

Reactant Vibrational Excitations Are More Effective than Translational Energy in Promoting an Early-Barrier Reaction $F + H_2O \rightarrow HF + OH$

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S Supporting Information

ABSTRACT: The exothermic $F + H_2O \rightarrow HF + OH$ reaction has a decidedly “early” or “reactant-like” barrier. According to a naïve interpretation of the Polanyi’s rules, translational energy would be more effective than vibrational energy in promoting such reactions. However, we demonstrate here using both quasi-classical trajectory and full-dimensional quantum wave packet methods on an accurate global potential energy surface that excitations in the H_2O vibrational degrees of freedom have higher efficacy in enhancing the reactivity of the title reaction than the same amount of translational energy, thus providing a counter-example to Polanyi’s rules. This enhancement of reactivity is analyzed using a vibrational adiabatic model, which sheds light on the surprising mode selectivity in this reaction.

The essence of chemistry is to convert reactants into products by utilizing available energies in various degrees of freedom to overcome the reaction barrier. However, it is well established that not all forms of energy are equal in promoting reactivity of bimolecular reactions, particularly those with an activated barrier. The different efficacies in promoting a reaction underscore the nonstatistical nature of many reactions and offer opportunities for controlling chemical processes by depositing energy into different modes.^{1,2} In 1972, Polanyi summarized succinctly the observations for atoms-diatom reactions in what are now called the Polanyi’s rules:³ For a reaction with an “early” (reactant-like) barrier, translational energy is more effective than vibrational energy in surmounting the barrier; and the reverse is true for a reaction with a “late” (product-like) barrier. These rules make intuitive sense and have been extensively tested in many systems and in most cases the predictions were upheld.

The extension of these rules to reactions involving polyatomic reactant molecules is not straightforward, as there are more than one vibrational mode in the reactants. While many observations have provided evidence in support of these rules,^{4–10} several recent experiments have offered examples with surprising departures from expectations. For instance, Liu and co-workers reported that the excitation of the C–H vibration in CHD_3 does not promote its reaction with F to form $HF + CD_3$,¹¹ which has an early barrier, but actually inhibits it. On the other hand, the same group also found that exciting the C–H vibration in CHD_3 was no more effective than the translational energy in promoting its reaction with

Cl,¹² which has a late barrier. Although reproduced by full-dimensional quasi-classical trajectory (QCT) calculations of Czako and Bowman,^{13,14} more recent quantum mechanical (QM) calculations found the violation of the Polanyi’s rules in the Cl + CHD_3 reaction is restricted to a small energy range.¹⁵ More importantly, it is still unclear if such surprising behaviors are exceptions or the rules. In either case, it is highly desirable to search for a more general paradigm to understand mode selectivity in chemical reactions, which requires detailed studies of other polyatomic reactions.

Here, we discuss a hydrogen abstraction reaction that is in many ways similar to the $F + CH_4$ system. The $F + H_2O \rightarrow HF + OH$ reaction with exothermicity -17.6 kcal/mol is of great importance in atmospheric chemistry¹⁶ and astrochemistry.¹⁷ Similar to the $F + CH_4$ system,¹⁸ the title reaction has a small barrier,¹⁹ consistent with weakly temperature dependent rate constants.²⁰ Experimental studies have found that the HF product is vibrationally excited but rotationally cold.^{21–23} On the other hand, the OH internal degrees were found unexcited, suggesting a spectator role during the reaction.^{24,25} These quantum state resolved observations are consistent with a simple abstraction mechanism for the title reaction.

