

PICOSECOND ANTI-STOKES RAMAN EXCITATION PROFILES AS A METHOD FOR INVESTIGATING VIBRATIONALLY EXCITED TRANSIENTS

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A method for estimating vibrational quantum numbers of vibrationally excited transients in solution is proposed. In this method, we calculate anti-Stokes Raman excitation profiles (REPs) which are characteristic of the initial vibrational states involved in the Raman process, and compare them with observed anti-Stokes intensities. We have applied this method to vibrationally hot molecules of canthaxanthin in the S_0 state and those of *trans*-stilbene in the S_1 state. For canthaxanthin, it has been found that the vibrationally excited transients are for the most part on the $\nu = 1$ level of the C=C stretching mode, and that excess vibrational energy is statistically distributed among all intramolecular vibrational modes. As for S_1 stilbene, vibrational transients are shown to be mostly on the $\nu = 1$ level for two vibrational modes examined, while the excess vibrational energy is probably localised on the olefinic C=C stretching mode.

Keywords: Anti-Stokes Raman scattering; time-resolved Raman spectroscopy; resonance Raman excitation profiles; vibrational relaxation; intramolecular vibrational redistribution

INTRODUCTION

In recent ultrafast studies in solution, knowledge on the intramolecular vibrational redistribution (IVR) processes is increasing. It has

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been suggested that the IVR processes might not be completed within a few picoseconds in some cases. It is important to specify the vibrational quantum states of observed vibrationally excited transients in order to clarify the mechanism of vibrational relaxation. Anti-Stokes Raman scattering arises from only those molecules which are populated in excited vibrational states. It can serve as a direct probe of the vibrational redistribution and/or cooling processes [1–4]. Frequency shifts of Raman bands can be qualitative measures of excess vibrational energy, but it is usually not easy to specify the quantum numbers since detailed information on anharmonic coupling is needed. In this paper, we try to obtain information on the energy levels on which vibrationally excited molecules are populated, using picosecond time-resolved anti-Stokes Raman spectroscopy.

If each vibrational state has a characteristic spectrum, the vibrationally excited transient can be identified. Resonance Raman excitation profiles (REPs) are characteristic of the initial state of the Raman transition; for example, the $\nu = 2$ to 1 anti-Stokes Raman transition of a vibrational mode may give an REP different from that of the $\nu = 1$ to 0 transition of the same mode. If observed Stokes REPs (which are usually due to the vibrationally ground state) are well reproduced by a model calculation, then anti-Stokes REPs may be predicted by the same model. We can then estimate the vibrational quantum number of a vibrationally excited transient by measuring the anti-Stokes REP of the transient and comparing it with calculated REPs.

VIBRATIONAL RELAXATION IN CANTHAXANTHIN

Vibrationally excited carotenoid molecules in the S_0 state are generated *via* internal conversion from the S_2 and S_1 states if excited with a visible light around 500 nm [1, 4]. The intensity of the anti-Stokes Raman band due to the 'in-phase' C=C stretch rises up to ≈ 12 ps, and then decays with a time constant of 15–20 ps. The rise of the intensity of an anti-Stokes Raman band can be attributed to an increase in the population of vibrationally excited transients on the associated energy level generated *via* internal conversion from the S_1 state. We analyzed the C=C stretching anti-Stokes Raman intensity

of canthaxanthin in benzene solution at 12 ps by the method proposed above [4].

In order to use the present method, the predictability of anti-Stokes REPs is presumed. We have verified this point for canthaxanthin by observing the cw-excited anti-Stokes and Stokes REPs and simulating them based upon the A term of Albrecht's formula (Franck-Condon mechanism). The observed REPs have been quantitatively reproduced by the simulation. REPs calculated by the same model for several anti-Stokes hot bands of the Franck-Condon active C=C stretching vibration of canthaxanthin are shown in Figure 1. Each REP in Figure 1 is characteristic of the initial state. The intensity of the anti-Stokes Raman band arising from the lowest excited level ($\nu_{\text{C}=\text{C}} = 1$) decreases monotonically when the Raman excitation is performed at a wavelength longer than 555 nm. On the other hand, the intensities of anti-Stokes Raman bands arising from higher excited levels are expected to increase when a longer wavelength is adopted for Raman measurements.

