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LINE SHAPE BEHAVIOR OF THE RESONANCE CARS IN Zn-TETRAPHENYLPORPHIN

Yukio ADACHI, Ryosaku IGARASHI, and Shiro MAEDA
Research Laboratory of Resources Utilization, Tokyo
Institute of Technology, Midori-ku, Yokohama 227

CARS of fluorescent Zn-tetraphenylporphin has been measured by ω_1 radiations in resonance with the first allowed transition near 600nm. An appreciably resonant line was observed at 1360cm^{-1} and the line shape changed remarkably by moving ω_1 within the absorbing region. The line shape behavior has been reasonably interpreted by picking out a doubly resonant term in the susceptibility expression, in which ω_1 and ω_3 are resonant with the 0-0 and 0-1 transitions respectively.

Coherent anti-Stokes Raman scattering(CARS) is an optical nonlinear process which gives resonant signals at Raman active frequencies of a molecule.[1] Two laser beams of frequencies ω_1 and ω_2 $(<\omega_1)$ are focused into a small sphere in the sample with an appropriate phase matching angle, being mixed in a four photon process to produce a coherent beam of anti-Stokes frequency $\omega_3=2\omega_1-\omega_2$. The CARS beam intensity is proportional to the absolute square of the third order susceptibility $\chi^{(3)}(-\omega_3,\omega_1,\omega_1,-\omega_2)$ defined by

$$P_\ell^{(3)}(\omega_3)=\chi_{\ell mno}E_m(\omega_1)E_n(\omega_1)E_o^*(\omega_2), \tag{1}$$

where $P_\ell^{(3)}(\omega_3)$ is the ℓ-component of third order nonlinear polarization and $E_m(\omega_1)$ etc. are the electric field components of incident radiations.

In the region of Raman resonance with an isolated vibrational requency Ω_r, the susceptibility has the form

$$\chi^{(3)}=\chi_{NR}^{(3)}+\chi_r/[\Omega_r-(\omega_1-\omega_2)-i\Gamma_r], \tag{2}$$

where Γ_r is the Raman linewidth and the polarization indices have been omitted. $\chi_{NR}^{(3)}$ is the non-resonant part due to all other electronic and vibrational levels, and χ_r is given by a perturbation expansion as follows:[2]

$$\chi_r=\frac{12NL}{\hbar^3}\sum_a\left(\frac{X_{ga}X_{ar}}{\omega_{ag}-\omega_3-i\gamma_a}+\frac{X_{ga}X_{ar}}{\omega_{ag}+\omega_1+i\gamma_a}\right)\sum_b\left(\frac{X_{rb}X_{bg}}{\omega_{bg}-\omega_1-i\gamma_b}+\frac{X_{rb}X_{bg}}{\omega_{bg}+\omega_2-i\gamma_b}\right). \tag{3}$$

In Eq.(3), N, L, X, and γ are the number density of the molecule, local field correction factor, transition moment, and damping constant respectively, and a and b denote the intermediate vibronic states. It is seen that the CARS intensity can be resonantly enhanced when either ω_1 or ω_3 approaches the transition frequency to an allowed excited level, and the effect may be most striking in the doubly resonant case arising for simultaneous $\omega_1\simeq\omega_{bg}$ and $\omega_3\simeq\omega_{ag}$.

Recently, there has been considerable interest in the resonance CARS,[3-7] and much attention has been given to the appearance of a negative peak. In the present note, we report the behavior of CARS line shape observed for Zn-tetraphenylporphin using ω_1 frequencies within the first absorption band shown in Fig.1. The measurement was carried out for the 7×10^{-4}mol dm^{-3} benzene solution with two dye lasers pumped by a nitrogen laser. Only one intense line was observed with appreciable resonance at about $\omega_1-\omega_2=1360\text{cm}^{-1}$, but the corresponding Raman spectrum was not obtained because of intense fluorescence. When the ω_1 was varied near the first smaller maximum of absorption, probably the 0-0 transition, the line shape showed a remarkable change from a negative peak to a positive one via a typical dispersive shape, as illustrated in Fig.2a. Such a line shape transformation has been reported for several systems$^{3-6)}$, but the present result is remarkable in that the negative/positive reversal has taken place within a much narrower frequency interval than known examples. This suggests that the damping constant γ is fairly small, being considerably smaller than the vibrational frequency Ω, so that the line shape behavior reveals the resonance with each vibronic level rather distinctly. Then, it is significant to treat the intermediate states a and b as separate vibronic states $|e,v\rangle$ in Eq.(3); that is

