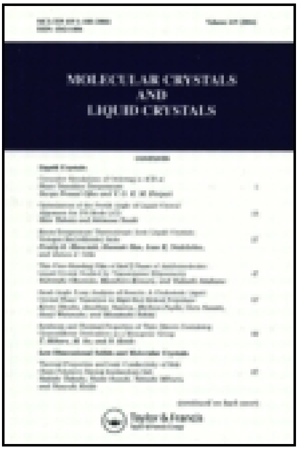

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Photoconductivity of Crystalline Iodoform II: Photocurrents Induced by a Two-Photon Absorption

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Photoconductivity of Crystalline Iodoform II: Photocurrents Induced by a Two-Photon Absorption

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Photogeneration of charge carriers in iodoform has been studied using a high power pulsed dye laser as an excitation source. In the region of 480–640 nm, i.e. that of weak absorption, the magnitude of the photogenerated charge follows a square light intensity dependence in the intensity range employed (up to 10^{23} photons/cm^{2}s). The spectral dependence of the photogeneration efficiency is similar to that observed for the *dc* photoconductivity at twice shorter wavelengths; the efficiency drops down, however, rapidly when the tail of the first absorption band of iodoform is approached. Temperature anomalies below 270 K render the exact determination of activation energies impossible.

Photoionization or collision ionization of singlet excitons are excluded from the considerations of the two-photon generation mechanism in iodoform. The most likely explanation of the mechanism of the creation of charges is a two-photon absorption to a higher excited state as a precursor of the initial charge carrier pair. The two-photon absorption cross section of crystalline iodoform is estimated to be *ca.* 2×10^{-50} cm^{4}s in the region of the maximum photogeneration efficiency (*ca.* 520 nm).

1 INTRODUCTION

In the preceding paper[1] we have reported on steady-state photoconduction in single crystals of iodoform. A high photogeneration efficiency has been observed and spectral characteristics of the photocarrier yield have been measured. This paper deals with the photoconduction in iodoform induced by short pulses of a tunable dye laser operated outside the regions of strong absorption of iodoform.

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Studies of intensity, wavelength and temperature dependences of photocurrents induced by weakly absorbed light pulses can contribute to the understanding of various charge carrier generation mechanisms.[2-8] An advantage of this technique is that multiple photon absorption takes place in the crystal bulk which allows one to distinguish between intrinsic photogeneration processes and surface effects.[9,10]

The literature data on the multiple photon generation of charge carriers in organics are scarce and even for anthracene—the best known organic photoconductor—there is some uncertainty with regard to detailed mechanisms of carrier production. A detailed study of the intrinsic bulk photoconductivity in anthracene induced by a high power dye laser has been reported by Bergman and Jortner[11] who determined the wavelength dependences of appropriate generation coefficients. Iodoform can be compared to anthracene in that it is a typical molecular crystal with regard to the character of intermolecular forces operating in the crystals, but it differs however from the more fully investigated aromatic compounds when the character of excited molecular states is considered.

Therefore it is of interest to study the photogeneration of charge carriers in iodoform using two photon-absorption excitation and to compare the results with those obtained recently for other organic molecular crystals.[12,13]

2 EXPERIMENTAL

Single crystals of iodoform (CHI_3) were prepared by sublimation as described earlier.[1] Platelets, usually *ca.* 50 mm^2 in area and *ca.* 1 mm thick were mounted in a thermostated cell between two identical electrodes made of indiumtin oxide covered quartz. The electrical and mechanical contact with electrodes was improved by using a few drops of silver paste at crystal edges.

Exciting light pulses of *ca.* 10 ns duration and energies up to 1200 μJoules per pulse were provided by a Molectron DL 200 dye laser pumped by a Molectron N_2 laser. A sample was irradiated through electrodes, the laser beam being parallel to the sixfold axis of the crystal. After suitable focusing the incident light intensity was *ca.* 1×10^{23} photons/cm^{2}s and could be controlled by attenuation with neutral density filters. A part of the light beam was deflected by a beam splitter to monitor the light intensity with a calibrated photodiode the output of which was displayed on one of the channels of a double-beam oscilloscope (Tektronix 555). The other channel was used to display an integrated photocurrent signal which was provided by a FET integrating preamplifier. Usually, five or more shots of the laser were recorded on a single oscilloscope photograph and results were averaged to give a single experimental point of a wavelength, temperature or voltage dependence of the generation efficiency.

