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TESTING CONDENSED-PHASE THEORIES OF PROTON TUNNELING IN CLUSTERS

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Abstract

Ultrafast measurements of proton transfer in clusters have provided a sufficient set of data to begin making critical comparisons with extensive condensed-phase studies. In this paper we show that the unique environment of clusters can potentially provide detailed information about condensed-phase properties not directly obtainable from condensed-phase studies. We discuss the mechanism of proton tunneling. A model is presented based on concepts developed for condensed-phase proton transfer, but which takes the additional step of treating the problem from a state-to-state level involving intermolecular and solvent modes that can strongly influence the tunneling probability. Some predictions are made for cluster proton transfer including; (1) mode-specific acceleration in the tunneling rate k, and (2) a structured dependence of k vs reaction free energy ΔG. Both predictions hold only when single-vibronic level excitation can be achieved and the vibrational relaxation rates are sufficiently slow, conditions that are well met in small clusters. Recent cluster results are in support of an important, but hitherto unverified, tenet in condensed-phase tunneling theory, namely the role of the hydrogen bond heteroatom symmetric stretch vibration, which modulates the tunneling barrier width.

Introduction

Many investigators have argued that research on molecular clusters provide special opportunities to understand detailed properties of the bulk phase. For the most part these promises have gone unfulfilled. Our interest in studying molecular clusters is motivated by the potential to understand chemical properties in solution at the level of single solvent molecules. In this paper, we present the case that clusters indeed can provide detailed information not directly attainable from condensed-phase studies. The unique environment of clusters holds several advantages to understanding molecular-level properties of condensed-phase, primary among these are: (1) solvent size and structure is well known, and (2) single-vibronic level excitation is possible permitting state-to-state measurements.

The particular problem we discuss here is the mechanism of proton transfer, and especially the role of vibrational and solvent modes on proton tunneling rates. In our experiments, we initiate a proton transfer by electronic excitation (excited-state proton transfer, ESPT) and measure PT rates as a function of varying solvent cluster conditions. More recently, we have been concerned with developing a theory of proton tunneling in clusters that embodies the most important concepts in condensed-phase theories, but which also treats the vibrational coupling in a manner consistent with the state-to-state

nature of the tunneling probabilities. Condensed-phase theories typically average over the state-to-state processes, conceding that they are untestable in the bulk. Clusters, however, offer the opportunity to examine these detailed pathways.

Background

Excited-state proton transfer (ESPT) reactions have been studied extensively in the condensed phase including several time-resolved experiments.[1,2] These reactions are strongly solvent dependent. The neutral acid AH (or AH*) and the conjugate base A^- (or A^{*-}) tend to be stabilized differently by the solvent, which means that the acidities of the ground and excited states can change markedly with different solvents. A solvent that is polar or that has a high proton affinity will favor the dissociated acid over the undissociated acid.

The first study of ESPT in a cluster was reported by Leutwyler, Cheshnovsky, and coworkers for 1-naphthol-$(NH_3)_n$.[3] These experiments were important because they showed that it is possible to investigate how individual solvent molecules progressively stabilize the product states. We represent proton transfer from the aromatic acid ROH (R = naphthyl or phenyl) as follows

$$ROH^*B_n \rightarrow RO^{*-} H^+B_n$$

which corresponds to a conversion from a locally excited S_1 state with a covalent O-H bond to an excited ion-pair state. B_n refers to the solvent cluster consisting of n molecules of base B. Leutwyler's group for naphthol,[3] and later Solgadi et al. for phenol[4] reported solvent size thresholds for reaction.

In our laboratory we have been interested in the picosecond dynamics of ESPT of phenol (PhOH) complexed to a variety of solvents.[5] The Zewail group[6] and the Bernstein and Kelley group[7] have been studying similar properties for 1-naphthol (1-NpOH). In all cases, a sharp onset to reaction occurs at some critical solvent size [n=5 for $PhOH^*(NH_3)_n$ and n=3 for $1\text{-}NpOH^*(NH_3)_n$]. The rates tend to be fairly constant for increasing solvent size despite the expectation of an increasing exothermicity (decreasing reaction free energy ΔG_0). This behavior we believe to correspond to the Marcus inverted region, as described below.

