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Absolute determination of the two-photon-absorption coefficient relative to the inverse Raman cross section*

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A new method for the direct measurement of two-photon-absorption (TPA) coefficients relative to known inverse Raman cross sections is reported. The method is independent of the laser-beam parameters utilized in the experiment. The TPA cross section of TiO_2, GaP, CdS, and $SrTiO_3$ due to simultaneous absorption of a photon at 14403 cm^{-1} and a photon at 17248 cm^{-1} was determined relative to the cross section of the 2855 cm^{-1} Raman mode of liquid cyclohexane. Accurate Raman cross sections may also be measured by the proposed method.

INTRODUCTION

With the development of high-power lasers, it has become possible to investigate many nonlinear (NL) optical processes. In particular, the two-photon-absorption (TPA) process by which two photons are simultaneously absorbed has been explored extensively. The selection rules for the TPA transitions are, in general, different from those of the one-photon transitions, and therefore, the measurement of the TPA properties of a material system is complementary to the linear measurements. A lot of information on the symmetry of the material eigenstates, including states which are unseen in linear spectroscopy, may be obtained from the relative values of the different components of the TPA tensor.[1]

Information about the magnitude of the transition matrix elements, the density of states, and the energy eigenvalues may be obtained from absolute measurements of the TPA coefficient and especially from its frequency dependence.[2] Unfortunately, these latter measurements are known to be difficult because of the strong dependence of the TPA process on the parameters of the laser used. This fact is reflected by the large scattering of the reported results in the literature.[2]

New techniques for absolute measurement of the TPA coefficient have been recently reported.[3-9] In the first kind of technique, the value obtained for the TPA coefficient is based on a good knowledge of the laser's parameters.[3,4] These measurements can be performed only with those particular lasers which may be quite well characterized, and therefore the spectral region of the measurement is very limited. The second kind of technique, which is independent of the laser parameters, is based on absolute calibration of the TPA coefficient by other known NL cross sections. This type of measurement may be carried out at different laser frequencies. This was done in Ref. 5 using the second-order NL susceptibility of quartz as the NL reference. A disadvantage of this specific calibration is the assumption that the quantum efficiency for the induced fluorescence by the absorption of one photon at 2ω is identical with the efficiency associated with TPA of two photons at ω. In Refs. 6–9 the calibration of the TPA cross section is done in relation to well-known Raman scattering cross sections. In contrast with all the other classical TPA techniques, this measurement, which utilizes a NL parametric mixing technique, is not associated with real material transitions and therefore stepwise multiphoton transitions do not interfere in the measurement[7] and the value for the TPA coefficient may be unambiguously obtained. Another simple normalization technique has been proposed recently[10] which is very useful for obtaining relative values of TPA coefficients of different materials independent of the properties of the laser used.[11] This method may give absolute TPA coefficients by using reference materials whose TPA coefficients have been measured by, for example, the method of Ref. 7.

The purpose of this paper is to report on a new method for the direct calibration of the TPA coefficient relative to well-known inverse Raman cross sections.[8,12,13] By this method we calibrated the TPA of CdS, GaP, $SrTiO_3$, and TiO_2 at 31 660 cm^{-1} relative to the Raman cross section of the strong 2855-cm^{-1} CH mode of liquid cyclohexane. Moreover, the dependence of the measurement on the laser parameters could be eliminated in a two-channel normalization experiment in ways similar to those used in Ref. 10, and thus very accurate and reliable TPA coefficients were obtained. This general method may also be used for the calibration of absolute Raman cross sections.