Dyes used and their tunability ranges were as specified by the manual of the dye laser.[14]

3 RESULTS

Preliminary measurements showed that iodoform crystals exhibit relatively strong photoconductivity when exposed to pulses of light with wavelengths in the range 480–640 nm, whereas virtually no photocurrent could be detected with the irradiation in the range 380–480 nm, i.e. within the first absorption band of crystalline iodoform (see Ref. [1]). To evaluate the nature of the long wavelength photogeneration process we have studied light intensity dependences of the magnitude of the generated charge at a few chosen wavelengths. Figure 1 shows typical results of such studies. It can be seen that slopes of the lines indicates a two-photon generation process dominates. The deviations of the slope from the theoretical value of two may be due in part to experimental errors, there may be nevertheless some other reasons for this behavior. Intensity dependences measured within the wavelength region of the one-photon generation have been found to be slightly sublinear,[1] which, together with the present results may indicate that some losses of carriers occur through bimolecular processes e.g. carrier recombination. It should be stressed that so-

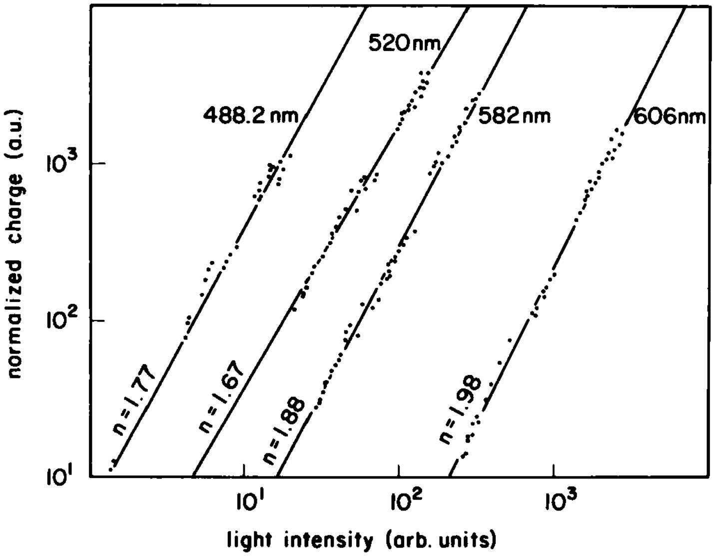


FIGURE 1 Light intensity dependences of the magnitude of the photogenerated charge. Excitation wavelengths and values of the least-square slopes of lines drawn through experimental points are given in the figure.

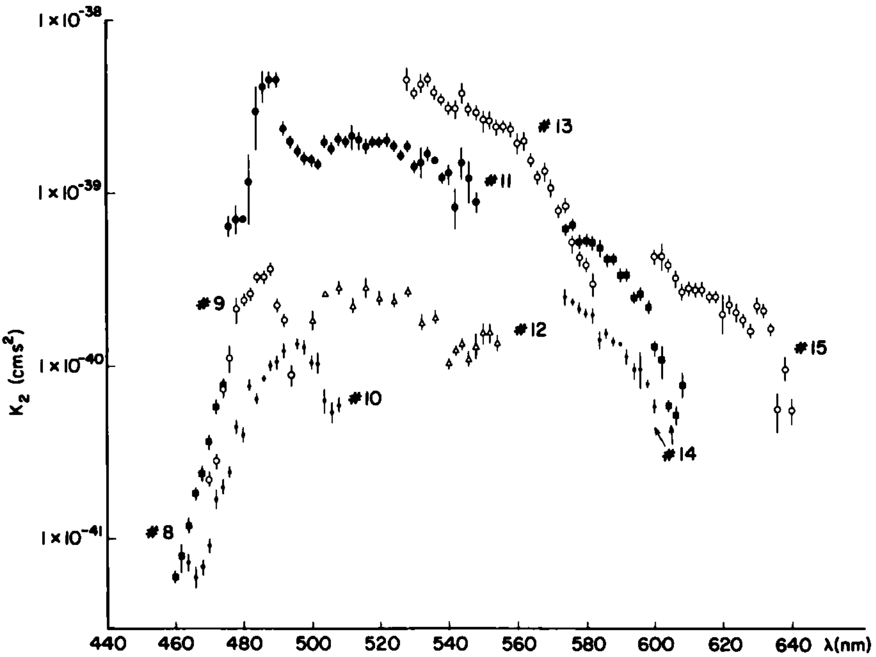


FIGURE 2 A set of uncorrected experimental data giving spectral dependences of the two-photon generation coefficient. Vertical sections denote mean errors in determination of K_2 at a given wavelength when results from a series of pulses were employed.

called germinate recombination i.e. that occurring between geminate charges forming an intial carrier pair which has not diffused apart to distances far enough to cancel the mutual Coulomb attraction, does not contribute to the intensity dependence. The germinate recombination is a first-order process with respect to the carrier concentration whereas the recombination taking place between free carriers is a second-order process and, at high concentrations of interacting charge carriers may give rise to a square root dependence of the carrier density on the rate of production of initial pairs. Results presented here and in[1] are not precise enough to make an attempt to calculate the recombination rate constant due to uncertainties in estimations of spatial distributions of carriers and relatively narrow ranges of intensities covered, the presence of recombination seems however to be of some importance especially at high photocurrent densities.

