

Mode Selectivity for a “Central” Barrier Reaction: Eight-Dimensional Quantum Studies of the $O(^3P) + CH_4 \rightarrow OH + CH_3$ Reaction on an Ab Initio Potential Energy Surface

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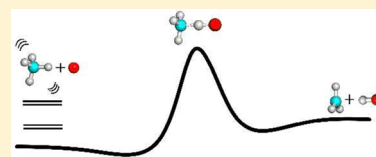
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Supporting Information

ABSTRACT: The dynamics of a combustion reaction, namely, $O(^3P) + CH_4 \rightarrow OH + CH_3$, is investigated with an eight-dimensional quantum model that includes representatives of all vibrational modes of CH_4 and with a full-dimensional quasi-classical trajectory (QCT) method. The calculated excitation functions for the ground vibrational state CH_4 agree well with experiment. Both quantum and QCT results suggest that excitation of the stretching modes of CH_4 enhances the reaction, while the bending and umbrella modes have a smaller impact on reactivity, again consistent with experimental findings. However, none of the vibrational excitations has comparable efficiency in promoting the reaction as translational energy.

SECTION: Kinetics and Dynamics



Polanyi's rules have been a guiding light for understanding mode and bond selectivity in gas-phase bimolecular reactions. On the basis of observations in atom–diatom reactions, Polanyi summarized in 1972 the role played by various forms of energy in promoting reactivity.¹ For a reaction with an “early” (reactant-like) barrier, for example, translational energy is more effective than vibrational energy. On the other hand, vibrational energy has higher efficacy in promoting reaction with a “late” (product-like) barrier. The extension of the Polanyi's rules to reactions involving polyatomic molecules is not straightforward. Indeed, the capacity of various reactant vibrational modes for promoting reactivity is likely to be different. Nevertheless, these rules have been largely upheld for such reactive systems,^{2–7} but exceptions have been reported recently for the $F/Cl + CHD_3$ reactions.^{8,9} The latter have been attributed to prereaction van der Waals complexes along the reaction path,^{10,11} although the latest quantum dynamical study on the $Cl + CHD_3$ reaction suggested that the violation of the Polanyi's rules is restricted to a small energy range.¹² However, most previous systems have either early or late barriers, and few have a “central” barrier, which is neither reactant-like nor product-like. In order to establish general rules of thumb for these complicated reactions, it is important to investigate such reactions.

The $O(^3P) + CH_4 \rightarrow OH + CH_3$ reaction, which represents an important initial step in hydrocarbon combustion,¹³ provides an ideal platform for studying reactions with a central

barrier. Its near thermoneutrality ($\Delta H^0 = 2.48$ kcal/mol)¹⁴ leads to a transition state that is neither reactant-like nor product-like. At the saddle point, approximately 14 kcal/mol above the $O(^3P) + CH_4$ potential minimum, the breaking C–H and forming O–H bonds are stretched by 0.2 Å relative to the corresponding bond lengths in the reactant CH_4 and the product OH .¹⁵ As a result, it presents a unique middle point between the much studied F and $Cl + CH_4$ reactions,^{11,16} which have clear early and late barriers, respectively. In some sense, the title reaction is similar to the much studied $H + CH_4 \rightarrow H_2 + CH_3$ reaction,^{17–21} although the former is of the heavy–light–heavy (HLH) type with a much smaller skew angle.

The title reaction has been extensively investigated experimentally.^{22–28} Recent molecular beam experiments have measured the excitation function,^{25,28} internal state distributions of both the CH_3 and OH products,^{23,24,27} as well as differential cross sections.^{25–28} The experimental data are consistent with a simple abstraction mechanism. In particular, the excitation function of the $O + CH_4$ reaction has a threshold of ~ 8 kcal/mol and increases monotonically with the collision energy.²⁸ In addition, the excitation of the C–H vibration in CHD_3 results in significantly enhanced reactivity for the $OH +$

Received: October 26, 2012

Accepted: December 4, 2012

Published: December 4, 2012

CD₃ channel.²⁵ Interestingly, however, bending excitations (ν_2 and ν_4) in CD₄ slightly inhibit the reaction.²⁶

