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Resonance heterodyne optical Kerr spectroscopy of solvation dynamics in water and D₂O

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Abstract

We have used the technique of time resolved resonance heterodyne optical Kerr effect to measure the ultrafast solvation dynamics of rhodamine 800 (R800) and 3,3'-diethylthia-tricarbocyanine bromide (DTTCB) in water and D₂O. We find a significant isotope effect in the picosecond range for R800 but we do not reveal it for DTTCB. We explain the R800 results by a specific solvation due to formation (breaking) of an intermolecular solute–solvent hydrogen bond. Another important part of the experimental data is a bimodal solvation correlation function with an ultrafast femtosecond component < 100 fs.

1. Introduction

Recently, interesting results have been obtained concerning the ultrafast solvation dynamics in liquids [1] and, particularly in liquid water [2–7]. It was found, experimentally [4], by molecular dynamical simulations and theory [5–7], that the solvation of a solute molecule (or ion) in water is bimodal. The solvation correlation function is Gaussian at short times and exponential at long times. Solvation studies are of great importance, since the time response of solvent molecules to the electronic rearrangement of a solute has an essential influence on the rates of chemical reactions in liquids [4,8] and, particularly in liquid water.

A question arises when and if the solvation dynamics of a solute in deuterated water is similar to water [6]. The Debye relaxation time, measured by dielectric relaxation technique for D₂O is slower

than H₂O at the same temperature [9]. Deuterated water is a more ordered liquid with a stronger hydrogen bond compared to normal water [10]. It was predicted that a significant isotope effect may be observed in ion solvation of normal and deuterated water in the (sub)picosecond range [6]. It was reported in Ref. [11] (see also Ref. [3]), that a small isotope effect exists in water for the longitudinal relaxation time.

Using the technique of the resonance heterodyne optical Kerr effect (HOKE) [12–14] we have studied the solvation dynamics of two organic molecules: R800 and DTTCB in normal and deuterated water in femto- and pico-second ranges. We found a rather significant isotope effect in the picosecond range for R800 but not for DTTCB. We attribute the R800 results to a specific solvation in rhodamine 800 due to the formation (breaking) of an intermolecular solute–solvent hydrogen bond. Another important

aspect of this study is that the solvation correlation function is bimodal with an ultrafast femtosecond component < 100 fs.

2. Theoretical background

Let us consider a molecule with two electronic states $n = 1$ and 2 in a solvent described by the Hamiltonian

$$H_0 = \sum_{n=1}^2 |n\rangle [E_n - i\hbar\gamma_n + W_n(Q)] \langle n|, \quad E_2 > E_1, \quad (1)$$

where E_n and $2\gamma_n = T_1^{-1}$ are the energy and the inverse lifetime of state n , $W_n(Q)$ is the adiabatic Hamiltonian of reservoir R (the vibrational subsystem of a molecule and a solvent interacting with the two-level electron system under consideration in state n).

The molecule is affected by an electromagnetic radiation of three beams

$$E(\mathbf{r}, t) = E^+(\mathbf{r}, t) + E^-(\mathbf{r}, t) \\ = \frac{1}{2} \tilde{\mathcal{E}}(\mathbf{r}, t) \exp(-i\omega t) + \text{c.c.},$$

where

$$\tilde{\mathcal{E}}(\mathbf{r}, t) = \sum_{m=1}^3 \mathcal{E}_m(t) \exp(i\mathbf{k}_m \cdot \mathbf{r}).$$

Since we are interested in the solvent–solute intermolecular relaxation, we shall single out the solvent contribution to $W_n(Q)$: $W_n(Q) = W_{nM} + W_{nS}$ where W_{nS} is the sum of the Hamiltonian governing the nuclear degrees of freedom of the solvent in the absence of the solute, and the part which describes interactions between the solute and the nuclear degrees of freedom of the solvent; W_{nM} is the Hamiltonian representing the nuclear degrees of freedom of the solute molecule.

In resonance HOKE spectroscopy [13], a linearly polarized pump pulse at frequency ω induces anisotropy in an isotropic sample. After the passage of the pump pulse through the sample, a linearly polarized probe pulse with polarization axis at $\pi/4$ rad from the pump field polarization, is incident on the sample. A polarization analyzer is placed after

the sample oriented at approximately $\pi/2$ (but not exactly) with respect to the probe pulse polarization. A small portion of the probe pulse that is not related to the induced anisotropy plays the role of a local oscillator (LO) with controlled magnitude and phase.

