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Ultraviolet two-photon absorption in alkali halides

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An experimental study of two-photon absorption (TPA) in RbBr, KBr, RbI, and KI was done with 10-nsec pulses from the second harmonic of a ruby laser ($2\hbar\omega = 7.12$ eV). The discrepancies found between the herein nanosecond and the previously known picosecond results indicate that optically generated free carriers must be accounted for in short-pulse measurements of TPA cross sections of alkali halides.

I. INTRODUCTION

Nonlinear optical processes are important in the investigation of many transparent materials. In particular, the two-photon-absorption (TPA) process attracts increasing scientific and technological interest. Because the selection rules for TPA transitions are, in general, different from those of one-photon transitions, TPA studies provide additional information about the band structure, the density of states, and the magnitude of the transition matrix elements of the solids. Unlike the linear-measurement case, absolute TPA coefficients can only be directly obtained by well-calibrated lasers.[1] Some recent techniques like the "two-channel normalization technique" enable one to perform accurate TPA measurements of relative cross sections.[2] Similar to the latter technique, utilizing two lasers of different frequencies, it is possible to obtain absolute TPA cross sections by calibration versus known Raman cross sections.[3-5]

With the recent technological developments in high-power uv lasers, measurements of nonlinear phenomena of various uv materials have gained increasing practical importance. In particular the study of the alkali halides are of much interest because the richness of phenomena in these materials. Color centers lasers and uv laser windows are two important uses of these systems.

This paper reports the measurements performed with four alkali halide crystals (RbBr, KBr, RbI, and KI) at room temperature. A 10-nsec laser (the second harmonic of a ruby laser) has been used to investigate the TPA process at the energy $2\hbar\omega = 7.12$ eV. In addition, the lack of TPA in KCl as expected from band-structure considerations was checked. The measurement was performed using standard one-beam method to obtain relative TPA cross sections. The results are compared with recent studies performed by Prior and Vogt[5] at $2\hbar\omega = 6.7$ eV, by Liu *et al.*[6] at $2\hbar\omega = 7.02$ eV, and earlier dispersive TPA measurements.[7,8]

II. EXPERIMENTAL PROCEDURE

The TPA measurements were carried out on rectangular prism-shaped crystals. Good optical quality samples were used in order to prevent damage due to the high-laser-power densities and to minimize stepwise absorption processes.

The experimental apparatus used in the measurements is schematically shown in Fig. 1. The uv light beam used for generation and monitoring the nonlinear absorption was the second harmonic of an electro-optically Q-switched ruby laser. The doubling of the ruby-laser frequency was per-

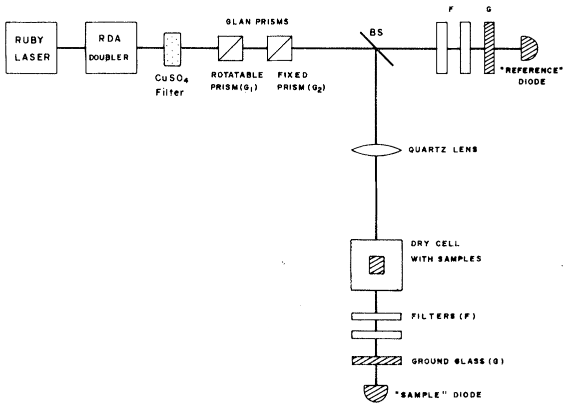

FIG. 1. Schematic diagram of the experimental layout.

formed in a temperature-tuned 90° rubidium dihydrogen arsenate (RDA) crystal with an efficiency of about 15%. The 2-MW uv beam at 3472 Å was filtered in a saturated solution of $CuSo_4$. The combination of two Glan air prisms [a rotatable prism (G_1) and a fixed one (G_2)] allows for a continuous variation of the uv light intensity while the polarization at the sample is held fixed. Because the TPA cross section is rather small, a quartz lens (L) was used to increase the light flux at the sample in order to enhance the effective nonlinear absorption. The examined crystal samples were located behind the focal plane of the lens to avoid damage caused by self-focusing. Under those experimental conditions no color centers were observed in the focal region. Two identical, large-aperture fast photodiodes (S-20 spectral response) were used for measuring the uv intensity before the sample in the "reference channel" and after the sample in the "sample channel". The ground-glass plates placed in front of the photodiodes are very essential in the measurement. The combination of those plates and the large-aperture photodiodes eliminates the major part of fluctuations in the ratio of the photodiodes readings caused by the shot-to-shot different laser speckle pattern. The crystal samples are placed in a dry cell (an oven at a temperature of about 40 °C). The special samples holder allows for fast change of the examined sample during the measurements. The signals are amplified, digitized, and punched on a tape which is later analyzed by a computer. In all cases the crystal [001] axis is along the laser electric field.