The evaluation of a spectral response curve for the two-photon photoconductivity in iodoform posed some experimental problems due to the necessity of a proper calibration of results obtained for various dyes with different light intensities employed. Figure 2 shows an example of a set of results obtained

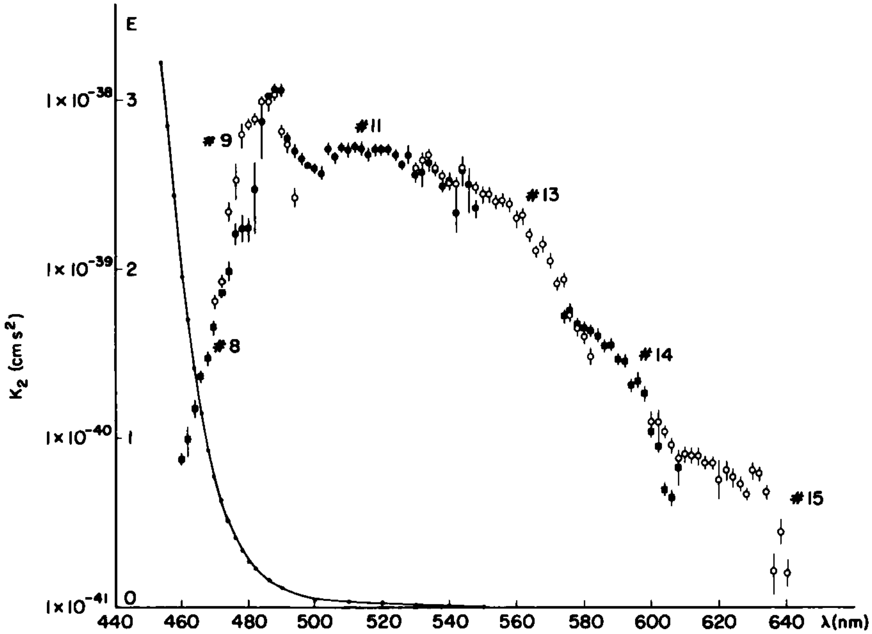


FIGURE 3 A master spectral dependence curve obtained from results of Figure 2 by normalizing the photogeneration efficiencies at the tunability limits of consecutive dyes. Full line shows the absorption threshold of a iodoform sample (*ca.* 0.15 mm thick).

with various dyes (numbered according to Ref. [14]) when no normalization was employed. It can be seen that although the scatter of results obtained within tunability ranges of consecutive dyes is not very large there are considerable deviations between results obtained within the same wavelength regions for different dyes. The obvious explanation of this spread of results is the difficulty of obtaining reproducible beam intensity profiles for different dyes. Some errors may also be introduced by the fluorescence background of the laser—especially at limits of the tunability ranges. Results given in Figure 2 could be normalized by vertical shifting of results obtained for different dyes to obtain an overlap of results in the regions where more than one dye could be used. The spectral response curve obtained in such a manner is presented in Figure 3. The ordinate axis is calibrated in the units of the experimental generation coefficient K_2 defined after[11] as follows

$$m = K_2 I^2 \qquad (1)$$

where m is the concentration of charge carriers produced by a pulse of the incident intensity I(photons/cm^{2}s). It should be noted the K_2 value is the product of the pulse duration τ(10^{-8} s in both this work and[11]) and a generation rate constant K_2'

$$K_2 = K_2'\tau \tag{2}$$

For quantitative comparison it was found that the K_2 values obtained for iodoform are about an order of magnitude higher than those reported for anthracene—*ca.* 10^{-39} cms^2.[11,12] Although absolute values of K_2 may be in error due to uncertainties in calculations of the incident light intensities (the geometry of the light beam, no correction for reflections from the sample surface, divergence of the beam etc.) this value for K_2 was supported by similar measurements of anthracene crystals in the same experimental setup. Magnitudes of charges generated in anthracene were found to be lower (*ca.* an order of magnitude) than in iodoform under the same experimental conditions.