The HOKE signal can be written in the form [14]:

$$J_{\text{HBT}} \sim -\text{Im} \int_{-\infty}^{\infty} \mathcal{E}_{\text{LO}}^*(t - \tau) \exp(i\psi) P_A^{(3)+}(t) dt, \quad (2)$$

where $\mathcal{E}_{\text{LO}}(t)$ and $P_A^{(3)+}(t)$ are the amplitudes of the positive frequency components of the LO field and the cubic polarization, respectively, ψ is the phase of the LO.

If the laser pulses are long compared with the inverse band-width of the absorption spectrum of the solute molecule in solution, the cubic polarization is related to the cubic susceptibility $\chi_{abcd}^{(3)}(\omega, \tau)$ ($a, b, c, d = x, y, z$) by the equation [15]

$$P_A^{(3)+}(t) = \sum_{bdc} \int_0^{\infty} d\tau_2 \chi_{abcd}^{(3)}(\omega, \tau_2) \cdot \frac{1}{8} \mathcal{E}_{2d}^*(t - \tau_2) \\ \times [\mathcal{E}_{3b}(t - \tau) \mathcal{E}_{1c}(t - \tau_2) \\ + \mathcal{E}_{1b}(t) \mathcal{E}_{3c}(t - \tau - \tau_2)], \quad (3)$$

where τ is the delay time of the probe pulse with respect to the pump one.

The cubic susceptibility can be represented as a sum of products of ‘‘Condon’’ $\chi_{\text{FC}\alpha,\varphi}^{(3)}(\omega, \tau_2)$ and a ‘‘non-Condon’’ $B_{abcd}^{\text{HT}\alpha,\varphi}(\tau_2)$ [15,16] parts

$$\chi_{abcd}^{(3)}(\omega, \tau_2) = \sum_{\alpha,\varphi} \chi_{\text{FC}\alpha,\varphi}^{(3)}(\omega, \tau_2) B_{abcd}^{\text{HT}\alpha,\varphi}(\tau_2), \quad (4)$$

where indices α, φ of $\chi_{\text{FC}}^{(3)}$ and B_{abcd}^{HT} show that the corresponding values are related to nonequilibrium processes in the absorption (α) or emission (φ) (for more details see below). The ‘‘Condon’’ factors $\chi_{\text{FC}\alpha,\varphi}^{(3)}(\omega, \tau_2)$ depend on both the excitation frequency ω and τ_2 , but they do not depend on the polarization states of exciting beams. The ‘‘non-Condon’’ terms $B_{abcd}^{\text{HT}\alpha,\varphi}(\tau_2)$ do not depend on ω , but depend on τ_2 and the polarizations of the exciting beams.

The origin of the ‘‘non-Condon’’ terms $B_{abcd}^{\text{HT}\alpha,\varphi}$ stems from the dependence of the dipole moment of the electronic transition on the nuclear coordinates

$D_{12}(Q)$. Such a dependence is explained by the Herzberg–Teller (HT) effect: mixing different electronic molecular states by nuclear motions.

Let us consider the spectra of R800 in water and other solvents (Fig. 1). This molecule has well structured spectra which can be considered as a progression with respect to an optically active (OA) high frequency vibration $\approx 1500\text{ cm}^{-1}$ [17]. The members of this progression are well separated, and their amplitudes rapidly attenuate when the number of the progression member increases (practically, as one can see from Fig. 1, the amplitude of the third member is very small). Such a behavior provides evidence of a small change of the molecular nuclear configuration on an electronic excitation. In other words, the Franck–Condon electron–vibrational interactions in rhodamine molecules are small.

The resonance Raman scattering studies of rhodamine dyes [18] display intense lines in the range of $\approx 1200\text{--}1600\text{ cm}^{-1}$ and the lowest-frequency one at 600 cm^{-1} in both alcohol and water solutions. Therefore, one can assume that the intramolecular vibrational contribution to the line broadening of the R800 in water in the range between the electronic transition frequency ω_{e1} and the first maximum is minimal. In our experiments the excitation frequency corresponds to this range ($\omega = 13986\text{ cm}^{-1}$).

As to the interactions with the solvent, they satisfy the slow modulation limit [15,16,19,20] in the spirit of Kubo's theory of the stochastic modulation [21]:

$$\tau_s^2 \sigma_{2s} \gg 1, \quad (5)$$

where $\sqrt{\sigma_{2s}}$ is the modulation amplitude and τ_s is the characteristic time of the attenuation of the correlation function of a stochastic modulation. Bearing in mind our comments concerning the role of the intra- and inter-molecular interactions, we can assume that criterion (5) is correct for the first maxima in both the absorption and luminescence spectra of the R800 in water. In the last case σ_{2s} is the central second moment of the first maximum.

