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Ultrafast relaxation and modulation in the oxazine dye nile blue

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Time-delayed four-wave mixing, using incoherent laser pulses 5 ns long and 350 Å wide, has been used to measure the optical phase relaxation of a large molecule (nile blue) in solution at 300 and 4.5 K. In the latter case an asymmetric response as well as a quantum beat (signaling a vibronic mode at 583 cm^{-1}) is observed. Its magnitude and shape gives its electron-vibron coupling factor $S=0.79$ together with the homogeneous relaxation time $T_2=43.7$ fs and the inhomogeneous relaxation time $T_2^*=13.3$ fs (full width of 940 cm^{-1}). Supporting evidence for the large value of S is presented.

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Femtosecond dye lasers have expanded the limits of ultrafast spectroscopy and fuel a continuing interest in optical properties of the oxazine dye nile blue. Time-resolved fluorescence measurements by up-conversion track a femtosecond spectral evolution followed by solvatochromic relaxation [1]. Recent photon-echo experiments using 6-fs pulses show optical coherence effects on the faster end of the femtosecond scale [2]. Previous echo experiments using pulses as short as 70 fs were unable to detect any coherence effects in nile blue even when cooled to 15 K [3]. That these same echo experiments had the potential to detect fast coherent effects was demonstrated by their results with the oxazine dye cresyl violet at 195 K and lower.

Another means of doing ultrafast spectroscopy is by exploiting the short noise spikes in a wide band non-transform limited laser. Fujiwara, Kuroda, and Nakatsuka [4] used a 40-Å-wide, 10-ns pulsed dye laser to study cresyl violet and confirmed that relaxation effects are observed at lower temperatures. This kind of experiment using noise fields retains the ability of detecting coherent quantum beats as was previously demonstrated by work performed in Na vapor using 16-Å-wide, 5-ns pulses [5]. In that work a 1.9-ps beat corresponding to the 6-Å fine structure of the $3P$ states was observed.

The two-pulse-echo experiments of Becker *et al.* produced a modulated response interpreted as due to quantum beats from 1850- and 555-cm^{-1} molecular vibrational modes in the S_1 excited state [2]. These modulations were identified by Bigot *et al.* [6] in the correlation function of their subsequent three-pulse-echo experiment although not evident in their plot of the echo intensity in the limit where two of the pulses were applied simultaneously.

We have used 350-Å-wide laser noise pulses 5 ns in duration to generate a coherent transient response by the time-delayed four-wave-mixing (TDFWM) technique. We confirm the lower-frequency modulation [2], but our 16-fs pulse intensity autocorrelation time did not provide sufficient bandwidth to excite any mode as high as 1850 cm^{-1}. In our analysis we use 583 cm^{-1} [7] for the lower vibrational mode and find an associated transition probability for the $0\rightarrow 1$ vibrational transition a factor of 5 larger than [2] used to fit their data. In terms of the electron-vibron coupling factor it means that $S=0.8$. Since this is comparable to unity our result implies that even the $0\rightarrow 2$ transition is appreciably excited and must be included in any photon-echo analysis.

Our results cited above were obtained with nile blue at 4.5 K in ethanol. The two-pulse experiments, on the other hand, were performed at room temperature with nile blue in ethylene glycol [2]. It is unlikely that either the dissimilar solvents or temperatures can account for the differences observed. When we worked at room temperature our results indicated that either $T_2 \ll 16$ fs or spectral diffusion was taking place on a short time scale compared to 1 ns. This limit must be reduced to 200 fs to accommodate the results of Ippen [3]. (Bigot *et al.* claim they found that spectral diffusion acts this fast [6].) Invoking spectral diffusion may have the advantage of explaining the otherwise puzzling result of Drabe, Cnossen, and Wiersma [8] that nile blue in a polymer at room temperature seems to be homogeneously broadened with $T_2=100$ fs [9].

The molecule nile blue has a molecular weight of 417.85 and a correspondingly rich vibrational spectrum which has been exposed by both hole-burning [7] and pump-probe experiments [10]. On using 6-fs pulses Fragnito *et al.* [11] find that the transmission is characterized by a 60-fs modulation showing that the mode at 583 cm^{-1} [7] is dominant.