The ratio of the signals (ρ) in the sample and reference channels is measured versus the uv light intensity. This ratio reflects the nonlinear absorption coefficients as shown below. The ratio ρ is given by

$$\rho=\frac{E_s}{E_R}=\frac{\int I_s(x,y,t)dx\,dy\,dt}{\int \eta I_R(x,y,t)dx\,dy\,dt}\ , \tag{1}$$

where the integration is over the beam cross section and pulse duration. $I_R(x,y,t)$ describes the laser original pulse which propagates in the z direction, η is the ratio between the reflectance to transmitance of the beam splitter (BS), and the intensity $I_s(x,y,t)$ is the solution of the TPA equation:

$$\frac{dI_s}{dz}=-\alpha I_s-\beta I_s^2\ , \tag{2}$$

where α and β are the one- and two-photon absorption coefficients, respectively. Assuming reflectance R at both sample faces, I_s is given by

$$I_s=(1-R)^2\exp(-\alpha d)I_R(1+\beta_{\text{eff}}I_R)^{-1} \tag{3}$$

and

$$\beta_{\text{eff}}=(1-R)[1-\exp(-\alpha d)]\beta/a\ ,$$

where d is the sample length. An expression for ρ as a function of I_R is obtained from Eqs. (1) and (3):

$$\rho=\frac{(1-R)^2\exp(-\alpha d)\int I_R(x,y,t)[1+\beta_{\text{eff}}I_R(x,y,t)]^{-1}dx\,dy\,dt}{\int \eta I_R(x,y,t)dx\,dy\,dt}\ . \tag{4}$$

The above expression for ρ has no general analytic solution. However, for a bell-shaped Gaussian-type beam and for a small effective TPA, a linear dependence of ρ and β is obtained:

$$\begin{aligned}\rho=\Bigg[(1-R)^2\exp(-\alpha d)\int_0^\infty r\,dr\int_{-\infty}^{+\infty}d\tau\exp[-(r/a)^2]\exp[-(\tau/b)^2]&\\ \times\{1-\beta_{\text{eff}}I_0\exp[-(r/a)^2]\exp[-(\tau/b)^2]\}\Bigg]&\\ \times\left[\eta\int_0^\infty I_0 r\,dr\int_{-\infty}^{+\infty}d\tau\exp[-(r/a)^2]\exp[-(\tau/b)^2]\right]^{-1}&\ ,\end{aligned} \tag{5}$$

and hence

$$\rho=(1-R)^2\eta^{-1}\exp(-\alpha d)(1-\beta_{\text{eff}}\sqrt{2}I_0)\ , \tag{6}$$

where I_0 is the maximum on-axis laser intensity. A linear dependence of ρ on I_0 is demonstrated in Fig. 2 for the various studied crystals.

With known laser parameters of inclusively absolute intensity, the TPA coefficients may be obtained utilizing Eqs. (4) or (6). However, in most systems the laser parameters do not exactly fit the assumptions on which Eq. (6) is based and the absolute peak intensity I_0 is practically unmeasurable. In such systems, relative TPA coefficients may be obtained by analyzing data similar to that

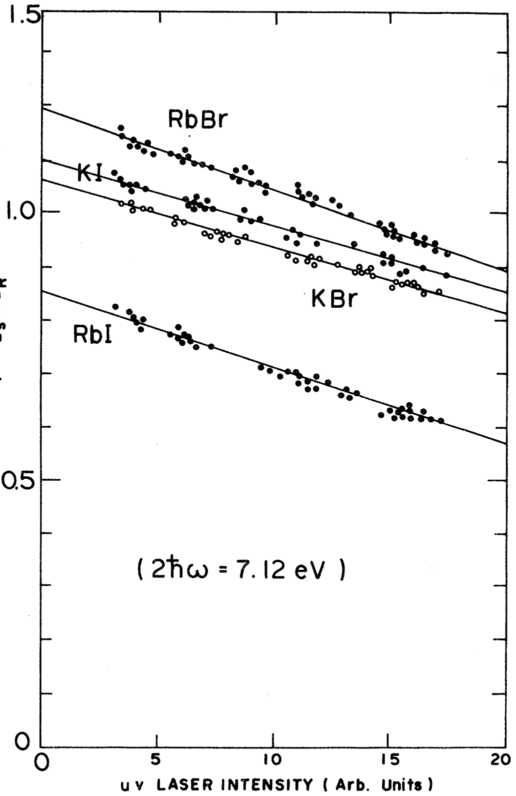

FIG. 2. Ratio of the signals in the sample and reference photodiodes as a function of the laser intensity for all studied materials.

of Fig. 2 with the aid of Eq. (6). It is assumed in this case that the laser parameters are stable during the measurement. This assumption is quite correct when the measurement of each sample is of short duration and the samples are rapidly changed during the measurement. More accurate relative TPA coefficients are obtainable by the two-channel normalization technique,[2] but using the method of the present paper results in faster data acquisition.