Suppose that the exciting pulses are Gaussian [19]:

$$\mathcal{E}_m(t) = \mathcal{E}_0 \exp\left[-(\Delta^2/2)(t-t_m)^2 + i\omega t_m\right],$$

with pulse duration of $t_p = 1.665/\Delta \gg \sigma_{2s}^{-1/2}$. The last criterion is well realized in our experiments,

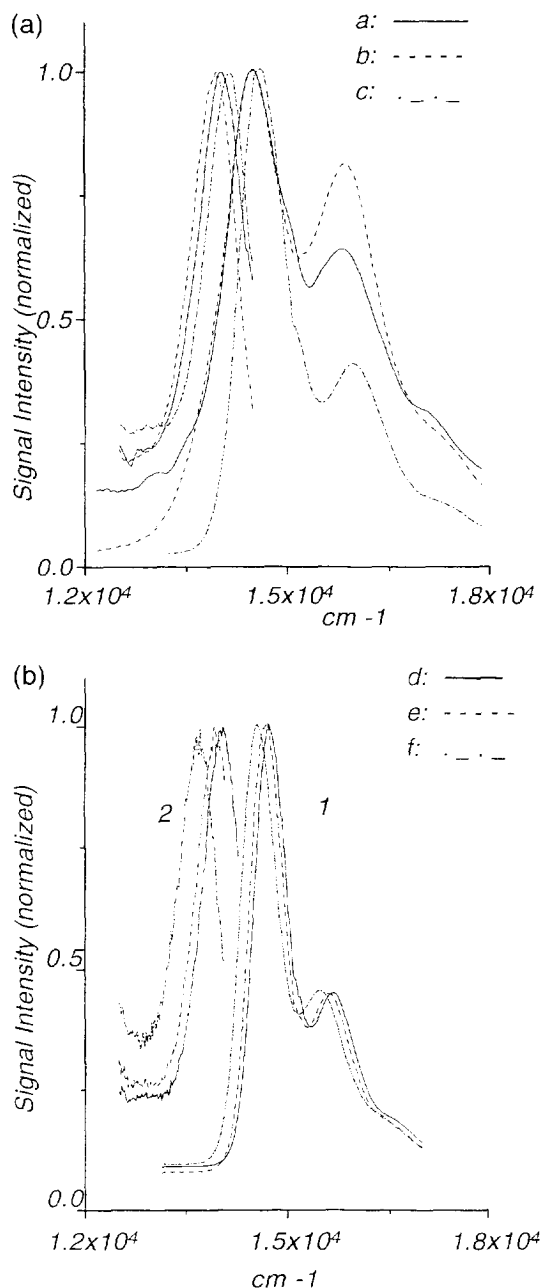


Fig. 1. Absorption (1) and emission (2) spectra of R800 in water (a), D_2O (b), ethanol (c), acetone (d), propylene carbonate (e), and dimethyl sulfoxide (f).

since $t_p \approx 100\text{ fs}$ (in the first series of our measurements $t_p \approx 150\text{ fs}$) and $\sigma_{2s}^{-1/2} \approx 14\text{ fs}$.

Let us discuss the role of non-Condon effects for R800 in H_2O and D_2O . The absorption spectra of

R800 in water and D₂O differ from the corresponding spectra in other solvents (Fig. 1). Solvents like H₂O and D₂O influence the relative intensities of spectral components in the absorption band. It can be described by the dependence of the dipole moment of the electronic transition D_{12} on a solvent coordinate $D_{12}(Q_s)$ [15], i.e. by the non-Condon effect. Thus, the electronic dipole moment dependence on a solvent coordinate must be a necessary component of our consideration. Moreover, the R800 absorption spectrum in D₂O differs from that of H₂O. The substitution of H by D influences the absorption spectrum shape. Thus, one can assume that the dependence $D_{12}(Q_s)$ is determined by the solute–solvent H-bond in water. The analytical form of the $D_{12}(Q_s)$ dependence is determined by invoking a specific model for the interaction.

Taking into account conditions (5) and $t_p \gg \sigma_{2S}^{-1/2}$, we can write the imaginary part of the Condon contributions $\chi_{FC\alpha,\varphi}^{(3)}(\omega, \tau_2)$ ($\psi=0$) in the form [19]:

$$\begin{aligned} \text{Im } \chi_{FC\alpha,\varphi}^{(3)}(\omega, \tau_2) \\ = -(2\pi^3)^{1/2} N L_L^4 \hbar^{-3} \exp(-\tau_2/T_1) \\ \times F_{S\alpha}^e(\omega - \omega_{el})(\sigma(\tau_2))^{-1/2} \text{Re } w(z_{\alpha,\varphi}). \end{aligned} \quad (6)$$