Theoretical studies of the reaction dynamics have been carried out using quasi-classical trajectory (QCT) methods,^{29–32} as well as reduced-dimensional quantum mechanical (QM) models up to seven dimensions (7D).^{17,33–38} In addition, a full-dimensional multiconfiguration time-dependent Hartree (MCTDH) calculation of the thermal rate constant has been reported.³⁹ However, these studies have all used semiempirical (some reduced-dimensional ab initio as well) potential energy surfaces (PESs)^{40,41} or semiempirical direct dynamics methods.²⁹ Recently, the first ab initio full-dimensional global PES has been developed by fitting a large number of accurate energy points,¹⁵ using a permutationally invariant polynomial method.⁴² The minimum-energy path for the reaction is depicted in Figure 1, with the geometries and

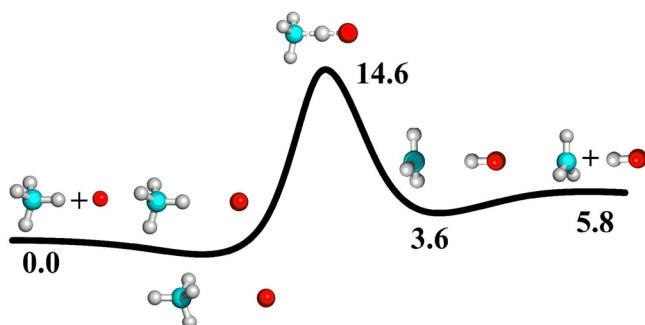


Figure 1. Schematic plot of the PES along the reaction path with the geometries and energies (in kcal/mol) of the stationary points.

energies of stationary points. QCT studies of the O + CHD₃ reaction have been reported on this PES by two of us,¹⁵ and the results are in good accord with the recent experiment by Wang and Liu.²⁵ However, due to possible large quantum effects (which are indeed found), such as tunneling and zero-point energy (ZPE), in this system, it is highly desirable to understand the reaction dynamics with a QM model. In this Letter, we report the first eight-dimensional (8D) QM reactive scattering calculations for this prototypical reaction on the new PES, along with full-dimensional QCT results.

The 8D QM model is similar to the pioneering work of Palma and Clary,³⁵ in which the C_{3v} symmetry of the CZ₃ moiety in the X + YCZ₃ → XY + CZ₃ reaction is maintained while other degrees of freedom are explicitly treated. This 8D model represents a realistic reduced-dimensional model for such a reaction because it includes representatives of all CH₄ vibrational modes, particularly the asymmetric stretching mode ignored in the 7D model.³⁸ A coordinate transform was recently introduced to render the CH₄ vibrational Hamiltonian more physically transparent and easier to discretize.⁴³ This new 8D Hamiltonian has already been applied to the H + CH₄ reaction with good agreement with experiment.⁴³ The QM calculations reported here were carried out with $J = 0$, and the integral cross section (ICS) was computed using the J -shifting approximation.⁴⁴ In addition, the QM ICSs have been multiplied by a factor of 4 to account for all possible reaction channels. The details of the QM model and parameters used in the calculations are given in the Supporting Information (SI). On the other hand, the QCT calculations are standard, as described in our earlier work.¹⁵ Neither ZPE correction nor product state resolution is imposed as a detailed analysis of the

state-to-state QCT calculations will be reported in a subsequent publication. All ICSs are multiplied by the electronic factor of 2/3 to account for the spin–orbit degeneracy of the reactants.

Figure 2 compares the calculated and measured ICSs for the ground vibrational state of CH₄, and the agreement is excellent.

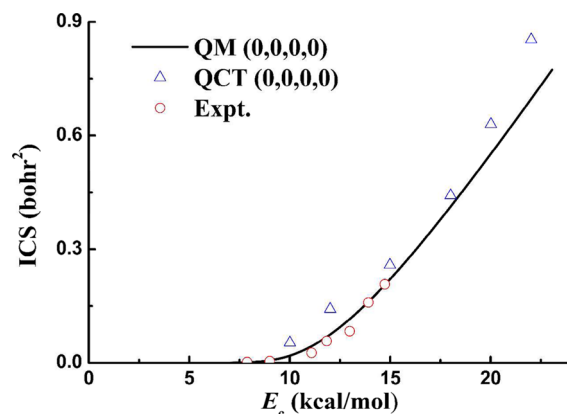


Figure 2. Comparison of the QM and QCT ICS for the ground vibrational state of CH₄ (0,0,0,0) with the experimental data, which was normalized with the QM values at 14.7 kcal/mol. The theoretical cross sections include the 2/3 degeneracy factor. Note that the experimental excitation function was derived from data in the CH₃($\nu = 0$) channel, which represents the dominant products.²⁸

