December, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **54**, *3691—3695 (1981)* 3691

The Application of Polarization Coherent Anti-Stokes Raman Spectroscopy to the Line-shape Analysis of Liquid Sample.

Ryosaku IGARASHI,* Fumisato IIDA,† Chiaki HIROSE,†† and Tsunetake FUJIYAMA
Institute for Molecular Science, Myodaiji, Okazaki 444
†*Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo 158*
††*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Midori-ku, Yokohama 227*

(Received May 22, 1981)

The polarization CARS spectra were observed for a few typical Raman lines at various experimental settings. Based upon the observed and calculated spectra, the usefulness and the validity of the polarization CARS method for the study of the overlapped Raman lines observed for a condensed system have been emphasized.

The coherent anti-Stokes Raman scattering (CARS) experiment is a new method of Raman spectroscopy which utilizes the nonlinear optical phenomena induced by the macroscopic third-order nonlinear polarization, $\vec{P}^{(3)}$. This type of spectroscopy has been extensively applied in a wide range of laboratories utilizing the feature of the nonlinear phenomena.[1–5] The polarization CARS is one application of the CARS method, one in which the direction of the polarization of the incident and the scattered light are properly chosen.[6–8]

One of the most important and difficult problems in the field of application spectroscopy lies in the analyses of the spectral lines which are composed of two or more different lines whose resonance frequencies are very close to each other in comparison with their linewidths. For the analyses of the condensed-phase spectra, it is often necessary to resolve an observed line into a number of lines by assuming symmetric lineshape functions, like a Lorentzian or a Gaussian. This method is indeed useful for practical purposes. In many cases, however, the assumption of the lineshape functions is arbitrary in nature and falls short of experimental proof. We started the present work with the belief that we could perform this line-separation into multi-components on a purely experimental basis if we used the polarization CARS method.

In this study, we observe a few typical overlapped Raman lines by the polarization CARS method and ascertain the usefulness and validity of the application of the polarization CARS method for the study of the overlapped Raman lines observed for condensed systems.

Theoretical

Third-order Susceptibility in Liquid. CARS arises from a third-order nonlinear polarization which is induced in the medium at the frequency when $\omega_3=2\omega_1-\omega_2$ by the incident lights, ω_1 and ω_2. This third-order nonlinear polarization at the ω_3 frequency can be expressed as:

$$\vec{P}^{(3)}(\omega_3)=\chi^{(3)}(\omega_3)\vec{E}(\omega_1)\vec{E}(\omega_1)\vec{E}^*(\omega_2), \tag{1}$$

where $\vec{E}(\omega_1)$ and $\vec{E}(\omega_2)$ are the amplitudes of the incident lights and where $\vec{P}^{(3)}(\omega_3)$ is the third-order susceptibility. As the CARS intensity is proportional to $|\vec{P}^{(3)}(\omega_3)|^2$, the CARS spectra are characterized by $\chi^{(3)}(\omega_3)$, which is a fourth-rank tensor. In general, $\chi^{(3)}(\omega_3)$ can be expressed as the sum of two terms:

$$\chi^{(3)}(\omega_3)=\chi^{\mathrm{NR}}+\chi^{\mathrm{R}}, \tag{2}$$

where χ^{NR} is an electronic or background susceptibility, and χ^{R}, a Raman susceptibility.

It has been established, for a spontaneous Raman scattering, that a totally symmetric Raman line is composed of two parts: an isotropic component and an anisotropic component. The linewidth of an anisotropic component is much broader than that of an isotropic one, because the isotropic linewidth is governed mainly by the reorientational relaxation process.[9] Therefore, it is preferable to write the χ^{R} of Eq. 2 in this form:

$$\chi^{\mathrm{R}}=\sum_{\mathrm{r}}\left(\frac{\chi^{\mathrm{rI}}}{\delta_{\mathrm{rI}}-\mathrm{i}\Gamma_{\mathrm{rI}}}+\frac{\chi^{\mathrm{rA}}}{\delta_{\mathrm{rA}}-\mathrm{i}\Gamma_{\mathrm{rA}}}\right), \tag{3}$$

where Γ_{rI} and Γ_{rA} are the linewidths of the isotropic and anisotropic components respectively; $\delta_{\mathrm{r}}=\omega_{\mathrm{r}}-(\omega_1-\omega_2)$; ω_{r} is the Raman frequency of the r-th vibrational mode. In the derivation of Eq. 3, we assumed that $\omega_{\mathrm{rI}}=\omega_{\mathrm{rA}}$.[10]

