

Finally, the method was applied to H₂O and gave 99% of the total binding energy of 10.08 eV at the equilibrium geometry.

These results are of considerable importance for the construction of accurate, economical surfaces for trajectory calculations, and will be described more fully in future publications.

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Photodissociation of partially solvated molecules in beams by the picosecond-jet technique: Hydrogen bond breakage

Peter M. Felker and Ahmed H. Zewail^{a)}

Arthur Amos Noyes Laboratory of Chemical Physics,^{b)} California Institute of Technology, Pasadena, California 91125

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In this communication we wish to report the measurement of photodissociation rates of jet-cooled solute-solvent complexes in various stages of solvation. The observation of fluorescence decays as a function of excess vibrational energy for isoquinoline (IQ), IQ-(methanol)_n, and IQ-(water)_n complexes reveals threshold behavior for the decay rates of 1:1 solute-solvent complexes. The thresholds at ~3 kcal/mol provide new information on the breakage of excited state hydrogen bonds.

Recently, we reported¹ the results of studies on the excitation and fluorescence spectra of jet-cooled IQ, and of jet-cooled IQ-(MeOH)_n and IQ-(water)_n hydrogen bonded complexes ($n=1, 2, \dots$). The studies revealed that IQ excited to the region of its $\pi\pi^*$ origin has a much shorter fluorescence lifetime than IQ-(solvent)_n complexes similarly excited. The interesting behavior of IQ fluorescence lifetime upon complexation suggests the possibility of extracting hydrogen bond dissociation kinetic parameters from the study of rates vs excess vibrational energy.

The characteristics of the picosecond-jet apparatus have been described elsewhere.² Briefly, a cw supersonic jet was formed by expanding 25–30 psi helium seeded with IQ through a 100 μm pinhole into an evacuated chamber ($P < 0.001$ Torr). Solvent vapor was introduced into the nozzle via a system similar to that de-

scribed in Ref. 1. The complexes were characterized by their dispersed fluorescence and excitation spectra, and by the dependence of excitation spectra on solvent concentration. For dispersed fluorescence and decay measurements the frequency-doubled output of a synchronously pumped cavity-dumped dye laser excited the jet. Fluorescence was collected through a monochromator and detected using a fast photomultiplier. Fluorescence excitation spectra were obtained using the frequency-doubled output of a nitrogen laser-pumped dye laser system.

The jet-cooled excitation spectrum of the origin region of IQ upon the addition of small amounts of methanol results in only one prominent band at 31 910 cm^{-1} (corresponding to a red shift of 19 cm^{-1} from the first prominent IQ band) besides those that appear with no methanol present (Fig. 1). This band has been assigned to the excited state origin¹ of an IQ-methanol₁ complex. (At higher methanol concentrations other bands arise in the origin region. These have been assigned to species involving more than one methanol molecule.¹) With water as solvent, a situation almost entirely analogous to that for methanol obtains, except that the excited state origin of the IQ-water₁ complex occurs at 31 933 cm^{-1} .

The fluorescence decay rates of the 1:1 IQ-solvent complexes as a function of excess vibrational energy in their excited states are shown in Fig. 2. The decay

rate for IQ is very fast at all energies for which data were taken.³ On the other hand, the rates for the two complexes both remain fairly steady and slow (compared to bare IQ) until "thresholds" are reached at $\sim 1000 \text{ cm}^{-1}$ excess energy and rapid increases begin.

The activation of an efficient decay channel in both the methanol and water complexes above 1000 cm^{-1} excess energy can be identified with the breakage of excited state hydrogen bonds for several reasons. First, taking the threshold energies as equal to the energies of the excited state hydrogen bonds, the value obtained ($\sim 3 \text{ kcal/mol}$) is close to ground state hydrogen bond enthalpies of similar complexes in solution.^{4,5} Second, our spectroscopic data in the jet pertaining to the hydrogen bond stretching vibration in the methanol species vs the water species indicate that the methanol species is more strongly bound in the ground and excited states than the water one.¹ The decay rate results are consistent with this, as judged by the greater decay rate for the water species at 1182 and 1405 cm^{-1} excess en-

