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Lifetime-Associated Two-Dimensional Infrared Spectroscopy Reveals the Hydrogen-Bond Structure of Supercooled Water in Soft Confinement

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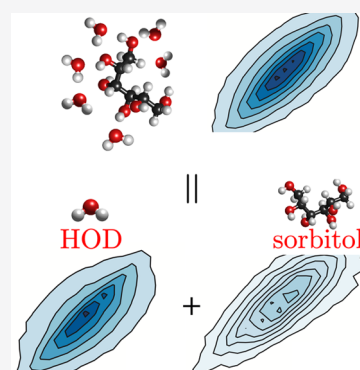
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ABSTRACT: We demonstrate a method to address the problem of spectral overlap in multidimensional vibrational spectroscopy and use it to investigate supercooled aqueous sorbitol solutions. The absence of crystallization in these solutions has been attributed to “soft” confinement of water in subnanometer voids in the sorbitol matrix, but the details of the hydrogen-bond structure are still largely unknown. 2D-IR spectroscopy of the OH-stretch mode is an excellent tool to investigate hydrogen bonding, but in this case it seems difficult because of the overlapping water and sorbitol contributions to the 2D-IR spectrum. Using the difference in OH-stretch lifetimes of water and sorbitol we can cleanly separate these contributions. Surprisingly, the separated 2D-IR spectra show that the hydrogen-bond disorder of soft-confined water is independent of temperature and decoupled from its orientational order. We believe the approach we use to separate overlapping 2D-IR spectra will enhance the applicability of 2D-IR spectroscopy to study multicomponent systems.



Hydrogen bonding plays a crucial role in many structured liquids, the most well-known case being liquid water and aqueous solutions. Infrared spectroscopy is ideally suited to investigate hydrogen-bond structure and dynamics in such systems because of the strong dependence of the OH-stretch frequency on the length (strength) of the OH...O bond.^{1–4} In particular, two-dimensional infrared (2D-IR) spectroscopy on the OH-stretch mode is often used to investigate water and aqueous solutions and has provided many new insights.^{5–17} In contrast to conventional infrared spectroscopy, 2D-IR spectroscopy allows separate observation of the homogeneous and inhomogeneous contributions to the OH-stretch line shape: roughly speaking, the homogeneous broadening provides information on the fast dynamical fluctuations of the H-bond structure while the inhomogeneous broadening mirrors the (quasi)static distribution of hydrogen-bond strengths.¹⁸ However, 2D-IR is difficult to use in the case of aqueous solutions where both the solvent and the solute contain OH groups, and their OH-stretch bands overlap strongly. Alcohol- and polyalcohol-water mixtures are typical examples of such systems: they exhibit complex behavior, including subnanometer molecular phase segregation¹⁹ and liquid-liquid transitions,^{14,20} but overlapping IR-absorption bands render the application of 2D-IR spectroscopy difficult.

Here, we show that this problem can be overcome by exploiting the different vibrational T_1 lifetimes of the OH-stretching modes of the different species in a mixture, and we apply this approach to study the anomalous H-bond structure of supercooled aqueous sorbitol solutions. Recent neutron and X-ray scattering experiments have shown that the structure of

water-sorbitol mixtures (70 wt % sorbitol, corresponding to a sorbitol molar fraction of $c \approx 0.19$) is extremely heterogeneous, with the water molecules forming small clusters (<2 nm) within the sorbitol amorphous matrix,^{21,22} which is characterized, in the supercooled phase, by the presence of nanometer/subnanometer voids that solidify at the glass-transition temperature ($T_g = 200$ K).^{21,22} Water is therefore in “soft” confinement in the sorbitol amorphous matrix and displays structural properties similar to those of water absorbed in porous silica substrates such as MCM41:²² crystallization is inhibited by the small size of the pores within which water molecules are segregated, rather than by the increase in the viscosity accompanying the liquid-to-glass transition.²² Remarkably, already at room temperature the orientational order of the H-bond network within the pores is larger than that of neat water, and it increases upon cooling, suggesting that the suppression of ice formation is not due to a reduction of water tetrahedrality,²² but the details of the hydrogen-bond structure remain elusive. As we will see, by exploiting the different T_1 of water and sorbitol OH-vibrations, we can cleanly separate the water and sorbitol 2D-IR spectra and so selectively probe the

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H-bond network of the nanoscopic water clusters across the supercooled phase and below T_g .

