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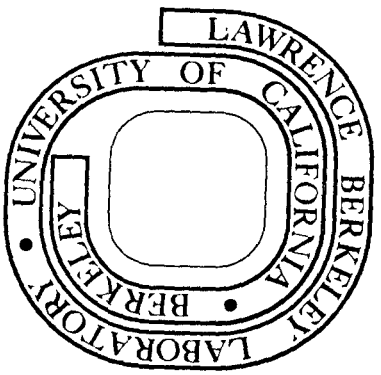

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POLARIZATION-SENSITIVE COHERENT ANTI-STOKES RAMAN SPECTROSCOPY

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ABSTRACT

We show that by using polarization coherent antiStokes Raman spectroscopy, the detection sensitivity of weak Raman modes is greatly enhanced. The spectra of the real part, the imaginary part, and the absolute magnitude of the resonant nonlinear susceptibility can be separately measured. Raman modes with cross-sections as low as 2×10^{-4} times that of the 992 cm^{-1} mode of benzene are detectable with less than 10 kW peak power lasers.

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A number of coherent nonlinear optical spectroscopic techniques have been developed in recent years,[1,2] which have clear advantages over spontaneous scattering techniques when high resolution is required, and/or when fluorescence or thermal radiative emission is strong. However, these coherent techniques have a rather limited sensitivity in detecting weak resonances, due to the strong background from the nonresonant nonlinear contribution. The major source of noise then comes from fluctuations in the power or the mode structure of the input lasers. In the case of coherent antiStokes Raman spectroscopy (CARS), variations of the basic scheme have been proposed to suppress this background,[3,4] but they make use of a third input beam so that three lasers are needed.

Recently, Akhamanov et al.[5] have shown that ellipsometric measurements of the antiStokes beam in a CARS experiment can yield information on the dispersion of the nonlinear susceptibility with a high accuracy. Such a scheme is attractive since polarization characteristics are independent of the laser intensity fluctuations. However it is a tedious process if the ellipsometric measurement is to be performed over the entire spectrum, as was done in Ref. 5.

In this letter, we show that with simple polarization arrangement in CARS, we can obtain a direct, continuously scanned spectrum which eliminates the nonresonant background and improves considerably the detection limit of weak Raman resonances. In addition, by admixing the resonant contribution with a controlled (and properly phase-shifted) proportion of the nonresonant part, we can obtain spectra which are linear in either the real or the imaginary part of the resonant susceptibility. This, of course, can be viewed as an optical heterodyne detection of the resonance,[6]

the local oscillator being provided by the nonresonant susceptibility.

Consider two input beams of frequencies ω_1 and ω_2 propagating in an isotropic medium along the $\hat{z}$ axis. The ω_1 beam is polarized along $\hat{x}$ and the ω_2 beam along a direction at an angle ϕ with $\hat{x}$. The nonlinear polarization at frequency $\omega_3 = 2\omega_1 - \omega_2$ is given by

$$P_x = 3\cos\phi[\chi^{NR}_{1111} + \chi^{R}_{1111}]E_1^2E_2^* \tag{1a}$$

$$P_y = 3\sin\phi[\chi^{NR}_{1221} + \chi^{R}_{1221}]E_1^2E_2^*. \tag{1b}$$

If χ^{NR} is real, then the direction of the nonlinear polarization arising from the nonresonant term χ^{NR} makes an angle

$$\alpha_{NR} = \tan^{-1}[(\chi^{NR}_{1221}/\chi^{NR}_{1111})\tan\phi] \tag{2}$$

with the $\hat{x}$ axis. Let $\hat{X}$ and $\hat{Y}$ be the axes parallel and perpendicular to the nonresonant part of the nonlinear polarization. Then, by using an analyzer along $\hat{Y}$ to detect the ω_3 signal, we can effectively suppress the nonresonant contribution.