In an isotropic medium, there are only two independent tensor components, $\chi^{(3)}_{1111}(-\omega_3:\omega_1,\omega_1,-\omega_2)$ and $\chi^{(3)}_{1221}(-\omega_3:\omega_1,\omega_1,-\omega_2)$, where 1 and 2 denote two distinguishable Cartesian axes. These tensor components are given by an orientational average of the susceptibilities of individual molecules. According to Yuratich and Hanna,[11] χ^{rI} and χ^{rA} of Eq. 3 for an electronic non-resonant condition are given by these relations:

$$\chi^{\mathrm{rI}}_{1111}=\frac{NL\alpha^2}{12\hbar}, \tag{4}$$

$$\chi^{\mathrm{rI}}_{1221}=0, \tag{5}$$

$$\chi^{\mathrm{rA}}_{1221}=\frac{3}{4}\chi^{\mathrm{rA}}_{1111}=\frac{NL}{12\hbar}\frac{\gamma_{\mathrm{s}}{}^2}{15}, \tag{6}$$

where α^2 is the mean value and $\gamma_{\mathrm{s}}{}^2$ is the symmetric part of the anisotropy of an usual Raman tensor. In this discussion we assumed that the antisymmetric part of the anisotropy is negligible. N is the number density of the Raman-active molecules, and L is the local-field correction factor.[1] It is important to add that the following relation holds approximately between the tensor components of χ^{NR}: it is known by the name of the Kleiman relation:

$$\chi^{\mathrm{NR}}_{1111}=3\chi^{\mathrm{NR}}_{1221}. \tag{7}$$

Polarization CARS. From the above discussion

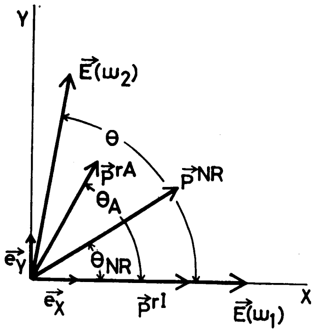

Fig. 1. Polarization directions for polarization CARS experiment.

it can be understood that the polarization, $\vec{P}^{(3)}(\omega_3)$, can be expressed as;

$$\vec{P}^{(3)}(\omega_3) = \vec{P}^{NR} + \sum_r (\vec{P}^{rI} + \vec{P}^{rA}), \tag{8}$$

where the superscripts correspond to those of Eqs. 2 and 3.

We set the experimental conditions as is shown in Fig. 1. One incident light, $\vec{E}(\omega_1)$, is linearly polarized to the X-direction, while the other incident light, $E(\omega_2)$, is polarized on the XY-plane at an angle; θ, with the X-direction. At this experimental setting, the terms of Eq. 8 are expressed by these relations:

$$\vec{P}^{NR} = 3\chi_{1111}^{NR} E_X^2(\omega_1) \{E_X(\omega_2)\vec{e}_X + \frac{1}{3} E_Y(\omega_2)\vec{e}_Y\}, \tag{9}$$

$$\vec{P}^{rI} = \frac{NL\alpha^2 E_X^2(\omega_1) E_X(\omega_2)}{4\hbar(\delta_{rI} - i\Gamma_{rI})}\vec{e}_X, \tag{10}$$

$$\vec{P}^{rA} = \frac{NL\gamma_S^2 E_X^2(\omega_1)}{60\hbar(\delta_{rA} - i\Gamma_{rA})}\left(\frac{4}{3} E_X(\omega_2)\vec{e}_X + E_X(\omega_2)\vec{e}_Y\right), \tag{11}$$

where $\vec{e}_X$ and $\vec{e}_Y$ are unit vectors in the directions of X and Y respectively. If we designate the angles between the X-axis and the vectors, $\vec{P}^{NR}$, $\vec{P}^{rI}$, and $\vec{P}^{rA}$, as θ_{NR}, θ_I, and θ_A respectively (see also Fig. 1), Eqs, 9, 10, and 11 lead to these relations:

$$\tan\theta_{NR} = \frac{E_Y(\omega_2)}{3E_X(\omega_2)} = \frac{1}{3}\tan\theta, \tag{12}$$

$$\tan\theta_I = 0, \tag{13}$$

and

$$\tan\theta_A = \frac{3E_Y(\omega_2)}{4E_X(\omega_2)} = \frac{3}{4}\tan\theta. \tag{14}$$