The QM ICS correctly predicted a reaction threshold of ~8 kcal/mol as well as the unique concave-up energy dependence observed in the experiment.²⁸ The reaction threshold is significantly lower than the classical and ZPE-corrected barriers (14 and 11 kcal/mol), signifying substantial tunneling. The QCT results are also in good agreement with the experiment, although slightly larger than the QM counterparts, which might be due to a number of factors such as the difference in dimensionality. The excellent overall agreement with experiment confirms again the accuracy of the PES.

To examine mode selectivity, the ICSs for several vibrational excited states of CH₄ are plotted in Figure 3 in both collision and total energy. For the latter, the QM vibrational frequencies of CH₄ are from our reduced-dimensional model, which are compared in the SI with those in the full-dimensional model, while the normal-mode frequencies on the PES were used in the QCT results. The vibrational state of CH₄ is denoted by (n_1, n_2, n_3, n_4) where the quantum numbers are for the symmetric stretching, bending, asymmetric stretching, and umbrella modes, respectively. As shown in the upper panel of the figure, both QM and QCT results indicate that excitations of both the symmetric and asymmetric stretching modes, (1,0,0,0) and (0,0,1,0), clearly enhance reactivity, with the former having higher efficacy. This observation is consistent with earlier reduced-dimensional QM models^{17,33,34,38} and experimental studies of the X + CH₄ reactions (X = F, Cl).^{4,5} Unfortunately, there has not been any experimental study on stretch excited CH₄ with O(³P), although C–H vibrationally excited CHD₃ has been investigated.²⁵ The enhancement observed here is consistent with that experiment²⁵ and subsequent theory.¹⁵ Interestingly, excitations in these two stretching modes do not enhance the reaction more than translational energy, as shown by the lower panel of Figure 3, at least in energies less than 23 kcal/mol.

As shown in Figure 3, our QM results indicate that the excitation in the CH₄ bend (0,1,0,0) promotes the reaction

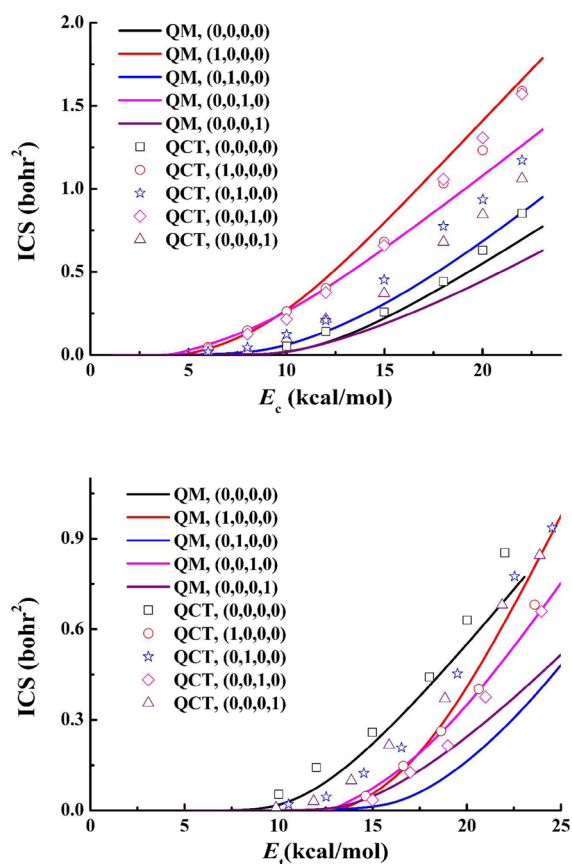


Figure 3. QM and QCT ICSs for the ground and various excited vibrational states of CH_4 , plotted in collision energy (upper panel) and total energy relative to $\text{O}(^3\text{P}) + \text{CH}_4$ (0,0,0,0) (lower panel). The ICSs include the 2/3 degeneracy factor.

