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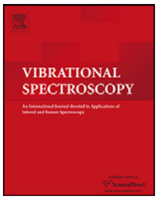

Electronic photon echo spectroscopy and vibrations

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ABSTRACT

Coupling between electronic and nuclear degrees of freedom in Rhodamine 800 has been studied using fluorescence line narrowing (FLN) and three-pulse photon echo peak shift (3PEPS). From the FLN measurement we extract the Huang-Rhys S-factors and frequencies of 16 Franck-Condon active vibrations clustered in two groups centred around 350 cm^{-1} and 1400 cm^{-1}. The five modes below 500 cm^{-1} covered by the excitation pulse spectral band create a complex beating pattern in the 3PEPS measurements. After determining the reorganisation energy of the modes involved in the peak shift measurement we are able to obtain the S-factors of the modes. The S-factors from two different experiments are in good agreement. The dephasing rates of these vibrations deviate significantly from the band-gap law. We propose that the main channel for the dephasing of the modes above 225 cm^{-1} is a second order process involving one phonon and a molecular vibration.

1. Introduction

Any condensed phase system is subject to coupling with environment rendering an explicit microscopic description impractical or even impossible [1,2]. In order to make progress, the system of interest and the so-called bath are separated and treated at different levels of theory. Quantum dynamics of such open systems coupled to the environment (bath) form a broad and active field of research covering deep issues like quantum dissipation, dephasing and even “arrow of time”. Separation of electronic and nuclear degrees of freedom (Born–Oppenheimer approximation) is a usual first step in molecular sciences. The typical outcome is a set of stationary electronic states which are of great importance for many studies. However, in order to understand reactions – transitions from one stationary state to another – one needs to also disentangle the couplings between the electronic system and the nuclear bath.

Nuclear dynamics is usually described via potential energy surfaces that govern the motion. Then the coupling between electronic and nuclear degrees of freedom manifests itself via changes of the nuclear potential energy surfaces in different electronic states. In the widely used linear harmonic Franck-Condon approximation the nuclear motions are described via harmonic normal modes with frequency ν_i. It is assumed that the modes and corresponding frequencies are the same for the different electronic states but the equilibrium nuclear coordinates can be shifted. In unit-less normal mode coordinates the shifts d_i determine the so-called Huang-Rhys S-factors: $S_i = d_i^2/2$ [1,2]. The reorganisation energy can be expressed as $\lambda_i = S_i \times h\nu_i$ and is a good measure of the coupling strength between a nuclear mode and an electronic transition.

S_i can be related to the Franck-Condon factors. This means that absorption and fluorescence spectra contain information about coupling between electronic and nuclear degrees of freedom. However, because of various broadening mechanisms related to dephasing and thermal activation, the room temperature absorption and fluorescence have heavily convolved information content with limited value. The lower thermal activation of over-damped nuclear motions at cryogenic temperatures makes spectral features more distinct compared to room temperature, but usually the inhomogeneous broadening reflecting the static disorder of the glass limits the resolution of the experiment. By selectively exciting a narrow distribution of the inhomogeneous profile it becomes possible to obtain fluorescence spectra that reveal distinct vibronic features [3–6]. The selective excitation of fluorescence with a narrow band laser at low temperature is referred to as fluorescence line narrowing (FLN) spectroscopy. As

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Abbreviations: ZPL, zero phonon line; 3PEPS, three-pulse photon echo peak shift; FLN, fluorescence line narrowing.

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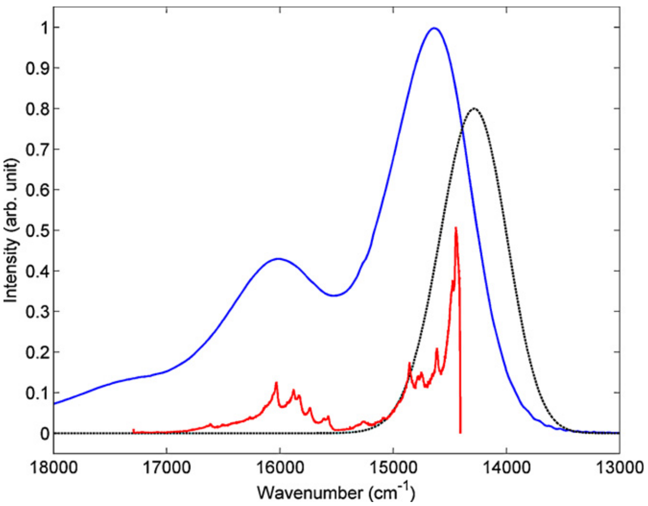

Fig. 1. Linear absorption spectra of Rhodamine 800 in ethanol at room temperature (blue solid). Also shown is the FLN spectra at 10 K reflected around the ZPL (red solid). The black curve provides the spectrum of the laser pulses used for the 3PEPS measurements. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

an example we show in Fig. 1, the room temperature linear absorption and low temperature FLN of Rhodamine 800. For ease of comparison, the FLN spectra have been reflected in respect of the zero phonon line (ZPL) position.