Here N is the density of the solute molecules, L_L is the Lorentz correction factor of the local field, $F_{S\alpha}^e(\omega - \omega_{el})$ is the equilibrium absorption spectrum of a chromophore,

$$\begin{aligned} w(z) = \exp(-z^2) \left[1 + (2i/\sqrt{\pi}) \int_0^z \exp(t^2) dt \right] \\ \text{is the error function of the complex argument [22],} \\ z_{\alpha,\varphi} = \{ i \Delta^2 [\tau_2(2 + S(\tau_2)) - t(3 + S(\tau_2)) + \tau] \\ + \omega - \omega_{\alpha,\varphi}(\tau_2) \} / (2\sigma(\tau_2))^{1/2}; \end{aligned} \quad (7)$$

$$\begin{aligned} \sigma(\tau_2) = \sigma_{2S} \{ 1 - S^2(\tau_2) + (\Delta^2/\sigma_{2S}) \\ \times [3 + 2S(\tau_2) + S^2(\tau_2)] \} \end{aligned} \quad (8)$$

is the time-dependent central second moment of the changes related to nonequilibrium processes in the absorption and the emission spectra respectively, at the active pulse frequency ω ,

$$\omega_{\alpha,\varphi}(\tau_2) = \omega_{el} \pm \frac{1}{2} \omega_{st} + S(\tau_2) \left[\omega - \left(\omega_{el} \pm \frac{1}{2} \omega_{st} \right) \right] \quad (9)$$

are the first moments of the transient absorption (α) and emission (φ) spectra, respectively, $\omega_{el} = (E_2 - E_1)/\hbar$, is the frequency of the purely electronic transition with corrections from the electronic degrees of freedom of the solvent [15,20], $u_s = W_{2S} - W_{1S}$, $\omega_{st} = 2\langle u_s \rangle$ is the solvent contribution to the Stokes shift between the equilibrium absorption and emission spectra, $\hbar^2 \sigma_{2S} S(t) = \langle u_s(0)u_s(t) \rangle - \langle u_s \rangle^2$, $S(t)$ is the normalized solute–solvent correlation function, $\sigma_{2S} = \hbar^{-2}(\langle u_s^2(0) \rangle - \langle u_s \rangle^2)$ is the contribution of the solvent to the second central moment of both the absorption and the luminescence spectra. The third term on the right-hand side of Eq. (8) which is proportional to Δ^2/σ_{2S} , plays the role of the pulse width correction to the hole or spike width. This term is important immediately after the optical excitation when $\tau_2 \approx 0$ and, therefore, $S(\tau_2) \approx 1$. The first term on the right-hand side of Eq. (7) which is proportional to $\Delta^2 \sim 1/t_p^2$, takes into account the contribution of the electronic transition coherence.

Formulae (6)–(9) correspond to a case where only the first maxima of the absorption and the emission spectra are taken into consideration. This simplification is justified due to the specific relative position of the excitation frequency ω with respect to the rhodamine spectra.

The cubic polarization for the HOKE experiment (y is the signal polarization axis, the probe pulse polarization is along the x axis and the pump pulse is at 45° with respect to both x and y) can be written in the form (see Appendix):

$$\begin{aligned} P_{A,y}^{(3)+}(t) \\ = \frac{1}{8} \sum_{\alpha,\varphi} \int_0^\infty d\tau_2 \chi_{FC\alpha,\varphi}^{(3)}(\omega, \tau_2) \\ \times \left[\frac{1}{5} B_S^{\alpha,\varphi}(\tau_2) | \mathcal{E}_{2,x}(1 - \tau_2) |^2 \mathcal{E}_{3,x}(t - \tau) \right. \\ + \left[B_0^{\alpha,\varphi}(\tau_2) + \frac{1}{30} B_S^{\alpha,\varphi}(\tau_2) \right. \\ \left. - \frac{1}{6} B_S^{\alpha,\varphi}(\tau_2) \right] \mathcal{E}_{1,x}(t) \mathcal{E}_{3,x}(t - \tau_2 - \tau) \\ \left. \times \mathcal{E}_{2,x}^*(t - \tau_2) \right], \end{aligned} \quad (10)$$

where values $B_{0,S,a}^{\alpha,\varphi}$ describing the non-Condon effects are determined by Eqs. (A.6) of the Appendix. For subsequent calculations we ought to choose a concrete dependence of $D(Q_s)$. When the dipole moment $D_{12}(Q)$ changes only its direction, but pre-

serves its modulus [15,16], the values $B_{0,S,a}^{\alpha,\varphi}$ are given by the following equations:

$$B_0^\alpha = B_0^\varphi = D_0^4/9; \quad B_a^\alpha = B_a^\varphi = 0,$$

$$B_S^{(m)}(\tau_2) = (D_0^4/2) \left\{ \frac{1}{3} + \exp \left[- \sum_j r_j^2 (1 - \Psi_j(\tau_2)) \right] \times \cos \left[\delta_{m\varphi} \sum_j r_j (1 - \Psi_j(\tau_2)) (\beta \hbar \omega_{St,j})^{1/2} \right] \right\}, \quad (11)$$

where $r_j = 2\alpha_j \sqrt{\langle Q_{Sj}^2(0) \rangle}$ are constants characterizing the correlations of the vector D_{21} with the j th intermolecular vibration, $D_0 = |D_{21}|$, $\omega_{St,j}$ is the contribution of the j th intermolecular motion to the total “intermolecular” Stokes shift ω_{St} ($\omega_{St} = \sum_j \omega_{St,j}$), $\Psi_j(\tau_2)$ is the normalized correlation function, corresponding to the j th intermolecular vibration which is related to the solvation correlation function $S(\tau_2)$ by Eq. (A.4). It is worth noting that the cosine term in the right-hand side of Eq. (11) for B_S^φ describes the interference of the Franck–Condon (dynamical Stokes shift) and the Herzberg–Teller relaxation dynamics.

3. Experimental details

A passively cw mode locked Ti:sapphire laser (Coherent, Mira) operating at 76 MHz providing tunable (720–800 nm) 70–100 fs pulses of 8 nJ, was used to measure solvation dynamics by heterodyne optical Kerr effect. Description of the experimental setup is given in Ref. [13]. The sample was measured in a rotating cell to avoid thermal contribution to the OKE signal. Unlike the nonresonant OKE measurement, which is used to measure the dynamics of liquids [12], the resonance measurements provide the solvation dynamics of probe molecules in solution. Rhodamine 800 was purchased from Exciton, 3,3-diethylthiatricarbocyanine bromide from Koch-Light and were used without further purification. $D_2O > 99.9\%$ was purchased from Aldrich.

4. Method of data analysis

Our aim is to determine the solvation correlation function by resonance HOKE spectroscopy. According to Eqs. (2)–(9) we need to know, for this purpose, the following characteristics of the steady-state spectra: ω_{el} and the solvent contribution to the Stokes shift between the equilibrium absorption and emission spectra ω_{St} . The latter is related to the solvent's contribution to the second moment σ_{2S} by the relation: $\omega_{St} = \hbar \beta \sigma_{2S}$. One can determine ω_{el} as the crossing point in the frequency scale of the equilibrium absorption and emission spectra of R800 ($\omega_{el} = 14235 \text{ cm}^{-1}$ for water and is about the same for D_2O).

The solvent contribution to the central moment σ_{2S} can be determined by the relation $\delta\Omega = 2\sqrt{2}\sigma_{2S} \ln 2$ where $\delta\Omega$ is the half-width of the first absorption maximum. In order to exclude from our consideration the contribution of the second maximum and the optically active vibration of the frequency $\approx 600 \text{ cm}^{-1}$, we determined $\delta\Omega$ as twice the distance (in the frequency domain) between the luminescence maximum and the right-hand side half maximum of the first luminescence maximum. Using this method, we obtain $\sigma_{2S} = 115416 \text{ cm}^{-2}$ for the water solution and therefore $\omega_{St} = \hbar \beta \sigma_{2S} = 550 \text{ cm}^{-1}$ which conforms with the experimentally measured value. For D_2O the relation $\omega_{St} = \hbar \beta \sigma_{2S}$ is an approximate one, and we suppose in this case $\sigma_{2S} = 123900 \text{ cm}^{-2}$.

Bearing this in mind, we fit our experimental data by Eqs. (2)–(11). We present the correlation function $S(\tau_2)$ in the form of a sum of a Gaussian and one or two exponentials

$$S(\tau_2) = a_1 \exp \left[-(\tau_2/\tau_G)^2 \right] + a_2 \exp(-\tau_2/\tau_{fe}) + (1 - a_1 - a_2) \exp(-\tau_2/\tau_e), \quad (12)$$

where τ_e is the decay time of the slow (picosecond) exponential. We relate it to the solute–solvent H-bond, and therefore connect the correlation function for the “non-Condon” intermolecular motion in the right-hand side of Eq. (12) with this exponential:

$$\Psi_j(\tau_2) = \exp(-\tau_2/\tau_e). \quad (13)$$

Comparing Eqs. (12) and (A.4), we can express the value $\omega_{\text{St},j}$ in Eq. (A.4) by the parameters a_1 , a_2 and ω_{St} :

$$\omega_{\text{St},j} = (1 - a_1 - a_2) \omega_{\text{St}}. \quad (14)$$

Correspondingly, the fitting parameters are a_1 , a_2 , τ_G , τ_{fe} , τ_e and $r^2 \equiv r_j^2$.

