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Dynamics of Bimolecular Reactions of Vibrationally Highly Excited Molecules: Quasiclassical Trajectory Studies

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Excitation functions from quasiclassical trajectory calculations on the $H + H_2O \rightarrow OH + H_2$, $H + HF \rightarrow F + H_2$, and $H + H'F \rightarrow H' + HF$ reactions indicate a different behavior at low and high vibrational excitation of the breaking bond. When the reactant tri- or diatomic molecule is in vibrational ground state or in a low vibrationally excited state, all these reactions are activated; i.e., there is a nonzero threshold energy below which there is no reaction. In contrast, at high-stretch excited-states capture-type behavior is observed; i.e., with decreasing translational energy the reactive cross-section diverges. The latter induces extreme vibrational enhancement of the thermal rate consistent with the experiments. The results indicate that the speed-up observed at high vibrational excitation is beyond the applicability of Polanyi's rules in their common form; instead, it can be interpreted in terms of an attractive potential acting on the attacking H atom when it approaches the reactant with a stretched X−H bond.

Introduction

Collisions of highly vibrationally excited molecules is commonly a topic in the field of unimolecular reactions,[1−5] where emphasis is laid on energy transfer, namely, when nonreactive but inelastic collisions change the energy content of the molecule that may undergo a unimolecular reaction. The possibility that the collisions of the excited molecules in the gas phase with *reactive* partners can show specific phenomena has traditionally not been considered as the colliders in unimolecular systems are selected to be inert. Bimolecular reactions of vibrationally excited molecules have become a subject of intense study recently, when experimental work indicated that a remarkable speed-up and state specificity can be observed when simple molecules in vibrationally excited states collide with reactive partners.[6−15]

According to the molecular beam experiments on the reaction of vibrationally excited water with H atoms,[6−13]

$$H + H_2O(00v) \rightarrow OH + H_2 \qquad \text{(R1)}$$

the vibrational excitation of the O−H stretch modes induces a remarkable state specificity: when the H atoms of the water molecule are tagged by isotope labeling, one can observe that the H or D atom is selectively abstracted depending on whether the O−H or O−D bond is vibrationally excited. In the corresponding experiments performed under thermal conditions[14,15] very large reaction rates were observed that correspond to thermal average reactive cross-sections of around 20 Å^2. Earlier classical trajectory[16−18] and quantum scattering[19] calculations indicate that reactivity increases with increasing excitation of the O−H stretch vibrational mode of water. This is not surprising as the reaction is characterized by a late barrier which, according to Polanyi's rules,[20−22] can be more easily surmounted if the atom to be abstracted vibrates with larger amplitude. The magnitude of the increase is, however, much larger than what one can expect on the basis of the bobsled effect that is beyond Polanyi's rules. The details of how and why the reactant in lower and higher vibrationally excited states reacts differently have not been investigated. It is not clear whether the extreme speed-up of the reaction is specific to the reaction of excited H_2O or can also happen in other systems. Accordingly, we studied the reactive cross-sections of reaction R1 and some other processes that are similar to it, namely, the reaction of H atoms with HF. The potential profiles for these two reactions are similar: the reaction is highly endoergic, and the potential barrier is late for both. Since the extra OH bond in H_2O is a well-behaved spectator bond and the masses are similar, one can expect similar dynamics.

In this paper we summarize the results of our theoretical studies on how the vibrational excitation increases the rate of the reaction. In the rest of the paper we first summarize the theoretical methods (section 2) and then present the results of the quasiclassical study of the dynamics of the $H + H_2O$ reaction in section 3 and those on the $H + HF$ abstraction and exchange processes (section 4). In section 5 we attempt to connect the enhancement of the rate to the properties of the potential surface.

