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The role of solvent and vibrations on proton tunneling in clusters

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Clusters are an important medium for studying properties of the bulk on an atomic or molecular level and for understanding departures from bulk-phase behavior as the system size approaches the single-molecule gas-phase limit. In this paper we investigate the role of solvent vibrations on proton tunneling by comparing emerging theories of tunneling in clusters to recent time-resolved measurements. Our ultimate goal is to develop a theory that is applicable to both the cluster and bulk-phase limits.

These discussions focus on excited-state proton transfer reactions (ESPT) of the form

$$ROH^* \cdots B_n \underset{k}{\longrightarrow} [RO^{*-} \cdots H^+B_n]_{ur} \underset{k_s}{\longrightarrow} [RO^{*-} \cdots H^+B_n]_r$$

where ROH is an aromatic acid (e.g., 1- and 2-naphthol, and phenol), B is a base-type solvent molecule, and n is the number of solvent molecules in the cluster. We assume a two-step process involving initial proton transfer followed by solvent reorganization from an unrelaxed ur to a relaxed r configuration. In a typical experiment, a molecular beam of clusters is photoexcited by a pump pulse and the evolution of reactant and product is monitored by a variably-delayed probe pulse using multiphoton ionization. Measurements are conducted by mass spectrometry or photoelectron spectroscopy.[1–3] The following observations summarize our understanding of ESPT in clusters:

(1) A distinct minimum cluster size is evident for ESPT, which is explained by a free energy $\Delta G_{0,n}$ that decreases in discrete steps for small values of n.[1–6] The reaction threshold for $PhOH(NH_3)_n$ occurs at $n = 5$ as observed in Fig. 1.[1,3] The onset occurs at $n = 3$ for 1-$NpOH(NH_3)_n$, as measured by Zewail *et al.*[4] and Kelley and Bernstein *et al.*,[5] and is due to the greater acidity of 1-NpOH relative to PhOH. In both cases, the reaction rate is fairly constant with increasing n.

(2) The measured rates of ESPT are relatively slow and increase with energy suggesting a barrier process.[1–5] The potential energy diagram in Fig. 1 indicates that the proton transfer state derives from a high-lying charge-transfer state of phenol that is stabilized by solvent molecules. A barrier arises from a surface crossing.

(3) A tunneling mechanism is evident by a strong proton/deuteron isotope effect for 1-NpOH[5] and PhOH[1] in $(NH_3)_n$. In phenol/ammonia at 2500 cm^{-1} vibrational energy the ESPT lifetimes for $n = 5$ and 6 range from 1–2.5 ns for deutero clusters versus about 60 ps for the protio clusters.[2] The observation of ESPT from the vibrationless levels of 1-$NpOH(NH_3)_n$ also supports a tunneling mechanism.[4,5]

(4) The proton is strongly coupled to product and solvent vibrational modes as evidenced by a large structural change that occurs after proton transfer. In time-resolved experiments using mass spectrometry and photoelectron spectroscopy, we measured a reorganization time of 300 ps and a reorganization energy of about 0.5 eV.[3]

Concerning proton tunneling models for clusters, Hineman *et al.* (HBKB)[5] considered a bound-to-continuum proton transition while we adopted a solvent-activated model[7] involving a bound-to-bound proton transition.[2] Recently, we extended the solvent-activated model to include coupling of the reaction coordinate to a manifold of product vibrations. The HBKB model, by assuming

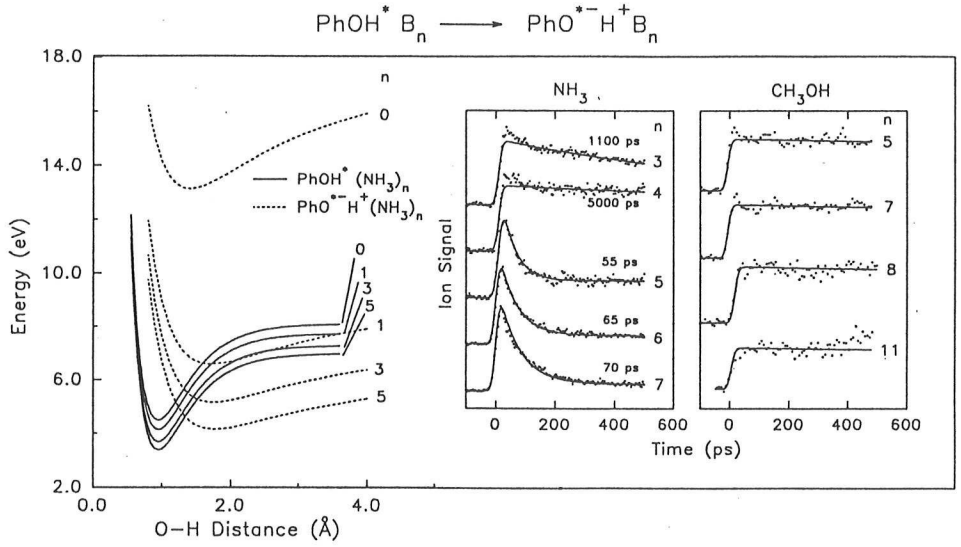

Figure 1. Approximate $PhOH(NH_3)_n$ cluster potential energy curves for the reactive PhO–H coordinate. Insert shows observed lifetime of the reactant $PhOH^*B_n$ (as measured by $PhOH^+B_n$ detection) in solvent clusters $(NH_3)_n$ and $(CH_3OH)_n$ at 2500 cm^{-1} internal energy.

