

Supporting Information for

Hydrophobic Collapse in N-methylacetamide-Water Mixtures

*Evgeniia Salamatova[†], Ana V. Cunha[†], Robbert Bloem^{‡#}, Steven J. Roeters[‡], Sander Woutersen[‡],
Thomas L. C. Jansen[†] and Maxim S. Pshenichnikov^{*†}*

[†]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen,
The Netherlands

[‡]Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904,
1098 XH Amsterdam, The Netherlands

*m.s.pshenichnikov@rug.nl

1. Types of the HB species

1.1 Group I. Group I includes the free NMA (f-NMA) and NMA donating one HB (1d-NMA) and consists of three different types.

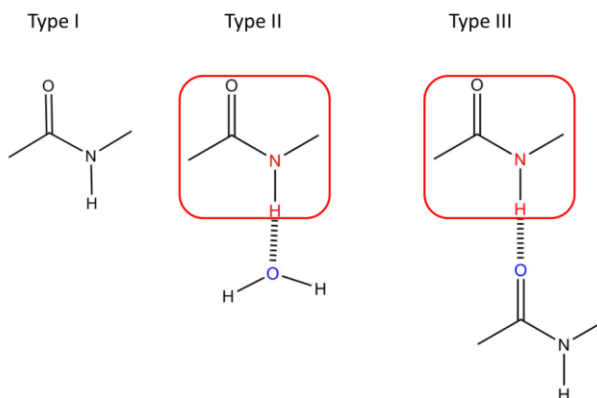


Figure S1 The schematic representations of NMA-water species, which were bundled in group I.

1.2 Group II. Group II includes the NMA-water species, which either accept one HB (1a-NMA) or donate one and accept one HB (1a-1d-NMA) and consists of six types.

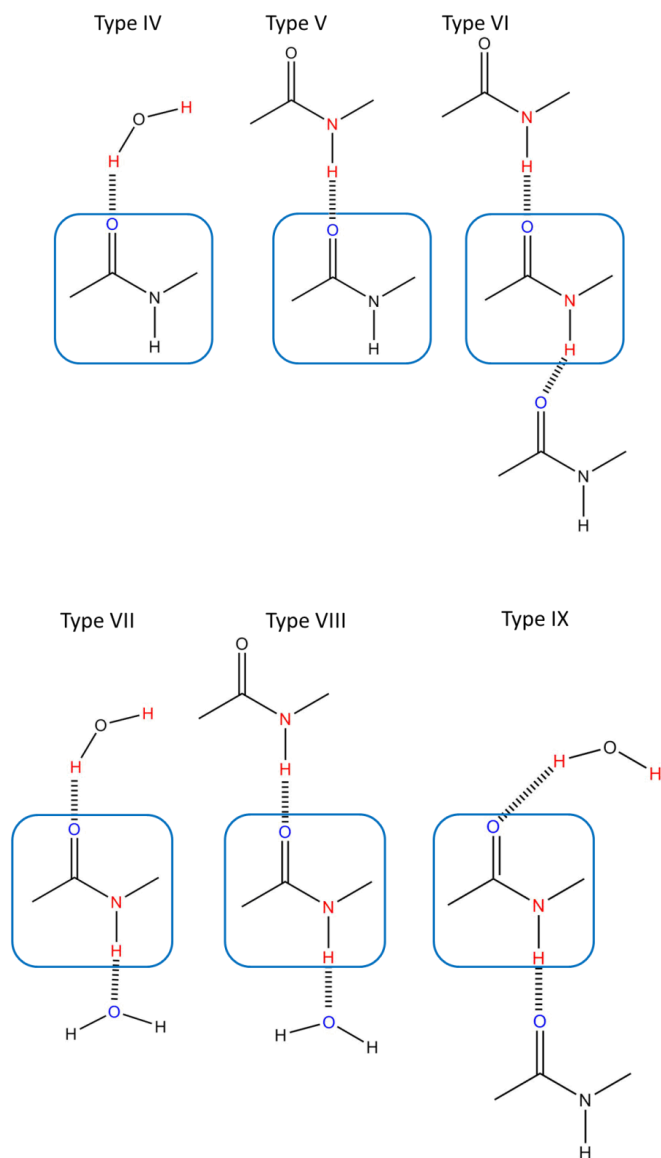


Figure S2 The schematic representations of NMA-water species, which were bundled in group II

1.3 Group III. Group III consists of the NMA-water species, which either accept two HBs (2a-NMA) or accept two and donate one HB (2a-1d-NMA). This group consists of nine types.