The wavelength dependence of K_2 is not very much different from that observed at twice shorter wavelengths for the photogeneration efficiency.[1] The carrier yield increases rapidly from 640 nm to 560 nm and reaches a plateau. Some deviations from a smooth behavior are evident at the limits of tunability ranges of dyes—most probably due to the fact that the intensity dependences are not exactly quadratic. This introduces the largest errors at the edges of the tunability ranges where the laser output is the lowest. A surprising feature of the spectral dependence is the peak at *ca.* 490 nm (see also Figure 4) which occurs just before the generation efficiency drops down rapidly with decreasing wavelength. The results presented in Figure 4 indicate that the appearance of this peak is reproducible, but its origin is unknown at present.

The short wavelength decrease of the photogeneration efficiency coincides with the threshold of the strong absorption of the crystal (plotted in Figure 3). One can explain this decrease by assuming that the ordinary one-photon absorption concurs with the two-photon process, the one-photon absorption leading to no photogeneration (this will be further discussed in the subsequent section). Therefore, to calculate the concentration of the produced charge carriers one has to replace Eq. 1 with

$$\bar{m} = K_2 \frac{l}{L} \int_0^L I^2 \exp(-2\epsilon x)\, dx = K_2 \frac{1 - \exp(-2\epsilon L)}{2\epsilon L} I^2 \tag{3}$$

where L stands for the sample thickness, ϵ is the extinction coefficient and $\bar{m}$ is the mean concentration of charge carriers produced. The above equation properly predicts the decrease of the observed generation efficiency when the sample absorption increases. The quantitative agreement between Eq. 3 and the experimental results can, however, be obtained only when the wavelength dependence of K_2 in the threshold region is accurately known, however qualitatively the agreement is satisfactory. At the present time the scatter of the results does not allow one to draw any conclusions about the behavior of K_2 in

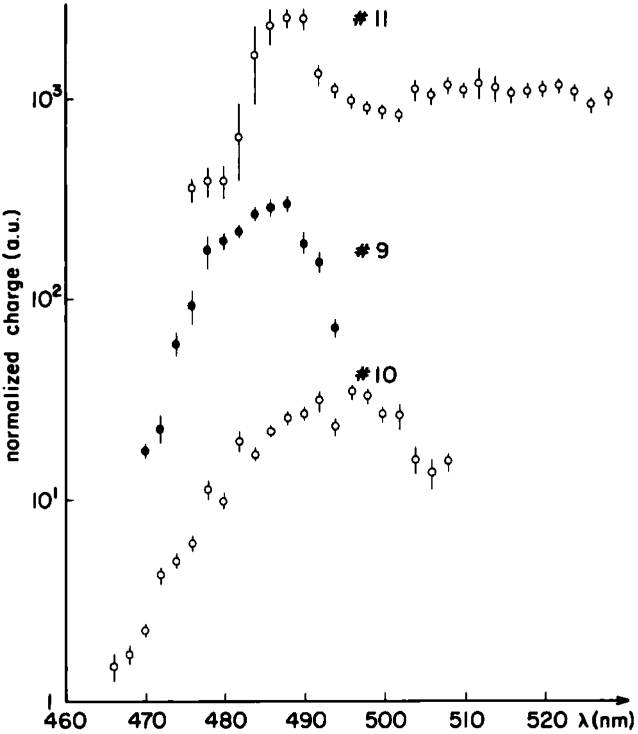


FIGURE 4 A fragment of the spectral dependence of the photogeneration efficiency showing a maximum at *ca.* 490 nm.

the region below 500 nm. One may, for example, suppose that the existence of the peak at *ca.* 490 nm is due to an experimental artifact, i.e. to the superposition of an increase of the two-photon generation efficiency onto a faster decrease of the absorption path due to the increase of the one-photon absorption coefficient. Checking of such a hypothesis would demand undertaking a systematic series of measurements for samples with different thicknesses.