THEORY

When two laser beams, a strong beam at ω_L and a weaker probe beam at ω_P interact in a NL material system, the strong beam induces a change in the complex refractive index at the probe frequency. The real part of this change is proportional to $n^{(2)}$, the self-focusing coefficient,[14,15] while the imaginary part of this change is responsible for NL loss or gain at ω_P.[14] The net gain or loss at ω_P is proportional to the imaginary part of the NL third-order susceptibility $\chi^{(3)}(-\omega_P, \omega_P, \omega_L, -\omega_L)$. Neglecting higher-order processes, the probe intensity may be described by[4]

$$\frac{dI_P}{dz} = -\alpha_P I_P - \beta I_L I_P , \tag{1a}$$

where

$$\beta = 32\pi^2\omega_P/(c^2 n_P n_L)\,\mathrm{Im}\chi^{(3)}(-\omega_P, \omega_P, \omega_L, -\omega_L) \; ; \tag{1b}$$

I_i and n_i $(i = P, L)$ are the laser intensities and the refractive indices at ω_P and ω_L, respectively; α_P in the linear absorption coefficient at ω_P; and c is the speed of light.

It is clear from Eqs. (1) that the NL process is enhanced whenever $\chi^{(3)}$ reaches a resonance.[16] We are dealing here with systems which are transparent at both ω_L and ω_P, and therefore only the resonances of $\chi^{(3)}$ which are associated with two-photon transitions (i.e., TPA or Raman) of the material system will be taken into account. For a system occupying the ground state, loss at ω_P (or a positive contribution to $\mathrm{Im}\chi^{(3)}$) occurs in the TPA case, i.e., when $\omega_P + \omega_L$ is close to two-photon transitions of the material. Raman transitions, however, may contribute to both gain and loss at ω_P. When $\omega_L - \omega_P$ is close to a Raman transition, and $\omega_L > \omega_P$, the Raman contribution to $\mathrm{Im}\chi^{(3)}$ is negative and is associated with gain. This gain is responsible for the strong amplification in the stimulated Raman effect.[17] When $\omega_P > \omega_L$, the sign of the Raman contribution to $\mathrm{Im}\chi^{(3)}$ is positive and the Raman transition is associated with absorption at ω_P. The latter process, which is usually called the inverse Raman effect,[8,13,16] is used in this work for the absolute calibration of the TPA coefficients. The cross section of the inverse Raman effect is a measurable quantity since it is directly proportional to the spontaneous Raman cross section.

We will now explain the details of the calibration procedure. We first solve Eq. (1) for a slab of NL material of thickness d and get for the transmitted energy

$$\begin{aligned} I_P(x, y, z = d, t) &= (1 - R_P)^2 I_P(x, y, z = 0, t - n_P d/c) \\ &\quad \times \exp\{-[\alpha_P d + \beta_{\mathrm{eff}} I_L(x, y, z = 0, t - n_L d/c)]\} , \\ \beta_{\mathrm{eff}} &= (1 - R_L)(1 - e^{-\alpha_L d})\beta/\alpha_L , \end{aligned} \tag{2}$$

where β is the TPA coefficient or the inverse Raman absorption coefficient and α_i, R_i, and n_i $(i = P, L)$ are the one-photon absorption coefficients, the reflectance and the refractive indices, respectively. In solution (2) we assume that only linear attenuation, and no back reflection, affects the strong beam at ω_L. The total transmitted energy of the probe pulse E_T is given by the integration of I_P over the pulse duration and the pulse cross section. Neglecting the dispersion of the refractive index, which is a good assumption for long pulses and thin samples, we get for E_T:

$$\begin{aligned} E_T = {} & \exp(-\alpha_P d)(1 - R_P)^2 \\ & \times \iint d\tau\, dx\, dy\, I_P(x, y, z = 0, \tau) \\ & \times \exp[-\beta_{\mathrm{eff}} I_L(x, y, z = 0, \tau)] . \end{aligned} \tag{3}$$

This expression clearly demonstrates the importance of the spatial and temporal overlap of the laser pulses in the measurement of β.