We study isotope-diluted (OH:OD \approx 0.02) aqueous sorbitol solutions with a sorbitol molar fraction $c = 0.19$. At this concentration crystallization is inhibited and the phenomenon of “soft” confinement is observed.²² The sample is prepared by mixing the appropriate amounts of sorbitol, D₂O, and H₂O (after mixing, the OH- and OD-groups were statistically distributed between water and sorbitol molecules). We study dilute isotopic OD/OH mixtures rather than isotopically pure liquids to prevent resonant energy transfer.^{5,23} For the experiments we put 2 μ L of liquid between two CaF₂ windows separated by a 25 μ m Teflon spacer, resulting in an OH-stretch absorbance less than 1 OD at room temperature. A liquid-nitrogen cryostat was used to control the temperature of the sample with a stability of ± 0.1 K. The cryogenic 2D-IR measurements were performed using a frequency-domain setup described previously.¹⁴ Further experimental details can be found in the Supporting Information.

In Figure 1 we show the linear IR absorption spectrum at several temperatures. At room temperature (295 K) the OH-

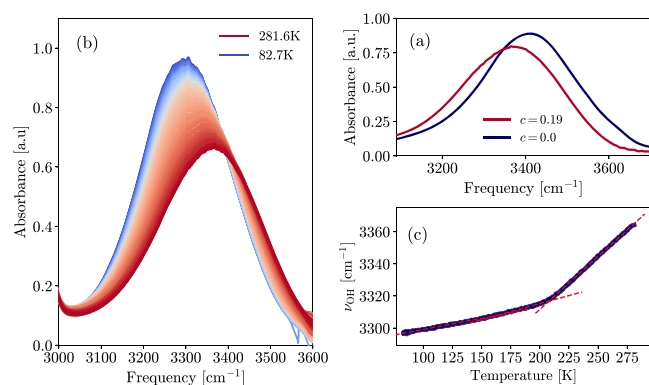


Figure 1. (a) IR absorption spectra of sorbitol solution (molar fraction $c = 0.19$) in HOD/D₂O (H/D \approx 2%) during cooling (1.5 K/min). (b) IR spectra of the OH-stretching mode with (red line) and without (blue line) sorbitol in solution as measured at room temperature. (c) Temperature dependence of the peak position of the OH stretching mode shown in panel a during the cooling. The red dashed lines are linear fits of the T -dependence of ν_{OH} . Three temperature regions can be identified: $T < 169$ K, 169 K $< T < 206$ K, and $T > 206$ K.

stretching band is located at a frequency lower than that of pure water (Figure 1a). The IR absorption spectra of water and sorbitol are strongly overlapped, and this makes a spectral analysis of the absorption band extremely difficult.

As can be observed in Figure 1b, upon cooling, the OH-stretching peak moves toward lower frequencies, indicating that the average H-bond length decreases. No crystallization was observed during the measurements, and the structural changes were completely reversible upon reheating the sample (Supporting Information, Figures S2 and S3). The T -dependence of the peak maximum of the OH-stretching band (ν_{OH}) is shown in Figure 1c. A sharp change in slope occurs at the glass-transition temperature ($T_g \approx 200$ K).^{21,22,24} An additional, smaller change in the T -dependence of ν_{OH} occurs around $T_g^\beta \approx 169$ K (see also the Supporting Information, Figure S4). The increase of the H-bond strength upon cooling is confirmed by the T -dependence of the HOH-

bending mode of water (Supporting Information, Figure S5) and by the temperature dependence of the THz absorbance.²⁵ The T -dependence of ν_{OH} around T_g can be explained by the sensitivity of the OH-stretch to the change in the thermal expansion coefficient of the mixture occurring at the glass-transition temperature.²⁶ A similar explanation can be invoked for T_g^β , which could indeed represent the second glass-transition of the solution, i.e., the temperature at which the Johari–Goldstein relaxation, a fast process characteristic of glass-formers,²⁷ arrests.^{24,28} Analogous observations have been made in several glass-formers, including pure sorbitol^{24,28,29} (see the Supporting Information for further details).