Methods

Reactive cross-sections for reactions with vibrationally excited reactants were calculated using the standard quasiclassical trajectory (QCT) method. The peculiarity of the calculations of the reaction of the triatomic water molecule is that trajectories are started from initial quantum states of H_2O which are represented by "root" trajectories. The latter are periodic trajectories in the internal phase space of water for which the calculated vibrational classical action variables for the three vibrational modes correspond to the selected quantum numbers +1/2 according to the Einstein−Brillouin−Kramers quantization rule. For low excited states of water we used the normal mode Hamiltonian. For higher vibrational states we used the local mode Hamiltonian—as the spectrum is better described by local

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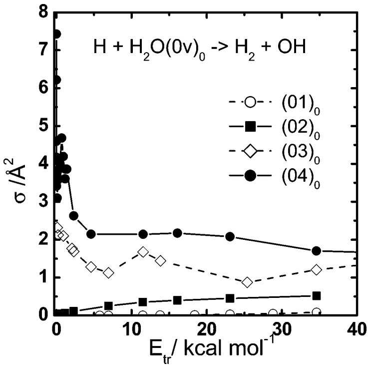

Figure 1. Excitation function for the $H + H_2O(0v)_0 \rightarrow OH + H_2$ reaction at varying OH stretch excitation (v) obtained on the WSLFH potential surface.

modes at higher excitation—so that the $(02)_0$, $(03)_0$, and $(04)_0$ excited states were described by 0 quantum in one O−H stretch and 2, 3, or 4 quanta in the other, and the bend mode is in the ground state (denoted by the subscript 0 after the parenthesis). In all calculations the connection between the orbital angular momentum and the initial impact parameter was considered to be purely classical. The calculations for the atom + diatom reactions were performed using an extensively modified parallel version of the VENUS code.[23] The atom + triatomic molecule reactions were calculated with the code used in ref 18.

Reaction of H Atoms with Vibrationally Excited Water Molecules. The $H + H_2O \rightarrow OH + H_2$ and the reverse reaction provide a testing ground for developing methods to treat reactions with four-atomic systems. Most of the earlier calculations have been performed on the WDSE potential surface,[24−26] but recently more precise surfaces appeared. The hybrid WSLFH surface[17] combines a spline-fitted reduced dimensional section of the surface with asymptotic reactant and product potentials derived from experiments using simple analytical and switching functions. This potential surface treats the two hydrogen atoms of the water molecules or, alternatively, the two H atoms of the diatomic H_2 as equivalent. The Ochoa−Clary (OC) surface,[27] which is based on the rotating bond order formalism,[28] treats all hydrogen atoms as equivalent, but the exchange reaction was not addressed and is not described correctly. The most recent and most extended is the YZCL2 potential surface,[29,30] which is based on the Shepard interpolation. This potential surface explicitly describes the exchange channel and considers all hydrogen atoms equivalent. There is a price for the increased accuracy, namely, that the calculation of the potential energy becomes more and more time-consuming in the cited order. In this work we used the WSLFH surface, because we focus our attention on the abstraction channel which is adequately described by this PES.