In a TDFWM experiment wide band noise pulses along $\mathbf{k}_1$ and $\mathbf{k}_2$ produce four-wave mixing signals along $\mathbf{k}_3=2\mathbf{k}_2-\mathbf{k}_1$ and $\mathbf{k}_4=2\mathbf{k}_1-\mathbf{k}_2$. In the limit that the longitudinal relaxation time $T_1 \gg T_2, \tau_c$ where T_2 is the transverse relaxation time and τ_c is the source correlation time then neglecting spectral diffusion the signal along $\mathbf{k}_3$ for

k$_2$ following **k**$_1$ by τ is given by [12,13]

$$I(\tau)\propto\sum_{m,n,m',n'}|P_m|^2|P_n|^2|P_{m'}|^2|P_{n'}|^2\int_0^\infty dt\int_0^\infty ds\,R(t-s)e^{-(\gamma_m t+\gamma_{m'}s)}e^{-i(\Delta_m t-\Delta_{m'}s)}$$
$$\times\int_0^\infty dt'\int_0^\infty ds'[R(\tau-t')c^{-(\gamma_n-i\Delta_n)t'}G^*(t-t')+R(\tau+t')e^{-(\gamma_n+i\Delta_n)t'}G^*(t+t')]$$
$$\times[R^*(\tau-s')e^{-(\gamma_{n'}+i\Delta_{n'})s'}G(s-s')+R^*(\tau+s')e^{-(\gamma_{n'}-i\Delta_{n'})s'}G(s+s')]\,, \tag{1}$$

where $\Delta_n=\omega-(\omega_{00}+n\Omega)$ is the detuning of the laser from level n, ω is the laser frequency, Ω is the mode frequency, and ω_{00} is the frequency of the $0\rightarrow 0$ transition, γ_n is the dephasing rate, $(1/T_2)_n$, of level n,

$$R(t)=\int_{-\infty}^{+\infty}\mathcal{E}^*(t)\mathcal{E}(t+\tau)d\tau=\frac{1}{2\pi}\int_{-\infty}^{+\infty}\mathcal{P}(\omega)d\omega \tag{2}$$

is the source correlation function, $E(t)$ is the electric field amplitude, $\mathcal{P}(\omega)$ is the source power spectrum, and $G(t)$ is the Fourier transform of the inhomogeneous line. According to [14] resonant Raman-scattering experiments show that the vibrational level structure of the S_0 and S_1 states are identical. This being the case, we can write, for a single vibronic mode,

$$\sum_n|P_n|^2e^{-i\Delta_n t}=e^{-i(\omega-\omega_{00})t}\sum_n|P_n|^2e^{in\Omega t}$$
$$=e^{-i(\omega-\omega_{00})t}p^2\sum_n\left|\frac{(-1)^n\alpha^n}{\sqrt{n!}}e^{-\alpha\alpha^*/2}\right|^2e^{in\Omega t}$$
$$=e^{-i\Delta t}p^2e^{-S(1-e^{i\Omega t})}\,. \tag{3}$$

where p is the dipole moment associated with the $0\rightarrow 0$ transition and $S=\alpha\alpha^*$ is the electron-vibron coupling factor. Equations (1) and (3) taken together give the four-wave mixing response if a single mode dominates. It simplifies in the limit of extreme inhomogeneous broadening where it becomes

$$I\propto p^8\int_0^\infty dt\int_0^\infty ds\,R(t-s)R^*(t-\tau)R(s-\tau)$$
$$\times e^{2S(\cos\Omega t+\cos\Omega s)}e^{-2\gamma(t+s)}\,. \tag{4}$$

We use this expression to fit the data for $\tau>0$ and thereby obtain S and T_2, having assumed that Ω is accurately known from hole-burning experiments. For $\tau<0$ the response is dominated by T_2^*, which we determine by using Eqs. (1) and (3) together with the values of S and T_2 previously obtained.

Single excitation pulses at 6220 and 350 Å wide and 5 ns long were obtained from the simplified spontaneous emission of a dye cell transversely pumped by a Nd:YAG laser. This output was split and a relative delay τ was introduced in an interferometric setup. The pulses were brought together at an angle of 10 mrad and recombined at the sample in an area of diameter 250 μm. Both parallel and antiparallel polarization excitation schemes were used to check for thermal effects. None were found. Pulse energies were in the range of 1 to 2 μJ and their power spectrum was monitored before and after the sample. The nile blue was dissolved in ethanol with a resulting optical density of 1. Both signals along **k**$_3$ and **k**$_4$ were recorded as a function of τ.

