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Destructive Interference of Imaginary Resonant Contributions to $\chi^{(3)}$[†]

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The first observation of destructive interference of imaginary contributions to $\chi^{(3)}$ from different resonances is reported. Destructive and constructive interferences were obtained between Raman and two-photon absorption (TPA) contributions in organic liquids. Accurate TPA and two-photon dispersion spectra of CS_2 obtained by using these interferences in $\chi^{(3)}$ are reported. The TPA experiment described is superior to the classical TPA experiments in its accuracy and in the fact that it lacks the uncertainties originating from scattering processes which compete with true TPA.

We report the first observation of destructive interference of imaginary contributions of different two-photon resonances to the complex nonlinear optical susceptibility $\chi^{(3)}$. It is shown that destructive and constructive interference can be achieved simply by interchanging the frequencies of the laser beams used in the measurements of $\chi^{(3)}$. Important uses are discussed for the reported interference effects in determinations of accurate absolute values for two-photon absorption (TPA) cross sections. We emphasize that the interferences reported here are between different two-photon contributions to $\chi^{(3)}$, possibly even from different materials. Bjorkholm and Liao[1a] and Stein *et al.*[1b] have observed destructive interference among the contributions of one-photon levels to a *single* TPA or Raman term, respectively.

The two experiments used for demonstrating the interference between the imaginary terms are specific examples of parametric mixing, where three electromagnetic fields $\vec{E}(\omega_i)$ $(i=a, b, c)$ produce a nonlinear polarization given by[2]

$$P_j^{(3)}(\omega_{\text{out}}=\omega_a+\omega_b+\omega_c)=\chi_{jklm}^{(3)}(-\omega_{\text{out}},\omega_a,\omega_b,\omega_c)E_k(\omega_a)E_l(\omega_b)E_m(\omega_c). \qquad (1)$$

This polarization generates a new field at ω_{out}.

In general, the third-order susceptibility $\chi^{(3)}(-\omega_{\text{out}},\omega_a,\omega_b,\omega_c)$ controls "four-photon" or "four-wave" processes. We consider here two specific cases, $\omega_{\text{out}}=\omega_1+\omega_1-\omega_2$ and $\omega_{\text{out}}=\omega_1-\omega_1+\omega_2$. The former involves three different waves and has been called three-wave mixing (3WM).[3] The latter we shall call the "Kerr effect" (KE) susceptibility. The name Kerr effect is most appropriate for the off-diagonal elements of $\chi^{(3)}(-\omega_2,\omega_1,-\omega_1,\omega_2)$ since these control the effective rotation of the polarization of the beam at ω_2 due to the presence of light at ω_1. Even though the third-order nonlinear susceptibilities are measured in parametric experiments where the material system does not change its quantum state, the importance of these susceptibilities is that different resonant contributions to $\chi^{(3)}$ are proportional to corresponding nonparametric two-photon scattering cross sections.[2] That is, when an intermediate frequency $\omega_1-\omega_2$ is near a Raman frequency ω_R of the material, the imaginary part of the resonant contribution is proportional to the Raman scattering cross section, and similarly for the TPA cross section when an intermediate frequency $\omega_1+\omega_2$ (or $2\omega_1$) is near a TPA transition frequency ω_t.

According to perturbation theory, in a simplified material system with one Raman and one TPA resonance close to $\omega_1-\omega_2$ and $\omega_1+\omega_2$ (or $2\omega_1$), respectively, and for frequencies far below any one-photon transition, the 3WM and the KE susceptibilities can be well approximated by[2,4]

$$\chi_{\mathrm{KE}}^{(3)}(-\omega_2,\omega_1,-\omega_1,\omega_2)=\chi_{\mathrm{NR}}^{(3)}(-\omega_2,\omega_1,-\omega_1,\omega_2)+\frac{T}{\omega_t-(\omega_1+\omega_2)-i\Gamma_t}+\frac{R}{\omega_{\mathrm{R}}-(\omega_1-\omega_2)+i\Gamma_{\mathrm{R}}}+\frac{R}{\omega_{\mathrm{R}}+(\omega_1-\omega_2)-i\Gamma_{\mathrm{R}}}, \tag{2a}$$

$$\chi_{3\mathrm{WM}}^{(3)}(-\omega_3,\omega_1,\omega_1,-\omega_2)=\chi_{\mathrm{NR}}^{(3)}(-\omega_3,\omega_1,\omega_1,-\omega_2)+\frac{T}{\omega_t-2\omega_1-i\Gamma_t}+\frac{2R}{\omega_{\mathrm{R}}-(\omega_1-\omega_2)-i\Gamma_{\mathrm{R}}}+\frac{2R}{\omega_{\mathrm{R}}+(\omega_1-\omega_2)+i\Gamma_{\mathrm{R}}}. \tag{2b}$$

