where the value at the lower limit T_0 has been dropped in comparison to the value at the upper limit. The accuracy of the approximation is illustrated in Fig. 5 where both (A8) and (A6) are compared with a numerical calculation of the integral (A1).

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Multiphoton Transitions in Ionic Crystals

I. M. Catalano, A. Cingolani, and A. Minafra
Istituto di Fisica dell'Universita', Centro Studi e Applicazioni in Tecnologie Avanzate, Bari, Italy
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Photoconductivity measurements in uncolored single crystals of NaCl, KCl, and KI are reported. The exciting source is the beam of a Q-switched ruby laser ($\hbar\omega = 1.78$ eV) and its second harmonic ($\hbar\omega = 3.56$ eV). The experimental results show clear evidence of multiphoton absorption processes. The nonlinear cross sections γ_n of two-, three-, four-, and five-photon transitions have been measured and compared with the cross sections predicted by the existing theories.

INTRODUCTION

In the present work we report the results of a study of multiphoton optical transitions in alkali halides.

The absorption process has been detected by means of the associated photocurrent. This method is indeed the only one capable of measuring absorption coefficients as low as 10^{-6} cm^{-1} or less. It may be noted that even with a flux of 10^{26} (photons/cm^2)/sec (which corresponds to about 30 MW/cm^2 of ruby light), the three-photon absorption coefficient is only 10^{-5} cm^{-1} and decreases very rapidly for higher-order transitions.

Other investigations of multiphoton transitions utilizing this technique are reported in the literature[1,2] with experimental results which differ markedly. Our aim was to determine the order of the transition (i.e., the number of photons which participate in the absorption process) and to evaluate the nonlinear cross section γ_n which can be compared with the cross section predicted by existing theories.

EXPERIMENTAL PROCEDURE

The experimental apparatus has been previously described.[3]

A Q-switched ruby laser ($\hbar\omega = 1.78$ eV) with a pulse duration of 20 nsec at half-power and 200-MW peak power was used to induce the photoconductivity. The maximum beam cross section was about 1.5 cm^2. The energy of every pulse was monitored with a photodiode intercepting a small fraction of the beam. The photocurrent pulse is integrated and the resulting voltage pulse is sent to a 556 dual-beam Tektronix oscilloscope with a 1A7A plug-in.

The absolute calibration of the measuring system has been obtained injecting a known amount of charge at the input and recording photographically the voltage output. A linearity test has been performed in the range of interest. The photodiode pulse is also integrated and displayed simultaneously on the other oscilloscope beam, thus giving the energy corresponding to the single photocurrent pulses. The photodiode has been calibrated and tested for linearity by measuring the energy of the laser pulses with a thermocouple calorimeter and the intensity was obtained approximating the photodiode pulse with a square pulse of 20-nsec duration.

To produce a different photon energy a $LiNbO_3$ second-harmonic generator (SHG) has been used in conjuction with the ruby laser. The SHG gives out about 10-MW maximum power at $\hbar\omega = 3.56$ eV and the residual ruby light is filtered out using a cell filled with an aqueous solution of $CuSO_4$.

Undoped monocrystals of NaCl, KCl, and KI, with typical dimension $0.8 \times 0.2 \times 1$ cm^3, were placed

in a parallel-plate capacitor which was charged to a voltage $V_0 = 1000$ V. To avoid space-charge effects, the voltage was applied to the capacitor only just before the start of the laser and the capacitor was shorted between the pulses. All measurements have been taken at room temperature, with the samples kept in a dry-nitrogen atmosphere.

The incident intensity I_ω of ruby laser for KCl and NaCl varied in the range 10–120 MW/cm^2. At an intensity level greater than 120 MW/cm^2 the crystals were damaged by the strong electric field associated with the laser beam and the photocurrent was no longer correlated with the incident intensity.

The maximum intensity for KI was 100 MW/cm^2. The second-harmonic intensity $I_{2\omega}$ for KI and NaCl varied in the range 0.1–12 MW/cm^2.

The photocurrent pulse has been also measured without integration in order to determine the decay time of the photoconductivity at different levels of irradiation. This measurement allows the selection of the right integration constant and, moreover, gives a parameter which is necessary to calculate the nonlinear cross section from the measured charge pulse.