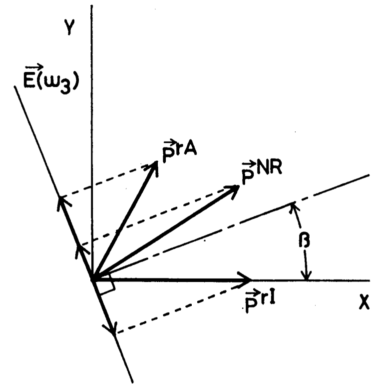

Fig. 2. Polarization direction of the CARS light which passed through the polarization analyzer.

The amplitude of the CARS light, $\vec{E}(\omega_3)$, is proportional to the polarization, $\vec{P}^{(3)}(\omega_3)$, so the observed amplitude, $\vec{E}(\omega_3)$, can have only one polarization state, which is defined by the vector-sum of $\vec{P}^{NR}$, $\vec{P}^{rI}$, and $\vec{P}^{rA}$. In this respect, the CARS light is obviously different from that of the spontaneous Raman scattering. As can be seen from Fig. 2, we can obtain various spectra by setting the polarization direction of the CARS light by putting a polarization analyzer in the path of the CARS light. If we cut off that light whose polarization direction makes an angle; β, with the X-axis, the amplitude, $E(\omega_3)$, which penetrates through the analyzer may be given by this relation:

$$E(\omega_3) \propto \{|\vec{P}^{NR}|\sin(\theta_{NR} - \beta) + \sum_r [|\vec{P}^{rI}|\sin(-\beta) + |\vec{P}^{rA}|\sin(\theta_A - \beta)]\}. \tag{15}$$

Especially, we can obtain "background-free" spectra if we set the experimental condition at $\beta = \theta_{NR}$.

Experimental

Apparatus for Polarization CARS Measurement. A schematic diagram of the polarization CARS spectrometer is shown in Fig. 3. A N_2 laser is oscillated at 337.1 nm with a peak output of 300 kW. The time-width of the N_2 laser is 7 ns, and the repetition rate is 4 Hz. This N_2 laser output is used to pump two dye lasers, 1 and 2, simultaneously. The frequency, ω_1, of the dye laser 1 is fixed at 19200 cm^{-1} (HWHM=0.4 cm^{-1}), while the frequency, ω_2, of the dye laser 2 (HWHM=0.6 cm^{-1}) is tunable. The directions of the polarization of ω_1 and ω_2 are adjusted by the use of two Glan-Laser prism polarizers, GP_1 and GP_2. The two light-beams, ω_1 and ω_2, are adjusted to be parallel with each other before a lens, L_1 (f=10 cm), and then focused into a sample cell. The phasematching angle is adjusted by sliding a mirror, M_1. The scattered light is selected out by the use of an appropriate aperture. The polarization direction of the CARS light is selected out by means of a Glan-Laser prism polarizer, GP_3. After being passed through a depolarizer, DP, the CARS light is focused into a monochromator (JEOL, Model U1 double-monochromator). Finally, the monochromated CARS light is detected by means of a photomultiplier (RCA-1P21) and averaged by the use of a laser photometer (Molectron, LP-20).