Values of K_2 given in Figure 3 have been obtained for electric fields about 6×10^3 V/cm. However it is important to know what is the overall electric field dependence of the photogeneration efficiency. As it has been seen, results[1] of steady-state photocurrents do not allow one to draw any conclusions about this dependence due to the predominance of space charge and trapping effects. In pulse measurements space charge effects may be easily controlled by limiting the amount of both the charge generated in a single pulse and accumulated during an experimental run to densities well below those corresponding to the capacitive charge at electrodes. Trapping effects in pulse meas-

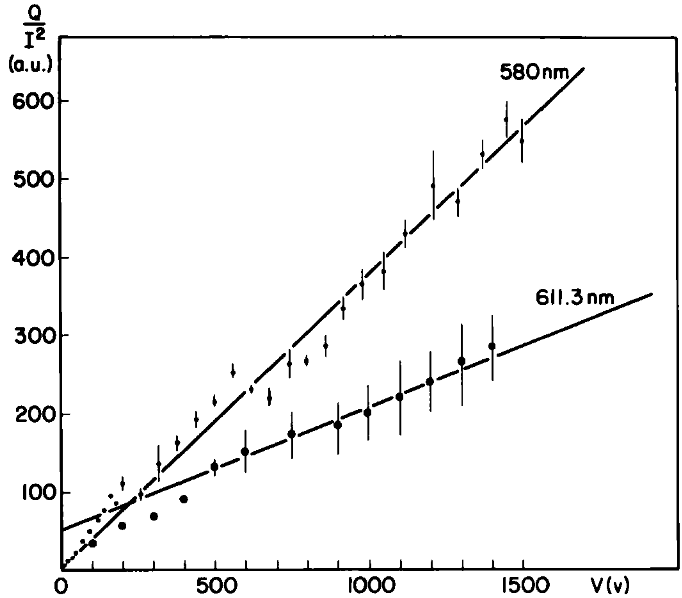


FIGURE 5 Examples of the electric field dependences of the photogenerated charge obtained for virgin iodoform samples at two wavelengths marked in the figure.

urements may be of some importance, especially at low fields if trapping times are shorter than the transit time of carriers. The charge collected at electrodes is then given by a Hecht-type relationship[15] superimposed on the field dependence of the generation rate. It is difficult to deduce from integrated current transients such as observed in this work whether the trapping effects contribute to the voltage dependence. However, in transient photocurrent measurements in which excitation with strongly absorbed light was used[16] shapes of hole signals indicated little hole trapping at room temperature for iodoform samples taken from the same batch. Thus, electric field dependences observed in this work may be supposed to be modified to only a little extent by trapping. Figure 5 shows typical examples of electric field dependences observed in this study. In some cases a slight sublinearity could be seen giving a positive intercept with the ordinate axis, in other cases the results yielded, practically zero intercept. In no case could the theoretical slope-to-intercept ratio predicted by the Onsager theory[17] be observed. This observation alone does not necessarily disprove the validity of the Onsager description of the dissociation of the initial charge carrier pair in iodoform. One can suppose that either experimental conditions do not allow monitoring of the unaffected field dependence of the photogeneration (due to the mentioned trapping effects or secondary recombination effects etc.) or the creation of the initial pair is a process which is also field dependent. In the latter case the overall field dependence would contain contributions of both photogeneration steps.

It must be mentioned that for the whole spectral region no differences were seen in magnitudes and shapes of signals obtained for positive and negative polarities of the sample front electrode. In view of the fact that for strongly absorbed light a rapid trapping of electrons could be seen[16] this result proves the hypothesis that the two-photon process observed is of a bulk nature. An independent corroboration of this hypothesis is given by the result that the magnitude of charge generated increases linearly with the sample thickness provided the electric field is being kept constant.

After prolonged measurements in which a substantial amount of trapped charges could be accumulated, some decrease of the photocurrent signal occurred indicating that trapped charges (most probably electrons) lowered the electric field inside the sample or act as recombination centers.

