PICOSECOND COHERENT STOKES AND ANTI-STOKES RAMAN SPECTRA
OF HOT S, TRANS-STILBENE IN SOLUTION: THE KINETICS
OF VIBRATIONAL COOLING IN THE PRESENCE OF “OPTICAL DEPLETION”

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The experimental results of time-resolved coherent resonance Stokes and anti-Stokes Raman scattering spectroscopy of the excited electronic S, state of trans-stilbene in ethanol are presented. The detected considerable changes in vibrational spectra due to “optical depletion” of the population of the S, state reflect the picosecond kinetics of vibrational-translational relaxation of vibrationally “hot” excited molecules.

1. Introduction

It is well established that the resonance excitation of a polyatomic molecule by a photon with energy exceeding the energy of the 0–0 pure electronic transition is accompanied by a fast intramolecular redistribution of the excess energy over all vibrational modes. This leads to the formation of an ensemble of vibrationally “hot” molecules in the excited electronic state, surrounded by “cool” molecules of the solvent, and subsequent dissipation of the vibrational energy into the heat “bath” of the solution (VT relaxation).

The main features of the intra- and inter-molecular vibrational energy redistributions in the ensemble of free molecules in the gas phase and in supersonic jets were well established using time-resolved fluorescence and other spectroscopic methods with pulsed laser excitation (see refs. [1,2] and references therein). However, the same investigations for molecules in the liquid phase have not been carried out until recently because of the lack of adequate experimental techniques and due to the fact that the corresponding relaxation processes are much faster in solutions (pico- and subpico-second range) than in the gas phase.

Such investigations have become possible due to recent progress in time-resolved vibrational spectroscopy techniques [3]. Gustafson et al. [4] have reported the first successful application of picosecond time-resolved resonance Raman (TRRR) scattering to the study of the excited electronic S, state of trans-stilbene in solution. Hamaguchi [5] observed TRRR spectra of vibrationally “hot” S, trans-stilbene molecules. The application of coherent resonance Raman scattering methods to the same problems offers additional advantages [6-8].

In the current paper we present the resonance coherent anti-Stokes and Stokes Raman scattering (CARS and CSRS) spectra of the excited S, state of trans-stilbene in solution and report the observation of considerable changes in these spectra, induced by the “optical depletion” of the population of the excited state. The “optical depletion” scheme was first proposed by Hamaguchi in ref. [5] to increase the temporal resolution of transient Raman spectroscopy.

The results of our recent polarization sensitive CARS experiments [9] have shown an anomalous increase of several components of the third-order susceptibility tensor \( \chi^{(3)} \) of trans-stilbene in ethanol under UV excitation. Namely, the anomalous depolarization ratio was observed to be \( |\chi^{(3)}_{111}/\chi^{(3)}_{1111}| \gtrsim 2.5 \) both for resonance electronic and Raman contributions; it is caused by the UV-pump-induced orientational anisotropy of the excited molecules, the UV pump being linearly polarized along the z-axis. Hence, it seems to be natural to use the geometry of CARS or CSRS probing, where only these enhanced
components will contribute to the signal. It takes place when the polarization vectors of the two probe beams in the CARS/CSRS scheme are perpendicular to each other, one of them (e.g. with tunable frequency $\omega_2$) being parallel to the UV-pump polarization plane. It is this scheme we deal with in our experiments.