Similarly to Ref. 10, we define $\rho(I_L)$, the ratio between the transmitted energies of the probe beams through two different samples A and B for identical laser pulses

$$\begin{aligned} \rho = {} & \frac{E_T^A}{E_T^B} \\ = {} & K \times \left(\exp(-\alpha_P^A d^A) \iint I_P \exp(-\beta_{\mathrm{eff}}^A I_L)\, d\tau\, dx\, dy\right) \\ & \times \left(\exp(-\alpha_P^B d^B) \iint I_P \exp(-\beta_{\mathrm{eff}}^B I_L)\, d\tau\, dx\, dy\right)^{-1} , \end{aligned} \tag{4}$$

where K is a constant independent of the laser intensity. Note that ρ is a complicated function of I_L and the beam overlap. If the strong laser beam is attenuated in sample A by a filter of transmission F, the factor I_L in the numerator of Eq. (4) should be replaced by FI_L. It is clear that when F obeys the relation

$$F = \beta_{\mathrm{eff}}^B / \beta_{\mathrm{eff}}^A , \tag{5}$$

the two integrands in Eq. (4) are identical and the ratio ρ *is independent of* I_L *and the characteristics of the beam overlap.* Therefore, since F can be found experimentally by checking the dependence of ρ on I_L, the ratio $\beta_{\mathrm{eff}}^B/\beta_{\mathrm{eff}}^A$ can be evaluated.

EXPERIMENT AND RESULTS

The TPA measurements reported here were calibrated using the 2855-cm^{-1} mode of cyclohexane. In Fig. 1 we illustrate our measurement of the inverse Raman absorption cross section of cyclohexane in the region $3000 > \omega_P - \omega_L > 2800$ cm^{-1}. This measurement was done by measuring the attenuation of the variable-frequency dye-laser probe beam[3,18,19] for a normalized intensity of the

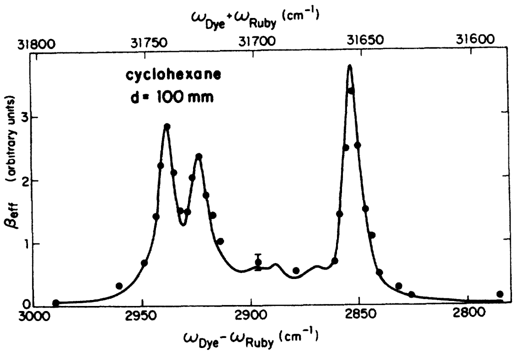

FIG. 1. Inverse Raman absorption coefficient for parallel probe and laser polarizations vs $\omega_P-\omega_L$ in a 10-cm cyclohexane cell (points), and the corresponding spontaneous Raman spectrum measured with a 5145-Å laser and 0.4-cm^{-1} spectrometer slits (solid line).

strong ruby laser beam. With the narrow linewidth lasers used, the measured spectrum of β_{eff} fits quite well a measurement of the spontaneous Raman scattering which is also presented in Fig. 1. The coincidence between the two spectra is a good check for the reliability of the experimental system.

The absolute Raman cross section of the 2855-cm^{-1} mode of cyclohexane measured in the blue ($\lambda_L = 4880$ Å) and reported by Colles and Griffiths[20] is used for calculating $\chi^{(3)}(-\omega_P, \omega_P, \omega_L, -\omega_L)$ using the relationship[14]

$$\chi^{(3)}(-\omega_s, \omega_s, \omega_L, -\omega_L) \propto \frac{1}{\omega_s^3 \omega_L} \frac{d\sigma}{d\Omega} . \tag{6}$$

No correction for the small dispersion of $\chi^{(3)}$ was introduced in the calculation of the inverse Raman absorption coefficient β from $\chi^{(3)}$. The cross section measurements in Ref. 20 are based on the Raman cross section of the 992-cm^{-1} mode of benzene reported by Skinner and Nilsen.[21] The latter cross section is slightly larger than the one reported by Kato and Takuma.[22] Therefore, the value of β for cyclohexane given here ($\beta = 0.0019$ cm/MW) may be somewhat high. Considering also experimental reproducibility, an uncertainty of about ±20% for the cyclohexane inverse Raman absorption coefficient β seems to be reasonable.

