + CH_3$ polyatomic reaction and its deuterated analogues, named PES-2002. The functional form was detailed elsewhere[1] and is implemented in a FORTRAN subroutine that can be found on our web pages.[11] In the calibration process we fitted some of the parameters of the analytical surface in order to reproduce the variation of the experimental thermal rate constants with temperature.

Given that there is a great variety of experimental information, this PES was widely tested,[1,12] reproducing the kinetics and dynamics behavior. Moreover, recent kinetics studies[7] from other laboratories lend support to this PES-2002 surface.

2.2. Quasiclassical Trajectory Calculations. Our (QCT) calculations[13-15] were carried out using a customized version of the VENUS96 code[16] that incorporates our analytical PES. The accuracy of the trajectories was checked by the conservation of total energy and total angular momentum. The integration step was 0.1 fs, with an initial separation between the H atom and the deuterated methane center of mass of 8.5 Å, and the vibrational and rotational energies were obtained from a 300 K distribution using the thermal sampling option in VENUS96. The reagent collision energies considered in the present work range from 16.1 to 46.1 kcal·mol^{-1} (0.7−2.0 eV).

First, the maximum value of the impact parameter, b_{max}, was computed by calculating batches of 10 000 trajectories at fixed values of the impact parameter, b, systematically increasing the value of b until no reactive trajectories were obtained. The b_{max} value thus obtained is 1.85 Å. Second, to compare experimental and theoretical QCT results, batches of 100 000 trajectories were calculated, where the impact parameter, b, was sampled from $b = b_{max}R^{1/2}$, where R is a random number in the interval [0, 1].

A serious drawback of the QCT method is its inability to properly treat the quantum mechanical zero-point energy (ZPE).[17-34] Many strategies have been proposed to approximately account for this quantum effect (see, for instance, refs 17−26, 31, and 32, and references therein), but no completely satisfactory procedure has emerged. Here, we employed a passive method,[26] consisting of discarding all reactive trajectories forming products with a total vibrational energy that is lower than the total harmonic ZPE of the products.

We perform a simple histogram binning of the trajectories that have not been discarded. Since we remove all trajectories with energies below the ZPE of the products, we consider the system to be in the vibrational ground-state bin whenever the

vibrational energy is lower than the energy of the first-excited vibrational state, while it is in the first excited state bin whenever the vibrational energy lies above the energy of the first excited state and below the energy of the second excited state. In other words, we take as vibrational quantum number the truncated integer of the real vibrational actions, instead of its nearest integer. However, the rotational number is taken, as usual, as the integer nearest to the computed rotational action. This approach will be denoted as histogram binning with simple ZPE correction (or HB-ZPE). Despite its simplicity, this method has been proven to work successfully for the similar $Cl + CH_4 \rightarrow HCl + CH_3$ reaction without compromising the statistical accuracy of the binning procedure.[35]

In the HB-ZPE procedure we only discard trajectories with a final vibrational energy below the total ZPE of the products, i.e., the sum of the ZPEs of HD and CD_3. Another more stringent criterion is the HB-DZPE (histogram binning with double ZPE correction) method, viz., discarding all trajectories that lead either to an HD with a vibrational energy below its harmonic ZPE or to a CD_3 with a vibrational energy below its harmonic ZPE. In this way we only count the reactive trajectories for which the nascent HD and CD_3 have vibrational energies above their respective harmonic ZPEs.

2.3. Quantum Scattering Calculations. It is still not possible to obtain detailed information like differential cross sections from a full-dimensional quantum dynamics calculation on a reaction involving six atoms. Therefore, reduced dimensionality quantum scattering calculations are employed here. We have chosen to use the so-called rotating line umbrella (RLU) model previously developed and extensively described by Yu and Nyman.[36-38] In the RLU model three degrees of freedom are treated explicitly quantum dynamically. For the $H + CD_4 \rightarrow HD + CD_3$ reaction, the forming H−D stretch vibration, the breaking C−D stretch vibration, and the umbrella type motion are treated explicitly.