The terms $\chi_{\mathrm{NR}}^{(3)}$ are real and smoothly varying; the second terms in Eqs. (2a) and (2b) are the resonant TPA contributions, and the last two terms in each equation are the Raman contributions. Only one Raman term in each equation will be resonant, depending on the sign of $\omega_1-\omega_2$. Thus, the sign of the imaginary part of the Raman contribution can be made positive or negative by making $\omega_1-\omega_2\sim\omega_R$ or $\omega_2-\omega_1\sim\omega_R$. We note the analogy of these two cases to the distinction between Raman and inverse-Raman processes.[5] Since the imaginary parts of the TPA terms do not change sign when the frequencies ω_1 and ω_2 are interchanged, we obtain constructive or destructive interference of imaginary contributions to $\chi^{(3)}$ depending on the sign of $\omega_1-\omega_2$. An unambiguous check of the perturbation expression [Eqs. (2a) and (2b)] is therefore available.

The interference effects were experimentally investigated in two different material systems: pure liquid CS_2 and mixtures of CS_2 and benzene. CS_2 was chosen for this experiment because of its large TPA cross section, while benzene was chosen because of its strong 992-cm^{-1} Raman mode. The experimental system for the 3WM susceptibility measurements was described by Levenson and Bloembergen.[6] The KE susceptibility measurements were done using a setup similar to the one described by Heiman *et al.*[7] Important differences in our system are the use of two narrow-band lasers and electronic recording of the signal versus $|\omega_1-\omega_2|$. By using the polarization arrangement of Ref. 7 in an isotropic material, one can measure the effective susceptibility

$$\chi_{\mathrm{eff}}^{(3)}(-\omega_2,\omega_1,-\omega_1,\omega_2)=\chi_{xxyy}^{(3)}(-\omega_2,\omega_1,-\omega_1,\omega_2)-\chi_{xyxy}^{(3)}(-\omega_2,\omega_1,-\omega_1,\omega_2). \tag{3}$$

The great advantage of measuring this effective susceptibility is that the nonresonant background term in Eq. (2a) is canceled,[7] but because of selection rules the resonant terms in general are not canceled.[7,8] Thus, the net TPA and Raman contributions are much more pronounced. In the 3WM experiment the tensor element $\chi_{xxxx}^{(3)}$ was measured, and in this case a real nonresonant background is present.

The experimental results of the KE susceptibility measurement are shown in Fig. 1. Clear effects of interference between the 992-cm^{-1} mode of benzene and the TPA contributions of CS_2 are seen. $\omega_1+\omega_2$ was kept the same so that the TPA contribution remained unchanged. For an appropriate ratio of TPA to Raman strength, the destructive interference exhibits a definite dip, as shown in Fig. 1(b). For other ratios the destructive and constructive interferences show up as different peak heights, as in Fig. 1(a).

The experimental results of the 3WM susceptibility measurements are shown in Fig. 2. The measurements were performed with $|\omega_1-\omega_2|$ in the vicinity of the strong 656-cm^{-1} mode of CS_2. In order to have the same TPA contribution for both $\omega_1>\omega_2$ and $\omega_1<\omega_2$, we held ω_1 fixed and used the two different values of ω_2 which obey $|\omega_1-\omega_2|\sim 656$ cm^{-1}. The sharp antiresonant structures in Fig. 2 are the result of the known destructive interference of the real part of the Raman term with the nonresonant term.[6] The shape of the antiresonant minimum depends on the magnitude of the imaginary part of the 3WM susceptibility, since the net real part of the 3WM susceptibility is very small in the minimum region. It can be seen from Fig. 2 that destructive and constructive interferences between the imaginary contributions occur for $\omega_1<\omega_2$ and $\omega_1>\omega_2$, respectively, as predicted by Eq. (2b).