$$\chi_r=\frac{12NL}{\hbar^3}\sum_v\left(\frac{X_{g0,ev}X_{ev,g1}}{\omega_{eg}+v\Omega_e-(\omega_1+\Delta)-i\gamma_e}\right)\sum_{v'}\left(\frac{X_{g1,ev'}X_{ev',g0}}{\omega_{eg}+v'\Omega_e-\omega_1-i\gamma_e}\right), \tag{4}$$

where Ω_e is the vibrational frequency of mode r in the e state, $\Delta=\omega_1-\omega_2=\omega_3-\omega_1$, and a single resonant electronic state e is assumed. On the other hand, the resonant intermediate states have been lumped into a single averaged state in the known examples with presumably large γ values. A notable point is that we now have a single predominantly resonant term in Eq.(4) corresponding to v=1 and v'=0, so that we may use a simpler approximate formula

$$\chi_r\simeq\frac{12NL}{\hbar^3}\left(\frac{X_{g0,e1}X_{e1,g1}}{\omega_{eg}+\Omega_e-(\omega_1+\Delta)-i\gamma_e}\right)\left(\frac{X_{g1,e0}X_{e0,g0}}{\omega_{eg}-\omega_1-i\gamma_e}\right). \tag{5}$$

Assuming $|\Omega_e-\Delta|/\gamma_e\ll1$ for Δ of appreciable Raman resonance, we obtain a very simple form of the susceptibility

$$\chi^{(3)}\simeq\chi^{(3)}_{NR}+\frac{C}{(u-i)(y-i)^2} \tag{6}$$

by employing the reduced frequencies defined by

$$u=[\Omega_r-(\omega_1-\omega_2)]/\Gamma_r, \qquad y=(\omega_{eg}-\omega_1)/\gamma_e \tag{7}$$

and

$$C=\frac{12NL}{\hbar^3}X_{g0,e1}X_{e1,g1}X_{g1,e0}X_{e0,g0}/\Gamma_r\gamma_e^2. \tag{8}$$

Then, it is straightforward to obtain the expression of resonance CARS line shape

$$\left|\frac{\chi^{(3)}}{\chi^{(3)}_{NR}}\right|^2\simeq1+2A\frac{(y^2-1)}{(y^2+1)^2}\left(\frac{u}{u^2+1}\right)+\left(A^2\frac{1}{(y^2+1)^2}-4A\frac{y}{(y^2+1)^2}\right)\left(\frac{1}{u^2+1}\right), \tag{9}$$

given by a single parameter $A=C/\chi^{(3)}_{NR}$. Fig.2b shows the calculated line shapes for A=0.5 by this formula. There is a fair correspondence between Figs.2a and 2b, convincing of the validity of present analysis at least qualitatively.

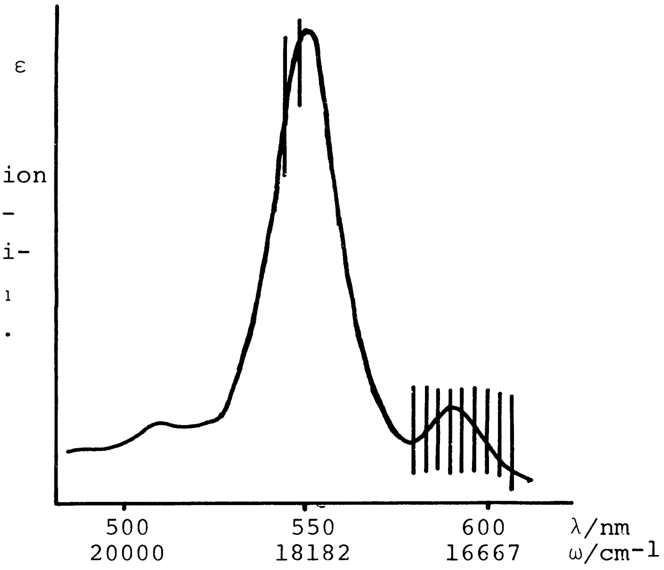

Fig.1 Visible absorption spectrum of Zn-tetraphenylporphin. Vertical lines indicate ω_1 corresponding to Fig. 2a.

