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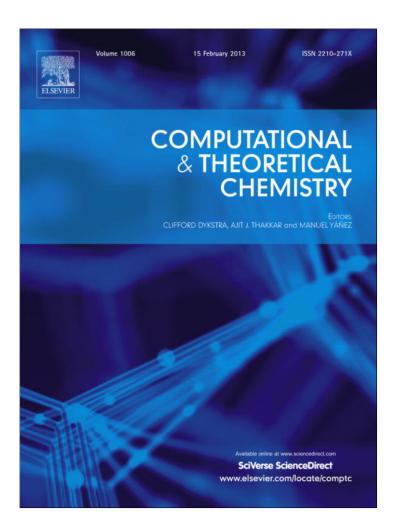
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The abstraction reaction of H and C-H stretch excited CHD₃: A QCT study on an ab initio based potential energy surface

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ABSTRACT

Using a recent ab initio based potential energy surface, PES-2009, quasi-classical trajectory calculations were performed to analyse the effects of the C–H stretch excitation on the reactivity and dynamics of the H + CHD $_3$ abstraction reaction at a collision energy of 1.53 eV. Firstly, we found that the C–H stretch mode excitation has little influence on the product rotational distributions and on the scattering distribution for both channels. However, it has significant influence on the product energy distribution for the CHD $_2$ + HD channel, indicating that the reaction shows mode selectivity, reproducing the experimental evidence. Finally, excitation of the C–H stretch by one quantum increases the reactivity of the vibrational ground-state for both channels reproducing the experimental evidence, although for the H-abstraction channel we report an enhancement of reactivity somewhat lower than other theoretical results.

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1. Introduction

The abstraction reaction of H and CHD_3 can evolve along two channels, H- and D-abstraction:

$$\begin{array}{c} H+CHD_3 \rightarrow CD_3 + H_2 \\ \rightarrow CHD_2 + HD \end{array}$$

To the best of our knowledge, only one experimental work, that by Zare's group. [1] has been carried out to study the effects of the C–H stretch vibrational excitation on the reactivity of this reaction. Those authors reported firstly that due to experimental difficulties, no clear preference for the H- or D-abstraction channel can be determined for the ground-state reaction, secondly that the C–H stretch excitation enhances the reactivity for both channels (no quantitative estimates were provided), and thirdly that the C–H stretch excitation is maintained in the CHD₂ product, which suggests mode selectivity.

Recently, three theoretical studies [2–4] have appeared to explain Zare's experiment. However, in comparing theory with experiment, one is simultaneously evaluating two approximations: the potential energy surface (PES), and the dynamical method (classical, quasi-classical, or quantum). Xie and Bowman [2] performed quasi-classical trajectory (QCT) calculations for the title reaction on the ZBB3 surface [5], which is obtained by a polynomial fitting of roughly 20,000 ab initio energies obtained with the

coupled cluster method, CCSD(T), with an aug-cc-pVTZ basis. At 1.53 eV, they found the C-H stretch vibrational excitation enhances the reactivity for both channels - by factors of 13.5 and 1.2 for the H- and D-abstraction channels, respectively. One year later, our group [3] performed QCT calculations on the PES-2002 surface [6], obtaining enhancements of 3.2 and 2.3 for these same two channels, respectively. Recently, Zhang's group [4] performed reduced dimensionality quantum (QM) calculations on the ZFWCZ surface [7], which uses a modified Shepard interpolation method based on CCSD(T)/aug-cc-pVTZ energies and CCSD(T)/ 6-311++G(3df,2pd) gradients. Those authors only studied the H-abstraction channel, finding that at 1.53 eV the C-H stretch vibrational excitation enhances the reactivity by a factor of 13.2, agreeing with Xie and Bowman's result, with both being greater than the enhancement found with the PES-2002 surface. Zhang et al. concluded that the PES-2002 surface is relatively less accurate.

We agree with that conclusion. Unfortunately, however, no comparison was made with our recent, and more accurate, PES-2009 surface [8]. Indeed, the major limitations of the old PES-2002 surface were, first, its semiempirical character (i.e., it was fitted to theoretical and experimental data), and second, the barrier height was too low, 12.9 kcal mol⁻¹, as compared with recent high-level ab initio calculations, 14.8–15.1 kcal mol⁻¹. Therefore, to correct the main deficiencies of the earlier PES-2002 surface, in 2009 we reported [8] the construction of a new analytical surface, PES-2009, which is fitted exclusively to very high-level ab initio calculations, and presents a barrier height of 15.0 kcal mol⁻¹. This surface basically consists of four London–Eyring–Polanyi (LEP) stretching terms, augmented by

