

Optical Stark Effect in Organic Dyes Probed with Optical Pulses of 6-fs Duration

P. C. Becker, R. L. Fork, C. H. Brito Cruz,^(a) J. P. Gordon, and C. V. Shank

AT&T Bell Laboratories, Holmdel, New Jersey 07733

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We report the first observation of the dynamic optical Stark shift on a femtosecond time scale. Pump pulses of 50-fs duration with peak intensities of 10^{11} – 10^{12} W/cm² were used to cause a Stark shift of the S_0 to S_1 transition in the organic dye molecule rhodamine-B. The perturbed spectra were observed with the use of probe pulses of 6-fs duration. The inferred effective transition dipole moment of 7 D is in good agreement with the value derived from the absorption line strength. At the higher pump powers, line-shape distortions and a reduction in the apparent line strength are also noted and discussed.

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We report the first observation of the optical Stark effect in large organic dye molecules in solution, probed on a femtosecond time scale. The optical Stark effect has been previously exploited in a number of gas-phase and condensed-matter systems.¹⁻⁴ Dye molecules have broad absorption lines with bandwidths on the order of tens of nanometers, which makes the Stark effect a difficult effect to study in these systems. However, the advent of high-intensity, ultrashort, coherent optical pulses⁵ has made it possible for the first time to directly observe the influence of intense optical fields on molecules in solution.

The optical Stark effect occurs when a high-intensity radiation field is coupled to a nearly resonant material system, resulting in shifts of the transition energies observed in absorption or fluorescence. The intensity-dependent absorption-frequency shift for a two-level system with a transition frequency ω_{21} is given by $\Delta\omega_{21} = \omega_p - \omega_{21} + \delta$, where

$$\delta = [(\omega_{21} - \omega_p)^2 + \Omega^2]^{1/2}. \quad (1)$$

$\Omega = \mu \cdot \mathbf{E}(\omega_p)/\hbar$ is the Rabi frequency and $\mathbf{E}(\omega_p) \times \cos(\omega_p t)$ is the pump electric field. For low pump intensities the shift of the absorption line relative to ω_{21} increases linearly with the pump intensity and at high intensities as the square root. To observe the Stark shift in organic dyes, a Rabi frequency comparable to the detuning is needed, which requires minimum intensities of 10^{11} W/cm², easily achievable with amplified femtosecond optical pulses.

The rhodamine dyes used in this study, sulforhodamine-640, rhodamine-6G, and rhodamine-B, have absorption peaks to the blue side of the 620-nm pump. The absorption bands of the molecules (FWHM \cong 25 nm) are composed of a number of vibronic transitions. Spectral hole-burning measurements have shown that the T_2 dephasing time in large dye molecules is on the order of 50–100 fs.⁶ This corresponds to a homogeneous linewidth of about 5 nm. An identification of the vibronic transitions that are contained within the S_0 to S_1 electronic transition, based on the room-temperature absorp-

tion line shape, was given by Schere, Seilmeier, and Kaiser.⁷

The experiment is done with a pump-probe technique with a pump of duration 50 fs, centered at 620 nm, and an energy of about 100 nJ, and a probe of duration 6 fs also centered at 620 nm. The pump and probe polarizations are parallel. The femtosecond pulses are produced by a colliding-pulse mode-locked laser and amplified in a copper-vapor laser pumped dye amplifier. These pulses are then split in two, one of them becoming the pump pulse; the other is sent through a short piece of optical fiber where it undergoes spectral broadening and is then compressed with a grating and prism-pair combination to form the probe pulse.⁵ The transmittance of the probe through the excited sample is monitored by an optical multichannel analyzer. Spectra are recorded as a function of the time delay between the pump and probe beams. The dyes are dissolved in ethylene glycol at concentrations which yield optical attenuations of less than $1/e$ when the dye solution is flowed through a jet with a thickness of 75 μm .