The nonlinear polarization components along $\hat{X}$ and $\hat{Y}$ are

$$P_X = \left\{3\chi^{NR}_{1111}\cos\phi/\cos\alpha_{NR} + 3\chi^{R}_{1111}\cos\phi\cos\alpha_{NR}(1 + \rho\tan\phi\tan\alpha_{NR})\right\}E_1^2E_2^* \tag{3a}$$

$$P_Y = -\left\{3\chi^{R}_{1111}\cos\phi\sin\alpha_{NR}[1 - \rho(\tan\phi/\tan\alpha_{NR})]\right\}E_1^2E_2^* \tag{3b}$$

where $\rho = \chi^{R}_{1221}/\chi^{R}_{1111}$. In many cases, the Kleinman symmetry is obeyed by

the nonresonant susceptibility, $\chi^{NR}_{1111} = 3\chi^{NR}_{1221}$. We then have $3\tan\alpha_{NR} = \tan\phi$ and Eq. (3) can be simplified. We note immediately from Eq. (3) that the output ω_3 signal is elliptically polarized because χ^R is complex. For a weak resonance with $|\chi^R| \ll |\chi^{NR}|$ so that the χ^R term in Eq. (3a) can be neglected, we can write

$$\theta = \theta' + i\theta'' = \frac{-P_Y}{P_X} \cong \frac{\chi^R_{1111}}{2\chi^{NR}_{1111}} \sin 2\alpha_{NR}[1 - \rho(\tan\phi/\tan\alpha_{NR})]. \qquad (4)$$

Then θ'', proportional to $\mathrm{Im}(\chi^R)$, gives the ellipticity, and θ', proportional to $\mathrm{Re}(\chi^R)$, gives the rotation of the major ellipse axis from $\hat{X}$ due to χ^R.

If we detect the ω_3 signal through an analyzer parallel to $\hat{Y}$, we obtain

$$I(\omega_3) \propto |P_Y|^2 \propto |\chi^R_{1111}|^2 \qquad (5)$$

with the nonresonant background completely eliminated. We can however also set the analyzer at a small angle θ_o away from $\hat{Y}$. The output is then given by

$$I(\omega_3) \propto |P_X \sin\theta_o - P_Y \cos\theta_o|^2 = |P_X \cos\theta_o|^2 |\tan\theta_o + \theta|^2. \qquad (6)$$

If $|\tan\theta_o| \gg |\theta|$, the output normalized against the component rejected by the analyzer becomes

$$I_{\parallel}/I_{\perp} \cong \tan^2\theta_o + 2\theta' \tan\theta_o. \qquad (7)$$

Aside from the $\tan^2\theta_o$ term, the spectrum is now dominated by the interference term which is proportional to θ' and hence to $\mathrm{Re}(\chi^R)$. We can also obtain the spectrum of $\mathrm{Im}(\chi^R)$ with a slightly different arrangement. Using a quarter wave plate with axes along $\hat{X}$ and $\hat{Y}$, we can shift the phase of P_X relative to P_Y by 90°. The normalized output is then given by $|i\tan\theta_o + \theta|^2$ with the interference term proportional to $\theta'' \propto \mathrm{Im}(\chi^R)$. Note that the signal-to-noise ratio can be optimized by adjusting θ_o, in a way similar to that discussed in Ref. 6.

The order of magnitude of these effects can be readily estimated from Eq. (4). Consider a resonance line with $\rho = 0$ and choose $\alpha_{NR} = 45°$. A weak resonance with $|\chi^R/\chi^{NR}| = 0.03$ will lead to a $|\theta| = 0.9°$, which is more easily detectable than the corresponding 3% variation of signal above the nonresonant background in the conventional CARS.

