

Four-wave spectroscopy of excited organic molecules

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The dispersion of the cubic nonlinear susceptibility of excited 1,4-diphenylbutadiene molecules has been measured. A comparison of the results with model-based calculations yields the mechanisms and time scales of the ultrafast relaxation processes for highly excited electronic states.

Studies of the relaxation and hidden structure of the absorption spectra of transitions between the electronic ground states (S_0) and a low-lying excited state (S_1^*) in organic molecules make extensive use¹⁻⁴ of the method (proposed in Refs. 5 and 6) of four-wave spectroscopy, which is based on measurements of the dispersion of the nonlinear cubic susceptibility $\chi^{(3)}$. In the present study we have used the methods of Refs. 5 and 6 for transitions between two excited electronic states of large molecules.

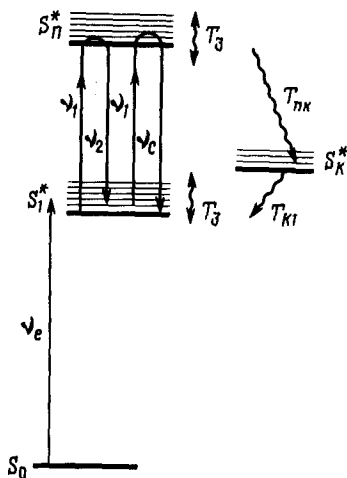


FIG. 1. Scheme of levels and transitions.

This approach has yielded data on the mechanisms and relaxation times of highly excited ($S_n^*, n > 1$) states. It is difficult to use other methods, e.g., ultrashort pulses, for this purpose because of the fast radiationless decay of S_n^* (an estimate based on the quantum yield of the $S_n^* \rightarrow S_0$ luminescence^{7,8} yields 10^{12} – 10^{14} s⁻¹).

In the experiments we used cyclohexane solutions of 1,4-diphenylbutadiene at room temperature. The dispersion of $\chi^{(3)}$ was measured in the $S_1^* \rightarrow S_n^*$ absorption band, which has a maximum at $\nu_m \approx 15\,000$ cm⁻¹ and a half-width $V \approx 2100$ cm⁻¹ (Ref. 9). The state S_1^* was filled by light pulses at the third harmonic of a nanosecond-pulse Nd:YAG laser with a frequency $\nu_e \approx 28\,200$ cm⁻¹, at resonance with the band of the $S_0 \rightarrow S_1^*$ transition. Four-wave mixing of the excited molecules was detected at the frequency $\nu_c = 2\nu_1 - \nu_2$, where ν_1 and ν_2 are the output frequencies of two dye lasers with a narrow band (the width of the output line was ≤ 0.3 cm⁻¹) pumped by pulses at the second harmonic from the same Nd:YAG laser (Fig. 1). We measured the intensity of the scattering signal (I_c) as a function of the frequency deviation $\Delta\nu = \nu_1 - \nu_2$ at $\nu_1 \approx 16\,000$ cm⁻¹, and we varied ν_2 over the range 15 000–17 000 cm⁻¹. The value of I_c at $\Delta\nu \approx 1$ cm⁻¹ was higher by a factor $\sim 10^5$ than the intensity of the “noise” signal detected in the absence of the ν_e light. We were thus able to eliminate the component of I_c due to scattering by unexcited molecules.

Figure 2 shows the results of these measurements, as plots of $\log|\chi^{(3)}|$ versus $\log|\Delta\nu|$ ($|\chi^{(3)}| \sim \sqrt{I_c}$). The similarity between the curves in Fig. 2 which correspond to the parallel (1) and orthogonal (3) polarizations of the light with ν_1 and ν_2 indicates that processes such as Brillouin scattering do not contribute to the frequency dependence of $\chi^{(3)}$ (Ref. 10). The linear region of the $(\log|\chi^{(3)}| \sim -\log|\Delta\nu|)$ curves, which can be seen even at $|\Delta\nu| \gtrsim 1.5$ cm⁻¹, is evidence of a “slow” picosecond stage of the energy relaxation from the S_n^* state to the S_1^* state.^{5,6} At frequency deviations in the interval 10 cm⁻¹ $\lesssim |\Delta\nu| \lesssim 100$ cm⁻¹, the slope of these curves becomes gentler. This behavior may be due to a realization of a three-level transition scheme (Fig. 1) and also a significant inhomogeneous broadening of the $S_1^* \rightarrow S_n^*$ absorption band.² Final-

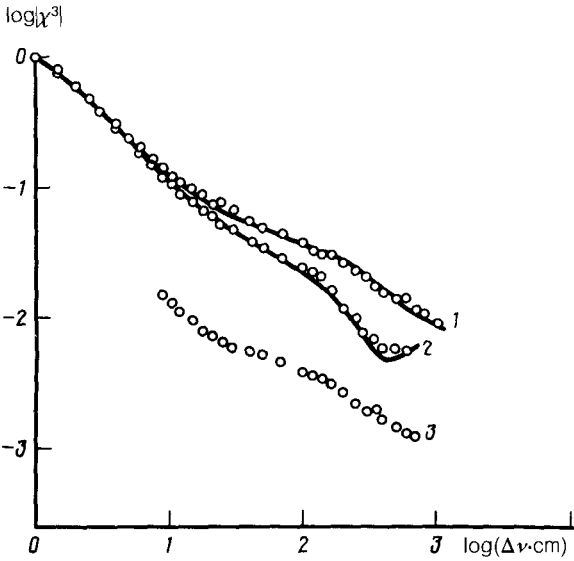


FIG. 2. Dispersion of $|\chi^{(3)}|$. 1,3— $\Delta\nu > 0$; 2— $\Delta\nu < 0$. Points) Experimental; curves) theoretical. 1,2—The polarizations of the exciting light with ν_1 and ν_2 are mutually parallel; 3—orthogonal.