EXPERIMENTAL RESULTS

As has been pointed out in the Introduction, the experiment aims to obtain information about (a) the order of the transition and (b) the magnitude of the nonlinear cross section.

For point (a) we have measured the dependence of the total charge Q induced by a single laser pulse as a function of the laser intensity.

The calculation of Ref. 3 may be extended to a multiphoton process involving n quanta, assuming for the generation rate $F(x)$ the expression

$$F(x) = N\gamma_n I^n/(1+\beta_n x)^{n/(n-1)} \quad ,$$

where

$$\beta_n = (n-1)(n\hbar\omega) I^{n-1} N\gamma_n \, ,$$

I is the incident flux in (photons/cm^2)/sec, N is the density of active atoms, and γ_n is the nonlinear cross section, defined by

$$W^{(n)} = N\gamma_n I^n \, ,$$

where $W^{(n)}$ is the transition rate for unit volume and γ_n is measured in cm^{2n} sec^{n-1}. With simple calculations one gets

$$Q = \frac{e V_0 V N}{a^2} \, \mu\tau^2 (1 - e^{-\tau_L/\tau}) \gamma_n I^n \, \frac{1-(1+\beta_n L)^{1/(1-n)}}{\beta_n L} \times \left(1 - \frac{2\xi}{\lambda} \, \frac{\xi \coth\frac{1}{2}\lambda - \ln(1+\xi \coth\frac{1}{2}\lambda)}{\xi^2 \coth^2(\frac{1}{2}\lambda)}\right) , \quad (1)$$

where $\xi = S(\tau/D)^{1/2}$, $\lambda = L/(\tau D)^{1/2}$, e is the electronic charge, V is the volume of the sample, τ is the lifetime of free electrons, μ is the electron mobility, D is the electron diffusion constant, S is the surface recombination velocity, τ_L is the laser pulse duration, L is the thickness of the sample in the beam direction, and a is the distance between the electrodes.

Using the values reported in the literature for the above parameters, the second term in the large parentheses may be shown to be negligible. Moreover, in our experimental conditions $\beta_n L \ll 1$, and

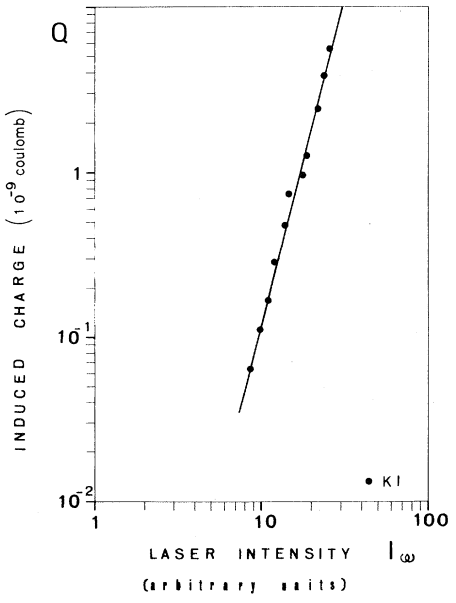

FIG. 1. Four-photon conductivity in KI.

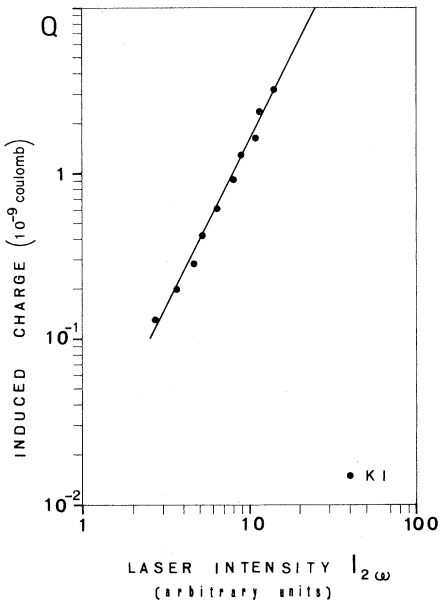

FIG. 2. Two-phonon conductivity in KI.