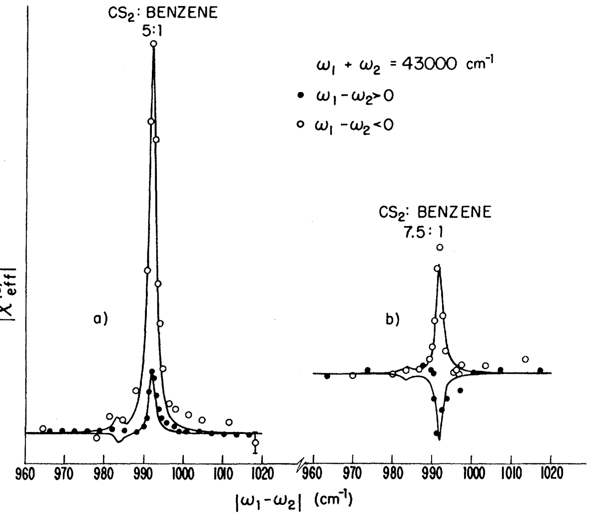

FIG. 1. Experimental (dots) and theoretical curves of $|\chi_{\rm eff}^{(3)}(-\omega_2,\omega_1,-\omega_1,\omega_2)|$ in CS$_2$-benzene mixtures. Destructive interference occurs for $\omega_1 > \omega_2$. The results for each mixture are drawn on different arbitrary scales.

The theoretical fits shown in Figs. 1 and 2 are based on expressions similar to Eq. (2). In the pure CS$_2$ case, accurate parameters for the shape of the rich Raman structure in the vicinity of the 656-cm^{-1} mode were taken from spontaneous Raman spectra measured with a laser at 5145 Å. The line shape of the benzene modes near 992 cm^{-1} is modified when benzene is mixed with CS$_2$. Spontaneous Raman data of a 2-parts CS$_2$, 1-part benzene mixture were used in fitting the curves in Fig. 1. For each mixture, both experiments were fitted with one value of R/T. The spontaneous spectra were fitted with imaginary Lorentzians, and the corresponding complex Lorentzians used for the Raman contributions to $\chi^{(3)}$.

An important use for the interference effects exhibited by the real and imaginary contributions[6] to $\chi^{(3)}$ is in accurate TPA cross-section measurements. Figure 3 illustrates a spectrum of the TPA cross section of pure CS$_2$ measured by the 3WM experiment. In addition, Fig. 3 shows the sum of the real part of the TPA contribution plus $\chi_{\rm NR}^{(3)}$. Since the Raman contributions to $\chi_{\rm NR}^{(3)}$ are negligibly small, this sum includes only TPA contributions. The two spectra are normalized to the known Raman strength of the CS$_2$ 656-cm^{-1} mode.[9] No dispersion corrections for this Raman strength were made. In regions of moderate TPA cross section, the use of both the destructive and constructive interference cases allows more accurate evaluations than are possible with only one

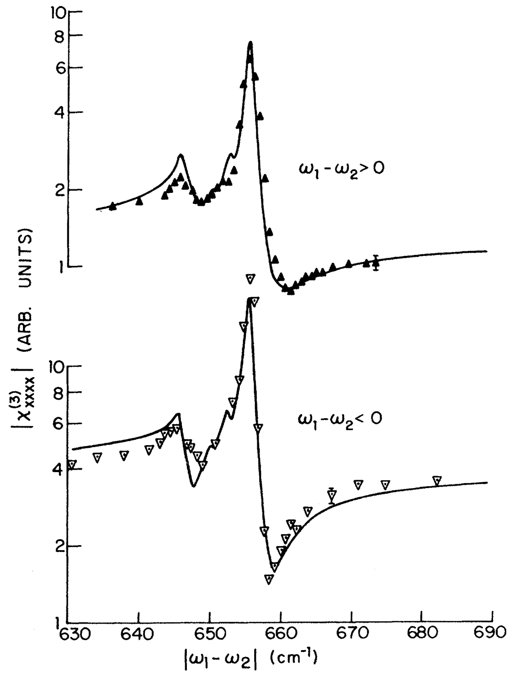

FIG. 2. Experimental points and theoretical curves of $|\chi_{xxxx}^{(3)}(-\omega_{\rm out},\omega_1,\omega_1,-\omega_2)|$ of CS$_2$ at $2\omega_1 = 44\,000$ cm^{-1}. Both theoretical curves were drawn using $\chi_{\rm NR}^{(3)} = (1.1+0.7i)\times 10^{-13}$ esu and laser linewidth 0.2 cm^{-1}.