Tunneling Model for Proton Transfer in Clusters

The details of our model of proton tunneling in clusters are described elsewhere.[8] In essense, it adapts the concepts of condensed-phase tunneling[9-11] to a state-to-state treatment based on radiationless transition theory.[12] For the present paper it suffices to understand qualitatively what elements are in the theory and why they are important. These are summarized in Fig. 1. A minimum of four nuclear coordinates is needed: (1) the O-H coordinate q_H, which is the reaction coordinate, (2) the O-N coordinate Q_N, in which the O···N symmetric stretch modulates the internuclear distance between potential minima, which in turn modulates the barrier height and width,[9,10] (3) the solvent coordi-

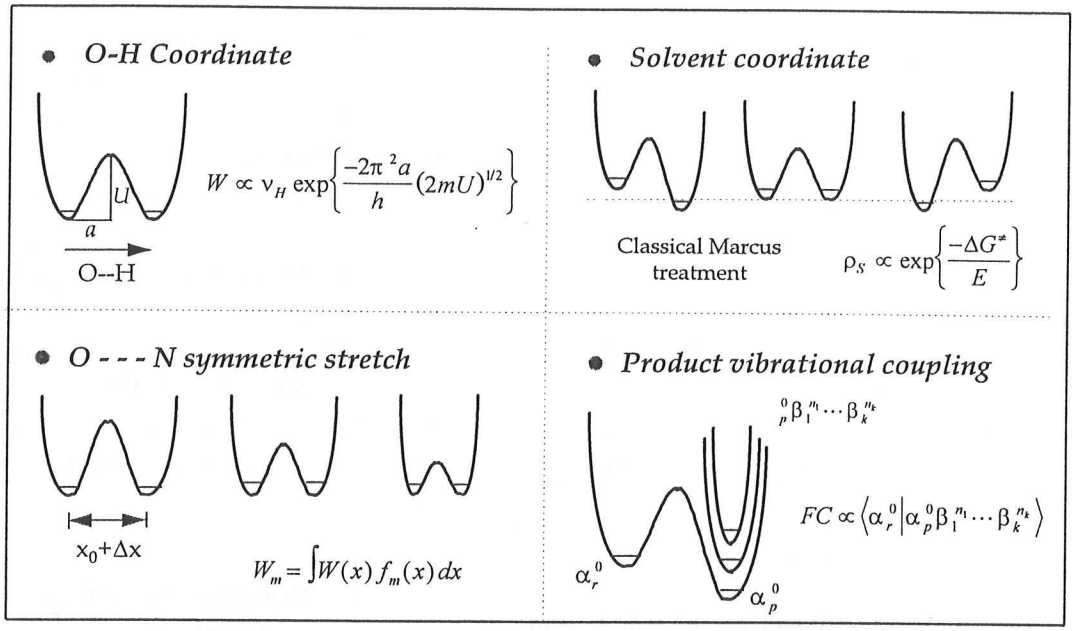

Figure 1. Diagrams that qualitatively show the important nuclear coordinates used in the present tunneling model. See text for details. Terms not defined in the text are as follows: ν_H, a, m, and U are O-H frequency, barrier width, reduced mass of tunneling particle, and barrier height, respectively. $f_m(x)$ is the vibrational probability amplitude for Q_N for quantum number m_N. $\Delta G^{\neq}$ is the solvent activation energy defined by Marcus theory and E is energy per mode in the cluster. FC are Franck-Condon factors for a vibrationless reactant where α is for the O-H vibration, and β_i are for all other modes *i*. m and n are quantum numbers for reactant and product, respectively.

nate S, in which solvent modes cause fluctuations in the relative energies of reactant and product,[11] and (4) coordinates corresponding to product accepting modes that reduce the electronic energy gap between reactant and product.[12] All coordinates, except for S are treated quantally in our treatment.[8]

Measured rates of proton transfer in $PhOH^*(NH_3)_n$ clusters are compared to various tunneling model calculations in Fig. 2. The ability to model tunneling rates as a function of ΔG_0 is a challenge to tunneling theories. Classical Marcus theory ignores the role of product vibrations and, consequently predicts a strong inverted region. This treatment is represented by the curve (- - -) in Fig. 2 and corresponds to considering the first three nuclear coordinates outlined above and in Fig. 1. A model that ignores both product vibrations and the Marcus concept of activated solvent, but which instead assumes a continuum of product states predicts a continuously increasing tunneling rate with $-\Delta G_0$. This calculation is represented by the curve (—) in Fig. 2 and corresponds to considering the first two coordinates outlined above. The model that includes all four nuclear coordinates is represented by the curve ($\cdot\ \cdot\ \cdot$) in Fig. 2 and gives the best agreement with experiment. This treatment is also consistent with experimental measurements of the dependence of k on internal vibrational energy and on deuteration.