A in-depth characterization of the H-bond structure can be provided by 2D-IR spectroscopy, but only if we can separate the overlapping water and sorbitol contributions. If the excited vibrational modes of the different molecular species decay with different rates, it should be possible to disentangle the individual contributions in a similar fashion as a difference in T_1 lifetime can be used to separate congested NMR spectra.^{30,31} To see if this approach is feasible for water–sorbitol mixtures, we determine the T_1 values of the OH-stretch mode of sorbitol and water using pump–probe measurements with broad-band (≈ 200 cm^{-1}) pump pulses centered at 3250 or 3365 cm^{-1} and at several temperatures in the range from 100 to 295 K. As shown in Figure 2a, upon excitation by the pump pulse, there is a strong negative absorption change around 3300 cm^{-1} due to bleach and stimulated emission of the $\nu_{\text{OH}} = 0 \rightarrow 1$ that decays on a picosecond time scale. A singular value decomposition analysis (see the Supporting Information, Figure S8) shows that the time- and frequency-dependent data can be described by two components, and from a global least-squares fit we find that the data can in fact be described by a sum of two exponential decays, with lifetimes $T_1 \approx 0.7$ ps and ≈ 1.6 ps (Figures 2b and S7, where the solid lines are the results of the fit and the blue and red dashed lines the water and sorbitol contributions). The decay-associated spectra are shown in Figure 2a. Considering a previous time-resolved study of the OD-stretch mode of water–sorbitol solution,³² we can assign the $T_1 \approx 0.7$ ps component to the OH-stretch mode of water and the 1.6 ps component to the OH-stretch mode of sorbitol. This previous study³² was of the OD-stretch mode of water–sorbitol solution, so the numerical values cannot be compared directly to ours (because the OH-stretch mode of a molecule generally decays much faster than the OD-stretch mode of its deuterated version); but just as here, it was found that the T_1 of water in the solutions is the same as the neat-water value and that the sorbitol T_1 is significantly longer. These previous OD-stretch experiments showed a third, fast (0.45 ps) OD-stretch component due to sorbitol, which we do not observe, probably because the OH-stretch analogue of this component decays too fast to be observable with our ~ 0.3 ps temporal resolution. The temperature-dependencies of the T_1 of water and sorbitol are plotted in panels c and d of Figure 2, respectively. The corresponding uncertainties, as extracted from the covariance matrix of the least-squares fit, are underestimates as systematic errors are not considered.

The large difference between T_1^{HOD} and T_1^{sorb} makes possible disentangling the water and sorbitol nonlinear 2D-IR responses in a fashion similar to that for the broad-band pump–probe measurements. Typical 2D-IR spectra, measured at pump–probe delays (Δt) corresponding to the T_1 values of water and