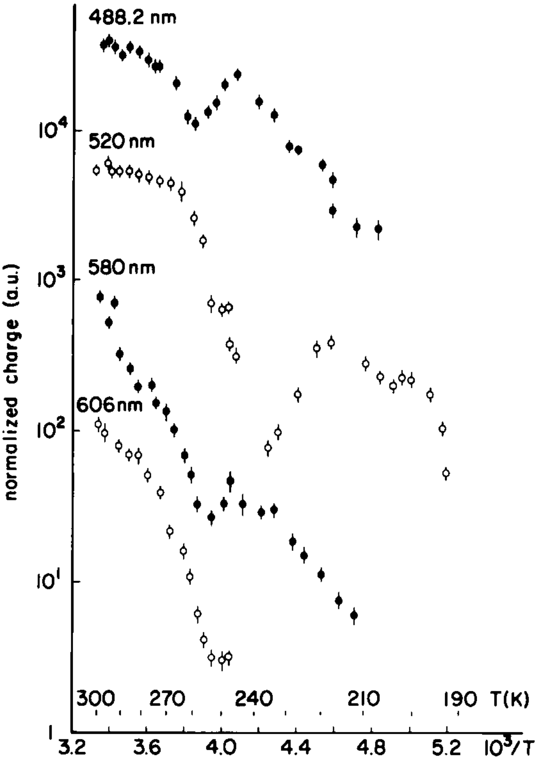
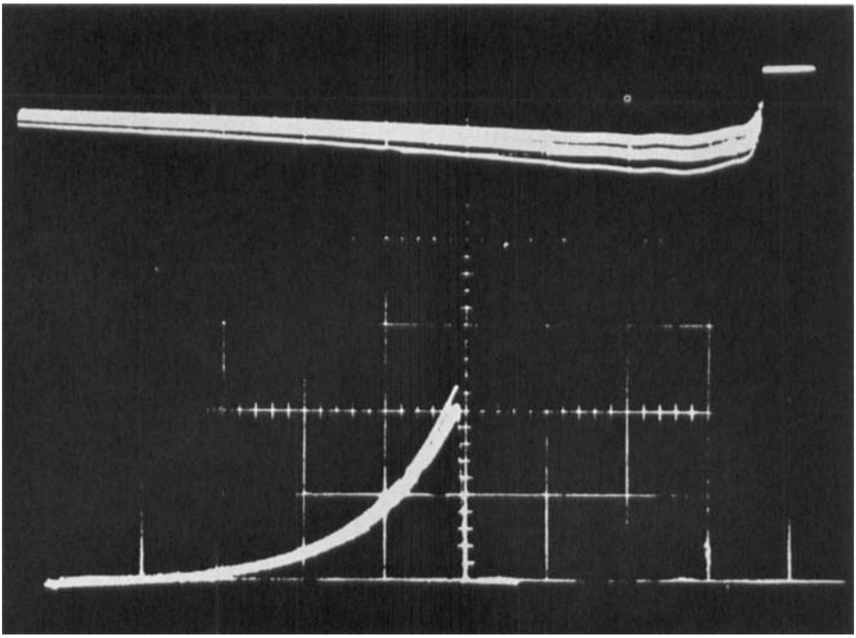


FIGURE 6 Temperature dependences of the photogeneration efficiency measured at wavelengths marked in the figure. The dependences are vertically shifted to facilitate comparison. Experimental points were obtained for cooling cycles.

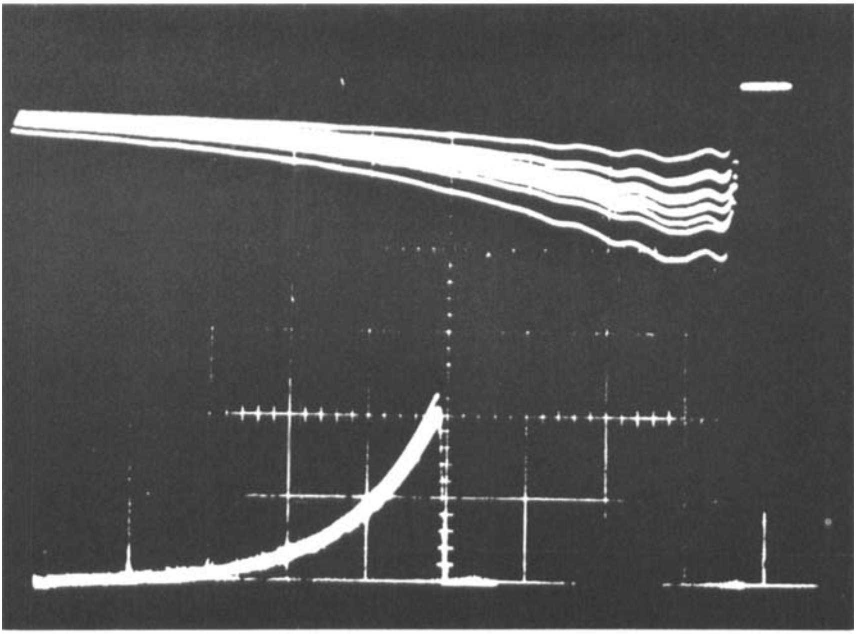
The temperature dependence of carrier generation efficiency was measured to give information concerning the energy of the generation process and its wavelength dependence. Figure 6 shows results of typical experiments. Distinct anomalies are seen below 270 K, which were found to depend slightly on the sample history. A hysteresis-like behavior was found on cooling-heating cycles. The phenomena observed occur in the temperature range where results of other studies of iodoform crystals[18] suggest a possibility of a phase transition. The anomalies obscur the trends of temperature variations of the photogeneration efficiency, it seems, nevertheless that the activation energy of the photogeneration does depend on the excitation wavelength as one should expect for the intrinsic generation (cf. [19]).