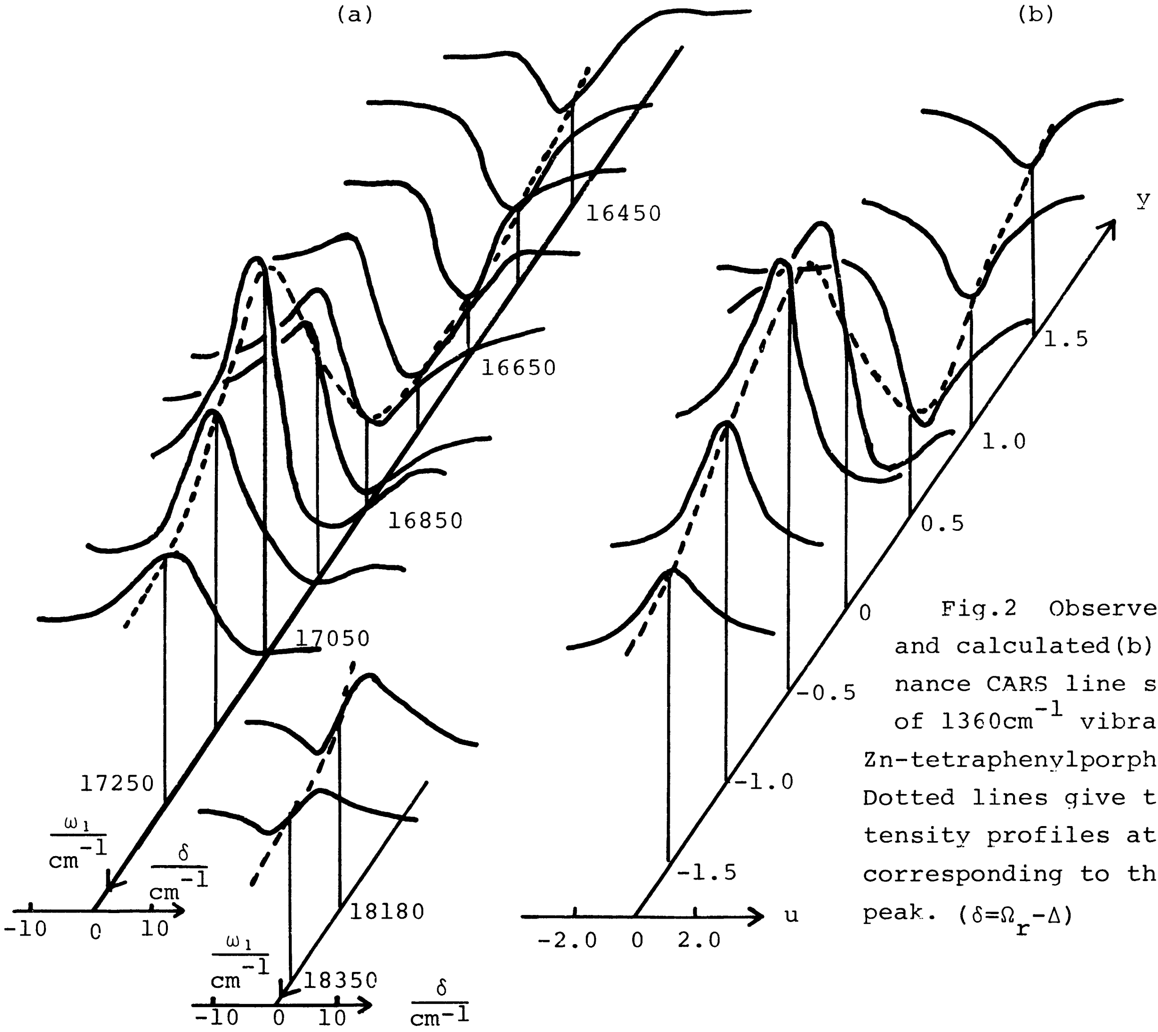

Fig.2 Observed(a) and calculated(b) resonance CARS line shapes of 1360cm^{-1} vibration of Zn-tetraphenylporphin. Dotted lines give the intensity profiles at $\delta(u)=0$ corresponding to the Raman peak. ($\delta=\Omega_r-\Delta$)

On the other hand, the observation by ω_1 near the principal absorption peak showed dispersion type line shapes of the reverse mode to the above, as also given in Fig.2a, suggesting the change in the sign of C between the 0-0 and 1-0 transition regions.

The present preliminary result seems to indicate a potentially interesting aspect of the resonance CARS. Besides, it may be pointed out that the resonance CARS has greater experimental flexibility than spontaneous resonance Raman, in that the parameter A given above can be deliberately changed by changing the sample concentration and solvent.

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