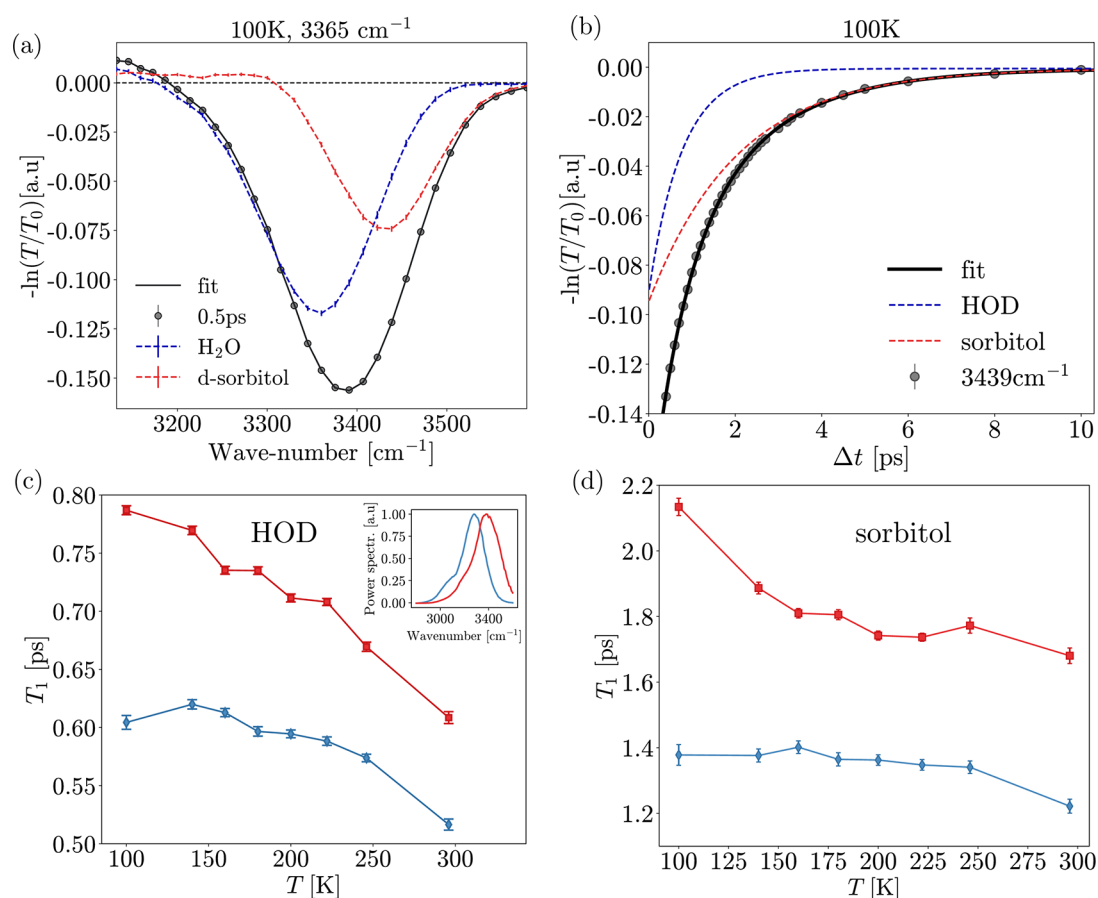


Figure 2. (a) Isotropic absorption change for sorbitol solution in HOD/D₂O as measured at 100 K with a broad-band pump pulse centered at 3365 cm⁻¹ (see inset in panel c) and for a pump–probe delay of $\Delta t = 0.5$ ps. The black solid lines is the curve obtained from the fitting procedure, while the blue and red dashed lines are the water and sorbitol contributions, respectively. Panel b shows isotropic absorption change at 3349 cm⁻¹ as a function of the pump–probe delay along with the fitting curves. The same color code as in panel a has been used. The vibrational lifetimes T_1 of the OH-stretching mode of water and sorbitol are reported in panels c and d. The red squares show the temperature dependence of T_1 as measured using the pump pulse at 3365 cm⁻¹ (red curve in the inset of panel (c)), while the blue diamonds refers to the values obtained from the measurements with the pump pulse centered at 3250 cm⁻¹ (blue curve in inset of panel c).

sorbitol, are shown in Figure 3a–d. The 2D-IR spectra show a strong negative absorption change associated with the $\nu_{OH} = 0 \rightarrow 1$ transition. The presence of two spectral components with different delay dependencies can be noticed by comparing panels a and c or panels b and d of Figure 3: for short pump–probe delays ($\Delta t = 0.7$ ps), the signal is dominated by the OH-stretching mode of HOD molecules, while for longer delays ($\Delta t = 1.6$ ps) the absorption bleach mostly reflects the sorbitol response. The investigated temperatures ($T \leq 270$ K) are sufficiently low that spectral diffusion is negligible on the time scale of the experiment, so that the delay dependence of the 2D-IR spectra directly reflect the vibrational relaxation of the excited states of the water and sorbitol molecules. It is then possible to extract the water ($\Delta\alpha_{\text{HOD}}$) and sorbitol ($\Delta\alpha_{\text{sorb}}$) 2D-IR spectra by fitting the time-dependent 2D-IR signal with a bimodal response function:

$$\Delta\alpha(\nu_1, \nu_2, \Delta t) = \Delta\alpha_{\text{HOD}}(\nu_1, \nu_2) \exp\left[-\frac{\Delta t}{T_1^{\text{HOD}}(\nu_1)}\right] + \Delta\alpha_{\text{sorb}}(\nu_1, \nu_2) \exp\left[-\frac{\Delta t}{T_1^{\text{sorb}}(\nu_1)}\right] + c(\nu_1, \nu_2) \quad (1)$$