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out-of-plane bending and valence bending terms and it was constructed by a multi-beginning least-squares optimisation of the parameters to CCSD(T)/cc-pVTZ energies and derivatives. The PES-2009 was subjected to great variety of tests [8–10], with both kinetics and dynamics (QCT and QM) results compared with the experimental information available for the H+CH4 reaction and its isotopomers. In general, PES-2009 reproduced the wide variety of experimental properties, which lent confidence to the surface. However, when comparing the excitation function for the three most recent surfaces, ZBB3 [5], ZFWCZ [7], and PES-2009 [8], Zhang et al. [7] found that for the H + CH₄ reaction at collision energies up to 1.0 eV the three surfaces show satisfactory agreement, while at higher collision energies PES-2009 overestimates this dynamical property. Nevertheless, this is not a serious problem in the present study, because we are analysing the effect of the C-H stretch vibrational excitation on the reactivity at 1.53 eV, and can reasonably assume that the overestimate will be compensated between the numerator (C-H stretch excited) and the denominator (C-H stretch

Therefore, in the current work using the PES-2009 surface we analyse the effect of the C–H stretch excitation on the title reaction, and we compare the results with the other theoretical studies [2,4].

2. Results and discussion

2.1. Enhancement of the reactivity by vibrational excitation

As a first test of the quality of the surface, we compared the enhancement of the reactivity when the antisymmetric C-H stretch mode is excited in the H + CH₄ reaction for which experimental data are available, which is not the case for the title reaction. Thus, at 1.52 eV, Zare's group [11] reported an enhancement of 3 ± 1.5. Using QCT calculations (i.e., the same dynamical method) the ZBB3 [12] and PES-2009 surfaces give similar results, 2.3 and 1.9, respectively, consistent with the experimental evidence. In sum, since these two surfaces were constructed using two totally different methods, the good agreement for this dynamical property at high energies, 1.52 eV, indicates firstly that they have a similar level of accuracy for studying the vibrational excitation, and secondly it confirms our hypothesis of a compensation in the overestimation of the C-H stretch-excited and ground-state reactivity. Note that the old PES-2002 surface predicts an enhancement of only 1.2, underestimating the experimental data.

Next, we analyse the title reaction, $H + CHD_3(\nu = 0, 1)$, whose potential energy surface is obviously the same as in the perprotio analogue. This reaction has been studied experimentally [1] and theoretically [2–4], although unlike the $H + CH_4$ reaction, the

Table 1 Reaction-cross sections ($bohr^2$) for the H- and D-abstraction channels of the H+ CHD $_3$ reaction at a collision energy of 1.53 eV, for the ground and the C-H stretch excited states.

	QCT/ ZBB3 ^a	QM/ ZFWCZ ^b	QCT/PES- 2009 ^c	QCT/PES- 2002 ^d
H-channel				
$\sigma(v=0)$	0.13	0.096	0.24	0.29
$\sigma(v=1)$	1.75	1.27	1.74	0.93
$\sigma(v=1)/\sigma(v=0)$	13.5	13.2	7.2	3.2
D-channel				
$\sigma(v=0)$	0.28	_	0.35	0.57
$\sigma(v=1)$	0.34	-	0.43	1.32
$\sigma(v=1)/\sigma(v=0)$	1.2	_	1.2	2.3

^a Ref. [2].

experimental information is only qualitative due to experimental difficulties. Table 1 compares the reaction cross sections at a collision energy of 1.53 eV from the present work (QCT/PES-2009) with Bowman's results [2] (QCT/ZBB3) and Zhang's results [4] (reduceddimensionality QM/ZFWCZ) for the H- and D-abstraction channels where available. The QCT/PES-2002 results [3] are also included for comparison. Firstly, one observes that, due to the issues commented on above, the results with the old PES-2002 surface are very far from the more recent values [2,4], and that the PES-2009 surface leads to a noticeable improvement. Secondly, the reaction cross section ratio of the C-H stretch ground-state D- and Habstraction channels is 1.4, which agrees well with the theoretical QCT/ZBB3 [2] results (2.1), although the experimental results [1] seem to suggest a lower ratio, since they observe "no clear preference for the H- or D-abstraction products". Thirdly, for the Dabstraction channel the QCT results on different surfaces, ZBB3 and PES-2009, give the same enhancement of reactivity with the C-H stretch excited mode – 1.2. Unfortunately, neither the reduced dimensionality QM/ZFWCZ results nor experimental data are available for comparison. Finally, greater differences between the surfaces are found in the H-abstraction channel. While Bowman et al. [2] and Zhang et al. [4] reported an enhancement factor of about 13, we obtain a factor of 7.2.