2. Experimental

The fourth harmonic of a picosecond cw-pumped, acousto-optically mode-locked and $Q$-switched Nd:YAG laser (266 nm, 40 ps pulse duration, 2.5 kHz repetition, 1 $\mu$J pulse energy, resonant with the $S_1\rightarrow S_0$ transition) was used for excitation of trans-stilbene [10]. The CARS/CSRS probing of the excited state was carried out simultaneously with the excitation. The second harmonic of a Nd:YAG (frequency $\omega_2 = 532$ nm, 60 ps, up to 20 $\mu$J/pulse) and a synchronously pumped dye laser (frequency $\omega_2 = 550-600$ nm, 60 ps, 1 $\mu$J/pulse), both resonant with the $S_n\rightarrow S_1$ transition were used to generate in the solution studied either Stokes, $\omega_S = 2\omega_2 - \omega_1$, or anti-Stokes, $\omega_A = 2\omega_1 - \omega_2$, coherent Raman signals. The polarization of the $\omega_2$ beam was parallel to that of the UV pump, the green $\omega_1$ beam being polarized perpendicular to the first two. A polarization analyzer in CARS/CSRS beam rejected stray light and dye-laser luminescence. Coherent Raman spectra were measured in the scanning regime with a spectral resolution of $\approx 0.5$ cm$^{-1}$, determined mainly by the dye-laser bandwidth. Tuning of the dye-laser frequency $\omega_2$ and synchronous tuning of the monochromator wavelength (according to $\omega_S$ or $\omega_A$ scanning) were performed in a step-by-step mode under the control of a microcomputer. The dye-laser wavelength-selecting element was a mirror in the first diffraction order of the intracavity grating, set at grazing incidence. The signal was detected by the computer-controlled time-gated single photon counting system. For each point the signal was measured twice: with UV excitation and without it. This allows a microcomputer to separate programmably the non-resonant electronic and Raman contributions of the solvent. The intensity of the probe pulses was adjusted using the set of two polarizers in $\omega_1$ beam, one being rotated and the second fixed. The

3. Results

CARS spectra of trans-stilbene in ethanol, taken in the above described polarization condition of probing are presented in fig. 1 in the presence of UV excitation (a) and without UV pump (b). Two Raman resonances of $S_1$ trans-stilbene with frequencies 1181 and 1242 cm$^{-1}$ correspond to the molecular normal
modes containing mainly C-phenyl stretch vibrations [4,5]. These resonances as well as the Raman line at 1150 cm\(^{-1}\) appear as deep, well-defined "dips" in the intense, slightly dispersive resonant background, created by the excited molecules. This unusual spectral bandshape in case (a) can be explained by interference effect between the following four independent coherent contributions to the CARS signal: (1) a purely non-resonant electronic susceptibility and (2) Raman resonances of the solvent (ethanol); (3) electronic and (4) Raman contributions of S\(_1\) trans-stilbene, the last two being resonantly enhanced. The relative phases of these susceptibilities are such that the interference between them results in mutual compensation of all the contributions at some points of CARS spectrum, especially dramatic for the 1181 cm\(^{-1}\) Raman line. Spectrum (a) is presented as it was obtained in the experiment without noise subtraction, curve (b) is smoothed. The CARS signal from S\(_1\) trans-stilbene considerably exceeds the non-resonant signal from ethanol (spectrum (b)) due to the resonance enhancement on the S\(_a\)\(-\)S\(_1\) transition. Note, that the number of excited molecules is as small as one per more than 2\(\times\)10\(^5\) molecules of the solvent.

In coherent Stokes spectra the same Raman lines of S\(_1\) trans-stilbene appear as maxima placed on the resonant electronic background (fig. 2) which means that the phases of the resonant contributions have changed. The CSRS spectra have been taken at the same experimental conditions as the CARS ones.

The frequencies of the maxima in CSRS spectra (figs. 2a, 2b and 2c) as well as those of the dips in CARS spectrum (fig. 1a) correlate well with the vibrational resonances of S\(_1\) trans-stilbene at 1150, 1181, 1242 and 1333 cm\(^{-1}\), determined by the transient resonance Raman spectroscopy in ref. [4]. The spectra (a), (b) and (c) were measured with various intensities \(I_1\) of the probe beam \(\omega_1\) and were normalized to the level of non-resonant background of the solvent. Of course, the signal level increases with the probe intensity increasing, the number of photon counts exceeding 3000 at the maximum of the 1181 cm\(^{-1}\) line in each spectrum. However the increase in \(I_1\) leads to a decrease of the normalized peak amplitudes, to a slight shift of the maxima to the low-frequency side and to a clear broadening of the Raman bands at 1181 and 1242 cm\(^{-1}\). As we understand, the above mentioned spectral changes reflect the kinetics of the vibrational deexcitation of the S\(_1\) excited molecules.