The effect of the zero-point energies of the degrees of freedom not treated in the RLU model is usually considered by including that zero-point energy in the potential energy surface. This is particularly important if, for instance, thermal rate constants or other absolute values of, for example, reaction cross sections are sought. In the present application we are only interested in angular distributions, i.e., relative magnitudes of the differential cross sections. Further, we are mainly studying trends as a function of collision energy. Therefore, the zero-point energy corrections can be neglected, which have been estimated to otherwise raise the vibrationally adiabatic barrier height by 1−2 kcal·mol^{-1} and to lower the endoergicity by 2−3 kcal·mol^{-1} in the present application.

Since the full derivation of the RLU model has been given previously,[36-38] it will not be repeated here. We therefore here only give values of those parameters that are varied in order to achieve converged results under different conditions or for different reactions. Using the symbols and terminology of ref 38, the hyperradius was propagated from 3.0 to 20.0 b using about 400 sectors and an adiabatic basis of 100 functions. The potential cutoff was set to 4.5 eV. The z-range was set to [−1.9, 1.9] b and treated with 60 Fourier DVRs, and 160 DVRs were used for the hyperangle φ. The C−D bond length of the unreactive bonds was held fixed at 2.06925 b. All RLU results presented here are for ground-state reactants forming ground-state products.

3. Results and Discussion

Here we will first discuss the barrier height of the potential and then present the calculated angular distributions.

TABLE 1: Barrier Height (kcal·mol^{-1}) Computed Using Different Levels of Calculation

method	barrier	ref	method	barrier	ref
CCSD(T)/QZ	15.3	39	CCSD(T)/QZ	14.9	44, 45
QCISD(T)/TZ	15.5	40	B3LYP	9.4	4
CCSD(T)/TZ	15.5	41	Extrapol. IB	14.4	1
QCISD(T)	15.6	4	Extrapol. SAC	14.2	1
SRP	14.8	42	PES-2002	12.9	1
CCSD(T)/TZ	14.8	43			

3.1. Barrier Height. In Table 1 we have collected computed ab initio barrier heights for the H + CH$_4$ reaction. Kraka et al.[39] reported ab initio calculations at the coupled-cluster level with single and double excitations, with a perturbative treatment of triple excitations, using basis sets of quadruple-ζ quality [CCSD(T)/cc-pVQZ]. Dobbs and Dixon[40] used the quadratic configuration interaction method with a triple-ζ plus polarization basis set [QCISD(T)/TZ+2p+f]. Kurosaki and Takayanagi[41] performed ab initio calculations similar to those of Kraka et al. although, with a smaller basis set.

Recently, Pu and Truhlar[42] using specific reaction parameters gave a classical barrier height of 14.8 kcal·mol^{-1}. Zhang et al.[43] presented ab initio calculations using the partially spin restricted coupled-cluster method with an augmented triple-ζ basis [RCCSD(T)/aug-cc-pVTZ] obtaining a barrier height of 14.8 kcal·mol^{-1}. Wu et al.[44,45] have also recently performed RCCSD-(T) calculations but with a larger basis (aug-cc-pVQZ), obtaining a barrier height of 14.9 kcal·mol^{-1}. Finally, Camden et al.[4] performed ab initio QCISD(T)/6-311G(2d, 2p) and DFT calculations using the B3LYP functional and a modest basis set (6-31G(d,p)).

The B3LYP barrier is very low, 9.4 kcal·mol^{-1}, and would thus be expected to overestimate the rate constant. All ab initio calculations[4,39−45] predict potential energy barrier heights in a narrow range, 14.8−15.6 kcal·mol^{-1}, with the most accurate value of 14.8 ± 0.2 kcal·mol^{-1}. However, some of these authors[39−41] concluded that on the basis of the experimental values, the calculated classical barrier is too high by up to 2.0 kcal·mol^{-1}. This is a general problem in computational chemistry and arises from only partially introducing the correlation energy and using incomplete basis sets. With this in mind, we used this estimation to start fitting the potential energy surface, which at the end of the fitting procedure gave a value of 12.9 kcal·mol^{-1} (0.56 eV), which is used in the analytic surface PES-2002.