At room temperature the signals were symmetric about zero delay and described by $I(\tau)\propto|\int d\omega\times e^{-i\omega\tau}\mathcal{P}(\omega)\times\mathcal{A}(\omega)|^2$ where $\mathcal{A}(\omega)$ is the absorption profile [3]; cf. our Fig. 1. This shows that the sample appears to be homogeneously broadened. It also serves as a check on our data processing and analysis.

At 4.5 K the signals were asymmetric and broadened; cf. Fig. 2. Variations in optical density from 0.5 to 3 and in power down to 0.1 μJ did not seem to alter the charac-

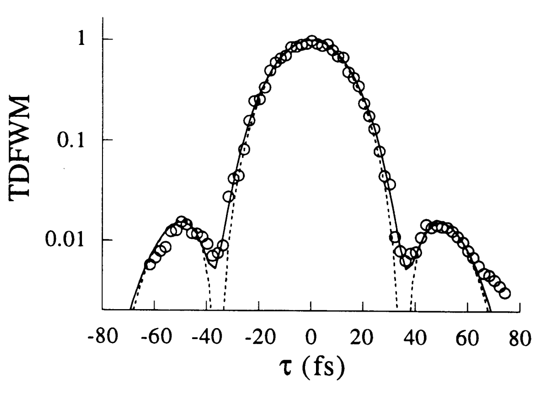

FIG. 1. The TDFWM response at room temperature is plotted as a function of the excitation pulse delay (open circles). For comparison, the Fourier transforms of both the square of the pulse power spectrum (dashed line) and the square of the product of the pulse power spectrum and absorption coefficient (solid line) are also shown.

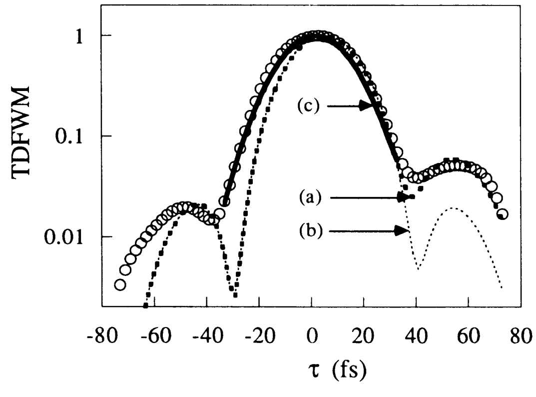

FIG. 2. The TDFWM response at 4.5 K is plotted as a function of the excitation pulse delay. The data are shown as circular points. $\Omega/2\pi c$ is set at 583 cm^{-1} in all calculations. Curve a: measured autocorrelation, $T_2^*=0$, $S=0.79$ (best fit to $\tau>0$), $T_2=43.7$ fs (best fit to $\tau>0$). Curve b: same as a but with S set to 0.15, $T_2=14.6$ fs (best fit to $\tau>0$). Curve c: $S=0.79$, $T_2=43.7$ fs as in a; $\tau_c=16.2$ fs (best Gaussian), $T_2^*=13.3$ fs (best fit for $|\tau|<33$ fs).

ter of the data.

Zero delay was determined to better than 0.5 fs by the symmetry requirement $I(\mathbf{k}_3,\tau)=I(\mathbf{k}_4,-\tau)$. We began by setting $T_2^*=0$ and $\Omega/2\pi c=583\ \mathrm{cm}^{-1}$ [7]; a nonlinear least-squares fit to Eq. (4) then gave $T_2=43.7$ fs and $S=0.79$ (cf. thick dotted line in Fig. 2). When Ω was allowed to vary as well, we found $\Omega/2\pi c=590\ \mathrm{cm}^{-1}$, $T_2=43.1$ fs, and $S=0.78$. Both of these fits were restricted to $\tau>0$ since the negative τ region is very sensitive to T_2^*. The source correlation function $R(t)$ was obtained via Eq. (2) from the measured power spectrum. It has a prominent bump on each side of the central peak. The left-hand bump is manifested clearly in Fig. 2 but the one on the right side is masked by the mode at $583\ \mathrm{cm}^{-1}$.