The saddle point on the potential surface for reaction R1 is slightly in the product $H_2 + OH$ valley. On the basis of Polanyi's rules, one can expect that vibrational excitation of the reactant's O−H bond will be favorable for the reaction. This is what we observe in QCT calculations on the WSLFH surface for the $H + H_2O(0v)_0$ reaction at low vibrational excitation ($v = 0$, 1, or 2) as shown in Figure 1. Qualitatively different excitation functions are obtained at high vibrational excitation ($v = 3$, 4), in agreement with the results reported earlier[16,17] for the OC potential surface.[27] While at low vibrational excitation the reactive cross-section is zero at low relative translational energy and there is a finite threshold for reaction, at high vibrational excitation, in contrast, the reactive cross-section diverges at low excitation energy and drops with increasing E_{tr}. At $v = 0$, 1, 2 the threshold energy decreases with increasing vibrational excitation, being about 17.3, 4.6, and 0.1 kcal mol^{-1}, respectively. The magnitude of the reactive cross-section increases with the initial relative translational energy, and at large E_{tr} it is approximately proportional to the initial vibrational quantum number. At $v = 3$ and 4 the limiting high-energy cross-section is also much larger than at lower v, but the large difference as compared to $v = 0$, 1, 2 is that the reactive cross-section decreases with increasing initial relative kinetic energy. At low E_{tr} the cross-section increases roughly according to an inverse power law with decreasing E_{tr}. The thermal rate coefficient calculated from the excitation functions for the $(04)_0$ state is in very good agreement with the experiments.[18] Excitation functions that diverge when the translational energy decreases generally characterize capture processes.[31] The opacity functions presented in Figure 2 corroborate this observation. At low relative translational energy larger reactive probability is observed at large impact parameters than in close to head-on collisions, indicating that the slowly moving reactants are attracted into a reactive arrangement. Increasing the initial relative translational energy, the reactive cross-section becomes larger at small impact parameters, which means that if the partners approach fast, the influence of the small attractive force is quickly overridden.

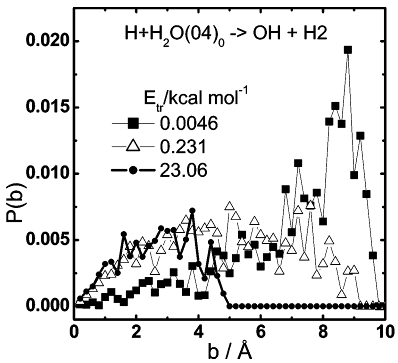

Figure 2. Opacity function for the $H + H_2O(04)_0 \rightarrow OH + H_2$ reaction at various initial relative kinetic energies.

Reaction of H Atoms with Vibrationally Excited HF Molecules. The potential surface for the

$$H + HF(v) \rightarrow F + H_2 \qquad (R2)$$

reaction is the best known of all chemical reactions beyond $H + H_2$. The 6-SEC surface of Truhlar et al.[32] and of Stark and Werner[33] are both based on ab initio calculations that cover almost all of the electron correlation energy. Similarly to H + water, the saddle point for this highly endothermic reaction is in the product valley. The three atoms are at a slightly bent arrangement at the saddle point. The H + HF saddle point is somewhat further out in the product valley, as the H−H bond length at the saddle point shows: it is 1.59 and 1.44 bohr, being about 0.15 and 0.03 bohr longer than the equilibrium H−H bond length for (R1) and (R2), respectively. We used both the 6-SEC and the SW surfaces, with somewhat different results. Here we report data obtained on the 6-SEC surface.

Figure 3 shows the excitation function for H abstraction from vibrationally excited HF at various initial vibrational quantum states of HF. Similarly to reaction R1, we found activated behavior at low vibrational excitation, up to $v = 2$, and capture type excitation function at higher vibrational excitation beginning with $v = 3$. The higher the vibrational excitation the higher is the reactive cross-section at any translational energy (so that the $\sigma - E_{tr}$ curves do not cross). The QCT method allows fine-tuning of vibrational excitation and determining more precisely

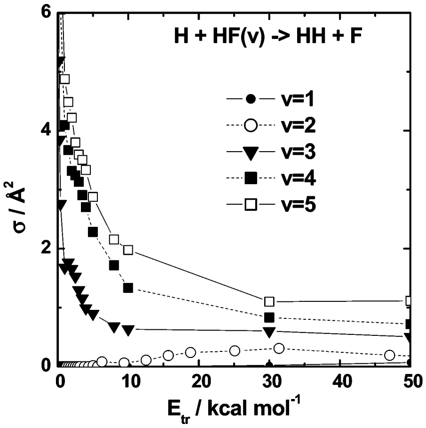

Figure 3. Excitation function for the $H + HF(v) \rightarrow F + H_2$ reaction calculated on the 6-SEC potential surface for different vibrational states v of HF.