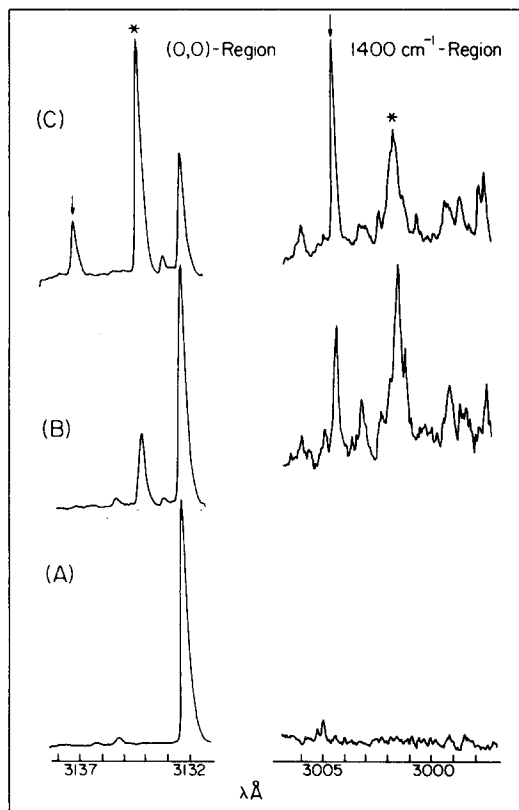


FIG. 1. Excitation spectra of jet-cooled IQ, and IQ-(methanol)_n complexes in the 0,0 and 1400 cm^{-1} regions as a function of methanol concentration. (a) no methanol, (b) relative methanol concentration ($\text{MeOH}_{\text{rel}} = 1$), (c) $\text{MeOH}_{\text{rel}} = 3$. For all spectra: nozzle to laser distance ($\equiv x$) = 3 mm, sample temperature (T) $\sim 65^\circ \text{C}$, fluorescence detection wavelength ($\equiv \lambda_{\text{det}}$) = 3300 \AA with 50 \AA bandpass. Each of the six spectra is scaled to the largest peak in that spectrum on the lower right which is scaled to the largest peak in the spectrum above it. Asterisks mark the 0,0 and 1405 cm^{-1} bands assigned to the 1:1 IQ-MeOH complex. Arrows denote the 31878 cm^{-1} origin and the 1405 cm^{-1} band assigned to the multiply solvated IQ-(MeOH)_n complex mentioned in the text.

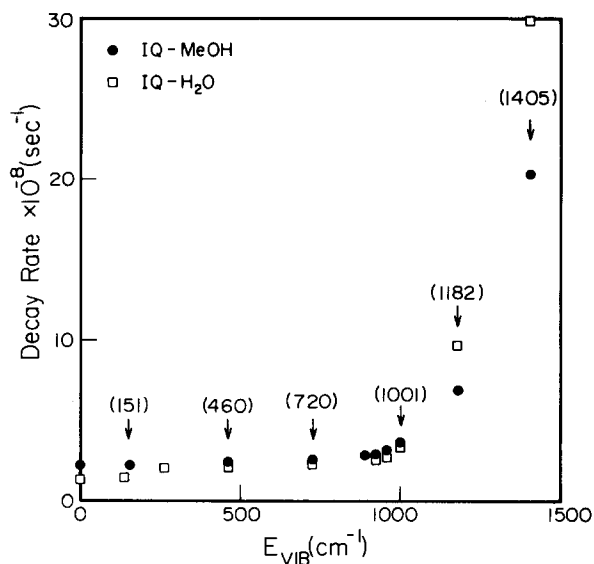


FIG. 2. Fluorescence decay rate vs excited state vibrational energy for 1:1 IQ-MeOH and IQ-H₂O complexes: $\lambda_{\text{det}} = 3300 \text{ \AA}$ with 50 \AA bandpass: $T \sim 65^\circ \text{C}$; $x = 3 \text{ mm}$. For both complexes, no change in rate was observed for the bands at $E_{\text{vib}} = 0$ and 1405 cm^{-1} as x varied from 3 to 6 mm. The numbers in parentheses denote excited state vibrational intervals of the methanol complex. The 460 , 720 , 1001 , 1182 , and 1405 cm^{-1} intervals can be correlated with intervals in the absorption spectrum of IQ vapor (Ref. 6).

ergy. Third, IQ-(methanol)_n and IQ-(water)_n species involving more than one solvent molecule have long fluorescence lifetimes even at $E_{\text{vib}} \sim 1400 \text{ cm}^{-1}$. We refer in particular to the absorptions at 33283 cm^{-1} for methanol (Fig. 1) and at 33306 cm^{-1} for water, which can be assigned to 1405 cm^{-1} vibrational intervals^{1,6} of the multiply-solvated MeOH and water species having origins at 31878 and 31899 cm^{-1} , respectively. For both these bands the observed lifetimes are about 9 ns, in contrast with the 475 and 340 ps measured for the 1:1 complexes at $E_{\text{vib}} = 1405 \text{ cm}^{-1}$. This behavior for the multiply-solvated species is understandable on at least two possible grounds: (1) stabilization of the >N:HOR bond by further complexation; and/or (2) an increase upon further complexation of bound-complex vibrational states relative to activated-complex states for a particular E_{vib} .