In the remainder of this paper we would like to focus on the Q_N coordinate and on the product vibrations that are Franck-Condon coupled to the reaction coordinate. These

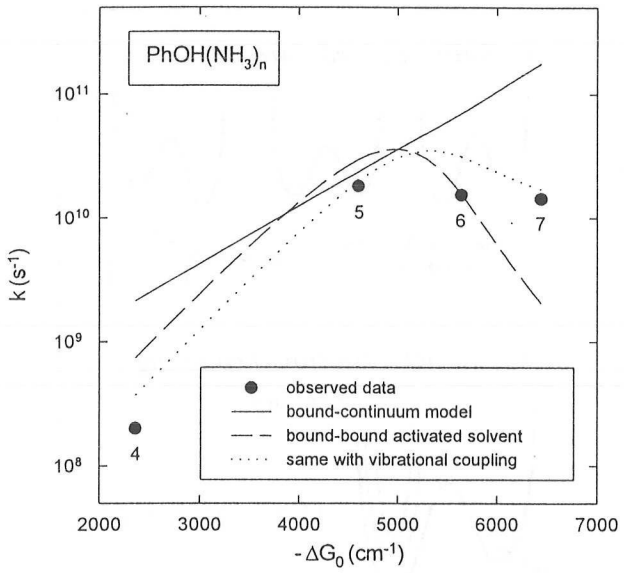

Figure 2. Observed and calculated dependence of k on cluster size n and ΔG_0 for PhOH*$(NH_3)_n$. Three tunneling models are compared and described in the text. Details and parameters used in the calculation are explained elsewhere.[8]

modes are the basis for considering the state-to-state tunneling probabilities and lead to interesting predictions that are testable in clusters, but not in condensed-phases, such as; (1) mode-specific acceleration in the tunneling rate k, and (2) a structured dependence of k vs reaction free energy ΔG_0. Both predictions hold only when single-vibronic level excitation can be achieved and the vibrational relaxation rates are sufficiently slow; conditions that are well met in small clusters.

Mode-Specific Tunneling in Clusters

The rates of proton transfer were calculated as a function of specific excitation of m_N quanta of the Q_N vibration. The results for different O-H barrier heights are given in Fig. 3. We also compare these state-specific tunneling rates to a calculation in which vibrational energy is redistributed statistically among all intermolecular modes of the cluster. The calculation is for a generic proton donor/acceptor pair with the properties given in the figure caption, but is loosely based on the PhOH*$(NH_3)_n$ system. For example, the statistical calculation is for a vibrational energy of E_{vib} = 2500 cm^{-1}, the energy corresponding to excitation of n=5 in Fig. 1.

Our tunneling model predicts a strong mode-specificity; the rate for m_N=1 is almost an order of magnitude greater than for the vibrationless level. The calculated rate for the m_N=1 level at 140 cm^{-1} is greater than the statistical rate at 2500 cm^{-1}. The latter case is affected by the large density of states. The probability of populating m_N is 0.13 for that case. Vibrational relaxation of the Q_N mode is not included in the calculation in Fig. 3, so actual mode-enhancements in rate may be less.

Experimental evidence for mode-specific ESPT may be found in the work by Fuke, Kaya and coworkers on the double proton transfer systems involving dimers of 7-azaindole (7AI) and 1-azacarbazole (1AC).[13] In these cases, the active mode Q_N is an N···N symmetric stretch. These frequencies are 120 and 114 cm^{-1}, respectively, in the $(7AI)_2$ and $(1AC)_2$ dimer excited states. Reaction times for $(7AI)_2$ are typically longer than 1 ps for all modes except the Q_N mode where lifetimes of 0.5 and 0.2 ps were determined for m_N = 1 and 2, respectively. The double proton transfer rates are much slower in $(1AC)_2$ dimers, but a strong mode-specificity is still observed. Reaction times of 330, 130, and 65 ps were measured for m_N = 0,1, and 2, respectively. Other modes had life-