4. Discussion

Actually, the probing pulse with frequency \(\omega_1\), resonant with the S\(_a\)\(-\)S\(_1\) transition is capable to effectively shorten the lifetime of molecules in the S\(_1\) state. Being transferred to the higher electronic state S\(_a\),
the molecules (at least a significant part of them) do not return back to the \( S_1 \) state. We observed the "optical depletion" of the \( S_1 \) state by measuring the corresponding attenuation of \( S_1 \) trans-stilbene fluorescence intensity at \( \lambda_n = 345 \) nm in the presence of the green quenching pulse.

More directly, we controlled the population of the \( S_1 \) state by measuring the dependence of the CSRS signal on the probe pulse intensity. This way we detect only those molecules which really contribute to the CSRS signal. The dependence of the signal at \( (\omega_1 - \omega_2) / 2\pi \tau = 1090 \) cm\(^{-1}\) with UV excitation, normalized to that of the unpumped sample, is presented in fig. 3a. This point of the CSRS spectrum is far enough from any Raman resonances of \( S_1 \) trans-stilbene, the contribution of the polarized Raman line of ethanol at 1095 cm\(^{-1}\) in the case of 90°-probing geometry being negligible, as follows from the CSRS spectrum of the unpumped sample (fig. 2d).

In the absence of any Raman resonances, the intensity of the CSRS signal from the UV-pumped solution can be described as being proportional to the squared modulus of the complex third-order nonlinear susceptibility:

\[
\frac{\chi^{(3)}_{CSRS}}{\chi^{(3)}_{unpumped}} \propto \frac{I^{max}}{I_1}
\]

\( I_1 \) is the probe laser intensity.

Fig. 3. (a) Probe \( \omega_1 \)-beam intensity dependence of the ratio of CSRS signal from the UV-pumped trans-stilbene solution to that from the unpumped solution at frequency \( (\omega_1 - \omega_2) / 2\pi \tau = 1090 \) cm\(^{-1}\). (b) The diagram on the complex plane, representing the real nonresonant contribution of ethanol \( \chi^{(3)NR}_{et} \) and complex resonant electronic contribution of \( S_1 \) trans-stilbene \( \chi^{(3)RE}_{S} \) into the net third-order susceptibility of the UV-excited solution at various probe \( \omega_1 \)-beam intensities \( I_1 \). The characteristic points in dependence (a) and in diagram (b) are marked by the numbers 1–4 respectively.
\[ I_{\text{CSRS}}^{\text{pumped}} \propto |\chi_2^{(3)}(\omega_1; \omega_2, \omega_2, -\omega_1)|^2, \]

where

\[ \chi_2^{(3)} = \chi_{\text{et}}^{(3)\text{NR}} + \chi_{\text{et}}^{(3)\text{E}}, \]

\( \chi_{\text{et}}^{(3)\text{NR}} \) is the non-resonant contribution of the solvent (ethanol) and \( \chi_{\text{et}}^{(3)\text{E}} \) is the resonant electronic \( S_1 \) trans-stilbene contribution into the net \( \chi_2^{(3)} \), \( \chi_{\text{et}}^{(3)\text{E}} \) being proportional to the number density of the excited stilbene molecules in the \( S_1 \) state. The square root of the measured ratio of the CSRS signal intensity from the UV-pumped solution to that from the unpumped one (fig. 3a) represents the following ratio of the corresponding amplitudes of complex susceptibilities:

\[ \sqrt{I_{\text{CSRS}}^{\text{pumped}} / I_{\text{CSRS}}^{\text{unpumped}}} = |\chi_{\text{et}}^{(3)\text{E}} + \chi_{\text{et}}^{(3)\text{NR}}| / |\chi_{\text{et}}^{(3)\text{NR}}|. \]

The observed dependence can be easily explained with the help of the diagram in fig. 3b. Here, on the complex plane, the non-resonant third-order susceptibility of ethanol \( \chi_{\text{et}}^{(3)\text{NR}} \) is presented as a vector with fixed length along the real axis \( \text{Re} \chi_{\text{et}}^{(3)\text{E}} \), and the complex resonant susceptibility of \( S_1 \) trans-stilbene \( \chi_{\text{et}}^{(3)\text{E}} \) is a vector with variable amplitude.