The pulse duration t_p in our experiments is $t_p \approx 70$ –150 fs, depending on the laser excitation wavelength. In the case of ultrafast OKE experiments, the decay time T_1 in Eq. (6) is replaced by the orientation relaxation time τ_{or} of the solute molecules, if the latter is shorter than T_1 . For rhodamine dyes $T_1 \approx 1$ –2 ns $> \tau_{\text{or}} \approx 150$ ps. We multiplied the experimental data by the factor $\exp(\tau/\tau_{\text{or}})$ and compared the theoretical and the experimental data for delay times $\tau \ll \tau_{\text{or}} \approx 150$ ps. Fig. 2 shows the computer fit results of the experimental data of R800 in H₂O and D₂O. The fit of the theoretical calculations to the experimental curves is good. The insert in Fig. 2 shows the solvation correlation functions $S(t)$ of R800 for H₂O and D₂O found by the computer fitting procedure.

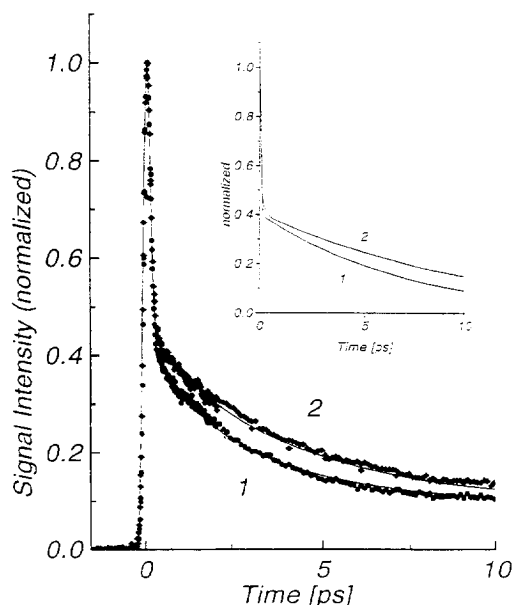


Fig. 2. HOKE signals for R800 in water (1) and D₂O (2). Dots and diamonds: experiment, solid lines: computer fit using Eqs. (2)–(4), (6), (8)–(15) for $t_p = 150$ fs, $r^2 = 2.5$, $\tau_G = 85$ fs; $a_1 = 0.6$ (1) and 0.44 (2), $a_2 = 0$ (1) and 0.156 (2), $\tau_{\text{fe}} = 146$ fs (2), $\tau_e = 6.8$ ps (1) and 10 ps (2). Insert: solvation correlation functions for H₂O (1) and D₂O (2).

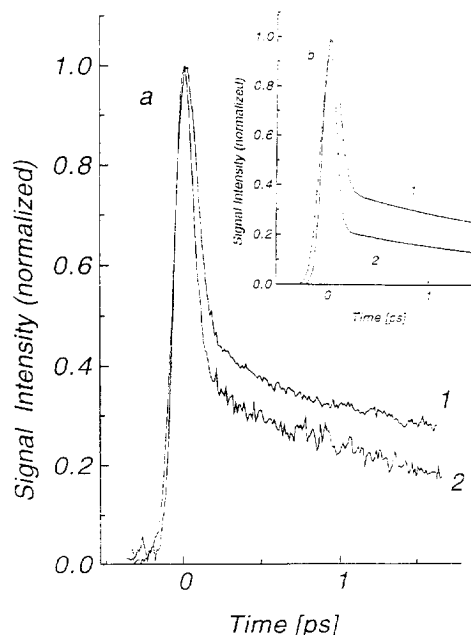


Fig. 3. Experimental (a) and calculated (b) HOKE signals for R800 in water for different excitation frequencies ω and pulse duration t_p . (a) $\omega = 13755$ cm⁻¹, $t_p = 125$ fs (1); $\omega = 13550$ cm⁻¹, $t_p = 100$ fs (2). (b) $\omega = 13831$ cm⁻¹, $t_p = 130$ fs (1); $\omega = 13441$ cm⁻¹, $t_p = 90$ fs (2).

We also carried out the corresponding measurements for R800 in water at different excitation frequencies ω (Fig. 3a). Fig. 3b shows theoretical spectra for different excitation conditions, i.e. ω and t_p for rhodamine 800 in water. We used the same parameter values of the previous fit (Fig. 2) for curves of Fig. 3b. One can see that the theoretical curves reproduce all the fine details observed in the experiment (in particular, the decrease in the amplitude of the slower signal component for “blue” excitations).