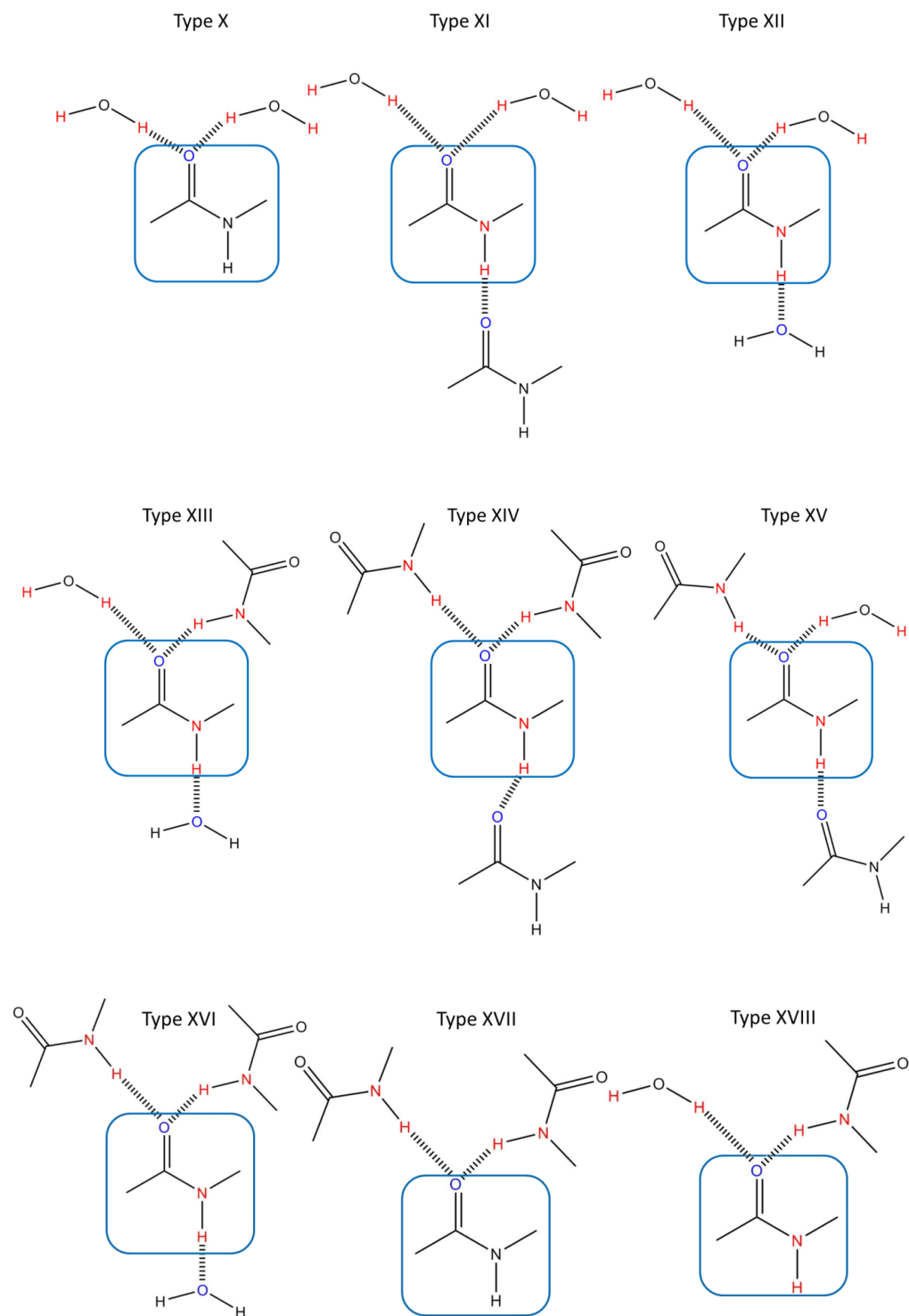


Figure S3 The schematic representations of NMA-water species, which were bundled in group III

1.4 Other NMA species. These NMA-water species are transient species found to either donate two HBs, or accept three HBs according to the used hydrogen bond criteria. These are not assigned to any of the groups I-III.