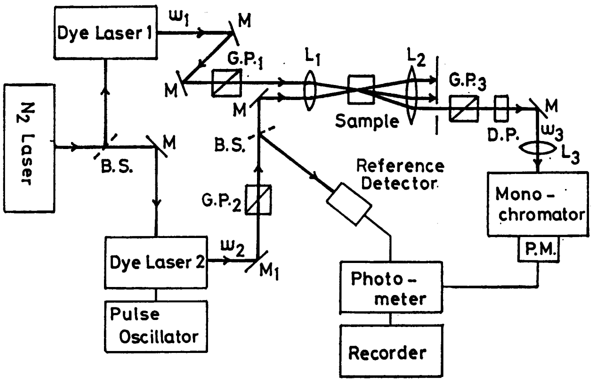

Fig. 3. Schematic representation of the experimental set-up.
BS: Beam splitter, M: mirror, GP: Glan prism, DP: depolarizer, PM: photomultiplier.

A part of the ω_2 is taken out by the use of a beamsplitter, BS, and used for the purpose of the normalization of the CARS light and for the triggering of the photometer. The depolarizer, DP, is used for the cancellation of the polarization characteristics of the monochromator.

Measurement of Ordinary Raman Spectra. The ordinary Raman spectra were recorded by a JEOL, JRS-400T Raman spectrophotometer equipped with an Ar$^+$-ion laser source (Spectra Physics, Model 164, 488.0 nm). A PL filter (Kenko) was used as a polarizer after being corrected for the polarization characteristics.

Sample. All the chemicals used in the present work were commercially available in a guaranteed grade and were used without further purification. The Raman spectra were observed for pure liquid toluene and chlorobenzene for a binary mixture (1 : 1 in volume) of them. The Raman spectra were also observed for pure liquid styrene.

Results and Discussion

For the purpose of dealing with the CARS lineshapes of Raman modes in liquid, we write the electric field of a CARS light being observed in this form:

$$E(\omega_3)=B\sin(\theta_{\mathrm{NR}}-\beta)+\sum_{\mathrm{r}}\left[\frac{R_{\mathrm{rI}}\sin(-\beta)}{\delta_{\mathrm{r}}-\mathrm{i}\Gamma_{\mathrm{rI}}}+\frac{R_{\mathrm{rA}}\sin(\theta_{\mathrm{A}}-\beta)}{\delta_{\mathrm{r}}-\mathrm{i}\Gamma_{\mathrm{rA}}}\right], \tag{16}$$

where:

$$B\propto|\vec{P}^{\mathrm{NR}}|=\sqrt{9+\tan^2\theta}\,\chi_{1111}^{\mathrm{NR}}E_{\mathrm{X}}{}^2(\omega_1)E_{\mathrm{x}}(\omega_2), \tag{17}$$

$$R_{\mathrm{rI}}\propto\frac{|\vec{P}^{\mathrm{rI}}|}{\delta_{\mathrm{r}}-\mathrm{i}\Gamma_{\mathrm{rI}}}=\frac{NL\alpha^2}{4\hbar}E_{\mathrm{X}}{}^2(\omega_1)E_{\mathrm{X}}(\omega_2), \tag{18}$$

and

$$R_{\mathrm{rA}}\propto\frac{|\vec{P}^{\mathrm{rA}}|}{\delta_{\mathrm{r}}-\mathrm{i}\Gamma_{\mathrm{rA}}}=\sqrt{16+9\tan^2\theta}\times\frac{NL\gamma_{\mathrm{S}}^2}{180\,\hbar}E_{\mathrm{X}}{}^2(\omega_1)E_{\mathrm{X}}(\omega_2). \tag{19}$$

Depolarized Raman Lines. A depolarized Raman line has only $\gamma_{\mathrm{s}}{}^2$ in the Raman tensor. Therefore, the polarization CARS spectra expected for this case are represented by this relation:

$$|E(\omega_3)|^2=\left|B\sin(\theta_{\mathrm{NR}}-\beta)+\frac{R_{\mathrm{A}}\sin(\theta_{\mathrm{A}}-\beta)}{\delta-\mathrm{i}\Gamma_{\mathrm{A}}}\right|^2. \tag{20}$$

The typical spectra expected for this case are illustrated in Fig. 4. It can be seen from the figure that the spectral features change dramatically with the change in β. It must be emphasized that this is the only case in which the Raman line is composed of only one component.