slightly, but the umbrella (0,0,0,1) excitation inhibits the reaction. These results are consistent with the experimental observation of Zhang and Liu, who reported slight inhibition of reactivity with one quanta in either of the two modes in CD_4 .²⁶ It should however be noted that not all CD_3 product channels were probed in the experiment; therefore, there might be some uncertainty in the data. On the other hand, both modes were found in the QCT model to promote the reaction, but to a lesser extent than the stretching modes. The QM–QCT discrepancy may stem from several factors. As discussed in the SI, for example, the bending mode is not well described by the 8D QM model as it destroys the C_{3v} symmetry. As a result, the bending frequency in the 8D model is significantly higher than that in full dimension. Nonetheless, the agreement with experiment is much better than earlier reduced-dimensional QM models, which predicted significant enhancement by exciting the bending and umbrella modes of CH_4 .^{17,33–35,38} The improved agreement with experiment can be presumably attributed to the accuracy of the PES.

With the theoretical results, we can now comment on the mode selectivity in this reaction. A naïve application of the Polanyi's rules would predict that the vibrational and translational energies should have roughly the same efficacy in promoting this reaction with a central barrier. This is obviously not the case here. To understand the mode selectivity in this reaction, one needs to think in terms of the coupling between vibrational modes and the reaction coordinate.⁴⁵ Our results above clearly indicated that both stretching modes are

strongly coupled with the reaction coordinate near the transition state, which is essentially the asymmetric stretch of the transferring H between C and O in this HLH system. It is well-known that in a vibrational adiabatic model, the frequency of the CH_4 symmetric stretching mode is significantly lowered when CH_4 is approached by a reactant such as Cl^{46} or $\text{O}^{41,47}$ as the vibration is coupled into the reaction coordinate. Thus, the adiabatic barrier associated with the symmetric stretching excited state is lower than that of the ground vibrational state, explaining its strong capacity to enhance the reactivity. On the other hand, the enhancement of the asymmetric stretching mode is more subtle as it is associated with a spectator mode in the vibrational adiabatic model.^{41,47} It has, however, been argued that this mode couples to other reactive modes nonadiabatically via Coriolis terms.⁴⁸ Our results also suggest that the influence of both the bending and umbrella modes on the reactivity is relatively small, suggesting that their couplings to the reaction coordinate are weak. This observation is in sharp contrast to an earlier reaction path analysis, which predicted strong enhancement of reactivity for umbrella excited CH_4 due to its strong coupling with the reaction coordinate.⁴¹ This failure underscores the complexity in the multidimensional dynamics.

In summary, we have presented 8D QM and full-dimensional QCT studies of the title reaction on an ab initio PES. The reasonably good agreement with available experimental results confirms the accuracy of the PES. In addition, the mode selectivity of the reaction has been investigated. Our results indicate that excitations in the stretching modes of CH_4 significantly enhance the reaction, with the symmetric stretch having a higher efficacy. On the other hand, excitations in the bending and umbrella modes have a smaller impact. Interestingly, none of the vibrational excitations are as efficient as translational energy in promoting the reaction. These results, along with recent observations on the $\text{F}/\text{Cl} + \text{CHD}_3$ reactions,^{8,9} suggest that conventional wisdom symbolized by the venerable Polanyi's rules may be in need of generalization. Theoretical studies of the reaction dynamics of these prototypical reactions will play an important role in shaping up our deeper understanding of bimolecular reactions with polyatomic molecules.

■ ASSOCIATED CONTENT

📄 Supporting Information

Detailed theory and additional results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

R.L. and M.Y. were supported by National Science Foundation of China (Projects 20921004, 21073229, and 20833007), G.C. by the Scientific Research Fund of Hungary (OTKA, NK83583) and the Bolyai Research Fellowship of the Hungarian Academy of Sciences, J.M.B. by the Department of Energy (DE-FG02-97ER14782), and J.L. and H.G. by the

Department of Energy (DE-FG02-05ER15694 to H.G.). We thank Prof. Kopin Liu for some stimulating discussions.

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