Very recently, we have developed a globally accurate potential energy surface (PES) for the ground electronic state of FH_2O ,²⁶ which correlates adiabatically to both the reactants and products of the title reaction. The PES, which was fit to approximately 30 000 dynamically weighted and Davidson corrected multistate, multireference configuration interaction¹⁹ points, with the permutation invariant polynomial method of Bowman and co-workers,²⁷ has a low (3.8 kcal/mol) reactant-like barrier (Figure 1). At low energies, this adiabatic reaction pathway is expected to dominate as the first excited electronic state, which also correlates adiabatically to the reactants and products of the title reaction, has a much higher barrier.¹⁹ QCT studies on this PES have reproduced most quantum-state-resolved experimental observations, thus validating the accuracy of the PES.²⁶ In addition, the dominance of backward scattering confirms the direct abstraction mechanism. Furthermore, we have demonstrated that a pre-reaction van der Waals well enhances reactivity at low energies due to stereodynamics.²⁸ In this work, we focus on the mode selectivity in this prototypical reaction using both QCT and QM wave packet approaches and

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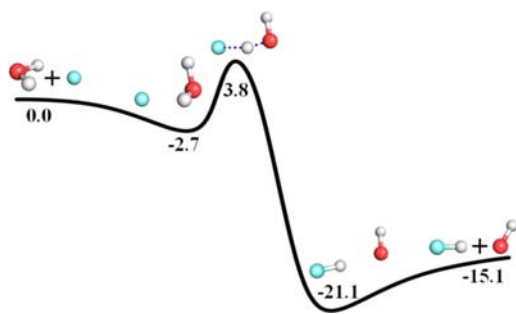


Figure 1. Schematic reaction path and stationary points for the $F + H_2O \rightarrow HF + OH$ reaction on the ground electronic state of FH_2O . Energies are in kcal/mol relative to reactants.

test the applicability of the Polanyi's rules in this atom-triatomic system.

Both the QCT and QM methods for calculating the reaction integral cross sections (ICSs) are well established,^{29,30} and the details of the calculations can be found in the Supporting Information (SI). Briefly, the QCT calculations were carried out using VENUS,³¹ in which the H_2O vibrational state was prepared using a normal mode approach implemented in VENUS. In the QM calculations, we used the flux-flux approach discussed in our recent work,^{32,33} based on the Chebyshev propagation.³⁴ We note here that the QM calculations are quite challenging due to the six-dimensional nature and, as a result, we have used the centrifugal sudden (CS) approximation^{35,36} in computing the $J > 0$ probabilities. Given the first-principles nature of the PES and QM dynamics, the results are highly reliable,³⁷ as illustrated by the recent work in another tetratomic reaction.³⁸

The H_2O molecule possesses three vibrational modes, which are commonly denoted by three quantum numbers (n_1, n_2, n_3) for the symmetric stretching, bending, and antisymmetric stretching normal modes, respectively. Figure 2 presents excitation functions in collision energy for various initial vibrational states of H_2O obtained from both the QCT and QM calculations. To compare the relative efficacies with respect to translational energy, they are also plotted in total energy referenced to the ZPE-corrected potential minimum in the reactant asymptote. As discussed in our earlier work,²⁸ the peak

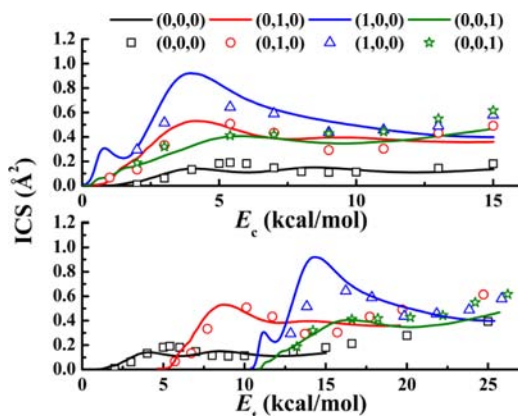


Figure 2. Reaction integral cross sections for various H_2O vibrational states obtained from both QCT (symbols) and QM (lines) calculations. These excitation functions are plotted in collision energy (upper panel) and total energy (lower panel). The latter is referenced to the $F + H_2O(0,0,0)$.

at low energy is due to the enhancement of reactivity by a pre-reaction van der Waals complex. For most energies, it is clear from the figure that excitations in all three vibrational modes of the H_2O reactant significantly enhance the reactivity of the title reaction and the vibrational excitations are more effective than translational energy. The symmetric stretching mode has the largest enhancement followed by the bending mode, while the antisymmetric stretching mode is least effective. In addition, the QCT and QM results are qualitatively consistent, although quantitative differences exist, which are presumably due to quantum effects such as tunneling not included in QCT, as well as to the approximate nature of the QM model.