ly, the asymmetry of the $|\chi^{(3)}|$ curves with respect to the sign of $\Delta\nu$ (cf. curves 1 and 2 in Fig. 2) is apparently due to a distortion of the dispersion curves by the “nonresonant” background, which becomes predominant at large frequency deviations, taking the form of a “nondispersing” pedestal and determining $\chi_{NR}^{(3)}$.

To determine the mechanisms and times of the relaxation processes from the state S_n^* , we carried out some model-based calculations and compared the results with the experimental behavior. The calculations were carried out for three-level (S_n^*, S_k^*, S_1^*) and two-level (S_n^*, S_1^*) schemes with an inhomogeneous broadening of the $S_1^* \rightarrow S_n^*$ band. Spectral diffusion at a rate T_3^{-1} was taken into account. We also carried out calculations for a three-level scheme with homogeneous broadening of the $S_1^* \rightarrow S_n^*$ band. The shapes of the experimental and theoretical curves agree best for the three-level scheme and a description of the dispersion of $|\chi^{(3)}|$ by^{2,6}

$$|\chi^{(3)}| = \left| \left[\frac{iK}{(1 + i\Delta T'_n)(1 + i\Delta T_2)} + \frac{M}{(1 + i\Delta T'_n)(1 + i\Delta T_n)} \right] \times \left[1 + \frac{T_{k1}}{2T_{nk}(1 + i\Delta T_{k1})} \right] + \chi_{NR}^{(3)} \right| \quad (1)$$

$$\frac{M}{K} = \frac{2T_n(J/\pi + i)}{\Omega T_2 T_3}$$

$$J = \frac{\omega_m - \omega_c}{\Omega} \left[\frac{\pi}{2} + \tan^{-1} \left(\frac{\omega_m}{\Omega} \right) \right] + \frac{1}{2} \ln \left[\frac{\omega_m^2 + \Omega^2}{\omega_c^3} \right],$$

where $\omega_j = 2\pi c\nu_j$ ($j = 1, 2, m, c$), $\Delta = \omega_2 - \omega_1$, and $\Omega = 2\pi cV$; K is a factor which is independent of Δ , $T_n^{-1} = T_{n1}^{-1}(T'_n)^{-1} = T_n^{-1} + T_3^{-1}T_2^{-1} = (2T_n)^{-1} + (T'_2)^{-1}T'_2$ is the phase relaxation time of the transition $S_1^* \rightarrow S_n^*$ and T_{n1} , T_{nk} and T_{k1} are the time scales of the energy relaxation among the S_n^* , S_k^* , and S_1^* states.

A least-squares fit of Eqs. (1) to the curves in Fig. 2 was made with the real value $\chi_{NR}^{(3)} = 0.0085|\chi^{(3)}(\Delta\nu = 1 \text{ cm}^{-1})|$, found from experimental values of $|\chi^{(3)}|$ at the extreme values of the frequency deviation ($\Delta\nu \geq 800 \text{ cm}^{-1}$). The relaxation times which were found, $T_n \approx 90$, $T_{nk} \approx 100$, $T_2 \approx T_3 \approx 20$ fs, and $T_{k1} \approx 9$ ps, are consistent with the conclusion that there is an inhomogeneous broadening of the absorption band of the $T'_n \rightarrow T'_n$ ($T_2^{-1}/\Omega \approx 0.13$) transition. They are also consistent with the experience of a "bottleneck": a long-lived state S_k^* , through which the S_1^* is filled for the most part in radiationless transitions from the S_n^* state (T_n is close to T_{nk}). The unusually large value of T_{k1} for highly excited states was confirmed by an independent experiment, in which we observed a bleaching of the $S_1^* \rightarrow S_n^*$ absorption band during exposure of the excited molecules to light at the frequency $16\,200 \text{ cm}^{-1}$ with a power density $\approx 100 \text{ MW/cm}^2$.

Comparing our data with the results of quantum-chemical calculations⁹ and measurements of the induced absorption in 1,4-diphenylbutadiene molecules,¹¹ we might suggest that the states S_1^* , S_k^* , and S_n^* have symmetries 1B_u , 1A_g , and 1A_g , respectively. In this case the times T_{nk} and T_{k1} found here from measurements of the dispersion of $\chi^{(3)}$ in the band of the allowed optical transition ${}^1B_u \rightarrow {}^1A_g$ ($S_1^* \rightarrow S_n^*$) of excited molecules correspond to the radiationless transitions ${}^1A_g(S_n^*)M^1A_g(S_k^*)M^1B_u(S_1^*)$.

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