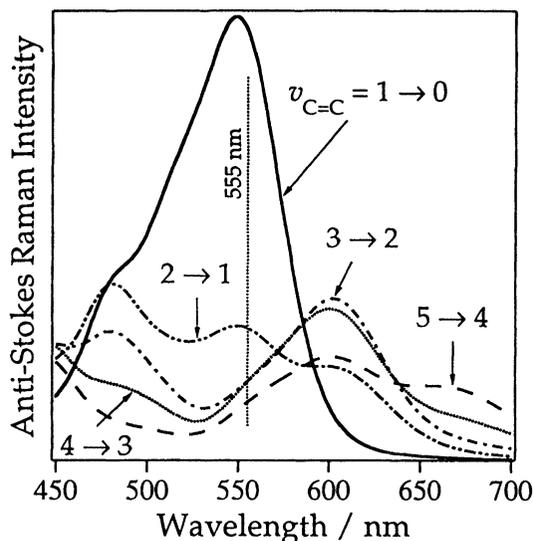


FIGURE 1 REPs of the C=C stretching band of canthaxanthin calculated for several anti-Stokes Raman transitions. Vibrational quantum numbers of other modes are set equal to zero.

We recorded a transient anti-Stokes Raman spectrum excited with picosecond pulses at 545 nm. Figure 2 (upper panel) shows the C=C stretching anti-Stokes Raman band observed for 555-nm probe with the pump light on and off. The pump-off spectrum reflects the intensity arising from the thermally distributed $\nu_{\text{C}=\text{C}} = 1$ level. If the pump-induced transient is on the $\nu_{\text{C}=\text{C}} = 1$ level, the probe-wavelength dependence of anti-Stokes Raman intensity arising from the pump-induced transients should be the same as that of the pump-off intensity. In this case, the pump-on/pump-off intensity ratio (hereafter denoted as R_λ where λ is the probe wavelength) should be unchanged

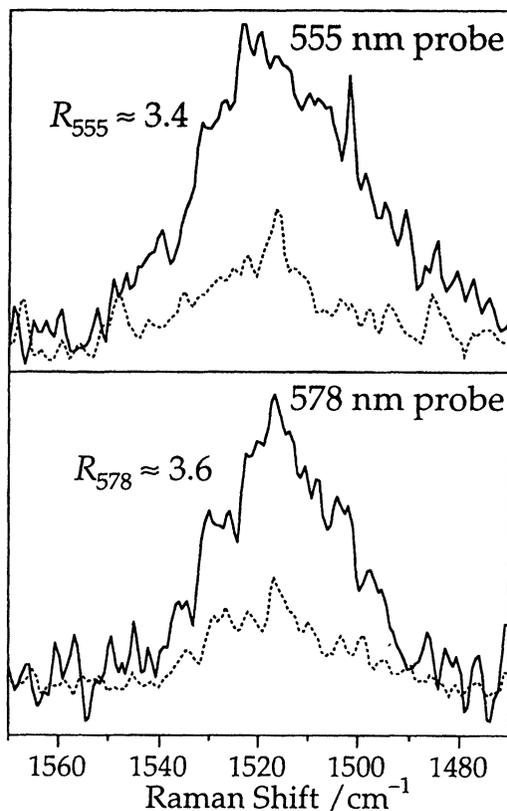


FIGURE 2 Transient anti-Stokes Raman band (C=C stretch) of canthaxanthin. Probe wavelength, 555 nm (upper panel) and 578 nm (lower panel). Solid and broken curves represent the pump (545 nm) on and off spectra, respectively.

for any probe wavelength. On the other hand, if the pump-induced transient is on a highly excited vibrational level, the anti-Stokes Raman intensity arising from the pump-induced transients is expected to increase for a probe wavelength longer than 555 nm. We observed anti-Stokes Raman spectra with 578-nm probe (Fig. 2, lower panel) and compared them with the 555-nm probe spectra. The observed R value seems to be independent of the probe wavelength ($R \approx 3.5$). This result leads us to a conclusion that the pump-induced anti-Stokes Raman intensity observed in the present study does not arise from highly excited vibrational states but mostly from the lowest excited vibrational state ($\nu_{C=C} = 1$).

Transient vibrational temperature can be estimated from the R_λ value. By comparing the transient temperature from the R_λ value and that theoretically calculated by assuming the Boltzmann distribution of excess vibrational energy, we have concluded that the excess energy is statistically distributed among all the intramolecular vibrational modes within 12 ps. The present result suggests that vibrational energy localised first on the C=C stretch is very rapidly redistributed among all vibrational modes.