To show that the right-hand bump of Fig. 2 really implies the presence of a strong vibronic mode, we replaced the parameter $S=0.79$ by the smaller value $S=0.15$ found in [2]. Again setting $\Omega/2\pi c=583\ \mathrm{cm}^{-1}$ and varying T_2 for the best fit, we found the thin dotted curve in Fig. 2, which does not fit the data well.

When $T_2^*>0$ the computation is time-consuming unless $R(t)$ is Gaussian. To determine T_2^* we took $R(\tau)\approx\exp(-t^2/2\tau_c^2)$ where $\tau_c=16.2$ fs to approximate the central peak of R as previously measured. Using our best values $\Omega/2\pi c=583\ \mathrm{cm}^{-1}$ [7] and $T_2=43.7$, $S=0.79$ from Fig. 2 (curve *a*), we now varied T_2^* to fit only the central peak ($|\tau|<33$ fs) of Fig. 2. In this calculation (thick solid curve) the sum in Eq. (1) was restricted to $n\leq 2$ and Δ_0 was set at $500\ \mathrm{cm}^{-1}$ to conform to the actual laser frequency. We found that $T_2^*=13.3$ fs.

The value of $T_2^*=13.3$ fs we obtain is quite reasonable and in agreement with estimates made elsewhere. It corresponds to a width of $\Delta\tilde{\nu}_{\mathrm{HWHM}}=\sqrt{\ln 2/2}/\pi c T_2^*=470\ \mathrm{cm}^{-1}$ in agreement with estimates $\Gamma_{\mathrm{inhom}}\approx 500\ \mathrm{cm}^{-1}$ made for the related cresyl violet in polyvinyl alcohol at low temperature [15,16]. It also conforms well to the measured absorption spectrum. A T_2^* much shorter makes the spectrum fall off too slowly on the red side; much longer and the structure of the 583-cm^{-1} mode is not washed out.

The value of $T_2=43.7$ fs measured at 4.5 K is too short to be understood as a thermally induced process. One possibility is that it is due to an ensemble of weak but numerous vibrational excitations which combine to produce the effect of a short T_2 [3]. Photon-echo measurements at room temperature find $T_2=65$ fs [2] and it is argued that this is the consequence of some non-Markovian relaxation process [6]. If so it would seem that T_2 at lower temperatures would be substantially increased rather than decreased as we measure. Another possible explanation is that there remains some residual spectral diffusion even at 4.5 K.

The mystery deepens when we compare with cresyl violet. Hole widths at low temperatures are of the order of $1\ \mathrm{cm}^{-1}$, are comparable with those in nile blue [7], and increase linearly with temperature [17]. Narasimhan, Pack, and Fayer, working with cresyl violet, have shown, using photon echoes, that the homogeneous linewidth is at least a factor of 5 narrower yet [18]. Weiner, Silvestri, and Ippen's work, however, using 70-fs pulses at 15 K finds that, though they are able to measure relaxation effects in cresyl violet, the dye nile blue relaxes too quickly to allow measurement [3]. This puzzle notwithstanding, Weiner, Silvestri, and Ippen [3] and Fujiwara, Kuroda, and Nakatsuka [4] find relaxation rates in cresyl violet orders of magnitude faster than found by Narasimhan, Pack, and Fayer [18] even though their excitation pulses are more to the red. Granted the techniques are different but since Weiner, Silvestri, and Ippen used a sequence of three 70-fs pulses sometimes all occurring within a 4-ps interval, which was the pulse duration in Fayer's two-pulse echo experiment, it is difficult to understand an observed relaxation rate in the former case more than 2 orders of magnitude faster than measured in the latter.