To illustrate these possibilities we have performed a CARS experiment with dilute mixtures of benzene in carbon tetrachloride. The experimental set-up is shown in Fig. 1. Two flashlamp-pumped dye lasers[7] were used to provide the two input beams at frequencies ω_1 and ω_2. One of them was set at a fixed wavelength $\lambda_1 = 5950$ Å with an intracavity interference filter and an etalon to reduce the linewidth to .2 cm^{-1}. The other was tuned with a telescope-grating combination, and its linewidth was less than .2 cm^{-1}. For the bulk of the experiments the output powers of these lasers were 7 kW at ω_1 and 3 kW at ω_2. The polarization of the ω_2 beam could be rotated with respect to that of ω_1 by a half-wave Fresnel rhomb, followed by a Glan-Thomson prism. The angle ϕ was adjusted so that $\alpha_{NR} \cong 45°$, in order to maximize $|\theta|$ in Eq. (4). The two beams were then focused at a small angle into the liquid cell and the antiStokes output was separated from the input beams by means of an iris and a monochromator, as usually

done in CARS experiments.

To obtain the spectrum of $|\chi^R|^2$, we should detect only the $\hat{Y}$ polarization component of the antiStokes output. A Glan-Thomson polarizer was put between the sample and the monochromator, and was adjusted to null the signal when $\omega_1 - \omega_2$ was off-resonance. Compensation for residual birefringence of the optics and the cell windows was achieved by means of a quarter-wave plate ($\lambda/4$) just in front of the polarizer. The background intensity due to χ^{NR} could be reduced by more than 10^4, so that very weak χ^R resonances were detectable. A typical spectrum is shown in Fig. 2a.

To obtain the spectra of $Re(\chi^R)$ and $Im(\chi^R)$, we should rotate the analyzer slightly away from the null position and measure the ratio of the intensities of the transmitted and rejected output beams. In the actual setup, the analyzer was placed after the monochromator, as depicted in Fig. 1. Then, the two orthogonal components, transmitted and reflected by the Glan prism, could be detected separately by two photomultipliers. A half-wave plate ($\lambda/2$) was put in front of the monochromator, and was rotated for adjusting θ_o. The ratio of the two photomultiplier signals was recorded as ω_2 was varied, and the result was insensitive to pulse-to-pulse laser fluctuations. Depending on the presence or absence of the quarter wave plate after the sample, the final signal output was proportional to $|i \tan\theta_o + \theta|^2$ or $|\tan\theta_o + \theta|^2$. Two spectra obtained with this method are shown in Figs. 2b and 2c, which gives a display of $Im(\chi^R)$ and $Re(\chi^R)$ respectively, through the interference terms. The lineshape in Fig. 2b is close to that of Fig. 2a, because the line is nearly a Lorentzian. It was also verified that the signal variation was inverted

with inversion of θ_o, which is a clear indication of the interference effect. The three spectra in Fig. 2 were obtained with the same mixture of 0.1% of benzene (by volume) in carbon tetrachloride. The absolute signal variations were in good agreement with Eq. (4), leading to $|\theta|_{max} = 1.1°$ (± 15%). Knowing $\rho = 0$ for this Raman mode of benzene and $\chi^{NR} = 45°$. we found $|\chi^R|_{max} = 3.8 \times 10^{-2}\ \chi^{NR}$. Taking into account the concentration of benzene, this value agrees within experimental error with a previous determination of $\chi^R(C_6H_6)/\chi^{NR}(CC\ell_4)$ by Levenson.[8]

Another application of this polarization CARS technique is illustrated in Fig. 3, which shows two spectra of 0.4M C_6H_6 in $CC\ell_4$ in the vicinity of the 992 cm^{-1} Raman mode. With the conventional unpolarized CARS (Fig. 3a) the isotopic line at 983 cm^{-1} appears only as a small peak (< 10%) above the strong wing of the main 992 cm^{-1} line. This is the case even at higher benzene concentration, because the strong background comes mainly from the real part of $\chi^{(3)}$ due to the strong 992 cm^{-1} line of benzene. To obtain the spectrum of Fig. 3b, the intensity was first nulled at 975 cm^{-1} and then the polarizer was slightly uncrossed (by ~ 2°) to allow for the optical heterodyning of weak resonances. The result is that the isotopic line appears very clearly and that even the second satellite line at 979 cm^{-1} is now distinctly visible.