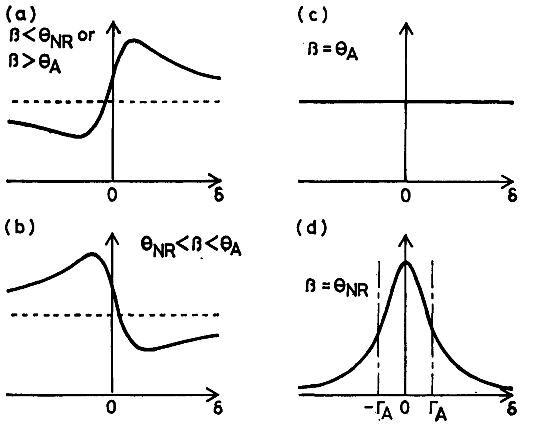

Fig. 4. Typical polarization CARS spectra for an isolated single Raman line.
Remark that (d) corresponds to a "background-free" spectrum.

Totally Symmetric Raman Lines. A totally symmetric Raman line is characterized by $\gamma_{\mathrm{s}}{}^2$ and α^2. Therefore, the polarization CARS spectra can be represented by this relation:

$$|E(\omega_3)|^2=\left|B\sin(\theta_{\mathrm{NR}}-\beta)+\frac{R_{\mathrm{I}}\sin(-\beta)}{\delta-\mathrm{i}\Gamma_{\mathrm{I}}}+\frac{R_{\mathrm{A}}\sin(\theta_{\mathrm{A}}-\beta)}{\delta-\mathrm{i}\Gamma_{\mathrm{A}}}\right|^2. \tag{21}$$

It must be emphasized that a totally symmetric Raman line is composed of two components, isotropic and anisotropic, although it seems to be a single line. Thus, Eq. 21 has two Raman-resonant terms, in good contrast to Eq. 20.

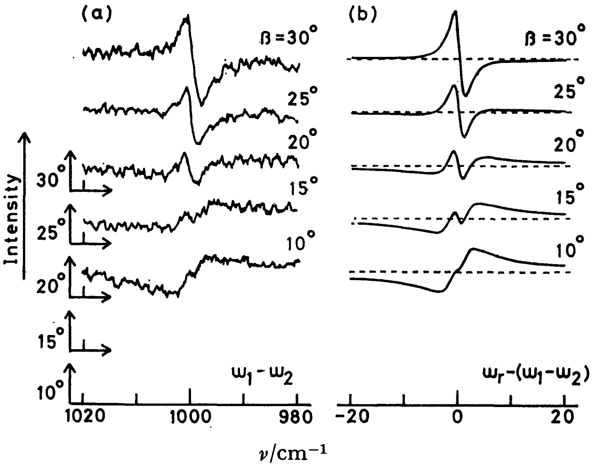

Fig. 5. Polarization CARS spectra for the 1000 cm^{-1} line of pure liquid styrene.
(a): Observed β-dependence, (b): Calculated β-dependence. The dotted lines indicate the background height; $B^2\sin^2(\theta_{\mathrm{NR}}-\beta)$.

As an example, we observed the polarization CARS spectra of the 1000 cm^{-1} Raman line of pure liquid styrene for various β-values. Figure 5(a) shows the results for the experimental settings of $\theta=85°$ and $\beta=$ 10, 15, 20, 25, and 30°. The spontaneous Raman spectra of this line, on the other hand, are characterized by these spectral parameters: the polarization degree is 0.05, and the lineshapes are Lorentzian, with $\Gamma_{\mathrm{I}}=$ 1.4 cm^{-1} for the isotropic line and with $\Gamma_{\mathrm{A}}=2.5$ cm^{-1} for the anisotropic line. Using these spectral parameters, the polarization CARS spectra were calculated for this Raman line: the results are illustrated in Fig. 5(b).[12] The good agreement between the observed and the calculated spectra indicates that the physical meaning of the damping factors, Γ_{I} and Γ_{A}, which appear in the CARS formulation is essentially the same as that of the half-widths in the spontaneous Raman scattering formulation.

It can be seen from Fig. 4 that we can clearly identify the existence of the two Raman components, the polarized and depolarized ones, by observing the polarized CARS spectra for various β-values. It is essential that, in the case of a totally symmetric Raman line, a Raman line should be considered to be overlapped lines whose frequencies are equal, but whose linewidths are different from each other.