Our value of $S=0.8$ is large when compared to $S=0.15$ obtained from two-pulse photon-echo experiments [2]. Other experiments, however, imply that our result is reasonable. The pump probe experiment of Fragnito *et al.* [11] has been analyzed by Pollard and co-workers [14,19] and they deduce that the coherent vibrational wave packet excited by the 6-fs pump pulse undergoes an excursion of $2D=3.0$ (cf. Fig. 3 of [14]). Here $D=\sqrt{2}\alpha$ is the reduced displacement of the ground- and excited-state harmonic potentials. Using their $\Omega/2\pi c=590\ \mathrm{cm}^{-1}$ leads to $S=\frac{1}{2}D^2=1.1$, which is even larger than our value. Another check on the reasonableness of our S relates to the Franck-Condon shift. The Stokes shift is the sum of the Franck-Condon shift (Stokes shift when $\Delta\mu=0$) and the solvatochromic shift ($\Delta\omega_S$). They are related by the Lippert-Mataga equation [20]

$$\Delta\omega_{\mathrm{Stokes}}=\Delta\omega_{\mathrm{FC}}+\frac{2(\Delta\mu)^2}{\hbar a^3}\left[\frac{\epsilon-1}{2\epsilon+1}-\frac{n^2-1}{2n^2+1}\right], \tag{5}$$

where $\Delta\mu$ is the difference in the dipole moment of the molecule in the ground and excited states, ϵ is the dielectric constant, and n is the index of refraction. The last term is $\Delta\omega_S$. Dutt *et al.* [21] have tabulated corresponding values of λ_a, λ_f, ϵ, and n for several solvents. The wavelengths correspond to the peaks in the absorption and fluorescence spectra, respectively. A plot of $\Delta\omega_{\mathrm{Stokes}}$ vs $\Delta\omega_S$ is closely fit to a straight line if their pyridine data is

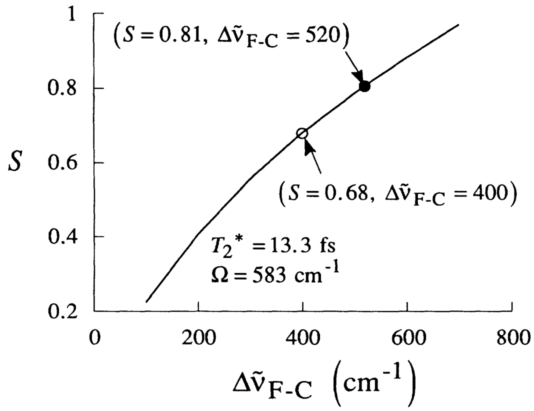

FIG. 3. The electron-vibron coupling factor for an inhomogeneously broadened molecule with the same single vibrational mode in both the ground and excited states is plotted as a function of its associated Franck-Condon shift.

excluded and on extrapolation leads to a Franck-Condon shift of 400 cm^{-1}. Including the pyridine data gives a Franck-Condon shift of 520 cm^{-1}. If the absorption spectrum is dominated by a single mode the Franck-Condon shift is directly related to S. For our situation, where inhomogeneous broadening dominates, the absorption is given by

$$\mathcal{A}(\omega)\approx\sum_{n=0}^{n=\infty}\frac{S^n}{n!}\exp[-(\omega-\omega_{00}-n\Omega)^2T_2^{*2}/2] \tag{6}$$

then $d\mathcal{A}(\omega)/d\omega=0$ at $\omega-\omega_{00}=\frac{1}{2}\Delta\omega_{\text{FC}}\equiv\omega_{\text{FC}}$. Therefore $S=S(\Delta\omega_{\text{FC}})$ is obtained as the solution to

$$\omega_{\text{FC}}=\frac{\Omega\sum_n n\,(S^n/n!)\exp[-(\omega_{\text{FC}}-n\Omega)^2T_2^{*2}/2]}{\sum_n (S^n/n!)\exp[-(\omega_{\text{FC}}-n\Omega)^2T_2^{*2}/2]}\,. \tag{7}$$

We plot the solution of this equation in Fig. 3. It is clear from the figure that our value of $S=0.79$ is supported by the Stokes shift data.

In conclusion, we have used incoherent laser noise to perform a TDFWM experiment in nile blue at 4.5 K which finds asymmetry and detects a quantum beat revealing the prominent vibrational mode at 583 cm^{-1} implying an electron-vibron factor an order of magnitude larger than previously measured. An analysis of pump-probe and Stokes shift data both support our measurement. Our measurement of T_2^* yields the inhomogeneous width as 940 cm^{-1}. Our measured T_2 is of the order of that obtained by room-temperature two-pulse photon-echo experiments which is surprising since all thermally activated processes should have been frozen out.

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