In conclusion, these spectra clearly demonstrate the sensitivity of polarization CARS for the detection of weak Raman modes. With our setup, the detection limit of benzene concentration in $CC\ell_4$ was 2×10^{-4} using the 992 cm^{-1} Raman mode, which is at least one order of magnitude improvement compared to other coherent Raman techniques.[6,9] With the use of more powerful lasers, such as YAG pumped dye lasers in the 100 kW -

1 MW range, the detection limit should be less than 10^{-5}, that is, one could detect concentrations as low as 10 ppm for molecules with scattering cross-sections similar to that of benzene. This technique should also be very useful in the case of gaseous media where the nonresonant background nonlinearity also constitutes a major obstacle to the detection of small concentrations of a given species.[2,10]

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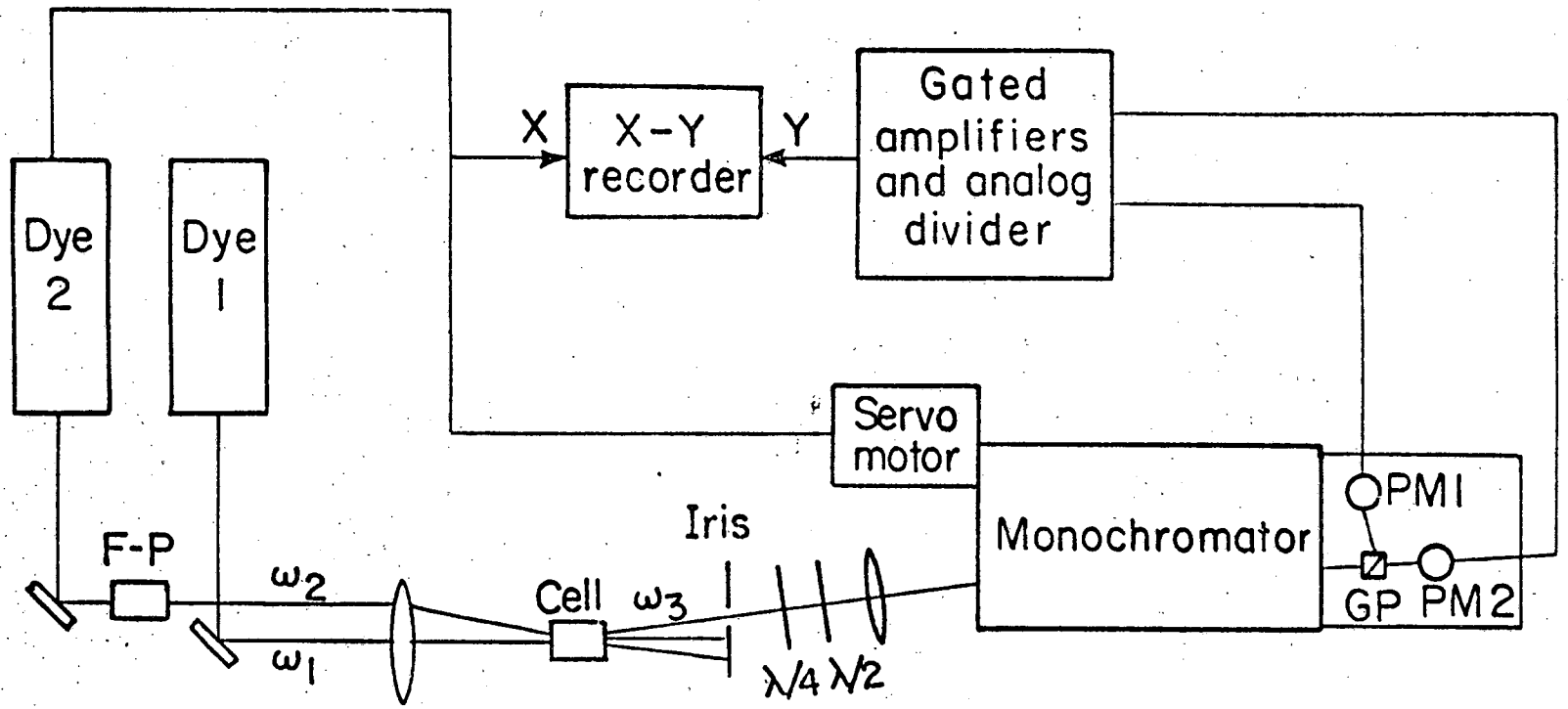
Figure Captions

