

Hydrogen Bond Enhancement of Fermi Resonances Explored with Ultrafast IR Two-Colour Pump-Probe and 2D-IR Spectroscopy

Christian Greve, Rene Costard, Henk Fidder, Erik T.J. Nibbering*

Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Strasse 2A, D-12489 Berlin, Germany
E-mail address: nibberin@mbi-berlin.de

Abstract: Ultrafast polarisation-resolved 2D-IR mapping the fundamental and first overtone N-H stretching manifolds, and two-colour IR pump-probe experiments following transient population dynamics characterize a key role of a Fermi resonance with the NH₂-bending in aniline-dimethylsulfoxide complexes.

OCIS codes: (320.7150) Ultrafast spectroscopy; (300.6250) Spectroscopy, condensed matter; (300.6340) Spectroscopy, infrared

Probing hydrogen stretching modes is a well-established means to explore hydrogen bonds. Couplings of these hydrogen stretching modes to fluctuating solvent degrees of freedom are reflected in the line broadening of hydrogen stretching transitions, which can be grasped by ultrafast 2D-IR spectroscopy. Determination of vibrational couplings with other intramolecular degrees of freedom provides a detailed insight into the potential energy surfaces of hydrogen-bonded systems. These vibrational couplings are reflected in vibrational energy flow pathways, which can be deciphered with ultrafast vibrational pump-probe spectroscopy. Recently, we presented a combined NMR, FT-IR, 2D-IR, and DFT study of adenosine-thymidine (A-T) base pairs in chloroform solution [1]. Based on our findings we concluded that a Fermi resonance of the N-H stretching modes of adenosine with the NH₂-bending degree of freedom results in an enhancement of the NH₂-bending first overtone transition, making it as strong as the N-H stretching transitions.

To further substantiate this interesting feature of this characteristic structural motif of hydrogen-bonded amino-groups, we have chosen the model system of aniline-*d*₅ (An) hydrogen bonded with one or two dimethylsulfoxide (DMSO) molecules in nonpolar CCl₄ (Fig. 1a). Using spectral decomposition of concentration-dependent linear and first overtone spectra of An and DMSO, it is possible to determine the equilibrium constants between An, An···DMSO and An···(DMSO)₂, and with that extract the spectra of the different species (Fig. 1b,c). Whereas An monomer has its symmetric and asymmetric N-H stretching transitions at 3395.5 cm⁻¹ and 3480.5 cm⁻¹, respectively, hydrogen bonding results in frequency downshifting of the N-H stretching transitions for An···DMSO and An···(DMSO)₂. The significant increase in absorption cross section of the fundamental N-H stretching manifold, and the decrease of oscillator strength of the associated first overtone N-H stretching manifold, are apparent in Fig. 1b,c. Although the oscillator strength increase of the N-H stretching modes in the region 3300-3500 cm⁻¹ is impressive, it nevertheless pales in comparison to the immense intensity increase of the overtone transitions near 3200 cm⁻¹.

Fig. 1d shows the 2D-IR spectra of An, An···DMSO and An···(DMSO)₂, for the parallel (ZZZZ) and perpendicular (ZZXX) polarisation geometries, measured with a heterodyne-detection 2D-IR photon echo set-up using the four-wave mixing geometry with diffractive optics. The magnitudes of positive and negative cross peaks compared to the diagonal peaks is on the same order of magnitude. As a result, and – more importantly – in contrast to the strongly overlapping peaks in the linear first overtone spectrum, it is possible to fully map out the vibrational energy levels of the fundamental and first overtone N-H stretching manifolds [2]. The reason for this is the connectivity of positive and negative contributions in a femtosecond 2D-IR spectrum that enables a full determination of Liouville space pathways taken by single-quantum transitions caused by the applied femtosecond IR pulses. The polarisation-resolved 2D-IR spectra support the relative orientations of the various IR transitions. Having established a mapping of the possible IR transitions between the ground, the fundamental and first overtone N-H stretching manifolds, a quantitative analysis of the fundamental, and first overtone N-H stretching manifolds can be achieved using a model vibrational Hamiltonian in a hybrid basis (local N-H stretching modes, normal bending mode; basis set notation $|v(\text{NH})_1, v(\text{NH})_2, \delta\rangle$). A proper description for all species is found using a coupling $J = -51 \text{ cm}^{-1}$ between the two local N-H stretching modes and a Fermi coupling between the NH₂-bending and the N-H stretching modes of $V = -37 \text{ cm}^{-1}$. The diagonal anharmonicity of the local N-H stretching mode is slightly larger for An···DMSO, $\Delta_{\text{HB}} = 88 \text{ cm}^{-1}$, than for An···(DMSO)₂, where it amounts to $\Delta_{\text{HB}} = 80 \text{ cm}^{-1}$, signifying a

