

Tunneling Mechanism for Excited-State Proton Transfer in Phenol-Ammonia Clusters

Jack A. Syage

The Aerospace Corporation, P.O. Box 92957/M5-754, Los Angeles, California 90009

Received: May 12, 1993; In Final Form: August 11, 1993*

Reaction rate measurements and modeling calculations are presented that support a tunneling mechanism for excited-state proton transfer (ESPT) in phenol-ammonia clusters. Rates of ESPT were measured by picosecond pump-probe resonance-enhanced multiphoton ionization in a molecular beam mass spectrometer. In earlier work on $C_6H_5OH \cdot (NH_3)_n$, we measured size-specific excited-state lifetimes and observed a decrease from 5 ns ($n = 4$) to 65 ps ($n = 5$). Here we report excited-state lifetimes for partially and fully deuterated clusters, $C_6H_5OD \cdot (ND_3)_n$ and $C_6D_5OD \cdot (ND_3)_n$, that are significantly longer (>1 ns for $n > 4$) than for the protiated clusters. The barrier to reaction is due to a crossing between a covalent state and a solvent-stabilized ion-pair state of phenol. A barrier model and tunneling calculations are presented in support of the experimental results.

1. Introduction

In the course of nature, few phenomena play as prominent a role as hydrogen bonding and proton transfer.¹ Biological roles are numerous. Hydrogen bonding is the cornerstone to genetic replication through DNA base pairing. Furthermore, photoinduced excited-state proton transfer (ESPT) has been implicated as a mechanism of transcription error that can lead to loss of genetic information.² The very specific nature of hydrogen bonding and proton transfer also largely accounts for the selectivity of enzymatic catalysis in proteins. In laboratory synthetic chemistry, acid and base conditions are often used to catalyze specific reaction pathways.

Proton- (and electron-) transfer reactions are especially intriguing because they can exhibit quantum-mechanical behavior (in particular barrier tunneling), even in large systems.³⁻⁷ The tunneling probability in condensed-phase systems is strongly dependent on solvent interactions. Static interactions account for the general shape of the potential energy surface and the equilibrium enthalpy of the reaction. Dynamic interactions such as solute-solvent vibrations and fluctuations in solvent orientation and lattice structure modulate the barrier width and the relative energy of the potential wells.

To understand the role of solvent effects on tunneling at the most fundamental level requires a means to study the immediate reactive site under specific conditions of energy and structure. These conditions suggest the use of molecular clusters. Ideally, by adjusting cluster conditions, choosing excitation energies, and employing mass spectrometric analysis, one can measure the effect of single molecules on the properties of small-to-medium-size clusters. These studies may be viewed as a microcanonical approximation of bulk-phase conditions where we control energy, solvent size, and time resolution.

Time-resolved studies of cluster chemistry can be traced back to the work of Felker and Zewail, who measured the picosecond dynamics of hydrogen-bond dissociation for the stepwise solvation of isoquinoline.⁸ Several groups are now investigating real-time dynamics in clusters.⁹⁻²¹ A number of these efforts involve excited-state proton transfer.^{10,17-21} The Zewail group first reported on the 1-naphthol-ammonia system and observed a distinct threshold to reaction at the level of three ammonia solvent molecules.¹⁰ This result was corroborated by Kelley, Bernstein, and co-workers.¹⁷ In a related series of experiments Bruker and Kelley measured proton-transfer rates in small solvent complexes formed in cryogenic argon matrices.²² They observed similar solvent-size dependence for 1-naphthol-ammonia; however, the rates

differed from the isolated clusters formed in molecular beams, presumably due to the polarizability of the Ar matrix.

Our proton-transfer work has focused on the molecule phenol in hydrogen-bonded solvent clusters.¹⁸⁻²⁰ It is interesting to note the difference in the critical solvent size for ESPT for 1-naphthol versus phenol in $(NH_3)_n$, these being $n = 3$ and $n = 5$, respectively. The pK_a^* values of excited state 1-naphthol and phenol are 0.5 and 4.1, respectively, which converts to an enthalpy difference of 0.22 eV.²³ Thus, additional ammonia solvent molecules are required to stabilize ESPT in phenol compared to 1-naphthol. Interestingly, time-averaged experiments on 1-naphthol^{24,25} and on phenol²⁶ in ammonia clusters indicated that both acids exhibit a critical solvent size for ESPT of $n = 4$. These experiments, which provided valuable spectroscopic and dynamic information on ESPT in these clusters, apparently are less suitable than time-resolved experiments for determining the minimum solvent size for inducing ESPT.

A particularly interesting problem is the shape of the reaction barrier along the O-H coordinate, which arises from a surface crossing between a covalent $O-H \cdots B_n$ potential and a solvent stabilized ion-pair $O^- \cdots H^+ B_n$ potential.¹⁸ In this paper, we present time-resolved measurements of ESPT in phenol- d_1 and phenol- d_6 in $(ND_3)_n$ clusters and compare them to the protio case. Because of the very strong dependence of barrier penetration on the reduced mass of an oscillator, tunneling reactions can exhibit very significant isotope effects and provide details about barrier heights and widths. We compare our measured rates to tunneling calculations based on two models: a bound-free potential for proton transition (gas-phase limit) and a bound-bound solvent-activated transition (condensed-phase limit). These models incorporate the dependence of the O $\cdots$ N vibration on the O-H potential¹⁷ and, in the latter case, the dependence of the solvent coordinate on the relative energies of the reactant and product. An interesting outgrowth of this analysis is that tunneling reactions should exhibit unusually pronounced mode-dependent reaction rates for those vibrations that cause modulation of the barrier width.

2. Experimental Section

The picosecond molecular beam apparatus has been described before,¹⁸⁻²¹ hence, only general details are given here. The molecular beam employs a temperature-controlled pulsed supersonic nozzle which serves as the cluster source. The central portion of the free-jet expansion passes through a 1-mm-diameter skimmer to produce a molecular beam of about 4-mm diameter at the ionization region of a time-of-flight mass spectrometer. The acceleration region is based on the three grid design for

* Abstract published in *Advance ACS Abstracts*, November 1, 1993.