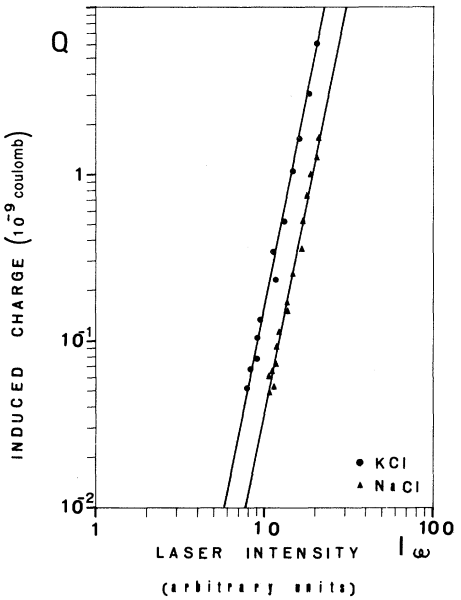

FIG. 3. Five-photon conductivity in KCl and NaCl.

therefore Eq. (1) reduces to

$$Q = \frac{e V_0 V N}{a^2} \mu \tau^2 (1 - e^{-\tau_L/\tau}) \gamma_n I^n , \tag{2}$$

which shows a $Q \propto I^n$ dependence.

In Fig. 1 the total charge Q is plotted versus I_ω for KI on a log-log scale. The straight line through the experimental points has a slope 4, which is consistent with a four-photon process, being the fundamental optical gap of KI 5.8 eV.[4,5] To confirm this, it is shown in Fig. 2 that the slope of a plot of Q vs $I_{2\omega}$ for KI, obtained with the SHG, is 2, i.e., a two-photon effect.

Figure 3 analogously represents the Q-vs-I_ω curves for KCl and NaCl, which have optical gaps of 8 and 8.1 eV, respectively.[4,5] These last results can be interpreted by a five-photon process.

In Fig. 4 a three-photon effect in NaCl excited by the second-harmonic radiation is represented.

From Figs. 1–4 and Eq. (2) it is possible to obtain γ_n, and the results are summarized in Table I.

The lifetime τ, which has been used in Eq. (2) to calculate γ_n, was measured from the decay of the multiphoton excited photocurrent. The experimental values therefore give a bulk lifetime, owing to weakness of the absorption process. The typical values obtained are of the order of 10^{-6} sec and it is worth noting that experimental values of τ, at room temperature in alkali halides, are not quoted in the literature.

DISCUSSION

Recently[6] a detailed calculation of the four-photon absorption rate, using a perturbative method and a Hartree-Fock approximation for the wave functions has been published.

The resulting formula at temperatures where the ionization by phonons may be important is

$$\gamma_4 = \frac{2^{27/2}}{63} \frac{\pi^3 \hbar^4 e^8}{n^4 c^4 m^2} \frac{P_{cv}^{\,2}}{(\hbar\omega)^{10}} \frac{(4\hbar\omega - E_g)^{3/2}}{m_{cv}^{\,3/2} N} \times \left((4\hbar\omega - E_g)^2 - \tfrac{28}{15} m_{cv} \frac{P_{cv}^{\,2}}{m^2} (4\hbar\omega - E_g) + \tfrac{28}{27} m_{cv}^{\,2} \frac{P_{cv}^{\,4}}{m^4} \right) , \tag{3}$$

where E_g is the fundamental optical gap, n is the refractive index, and $P_{cv}^{\,2}$ is the square of the matrix element of momentum operator, which may be assumed to be $\simeq \frac{3}{4} E_g m^2 / m_{cv}$. m_{cv} is the reduced mass of valence and conduction bands, which in alkali halides is about equal to the conduction effective mass. The other symbols have the usual meaning.

From this formula for KI one obtains $\gamma_4 = 6.8 \times 10^{-114}$ cm^8 sec^3, which is in agreement with our experimental value. Unfortunately, experimental data from other laboratories are not available to check our results.

The two-photon transition in KI has been a good test for the accuracy of our measurements. Indeed, the γ_2 reported in Table I ($\gamma_2 = 5 \times 10^{-49}$ cm^4 sec) is the same which has been found for two photon process by other authors.[7–9]

The values of γ_5 in Table I are not consistent with that of Ref. 1, in the case of NaCl. In fact,

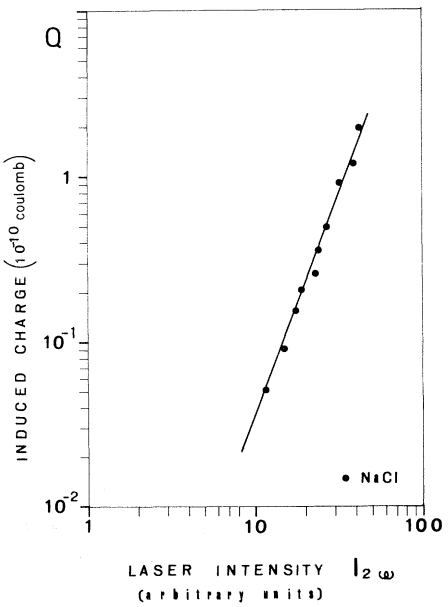

FIG. 4. Three-photon conductivity in NaCl.