Let us analyze these values from a kinetic point of view. On one hand, PES-2002 reproduces the behavior of the experimental measurements of thermal rate constants and kinetic isotope effects, which are a very sensitive test of different features of the potential energy surface, such as barrier height and width, zero-point energy, and tunneling effect. Moreover, recently Zhao et al.[7] applied the quantum instanton approximation for thermal rate constants to this reaction using our PES-2002. They found that the quantum instanton rates show good agreement with available experimental data over the wide temperature range 200−2000 K. We however also note that Pu and Truhlar[42] with a barrier height of 14.8 kcal·mol^{-1} obtained good agreement with the available experimental rate constants from 250 to 2400 K using parametrized direct dynamics. On the other hand, Wu et al.[44,45] with the same barrier height, 14.8 kcal·mol^{-1}, and using accurate quantum dynamics calculations found that the theoretical results underestimate the experimental rate constants by a factor of 2−4 over the temperature range 250−500 K. Therefore, it is not only the barrier height, but also the shape of the potential, i.e., the drop toward reactants and products,
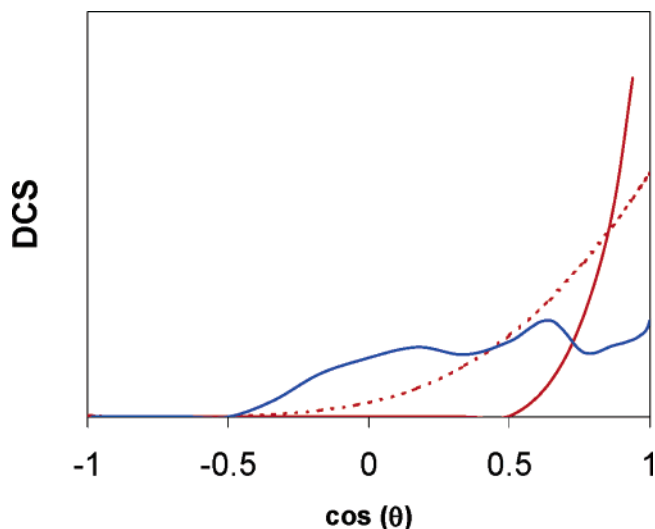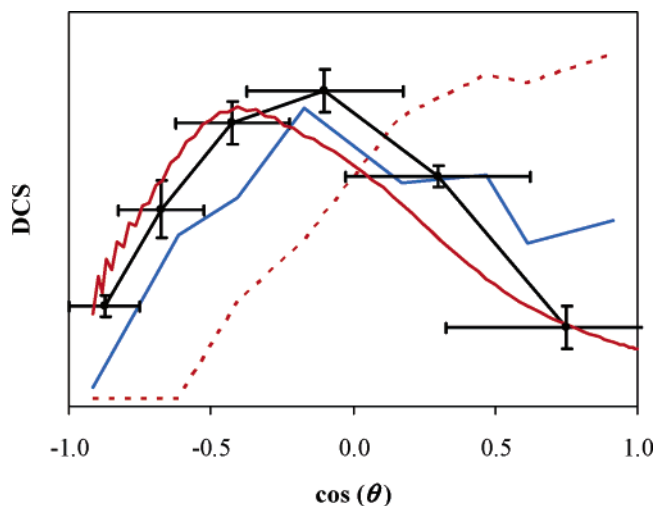

Figure 1. CD$_3$ product angular distribution (with respect to the H incident) for the H + CD$_4$ → HD + CD$_3$ reaction at 16.1 kcal·mol^{-1}: dashed line, QCT calculations on the PES-2002 surface; red line, QM calculations on the PES-2002 surface; blue line, QCT calculations on the B3LYP/6-31G(d,p) surface.[4] The scattering distributions are normalized so that the area is the same.

what will determinate the final result. This is especially true at low temperatures, where tunneling could make the rate constant more dependent on the shape of the PES than on the barrier height. Obviously, in a straight comparison between theory and experiment, the theoretical method used (for instance variational transition-state theory or quantum dynamics method) and the uncertainties associated with experiment must be taken into account.

Although the PES-2002 surface presents some flaws and it shows discrepancies with accurate ab initio barrier heights and experimental product scattering distributions when QCT calculations are used, the reasonable qualitative (and sometimes quantitative) reproduction of a wide variety of kinetic and dynamic experimental data allows us to believe that this analytical surface is well-balanced and most features are reasonably well described.