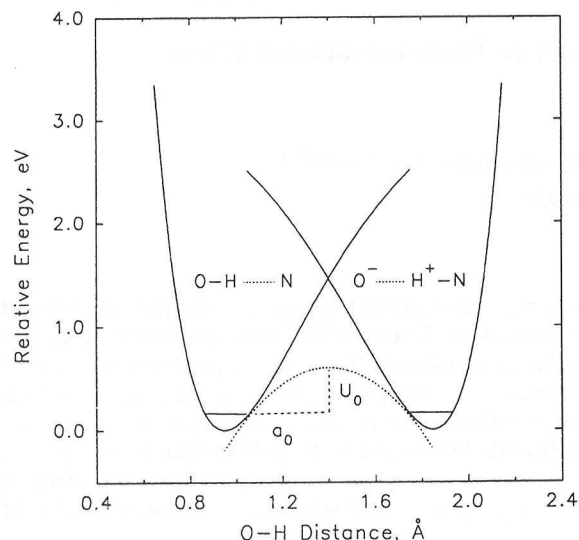


Figure 1. Barrier to ESPT arising from the crossing of a covalent and ion-pair potential. A parabolic barrier, used for calculating tunneling rates, is fitted to the crossing region; a_0 and U_0 are the barrier half-width and height measured from the vibrationless level of O-H.

space focusing. We use 1-cm grid spacings, a 1-m drift tube, and extraction and acceleration fields of 200 and 1800 V/cm, respectively. The ion signal is detected by a dual-microchannel plate detector and recorded using a boxcar gated integrator/averager. The deuterated phenols (Merck Sharpe & Dohme Isotopes, 98 atom % D minimum isotopic purity, used as is) were contained in a sample holder in the pulsed nozzle and heated to about 50 °C. Samples of ND₃, varying in concentration from 1 to 10% in He, were prepared in a 2-L high-pressure cylinder and allowed to flow at about 35 psi over the phenol contained in the pulsed valve. It was necessary to use ND₃ instead of NH₃ to avoid contamination of the deuteriophenols by proton exchange with ammonia. The flow mixture, at a typical backing pressure of 35 psi, was expanded through a nozzle with a 750- μ m-diameter aperture and 60° (full angle) conical throat.

The picosecond laser is based on a pulsed (10 Hz) active/passive mode-locked Nd:YAG laser, which produces output at 532 nm (25-ps pulses), 355 nm (25 ps), and 266 nm (18 ps). Time-resolved spectra were recorded by delaying a probe pulse λ_2 relative to a pump pulse λ_1 using a scanning optical delay line.¹⁸ We refer to the sequence and the delay time t by the designation $\lambda_1-t-\lambda_2$. Calculated curves are fitted to the data using a convolution that assumes a Gaussian-shaped instrument function (typically 25–30 ps, fwhm). A minute deviation from flatness in the particular delay line used in these experiments prevented accurate measurements of long decay times (greater than 1 ns). The deviation is insignificant over short travel distances and, therefore, did not affect short time measurements (less than 200 ps).

3. Background

(3.1) Potential Energy Curves. The potential surface and barrier to proton transfer derives from a curve crossing involving a short-range O-H covalent bonding potential (e.g., S_0 , S_1 , and ground-state cation) and a long-range Coulombic O-H⁺ ion-pair potential.¹⁸ We will examine the potential along three coordinates, the O-H coordinate, q_H , which is the reaction coordinate, the O...N coordinate, Q_N , which affects the barrier properties, and the solvent coordinate, S , which affects the relative energies of reactant and product. We represent the potential along the q_H coordinate in Figure 1. The example shown is for a fixed O...N

distance of 2.8 Å and a fixed solvent coordinate for which the reactant and product energies are isoenergetic. Figure 1 will serve as a starting point for examining the mechanism of tunneling for ESPT in phenol-ammonia clusters. There are three important questions that need to be addressed: (1) what is the splitting at the crossing point, (2) how does the barrier vary with changes in Q_N (e.g., due to O...N symmetric stretch), and (3) how does the O-H potential vary with changes in solvent coordinate S ? These points are discussed in turn.

(1) Juanós i Timoneda and Hynes calculated electronic couplings for the neutral and ion-pair potentials of a model OH-N complex and obtained a value of about 1 eV for O...N distances of 2.8 Å (a calculated coupling of 0.7 eV at 3.0 Å indicates the sensitivity of the coupling to Q_N).⁵ Using this splitting for our potential model leads to a barrier height of 0.4 eV measured from the vibrationless level. We represent the barrier in Figure 1 by a parabolic function that has an equilibrium barrier height and width of U_0 and $2a_0$, respectively. We choose this shape because it simplifies the tunneling calculations described later.

(2) Typical O-H...N linear hydrogen bond distances are about 2.8 Å.²⁷ An early calculation on PhOH-NH₃ predicted minima along the q_H coordinate at 1.0 and 1.8 Å,²⁸ which is consistent with an equilibrium Q_N^0 value of 2.7–2.8 Å assuming typical O-H and N-H bond lengths of 0.95–1.0 Å. More recent determinations of Q_N^0 from spectroscopic measurements of naphthol-NH₃ range from 2.6–2.9 Å.^{29,30} The value of a_0 in Figure 1 is determined to be 0.30 Å based on the spacing between minima of 0.8 Å and the O-H vibrationless amplitude of 0.10 Å.³¹ The point to note is that the barrier width and height depend directly on the Q_N coordinate. For example, the symmetric O...N van der Waals stretch mode will modulate a and U from their equilibrium values, which can lead to enormous enhancements in the tunneling probability during the compression phase of the vibration. This effect is an important part of the tunneling model discussed below.

(3) The potential in Figure 1 assumes a solvent configuration that is fixed such that the minimum energies are the same (we will call this solvent configuration S^*). The equilibrium solvent geometry, however, will certainly be different for the covalent and ion-pair states. Schematic representations of the the O-H potential for equilibrium solvent configurations of the reactant and product, S_r and S_p , respectively, are given in Figure 2a. This picture is important because it implies that proton transfer requires solvent motion to reduce the energy of the product state. A convenient way to represent the solvent configuration energy is to plot the minimum energies of the reactant (covalent) and product (ion-pair) potentials as a function of solvent coordinate S as shown in Figure 2b. This view indicates that there is an activated solvent configuration S^* at energy ΔG^* for bringing the reactant and product minimum energies (or vibrationless levels) into resonance. The importance of this condition for promoting proton tunneling is examined below. The free energy difference $\Delta G_r - \Delta G_0$ is commonly referred to as the solvent reorganization energy λ .