Apparently, the results presented in Figure 2 do not conform to the conventional wisdom as stipulated by the Polanyi's rules, which predict that translational energy should be more effective than internal excitation of the reactant for this early barrier reaction. Interestingly, both experimental^{4,5} and theoretical studies^{39,40} found vibrational excitations of H_2O also enhance reactivity for $H + H_2O \rightarrow OH + H_2$, which is consistent with Polanyi's rules since this reaction has a late barrier.

To understand this surprising phenomenon, we turn to the analysis of the reaction path model,⁴¹ in which the PES is approximated by the minimum energy path (MEP) along the reaction coordinate and $(3N - 7)$ generalized normal modes orthogonal to the reaction coordinate. Assuming vibrational adiabaticity, the state-specific reactivity is determined by the barrier height on the vibrational-state selected effective potentials obtained by adding the corresponding vibrational frequencies to the MEP. In Figure 3, the generalized vibrational

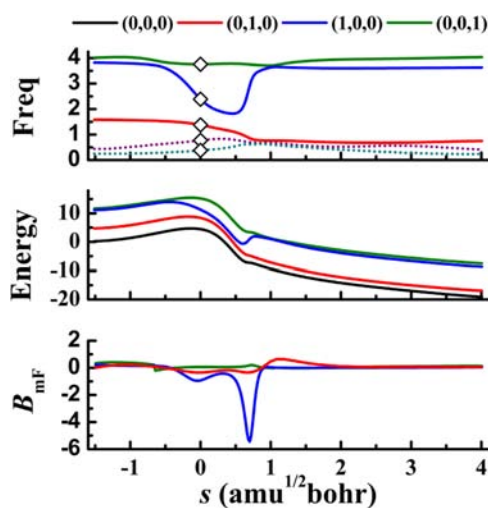


Figure 3. Generalized vibrational frequencies (upper panel), vibrational-state specific minimum energy paths (middle panel), and the couplings between vibrational modes and the reaction coordinate (lower panel) calculated on the PES between the pre- and post-reaction van der Waals complexes. The dotted lines are for low-frequency modes. The units are given in frequencies (10^3cm^{-1}), energy (kcal/mol), B_{mF} ($\text{amu}^{-1/2} \text{bohr}^{-1}$). The diamonds indicate the position of the saddle point.

frequencies along the reaction path (upper panel) and vibrational-state selected effective potentials (middle panel) computed using POLYRATE⁴² are shown. (The details of the reaction path calculations and the geometric information of the MEP are given in the SI.)

From the upper panel of Figure 3, it is interesting to note that the symmetric stretching mode of the H_2O reactant ($s < 0$)

undergoes dramatic changes as the two reactants move closer. This generalized normal mode is localized near the transition state ($s = 0$) to the O–H stretching mode directed toward the incoming F atom, in strong coupling with the reaction coordinate. As a result, the frequency of this “reactive mode” is almost halved at the transition state. It eventually transforms into the H–F vibration in the product side ($s > 0$) and its frequency recovers. In the mean time, the bending mode of H_2O also changes significantly along the reaction coordinate, and eventually turns into the rotation of HF. The large changes of the frequencies in these two modes are indicative of strong couplings with the reaction coordinate, as shown in the bottom panel of Figure 3, where the couplings (B_{mF}) are plotted. On the other hand, the antisymmetric stretching mode of H_2O is a “spectator mode” in this vibrationally adiabatic model, which localizes to the nonreactive OH vibration with nearly the unchanged frequency throughout the reaction. The localization of the normal stretching vibrations is a well-established phenomenon for H_2O due to a Darling–Dennison resonance.⁴³

The enhancement of reactivity by exciting the symmetric stretching and bending modes of H_2O can be rationalized, at least partly, by the lower barriers (3.04 and 4.31 kcal/mol for the two modes) than that on the ZPE corrected MEP (4.70 kcal/mol). The lowering of the barriers stems from the reduction of the corresponding vibrational frequencies near the transition state. The enhancement by exciting the antisymmetric stretching mode of H_2O , which is smaller than the other two modes, is more complicated because the corresponding barrier does not differ significantly from the ZPE corrected MEP. It is likely that enhancement is due to a vibrationally non-adiabatic mechanism,^{44,45} which would also lower the effective barrier.

