

Exciton delocalization in the amide I band of a protein-like liquid

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The exciton delocalization in the amide I band of neat N-methylacetamide is studied with 2D IR spectroscopy. The spectra consist of a diagonally elongated peak and a narrower shoulder assigned to delocalized excitons. According to the inverse participation ratio, the excitons are delocalized over tens of amide I oscillators.

Proteins are the engines of living systems. Even though they are complex, they can be mimicked by a simple peptide building block, N-methylacetamide (NMA). Here, we study the amide I mode of neat NMA (<3% water molar concentration) in order to gain fundamental understanding of protein - protein interactions. Two-dimensional infrared spectroscopy (2DIR) is sensitive to structural heterogeneity and dynamics and, thus, ideal to study the complex picture of exciton delocalization over multiple individual amide I oscillators [1]. At the theory side, we combine Molecular Dynamics (MD) with response function calculations [2] to obtain absorption and 2DIR spectra of the amide I mode of NMA. Experimental and theoretical spectra are in qualitative agreement (see Figure) although the computed spectra are ~25% narrower. The bump on the red flank of the experimental spectrum is most probably caused by residual water bend vibrations. The main peak is diagonally elongated due to heterogeneity of hydrogen bond network. A narrow shoulder in the blue side of the spectra arises according to theory from the excitonic coupling. The high degree of exciton delocalization is shown by the inverse participation ratio suggesting delocalization over tens of amide I oscillators. The present results are well in line with a previous study on the anisotropy decay in NMA [3], where the slow decay time is caused by preferential parallel alignment of the transition dipoles of the coupled molecules.

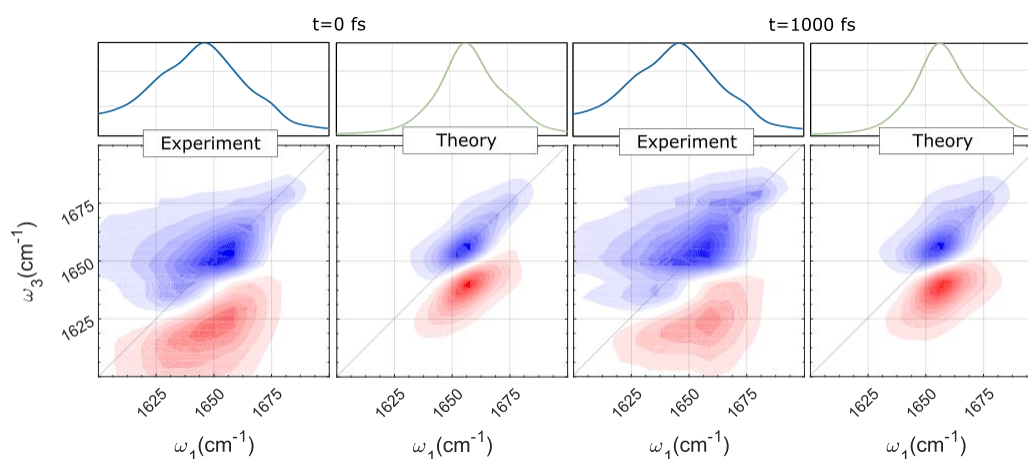


Figure 1. The linear (top panel) and 2D IR (bottom panel, perpendicular pump-probe polarization) spectra of liquid NMA at ~300 K at two waiting times.

[1] T. Miyazawa, J. Chem. Phys. 32:1647 (1960)

[2] C. Liang and T. L. C. Jansen, J. Chem. Theory. Comput. 8:1706 (2012)

[3] M. R. Panman and D. J. Shaw and B. Ensing and S. Woutersen, Phys. Rev. Lett. 13:207801 (2014)