In the course of measurements of temperature dependences an interesting effect has been observed. When temperature is lowered in the vicinity of *ca.* 220 K distinct oscillations of the current emerge (Figure 7 a–c) which are superimposed onto the signal. The form of the oscillations was found to be reproducible from one laser shot to another. The effect disappears when temperature is raised again. The observed phenomenon is similar to photoinduced piezoe-

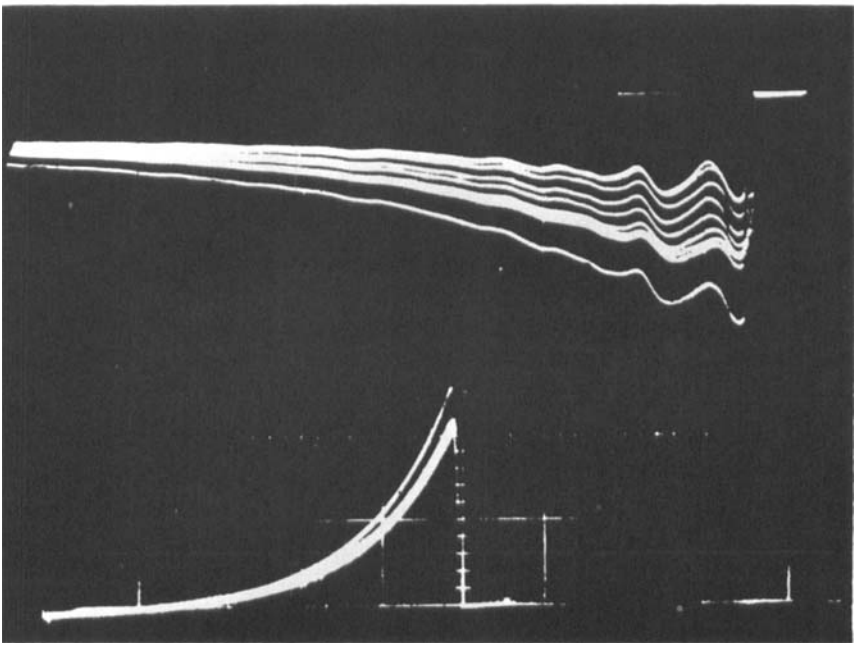


(a)

FIGURE 7 Evolution of the photocurrent signal at low temperatures. The upper oscilloscope beam shows the integrated photoiode signal whereas the lower beam displays the photocurrent signal. A series of laser pulses were fired for each of the pictures. Temperatures amount to 219, 210 and 207 K for the pictures a, b and c, respectively. The time basis is 50 μs/div.



(b)



(c)

lectric oscillations which were observed under similar conditions in piezo- or ferroelectrics.[20,21] It may indicate that at low temperatures samples of iodoform behave as piezoelectrics; the light induced mechanical oscillations give rise to an oscillative behavior of charges induced at electrodes. A long time constant of the preamplifier used (necessary to perform the integration of the photocurrent) did not allow us to follow the relatively high frequency oscillation modes which might take place in plane-parallel samples. It is rather a combination of various oscillation modes which is actually observed. The observation of the piezoelectric behavior puts forward an interesting question relating to the origin of the effect. One can suppose that either iodoform crystals while being non-piezoelectric at room temperature, undergo a phase transformation to a piezoelectric phase or that the piezoelectric behavior at low temperatures is due to electret-like effects of trapped charges. The former hypothesis relates to the fact that the room temperature structure of iodoform crystals[22,23] involves orientational disorder which causes the space group of the crystal $P6_3$ (non-centrosymmetric) to be practically $P6_3/m$ (centrosymmetric). The postulated phase change would thus involve ordering of the structure at low temperatures and there is indeed evidence for a phase-change in this temperature range. On the other hand, piezoelectric effects may also be observed due to a permanent polarization induced by charges trapped in the vicinity of electrodes. Although this explanation seems less likely in view of the reversibility of the effect, the final interpretation can only be given after completing the studies of iodoform crystals by more direct methods of phase transition detection.

4 DISCUSSION

The two-photon mechanism of generation of charges in iodoform may be explained by taking into account both the results presented in the preceding paper[1] and information on multiphoton generation mechanisms in other compounds. A square light intensity dependence of the magnitude of the generated charge may be anticipated in three cases:

i) a two-photon absorption may take place, either directly to a crystal CT state,[19] i.e. yielding a charge carrier pair or to a higher excited state which may autoionize: directly or through intermediates.

ii) a one-photon absorption may lead to the creation of an exciton (provided the photon energy is sufficient) and another photon may photoionize the exciton.

iii) for sufficiently high concentrations of one-photon produced excitons a collision ionization may take place leading to the creation of charge carrier pairs.