The TPA measurements were done using a two-channel normalization technique[10] and the conventional TPA technique.[3,18,19] The experimental setup for the two-channel normalization measurements is shown in Fig. 2. A multimode ruby laser is used as a source for the strong beam at ω_L and for pumping (after doubling the frequency) a visible dye laser (ω_P). An intracavity telescope in the dye laser is used for narrowing the output below 0.5 Å.[23] The beams of the ruby and the dye laser are combined by a dichroic mirror (DM). A glan prism (GS) splits the collinear beams into the cyclohexane cell (S_A) and the examined sample (S_B). After filtration by the cutoff filters (F_i), the two probe beams are detected by two HP 5082-4220 diodes. A plate of ground glass (G) is inserted in front of each diode in order to minimize the effect of the nonuniformity of the laser beam and the diode's active area. The signals are amplified, digitized and punched on a tape which is later analyzed by a computer.[9] The relative intensity of the ruby laser beam in the samples (i.e., the value of F) may be varied by rotating the double Fresnel prism (DFP) used as a half-wave plate. For a given value of F, the ratio $\rho(I_L)$ is measured for different ruby intensities which are obtained by inserting filters (VA) in the ruby beam. An iris in front of the splitting prism GS is a critical component in the TPA measurement. By proper setting of this iris the overlap integral [Eq. (3)] is maximized.

Figure 3(a) shows our results for ρ for CdS-cyclohexane and for CdS-TiO$_2$. It is seen from the figure that the appropriate values of F for which ρ is independent of I_L are $2.2 < F < 2.56$ and $F \cong 1.4$ for CdS-C$_6$H$_{12}$ and CdS-TiO$_2$, respectively. Using Eq. (5) and the linear data of the samples given in Table I, we obtain the values $\beta_{CdS} = 0.056 \pm 0.006$ cm/MW and $\beta_{CdS}/\beta_{TiO_2} \cong 2.4$. In a similar way we normalized β of SrTiO$_3$ versus cyclohexane, $\beta_{SrTiO_3} = 0.003 \pm 0.001$ cm/MW.

Using the conventional TPA technique we measured the TPA coefficients of CdS, TiO$_2$, and GaP relative to the inverse Raman cross section of cyclohexane. The TPA coefficients were obtained by comparing the transmission of the samples at

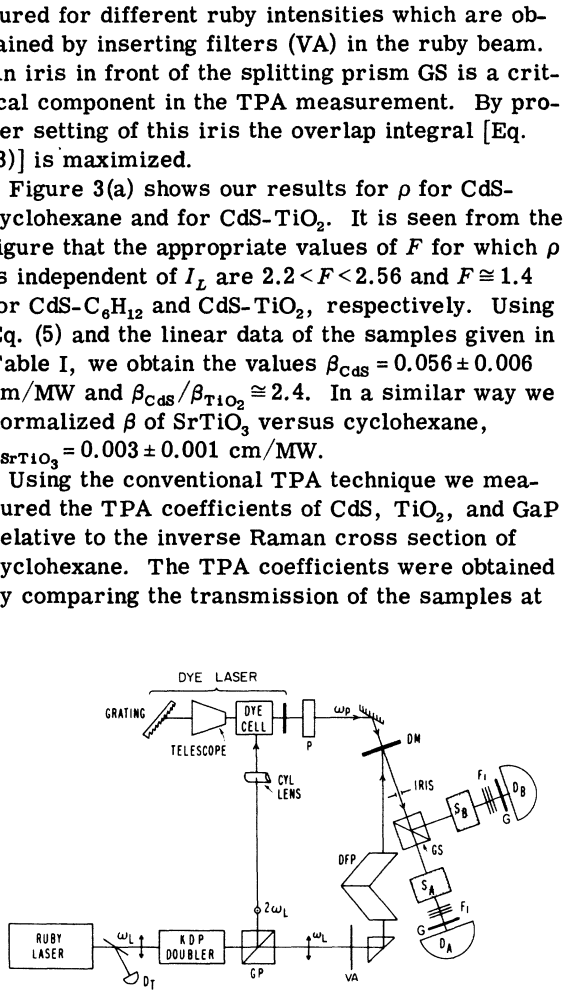

FIG. 2. Two-channel normalization experimental setup. GP and GS are glan prisms, DFP is a double Fresnel rhomb used as a half-wave plate, P is a polarizer with polarization axis at 45° to the vertical, DM is a dichroic mirror, S_A and S_B are the cyclohexane cell and the examined sample, respectively, F_i are cutoff filters, VA is a variable filter, G are ground glass plates, and D_A and D_B are photodiodes with the attached electronics.