To analyse whether this reaction (ground state and C–H vibrationally excited) presents intramolecular vibrational redistribution (IVR) in the entry channel, we computed the average energy on each normal mode to obtain information on the temporal evolution of this energy along the first steps of the reaction. In both the CHD₃ ground-state and with the C–H stretch mode excited by one quantum, our classical trajectory calculations show that no transfer of energy is observed in the first steps for this reaction and we conclude that the intramolecular vibrational redistribution will be small or negligible, in accordance with Camden et al.'s suggestion based on experiment [1]. These results with the PES-2009 surface agree with those obtained by our group with the PES-2002 surface [13].

In sum, for the C–H stretch excitation in the $\rm H + CH_4$ reaction the PES-2009 surface reproduces both the experimental data and other theoretical results which used different PESs. Moreover, for the title reaction, it reproduces the qualitative experimental evidence that the C–H stretch excitation enhances the reactivity for both channels, and agrees with recent theoretical calculations (especially for the D-abstraction channel).

To explain the discrepancy between our results and those from Xie and Bowman [2] for the H-abstraction channel, given that no quantitative experimental data on the enhancement factor is available, we will resort to the results from the similar $Cl + CHD_3(v = 0,1)$ reaction. For the latter, a severe theory/experiment comparison [14,15] has been performed, which could shed some light to the present reaction. When the hydrogen-abstraction state-to-state reaction $Cl + CHD_3(v = 1) \rightarrow HCl + CD_3(v = 0)$ was analysed, both the crossed-beam experiment [14] and the QCT calculations [15] at a collision energy of 8 kcal $\overline{\text{mol}}^{-1}$ showed a good agreement. However, when all the vibrational excited CD₃ products are included (as it is also the case for the title reaction), while theoretical results showed an enhancement factor v = 1/v = 0 of about 3, the experimental finding [16] was 1.4, i.e., theory overestimates experiment by a factor of two. Kopin Liu noted [17] that this disagreement could be due to differences in the CD₃ product vibrational distribution. So, while experimentally Liu et al. [16] reported that $CD_3(v=0)$ accounts for about 63% of all the CD_3 product, theoretical results [15] predict that only about 30% of the CD₃ product is in its ground state, i.e., theory predicts about twice the CD₃ vibrational excitation observed experimentally.

In the case of the H + CHD₃(v = 1) \rightarrow CD₃ + H₂ reaction, we have performed a similar analysis, finding that while the PES-2009

^b Ref. [4].

^c This work.

d Ref. [3].

surface presents a fraction of energy in vibration of 6% for the CD₃ product, the ZBB3 surface presents a value of 10%, i.e., about twice that obtained with our surface. If we assume that the previous analysis for the $Cl + CHD_3(v = 0, 1)$ reaction on the influence of the CD₃ vibrational population can also be applied here, we can presume that the discrepancies between the PES-2009 and ZBB3 enhancement factors for the title reaction are related to the different vibrational excitation of the CD3 product. If we also assume that the overestimation of the product vibrational excitation observed in the Cl + CHD₃(v = 1) reaction will also be found in the $H + CHD_3(v = 1)$ reaction given that both surfaces are constructed in a similar fashion, then it is also possible that our results be closer than those from the ZBB3 surface to a future quantitative experiment that includes all the CD3 vibrational states. Note that for the D-abstraction channel (i.e., for the CHD₂ product), PES-2009 and ZBB3 give a similar fraction of energy in product's vibration, 14% and 15% respectively, which agrees with the similar enhancement factor found for this path with both surfaces, 1.2, thus reinforcing the earlier argument. Therefore, future experimental work is needed to elucidate whether our conclusions on the disagreement between the results for the hydrogen channel are correct. Unfortunately, a similar analysis cannot be performed on the ZFWCZ surface to shed some more light on this subject.

2.2. Product energy partition

The QCT results for the ground-state and vibrationally excited $CHD_3(\nu)$ reactant at a collision energy of 1.53 eV are listed in Table 2 for the two channels, hydrogen channel $(CD_3 + H_2)$ and deuterium channel $(CHD_2 + HD)$. Unfortunately, there is no experimental data for comparison, but we observe that when the C–H stretch mode is excited by one quantum the vibrational excitation of the product increases by a factor of 2 for the hydrogen abstraction and 7 for the deuterium abstraction with respect to the ground-state. This behaviour agrees qualitatively with the experimental results of Camden et al. [1], indicating that the C–H stretch mode preserves its character along the reaction.