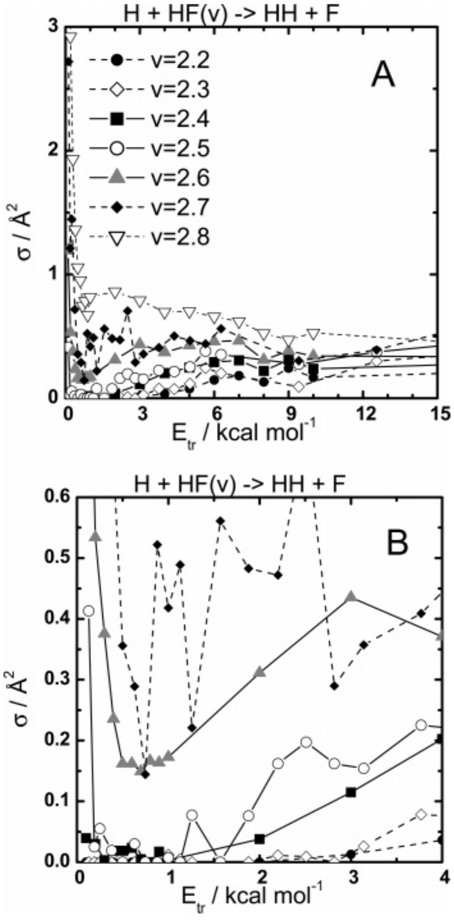

Figure 4. Same as Figure 3 but at noninteger HF vibrational "quantum numbers": (A) global view; (B) low-energy region (the assignment of symbols to quantum numbers is in A).

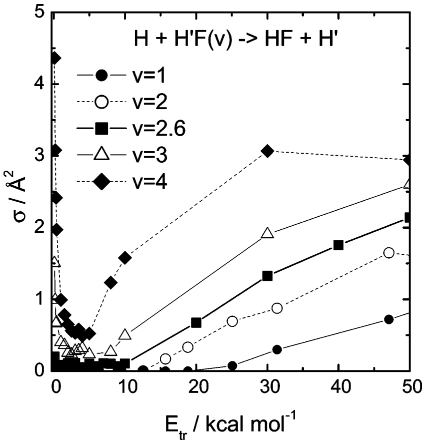

Figure 5. Excitation function for the $H + H'F(v) \rightarrow FH + H'$ reaction at various vibrational quantum states of HF obtained on the 6-SEC potential surface.

when the reaction switches from activated to capture-like. The excitation functions calculated at noninteger vibrational quantum numbers are shown in Figure 4. Examining Figures 3 and 4, one finds that at very high vibrational excitations ($v = 5, 4, 3$) at low initial relative translational energy the cross-sections drop smoothly with increasing E_{tr} and follow an inverse power law up to around $E_{tr} = 1$ kcal mol^{-1}. As the vibrational excitation decreases below $v = 3$ (Figure 4), a dip appears in the excitation function at around $E_{tr} = 1$ kcal mol^{-1}, above which the reactive cross-section increases first and then passes a local maximum and continues the pattern started at low translational energies, i.e., drops further. Decreasing the vibrational excitation further, the dip becomes deeper, the slow increase of the cross-sections after the minimum becomes faster, and the local maximum shifts to higher translational energies and becomes flatter. At $v = 2.5$ or 2.4 the minimum on the excitation function goes down to zero between about $E_{tr} = 0.5$ and 2 kcal mol^{-1}. On the low-energy side of the minimum the cross-section increases sharply at $v = 2.5$ and moderately at $v = 2.4$, while on the high-energy side the increase is much less sharp. A further decrease of the vibrational excitation leads to well-defined activated behavior, with zero cross-section up to a threshold energy with $E_{threshold} \approx 1$ kcal mol^{-1} at $v = 2.2$ and $E_{threshold} \approx 3$ kcal mol^{-1} at $v = 2.1$. From this one can conclude that the switch from activated to capture-type occurs at about $v = 2.5$, which corresponds to an HF vibrational energy of 34.6 kcal mol^{-1}, which is only a little bit higher than the classical barrier for the reaction (32.7 kcal mol^{-1}). The final state distributions for the H_2 product of this reaction are peaked at $v = 0$ independently of the initial vibrational excitation, indicating that the process is vibrationally highly nonadiabatic.

