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Transient polarization four-photon "non-Condon" spectroscopy of electronic transitions in complex molecules

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Abstract

We show both theoretically and experimentally that resonance transient grating spectroscopy (RTGS) is a good method for the investigation of ultrafast solvation dynamics of large probe molecules in solutions. We have studied the solvation dynamics of LDS 750 in many solvents in a broad time range by RTGS and by induced optical Kerr effect spectroscopy. We propose a new method for the investigation of non-Condon effects in solvation: transient polarization four-photon spectroscopy.

1. Introduction

Recently, the ultrafast solvation dynamics of a large dipolar probe molecule has been investigated by resonance transient grating spectroscopy (RTGS) [1-3]. In this method two pump pulses with wave vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ and frequency ω create a light-induced grating in the sample under investigation with a wave vector $\boldsymbol{q} = \boldsymbol{k}_1 - \boldsymbol{k}_2$. The grating effectiveness is measured by the diffraction of a time-delayed probe pulse ω, $\boldsymbol{k}_3$ with the generation of a signal with a new wave vector $\boldsymbol{k}_s = \boldsymbol{k}_3 \pm \boldsymbol{q}$. Here we show that the RTGS is a good method for the investigation of solvation dynamics in the subpicosecond–subnanosecond range.

Furthermore, we show that using RTGS and resonance-induced optical Kerr effect (OKE) discovers new possibilities in resonance four-photon spectroscopy: it permits the study of Herzberg–Teller (HT) effects (mixing different electronic molecular states by nuclear motions, the so called non-Condon effects). The latter can be explained as following: if the electronic functions are independent on the nuclear coordinates ("Condon" approximation), then, the signal time dependence in transient resonance four-photon spectroscopy does not depend on the polarization of the exciting pulses. In the opposite case, when the electronic wave functions and, consequently, the dipole moment of the electronic transition depend on the nuclear coordinates $\boldsymbol{D}_{12}(\boldsymbol{Q})$ (due to the HT interactions), the signal generally depends on the polarization of the exciting pulses. The comparison of both the signal of the RTGS excited by pulses with parallel polarizations and the signal of the resonance-induced OKE, can provide pertinent information about the contribution of the HT interactions.

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2. Model and general expressions

We consider a solute/solvent system with two electronic states $|1\rangle$ and $|2\rangle$ of the probe molecule giving rise to broad structureless electronic spectra. The duration of the laser pulses (>150 fs) is longer than the reciprocal bandwidth of both the absorption and the luminescence spectra and longer than intramolecular vibrational relaxation times. We shall also consider the translational and the rotational motions of the liquid molecules as classical, at room temperature.

We have shown [4] that the cubic susceptibility of such a system $\chi^{(3)}_{abcd}(\omega,\tau)$ ($a, b, c, d = x, y, z$) describing the generation of the signal $\boldsymbol{k}_s$, can be represented as a product of a "Condon" $\chi^{(3)}_{\mathrm{FC}}(\omega,\tau)$ and a "non-Condon" $B^{\mathrm{HT}}_{abcd}(\tau)$ contribution:

$$\chi^{(3)}_{abcd}(\omega,\tau) = \chi^{(3)}_{\mathrm{FC}}(\omega,\tau) B^{\mathrm{HT}}_{abcd}(\tau), \tag{1}$$

where τ is the probe pulse delay time.

The "Condon" factor $\chi^{(3)}_{\mathrm{FC}}(\omega,\tau)$ depends on both the excitation frequency ω and the probe pulse delay time τ, but it does not depend on the polarization states of the exciting beams. The "non-Condon" term $B^{\mathrm{HT}}_{abcd}(\tau)$ does not depend on ω but depends on τ and the polarizations of the exciting beams.

In accordance with expression (1), one can distinguish between Condon and non-Condon spectroscopy of the solvation dynamics.

