1F2a

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

○Yasunori Miyazaki[1], Yoshiya Inokuchi[1], Takayuki Ebata[1], Milena Petchovic[2]

1) Grad. Sc. Sci., Hiroshima Univ. 2) Faculty of Phys. Chem., Univ. of Belgrade

It is well-known that the OH stretching mode is very sensitive to surrounding environments. In particular, the formation of hydrogen bonding results in a large redshift and broadening of the OH stretching absorption band. The former is ascribed by reducing the force constant of the OH bond and the latter by vibrational energy relaxation (VER). In the present study, a comparative study of VER between hydrogen and deuterium exchanged monohydrated phenol complexes is investigated in a supersonic molecular beam. The direct time-resolved measurement of energy redistribution from the phenolic OH/OD stretching mode of the phenol-d_0-H_2O/phenol-d_1-D_2O complex is performed by picosecond IR-UV pump-probe spectroscopy (Fig 1).

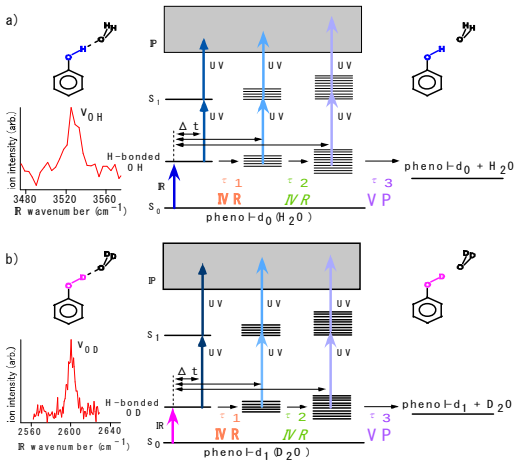

Fig 1: pump-probe experiment

Two complexes follow the same relaxation process that begins with the intramolecular vibrational energy redistribution **IVR** (τ_1) and the intermolecular vibrational energy redistribution *IVR* (τ_2), which give rise to the vibrational predissociation VP (τ_3). The observed lifetime of each component in the hydrogen system is 3 – 4 times shorter than the one in the deuterated system, as seen in Table 1. This difference is discussed by anharmonic force field and RRKM theory. Anharmonic analysis emphasizes that **IVR** and *IVR* are closely related to the relaxation route derived from the specific interaction of intra- and intermolecular vibrational modes between phenol and water. Moreover, the RRKM calculation predicts a different aspect of energy randomization that leads the vibrational predissociation in two complexes.

Table1: fitting parameters of each complex

complex	stretching mode	frequency (cm^{-1})	excess energy (cm^{-1})	**IVR** τ_1 (ps)	*IVR* τ_2 (ps)	VP τ_3 (ps)
phenol-d_0-H_2O	ν_{OH}	3630	1530	4*	<10	25
phenol-d_1-D_2O	ν_{OD}	2600	600	12	24	100

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