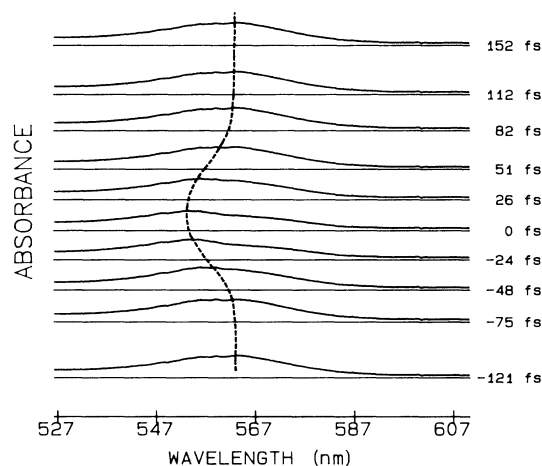


FIG. 1. Experimental absorption spectra of rhodamine-B during the passage of an intense 50-fs pump pulse, recorded with the 6-fs probe pulse.

Figure 1 shows the experimental absorption spectra obtained in the case of rhodamine-B ($\omega_{21} \cong 565$ nm) for different relative time delays between the pump and probe beams. The spectra observed are 6-fs snapshots taken during the passage of the 50-fs pump pulse. A fast shift to the blue in the line center is clearly observed as the pump pulse travels through the medium. At the peak of the pump pulse, the shift is maximized and reaches a value of about 9 nm (280 cm^{-1}). Changes in the line shape are also present.

Useful information is provided by investigation of the optical Stark shift as a function of pump intensity. Figure 2 is a plot of the Stark shift as a function of pump intensity for the dye rhodamine-B. The data points were obtained from a single experimental run, the intensity being varied by replacement or removal of neutral density filters from the pump beam path. The low-intensity points follow a linear dependence on intensity, as expected from Eq. (1). All the experimental points, except the last two, were fitted by Eq. (1) and the result is shown as a smooth curve.

From the plot of the line-center shift as a function of intensity, we can obtain an effective dipole moment for the rhodamine-B dye molecule. At low pump intensities, the Stark shift of a multilevel system can be readily calculated with second-order perturbation theory. Since in our case the pump is well off resonance, the pump detuning is approximately the same for all the vibronic transitions of the S_0 to S_1 electronic transition, and the Stark shift of state n (energy E_n) is given by

$$\Delta E_n \approx \sum_m |\langle n | \boldsymbol{\mu} \cdot \mathbf{E}(\omega_p) | m \rangle|^2 / 4\Delta, \quad (2)$$

where n denotes an S_0 state and m an S_1 state, or vice versa. Δ is the average detuning of the pump and is equal to $(E_n - E_m)_{av} + \hbar\omega_p$ if n is in the ground state and to $(E_n - E_m)_{av} - \hbar\omega_p$ if n is in the excited state.

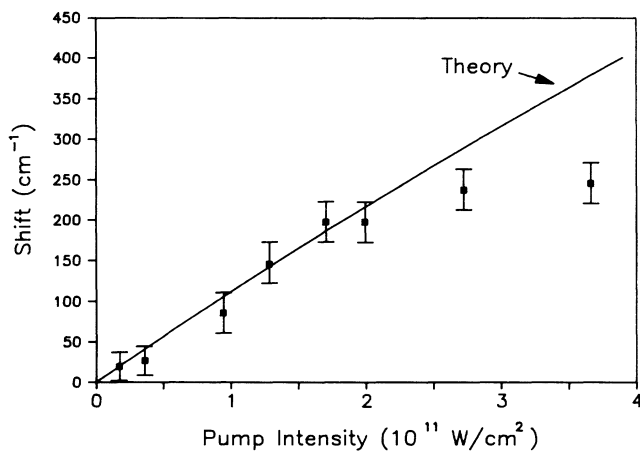


FIG. 2. Stark shift of the absorption-line center for rhodamine-B as a function of the pump intensity. The smooth curve is the best fit of Eq. (1) to the first six experimental points and yields an effective dipole moment of 6 D.

The peak of the vibronic transition manifold will thus be shifted by the amount

$$\Delta E \approx \sum_m |\langle n | \boldsymbol{\mu} \cdot \mathbf{E}(\omega_p) | m \rangle|^2 / 2\Delta, \quad (3)$$

where we assumed that the excited-state shift is equal and opposite to the ground-state shift. $\sum_m |\langle n | \boldsymbol{\mu} \cdot \mathbf{E}(\omega_p) | m \rangle|^2$ represents the integrated absorption from a vibronic state of the S_0 manifold to the S_1 manifold. This expression shows that at low intensities the shift of the peak of the vibronic transition manifold appears identical to that of an effective two-level system. If we average over the distribution of molecular orientations in a liquid, the rate of change of the Stark shift with respect to pump intensity is given ($I = \frac{1}{2} cn_0 \epsilon_0 \times |\mathbf{E}(\omega_p)|^2$) by

