

Vibrational spectra of “hot” molecules in an excited electronic state: measurement of picosecond cooling kinetics by means of coherent Raman scattering

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The spectra of the coherent resonant Stokes Raman scattering of trans-stilbene in an excited electronic state in a solution have been measured with picosecond time resolution. The changes in the spectra produced as a result of a photoinduced reduction of the lifetime of the S_1 state reflect the kinetics of the “cooling” of the vibrational subsystem of the excited molecules.

This is the first report of a study of the picosecond cooling kinetics of vibrationally “hot” trans-stilbene molecules in a solution carried out by a method of resonant coherent Stokes scattering of light and a technique of a photoinduced reduction of the lifetime of the S_1 excited state.

1. The resonant excitation of the electronic states of polyatomic molecules during absorption of photons with an energy exceeding the energy of the purely electronic 0–0 transition is accompanied by a fast (subpicosecond, in the case of molecules in solu-

tion) intramolecular redistribution of the excess excitation energy among vibrational states. In other words, this excitation is accompanied by the formation of an ensemble of vibrationally "hot" molecules in an excited electronic state, surrounded by "cold" solvent molecules, and by a subsequent cooling of the vibrationally excited molecules (VT relaxation).

The basic characteristics of the intramolecular and intermolecular redistributions of vibrational-excitation energy in an ensemble of free molecules in the gas phase and also in gas jets have been established in the particular cases of several organic molecules by means of fluorescence spectroscopy with laser excitation and time resolution.¹ Other spectroscopic methods have also been used.² However, there have so far been no corresponding studies for molecules in a solution, because of the lack of appropriate experimental apparatus and also because the time scales of the corresponding relaxation processes are considerably shorter in a liquid (in the picosecond and subpicosecond ranges).

Research of this sort has now become possible because of technological progress in the generation of ultrashort optical pulses and the development of methods of time-resolved Raman spectroscopy.³ Gustafson *et al.*⁴ have reported the first successful use of picosecond Raman spectroscopy to study an excited electronic state of trans-stilbene in a solution. Hamaguchi⁵ has observed Raman spectra of vibrationally hot trans-stilbene molecules in the S_1 state.

For the present study of the vibrational spectra of trans-stilbene in a solution we have used the technique of coherent Raman spectroscopy, which offers a signal-to-noise ratio and a spectral resolution significantly better than in conventional Raman scattering.^{6,7}

2. The molecules are excited by a pulse at the fourth harmonic of a Nd:YAG laser ($\lambda_B = 266$ nm, $E_B = 0.5$ μ J). The excited state is probed directly during its excitation, by means of pulses at the second harmonic of a Nd:YAG laser (of frequency ω_1 ; $\lambda_1 = 532$ nm, $E_1 \ll \mu$ J) and from a synchronously pumped dye laser (of frequency ω_2 ; $\lambda_2 = 550$ – 600 nm, $E_2 \approx 1$ μ J). The length of the pulses was ≈ 60 ps, and the repetition frequency was⁸ 3 kHz. The UV excitation light and the coherent Stokes Raman scattering probe (Fig. 2a) were focused in a free jet of an ethanol solution of trans-stilbene, 300 μ m thick. The diameter of the probed region was about 50 μ m. Coherent Raman spectra were measured with a resolution ≈ 0.5 cm^{-1} ; the signal at the Stokes frequency $\omega_s = 2\omega_2 - \omega_1$ was recorded. The signal of coherent Stokes Raman scattering was detected by a method involving the counting of single photons by a strobe technique.

