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Solvation dynamics of rhodamine 800 in water and D_2O

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Abstract

Time-resolved resonance heterodyne optical Kerr-effect spectroscopy is employed to measure the solvation dynamics of rhodamine 800 in water and D_2O. Unlike other large dye molecules, rhodamine 800 solvation dynamics in water exhibits a long-time component which we attribute to hydrogen-bond formation (breaking). We also find a rather unusual large isotope effect which does not exist in other dyes. An important part of the experimental data is a bimodal solvation correlation function with an ultrafast femtosecond component < 100 fs.

Keywords: Solvation dynamics; Isotope effect; Ultrafast spectroscopy

Solvation dynamics has been extensively studied in the last decade. Most of these studies are based on time-resolved luminescence techniques. Only limited number of studies were conducted on the most common liquid, water [1–5]. It was found experimentally [2], by molecular dynamical simulations and theory [3–5] that the solvation of a solute molecule in water is bimodal. The solvation correlation function is Gaussian at short times and either exponential or nonexponential at long times.

Experimental studies of the solvation dynamics in both water and D_2O of a particular solute molecule have shown a very small difference in their dynamics. This finding is surprising since water and D_2O differ in many other respects [4, 6, 7].

Using resonance heterodyne optical Kerr (HOKE) spectroscopy [8–10], we have studied the solvation dynamics of rhodamine 800 (R800) in water and D_2O with a time resolution better than 100 fs.

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 spectroscopy. Description of the experimental setup is given in Ref. [9]. 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 [8], the resonance measurements provide the solvation dynamics of the probe molecules in solution.

Our aim is to determine the solvation correlation function by resonance HOKE spectroscopy. The HOKE signal can be expressed by the cubic polarization [10]. The latter has been calculated by theory [11, 12].

We present the correlation function of the solvation dynamics $S(\tau_2)$ in the form of a sum of a

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Gaussian and one or two exponentials:

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

where τ_e is the decay time of the slow (picosecond) exponential. We relate it to the solute–solvent H-bond.

The pulse duration t_p in our experiments is $t_p \approx 70$–150 fs, depending on the laser excitation wavelength. Fig. 1(a) shows the computer-fit results of the experimental data of R800 in H_2O and D_2O. The fit of the theoretical calculations to the experimental curves is good. Fig. 1(b) shows the solvation correlation functions $S(t)$ of R800 for H_2O and D_2O found by the computer fitting procedure.

The correlation solvation functions for R800 in water and D_2O consist of two main components: an ultrafast Gaussian one with $\tau_g \sim 85$ 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 D_2O is also 60%. This value is close to that observed by Fleming et al. (~50%) for coumarin 343 solvation in liquid water [2]. Its duration (85 fs) is about 1.7 times longer than that observed in Ref. [2].

Let us consider the slow components of the correlation functions for H_2O and D_2O (Eq. (1)) ($\tau_e = 6.8$ ps for H_2O and $\tau_e = 10$ ps for D_2O). They are close to the Debye relaxation times τ_D for these solvents (8.27 and 10.37 ps, respectively [6]). Such long components have not been observed in recent studies of solvation dynamics of other solutes in water [1, 2]. We interpret our observations as a specific solvation related to the formation (or breaking) of an intermolecular solute–solvent hydrogen-bond between R800 and water molecules. The situation is similar to that observed by Berg et al. [13, 14] 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 [14–16]. In computer simulations the autocorrelation time of hydrogen bonds in water is 5–7 ps [14, 17]. Thus, the assumption that the slowest solvation is related to the reorganization of a hydrogen bond, seems rather plausible.

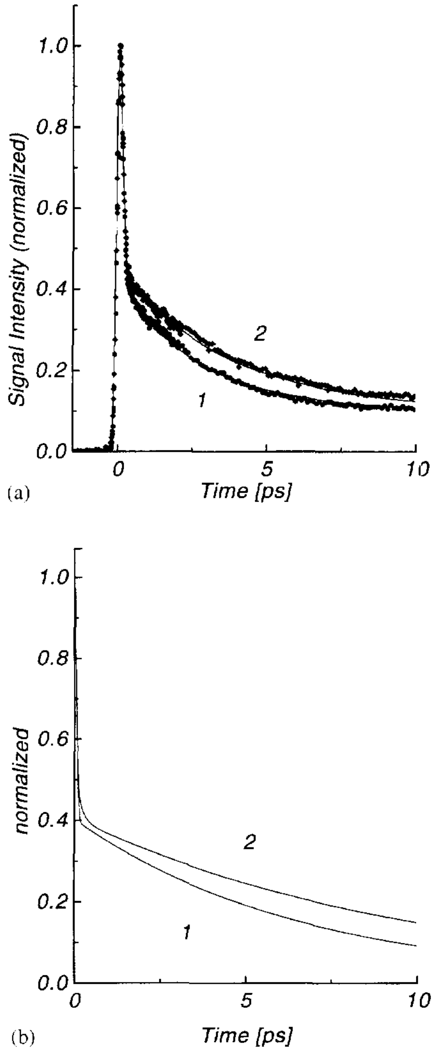

Fig. 1. (a) HOKE signals for R800 in water (1) and D_2O (2): (Dots and diamonds) experimental data; (solid lines) computer fit for $t_p = 150$ fs, $\tau_g = 85$ fs; $a_1 = 0.6$ (1) and 0.44 (2), $a_2 = 0$ (1) and 0.156 (2), $\tau_{fe} = 146$ fs (2), $\tau_e = 6.8$ ps (1) and 10 ps (2). (b) Solvation correlation functions for H_2O (1) and D_2O (2).

The experimental data for R800 show a significant isotope effect in water (~32% for times τ_e in contrast to study [13] 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 [18].

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