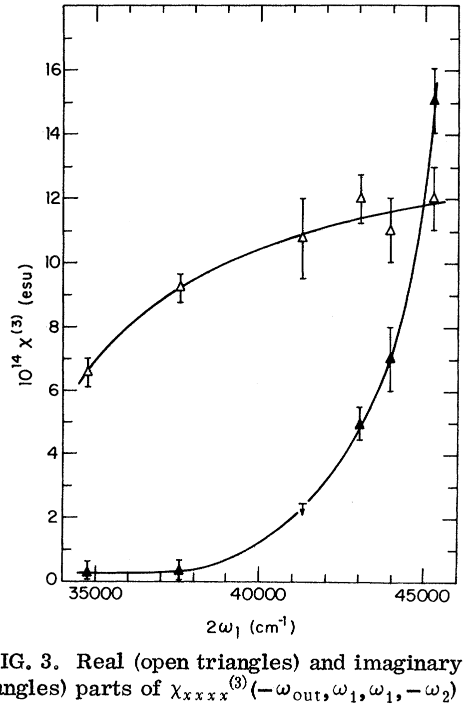

FIG. 3. Real (open triangles) and imaginary (solid triangles) parts of $\chi_{xxxx}^{(3)}(-\omega_{\rm out},\omega_1,\omega_1,-\omega_2)$ of pure CS$_2$. The TPA cross section is proportional to Im$\chi^{(3)}$. At $2\omega_1 = 41\,320$ cm^{-1} just an upper limit for Im$\chi^{(3)}$ was obtained by destructive interference measurement.

case. For strong or weak TPA strengths, however, the use of both experimental cases is essential, since only one or the other is sufficiently sensitive to the TPA contribution. In the KE susceptibility measurement, the fitting of both the destructive and constructive cases with the same values for the TPA and Raman contributions assures the absence of unwanted background due to various experimental misalignments.

Our TPA dispersion measurement is quite close to a recent measurement of Owyoung[10] and also to that of Levenson and Bloembergen.[6] This agreement is excellent considering that each of these three measurements used different calibration standards. The large TPA cross section ($\beta = 11 \times 10^{-51}$ cm^4 sec/photon molecule at $2\omega_1 \approx 45\,000$ cm^{-1}) suggests the presence of an allowed electronic TPA transition, and the shape of the TPA curve is similar to that of the one-photon cross section versus $2\omega_1$.[11] This evidence supports the assignment of the strong band in CS_2 at ~ 50 000 cm^{-1} as a $^1B_2$ electronic state.[12]

At present, no other method for TPA measurement can give cross sections as accurately as the one described here. This is mainly due to the noncritical dependence of the measurement on the laser-beam characteristics. In addition, the classical TPA measurements suffer from the difficult problem of distinguishing the TPA process from other competitive scattering processes. In most of the practical cases there is no satisfactory solution to this problem. No such problems exist in the parametric experiments, where the unwanted scattering processes which contribute in the classical TPA experiments do not contribute coherently to the signal. An additional advantage of the TPA parametric measurement is the possibility of using a reference material with a nondispersive susceptibility to normalize the output signal.[3,6] By this normalization, the critical nonlinear dependence of the measurement on the coherence of the sources or on the beam overlap is minimized.

We do not have absolute values for the TPA contribution to the KE susceptibility because the Raman cross section of benzene molecules is different in CS_2 than in pure benzene and has not yet been measured. However, as $\omega_1 + \omega_2$ varies from 35 770 cm^{-1} to 43 000 cm^{-1} the TPA contribution to the KE susceptibility changes by a factor 1.8 ±0.5, while the TPA contribution to the 3WM susceptibility changes by a factor 17 ± 5. This difference in dispersion between the TPA contributions to the KE and 3WM susceptibilities can be crudely explained by reference to the polarization dependence of the TPA as worked out by McClain[13] and the symmetry properties of the excited states of CS_2.[14]

In conclusion, the destructive interference between different imaginary contributions to $\chi^{(3)}$ is reported for the first time. The usefulness of this interference in the measurement of accurate TPA cross sections has been discussed. These accurate values may then be used as references in the more convenient standard TPA experiments by use of the normalization technique of Lotem, Bechtel, and Smith.[15] These interference effects, and especially the method of changing the sign of the imaginary part of the Raman resonant denominators, may become very useful tools in resonance 3WM investigations since the variation of the now complex Raman strengths cannot be fully determined by classical Raman spectroscopy. We anticipate that further uses of the interference effects described here will also be developed.

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