(3.2) Tunneling Model. We examine two views of proton tunneling in clusters. The first is a solution-phase picture that introduces the concept of solvent motion and reorganization energy to facilitate tunneling. This picture is based on the potential model in Figure 2 for solvent activation. Proton tunneling is treated as a bound-bound transition and occurs when the solvent attains a configuration for which the reactant and product states are degenerate. An alternative view of proton tunneling, advanced by Hineman, Bruker, Kelley, and Bernstein (HBKB) for 1-naphthol-ammonia clusters, is to assume that the product potential is unbound (e.g., a gas-phase free-particle dissociation).¹⁷ This strategem removes the restriction for solvent motion to bring two bound states into resonance. The justification given for the bound-free approach is (1) proton transfer occurs from the vibrationless level of cold clusters for which there cannot be significant solvent

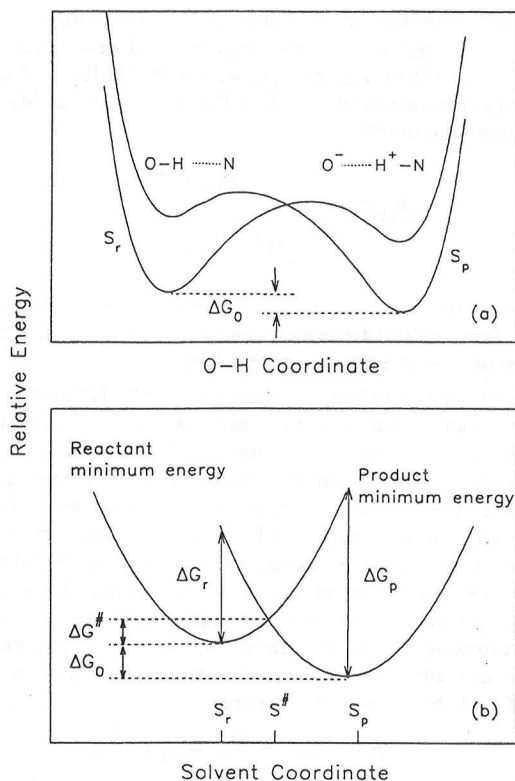


Figure 2. (a) Schematic representation of the potential energy along the O-H coordinate for fixed solvent configurations S_r and S_p . (b) Reactant and product minimum energy as a function of solvent coordinate S . ΔG^* is the free energy of activation for achieving resonance between the reactant and product minimum (vibrationless) energy. ΔG_0 is the free energy of reaction for an equilibrating solvent. ΔG_r and ΔG_p are the free energies of reaction for fixed-solvent configurations S_r and S_p , respectively.

motion and (2) there are a large number of product vibrations, including intermolecular and solvent modes, that couple to the O-H coordinate and that can accept energy corresponding to mismatches between the vibrationless reactant and product states along the O-H coordinate. Although the proton clearly goes to a bound state of the product, the use of a free-particle product potential simplifies the analysis.

Perhaps an acceptable picture that is intermediate to the two just described is to consider a high density of product-bound states (those states that couple to the product N-H bond). The appeal of this picture is that it retains the essence of a solvent-assisted bound-bound transition yet recognizes that the solvent interaction need not be very large, just large enough to shift energies by an amount equal to the inverse of the density of product states coupled to the O-H coordinate. This treatment is really the same as the activated-solvent model of proton transfer, except that the density of product states method conveniently prevents the free energy of solvent activation ΔG^* in Figure 2a from becoming too large.

Tunneling is sensitive to many coordinates of a multidimensional potential surface.⁵⁻⁷ A tractable approach that encompasses the essential features of proton tunneling is to treat the O-H and O...N coordinates, q_H and Q_N , respectively, as quantized motions, and the solvent coordinate as a classical parameter. This model will necessarily introduce parameters that are experimentally ill defined. The objective is not to obtain quantitative agreement with experiment but rather to examine how sensitive tunneling rates are to these different parameters. By exploring the range of results (parameter space), we should be able to test the reasonableness of our potential energy picture. Furthermore, the model should suggest what experimental parameters are worth measuring in future work.

Solvent-activated proton transfer: Borgis and Hynes⁶ and Cukier and Morillo⁷ have shown that in the limit of slow solvent

motion the rate constant for proton tunneling can be expressed as

$$k = \frac{2\pi}{h} C^2 \left(\frac{\pi\beta}{\lambda} \right)^{1/2} \exp[-\beta\Delta G^*] \quad (1)$$

where $2C$ is the tunneling splitting for a symmetric double-well potential. β is defined as $(k_b T + E_{vib}/s)^{-1}$, where T is the initial cluster temperature (k_b is the Boltzmann constant), E_{vib} is the vibrational excitation energy in S_1 , and s is the number of effective degrees of freedom in the cluster that contribute to the heat capacity. We have arranged the terms in eq 1 to resemble a Golden Rule rate equation (i.e., $k = (2\pi/h)C^2\rho$ where ρ is the density of states at some given energy). This suggests the interesting interpretation that the product of the square root and exponential term is a density of states. The condition for slow solvent motion (i.e., slow energy modulation limit by bath fluctuations), for which eq 1 is valid, is $(2\lambda/\beta)^{1/2} \gg h\nu_L$ where ν_L is the inverse of the correlation time for solvent fluctuations. For hydrogen-bonded solvents at low temperature, we equate ν_L to typical intermolecular solvent vibrational frequencies (about 100 cm^{-1}). The left-hand side of the inequality is about 500 cm^{-1} based on values of λ and β estimated later.