The observed higher efficiency of the symmetric stretching mode in enhancing reactivity than the antisymmetric stretching mode is quite similar to observations in the Cl + CH_4 reaction^{6–9} and dissociative chemisorption of methane on Ni,¹⁰ both have a late barrier. Reaction path analyses for these reactions^{45–48} have identified qualitatively similar behaviors shown in Figure 3. Specifically, the symmetric stretching mode of methane is the “reactive mode”, which lowers its frequency drastically near the transition state, while the antisymmetric stretching mode remains a spectator, but presumably undergoes vibrationally non-adiabatic transitions to reactive modes. Similar effects of bending excitation were also observed. Interestingly, Halonen et al. showed that the symmetric stretching wave function “rotates” toward the reaction coordinate while the asymmetric stretching wave function away from the reaction coordinate.⁴⁶ These reactions with different locations of the transition state share the same pattern in terms of coupling of vibrational modes with the reaction coordinate.

It is clear from the above analysis that the mode selectivity in this system is far more complicated than atom–diatom systems based on which the Polanyi’s rules were established. As pointed out by several authors,^{49–51} it might be more appropriate to predict the mode selectivity by examining coupling between the generalized vibrational modes and the reaction coordinate, which of course was the essence of the original Polanyi’s rules. In the title reaction, it is shown that the symmetric stretching and bending modes of the H_2O reactant are strongly coupled with the reaction coordinate, despite the early barrier. As a result, their roles in enhancing the reactivity can be readily understood. However, the coupling with the reaction

coordinate is apparently not the only criterion, as it cannot explain the enhancement of the antisymmetric stretching mode in our system. As discussed above, the latter is presumably due to vibrational non-adiabaticity which leaks energy into the reaction coordinate. The energy flow between different vibrational modes during the reaction can be considered as a manifestation of the intramolecular vibrational energy redistribution (IVR).

Since the title reaction shares many similarities with the F + CH_4 reaction, it is interesting to note that the excitation in CH stretch actually inhibits the F + $\text{CHD}_3 \rightarrow \text{HF} + \text{CD}_3$ reaction.¹¹ Czakó and Bowman have shown based on QCT calculations on an accurate full-dimensional PES that the inhibition can be attributed to stereodynamics controlled by various pre-reaction van der Waals complexes.¹³ The title reaction has also a pre-reactive van der Waals complex, and as we demonstrated in our recent work,²⁸ the stereodynamical force between F and H_2O is stronger and favorable for steering the system toward the transition state. To understand the influence of the van der Waals complex, we have carried out QM calculations on a modified PES in which the van der Waals well was artificially removed.²⁸ The results, shown in SI, indicated that the mode selectivity remains, suggesting a minor role for stereodynamics and reinforcing the notion that the mode selectivity is largely determined by couplings with the reaction coordinate at the transition state.

To summarize, it is clear that the Polanyi’s rules for atom–diatom reactions need be extended for reactions involving polyatomic molecules. The examples discussed here and elsewhere suggest that instead of using the location of the barrier as the criterion to predict the efficacy of the form of energy in promoting reactivity, the coupling of the vibration with the reaction coordinate presents a better predictor. Ultimately, however, full-dimensional dynamics is needed to account for experimental observations accurately, as strong energy flow between different modes may be present in many multidimensional systems.

■ ASSOCIATED CONTENT

📄 Supporting Information

Details of theoretical methods 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.

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