3E3 Vibrational energy relaxation of phenol-water complex studied by picosecond time-resolved IR-UV pump-probe spectroscopy

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It is well-known that the OH stretching vibration is very sensitive to the surrounding environment. The characteristic property is the propensity to form the hydrogen bond with protic solvent, which results in a redshift and spectral broadening of the absorption band. Thus, hydrogen bond alters the chemical property and dynamics i.e. a remarkable acceleration of vibrational energy relaxation (VER). However, such solute-solvent interaction masks the detailed mechanism of energy redistribution. We used jet-cooled phenol-d_0-H_2O/phenol-d_1-D_2O to investigate ground-state VER of the hydrogen-bonded phenolic OH/OD stretching vibration. We applied picosecond IR-UV pump-probe spectroscopy (Fig 1.) and discussed the internal energy redistribution by anharmonic force field and RRKM theories. Hereafter, phenol-d_0-H_2O and phenol-d_1-D_2O are denoted as the hydrogen system and the deuterium system, respectively.

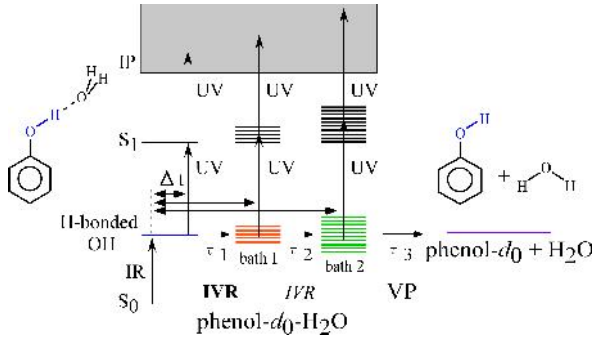

Fig 1. scheme of pump-probe experiment of phenol-d_0-H_2O

The mixture of phenol and water vaporized in the pulsed nozzle are adiabatically expanded into vacuum in He carrier gas and collimated by a conical skimmer to generate a supersonic molecular beam. Two lasers are introduced into a jet-cooled complex coaxially with a certain time delay $\triangle$t. Picosecond IR laser pulse pumps the phenolic OH/OD stretching vibration of the complex. Picosecond UV laser pulse ionizes the complex by R2PI method and monitors the population change of the pumped level and energy-redistributed levels. The lifetime is determined by convoluting the obtained decay curve with a Gauss-shaped laser pulse of 12 ps (HWFM).

We adapted the same three-step relaxation model to explain the relaxation process of the phenol-water complex as other phenol-solvent complexes[1]. Fig 2. shows the transient R2PI spectra of the deuterium system after the IR excitement of the OD stretch at 2600 cm^{-1}. An obvious energy flow is observed that the ion intensity of OD_1^0 transition decreases whereas the broad continuum starts to appear in the higher energy region as the delay time increases. The broad continuum contains all vibronic transitions from the energy-redistributed levels, bath 1 and bath 2. No ion signal is obtained after 280 ps because the complex dissociates by breaking of the hydrogen bond. The time evolution of the OD_1^0 transition is shown in Fig 3a and the convolution of the decay curve yields 14 ps of the **IVR** lifetime (τ_1). Figs 3b-d are the time evolutions of the broad continuum

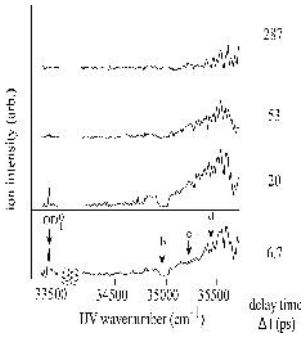

Fig 2. transient R2PI spectra of phenol-d_1-D_2O

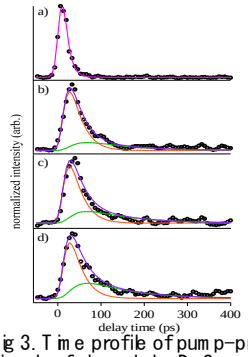

Fig 3. Time profile of pump-probe signals of phenol-d_1-D_2O

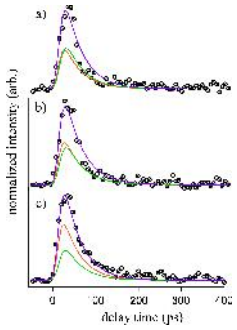

Fig 4. Time profile of pump-probe signals of phenol-d_0-H_2O

measured at three different UV wavenumbers and a fitting of the decay curves gives 24 ps of the *IVR* lifetime (τ_2) and 100 ps of the VP lifetime (τ_3). The same experiment is carried out for the hydrogen system. Because of the laser condition, we used the estimated **IVR** lifetime (τ_1) from the bandwidth, which is 4 ps[2]. Figs 4a-c are the time evolutions of the broad continuum measured at three different UV wavenumbers that yield 6 ps of the *IVR* lifetime (τ_2) and 40 ps of the VP lifetime (τ_3) by the convolution of the decay curves. In short, the hydrogen system has overall shorter lifetimes than the deuterated system as seen in Table 1.

The difference on relaxation lifetime is discussed by anharmonic force field and RRKM theory. Anharmonic analysis emphasizes the accessibility of energy flow among the vibrational modes, that is, the relaxation pathway. The OH stretching vibration is more likely to couple with intra- and intermolecular vibrational modes than the OD stretching vibration. It turns out to be a faster relaxation rate of the internal energy redistribution in the hydrogen system and supports our ps lifetime study. Since VER occurs much faster than the dissociation, we calculated the dissociation lifetime using the RRKM theory. Fig 5. illustrates the potential energy diagram of phenol-water complex along the hydrogen bond coordinate. Although several assumptions such as rigid-rotor model, harmonic oscillator, and equal hydrogen-bond dissociation energy are made, the calculation reproduces the quantitative tendency of τ_3 as seen in Table 1. Most importantly, both complexes are predicted to show RRKM behavior and dissociate only after the IR excitation energy is completely randomized over the whole body of the complex.

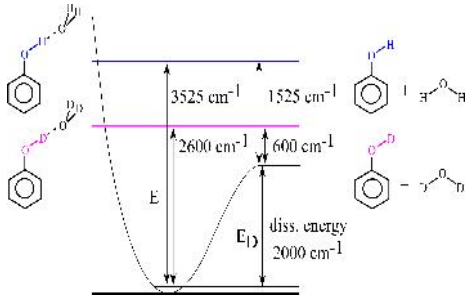

Fig 5. potential energy diagram of phenol-water complex

Table 1: experimentally determined lifetime and RRKM-lifetime of the two phenol-water complexes

complex	stretching mode	frequency (cm^{-1})	excess energy (cm^{-1})	**IVR** τ_1 (ps)	*IVR* τ_2 (ps)	VP τ_3 (ps)	VP τ_3(RRKM) (ps)
phenol-d_0-H_2O	ν_{OH}	3525	1525	4	6	40	100
phenol-d_1-D_2O	ν_{OD}	2600	600	12	24	100	330

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2. A. Doi and N. Mikami, *J. Chem. Phys*. **129**, 154308 (2008).