Fig. 1 Schematic of the experimental set-up; F-P is a half-wave Fresnel rhomb followed by a polarizer, GP is a Glan-Thomson prism. PM1 and 2 are photomultipliers.

Fig. 2 Polarization CARS spectra of .011 M benzene in carbon tetrachloride (a) background suppression; (b) and (c) interference between a small fraction of the coherent background and the imaginary (b) or the real part (c) of the Raman contribution.

Fig. 3 CARS spectra of .4 M benzene in carbon tetrachloride in the vicinity of the strong 992 cm^{-1} Raman mode (a) unpolarized detection (b) transmitted signal through a quarter-wave plate and a slightly uncrossed polarizer — arbitrary scale between (a) and (b).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Dye 1
X
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Y
Gated amplifiers and analog divider
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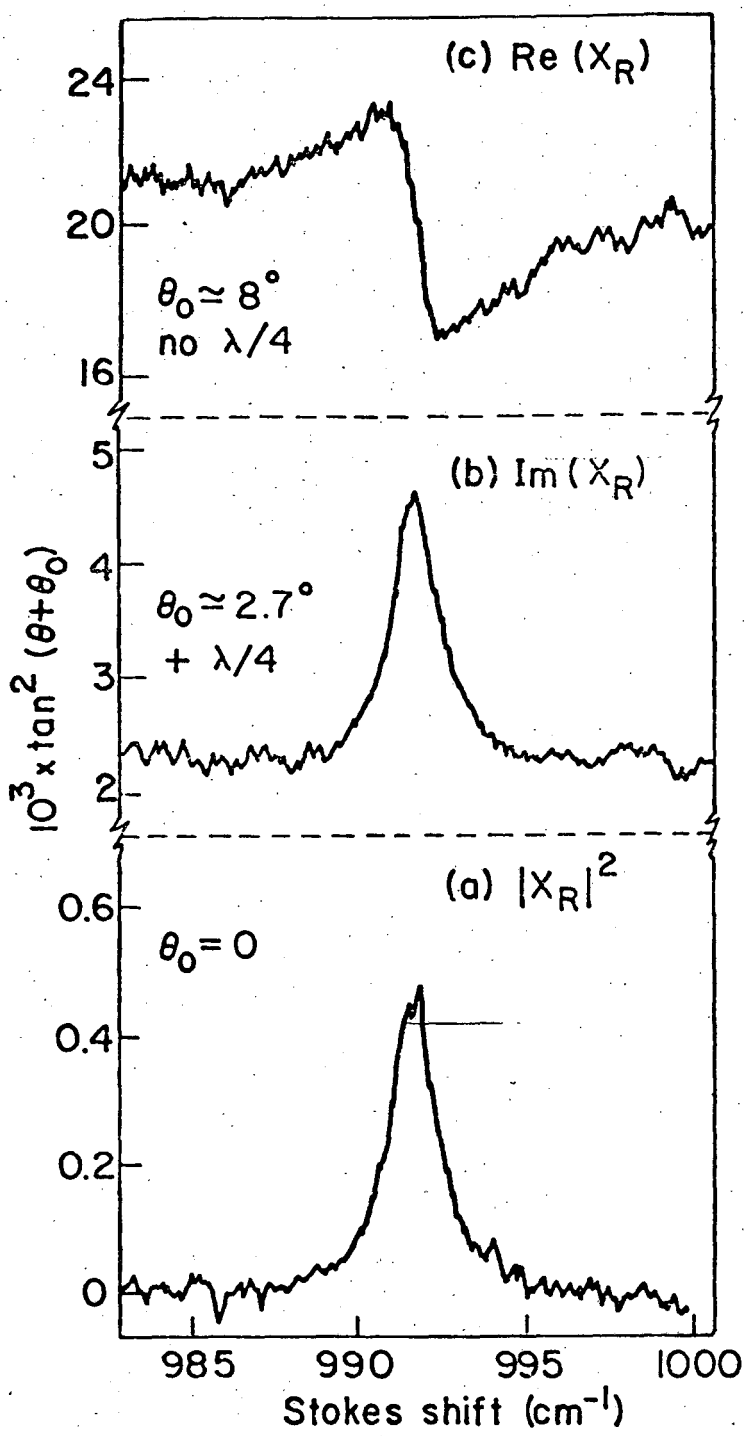
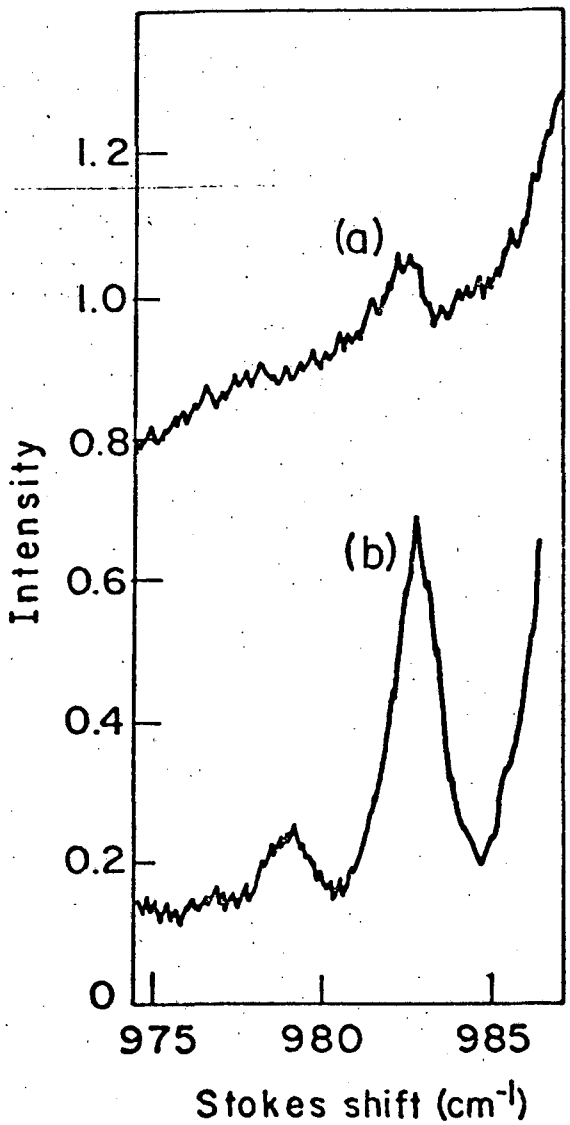

(c) Re (X_R)
24
20
16
$\theta_0 \simeq 8°$
no $\lambda/4$
(b) Im (X_R)
5
4
3
2
$\theta_0 \simeq 2.7°$
+ $\lambda/4$
$10^3 \times \tan^2(\theta+\theta_0)$
(a) $|X_R|^2$
0.6
0.4
0.2
0
$\theta_0 = 0$
985
990
995
1000
Stokes shift (cm^{-1})

XBL791-5629



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