5. Discussion

The correlation solvation functions for R800 in water and D₂O consist of two main components: an ultrafast Gaussian one with $\tau_G \approx 85$ fs < 100 fs, and a slow one with an exponential decay of a few picoseconds. Only a small part of the fast signal component can be explained by the coherent spike. The main contribution to it is due to the hole-burning effect.

The amplitude of the Gaussian component is about 60% for water, and the sum of a Gaussian and a fast exponential for D₂O is also 60%. This value is close to that observed by Fleming et al. ($\approx 50\%$) for coumarin 343 solvation in liquid water [4]. Its duration (85 fs) is about 1.7 times longer than that observed in Ref. [4]. The large difference can be explained as follows. The solvation, observed in Ref. [4], has been interpreted as an ion one [6]. According to Ref. [6], dipole solvation is slower than the ion one. Therefore, if in the case of R800, the solvation is due to dipole or higher multipole interactions, its fast component is slower than in the case of ion solvation. The fast exponential of 146 fs for D₂O corresponds to that observed for water solvation in Refs. [3,4].

Let us consider the slow components of the correlation functions for H₂O and D₂O (Eq. (12)) ($\tau_c = 6.8$ ps for H₂O and $\tau_c = 10$ ps for D₂O). They are close to the Debye relaxation times τ_D for these solvents (8.27 ps and 10.37 ps, respectively [9]). Such long components have not been observed in recent studies of solvation dynamics of other solutes in water [3,4]. We interpret our observations as a specific solvation related to formation (or breaking) of an intermolecular solute–solvent hydrogen bond between R800 and water molecules. The situation is similar to that observed by Berg and coauthors [23,24] on specific solvation dynamics of resofurin in alcohol solutions. In hydrogen-bonding solvents, the longest component of the Debye dielectric relaxation is assumed to be related to the rate of hydrogen-bond reorganization of the solvent [24–27]. According to Ref. [25], the time τ_D may reflect translation in water. In computer simulations the autocorrelation time of hydrogen bonds in water is 5–7 ps [24,28]. Thus, the assumption that the slowest solvation is related to the reorganization of a hydrogen bond, seems rather plausible. The experimental data for R800 show a significant isotope effect in water ($\approx 32\%$ for times τ_c), in contrast to Ref. [23] in which an isotope effect in deuterated ethanol was not observed. It would be expected in view of the larger number of H-bonds that water makes [29].

The hydrogen-bond formation (or breaking) assumption correlates with occurrence of non-Condon effects. The dependence $D(Q)$ is essential for a large change in Q . This is the case of hydrogen-bond

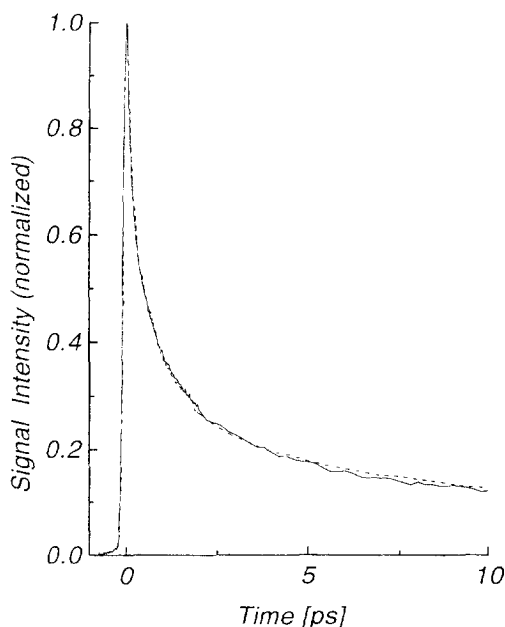


Fig. 4. HOKE data for DTTCB solutions in water (solid line) and D₂O (dotted line); $t_p = 70$ fs, $\omega = 13330$ cm⁻¹.

formation (or breaking) where a large Q is accompanied by a large hopping distance (3.3 Å for water [25]) and a small activation energy.

In Fig. 4 the HOKE data for DTTCB solution in water and D₂O are shown. These data reflect only fast dynamics of solvation (nonspecific one) and do not show any significant isotope effect.

6. Summary

Using the technique of time resolved HOKE, we have studied the ultrafast solvation dynamics of R800 and DTTCB in water and D₂O. According to our findings, the time dependence of the HOKE signal for R800 at the frequency domain under consideration, is determined mainly by solute–solvent interactions. The significant change in the HOKE signal during the first ≈ 100 fs is determined largely by the transient hole-burning effect. A biphasic behavior of the solvation correlation function is essential for a good fit with the experimental data. The fast component of solvation dynamics for both R800 and DTTCB is determined by the nonspecific solvation. The slowest component for R800 (which is close to

the Debye relaxation time) is determined by a specific solvation related to formation (or breaking) of an intermolecular solute–solvent hydrogen bond. Correspondingly, we observe a significant isotope effect for the R800 solution, and do not observe an isotope effect for DTTCB, which does not seem to form a solute–solvent hydrogen bond.