All the above processes have been studied in detail for anthracene crystals and the most comprehensive treatment of them is that of Bergman and Jortner.[11] It is well established that in anthracene both photoionization and collision ionization of singlet excitons are charge carrier production pathways, the relative importance of the two processes depending on the absorption coefficient. It can be easily shown that the probability of the photoionization is proportional to the absorption coefficient whereas the probability of the collision ionization is proportional to the square of the absorption coefficient. This essentially rules out the possibility that the two-photon photogeneration in iodoform may involve singlet excitons since the photogeneration yield is found to decrease rapidly when the absorption coefficient of the crystal increases. This indicates that excited states which are formed by absorption within the first absorption band of crystalline iodoform are not only unlikely to autoionize or produce carriers by extrinsic processes (interaction with traps or with the surface) but also will not be photoionized. The most likely explanation of these features which set properties of iodoform in sharp contrast to those of anthracene and related compounds is that the lifetime of the first excited state is extremely short and thus the mean diffusion length and the steady-state concentration are too low to allow the photoionization or collision ion ization to take place. This is not surprising since it is known that iodoform dissociates readily[24,25] in the gas phase or in solution when irradiated to give free radicals. Thus, it may be anticipated that the potential energy curve for the first excited state of iodoform has no minimum.

One cannot exclude the possibility that there is a lower lying triplet state of iodoform which is not detected by the crystal absorption studies due to a low value of the absorption coefficient. Such a state, if sufficiently stable, might contribute to the photogeneration by a two-photon process. It would be tempting to interpret the maximum of the photogeneration efficiency at *ca.* 490 nm as the result of photoionization of triplet excitons formed by a one-photon absorption. The triplet photoionization process would be, however, superimposed on the broad photoresponse curve which cannot be reasonably explained by invoking the existence of intermediate exciton states. As mentioned in[1] there are no literature data about the existence and stability of triplets in iodoform and the hypothesis that a metastable excitonic state may be formed by absorption of light of *ca.* 490 nm lacks independent spectroscopic evidence.

The most reasonable explanation of the results obtained is that the two-photon process observed is the analogue of the process observed for twice shorter wavelengths and that a true two-photon absorption (i.e. involving a virtual state and not an exciton state as an intermediate) takes place. The similarity between the thresholds of the one-photon quantum yield and the two-photon generation efficiency indicates that the same precursor state is involved in both processes.

As mentioned in[1] one cannot specify at the present time whether the precursor state is a localized exciton which autoionizes or the state has a character of a delocalized charge carrier pair. The problem of the relevance of the free radicals involvement in the process is also still obscure. Further studies should help to clear these points.

A relatively high value of the experimental two-photon generation coefficient reaching 8×10^{-39} cms^2 is an effect of a relatively high value of the quantum yield of production of charge carriers from the precursor state. The yield has been estimated in[1] to be not lower than 6×10^{-3} charge carriers/photon absorbed at fields similar to those used in this study.

For the direct two-photon absorption as the generation pathway one can express the value of K_2 as

$$K_2 = \tau \sigma_2 N \eta \tag{4}$$

where τ is the duration of the light pulse, σ_2 stands for the two-photon absorption coefficient, N is the density of iodoform molecules and η stands for the quantum yield. Setting $\tau = 10^{-8}$ *s*, $N = 6 \times 10^{21}$ cm^{-3} and K_2 and η as given above one obtains *ca.* 2×10^{-50} cm^{4}s for the two-photon absorption coefficient. This value may be compared with *ca.* 10^{-48} cm^{4}s—being a typical value of the coefficient for anthracene.[26] Speiser and Kimel[27] studied the two-photon absorption in iodoform in solution at 694 nm monitoring the amount of photochemically liberated iodine as a function of a ruby laser power. Values given in[27] for σ_2 are about 9×10^{-49} cm^{4}s. Although the straightforward comparison between these values and that derived from Eq. 4 is impossible due to differences in the wavelength, state of iodoform molecules and uncertainties in the estimation of K_2 and η, one can suppose that the value given by Speiser and Kimel may be overestimated. As pointed out by Kornweitz *et al.*[25] irradiation of iodoform solutions with ruby laser may give rise to free radical chain reactions when traces of iodine and oxygen are present. Such chain reactions, if present in experiments described in,[27] would increase the quantum yield of iodine production and lead to the overestimation of σ_2.

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