The switch from activated to capture-type behavior seems not to be restricted to the H + HF abstraction reaction. The excitation function for the exchange reaction of the same reactants,

$$H + H'F(v) \rightarrow FH + H' \qquad \text{(R3)}$$

is shown in Figure 5 at various vibrational quantum numbers. An activated behavior can be seen for $v = 1$ and 2, and above $v = 3$ capture-type cross-sections are observed. On the high-v excitation functions the minimum that was seen on the abstraction excitation functions only at low v is much more expressed. The switch between the activated and capture-type behavior is at around $v = 2.7$, somewhat higher than for the abstraction reaction, in agreement with the somewhat higher barrier for exchange.

Reverse Reactions

As the change of the excitation function from activated to capture-type is not unique to the $H + H_2O$ reaction where it was first observed, it seems to be promising to check other reactions. The reverse reactions to (R1) and (R2) can serve as good test cases as there are good potential surfaces for both, and they differ significantly from the cases seen so far. Both the $OH + H_2$ and the $F + H_2$ reactions are very exothermic and are characterized by a low and early barrier. For such reactions Polanyi's rules predict that translational excitation

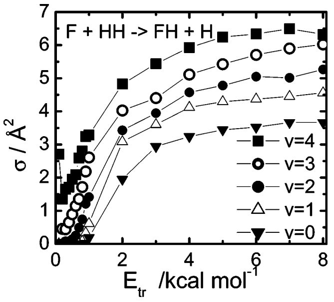

Figure 6. Excitation function for the F + $H_2(v)$ → H + HF reaction at various vibrational quantum states of H_2 obtained on the 6-SEC potential surface.

promotes the reaction more efficiently than vibration, but the conventional use of the rules does not consider the effect of varying the magnitude of the vibrational energy. In an earlier study of the OH + $H_2(v)$ reaction on the OC potential surface,[34] activated behavior was reported at $v = 0$ while capture-type reactivity at $v = 1$. Here we studied the F + $H_2(v)$ reaction for $v = 0-4$ (Figure 6). The threshold energy is very low even for the reaction of H_2 in the vibrational ground state (around 0.9 kcal mol^{-1} at this QCT approximation) in accord with the low barrier on the PES and quickly decreases to 0.6 and 0.2 kcal mol^{-1} at $v = 1$ and 2, respectively. There is a switch from activated to capture-type behavior for this reaction also; it occurs between $v = 2$ and 3, where the threshold disappears and the cross-section quickly increases with the decrease of the initial relative translational energy.