III. RESULTS AND DISCUSSION

Figure 2 shows a set of data results used in calculating the TPA coefficients of RbBr, KBr, KI, and RbI. Using four values of ρ at two laser intensities, the ratio $\beta(\text{crystal}_1)$: $\beta(\text{crystal}_2)$ is directly obtained by Eq. (6). The relative TPA coefficients of the four crystals studied in this work are shown in Table I. Also shown in the table are the TPA results of Refs. 5 and 6. In analyzing the TPA results we have used the data of the two latter references and the results of measurements performed more than a decade ago.[7,8] The broad-band measurement of KI (Ref. 8) is a good reference for dealing with the dispersion of β. We therefore use KI as the TPA reference crystal. In all the references noted above the uncertainty of the relative TPA cross section values is, of course, smaller than that of their absolute data. In the case of Refs. 7 and 8 where the dispersion of β was measured in the vicinity of 6 eV using a ruby laser and a flash lamp, we believe that due to experimental difficulties their results reflect, in general, the correct dispersive, but not the absolute behavior of the TPA coefficients. We note that in comparing the low-temperature results to room-temperature data, the crystals' energy-band shifts versus temperature should be taken into account.

Inspection of Table I shows the similarity in the TPA coefficients ratios in the present work and in Refs. 5 and 6. The results of Ref. 6 cited in the table were obtained by the two-channel normalization technique with uncertainties of less than 10%. This measurement is the only one performed with psec laser pulses.

The present results may be analyzed in comparison with the other published data. Thus, we first deal with the work of Fröhlich and Staginnus[7] who have measured RbBr, KBr, and RbI at 10 and 80 K. When the temperature correction is considered, a value close to 1 in the vicinity of 7 eV is expected for β(RbBr):β(KBr). We obtained a close value for that ratio. For RbI, if we assume a monotonic rise of β beyond the experimental limit (7 eV) of Ref. 7, and with the same slope, a ratio $\beta(\text{RbI}):\beta(\text{KBr}) > 3$ is expected in contradiction with our measured value of less than 1. An explanation

TABLE I. Comparison between the relative TPA coefficients of the various studied materials. Reference 5 refers to measurements at 6.7 eV while Ref. 6 reports results obtained with a psec laser at 7.02 eV.

	Crystal length d (cm)	β(crystal):β(KI) Present work	Ref. 6	Ref. 5
RbBr	1.0	0.55	0.305	0.62
KBr	0.74	0.64		0.45
RbI	1.0	0.51	0.668	
KI	0.47	1	1	1

for the larger ratio value extrapolated from Ref. 7 might be a strong negative slope of β(RbI) beyond 7 eV or more likely the influence of F-center generation which affects the effective nonlinear absorption.

The present results for KI can be compared to the results of Refs. 5 and 6 if one takes into account the dispersion measurements of Park and Stafford.[8] From the latter reference, the value β(7.02 eV):β(6.7 eV)$\simeq$1.2 is expected but the result based on Refs. 5 and 6 is $\sim$0.8 for the same ratio.[9] For RbBr we expect a ratio β(7.02 eV):β(6.7eV) $\gg$1 from the data of Ref. 8, but from Refs. 5 and 6 we obtain for the same ratio a value $\sim$0.4. Those discrepancies in KI and RbBr cannot be simply explained by experimental uncertainties. It seems that the psec TPA value for RbBr is smaller by a factor of $\sim$2 from that of the nsec measurements. This statement is also supported by the fact that the psec result for β(RbI):β(KI) is close to the nsec results while β(RbBr):β(KI) is smaller by a factor of $\sim$2.

The high laser intensities in the psec experiments should be the cause for the discrepancies. Free-carrier generation and trapping rates might affect differently the nsec and psec pulse measurements. Both effects are known to play an important part in semiconductor nonlinear absorption.[10] In the case of alkali halides, however, there still is a nonresolved conflict between Refs. 11 and 12 which estimate free-carrier lifetimes of 1 μsec and a few psec, respectively. An explanation for this difference is that carrier lifetimes must depend on impurity concentration as well as carrier density. The present measurements were performed using the same samples as in Ref. 6 and so the carrier density must be the cause for the above-mentioned discrepancies. We expect an inverse dependence of the carrier lifetime on the carrier density and then a stronger influence on the psec TPA cross section. Further experiments on laser peak power dependence would be necessary to clarify this point.

In comparison to theoretical predictions, our results for the ratio β(RbI):β(RbBr):β(KI) fit the corresponding calculated values 0.6:0.7:1 well, based on the Keldysh formula with a parametrically fitted effective mass.[6] The recent theoretical work of Vaidyanathan *et al.*[13] who have calculated the TPA's of KI and RbI using various models, shows that the Keldysh model gives a correct order of magnitude for the TPA ratio of the latter two crystals.

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