3. "Condon" nonlinear spectroscopy

The "Condon" factor is given by

$$\chi^{(3)}_{\mathrm{FC}}(\omega,\tau) \sim \exp(-\tau/T_1)\,[A_\alpha(\omega,\tau) + A_\varphi(\omega,\tau)], \tag{2}$$

where the exponential term describes the signal decay due to the relaxation of the population grating (T_1 is the lifetime of the excited electronic state $|2\rangle$). The terms $A_{\alpha,\varphi}(\omega,\tau)$ are strongly coupled with the solvation dynamics in the ground (α) or in the excited (φ) electronic states. If one neglects the intramolecular degrees of freedom, then the values of $A_{\alpha,\varphi}$ are determined by the photoinduced changes related to the nonequilibrium solvation processes in the absorption ($F_{s\alpha}$) and the emission ($F_{s\varphi}$) spectra, respectively, at the active pulse frequency ω, as well as by the corresponding changes in both spectra of the refraction index $X_{s\alpha,\varphi}$.

In the general case, taking into account the intramolecular degrees of freedom, we obtain that the values of $A_{\alpha,\varphi}(\omega,\tau)$ are determined by 2-D convolutions of the intramolecular spectrum $F_{\mathrm{M}}(\omega')$ (which does not depend on time due to faster intramolecular relaxation) with the spectra $F_{s\alpha,\varphi}$ and $X_{s\alpha,\varphi}$:

$$\begin{aligned} A_{\alpha,\varphi}(\omega,\tau) &= \iint \mathrm{d}\omega'\mathrm{d}\omega''\, F_{\mathrm{M}}(\omega')F_{\mathrm{M}}(\omega'') \\ &\quad \times F^{\mathrm{e}}_{s\alpha}(\omega-\omega_{21}-\omega'')\,[F_{s\alpha,\varphi}(\omega-\omega_{\alpha,\varphi},\tau) \\ &\quad + \mathrm{i}2(\pi)^{-1/2}\, X_{\alpha,\varphi}(\omega-\omega_{\alpha,\varphi},\tau)]. \end{aligned} \tag{3}$$

Here the frequencies $\omega_{\alpha(\varphi)} = \omega_{21} \pm \omega' + (\omega - \omega_{21} - \omega'')\,S(\tau) - \delta_{\alpha(\varphi),\varphi}\,\omega_{\mathrm{st}}(1 - S(\tau))$ are determined by the correlation function $S(\tau)$ of the solvation process, ω_{21} is the frequency of the Franck–Condon transition 1 → 2, ω_{st} is the solvent contribution to the Stokes shift of the equilibrium absorption and emission spectra, δ_{mn} is the Kronecker symbol.

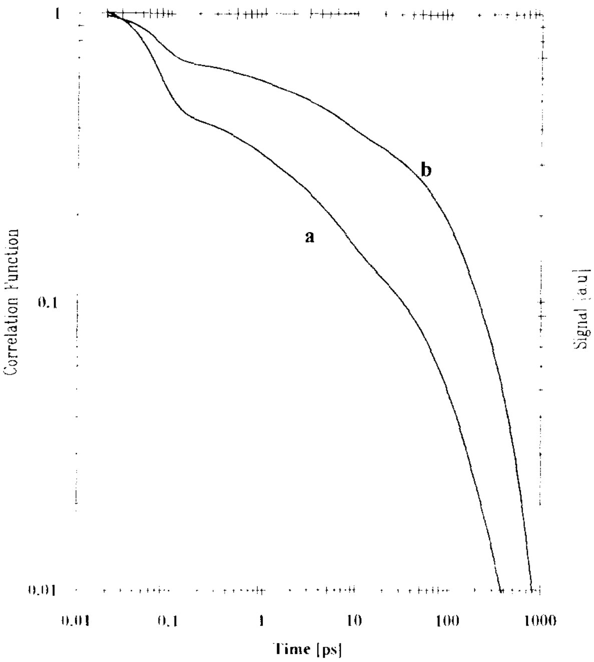

Fig. 1. The calculated signal intensity $J_s(\tau)$ for RTGS (a) and the corresponding correlation function $S(\tau)$ (b).

