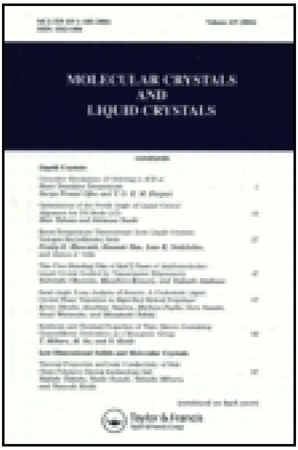

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Photoconductivity of Crystalline Iodoform I.

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Photoconductivity of Crystalline Iodoform I.

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Steady state photoconduction in iodoform has been studied between 210—400 nm. The photoconduction threshold is at 345 nm whereas the crystal absorption extends up to 480 nm. The photoconductivity action spectrum shows a steep rise of the photo carrier generation efficiency in the range 345—290 nm and a plateau at shorter wavelengths. Current-voltage characteristics measured under steady illumination show a square dependence of the photocurrent on applied voltage showing the influence of space charge effects. Electron photocurrents are three orders of magnitude lower than hole photocurrents. The lower limit of the photogeneration quantum yield is estimated as 6×10^{-3} charge carriers/photon with an applied field of 1×10^4 V/cm.

The mechanism of the photogeneration process is discussed, and it is suggested that it is intrinsic in nature. The possibility that free radicals formed by photodissociation of iodoform molecules contribute to the photogeneration is also discussed.

INTRODUCTION

Although there is a prolifiery of organic compounds, relatively few have found application in active devices developed by electronics industries. Their potential use in low cost photovoltaic cells however has stimulated interest in their electronic properties, particularly those related to photogeneration and photoconduction.

The photogeneration processes in organics have been studied for a long time, but details of these processes are, however, not yet well understood. One can distinguish between intrinsic and extrinsic creation of charge carriers,

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with the extrinsic processes involving interactions of neutral excitons with lattice imperfections or with electrodes of perhaps lesser theoretical interest. Intrinsic photogeneration has been studied in some detail for anthracene[1–5] and one of the major achievements of these studies is the demonstration of the applicability of the Onsager model of the field assisted dissociation of a pair of charges[6] and thus the description of the electric field dependence of the photogeneration yield. The mechanism of the formation of the initial charge carrier pair is, however, obscure. The hypotheses that charge carrier pairs may be formed by autoionization of metastable neutral exciton states[7] were tested[5] but the attempts to describe the process in terms of the model put forward by Knights and Davis[8] were unsuccessful.

Bounds and Siebrand[9] have offered an alternative explanation of the primary photogeneration step in anthracene arguing that a direct absorption of light may lead to the formation of charge-transfer excitons—i.e. the initial associated charge pairs. This model seems to be suitable for the interpretation of the photoconductive properties of crystals of anthracene but any generalization of the model for a wider class of substances is unfounded at present.

A different approach to this generation problem has been suggested by Hong and Noolandi[10] who extended the Onsager model to account for the possibility that the initial charge carrier pair may bear a character of a lowest excited state. By introducing a finite recombination rate at a sphere of a finite radius they[10] quantitatively interpreted the photogeneration and fluorescence quenching results for phthalocyanine.[11,12] Again, it is not clear whether the approach may be successful in interpreting results for other substances.

A major drawback in the application of any of the theoretical models to experimental results is the complex character of photoconduction processes in organics. Apart from the differences between intrinsic and extrinsic processes which are not always easily distinguished experimentally, there are also complications due to exciton-exciton, exciton-photon or exciton-charge carrier interactions and trapping and space charge effects.[13,14]

In this paper we describe the results of studies of the steady-state photoconductivity in single crystals of iodoform (CHI_3), a compound which is found to exhibit high photogeneration yields and interesting photoconductive characteristics. An accompanying paper deals with the results obtained by a two-photon absorption.[13]

Iodoform is an interesting candidate for experimental and theoretical studies of generation and transport of charge carriers. Unlike most other organics studied, the chemical structure is not related to the arch type organic, anthracene, but some of the important physical properties are known. Iodoform crystallizes in a hexagonal space group,[15–17] and there are indications that the crystals structure may involve an orientational disorder with regard to the direction of the C—H bond (and the dipole moment).[17]

EXPERIMENTAL

Iodoform, commercial or synthesized in the laboratory of the Institute of Organic and Physical Chemistry of the Technical University of Wroclaw, was purified by multiple vacuum sublimation. Attempts to use any other purification procedures (recrystallization, zone melting) proved unsuccessful. The efficiency of purification was improved by carrying a sublimation through a layer of activated carbon.[18] A slow final sublimation carried out in a large-diameter tube usually yielded perfectly faceted hexagonal single crystalline plates of iodoform. The largest faces of the platelets were, as a rule, perpendicular to the sixfold axis. This orientation could be readily checked with a polarization microscope.