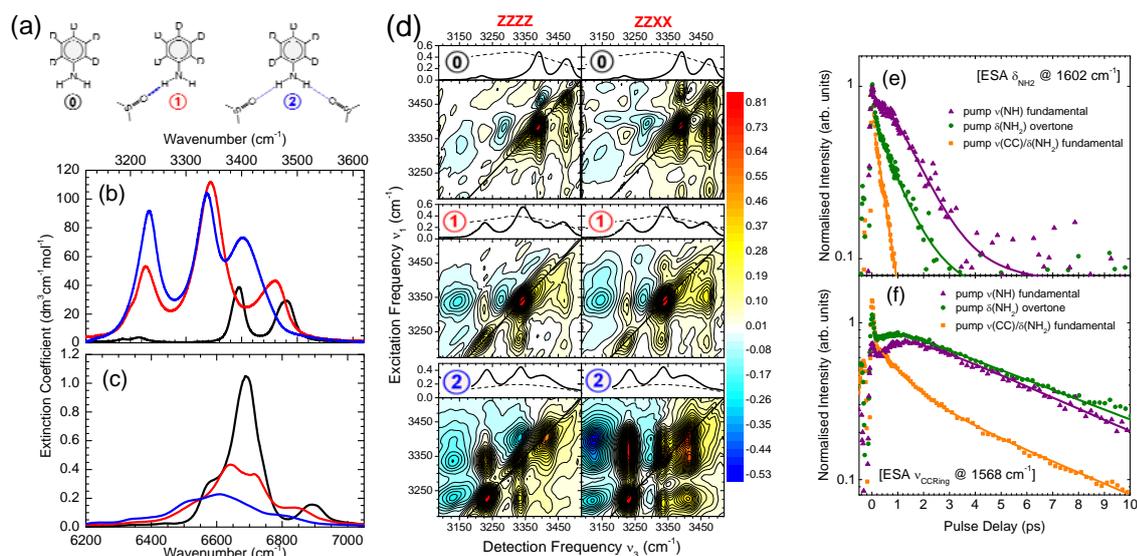


Figure 1: (a) Chemical structures of An, An...DMSO and An...(DMSO)₂; (b,c) linear decomposed spectra of fundamental and first overtone transitions, color code according to chemical structures; (d) 2D-IR spectra for (ZZZZ) and (ZZXX) polarization geometries, linear spectra shown above the 2D-IR spectra; (e,f) transient pump-probe signals of the NH₂-bending and C=C ring stretching modes of An...(DMSO)₂ for different excitation conditions.

slightly stronger hydrogen bond in single hydrogen-bonded An...DMSO than the individual hydrogen bonds in the double-hydrogen bonded An...(DMSO)₂. From this analysis using the hybrid basis set we can make clear why a symmetrized N-H stretching representation $|v(\text{NH})_s, v(\text{NH})_{as}\rangle$ is more appropriate for An and An...(DMSO)₂, and that a local mode representation $|v(\text{NH})_f, v(\text{NH})_b\rangle$ makes more sense for An...DMSO. In addition, the nature of the eigenstates changes for the first overtone manifold as well due to a different degree of interplay of intermode couplings and diagonal anharmonicities. A similar observation was found for adenosine monomer [3].

Fermi resonances with bending overtones have been postulated to play a key role in the vibrational energy redistribution of hydrogen stretching oscillators, ranging from C-H stretching modes in organic molecules [4] to the O-H stretching modes in liquid water [5]. Using single and two-colour pump-probe measurements we have investigated the population kinetics of the N-H stretching manifold as well as the C=C ring mode at 1573 cm⁻¹, and the NH₂-bending band located in the range of 1617-1641 cm⁻¹. The N-H stretching lifetime is 5.5 ps in free An, and shortens to 0.6-0.9 ps in An...(DMSO)₂. Such a drastic lifetime shortening is not found for the NH₂-bending mode fundamental, which decreases from 0.6 ps in An to 0.44 ps in An...(DMSO)₂. Interestingly, both the C=C ring mode and the NH₂-bending mode show a delayed rise in red-shifted transient absorption when the pump pulse excites the Fermi resonance enhanced NH₂-bending overtone, which becomes even more accentuated when the initially excited modes are the N-H stretching transitions. These findings strongly suggest a dominant vibrational energy flow pathway scenario from the fundamental N-H stretching via Fermi resonances involving the NH₂-bending mode to the fundamental NH₂-bending and the C=C ring stretching states.

References

- [1] C. Greve, N. K. Preketes, H. Fidder, R. Costard, B. Koeppel, I. A. Heisler, S. Mukamel, F. Temps, E. T. J. Nibbering and T. Elsaesser, "N-H stretching excitations in adenosine-thymidine base pairs in solution: Pair geometries, infrared line shapes and ultrafast vibrational dynamics," *J. Phys. Chem. A* **117**, 594-606 (2013).
- [2] C. Greve, E. T. J. Nibbering and H. Fidder, "Hydrogen bonding induced enhancement of Fermi resonances: A linear IR and nonlinear 2D-IR study of aniline-d₅," *J. Phys. Chem. B* **117**, 15843-15855 (2013).
- [3] C. Greve, N. K. Preketes, R. Costard, B. Koeppel, H. Fidder, E. T. J. Nibbering, F. Temps, S. Mukamel and T. Elsaesser, "N-H stretching modes of adenosine monomer in solution studied by ultrafast nonlinear infrared spectroscopy and ab-initio calculations," *J. Phys. Chem. A* **116**, 7636-7644 (2012).
- [4] D. Dlott, "Vibrational energy redistribution in polyatomic liquids: 3D infrared-Raman spectroscopy," *Chem. Phys.* **266**, 149-166 (2001).
- [5] S. Ashihara, N. Huse, A. Espagne, E. T. J. Nibbering and T. Elsaesser, "Ultrafast structural dynamics of water induced by dissipation of vibrational energy," *J. Phys. Chem. A* **111**, 743-746 (2007).