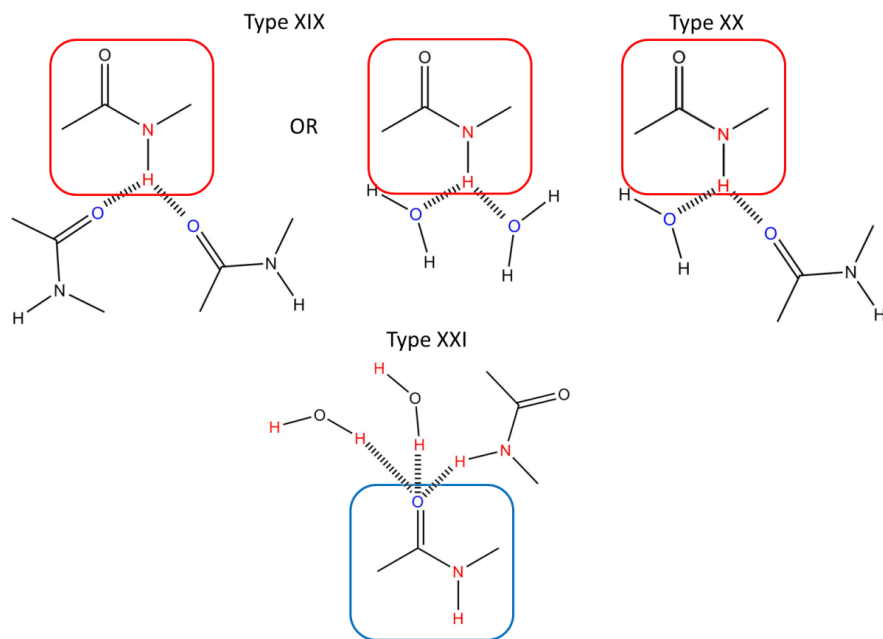


Figure S4 The schematic representations of transient NMA-water species, which were not assigned to any of the three groups.

2. 2D IR spectra of NMA-water mixture at different waiting times and CLS analysis