To compare our results with theory, preliminary RRKM calculations of the dissociation kinetics of IQ-methanol₁ and IQ-water₁ species were performed. We used, in part, experimentally determined hydrogen bond vibrational frequencies¹ and the algorithm of Hase and Bunker.⁷ The calculated rates were found to closely fit the observed rates at 1182 and 1405 cm^{-1} given activation energies of about 2.9 and 2.8 kcal/mol for the two species, respectively. How this relates to energy flow in the molecules is currently under investigation.

In summary, the ability to study the time-resolved kinetics of bond breakage under isolated molecule conditions can yield important information regarding the energies of bonds and the dependence of the rate of bond breakage upon excess energy for molecules in different

stages of solvation. A full account of this work and work on other species will be published later.

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^{b)} Contribution No. 6768.

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NOTES

Polarization model for NH₃-H-H₂O proton transfer reaction

Carl W. David

Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268

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The polarization model for water¹ was extended to ammonia² and its polymers³ up to and including the hexamer. Haymet and Oxtoby⁴ have recently criticized the polarization model as lacking in theoretical foundation, especially in the intermediate internuclear separation domain. With the appearance of the study by Scheiner⁵ in which the proton transfer reaction between ammonia and water is studied with great accuracy, it becomes possible to test the polarization model accuracy exactly in the domain of distances in which Oxtoby has claimed that the polarization model fails. In this Note, we report the polarization model results, comparable to those of Scheiner, which do indeed indicate the poor agreement with *ab initio* computations.

Prior to undertaking our computation, we were forced to recalibrate the model for NH₃ so that the proton affinity in the model more nearly represented state of the art values. The newer values, cited by Scheiner, indicate that an appropriate value for the proton affinity of ammonia should be 221 kcal/mol. We have therefore recalibrated our polarization model to insure that this value is properly incorporated into the functions (previous calibration was to 201 kcal/mol). All the polarization model functions have been slightly modified in order to achieve agreement with monomer results. The new functions are listed at the end of this note, and we refer to them as the PM(N₃) set of calibration functions.

The removal of a proton from the ammonium cation, and its transfer to a water molecule, involves computations in which the N-H and the O-H distances vary over values far in excess of the bond lengths (typically about an angstrom). Thus the computations of the potential energy of the system NH₃-H-H₂O as the central proton shifts, as a function of the N-O (fixed) separation is a computation directly in the domain under ques-

tion. Contrary to Scheiner, we have fully relaxed the five protons not involved in the "reaction" so that technically our values for the activation barrier for proton transfer from ammonia to water should be lower than his values. They are higher. Figure 1 shows the potential energy profiles obtained at 3.1 and 2.9 Å N-O separation. The activation barrier is significantly higher (about double) that obtained by quantum mechanical computation.

We conclude that the argument of Haymet and Oxtoby,

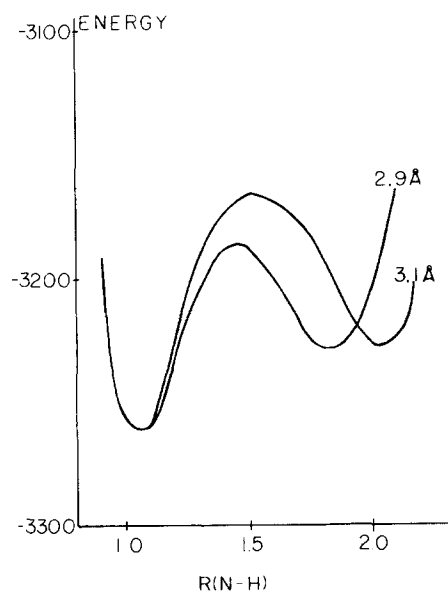


FIG. 1. The potential energy for the transport of a proton from NH₄⁺ to water. The ordinate is the N-H distance, in Å and the two curves correspond to fixed N-O distances of 3.1 and 2.9 Å.