The tunneling splitting for an O-H symmetric double-well potential with a parabolic barrier is given by⁴

$$2C = (h\nu_1/\pi) \exp[-\Omega] \quad (2a)$$

where ν_1 is the O-H stretch frequency and

$$\Omega = (\pi^2 a/h)(2mU)^{1/2} \quad (2b)$$

It is worth noting that the tunneling frequency for this case is defined as $\nu_t = 4C/h$,⁴ which allows us to interpret the remaining part of eq 1 as the probability of solvent being in a configuration S^* that gives rise to a tunneling resonance. The reason C also appears in the latter definition is that the effective energy range of coupled solvent accepting modes for proton transfer depends linearly on ν_t based on the uncertainty principle. By a Golden Rule argument, the number of bath states that are active or coupled depends on the strength of the coupling C . Inserting eqs 2 into eq 1 leads to the tunneling rate constant

$$k = \frac{h\nu_1^2}{2\pi} \exp[-2\Omega] \left(\frac{\pi\beta}{\lambda} \right)^{1/2} \exp[-\beta\Delta G^*] \quad (3)$$

The solvent free energy of activation ΔG^* is illustrated in Figure 2b. For parabolic potentials the term is given by

$$\Delta G^* = (\lambda + \Delta G_0)^2/4\lambda \quad (4)$$

where the solvent reorganization energy λ is defined as $\Delta G_r - \Delta G_0$ in Figure 2b. ΔG^* has an interesting dependence on the reaction free energy (driving force) ΔG_0 , which we summarize as follows: (1) $\Delta G_0 = 0$, in which case $\Delta G^* = \lambda/4$, (2) $\Delta G_0 = -\lambda$, in which case $\Delta G^* = 0$, and (3) $\Delta G_0 < -\lambda$, in which case the value of ΔG^* increases again. The latter situation is the so called Marcus "inverted region".³²

Bound-free proton transfer: For reasons discussed earlier, HBKB adopted a bound-free model to explain their tunneling results for 1-naphthol/ammonia clusters. The escape probability for a bound proton separated from a dissociative potential by a parabolic barrier is given by⁴

$$k = \nu_1 \exp[-\Omega] \quad (5)$$

HBKB defined q_H as the reactive coordinate and incorporated the effect of the O...N vibrational coordinate Q_N in modulating the barrier height and width. In so doing, they obtained expressions for $k(E)$ by averaging over the probability of populating ν quanta of the O...N stretch. The integration over

the O...N vibrational wave functions involves the exponential term in eq 5 because of the barrier parameters in the term Ω . The exponential term also appears in the condensed-phase tunneling rate constant eq 3, so the HBKB treatment of Q_N will also be adapted for that case as well. For convenience we define the exponential term as

$$A = \exp[-2\Omega] = \exp[-(2\pi^2 a/h)(2mU)^{1/2}] \quad (6)$$

It is worth noting that by this definition $A = (2C/h\nu_1)^2$.

Averaging over Q_N : The O-H stretch mode, having a frequency of 3500 cm^{-1} ,³³ is not acutely excited in these studies, so tunneling occurs from the origin of the O-H potential. What facilitate tunneling are vibrations that compress the O...N distance, thereby reducing the barrier height and width. For simplicity, we consider only the O...N stretch mode although other vibrations such as the O-H-N bend mode could be important. The O...N stretch has an S_1 frequency of 182 cm^{-1} in PhOH-NH₃ (reduced mass $\mu = 14 \text{ amu}$).³⁴ Assuming the same force constant for PhOH-(NH₃)₅ and assuming a rigid solvent, leads to a frequency of 102 cm^{-1} ($\mu = 44 \text{ amu}$).³⁵ However, the solvent will most likely deform somewhat in response to the O-N stretch thus decreasing the effective reduced mass (this assumes that there are solvent modes of higher frequency than the O-N frequency). We choose an intermediate frequency value of 140 cm^{-1} , which corresponds to an effective reduced mass of 23 amu . The tunneling rate is not excessively sensitive to moderate variations in this value.

Following HBKB, we evaluate A as a function of O...N distance and integrate over the wavefunction for ν quanta of O...N stretch:

$$A(\nu) = \langle \psi_\nu | A(x) | \psi_\nu \rangle = \int_{-\infty}^{\infty} A(x) f_\nu(x) dx \quad (7)$$

where x is the deviation of the O...N distance from the equilibrium position. The $A(x)$ dependence derives from the $a(x)$ and $U(x)$ dependences, which are easily evaluated for a parabolic barrier.^{17,36} The O...N vibrational amplitude probability $f_\nu(x)$ is given by

$$f_\nu(x) = |\psi_\nu|^2 = |N_\nu H_\nu(\alpha^{1/2}x) \exp(-\alpha x^2/2)|^2 \quad (8)$$

where

$$N_\nu = \left[\frac{1}{2^\nu \nu!} \left(\frac{\alpha}{\pi} \right)^{1/2} \right]^{1/2} \quad (9a)$$

$$\alpha = \frac{4\pi^2 \mu \nu_2}{h} \quad (9b)$$

and ν_2 is the O...N oscillator frequency and $H_\nu(\alpha^{1/2}x)$ are the Hermite polynomials. Substituting eqs 6, 8, and 9 into eq 7 gives the expression

$$A(\nu) = \gamma N_\nu^2 \int_{-\infty}^{\infty} H_\nu(\alpha^{1/2}x)^2 \exp(-px^2 + 2qx) dx \quad (10)$$

where

$$\gamma = \exp(2qa_0) \quad (11a)$$

$$q = (\pi^2/h)(2mU_0)^{1/2} \quad (11b)$$

$$p = \alpha - q/2a_0 \quad (11c)$$

Equation 10 can be integrated analytically; however, the computation becomes extremely tedious for increasing ν because of the squared Hermite polynomial term. We used a symbolic algebra routine to evaluate eq 10 up to $\nu = 5$.^{37,38}

The value $A(E)$ at energy E is then determined by the expression

$$A(E) = \sum_\nu P_\nu(E) A(\nu) \quad (12)$$

where $P_\nu(E)$ is the population probability of ν quanta of O...N stretch at energy E . $P_\nu(E)$ can be evaluated by direct counting methods; however, the frequencies for the intermolecular vdW

modes, which will dominate the density of states, are not all known. Because these modes are of low frequency and we are interested in high total vibrational energy, we follow HBKB and use a classical expression for calculating $P_\nu(E)$ based on the Marcus-Rice approximation³⁹

$$P_\nu(E) = \frac{[(E - E_\nu)/E]^{s-2}}{\sum_\nu [(E - E_\nu)/E]^{s-2}} \quad (13)$$

where E_ν is the energy of the specific vdW mode (i.e., the O...N stretch fundamental frequency) and s as defined earlier is the number of effective degrees of freedom.