2.1. Experimental spectra of NMA-d₁/D₂O mixture at X = 0.5

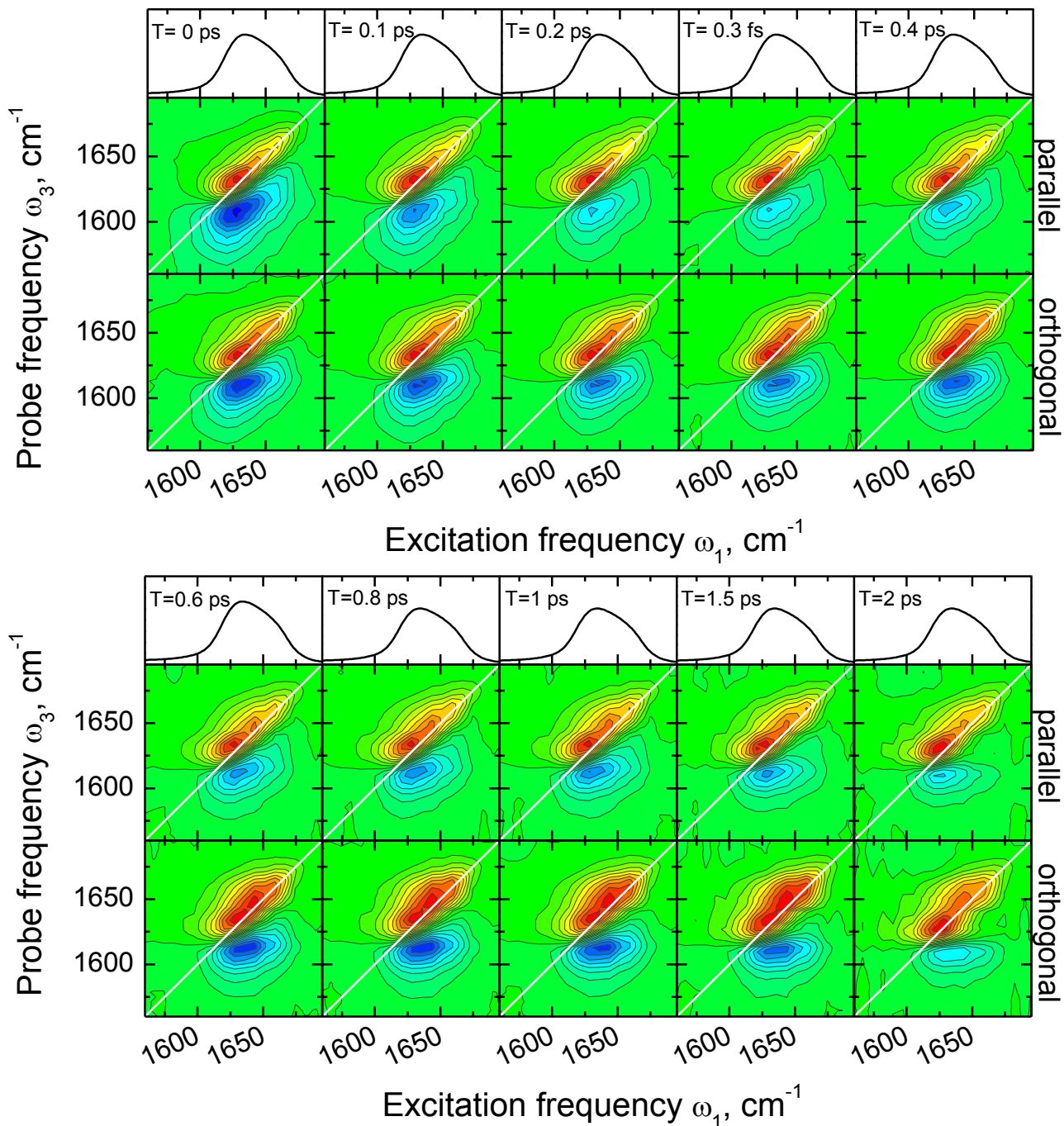


Figure S5 2D IR experimental spectra of NMA-d₁/D₂O solution at different waiting times and two different polarizations. The equidistant contours are drawn with 10% steps from the maximal amplitude