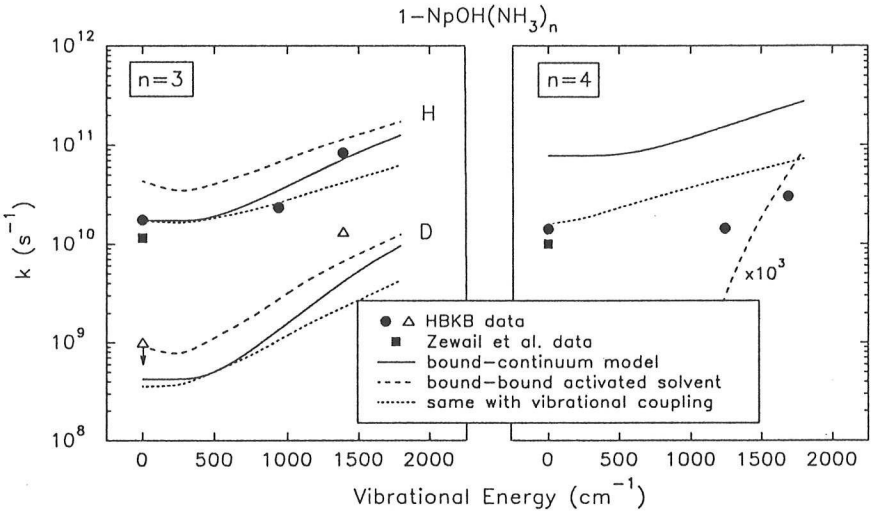

Figure 2. Calculated energy dependence of k by the three models of tunneling and comparison to measurements for 1-$NpOH(NH_3)_n$ and 1-$NpOD(ND_3)_n$. See Ref. 2 for details,

a continuum of product states, does not predict a rate dependence on ΔG_0, other than that due to changes in the O–H barrier. The activated solvent model predicts a steep dependence of k on ΔG_0 and an exaggerated inverted region. The inverted region becomes less severe when vibrational coupling is included. Our treatment of the manifold of product accepting states is based on a Franck-Condon treatment common to radiationless transition and resembles a structured quasicontinuum.[2]

Calculated results are compared to experiment in Figs. 2 and 3. The HBKB model agrees well with the vibrational energy dependence of k for 1-$NpOH(NH_3)_n$ and 1-$NpOD(ND_3)_n$. However, it is unsuccessful in predicting the relative rate for $n = 3$ versus $n = 4$,[2,5] due to the use of a product continuum, which assumes that k is independent of ΔG_0. The bound-bound tunneling models, on the other hand, predict a strong dependence of k on ΔG_0. For $n = 3$ in Fig. 2, the solvent-activated bound-bound tunneling model predicts a decrease in $k(E)$ for small E followed by an increase at larger E. The downturn is a peculiarity of the classical solvent model when the solvent barrier is

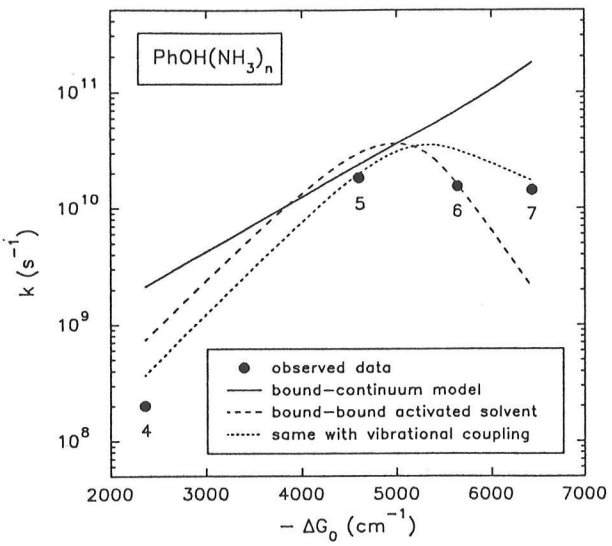

Figure 3. Calculated dependence of k on cluster size n and ΔG_0 by the three models of tunneling and comparison to measurements for $PhOH(NH_3)_n$. See Ref. 2 for details

at a minimum. For $n = 4$, ΔG_0 decreases by about 0.3 eV as determined from stepwise solvation energies reported elsewhere.[1,3] Hence, ΔG_0 enters the inverted region where the activated-solvent model predicts very slow rates and a highly exaggerated $k(E)$ energy dependence. Including the coupling of product vibrations to the O–H coordinate overcomes this problem as illustrated in Fig. 2. A moderate and smoothly varying $k(E)$ energy dependence is obtained.

An important feature to note is that the bound-bound models are in better agreement with the absolute value of k for $n = 4$ better than is the bound-continuum model. This is seen more clearly in Fig. 3 where the calculated results are compared to the measured cluster size dependent rate constants for $PhOH(NH_3)_n$ (Fig. 2). As noted earlier, k is relatively insensitive to n and ΔG_0 for 1-$NpOH(NH_3)_n$ and $PhOH(NH_3)_n$, an observations that at first seemed baffling. The HBKB bound-continuum model predicts an exponentially increasing k with ΔG_0 due to a decrease in the barrier height and width along the O–H coordinate. The activated-solvent models have an additional dependence on ΔG_0 that appears in the solvent activation energy. However, in the absence of product vibrational coupling, the dependence is exaggerated (Fig. 3). With vibrational coupling added to the model, the effect is moderated and more realistic.

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