Two Closely Located Totally Symmetric Raman Lines. In a case where two Raman lines are located very close to each other, we must consider the overlapping of four Raman lines: two isotropic components and two anisotropic components. As a model system, the binary mixture of toluene and chlorobenzene was chosen, because liquid toluene shows a Raman line at $\omega_r=1004$ cm^{-1}, with a depolarization degree of $\rho=0.018$ and with half-widths of $2\Gamma_I=2.1$ cm^{-1} and $2\Gamma_A=4.2$ cm^{-1}, while liquid chlorobenzene shows a Raman line at $\omega_r=1002.8$ cm^{-1}, with a depolarization degree of $\rho=0.025$ and with half-widths of $2\Gamma_I=1.5$ cm^{-1} and $2\Gamma_A=3.8$ cm^{-1}. These two Raman lines are assigned to the C–C stretching vibrations of the benzene rings and have almost equal intensities.

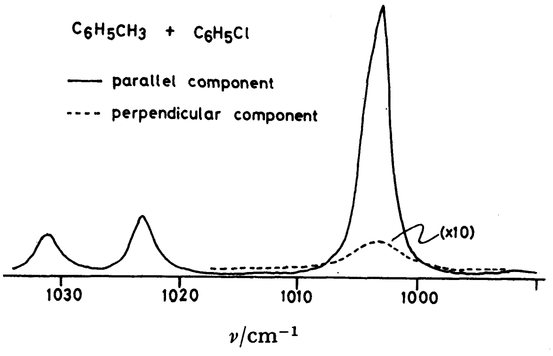

Fig. 6. Observed spontaneous Raman spectra for the binary mixture of toluene and chlorobenzene, (1 : 1 mixture in volume).

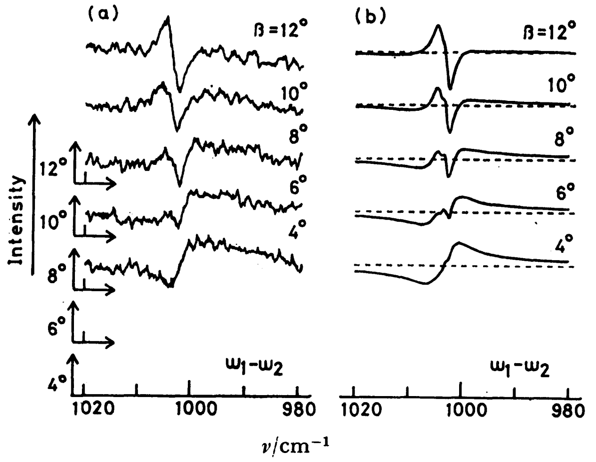

Fig. 7. Polarization CARS spectra for the binary mixture of toluene and chlorobenzene, (1 : 1 mixture in volume).

(a): Observed β-dependence, (b): Calculated β-dependence. The dotted lines indicate the background height, $B^2 \sin^2 (\theta_{NR}-\beta)$.

Figure 6 shows the Raman spectra observed for the binary solution of toluene and chlorobenzene. In this figure, two Raman lines are overlapped with each other at about 1000 cm^{-1}. It can be seen from the figure that it is almost impossible to separate this line into two Raman lines without knowing accurate spectral information about these individual lines. Figure 7(a) shows the observed polarization CARS spectra for $\theta=85°$ and for $\beta=4$, 6, 8, 10, and 12°. Figure 7(b) shows the results of the simulative calculation of the corresponding spectra on the basis of the above spontaneous Raman data. It can be seen from this figure that the overlapping of two Raman lines can easily be surmised by means of the asymmetric feature of the polarization CARS spectra. That is, the positive and negative peaks are quite different from each other both in shape and area, in good contrast with the spectra given in Fig. 5.[13)]

Concluding Discussion. In the preceding paragraphs, the polarization CARS spectra have been discussed for three different cases: (1) a spectrum is composed of only one Raman line and only one component; that is to say, the line corresponds to one vibrational mode and one component: (2) a spectrum is composed of one Raman line which can be assigned to one vibrational mode, but is made from two components, namely, isotropic and anisotropic components, and (3) a spectrum corresponds to two overlapped Raman lines, each of which is made from isotropic and anisotropic components. From the results obtained, we can draw a few important conclusions with respect to the application of the polarization CARS method to the analysis of the overlapped Raman lines.