Estimation of tunneling parameters: The O-H potential and barrier parameters have already been examined in section 3.1. Here we examine solvent parameters. We assume that only intermolecular vibrational and rotational (or reorientational) modes are of sufficiently low frequency to be effective oscillators in low temperature clusters and, therefore, define $s = 6n - 6$, where n is the number of molecules in the cluster.⁴⁰ All other modes (i.e., intramolecular modes) are assumed to be of significantly higher frequency to be significantly less important to the effective density of states. For the cluster size PhOH-(NH₃)₅, one obtains $s = 30$. The average thermal energy is $\langle E_{th} \rangle = sk_bT$ and the average total energy E is

$$E = \langle E_{th} \rangle + E_{vib} = s/\beta \quad (14)$$

The value of k_bT can be estimated using Klotz's evaporative cooling model,⁴¹ which holds that $k_bT = D_0/\gamma$, where D_0 is the monomer-cluster bond energy and γ is called the Gspann parameter and has a nearly universal value of about 25.⁴² For the medium-size clusters studied here ($n \geq 5$) we assume a value of $D_0 = 1200 \text{ cm}^{-1}$ corresponding to the binding energy of the neutral (NH₃)₂ dimer.⁴³ The resulting value of $k_bT = 50 \text{ cm}^{-1}$ (or about 75 K) assumes that clusters cool only evaporatively, when in fact collisional cooling can be quite effective. Therefore, we consider the cluster temperature obtained by the Klotz evaporative cooling model to be an upper limit and use half this value (i.e., $k_bT = 25 \text{ cm}^{-1}$) as an input for calculations. At these low temperatures, the calculated tunneling rates are not overly sensitive to k_bT .

The solvent reorganization energy λ is an important parameter that is difficult to determine. We expect it to be relatively small since the equilibrium solvent configuration for reactant and product should be similar (i.e., lie in a similar region of Franck-Condon space). Assuming that several quanta of intermolecular modes (typically $\sim 100 \text{ cm}^{-1}$ each) are necessary to cause an interchange between reactant and product solvent configuration, we estimate a lower limit of $\lambda \geq 1000 \text{ cm}^{-1}$. This is consistent with values of λ determined from spectral data for ESPT of 3-hydroxyflavone in polar liquids.⁴⁴ An upper limit for λ is estimated from time-resolved shifts in the photoelectron spectrum of phenol-ammonia clusters of about 4000 cm^{-1} .²⁰ For our calculations we choose a value of $\lambda = 2000 \text{ cm}^{-1}$. The reaction free energy ΔG_0 is assumed to be slightly exothermic for the $n = 5$ cluster given the fact that the $n = 4$ cluster size is unreactive. We assign ΔG_0 a value of -1000 cm^{-1} based on the incremental increase in the proton affinity of the ammonia cluster from $n = 4$ to $n = 5$.¹⁸

4. Results and Discussion

(4.1) Experimental Measurements. The time dependence of excited-state reactant PhOH*(NH₃)_n is measured by detecting the parent-ion signal PhOH⁺(NH₃)_n as a function of the pump-probe delay time t . As discussed in earlier work, ionization of excited-state reactant leads almost exclusively to parent ion, whereas ionization of excited-state product PhO⁺-H⁺(NH₃)_n

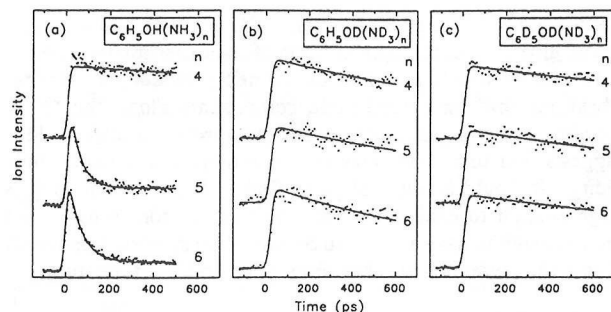


Figure 3. Effect of deuteration on the excited-state lifetime of $\text{PhOH}^+(\text{NH}_3)_n$ ($n = 4-6$). The data were fitted to single-exponential functions with the following lifetimes: (a) 5.0 ns ($n = 4$), 55 ps ($n = 5$), 65 ps ($n = 6$); (b) 1.5 ns ($n = 4$), 1.5 ns ($n = 5$), 1.1 ns ($n = 6$); (c) 2.4 ns ($n = 4$), 2.0 ns ($n = 5$), 2.4 ns ($n = 6$).

leads to extensive dissociative ionization to $\text{PhO} + \text{H}^+(\text{NH}_3)_{n-m} + m(\text{NH}_3)$.^{18,19} The parent-ion signal decays by the rate of ESPT, but to a plateau level determined by the fraction of product cluster ion that does not dissociate upon ionization. For 532-nm ionization (a two-photon process), the undissociated fraction is small, so the parent-ion signal decays to a level near the baseline (Figure 2a). For lower energy ionization, the plateau level is higher and the decay is less distinct.^{18,19,45} We expect the above behavior to apply to the deuterated clusters as well, in which case ESPT should be detectable if it occurs.

The measured rates of ESPT in phenol- d_1 and phenol- d_6 in $(\text{ND}_3)_n$ clusters are compared to measurements for phenol- $(\text{NH}_3)_n$ in Figure 3. In the latter case (Figure 3a), a distinct onset to ESPT occurs at $n = 5$ as discussed in detail in previous work.¹⁸ The lifetimes for $n = 5$ and $n = 6$ are about 60 ps. The calculated curves in Figure 3a were fitted to a single-exponential function that decays to a plateau level described above. The deuterated cluster measurements in Figure 3b,c do not show evidence of fast decay for $n > 4$. Instead, lifetimes of about 1.5 and 2.4 ns, respectively, are observed. These curves were fitted to single-exponential decays without including an asymptotic plateau level. Also because of a slight deviation on the long-time behavior introduced by the delay line (cf. Experimental Section), we report these lifetimes to an uncertainty of $\pm 50\%$. Despite the uncertainty, the isotope effect is clearly greater than an order of magnitude, which is strong evidence of a tunneling mechanism.

(4.2) Comparison with Calculations. Calculated tunneling rate constants as a function of vibrational photoexcitation are presented in Figure 4 for the HBKB bound-free gas-phase model (---) and the bound-bound activated-solvent model (—). Experimental data points from the measurements in Figure 3 are included for comparison. The agreement on an absolute scale is good, though probably fortuitous. We have not adjusted any parameters. For example, the barrier values a_0 and U_0 were determined strictly from the best determination of the covalent and ion-pair potentials along the O-H coordinate and the calculated barrier splitting. However, the choice of solvent-related parameters (e.g., λ , ΔG_0 , $k_b T$, s), was somewhat more arbitrary, which if varied by reasonable amounts could have an aggregate effect on k of greater than an order of magnitude.