where c is a small contribution accounting for the temperature increase after the vibrational relaxation has occurred. The fitting procedure was performed using only the data in the 0.7–10 ps time-window to avoid coherent coupling effects,³³ and T_1^{HOD} and T_1^{sorb} were fixed to the values obtained from the broad-band pump–probe measurements. The temperature and ν_{pump} -dependence of the vibrational relaxation times was accounted for by interpolating the data plotted in Figure 2c,d. The resulting least-squares fits are shown in Figures S9 and S10, while the water (HOD) and sorbitol 2DIR spectra extracted from the 2D-IR spectra in Figure 3a,b are shown in Figure 3e–h.

For both water and sorbitol, the 2D-IR spectra are elongated along the diagonal. This indicates that the absorption band is inhomogeneously broadened;¹⁸ that is, there is a broad distribution of vibrational center frequencies, and therefore, the hydrogen-bond network is characterized by a strong structural disorder. Quantitative information can be obtained by analyzing the component-2DIR spectra of water and sorbitol with a Bloch line-shape model, in which the OH-groups are characterized by a Lorentzian homogeneous broadening and center frequencies (ν) distributed according to a Gaussian.³⁴ This model describes the experimental 2DIR spectra very well (see Figure 3i–l), and from a global least-

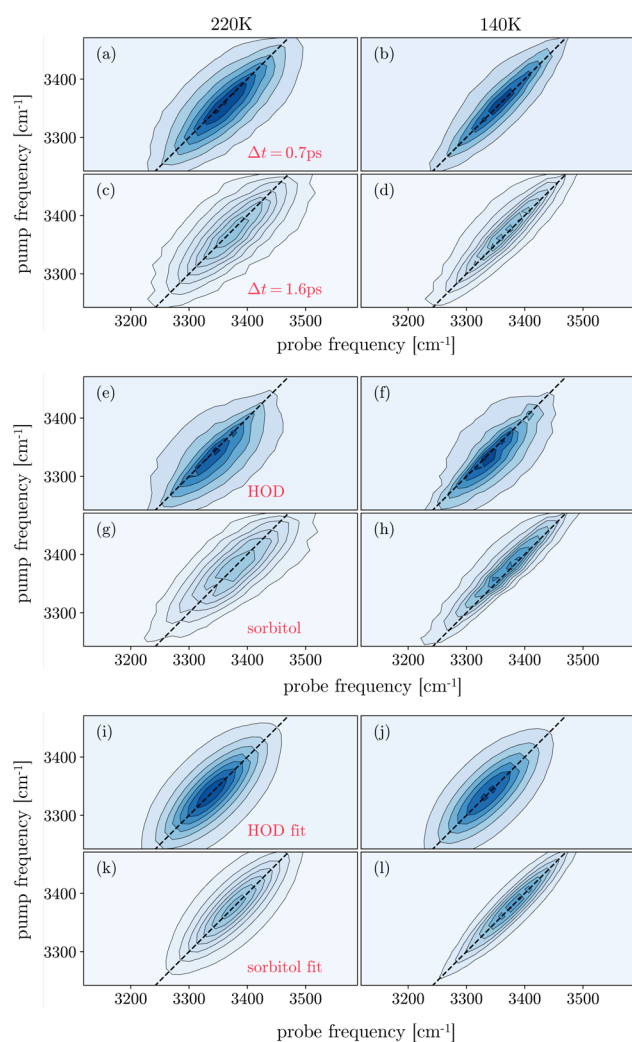


Figure 3. (a and b) 2D-IR spectra measured at 220 and 140 K, respectively, for a pump–probe delay of $\Delta t = 0.7$ ps. (c and d) 2D-IR spectra at the same temperatures as in panels a and b but for $\Delta t = 1.6$ ps. (e and f) Extracted HOD components of the 2D-IR spectra at 220 and 140 K. (g and h) Sorbitol components of the 2D-IR spectra at 220 and 140 K, respectively. (i and j) Results of a least-squares fit of a Bloch line shape model to the data shown in panels e and f. (k and l) Results of a least-squares fit of a Bloch line shape model to the data shown in panels g and h. The black dashed lines show the main diagonal of the 2D-IR spectra.