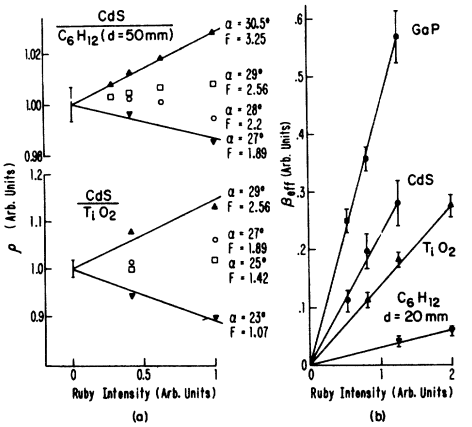

FIG. 3. (a) ρ, the ratio between the transmitted energies in the samples CdS-cyclohexane and CdS-TiO_2 vs ruby laser intensity. Each value of F corresponds to a setting angle α of the DFP. (b) β_{eff} vs ruby intensity, as we measured by the conventional TPA technique. Each data point represents the average of ~ 10 laser shots except the TiO_2 and cyclohexane with ~ 50 shots.

ω_P for different values of I_L. In order to minimize the drift in the experimental conditions, the samples were mounted on a special holder which allowed us to switch samples rapidly. The results of this measurement are shown in Fig. 3(b) and are tabulated in the fifth column of Table I. For comparison the results of the two-channel normalization measurements are listed in the fourth column of this table. The error bars in Fig. 3 represent the standard deviation of ρ and β_{eff}. The uncertainty in the data points for cyclohexane and TiO_2 shown in Fig. 3(b) are relatively small because of the large number of laser shots (~50) averaged at each of these data points.

The value $\beta_{CdS} = 0.071 \pm 0.015$ cm/MW and the ratio $\beta_{CdS}/\beta_{TiO_2} = 2.6 \pm 0.6$ obtained by the conventional TPA technique fits very well the results of the two-channel normalization measurement. The uncertainty in the former measurement is, of course, larger than that of the two-channel experiment.

Our measured value for β_{zz} of TiO_2 at $\omega_L + \omega_P = 31\,660$ cm^{-1} is about seven times larger than the value $\beta_{zz} = 0.0034$ cm/MW obtained by Waff and Park[24] (who used a Nd-glass laser and flash lamp) at the same two-photon energy, and about three times larger than $\beta_{xx} = 0.0065$ cm/MW, obtained by Penzkofer and Falkenstein[25] at $2\omega = 31\,950$ cm^{-1} using a picosecond laser source. (β_{xx} and β_{zz} represent the TPA coefficient for linearly polarized photons, polarized along the x axis and the z axis of the crystal, respectively.) No TPA data at $\omega_L + \omega_P \sim 32\,000$ cm^{-1} for the other crystals investigated in this work have been published in the literature.

A comparison of our TiO_2 results with those of Refs. 24 and 25 should be carefully made. We note that the most fundamental physical quantity to be compared is $\chi^{(3)}$ and not β, which includes a trivial frequency factor [see Eqs. (1)]. The large deviation of the result of Ref. 24 probably originates from the severe complications which arose in their experiment in the determination of the overlap integral [Eq. (3)]. The deviation of the results of Ref. 25, however, cannot be explained by the different laser frequencies used, by the small difference between the two-photon energies or by the different electric field polarizations used, which according to Ref. 24 result in the ratio $\beta_{zz}/\beta_{xx} = 1.25$. Dispersion in the TPA coefficient which originates from the one-photon denominators in $\chi^{(3)}$ is also unlikely as an explanation for this deviation since the measurements were done

TABLE I. Sample properties and TPA results.