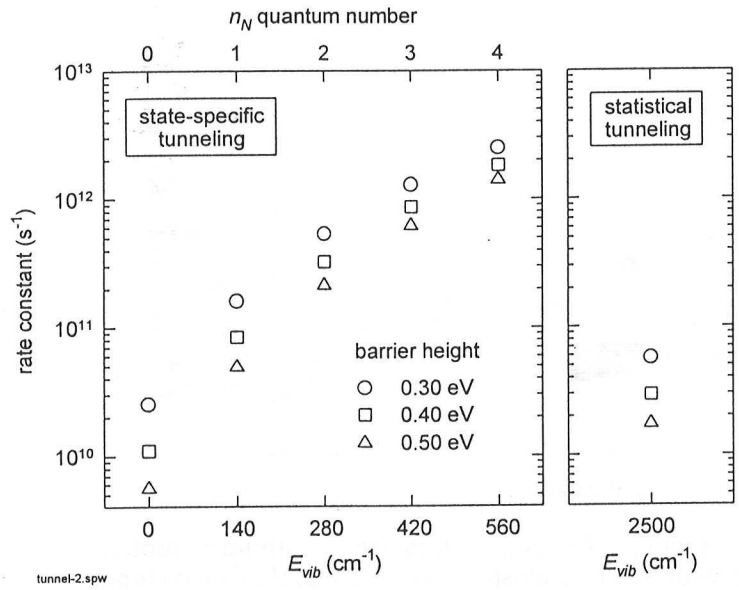

Figure 3. Calculated tunneling rate constants for mode-specific excitation of the Q_N vibrational coordinate. Calculation assumes a harmonic oscillator of frequency 140 cm^{-1}. The statistical calculation at 2500 cm^{-1} vibrational energy is based on redistribution to all intermolecular vibrational and rotational modes using a simple Marcus-Rice classical expression.[8]

times of about 300 ps. In both the 7AI and 1AC dimers, a strong deuterium effect was observed, which is further evidence of a tunneling mechanism.

The effectiveness of mode-specificity depends on the competition between the rate of vibrational relaxation vs tunneling. Bruehl and Hynes recently calculated vibrational relaxation rates for a model A-H···B hydrogen bond complex in polar solvent.[14] They considered the proton stretch motion (over a 2500-3500 cm^{-1} range), the proton bend (from 1000-1700 cm^{-1}), and the symmetric stretch (from 100-300 cm^{-1}). Vastly different relaxation times are calculated. The major trend is for relaxation rate to increase steeply with decreasing vibrational frequency due to the increasing spectral density of solvent modes at lower frequency. For example, the proton stretch and the symmetric stretch are calculated to relax on the order of 10 ns and 100 fs, respectively.

These calculations would seem to rule out the possibility of observing mode-selective ESPT by direct excitation of the symmetric stretch, except that the relaxation rate may be much slower in clusters. The groups of Leutwyler[3,15] and Mikami[16] have assigned vibronic bands in the S_1 excitation spectra of PhOH-B (B = H_2O and NH_3) to the symmetric stretch mode. The linewidths are less than a few wavenumbers, which correspond to relaxation times much greater than a picosecond, and very likely tens to hundreds of picoseconds for dimers at low energy. A study of relaxation time in clusters vs number of solvent molecules would be very important.

A structured k vs ΔG_0 dependence in the Marcus inverted region

Classical Marcus theory assumes the free energy of reaction ΔG_0 is absorbed by solvent modes. A reaction is then most efficient when $-\Delta G_0$ equals the solvent reorganization energy λ_S. The reorganization energy is the difference in solvent energy for a configuration that is in equilibrium for the reactant vs the product. The solvent energy is