We plot in Fig. 1 the calculated signal intensity $J_s(\tau) \sim |\chi^{(3)}_{FC}(\omega,\tau)|^2$ (curve a) corresponding to the correlation function $S(\tau)$ (curve b). One can see that the dependences of $S(\tau)$ and $J_s(\tau)$ are very similar (but not identical), and that the signal $J_s(\tau)$ reflects the fine details of $S(\tau)$.

Resonance-induced OKE and RTGS techniques were employed to study the solvation dynamics of large dipolar probe molecules in highly associative liquids. The experimental systems are described elsewhere [3]. The laser system provided 635 nm–140 fs amplified (15 μJ) pulses at 1 kHz rate. LDS 750 (styryl 7) was used as a probe molecule and the solvents used are monools-methanol ethanol, propanol and diols-1,2-ethanediol, 1,3-propanediol and 1,4-butanediol.

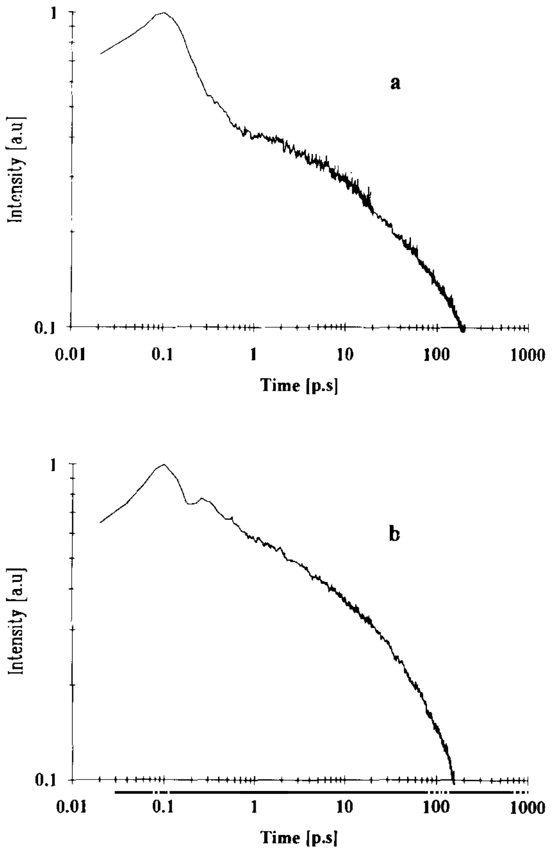

Fig. 2. The experimental signal intensity of LDS 750 in 1,3-propanediol for RTGS (a) and induced OKE spectroscopy (b) as a function of time delay between the pump pulses and the probe pulse.

Fig. 2(a) shows the time-resolved signal of LDS 750 in 1.3-propanediol measured by RTGS on a log–log scale where the time scale spans three decades. The experimental signal can be fitted by a short Gaussian component ~ 100 fs followed by several exponential components with decay time of 600 fs, 5 ps, 30 ps, 200 ps and 500 ps. The fact that we observe more than one relaxation time is in agreement with the dielectric relaxation properties of alcohol [5]. The longest decay component of the RTGS signal (500 ps) is by a factor of two shorter than the excited lifetime of LDS 750 in 1,3-propanediol measured by time-resolved fluorescence technique. The factor of two arises since the RTGS signal is proportional to $|\chi^{(3)}|^2$ while $\chi^{(3)}$ itself decays as $\exp(-t/T_1)$ (see Eq. (2)). Similar data were obtained for 1,4-butanediol but with 600 fs, 5 ps, 70 ps, 250 ps and 550 ps decay times.