First, it has been shown that polarization CARS spectra should be analyzed by considering both isotropic and anisotropic scattering processes. It is essential to consider the difference between the isotropic and anisotropic linewidths. Therefore, the separation of the overlapped Raman lines into the individual vibrational lines is not so simple as has been described by Koroteev *et al.*[8)] The apparent splittings in the CARS spectra cannot directly be related to the band-overlapping in ordinary Raman spectra.

Secondly, a polarization CARS method can be a useful technique to compare the isotropic and anisotropic components which are related to the same vibrational mode, because we can observe isotropic and anisotropic components separately by using a proper experimental setting. If we set $\beta=\theta_A$ or $\beta=\theta_I$, we can obtain a purely isotropic spectrum or a purely anisotropic spectrum respectively. For other angles, the spectra exhibit rather complicated features, namely, mixtures of isotropic and anisotropic spectra. As we can change the ratio of R_I and R_A properly by changing the θ, this method is extremely useful for the analysis of a Raman line whose depolarization degree is very small.

Thirdly, it has been shown that the polarization CARS spectra are quite sensitive to the change in the spectral parameters of component lines. Although the analyses of polarization CARS spectra themselves are rather complicated and difficult when several Raman modes are overlapped, the simultaneous use of spontaneous Raman and polarization CARS spectra is a very promising method for the separation of the overlapped Raman lines into their component lines. We can ascertain the validity of the line-separation of overlapped ordinary Raman lines by simulating polarization CARS spectra using the spectral parameters obtained from the line-separation of ordinary Raman spectra. It must be emphasized, however, that this process is purely experimental.

References

1) M. D. Levenson and N. Bloembergen, *Phys. Rev. B*, **10**, 4447 (1974).

2) H. Lotem, R. T. Lynch, Jr., and N. Bloembergen, *Phys. Rev. A*, **14**, 1748 (1976).

3) J. W. Nibler and G. V. Knighten, "Coherent Anti-Stokes Raman Spectroscopy," in "Raman Spectroscopy of Gasses and Liquids," Topics in Current Physics, ed by A. Meber, Springer-Verlag (1979) Vol. II.

4) R. Igarashi, Y. Adachi, and S. Maeda, *J. Chem. Phys.*, **72**, 4308 (1980).

5) M. Shimizu, R. Igarashi, Y. Adachi, and S. Maeda, *J. Chem. Phys.*, **73**, 612 (1980).

6) S. A. Akhmanov and N. I. Koroteev, *Sov. Phys. JETP*, **40**, 650 (1975).

7) S. A. Akhmanov, A. F. Bunkin, S. G. Ivanov, and N. I. Koroteev, *Sov. Phys. JETP*, **47**, 667 (1978).

8) N. I. Koroteev, M. Endemann, and R. L. Byer, *Phys. Rev. Lett.*, **43**, 398 (1979).

9) F. J. Bartoli and T. A. Litovitz, *J. Chem. Phys.*, **56**, 404 (1972).

10) C. H. Wang and J. Mchale, *J. Chem. Phys.*, **72**, 4039 (1980).

11) M. A. Yuratich and D. C. Hanna, *Mol. Phys.*, **33**, 671 (1977).

12) The relative magnitude of R_I or R_A to B was determined from the simulation. The final parameters used for the simulation were: $\Gamma_I = 1.4\ \mathrm{cm}^{-1}$, $\Gamma_A = 2.5\ \mathrm{cm}^{-1}$, $R_I = 1.07B$, $R_A = 0.65B$, and $\omega_r = 1000.0\ \mathrm{cm}^{-1}$.

13) The relative magnitudes of R_I and R_A to B were determined from the simulation. The final parameters were: $R_I = 1.03B$ and $R_A = 0.21B$ for toluene, and $R_I = 1.00B$ and $R_A = 0.30B$ for chlorobenzene.