Solvent Environment Revealed by Positively Chirped Pulses

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Abstract The spectroscopy of large organic molecules and biomolecules in solution has been investigated using various time-resolved and frequency-resolved techniques. Of particular interest is the early response of the molecule and the solvent, which is difficult to study due to the ambiguity in assigning and differentiating inter- and intra-molecular contributions to the electronic and vibrational populations and coherence. Our measurements compare the yield of fluorescence for two laser dyes IR144 and IR125 as a function of chirp. While negatively chirped pulses are insensitive to solvent viscosity, positively chirped pulses are found to be uniquely sensitive probes of solvent viscosity.

1 Introduction

Understanding molecular dynamics soon after photon absorption, taking into account the solvent environment surrounding the molecule, is central to predicting the course of chemical reactions and biophysical processes. The relevant timescales regarding photo-excitation in solution are determined by the inter- and intra-molecular interactions and their corresponding energy fluctuations, which occur in the 10–100 fs regimes [1, 2]. The multiple inter- and intra-molecular processes occurring during this time, convoluted by inhomogeneous broadening as well as the spectral and temporal response function of the experimental setup complicate assignment of the observed decay processes. Here we focus on the optical response from IR125 to IR144, which have been studied in solution as a function of temperature and solvent. The organic dye molecule IR125 undergoes non-polar

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solvation, while IR144 undergoes polar solvation given the reduction in its dipole moment upon excitation. The difference between both molecules is caused by the piperazine functional group in IR144 [3]. Three-pulse photon-echo peak shift (3PEPS) measurements revealed a solvent independent coherent response for times <0.1 ps, described as inertial, followed by a solvent dependent component changing from 4.04 to 1.36 ps in ethylene glycol at 297–397 K [4]. Our goal is to find spectroscopic probes [5] of solvation environment that are sensitive and easier to implement in a microscope, in particular we evaluate here chirped femtosecond pulses. These single-beam methods will be of paramount importance when investigating microenvironment effects on single molecules, due to the relative ease of the experimental implementation.

2 Experimental

Pulses from a femtosecond regeneratively amplified Ti: Sapphire laser producing 25 nm FWHM, (corresponding to 36 fs when transform limited) were used. Pulses were compressed and shaped using a pulse shaper (MIIPS-HD, Biophotonic Solutions Inc.) placed after the amplifier. A chirped-pulse scan consisted of recording molecular emissions as a function of φ'', the spectral chirp from negative to positive 20,000 fs^2, for $\varphi(\omega) = 0.5\varphi''(\omega - \omega_0)^2$. In a sense, a chirp scan can be interpreted as two-color time-resolved measurements for which early changes such as those occurring at 100 fs are observed near 1,000 fs^2.

3 Results and Discussion

Measurements of the dependence of integrated fluorescence intensity (detected at 90°) were recorded as a function of chirp. Results for both dyes dissolved in ethylene glycol at different temperatures are shown in Fig. 1. A secondary axis denoting the pulse duration of the chirped pulses has been provided in the figures to help elucidate the timing of the inter-and intra-molecular processes taking place during the chirp scans. The data is normalized on the asymptotic values of the chirp effect. The curves were normalized on the asymptotic values attained for negative chirp. Measurements for the two different dyes dissolved in ethylene glycol were performed at 278, 294 and 323 K and have been color coded as blue, black and red respectively. Negative chirp experiments can be thought of as being similar to pump-probe measurements, in which the bluer wavelength pump precedes the redder wavelength probe. This observation is consistent with pump-probe measurements comparing IR144 in methanol and ethylene glycol, and finding no difference. Positive chirp, on the other hand, yields different dynamics as a function of temperature. When exploring IR125 fluorescence, we find that colder solvent leads to enhanced fluorescence near 800 fs^2. This enhancement is not observed at higher

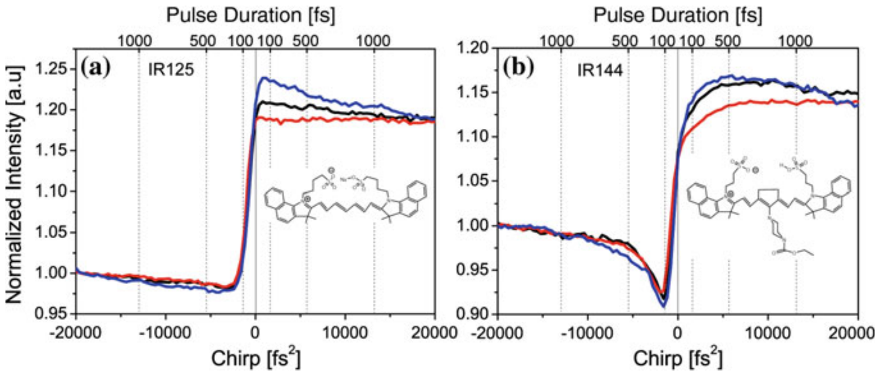

Fig. 1 Integrated fluorescence response to chirped pulses for **a** IR125 and **b** IR144 in ethylene glycol at three temperatures: 278 K (*blue*), 294 K (*black*), and 323 K (*red*)

temperatures. A similar fluorescence enhancement for colder solvent is observed for IR144, however, the maximum fluorescence is reached around 5,000 fs^2 which corresponds to 500 fs. The overall difference in the shape and decay rates between the two dyes can be attributed to molecular properties of the probe molecules. IR144 undergoes a change in dipole moment upon excitation and therefore undergoes polar solvation, which depends on solvent reorientation.

This accounts for the slower dynamics of IR144 in ethylene glycol. IR125 on the other hand undergoes non-polar solvation due to the absence of any significant change in dipole moment upon excitation. The viscoelastic model for non-polar solvation predicts a rapid viscosity independent inertial response and slower viscosity dependent diffusive dynamics following excitation. Our positive chirp findings for IR125 are consistent with the rapid viscosity independent inertial response (rise close to zero chirp) followed by the slower viscosity dependent diffusive dynamics observed as pulse duration increases. In contrast, the dipolar response of IR144 depends on solvent reorientation, a process that is viscosity dependent, and thus delaying the point where maximum fluorescence is observed. The ability of phase shaped laser pulses to probe the solvent environment is particularly exciting given the relative ease of these experiments compared to the much more complicated four wave mixing setups. We plan to take advantage of chirped pulses to probe solvent environment effects of probe molecules in interesting environments such as protein pockets, membranes and under single molecule conditions.

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