Discussion

Our QCT calculations on atom-transfer reactions indicate that the excitation functions for the reaction of an atom with a vibrationally excited reactant undergoes a qualitative change as the vibrational excitation increases, independently whether the reaction is exothermic or endothermic. For an endothermic reaction at low vibrational excitation we see the expectations based on Polanyi's rule to be fulfilled. Namely, at low translational energy there is no reaction, the cross-section increases above zero at a high threshold and increases slowly and monotonically with the initial relative translational energy. The threshold energy decreases as the vibrational excitation increases, and the rate of increase of the cross-sections above the threshold energy is similar at different vibrational energies. The same amount of energy is more efficient for enhancing reactivity if invested in the form of vibrational energy than in the form of translational energy, which is one formulation of Polanyi's rule. At high vibrational excitation energy a different type of excitation function is observed. The cross-section is very large at low relative translational energy and drops quickly, at a close to inverse power law with increasing E_{tr}. The decrease slows down when E_{tr} increases to around a few kilocalories per mole. In certain cases (H + HF abstraction) the excitation functions keep decreasing monotonically, but more and more slowly as E_{tr} increases. In several cases (H + HF exchange, H + H_2O abstraction, F + H_2 abstraction), however, a well-defined minimum can be observed. The cross-sections start to increase again after the minimum and may pass a flat maximum. The composite nature of the excitation function indicates that there are two different features that determine its shape: one that is responsible for the divergence of the cross-section with decreasing E_{tr} at low relative kinetic energies and one that causes the slow increase at larger kinetic energies. The latter is very probably the manifestation of Polanyi's rule, similarly to what we described for low vibrational excitation. On the basis of the regular trajectory plots with various vibrational excitation, it is easy to understand that as the amplitude of the reactant's vibrational motion increases, the reaction rate should increase. However, that picture would not explain why the reactive cross-section should diverge at low translational energy: it looks like the beneficial effect of the increased vibrational amplitude can be better manifested if the reactants approach slowly. Capture-type excitation functions are characteristic of collisions between partners that exert an attractive force on each other. Investigating potential surfaces for atom-transfer reactions, one can find that there is an attractive interaction between a vibrationally highly excited molecule and an atom for situations that do not occur when the reactant is not vibrationally highly excited, namely, when the breaking bond is significantly stretched. The existence of such an attraction was shown for several ab initio potential surfaces for H + H_2O,[16,17] but it is not unique to that reaction. Figure 7 shows the potential experienced by the H atom approaching the H atom of an HF molecule when the F−H bond is extended to the length corresponding to the saddle point of the 6-SEC PES. The potential is attractive already at large distances. Due to the large vibrational amplitude of a highly stretch-excited molecule the reactive bond can often be relatively long, and if the attacking atom arrives at the right phase, "passing the barrier" is a smooth downhill walk. Such an attraction can also be observed for the exchange reaction.

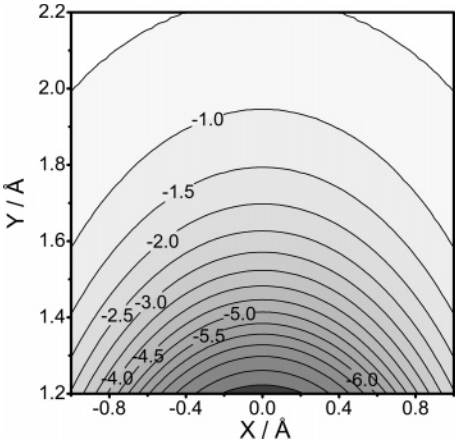

Figure 7. Cross-section of the potential surface of the H+ HF(v) → H_2 + F reaction taken at the HF bond length of 1.3 Å. The potential felt by an H atom at coordinates X and Y approaching the H of HF positioned at the origin of the coordinate system is plotted as a function of the location of the attacking H. The H−F bond points down along the Y axis. Contour lines are spaced 0.5 kcal mol^{-1} from each other. The energy is referred to an HF molecule expanded to 1.3 Å and an H atom at the infinity.

The idea that the vibrational enhancement of the rate is due to the attractive potential for excited vibrational states of the reactant is closely related to the observations made long ago on the basis of transition-state theory.[35,36] Pollak[35] found that for vibrationally highly excited reactants, as usual, in addition to the attractive periodic orbit dividing surface (*pods*) there are repulsive *pods*' also. If the vibrational excitation is high, the repulsive *pods* is way out in the reactant valley, and the corresponding adiabatic barrier is shallow. On the basis of this theory, one can explain why dynamical thresholds are observed in reactions with vibrationally excited reactants. The simplicity of the theory and its success for mostly collinear reactions has a real appeal. However, to reconcile the existence of a vibrationally adiabatic barrier with the capture-type behavior—which seems to be supported by the agreement of the calculated and experimental rate coefficients[18]—needs further study.

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