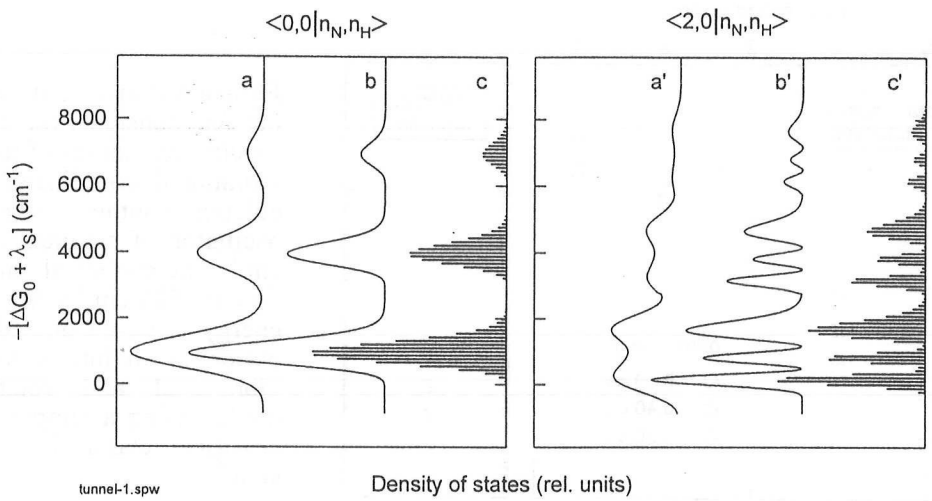

Figure 4. (a,a') Calculated Franck-Condon factors for an arbitrary proton transfer system consistent with previous clusters experiments. (b,b') envelope of the density of states. (c,c') envelope of the density of states after convolving a classical Marcus-Boltzmann distribution for solvent mode excitation at 300K. The left and right hand plots correspond to vibrationless and m_N=2 single-vibronic level excitation. Vibrational frequencies and reorganization energies used in the FC calculations are: n_N = 110 cm^{-1}, n_H = 3500 cm^{-1}, λ_N = 1000 cm^{-1}, and λ_H = 1500 cm^{-1}.

usually treated classically, but it involves vibrational energy and could very well be represented by Franck-Condon (FC) factors for the solvent modes. In that case the solvent reorganization energy is the amount of vibrational excitation imparted to the solvent when converting from the reactant to the product equilibrium geometry. As $-\Delta G_0$ becomes less than or greater than λ_S, the efficiency or rate of reaction decreases. The latter condition is called the Marcus inverted region. Experimentally, there is very little evidence of a Marcus inverted region.[17] Rates of electron transfer and proton transfer reactions tend to reach plateau levels rather than decrease in the inverted region. This behavior is thought to be due to the coupling of inter and intramolecular vibrations of frequencies greater than the solvent modes. Attempts have been made to model these interactions that in essense allow larger exoergicities to proceed efficiently.[18]

The vibrations that couple to the reaction coordinate can be described by FC factors. The vibrations that are important are simply those that are required for the reactant to reach the equilibrium geometry of the product. For the proton transfer reactions considered here, the most important coupling modes are the O-H and H-N vibrations, and the O···N symmetric stretch, as we have described above. Bending modes can also participate, but we know less about them, so we ignore them at this time. Interestingly, if the geometries of reactant and product were known, then all the FC couplings could be determined and the reactant rates modeled with new accuracy. A rule thumb for assessing the Marcus inverted region may then be stated as follows. *If the reactant and product geometries are the same, one should observe a strong inverted region. If the geometries*

are different, indicating product vibrational excitation, the inverted region should be less apparent.

The premise that product vibrations modify the Marcus inverted region is difficult to test in condensed-phase systems because of the thermal average of energy states. As we have shown above, the tunneling probability is inherently a state-to-state property. Theories typically treat these states classically because experiments cannot resolve the state-to-state processes; however this treatment fails to uncover the fundamental physics. The state-to-state tunneling rates outlined above and discussed in greater detail elsewhere[8] were formulated to model cluster experiments where state-to-state processes can be followed. The mode-specific measurements of proton transfer in dimers by Fuke, Kaya, et al.,[13] discussed above, are an important step toward testing these concepts.

Another outcome of our state-to-state tunneling model is the prediction of a structured dependence of k with ΔG_0 for clusters in the inverted region. The effect is strongest for single-vibronic level excitation, particularly for the vibrationless level. In Fig. 4 are calculations of the product density of states, which is to say the vibrations of the product that will be excited by proton transfer. The stick figures, Figs. 4a,a' represent the FC factors for Q_N and q_H product excitation for an assumed geometry change (or vibrational reorganization energy λ_N and λ_H, respectively). For vibrationless excitation of the reactant $<m_N,m_H| = <0,0|$, the FC distribution in the product is very structured. Consequently, k, which is proportional to the vibrational overlaps, will also vary with ΔG_0 in a similar manner. For overtone excitation of Q_N (for example $<m_N,m_H| = <2,0|$), the FC distribution is more oscillatory. The FC envelope is outlined by curves b,b'. If we convolve a classical solvent mode distribution using a Marcus-Boltzmann function at 300K, then the structure is smoothed out as seen in by curves c,c'. For a true thermal sample, a distribution of reactant vibrations would be populated and the oscillations in the density of states would average out. In clusters, however, the oscillatory nature of k vs ΔG_0 should persist. Now there is no convenient way to vary the ΔG_0 without affecting other properties of the clusters, however, a series of well controlled experiments might reveal the effect predicted here.

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