	α [a] (cm^{-1})	d (cm)	Reflectivity [b] (%)	β [c] (cm/MW)	β [d] (cm/MW)	Crystal orientation [e]
CdS	0.06	0.47	17	0.056 ± 0.006	0.071 ± 0.015	$\vec{E} \parallel [110]$; $\hat{k} \parallel [001]$
GaP	1.45	0.4	28		0.25 ± 0.07	$\vec{E} \parallel [111]$; $\hat{k} \parallel [011]$
TiO_2	0.07	0.9	23	0.023 ± 0.004	0.027 ± 0.006	$\vec{E} \parallel [001]$; $\hat{k} \parallel [100]$
$SrTiO_3$	0.30	0.8	16	0.003 ± 0.001		$\vec{E} \parallel [1\bar{1}0]$; $\hat{k} \parallel [001]$
Cyclohexane	< 0.01		4	0.0019 [f]	0.0019 [f]	Liquid phase

[a] Absorption constant at the ruby laser wavelength 6943 Å, measured in a Cary 14 spectrophotometer.

[b] Calculated from index of refraction data.

[c] Our results using the two-channel normalization measurements presented in Fig. 3(a).

[d] Our results using the conventional TPA measurements [Fig. 3(b)].

[e] $\vec{E}$ represents the electric field of the lasers and $\hat{k}$ is the propagation direction of the lasers.

[f] Based on the data of Ref. 20, see text.

with laser frequencies far enough from the band gap (3.75 eV)[24] to ensure no resonant behavior.[16] Also, no $[\chi^{(2)}]^2$ contribution to $\chi^{(3)}$,[9,12] a contribution which depends on the beam polarization and propagation vector, is expected in TiO_2 which exhibits inversion symmetry. Two steps sequential one-photon absorption contributions to β and absorption caused by two-photon generated holes may, however, influence differently the measurements in the nanosecond and picosecond regimes.[4,7,26] We conclude, therefore, that the latter effects and the possibility that the laser pulses in Ref. 25 were not well characterized may explain the deviation of their TiO_2 TPA results from ours.

DISCUSSION AND CONCLUSIONS

The TPA coefficient and the Raman cross section are important material parameters. Accurate values of TPA coefficients and especially their spectral dependence will be useful for stimulating further theoretical calculations of two-photon phenomena. In particular, existing theoretical models of matter such as the "empirical pseudopotential method"[27] may be checked by comparing the theoretical β based on the specific model with the experimental one. We note that one-photon spectroscopy above the material band gap shows surface effects because of the small penetration depth. The TPA measurement, however, reflects in the same spectral region only the bulk properties of the material. Therefore, a comparison of the TPA experimental results with theoretical models is more direct than in the one-photon case. Experimentally, accurate TPA coefficients may be used for the characterization of pulsed laser beams.[25] This may be done by checking the interaction of the strong beam with a probe beam whose parameters are well known (cw dye laser beam, for example) in a NL absorber. The measured value of E_T [see Eq. (3)] may give important information on the spatial and temporal properties of the strong beam. In particular, absolute peak-power values, which are very important in multiphoton processes, may be obtained by this method. Accurate Raman cross sections may be used for measuring average concentrations of molecular species over long atmospheric paths using stimulated Raman gain[19] or inverse Raman loss experiments.

The calibration method described here is very useful for reliable measurements of TPA coefficients. Raman cross sections may also be calibrated by the same method. In this case, inverse Raman absorption as well as stimulated Raman gain may be utilized in the measurement. The use of a probe beam in the absorption measurement has an advantage over the standard one-beam TPA methods. In the one-beam case, any small loss in the laser beam caused by other NL processes may strongly influence the measured cross section. Such perturbations which influence the strong laser beam have only a minor effect on the probe beam.

In conclusion, we have described a technique which allows simple measurement of TPA coefficient and Raman cross section, relative to known inverse Raman cross sections. The use of the two-channel normalization experiment enables one to eliminate the dependence of the NL absorption on the laser intensity, thereby removing the usual problems associated with absolute intensity measurements. Additionally, this normalization alleviates sources of errors due to irreproducible laser pulse spatial and temporal profile, allowing the measurement to be made with simple uncontrolled lasers.

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