The tunneling parameters used here differ somewhat from HBKB.¹⁷ We use an O-H fundamental frequency of 3500 cm^{-1} rather than 3000 cm^{-1} based on measurements by the Felker group.³³ We assume an equilibrium barrier half width of $a_0 = 0.30$ Å rather than 0.20 Å. The latter value used by HBKB was based on an O...N equilibrium distance of 2.6 Å reported by Pratt and co-workers for 1-naphthol bound to one ammonia.³⁰ Other reports, however, indicate that this distance may be in the range 2.8–2.9 Å.^{28,29} Finally, because we worked at higher vibrational energy than HBKB, it was necessary for us to include contributions to eq 12 up to $v = 5$.^{37,38} The $P(v)$ distribution for the O...N vibration at $E_{\text{vib}} = 2500$ cm^{-1} was determined from eq

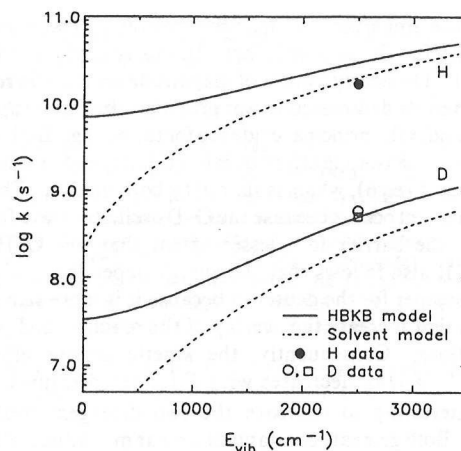


Figure 4. Comparison of calculated tunneling rates to observed rates for deuterated (D) and nondeuterated (H) clusters for $n = 5$ NH_3 molecules. Parameters for calculations are as follows: $\nu_1 = 3500$ cm^{-1} (O-H), 2475 cm^{-1} (O-D); $\nu_2 = 140$ cm^{-1} ; $\mu = 23$ amu; $a_0 = 0.30$ Å (O-H), 0.32 Å (O-D); $U_0 = 0.40$ eV (O-H), 0.53 eV (O-D); $E = 2500$ cm^{-1} ; $s = 30$; $k_b T = 25$ cm^{-1} ; $\lambda = 2000$ cm^{-1} ; $\Delta G_0 = -1000$ cm^{-1} . The values of a_0 and U_0 are different for the O-H and O-D oscillators because the vibrationless levels lie at different energies. The symbols ●, ○, and □, represent the measured lifetimes for $n = 5$ in Figures 3a–c, respectively.

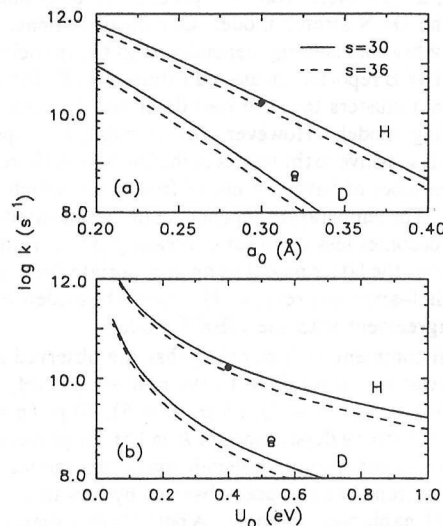


Figure 5. Dependence of calculated k for the activated-solvent model on barrier parameters a_0 and U_0 . Curves are presented for $s = 30$ (—) and 36 (---). See Figure 4 caption for parameters and symbol assignments.

13 to be 0.715, 0.208, 0.057, 0.015, 0.0036, and 0.0008 for $P(v = 0)$ to $P(v = 5)$, respectively). Although the population probability at higher v is very small, the tunneling term $A(v)$ is very large so that the contribution to the overall k from $v = 5$ was for some cases as large as 10%. Finally, HBKB assume sufficiently cold clusters to ignore thermal energy, whereas we have allowed for a modest amount of thermal energy through the $k_b T$ term of E (eq 14).

The sensitivity of k to varying values of a_0 , U_0 , and s is examined in Figure 5. Only small adjustments in these parameters are needed to obtain an excellent match between calculated and measured values of k . However, because of the approximations of the theory, it is probably not justified to extract values of U_0 and a_0 by fitting calculated rates to observed rates. Instead we consider the good agreement to indicate that the potential model in Figure 1 is not unreasonable. The sensitivity of k on values of s are indicated in Figure 5 for $s = 30$ and $s = 36$. The latter value was chosen because it represents the number of intermolecular modes for the next larger cluster size that undergoes ESPT, namely, $\text{PhOH} \cdot (\text{NH}_3)_6$. Hence, the effect on k due to increasing cluster size can be roughly examined.

The more important comparison between experiment and theory concerns the isotope effect. In this regard there is good agreement. The nearly 2 order of magnitude decrease in reaction rate observed for deuterated versus protiated clusters is supported by theory and is the principal evidence for tunneling. Both models predict the same isotope effect because this dependence is due to the function A (eq 6), which is shared by both models. The mass dependent effect occurs because the O—D oscillator wave function penetrates the barrier to a lesser extent than the O—H wave function. It also follows that the energy dependence of k with E will be steeper for the deuteron because it is more sensitive to properties that increase the overlap of the reactant and product wavefunctions. Consequently, the kinetic isotope effect, as measured by k_H/k_D decreases with E (or temperature).

It is interesting to compare the two divergent models of tunneling. Both give rate constants of similar magnitude, although as discussed above variations in the solvent parameters would significantly change the absolute magnitude of k . Both models predict the same isotope effect, but that is because this dependence is due to the function A (eq 6), which both models share. The two models differ greatly, though, in the energy (or temperature) dependence. The activated-solvent model has a much steeper energy dependence owing to the barrier to solvent reconfiguration (Figure 2b). The energy dependence in the HBKB model, on the other hand, arises solely from the probability of populating v quanta of the O...N stretch mode. Our measurements did not explore the vibrational energy dependence on the tunneling rate. However, HBKB reported measured values of $k(E)$ for 1-naphthol-ammonia clusters that are well described by their bound-free tunneling model. However, the calculated temperature dependence is sensitive to the values of the O...N stretch frequency ν_2 and the number of bath degrees of freedom s , which are not well-known. The temperature dependence of the activated-solvent model also becomes less steep for decreasing $\Delta G^\ddagger$. Hence, one cannot rule out the latter model as an appropriate description of the 1-naphthol-ammonia results. However, the evidence to date is in good agreement with the HBKB model.