$$d(\Delta E)/dI = \frac{3}{5} \mu_{12}^2 / cn_0 \epsilon_0 \Delta_n, \quad (4)$$

where the effective dipole moment is $\mu_{12}^2 = \sum_m |\langle n | \boldsymbol{\mu} \times | m \rangle|^2$, and n_0 is the index of refraction of the solution. Using the experimental data of Fig. 2, we then obtain an effective dipole moment for the rhodamine-B dye molecule S_0 -to- S_1 transition:

$$\mu_{12} \approx 2 \times 10^{-29} \text{ C m} \approx 7 \text{ D.}$$

This effective dipole moment compares well to the value of $\mu_{12} \approx 8$ D determined from the measured peak absorption cross section of 3.4×10^{-16} cm^2 for rhodamine-B. The primary source of uncertainty in the estimate of μ_{12} is the absolute value of the intensity and leads to a relative uncertainty of $\pm 50\%$. Note also that contributions to the excited-state shift from transitions from the S_1 excited state to higher-lying states have been neglected.

At high pump intensities we observe from Fig. 2 that the signal saturates and deviates from the square-root dependence. The Stark shift in this region is significantly lower than expected from Eq. (1), if we use the

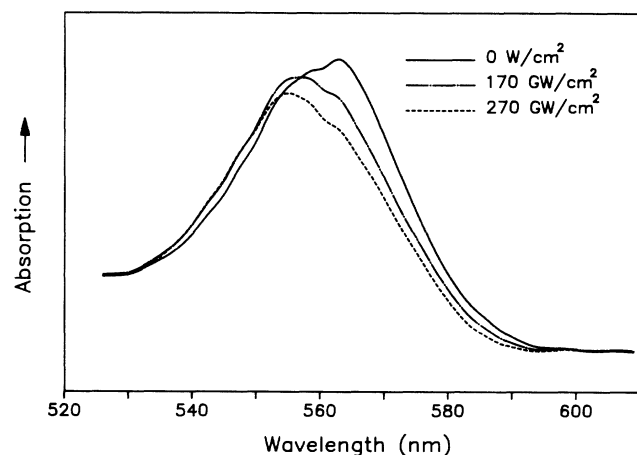


FIG. 3. Absorption line of rhodamine-B at the peak of the pump pulse for three different values of pump intensity.

previously estimated effective dipole moment. At these high intensities, the multilevel character of the line becomes important, the line shape begins to distort significantly, and the simple two-level approximation breaks down.

Figure 3 shows three traces of the absorption spectrum of rhodamine-B at different peak pump intensities. It is clear that as the pump intensity rises there is a decrease in the integrated absorption, evidenced by a lowering of the area under the absorption line. The integrated absorption decreases steadily as the pump intensity increases. The loss of integrated absorption is virtual in that the absorption spectra immediately before and after the passage of the pump are identical.

This effect can be qualitatively understood within an already well-known framework for the steady-state interaction of a strong pump and a weak probe with a two-level system.^{8,9} Since the pump detuning from the molecular resonance is large, the molecular system responds nearly instantaneously to the pump field. At any given moment during the passage of the pump, the system can then be analyzed with the steady-state treatment of Mollow.⁸ Since the solution developed in Ref. 8 is linear in the probe field, each frequency component of our large-bandwidth probe can be considered separately. With use of the parameters of our experimental conditions it is found that the integrated absorption strength of the shifted line does indeed decrease as the Rabi frequency increases. Physically, this is due to the fact that the strong pump creates a nonnegligible virtual population in the excited state, which correspondingly reduces the apparent line strength.¹⁰

In conclusion, we report the first measurements of the optical Stark effect in organic dyes in solution on a femtosecond time scale. We have used the effect to estimate an effective dipole moment of the rhodamine-B dye mol-

ecule, and have found that at high peak pump intensities the absorption line can be significantly perturbed. The demonstration of the dynamic Stark shift in a large molecule in solution on a femtosecond time scale raises the interesting possibility of the switching of molecular transitions on or off resonance for various optical or spectroscopic applications.

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^(a)On leave from Instituto de Física, University of Campinas, Campinas, 13100 São Paulo, Brazil.

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