3. The intensity of the coherent Stokes signal is given by

$$I_s \sim |\chi^{(3)}(\omega_s; \omega_2, -\omega_1, \omega_2)|^2 I_1 I_2^2 = |\chi^e + \chi^E + \sum_j \chi^{R_j}|^2 I_1 I_2^2, \quad (1)$$

where I_1 and I_2 are the intensities of the probing light at the frequencies ω_1 and ω_2 , respectively. The nonlinear susceptibility $\chi^{(3)}$ is determined by the contributions of the solvent (χ^e), the electron susceptibility (χ^E), and the vibrational resonances χ^{R_j} of the molecules under study. The frequencies ω_1 , ω_2 , and ω_s fall in the band of induced

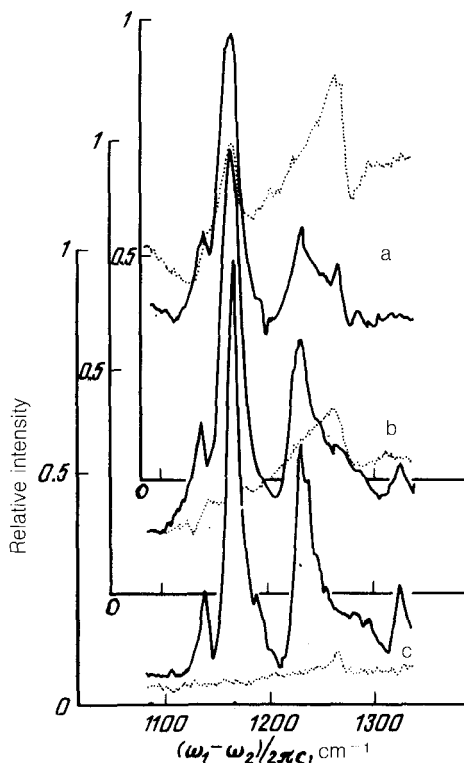


FIG. 1. Spectra of the resonant Stokes coherent scattering of light by trans-stilbene in the S_1 state in ethanol at various intensities of the probing light, I_1 : a— $I_1 = I_{\max}$; b— $I_1 = 10^{-1} \cdot I_{\max}$; c— $I_1 = 10^{-3} \cdot I_{\max}$. Dotted lines—Spectra without excitation; solid lines—coherent Stokes Raman scattering spectra with UV excitation ($\lambda_R = 266$ nm; $\Delta t = 0$; concentration of 1 mM).

absorption from the S_1 state, which peaks at 585 nm (Ref. 9). The conditions for a resonant amplification of the coherent Raman-scattering signal are thus satisfied.

4. Figure 1 shows spectra of the coherent Stokes Raman-scattering spectra of the trans-stilbene solution over the region 1100–1350 cm^{-1} . The spectra measured without the UV excitation (the dashed lines) are due primarily to the signal from the solvent (the Raman lines of stilbene are not seen against its background). The peaks in the spectra of the resonant coherent Stokes Raman scattering with UV excitation (the solid lines) correspond quite well to the vibrational resonances of the S_1 states of trans-stilbene with frequencies of 1150 cm^{-1} , 1181 cm^{-1} , 1242 cm^{-1} , and 1333 cm^{-1} , found from data on resonant Raman scattering in Ref. 4. Spectra a, b, and c were measured at various intensities I_1 of the probing light of frequency ω_1 . With increasing I_1 , we observe a decrease in the relative amplitude of the peaks, a shift of the peaks, and changes in the widths of the lines at 1181 and 1242 cm^{-1} . We believe that these changes reflect the kinetics of the cooling of the vibrational subsystem of the molecule in the S_1 state.

5. Specifically, the probing pulse at the frequency ω_1 , in a resonant interaction with molecules in the S_1 state, is capable of effectively reducing the average time τ_{S_1} spent by the molecules in this state, sending some of them into higher-lying electronic states⁵ S_n , from which they do not subsequently return to the S_1 state. We monitored

the decrease in the number of molecules being probed with increasing I_1 by measuring the intensity of the fluorescence from the S_1 state at the wavelength $\lambda = 345$ nm. The more than fivefold decrease in this intensity over the range of I_1 accessible in these experiments is evidence that τ_{S_1} decreases from ≈ 50 ps, at a negligible photoinduced quenching, to ≈ 10 ps at the maximum intensity I_1 .