3.2. CD$_3$ Angular Distributions. *(A) Low Collision Energy (0.7 eV).* As our PES-2002 surface was calibrated to reproduce thermal rate constants, we shall begin by analyzing its behavior at the lowest energy studied here, viz. 16.1 kcal·mol^{-1} (0.7 eV). The angular scattering distributions of the CD$_3$ ($v' = 0$) product with respect to the incident H atom (obtained as the differential cross section, DCS) are plotted in Figure 1 for the QCT and QM calculations using our PES-2002. Both dynamics methods yield predominantly forward scattered CD$_3$, suggesting a rebound mechanism associated with low impact parameters. At this low energy, the QCT calculations on the B3LYP surface from Camden et al.[4] give a similar behavior, although somewhat more sideways scattered.

We will see below that increasing the collision energy tends to move the angular distribution from forward toward sideways/backward scattered. Therefore, the increased sideways scattering on the B3LYP surface could be attributed to its lower barrier height, since for a given collision energy the system will have more kinetic energy in the transition state region than when using the PES-2002 surface. Unfortunately, at this collision energy there is no experimental data for comparison, but the agreement between different dynamics methods (QM and QCT) and different surfaces (PES-2002 and B3LYP), together with the analogy to other similar gas-phase hydrogen abstraction
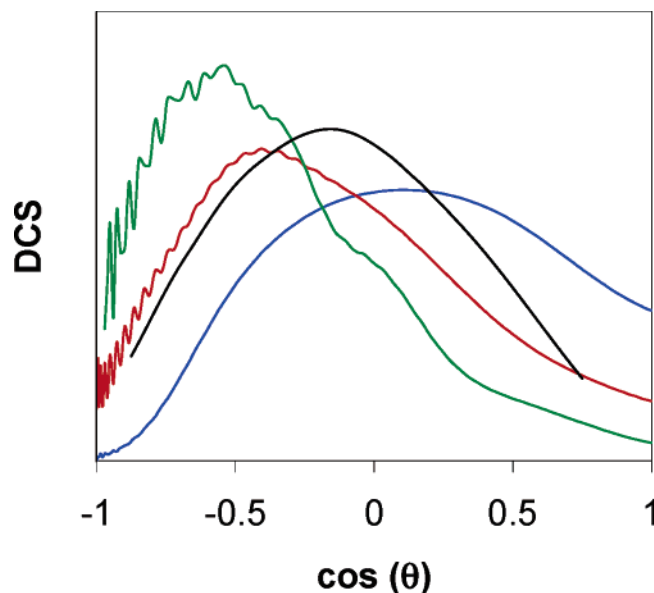
Figure 2. CD_3 product angular distribution for the $H + CD_4 \rightarrow HD + CD_3$ reaction at 27.8 kcal·mol^{-1}: black line, experimental results,[3–5] including error bars; blue line, QCT calculations on the B3LYP surface;[4,5] dashed line, QCT calculations on the PES-2002 surface; red line, QM calculations on the PES-2002 surface. The black and blue lines have been read directly from the original figures in the corresponding publications. The scattering distributions are normalized so that the area under the common regions is the same.

reactions (for instance, $Cl + CH_4$),[35] seems to confirm the mechanism at low energies and the capacity of the PES-2002 surface to reproduce dynamics features as sensitive as differential cross sections in the energy range for which it was calibrated.

(B) High Collision Energies (1.0−2.0 eV). Experimentally,[3–5] the scattering angular distribution of the CD_3 product was measured with respect to the incident H atom (obtained as the differential cross section, DCS) at two rather high collision energies, 1.2 and 1.95 ± 0.05 eV. It was found that the scattering is mainly sideways and backward, suggesting a stripping mechanism at large impact parameters. This behavior at high energies strongly contrasts with the behavior at low energies.