VIBRATIONAL RELAXATION IN *TRANS*-STILBENE

As another example, we have studied vibrationally excited transients of *trans*-stilbene in the S_1 state in a butanol solution. *Trans*-stilbene is directly excited by ultraviolet light to the vibrationally excited S_1 state if the pump photon has a sufficient excess energy [2, 3]. We observed picosecond anti-Stokes Raman spectra of the excited stilbene, with a pump wavelength chosen to give the excess vibrational energy of 5200 cm^{-1} . With the pump wavelength fixed, the probe-wavelength dependence of picosecond anti-Stokes Raman intensities at 0 ps delay time was recorded and compared with simulated anti-Stokes REPs, to examine the vibrational quantum numbers of the transients.

The observed and simulated anti-Stokes REPs of the transient are compared as a normalized intensity ratio of two Raman bands (a band attributed to the olefinic C=C stretch and that attributed to the C—Ph stretch), defined as $r_\lambda = (I_{C=C}(\lambda)/I_{C-Ph}(\lambda))/(I_{C-Ph}(\lambda_0)/I_{C=C}(\lambda_0))$ where λ_0 is a reference probe wavelength. Figure 3 shows

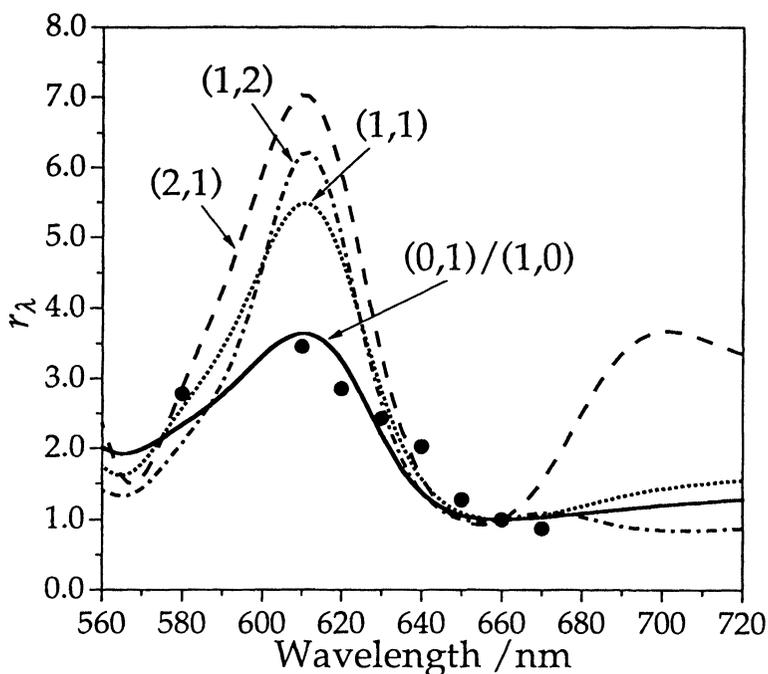


FIGURE 3 Probe wavelength dependence of r_λ , observed (circles) and calculated. The curve denoted as (n_1, n_2) is calculated for the initial vibrational level with the C=C and C—Ph stretching quantum numbers of n_1 and n_2 , respectively; $(0, 1)/(1, 0)$ is calculated on the assumption that the C=C stretching band arises from the $(1, 0)$ level and the C—Ph band from $(0, 1)$.

the simulated r_λ 's ($\lambda_0 = 660$ nm) for several initial levels included in the anti-Stokes Raman process. The observed r_λ at 0 ps delay time is also shown in this figure (filled circles). The observed points are reproduced satisfactorily by the curve calculated on the assumption that the two anti-Stokes Raman bands arise from the lowest excited vibrational levels. This result indicates that the observed vibrationally excited transients are for the most part in the lowest excited vibrational levels, as far as the C=C and C—Ph stretches are concerned.

On the other hand, a further analysis of the relative anti-Stokes intensities suggests that the excess vibrational energy is not statistically distributed among intramolecular vibrational modes. The excess

energy seems to be localised on the C=C stretching mode immediately after the photoexcitation.

CONCLUDING REMARKS

In the present study we have shown that anti-Stokes REPs can be used for estimating vibrational quantum numbers of transients. For both of the two systems studied, we have found that the observed transients are in the lowest vibrationally excited states of the Raman-active high-frequency modes. This result is phenomenologically similar to Kasha's rule for electronic excitations, and may possibly be common to a wide range of vibrationally excited transients. It is important to extend the study to a wider range of molecules and to directly observe highly excited transients and their relaxation.

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