2.2. Theoretical coupled spectra of NMA/water mixture at $X = 0.3$

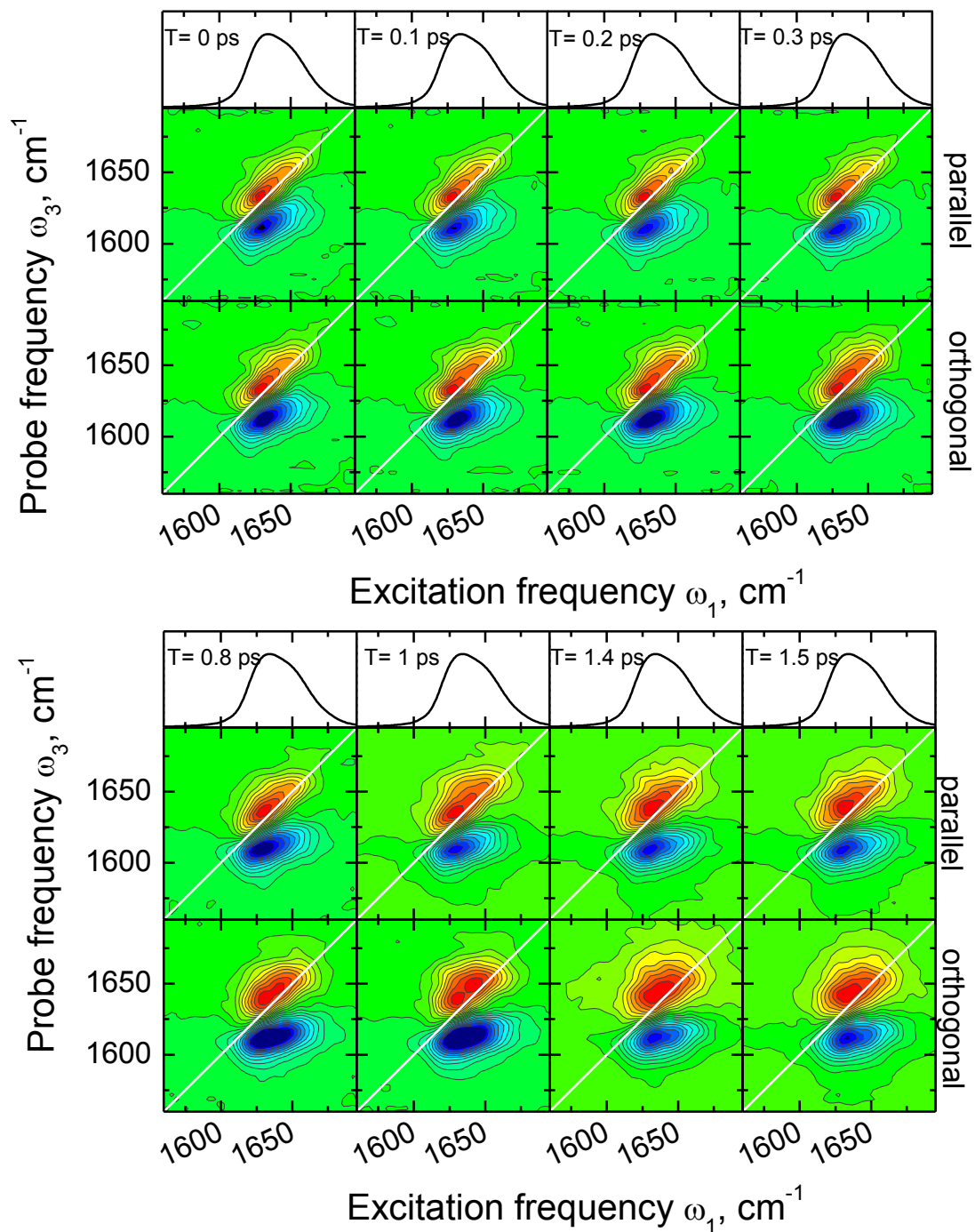


Figure S6 2D IR theoretical coupled spectra of NMA/water solution at different waiting times and two different polarizations. The equidistant contours are drawn with 10% steps from the maximal amplitude

