Supporting Information

Correlating Infrared and X-ray Absorption Energies for Molecular-Level Insight into Hydrogen Bond Making and Breaking in Solution

Mirabelle Prémont-Schwarz†, Simon Schreck‡||, Marcella Iannuzzi§, Erik T. J. Nibbering†, Michael Odelius#, Philippe Wernet‡

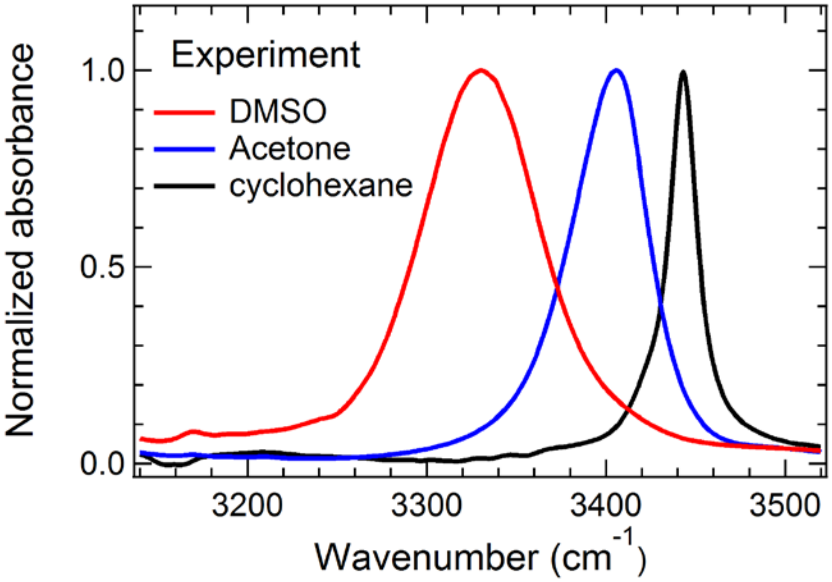
† Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2 A, 12489 Berlin, Germany

‡ Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Albert-Einstein-Str. 15, 12489 Berlin, Germany

|| Institut für Physik und Astronomie, Universität Potsdam, Karl-Liebknecht-Strasse 24-25, 14476 Potsdam, Germany

§ Institute of Physical Chemistry, University of Zurich, Winterthurerstr. 190, CH-8057 Zurich, Switzerland

Department of Physics, Stockholm University, AlbaNova University Center, 106 91 Stockholm, Sweden



Supporting Figure S1: Measured infrared absorption spectra in the N-H stretching region of N-methylaniline (NMA) in DMSO, acetone and cyclohexane.

For comparison of the calculated to the experimental IR absorption spectra we have shifted the calculated spectra by aligning the calculated frequency of the isolated NMA molecule, 3610.3 cm^{-1}, with the value from the cyclohexane solution, 3442.0 cm^{-1}, shown in Fig. S1.

Sampling of configurations from the ab initio molecular dynamics simulations

For dynamical sampling, we extracted 100 configurations regularly distributed over each of the ab initio molecular dynamics simulations of N-methylaniline, NMA, in DMSO or acetone. In addition, a short sequence of configurations was studied in detail to investigate the spectral response to a hydrogen-bond exchange. All calculations were based on a density functional formalism. For the x-ray spectrum simulations presented in the main text, we used the half-core-hole, HCH, transition potential method (72) as implemented in the fully periodic simulation models in CP2K. For comparison, we also performed XAS simulations of clusters with the HCH method in StoBe (73) and the TDDFT method in ORCA (74). Also, the IR spectrum calculations in Gaussian09 were performed on clusters.

Clusters of the solvated *NMA* were cut-ouf from the periodic model by including molecules around the solute, which had any atom, apart from hydrogen, within a 5 Å radius of the nitrogen atom in NMA. For the interpretation of the x-ray absorption spectra, we also prepared more restrictive cut-outs from the same configurations including either only the solute, *only NMA*, or the solute and the nearest hydrogen-bond accepting solvent molecule, *NMA+1SOLV.MOL*.

Calculations of IR spectra of the N-H stretching mode

The calculated IR spectra in Fig. 1b reasonably well reproduce the experimental red-shifts observed in Fig. 1a in the paper. However the spectral shapes are too broad. The present model is limited by cluster size, simulation time and the neglect of motional narrowing, but the simulated IR spectra served the purpose of showing that the essential features of the solvation of NMA is captured by the MD simulation as an indication of realistic hydrogen bond environments. Below we also investigate the origin of the red-shifts with the minimal solvation model NMA+1SOLV.MOL.

Calculations of nitrogen K-edge X-ray absorption spectra

In CP2K, we used the BLYP functional and a pseudopotential description, GTH-BLYP in combination with the TZVP-GTH basis set. An all-electron description with the 6-311++G2d2p basis set of the nitrogen atom, enabled the core-level spectrum calculations.