2.3. Rotational distributions of the bimolecular products, H₂ and HD

As we mentioned above, in our calculations at this collision energy the CD_3 and CD_2H products mostly appeared in their respective vibrational ground state, v=0. The QCT vibrationally resolved $H_2/HD(v=0)$ rotational distributions are plotted in Fig. 1. In general, the rotational distributions for the HD product (deuterium abstraction) are slightly hotter than for H_2 (hydrogen abstraction), and C–H vibrational excitation does not change this tendency. Unfortunately, there are no experimental values for comparison, but these results agree with the only available theoretical results [2].

Table 2Product^b vibrational distribution (in percentages)^a for the H- and D-abstraction channels of the H+ CHD₃ reaction at a collision energy of 1.53 eV, for the ground and the C-H stretch excited states.

	f_V (CD ₃ or CHD ₂)	f_R (CD ₃ or CHD ₂)	f_V (H ₂ or HD)	f_R (H ₂ or HD)	f_T
H-channel ν = 0 ν = 1	3 6	2 1	2 2	18 16	75 75
D-channel v = 0 v = 1	2 14	2 3	7 10	18 15	71 58

^a Calculated maximum error: ±1.

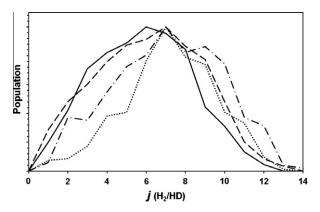


Fig. 1. Rotational populations for the diatomic product of the H + CHD $_3$ reaction at a collision energy of 1.53 eV. The distributions are scaled to the same maximum value. The H-abstraction, that leads to the CD $_3$ + H $_2$ products, is shown as a solid line when the reactants are in their vibrational ground state and as a dashed line when the reactants are in the first excited vibrational state. The D-abstraction, that leads to the CHD $_2$ + HD products, is shown as a dotted line when the reactants are in their vibrational ground state and as a dotted-dashed line when the reactants are in the first excited vibrational state.

2.4. Product angular distribution

The product angular distribution is doubtless one of the most sensitive dynamics properties with which to test the quality of the surface. The QCT angular scattering distribution of the CD₃ and CD₂H products with respect to the incident atom (obtained as the differential cross section, DCS, which was fitted using the Legendre moment method [18]) is plotted in Fig. 2. However, in an earlier study on the Cl + CH₄ reaction [19] we observed that the product rotational distribution obtained with QCT calculations greatly influences the angular scattering distribution, and only when the lowest rotational numbers are considered the experimental distribution is reproduced. Therefore, in the present study we assume this behaviour, and the product scattering distribution is analysed using only trajectories with the lowest j values $(0 \le j \le 2)$.

While the H-channel presents a clear backward tendency, the D-channel presents in addition sideways scattering, and this tendency is independent of whether or not the CHD₃ reactant is vibrationally excited. Our results agree qualitatively with the only available theoretical results [8], although in our study the back-

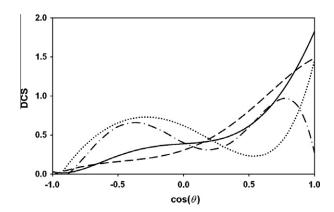


Fig. 2. Product angular distribution for the $H + CHD_3$ reaction at a collision energy of 1.53 eV for both channels. The H-abstraction, that leads to the $CD_3 + H_2$ products, is shown as a solid line when the reactants are in their vibrational ground state and as a dashed line when the reactants are in the first excited vibrational state. The D-abstraction, that leads to the $CHD_2 + HD$ products, is shown as a dotted line when the reactants are in their vibrational ground state and as a dotted-dashed line when the reactants are in the first excited vibrational state.

^b Products depend on the channel. fV, fR, and fT stand for vibrational, rotational, and translational contributions, respectively.

ward tendencies are more pronounced. Unfortunately, there is no experimental information on the title reaction for comparison.

3. Conclusions

Using QCT calculations on an analytical potential energy surface, PES-2009, which is based exclusively on high-level ab initio calculations, in the present work we have analysed the role of the C-H stretching vibrational excitation on the dynamics of the H + CHD₃ reaction. We found that the diatomic product rotational distributions and the product angular distributions are insensitive to this C-H excitation, and that when the C-H stretch mode is excited by one quantum the C-H stretch excitation is maintained in the CHD₂ product (D-abstraction channel), which suggests mode selectivity, in agreement with experiment. Finally, the C–H stretch excitation enhances the reactivity with respect to the vibrational ground-state for both channels, and agrees with recent theoretical calculations (especially for the D-abstraction channel). However, further theoretical and experimental (which nowadays are only qualitative) studies are needed to understand the disagreement for the H-abstraction channel.

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