As a final comment, it is puzzling that the observed rates of ESPT are relatively insensitive to the number of NH_3 solvent molecules [e.g., 55 ps ($n = 5$), 65 ps ($n = 6$), 70 ps ($n = 7$)],¹⁸ considering the strong dependence of k on barrier properties and the significant effect of single molecules on the energetics in small clusters. This trend has also been observed by Zewail et al.¹⁰ and HBKB¹⁷ for 1-naphthol/ammonia. A possible explanation is that there are two opposing effects on k with n that may counteract each other. For increasing n , one expects a lowering of the barrier height, which would increase the values of $A(v)$. However, the density of states increases with n , which shifts the $P(v)$ distribution to lower values of v . The overall effect on $k(E)$ may be small. As an illustration, we consider the case of $\text{PhOH} \cdot (\text{NH}_3)_n$ for $n = 5$ and 6. For a reduction in the barrier height of 0.05 eV [e.g., $U_0 = 0.40$ eV, $s = 30$ ($n = 5$); $U_0 = 0.35$ eV, $s = 36$ ($n = 6$)] one obtains the same calculated lifetime of 16 ps (Figure 5b). Another explanation why the expected increase in k with n is not observed is that the Marcus inverted region may be moderating rate. This behavior is predicted for the condition $\Delta G_0 > -\lambda$, which is likely to apply in small clusters where the stepwise solvation energies of the ion pair are relatively large.

5. Summary and Conclusions

Time-resolved measurements of ESPT in phenol-ammonia^{18,19,45} and naphthol-ammonia clusters^{10,17} are helping to elucidate the properties of the reaction barrier and in particular the importance of tunneling. The principal evidence in support of tunneling in this work is a dramatic slowing of reaction rate for transfer of a deuteron versus a proton. A three-coordinate tunneling model is adapted to a barrier picture composed of the crossing of a Morse-type covalent potential and a solvent-stabilized

Coulombic-type ion-pair potential. Calculations based on this model give a consistent explanation of the experimental results.

It is interesting to note that the tunneling model predicts that vibrations that have amplitude components along the O...N coordinate can significantly accelerate proton transfer. This suggests that tunneling rates should exhibit strong mode specificity. It would be interesting to find a cluster system that is large enough to exhibit solvent-stabilized proton transfer, yet small enough to have a resolved S_1 excitation spectrum, in which to test the possibility of observing mode-specific tunneling.

Acknowledgment. I am grateful to Profs. D. F. Kelley and J. T. Hynes for discussions on tunneling, Prof. P. M. Felker for discussions on structures in clusters, and Dr. T. S. Rose for help in the symbolic integrations. I thank Prof. A. H. Zewail for communicating his latest results on 1-naphthol-ammonia prior to publication. This work was supported by the Aerospace Sponsored Research program.