squares fit to $\Delta\alpha_{\text{HOD}}$ and $\Delta\alpha_{\text{S}}$, we obtain the half-width at half-maximum of the Lorentzian line shape (γ), accounting for the homogeneous broadening, and the standard deviation of the central frequency distribution (σ), representing the inhomogeneous contribution to the line shape. The T -dependence of γ and σ for water (blue dots) and sorbitol³⁵ (red squares) are shown in Figure 4. The homogeneous width γ , which represents the fast fluctuations in the H-bond structure, decreases upon cooling for both water and sorbitol, but interestingly, only the sorbitol response is sensitive to the T_g of the mixture, while no change in the slope is observed for water. This observation supports the picture suggested in ref 22, that on approaching T_g the mobility of water molecules decouples from the macroscopic viscosity. The inhomogeneous broadening, which reflects the hydrogen-bond strength distribution, is, in contrast, almost insensitive to T (apart from a small gradual increase in the case of sorbitol). Thus, while the

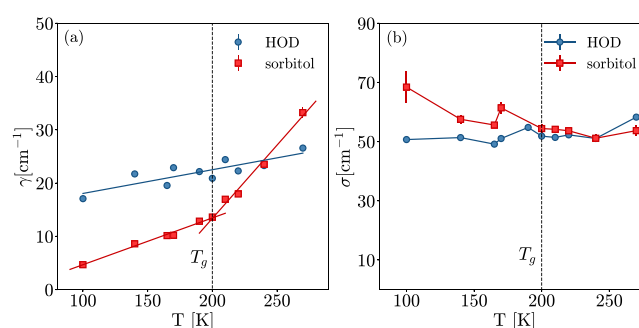


Figure 4. Temperature dependence of the spectral parameters obtained from least-squares fits of a Bloch model to the sorbitol and water components of the 2D-IR spectra. Panel a: Lorentzian half-width γ . The solid lines are a guide to the eyes. Panel b: standard deviation σ of the distribution of central frequencies. The values extracted for HOD and sorbitol are plotted as blue circles and red squares, respectively. The black dashed lines indicate the glass transition temperature (T_g) of the mixture.

average H-bond strength of the water molecules increases upon cooling (Figure 1c), the width of the associated distribution does not change noticeably. This surprising result indicates that the H-bond-strength distribution and the orientational order within water clusters are independent, because the tetrahedrality of the H-bond network has been shown to increase significantly on approaching T_g .²²

Another intriguing aspect emerging from our transient absorption measurements is the increase of T_1^{HOD} with decreasing T . In neat water, when the H-bond strength increases (i.e., ν_{OH} redshifts) the vibrational relaxation becomes faster³⁶ as the energy gap with low-energy intramolecular modes (such as the overtone of the HOH-bend) reduces.³⁷ Here we observe the opposite trend (Figure 2). This trend might be explained if we consider another possible route for vibrational relaxation, e.g., the direct coupling of the OH-stretch with the H-bond network modes.³⁸ The soft confinement might indeed prevent the formation of an extended H-bond network as in the case of pure water, thus reducing the coupling between the OH-stretching mode and low-frequency modes.

To summarize, we have used 2D-IR spectroscopy to investigate the hydrogen-bond structures of water in soft confinement. Exploiting the different vibrational lifetimes of the OH-stretching mode of water and sorbitol, we can cleanly separate the nonlinear responses of sorbitol and of the water clusters. We find that the average hydrogen bond length decreases upon cooling, and its dependence is sensitive to the liquid-to-glass transition of the solution. In contrast, the distribution of hydrogen bond strengths is almost temperature-insensitive and decoupled from the orientational order. The method here introduced can be applied to any mixture of molecules with overlapping 2D-IR spectra, provided that the T_1 values of the spectrally overlapping modes are sufficiently different. We therefore believe it can become a valuable tool to investigate mixtures or other multicomponent systems by means of 2D-IR spectroscopy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.1c01595>.

Experimental details, absence of crystallization during FTIR measurements, *T*-dependence of the OH-stretching band, HOH bending mode of water, examples of fitting curves of transient absorption data, and absence of spectral diffusion (PDF)

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Notes

The authors declare no competing financial interest.

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