TABLE I. Nonlinear cross section γ_n for multiphoton absorption in alkali halides (units cm^{2n} sec^{n-1}).

Sample	$\hbar\omega = 1.78$ eV	$\hbar\omega = 3.56$ eV
KI	$\gamma_4 = (2 \pm 0.8) \times 10^{-114}$	$\gamma_2 = (5 \pm 0.5) \times 10^{-49}$
KCl	$\gamma_5 = (2.4 \pm 1.2) \times 10^{-140}$	...
NaCl	$\gamma_5 = (1.8 \pm 0.9) \times 10^{-140}$	$\gamma_3 = (1 \pm 0.3) \times 10^{-80}$

these authors find $\gamma_5 \simeq 5 \times 10^{-138}$ cm^{10} sec^4, which is greater than our value by two orders of magnitude. This disagreement is partially due to the numerical value of τ (4×10^{-8} sec) assumed by these authors in the calculation of γ_5, which differs from our experimental determination ($\sim 10^{-6}$ sec).

It is to be noted that our value is consistent with their approximate calculation, which gives $\gamma_5 = 0.5 \times 10^{-140}$ cm^{10} sec^4. However, the formula seems not applicable, since the approximation reported is not fulfilled. On the other hand, we were unable to repeat their calculation in order to investigate the significance of the involved approximation.

The γ_3 of Table I is in good agreement with the experimental value for Al_2O_3,[1] for which $\gamma_3 = 1.4 \times 10^{-80}$ cm^6 sec^2.

Recently[10] a calculation of the three-photon absorption coefficient has been made using perturbation theory.

Assuming a four-parabolic-band model with direct gap, in the case for which the three photons have the same energy, the result found is

$$\gamma_3 = \frac{4\pi^2\hbar^5 e^6}{n^6 m^6 c^3 N} \frac{1}{(\hbar\omega)^3 \alpha_c^{3/2}} \frac{36\,|(1+\mathcal{P}_{nm})P_{cm}P_{mn}P_{nv}|^2}{[\Delta n - \hbar\omega + (\alpha_n/\alpha_c)(3\hbar\omega - E_g)]^2} \times \frac{(3\hbar\omega - E_g)^{1/2}}{[\Delta m - \hbar\omega + (\alpha_m/\alpha_c)(3\hbar\omega - E_g)]^2}, \quad (4)$$

where P_{ij} is the momentum matrix element between bands i and j (v is the valence band, c is the conduction band, and m and n are upper bands), $\mathcal{P}_{nm}$ is an operator indicating permutation on states n and m, $\alpha_i = \hbar^2/2m_i$ (m_i is the effective mass in band i), and Δn and Δm are the energy differences between the minima of bands n and m, respectively, and the valence band which we assume to be flat.

The evaluation of Eq. (4) requires a knowledge of the band structure of the material. Since the band structure of NaCl is not known in detail, we have approximated Δm and Δn with E_g, and assuming also α_m and $\alpha_n = \alpha_c$, we obtain $\gamma_3 = 2.6 \times 10^{-80}$ cm^6 sec^2. This result, in spite of the used approximations, is in reasonable agreement with our experimental γ_3.

We can conclude that the photoconductivity measurements have given clear experimental evidence of multiphoton processes in ionic crystals up to the fifth order, and that the experimental nonlinear cross sections γ_2, γ_3, and γ_4 are in satisfying agreement with the theoretical calculations. Regarding this last statement, it is to be noted that Eq. (1) is based on a very simple model which does not take into account, for example, space-charge effects. On the other hand, the theoretical calculations are also based on approximative models (this is particularly true for γ_5) and involve parameters which often are not completely known.

ACKNOWLEDGMENTS

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