The amplitude of \( \chi_{\text{et}}^{(3)\text{E}} \) changes proportionally with the population of the \( S_1 \) state, being maximum, \( \chi_{\text{et}}^{(3)\text{E}} \), at minimum intensity \( I_i \), and minimum, \( \chi_{\text{et}}^{(3)\text{E}} \), at maximum depletion of the \( S_1 \) state, i.e. at maximum \( I_i \). The measured ratio, given by eq. (3), is proportional, according to eq. (2), to the length of the net \( \chi_2^{(3)} \) vector. The characteristic points (1–4) on curve 3a correspond to those, marked at the diagram in fig. 3b. Measuring the ratio at point 3, which corresponds to the minimum of \( |\chi_2^{(3)}| \), we can calculate the angle \( \theta \) between the two vectors, \( \chi_{\text{et}}^{(3)\text{E}} \) and \( \chi_{\text{et}}^{(3)\text{NR}} \), which characterizes the phase shift between the resonant electronic susceptibility, \( \chi_{\text{et}}^{(3)\text{E}} \) and the real non-resonant contribution, \( \chi_{\text{et}}^{(3)\text{NR}} \), \( \theta = -(120 \pm 10)^\circ \).

This analysis allows us to evaluate the maximum laser-induced depletion of the population of the \( S_1 \) state: for our experimental conditions we have the ratio \( |\chi_{\text{et}}^{(3)\text{E}} / \chi_{\text{et}}^{(3)\text{E}}| \approx 5 \). It means that the population of the \( S_1 \) state is reduced by a factor of 5 as a consequence of the action of \( \omega_1 \) radiation. This depletion is equivalent to the effective shortening of the \( S_1 \) lifetime from 50 ps without depletion [12] to about 10 ps at maximum \( I_i \).

With optically induced \( S_1 \) lifetime shortening, the portion of vibrationally unrelaxed ("hot") molecules in solution increases. This leads to the observed changes in the vibrational spectra of the excited molecules (fig. 2), which are analogous to that induced by a temperature increase. The dependence of the bandwidths of the Raman lines at 1242 and 1181 cm\(^{-1}\) on the probe intensity \( I_i \) are presented in fig. 4. The fwhm of the first band increases by \( \approx 60\% \) (from 17 to 28 cm\(^{-1}\)) and of the second one by \( \approx 70\% \) (from 14 to 24 cm\(^{-1}\)). These changes exceed considerably the experimental errors; they cannot be attributed to possible interference effects, either.

We observed the same shift and broadening of the Raman lines in CARS spectra, when increasing the probe intensity. We defer the details to a later publication because of the difficulties in the interpretation of the complicated shape of the spectrum.

Hamaguchi has observed earlier the broadening of the transient resonance Raman line at 1566 cm\(^{-1}\) as well as the frequency shift of the 1181, 1242 and 1566 cm\(^{-1}\) lines [5] under the optical depletion of trans-stilbene \( S_1 \) state population by the probe pulse. Our CARS and CSRS measurements of the spectral changes due to probe intensity variation, having been performed with much higher signal-to-noise ratio and much better spectral resolution, are in good agreement with that of Hamaguchi.
5. Conclusion

It is worthy to stress, in conclusion, that time-resolved coherent resonance Raman spectroscopy (both in Stokes and anti-Stokes variants) along with the anisotropic excitation of the molecules and the enhanced time resolution by optical depletion is very effective for the study of the vibrational dynamics of polyatomic molecules.

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References