In many cases we are interested in electronic dynamics at room temperature. In order to overcome the room temperature spectral congestion and obtain information about the system–bath interaction it is necessary to explicitly follow the dephasing dynamics. Exploiting the ability to evolve the electronic system in both coherences and population, a three-pulse photon echo experiment is able to measure the system–bath interaction. Of particular importance is the three-pulse photon echo peak shift experiment (3PEPS) [7–14], which directly leads to the first approximation for the system–bath interaction autocorrelation function in the time domain. In this work we use both FLN and 3PEPS to obtain detailed quantitative information of how do the molecular vibrations and the solvent motions couple to an electronic transition of a chromophore. We demonstrate that the S_i acquired by different methods is identical.

2. Materials and methods

The FLN measurements were conducted in a flowing helium cryostat (Janis STVP-400) and the spectra were recorded by a 0.32 m spectrograph (Triax 320, Jobin Yvon) combined by a liquid nitrogen cooled CCD. The sample was excited at 713.8 nm with a NdYAG laser (Millennia ProX, Spectra Physics) pumped continuous wave Ti:Sapphire laser (Spectra Physics 3900S) with a line width of less than 0.1 cm^{-1}. The power density was kept low enough to avoid hole-burning effects in the spectra. Usage of a 1200 lines/mm grating blazed at 750 nm resulted in a spectral resolution of 0.1 nm. The optical density at the peak of the absorption spectra was 0.3 and the fluorescence was collected perpendicularly in respect to the excitation beam.

The photon echo set-up and methodology has been described before [15]. In the present experiment the NOPA was set to 700 nm generating pulses of 34 nm bandwidth. The time domain characterization of the pulses was done via second order autocorrelation in a 100 μm BBO crystal. The autocorrelation had a Gaussian shape with a FWHM of 29 fs resulting in almost perfectly transform limited pulses. The total energy per pulse was estimated to be 2.5×10^{14} photons/cm^2. The optical density of the sample was 0.15 at the excitation wavelength and the measurements were performed in a 0.2 mm quartz cell to avoid pulse propagation effects [16–18].

Rhodamine 800 (Sigma–Aldrich) was dissolved in ethanol for all measurements.

3. Results and discussion

In FLN the system–bath interaction strength is related to the ratio of the intensities of the sideband and the ZPL. Since the ZPL emission is contaminated by scattering of the exciting laser, additional information is needed. This information can be obtained from simulations. In earlier studies either the temperature dependence of the linear absorption spectra [5] or the wavelength dependence of the FLN spectra [6] has been simulated. Here we make use of the temperature dependence of the vibrational sidebands of the FLN spectra together with the linear absorption spectra, to determine the unit-less shift of the minima of the normal modes that couple to the electronic transition (see Table 1). We also find that the Gaussian inhomogeneous broadening has a FWHM of 550 cm^{-1} and the maximum at 14500 cm^{-1} (689.7 nm). Both the ZPL and the vibrations were constructed using a Lorentzian line with a FWHM of 4 cm^{-1}. The low frequency over-damped phonon modes were described via spectral density consisting of the Debye density of phonon states multiplied by an exponential cutoff. In Fig. 2, the measured and calculated FLN spectra of Rhodamine 800 at three temperatures are presented.

The strength of the FLN measurement is the very reliable quantitative information about the fast parts of the system–bath interaction – coupling to the molecular vibrations. The ability to accurately determine low frequency dynamics in FLN critically depends on the removal of the resonant scattering from the detected signal. The removal is never perfect; consequently the FLN is not ideal to reveal slower bath dynamics. The issue is particularly problematic in liquid phase where there is no clear borderline between slow and fast motions of the bath. However the complementary use of FLN and 3PEPS can help to circumvent this problem, as the photon echo approaches the problem from the opposite end, and is more suited to study the slower parts of the dynamics. Even though in the harmonic approximation the two measurements should show the same dynamics, the respective strengths and weaknesses of the two methods lead to quite different low frequency spectral densities.

The 3PEPS of Rhodamine 800 in Fig. 3 has decaying and oscillating components. According to the 3PEPS theory the decaying component has inertial (Gaussian) and diffusive (expo-

Table 1
Frequencies, dimensionless displacements and reorganisation energies of the normal modes used in the simulations. The total reorganisation energy of all vibrational modes is equal to 832 cm^{-1}.

ν_i (cm^{-1})	90	165	225	290	356	392	465	870
d_i	0.536	0.280	0.523	0.255	0.427	0.343	0.498	0.198
λ_i (cm^{-1})	12.9	6.5	30.8	9.5	32.5	23.0	57.6	17.0
ν_i (cm^{-1})	1180	1220	1342	1440	1490	1550	1640	2220
d_i	0.313	0.182	0.394	0.430	0.396	0.024	0.460	0.181
λ_i (cm^{-1})	57.9	20.3	104.0	133.0	116.6	0.45	173.2	36.2