The angular scattering distributions of the CD_3 ($v' = 0$) product with respect to the H incidence (obtained as the differential cross section, DCS) are plotted in Figure 2 at 27.8 kcal·mol^{-1} for the QCT and QM calculations using our PES-2002, along with experimental results[3,4] and other QCT theoretical calculations[3,4] using a DFT surface [B3LYP/6-31G(d,p)] for comparison. When QCT calculations were performed on our PES-2002, predominantly forward scattered CD_3 was obtained, in strong contrast to the experimental evidence. Therefore, a priori, one would think that the discrepancy is due to the PES. However, when RLU quantum-mechanical scattering calculations are performed on our PES-2002, good agreement is obtained with the experimental data, taking into account the experimental error bars. A priori, this result may appear surprising, since the reduced dimensionality model is expected to work best at low energies, while at high energies quantum effects are less important and the collinear constraint of the model is less well founded. We do not have sufficient information here to conclude whether the agreement is fortuitous or is commonplace.

To shed more light on this question, in Figure 3 we analyze the DCSs of the CD_3 ($v' = 0$) products at several high energies, from 23.1 to 32.6 kcal·mol^{-1}, using reduced dimensionality QM calculations. The QM calculations reproduce the experimental tendency, i.e., the scattering moves backward with increased collision energy. Experimentally when the collision energy

Figure 3. CD_3 product angular distribution (with respect to the incident H) for the $H + CD_4 \rightarrow HD + CD_3$ reaction at different collision energies using reduced dimensionality QM calculations on the PES-2002 surface: black line, experimental values at 27.8 kcal·mol^{-1} from ref 3; blue, red and green lines are QM calculations at 23.0, 27.8, and 32.2 kcal·mol^{-1}, respectively. The scattering distributions are normalized so that the area under the common regions is the same.

increases, the CD_3 average scattering angle shifts from sideways ($\langle\cos\theta\rangle = -0.07 \pm 0.10$ at 27.8 kcal·mol^{-1}) to backward hemisphere ($\langle\cos\theta\rangle = -0.20 \pm 0.09$ at 45.0 kcal·mol^{-1}).

Finally, for the purpose of comparison, we analyze the role played by the ZPE in the QCT results. As was indicated in section 2, one of the more serious drawbacks of QCT calculations is the zero-point energy (ZPE) problem.

It has been pointed out that the binning procedure can affect the conclusions of QCT calculations significantly,[46] and in our earlier work,[35] different binning methods were checked. First, we tested the widely used Gaussian-weighted binning procedure,[46,47] which has the disadvantage that it effectively reduces the number of reactive trajectories (since some trajectories have an almost zero weight) and more trajectories are required to give the same statistical accuracy as the HB-ZPE method.[48] Second, we checked the influence of the way that reactive trajectories with vibrational energies below the ZPE of products are eliminated. We used the HB-ZPE and HB-DZPE methods. Finally, we compared these binning procedures with the simplest method, the widely used histogram binning with no ZPE correction whatsoever.

At all energies studied in this paper we obtained a similar picture to that of the QCT calculations with the HB-ZPE consideration, and they are not represented here. Therefore, for this polyatomic $H + CD_4$ reaction the discrepancy at high energies between QCT and experiment when using the PES-2002 is not due to whether the quantum mechanical ZPE effect is taken into account, since it seems to have a negligible effect on the scattering distributions.

4. Conclusions

In this work we have performed a dynamics study employing quasiclassical trajectory (QCT) and 3D-quantum-scattering (QM) calculations on a potential energy surface (PES-2002) previously developed in our group for the reaction of a hydrogen atom with methane and its deuterated analogues, focusing on the product angular distribution at several collision energies.

Analysis of the H + CD$_4$ → HD + CD$_3$ Reaction

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First, at low collision energies, 16.1 kcal·mol^{-1}, for which the PES-2002 surface was calibrated, QCT and QM calculations on this surface and QCT calculations on a DFT surface gave that the CD$_3$ products scatter forward. Unfortunately, there are no experimental data for comparison, but the good agreement between different dynamics methods on different surfaces confirms a rebound mechanism.

Second, at high energies on the PES-2002 surface, only when reduced dimensionality QM calculations are performed are the experimental product angular distributions reproduced.

Third, the PES-2002 surface in combination with QM calculations shows that the CD$_3$ angular distribution switches from forward to backward with increasing collision energy, indicating a slow change of the dominant mechanism from a rebound mechanism at low energy to backward scattering at high energy, reproducing the experimental tendency.

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