This photoinduced decrease in the lifetime of the S_1 state is reflected in the coherent Stokes Raman-scattering spectra (Fig. 1). The excess vibrational energy imparted to the trans-stilbene molecule during the absorption of a photon with $\lambda = 266$ nm is ≈ 7000 cm^{-1} . This figure corresponds to the pumping of an excess energy ≈ 100 cm^{-1} into each vibrational mode, i.e., to an ≈ 150 -K increase in the vibrational temperature of the molecule during the UV excitation. The time spent by the molecule in the S_1 state is sufficient for the transfer of a significant fraction of the excess energy to the surroundings, and it is also sufficient for the cooling of the molecule itself. A reduction of this time obviously leads to an increase in the fraction of the energy which remains in the vibrationally excited molecule and which should therefore be manifested in the vibrational spectra in the same way that temperature-induced effects are manifested in these spectra: as a shift of the lines to the low-frequency region and a broadening of these lines. This is what is observed experimentally.

Figure 2b shows the half-widths of the lines at 1181 and 1242 cm^{-1} versus the intensity I_1 . We see that the half-width of the first of these lines increases $\approx 70\%$ (from 14.5 to 24 cm^{-1}), while that of the second increases $\approx 60\%$ (from 17.5 to 28 cm^{-1}). These changes are substantially greater than the experimental error. The shifts of the centers of the lines which are detected are also beyond explanation in terms of interference effects in the spectrum of the coherent Raman scattering (a numerical simulation showed that the latter effects do not exceed 2–3 cm^{-1}).

6. In summary, the observed changes in the spectra of coherent Stokes Raman

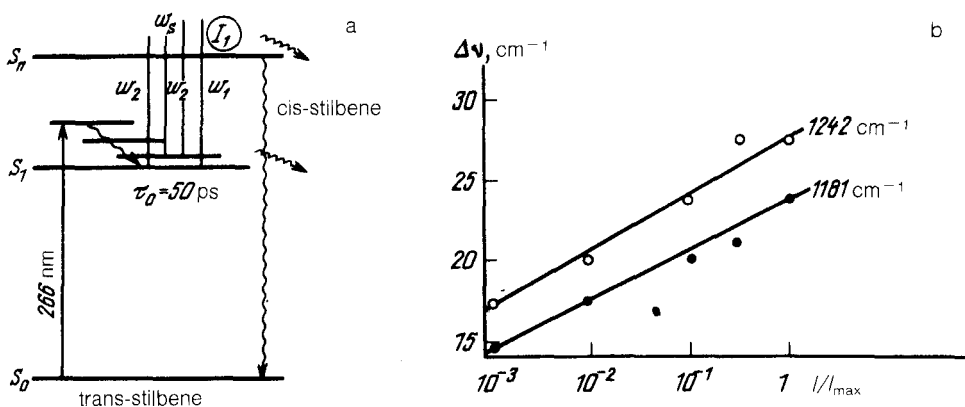


FIG. 2. a—Diagram of the excitation and the coherent-Stokes-Raman-scattering probing of the exciting S_1 state of the trans-stilbene molecule; b—width at half-maximum of the coherent Stokes Raman scattering lines at 1181 and 1242 cm^{-1} versus the intensity of the probing light, I_1 .

scattering during a photoinduced decrease in the lifetime of the S_1 state of trans-stilbene are caused by molecules in which a vibrational-translational relaxation has not gone to completion. In the present letter we have been discussing the data on the Stokes coherent Raman scattering; corresponding results were obtained in the anti-Stokes version of coherent Raman scattering (CARS), but in that other case the shape of the spectrum is markedly different from that in Fig. 1 [because of different conditions for the interference of the χ^E and $\chi^{R'}$ contributions to (1)]. A corresponding analysis of the CARS spectra observed is being carried out.

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