The RTGS data between ~ 50 and 200 ps match quite nicely to the solvation dynamics measured by time-resolved fluorescence measurements [3]. The short time scale dynamics of the RTGS signal of LDS 750 in acetonitrile [3] is very similar to the time-resolved fluorescence experiments of the Chicago group [6].

One can see that the experimental (Fig. 2(a)) and the theoretical (Fig. 1(a)) behavior of the signal are similar. Thus, RTGS can be used for the ultrafast study of the solvation dynamics.

4. "Non-Condon" nonlinear spectroscopy

The importance of the study of non-Condon effects is related with the experimental observation [6] that the transition dipole moment rotates during the fast initial stage of probe solvation. Using the general theory [4], we obtained expressions for the signals in RTGS and OKE methods, taking into account non-Condon terms $B^{HT}_{abcd}(\tau)$:

$$J_{RTGS}(\tau) \sim |\chi^{(3)}_{FC}(\omega,\tau)|^2 \, |B_0(\tau) + \tfrac{2}{15} B_s(\tau)|^2 \tag{4}$$

and

$$J_{OKE}(\tau) \sim |\chi^{(3)}_{FC}(\omega,\tau)|^2 \, |B_s(\tau)|^2, \tag{5}$$

where $B_0(\tau)$ and $B_s(\tau)$ are functions of the scalar (0) and the symmetrical (s) parts of the tensor $\sigma_{ab}(Q) = D^a_{12}(Q/2)\, D^b_{21}(Q/2)$, respectively.

One can see from Eqs. (4) and (5) that the time dependences of the signals $J_{\mathrm{RTGS}}(\tau)$ and $J_{\mathrm{OKE}}(\tau)$ are different. The signal $J_{\mathrm{OKE}}(\tau)$ is determined by a function of the symmetrical part of the tensor $\sigma_{ab}(B_s(\tau))$, while $J_{\mathrm{RTGS}}(\tau)$ is determined by a linear combination of functions of the symmetrical (B_s) and the scalar (B_0) parts of the tensor σ_{ab}, respectively.

When the dipole moment $\boldsymbol{D}_{12}(\boldsymbol{Q})$ changes only its direction, but preserves its modulus $|D_{12}(\boldsymbol{Q})|$ (when $\boldsymbol{Q}$ is changing), the function of the scalar part, $B_0(\tau)$, is constant. In such a case, the DC level of the $J_{\mathrm{RTGS}}(\tau)$ signal will be larger than in $J_{\mathrm{OKE}}(\tau)$.

The model calculations confirm this conclusion. We have considered a molecule, where the direction of its transition moment depends on the excitation of intermolecular motions. We have obtained that

$$J_{\mathrm{RTGS,OKE}}(\tau) = |\chi_{\mathrm{FC}}^{(3)}(\omega,\tau)|^2 \, |C_{\mathrm{RTGS,OKE}} + \exp[-r^2(1 - S(\tau))]|^2, \qquad (6)$$

where $C_{\mathrm{RTGS}} = 2$, $C_{\mathrm{OKE}} = \frac{1}{3}$, r is a constant characterizing the correlation of the vector $\boldsymbol{D}_{12}$ with the intermolecular motion. It is worth noting that the attenuation of the time-dependent part of the non-Condon term is determined by the correlation function $S(\tau)$ of the solvation process (see Eq. (6)).

Figure 2(b) shows the time-resolved resonance OKE signal of LDS in 1,3-propanediol. As can be seen from Fig. 2, the OKE signal differs from the RTGS signal. The difference between the RTGS and OKE signals can reflect the correlation of the dipole moment $\boldsymbol{D}_{12}$ with solvation dynamics, although we cannot rule out other plausible mechanisms.

In conclusion, we showed theoretically and experimentally that RTGS is a good method for the investigation of solvation dynamics in a broad time range: from subpicosecond to subnanosecond. We measured the solvation dynamics of LDS 750 in many solvents and a broad time range. We have proposed a new method for the investigation of HT effects in solvation: transient polarization four-photon spectroscopy.

Acknowledgements

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