Acknowledgement

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Appendix

Let us consider the non-Condon terms in Eq. (4) for $\chi_{abcd}^{(3)}(\omega, \tau_2)$. They have the following forms [15]:

$$B_{abcd}^{\text{IT}(m)}(\tau_2) = \int \int d\boldsymbol{\mu} d\boldsymbol{\nu} \langle \tilde{\sigma}_{ab}(\boldsymbol{\nu}) \tilde{\sigma}_{dc}(\boldsymbol{\mu}) \rangle_{\text{or}} \times \exp \left\{ -2 \sum_j \left[\langle Q_{Sj}^2(0) \rangle \times (\mu_j^2 + \nu_j^2 + 2\mu_j \nu_j \Psi_{Sj}(\tau_2)) + i \delta_{m\varphi} d_{Sj} \nu_j (1 - \Psi_{Sj}(\tau_2)) \right] \right\}, \quad (\text{A.1})$$

where $m = \alpha, \varphi$; $\delta_{m\varphi}$ is the Kronecker delta,

$$\tilde{\sigma}_{ab}(\boldsymbol{\nu}) = \frac{1}{(2\pi)^M} \int d\mathbf{Q}_S \sigma_{ab}(\mathbf{Q}_S) \exp(-i\boldsymbol{\nu} \cdot \mathbf{Q}_S), \quad (\text{A.2})$$

is the Fourier-transformation of the tensor

$$\sigma_{ab}(\mathbf{Q}_S) = D_{12}^a(\mathbf{Q}_S/2) D_{21}^b(\mathbf{Q}_S/2), \quad (\text{A.3})$$

$\Psi_{Sj}(\tau_2) = \langle Q_{Sj}(0) Q_{Sj}(\tau_2) \rangle / \langle Q_{Sj}^2(0) \rangle$ is the correlation function, corresponding to coordinate Q_{Sj} . If this vibration is an optically active one, then the solvation correlation function $S(\tau_2)$ is related to the correlation functions $\Psi_j(\tau_2)$. In the classical case

(which is only considered in this work) this relation is

$$S(\tau_2) = \sum_j \omega_{St,j} \Psi_j(\tau_2) / \omega_{St}, \quad (\text{A.4})$$

where $\omega_{St,j}$ is the contribution of the j th intermolecular motion to the whole “intermolecular” Stokes shift ω_{St} ($\omega_{St} = \sum_j \omega_{St,j}$). $S(\tau_2)$ can be considered as an average of the values $\Psi_j(\tau_2)$ distributed with the density $\omega_{St,j} / \omega_{St}$. If the non-Condon contribution is due to a non-OA vibration which does not contribute to the Stokes shift ω_{St} , then $\Psi_j(\tau_2)$ is not related to $S(\tau_2)$.

The second addend in the square brackets in Eq. (A.1) describes the interference of the Franck–Condon and Herzberg–Teller contributions. The value of the parameter d_{Sj} can be expressed by the following equation:

$$|d_{Sj}| = (\hbar \omega_{St,j})^{1/2} / \omega_{Sj}. \quad (\text{A.5})$$

For freely orientating molecules, the orientational averages $\langle \tilde{\sigma}_{ab}(\boldsymbol{\nu}) \tilde{\sigma}_{dc}(\boldsymbol{\mu}) \rangle_{\text{or}}$ can be expressed by the tensor invariants $\tilde{\sigma}^0$, \tilde{h}_s and \tilde{h}_a (see Ref. [15]).

Let us consider the HOKE experiment. Using Eqs. (3), (4), (A.1) and Eqs. (47)–(56) of Ref. [15] we obtain Eq. (11) of the main text where

$$B_{0.S.a}^{(m)}(\tau_2) = \int \int d\boldsymbol{\mu} d\boldsymbol{\nu} \exp \left\{ -2 \sum_j \left[\langle Q_{Sj}^2(0) \rangle \times (\mu_j^2 + \nu_j^2 + 2\mu_j \nu_j \Psi_{Sj}(\tau_2)) + i \delta_{m\varphi} d_{Sj} \nu_j (1 - \Psi_{Sj}(\tau_2)) \right] \right\} \cdot \begin{cases} \tilde{\sigma}^0(\boldsymbol{\nu}) \tilde{\sigma}^0(\boldsymbol{\mu}) \\ h_s(\boldsymbol{\mu}, \boldsymbol{\nu}) \\ h_a(\boldsymbol{\mu}, \boldsymbol{\nu}) \end{cases} \quad (\text{A.6})$$

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