2.3. Theoretical uncoupled spectra of NMA/water mixture at $X = 0.3$

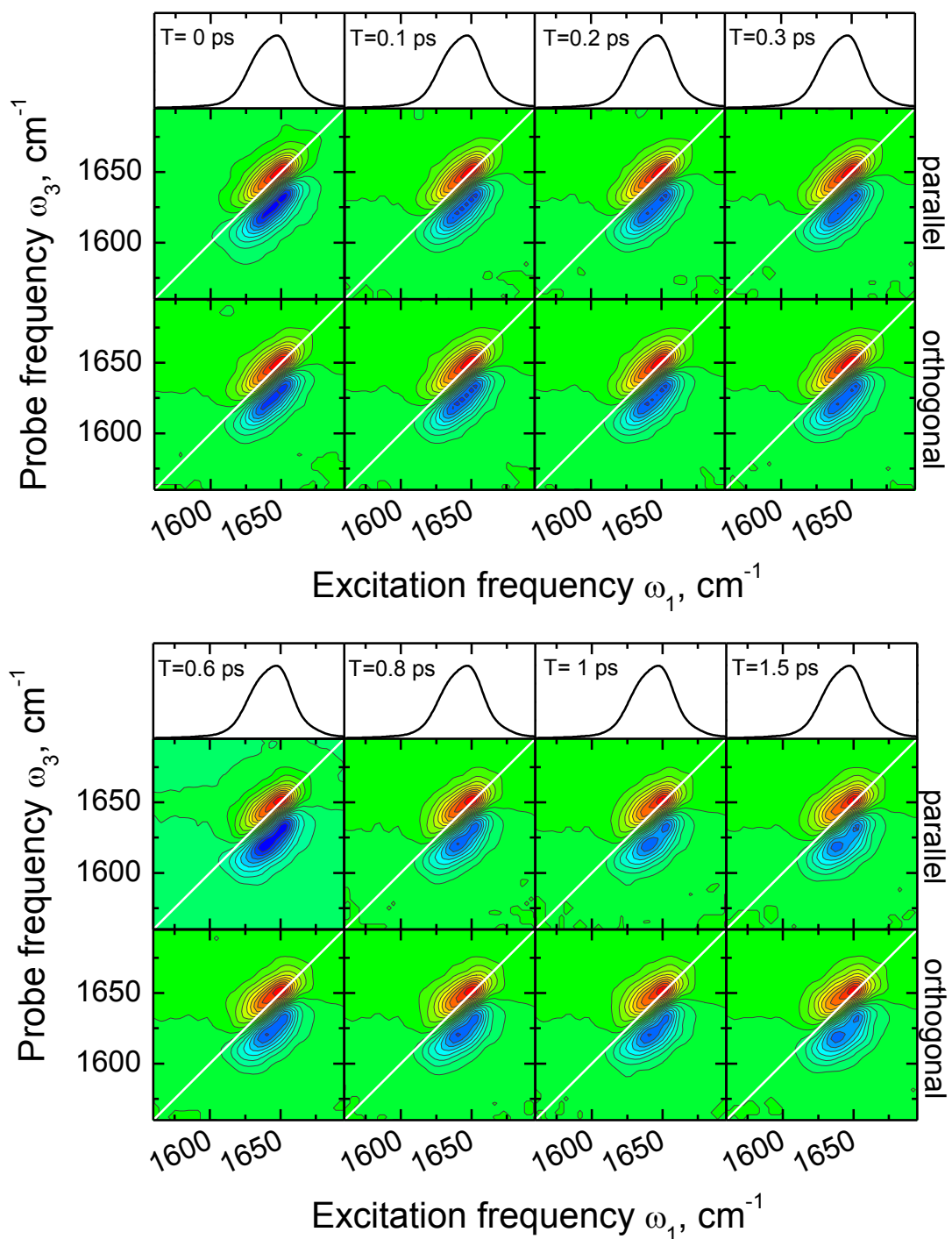


Figure S7 2D IR theoretical uncoupled spectra of NMA/water solution at different waiting times and two different polarizations. The equidistant contours are drawn with 10% steps from the maximal amplitude

2.4. CLS analysis of the 2D IR spectra, calculated from the bleaching region

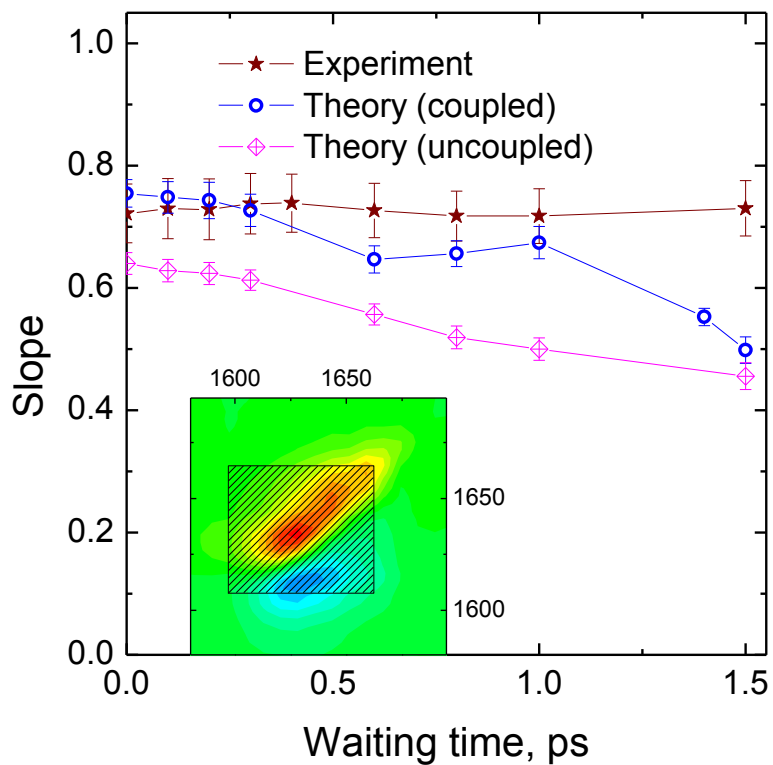


Figure S8 CLS analysis of 2D spectra (parallel polarization) in the amide I region at the frequency region of the bleaching spectra for experimental and simulated spectra