References and Notes

- (1) Caldin, E.; Gold, V. *Proton-Transfer Reactions*; John Wiley & Sons: New York, 1975.
- (2) Löwdin, P. O. *Adv. Quantum Chem.* **1966**, *2*, 213.
- (3) Rentzepis, R. M.; Barbara, P. E. *Adv. Chem. Phys.* **1981**, *47*, 627.
- (4) Bell, R. P. *The Tunnel Effect in Chemistry*; Chapman-Hall: New York, 1980; Chapter 2.
- (5) Juanós i Timoneda, J.; Hynes, J. T. *J. Phys. Chem.* **1991**, *95*, 10431.
- (6) Borgis, D. C.; Lee, S.; Hynes, J. T. *Chem. Phys. Lett.* **1989**, *162*, 19.
- (7) Borgis, D. C.; Hynes, J. T. *Chem. Phys.* **1993**, *170*, 315.
- (8) Borgis, D. C.; Hynes, J. T. *J. Chem. Phys.* **1991**, *94*, 3619.
- (9) Cukier, R. I.; Morillo, M. J. *Chem. Phys.* **1990**, *91*, 857.
- (10) Morillo, M.; Cukier, R. I. *J. Chem. Phys.* **1990**, *92*, 4833.
- (11) Makri, N.; Miller, W. H. *J. Chem. Phys.* **1989**, *91*, 4026.
- (12) Felker, P. M.; Zewail, A. H. *Chem. Phys. Lett.* **1983**, *94*, 454.
- (13) Willberg, D. M.; Gutmann, M.; Breen, J. J.; Zewail, A. H. *J. Chem. Phys.* **1992**, *96*, 198.
- (14) Gutmann, M.; Willberg, D. M.; Zewail, A. H. *J. Chem. Phys.* **1992**, *97*, 8037, 8048.
- (15) Breen, J. J.; Peng, L. W.; Willberg, D. M.; Heikal, A.; Cong, P.; Zewail, A. H. *J. Chem. Phys.* **1990**, *92*, 805.
- (16) Ray, D.; Levinger, N. E.; Papanikolas, J. M.; Lineberger, W. C. *J. Chem. Phys.* **1989**, *91*, 6533.
- (17) Papanikolas, J. M.; Gord, J. R.; Levinger, N. E.; Ray, D.; Vorsa, V.; Lineberger, W. C. *J. Phys. Chem.* **1991**, *95*, 8028.
- (18) Cassasa, M. P.; Stephenson, J. C.; King, D. S. *J. Chem. Phys.* **1988**, *89*, 1966.
- (19) Fuke, K.; Keizo, K.; Misaizu, F.; Kaya, K. *J. Chem. Phys.* **1991**, *95*, 4074.
- (20) Baumert, T.; Röttgermann, C.; Rothenfusser, C.; Thalweiser, R.; Weiss, V.; Gerger, G. *Phys. Rev. Lett.* **1992**, *69*, 1512.
- (21) Sipior, J.; Sulkes, M. *J. Chem. Phys.* **1988**, *88*, 6146.
- (22) Teh, C. K.; Sipior, J.; Sulkes, M. *J. Phys. Chem.* **1989**, *93*, 5393.
- (23) Arnold, S.; Sulkes, M. *J. Phys. Chem.* **1992**, *96*, 4768.
- (24) Wittmeyer, S. A.; Kazishka, A. J.; Topp, M. R. *Chem. Phys. Lett.* **1989**, *154*, 1.
- (25) Kazishka, A. J.; Shchuka, M. I.; Wittmeyer, S. A.; Topp, M. R. *J. Phys. Chem.* **1991**, *95*, 3663.
- (26) Wei, S.; Purnell, J.; Buzza, S. A.; Stanley, R. J.; Castleman, Jr., A. W. *J. Chem. Phys.* **1992**, *97*, 9480.
- (27) Hineman, M. F.; Brucker, G. A.; Kelley, D. F.; Bernstein, E. R. *J. Chem. Phys.* **1992**, *97*, 3341.
- (28) Syage, J. A.; Steadman, J. J. *J. Chem. Phys.* **1991**, *95*, 2497.
- (29) Steadman, J.; Syage, J. A. *J. Chem. Phys.* **1990**, *92*, 4630.
- (30) Steadman, J.; Syage, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6786.
- (31) Steadman, J.; Syage, J. A. *J. Phys. Chem.* **1991**, *95*, 10326.
- (32) Syage, J. A.; Steadman, J. J. *Phys. Chem.* **1992**, *96*, 9606.
- (33) Syage, J. A. *Chem. Phys. Lett.* **1993**, *202*, 227.
- (34) Syage, J. A.; Steadman, J. J. *Chem. Phys. Lett.* **1990**, *166*, 159.
- (35) Syage, J. A. *Ultrafast Spectroscopy in Chemical Systems*; Simon, J. D., Ed.; Kluwer Academic Press: New York, in press.
- (36) Brucker, G. A.; Kelley, D. F. *J. Chem. Phys.* **1989**, *90*, 5243.
- (37) Brucker, G. A.; Kelley, D. F. *Chem. Phys. Lett.* **1989**, *136*, 213.
- (38) Harris, C. M.; Selinger, B. K. *J. Phys. Chem.* **1980**, *84*, 1366.
- (39) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131.
- (40) Cheshnovsky, O.; Leutwyler, S. *J. Chem. Phys.* **1988**, *88*, 4127.
- (41) Knochenmuss, R.; Cheshnovsky, O.; Leutwyler, S. *Chem. Phys. Lett.* **1988**, *144*, 317.
- (42) Droz, T.; Knochenmuss, R.; Leutwyler, S. *J. Chem. Phys.* **1990**, *93*, 4520.
- (43) Jouvet, C.; Lardeux-Dedonder, C.; Richard-Viard, M.; Solgadi, D.; Tramer, A. *J. Phys. Chem.* **1990**, *94*, 5041.
- (44) Solgadi, D.; Jouvet, C.; Tramer, A. *J. Phys. Chem.* **1988**, *92*, 3313.
- (45) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman: San Francisco, 1960.
- (46) Matsuyama, A.; Imamura, A. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2196.
- (47) Connell, L. L.; Ph.D. Thesis, University of California, Los Angeles, 1992.

- (30) Plusquellic, D. F.; Tan, X.-Q.; Pratt, D. W. *J. Chem. Phys.* **1992**, *96*, 8026.
- (31) The amplitude, defined as the maximum deviation from the equilibrium position, is given by $(h/\nu\mu)^{1/2}/2\pi$.
- (32) Marcus, R. A. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7. Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.
- (33) Hartland, G. V.; Henson, B. F.; Venturo, V. A.; Felker, P. M. *J. Phys. Chem.* **1992**, *96*, 1164.
- (34) Mikami, N.; Okabe, A.; Suzuki, I. *J. Phys. Chem.* **1988**, *92*, 1858. Schültz, M.; Bürgi, T.; Leutwyler, S.; Fischer, T. *J. Chem. Phys.* **1993**, *98*, 3763.
- (35) $\nu = (k/\mu)^{1/2}/2\pi$.
- (36) If one assumes that only the amplitude, but not the curvature, of the inverted parabola changes with O...N motion, then it follows that $U(x) = U_0(1 + x/2a_0)^2$ and $a(x) = a_0(1 + x/2a_0)$.
- (37) *Mathematica*; Wolfram Research, Inc.: 100 Trade Center Dr., Champaign, IL 61820-7237. Equations for $v = 1-5$ are available upon request.
- (38) Transcription errors entered into the equations reported by HBKB (Appendix of ref 17). For $v = 2$, line 1, the term $\mu\omega/2\hbar p$ should be $2\mu\omega/\hbar p$ (note that ω equals $2\pi\nu_2$ in this work). For $v = 2$ and $v = 3$, line 2, the numeral 12 should read 24. Also, because a factor of two inadvertently entered into their calculations, the calculated rates reported are half of their correct values.
- (39) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley: New York, 1972.
- (40) Wei, S.; Tzeng, W. B.; Castleman, Jr., A. W. *J. Phys. Chem.* **1991**, *95*, 585.
- (41) Klots, C. E. *J. Chem. Phys.* **1985**, *83*, 5854. Klots, C. E. *Z. Phys. D* **1987**, *5*, 83. Klots, C. E. *Acc. Chem. Res.* **1988**, *21*, 16.
- (42) The term γ derives from an Arrhenius equation $\gamma = \ln A - \ln k_e = D_0/k_bT$, where A is a preexponential factor (typically 10^{15} s^{-1}), k_e is the evaporative rate constant for loss of the last monomer before photoexcitation and is taken to be the inverse of the drift time to the excitation region ($50 \mu\text{s}$ in our case), and D_0 is the activation energy for loss of the last monomer.
- (43) Ceyer, S. T.; Tiedemann, P. W.; Mahan, B. H.; Lee, Y. T. *J. Chem. Phys.* **1979**, *70*, 14. Greer, J. C.; Ahlrichs, R.; Hertel, V. *Chem. Phys.* **1989**, *133*, 191.
- (44) Swinney, T. C.; Kelley, D. F. *J. Chem. Phys.* **1993**, *99*, 211.
- (45) Hineman, M. F.; Kelley, D. F.; Bernstein, E. R. *J. Chem. Phys.* **1993**, *99*, 4533.