In the StoBe code (73) the Becke Perdew gradient-corrected exchange and correlation functionals (75, 76) were used. The half core-hole transition potential method (72) was used in combination with a double-basis set procedure in which, after convergence, the basis set was augmented with a large, diffuse basis set to better describe Rydberg and continuum states (77). The carbon and hydrogen atoms were described with triple-ζ valence basis sets, including polarization functions, (78) except for the core-excited nitrogen atom, which is described using a flexible IGLO basis set (79). The oxygen and sulfur atoms were described using effective core potentials (80) ECPs in conjunction with a 311/ 211 basis set for the valence electrons for oxygen, and 311/211/1 for sulfur. The ECPs slightly reduces the computational effort, and have little significant effect on the final XA spectrum. The auxiliary basis sets used were 5,2;5,2 for oxygen, and 2,3:2,3 for sulfur and 3,1;3,1 for hydrogen, where the nomenclature NCs , NCspd ; NXCs , NXCspd- indicates the number of s and spd functions used to fit the Coulomb and exchange correlation potentials, respectively.

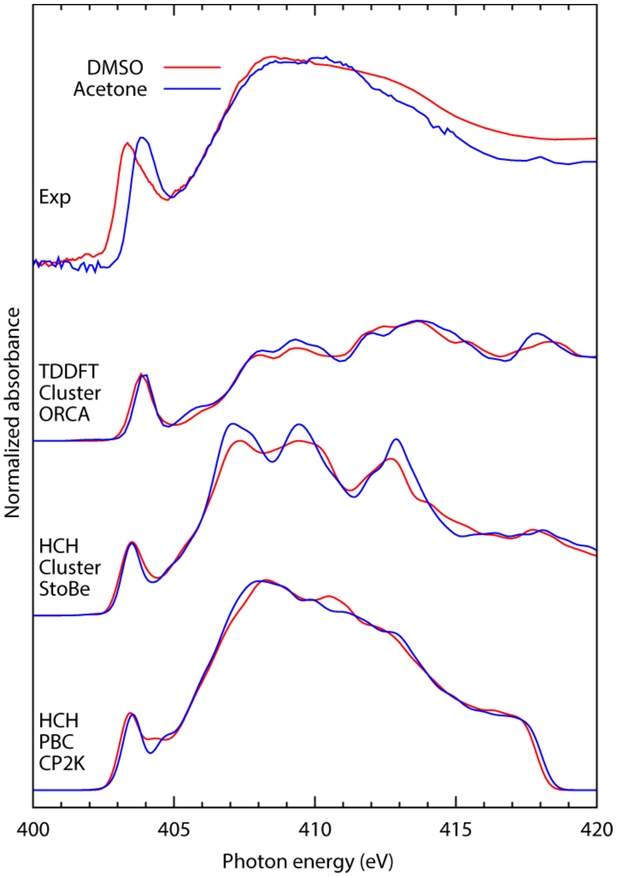
In ORCA (74), we performed time-dependent (TD-)DFT calculations using Beck-Perdew gradient-corrected exchange and correlation functionals (75, 76) within the ZORA approximation (81). The simulated spectra are based on 4000 core-excitations calculated with the def2-TZVP(-f) basis set (82). The computational speed was increase with an auxiliary basis sets for Ahlrichs Coulomb density fitting.

The discrete spectra were convoluted as described in the main text and an ad-hoc constant energy shift were applied to the XA spectra calculated in Cp2k(+0.3 eV), Stobe(+0.8 eV) and ORCA(+22.7 eV) for a rough alignment with the experimental data.

In StoBe, we also attempted to add a delta-Kohn-Sham energy correction (83) to the HCH spectrum for each configuration to improve the accuracy of the HCH results and to see if it would enable us to reproduce the experimentally observed XAS pre-edge shift. The delta-Kohn-

Sham correction amounts to shifting each individual spectrum by an explicit calculation of the energy differences between the ground state and the lowest core-excited state. However, since the lowest core-excited state in the HCH calculation of NMA in acetone corresponded to a solute-to-solvent transition, the method was not applicable. Furthermore, attempts to align the transitions with dominant pre-edge intensities in the HCH calculations to the explicit core-excitation energies also gave unreliable results.

In Fig. S2, the results from HCH/CP2K, using the fully periodic model, are compared to the results from HCH/StoBe and TDDFT/ORCA, using small clusters. We ascribe the sharpness of the features in the region 407-413 eV in the spectra from Stobe to the finite-size effect and to minor extent to differences in the basis sets. These spectral differences between the CP2K and Stobe and ORCA calculations are not important for the present purpose. We notice that the pre-edge features are in good agreement between the different computational frameworks, but that none of the spectrum simulations techniques reproduce the experimentally observed solvent dependence. In Fig. S3, we present the comparison of sampled XAS spectra of the NMA(solv.mol.)$_x$ clusters with spectra of only the NMA molecule and the NMA hydrogen bonded to a single solvent molecule NMA+1solv.mol. Thereby, we can clearly associate the pre-edge shift with the NH-O hydrogen bond, but we do not see any solvent dependence.



Supporting Figure S2: Nitrogen K-edge x-ray absorption spectrum for N-methylaniline (NMA) in DMSO and acetone. The experimental data are compared to cluster calculations for HCH-STOBE and TDDFT-ORCA and to fully periodic calculations HCH-CP2K.

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