Alternatively, large bulky crystals of iodoform were grown by the sublimation method of Radomska *et al.*[19] Samples of desired orientation and size (usually 0.5–0.8 mm thick) were cut with a wire saw. For all measurements reported in this paper samples with faces perpendicular to the sixfold axis were used. When necessary, crystal faces were gently polished with a tissue soaked with a mixture of chloroform and ethyl ether. This procedure was found to introduce no detectable change to experimental results as compared with results obtained on crystals with fresh surfaces. At all steps of the purification, crystal growth and sample handling, excessive contact with the ambient light was carefully avoided.

For the photoconductivity measurements sandwich- or surface-type electrode arrangements were used, the electrodes being prepared by evaporation of gold through suitable masks in vacuo. Samples were mounted in a thermostated chamber with quartz windows and appropriate electrical connections. The chamber was filled with nitrogen. A Keithley 240 A high voltage supply and a Keithley 616 electrometer were used. The excitation was provided by a 1 k W xenon arc the light of which was passed through a 0.25 m grating monochromator. To ensure a complete rejection of the stray light which was important for measurements in the short wavelength region, suitable interference filters were used in front of the monochromator together with either a gaseous chlorine filter[20] at wavelengths shorter than 280 nm or a bandpass filter UV-D 25 at wavelengths longer than 260 nm. A small part of the light beam (*ca.* 2.5%) was deflected by a quartz beam splitter to quantitatively measure the light intensity with a radiometer (EG & G 580-25 A and 585-62). In calculations of the incident light intensity impinging on the iodoform sample, corrections were made for the calibration of radiometer, wavelength-dependent values of the reflection coefficient of quartz, losses at cryostat windows and the absorption of the top gold electrode (the transmittance of the electrode usually amounted to *ca.* 30%). Light intensity could be varied with a set of fine wire mesh filters placed in front of the monochromator. In all measurements steady-state values of the photocurrent were read by recording the current vs. time after opening the shutter. Usually the current rose monotonically to reach the steady-state value in a few minutes, or, if not after the initial build-up, there was a decay to the stationary value.

3 RESULTS

Preliminary experiments have shown that iodoform crystals exhibit a strong photoresponse when irradiated with light of wavelengths shorter than *ca.* 340 nm (3.65 eV). Figure 1 shows a typical spectral dependence of the photocurrent for the sandwich-type electrode arrangement (applied field = 1×10^4 V/cm) and a similar plot obtained for a surface electrode arrangement. The photocurrent rises steeply with the increasing photon energy up to *ca.* 290 nm (4.25 eV) and reaches a weakly structured plateau. There is no photoeffect for wavelengths longer than *ca.* 350 nm, although iodoform crystals absorb light within the whole UV region reaching far into the visible. Figure 2 shows the absorption spectra of iodoform in a heptane solution and as a pure crystal. The solution spectrum is similar to those reported in the literature[21,22] whereas the crystal spectrum is different from that reported,[23] especially in the long wavelength region. A separate report will give an analysis of the major features of these absorption spectra, but it must be mentioned here that the shape of the spectrum in the long wavelength region has been found to depend strongly on sample preparation.

In order to ensure the single-photon nature of the photoconduction light intensity dependences have been measured, with intensities in the range 10^{12}—10^{14} photons/cm^{2}s. Figure 3 shows some typical results. The dependences are, as a rule, slightly sublinear. This feature has not been taken into account in calculations of the spectral dependences of the photogeneration yield given in Figure 1 which were obtained by implying a linear relationship between the photocurrent and the photon flux. This sublinearity might have introduced a small systematic error in the results. The origin of the sublinear behavior of the photocurrent vs. the light intensity is, most probably, the recombination of free charge carriers within the generation region of the sample. The fact that the slope of log-log-dependences in Figure 3 differs more from unity the higher the current, is consistent with this interpretation.

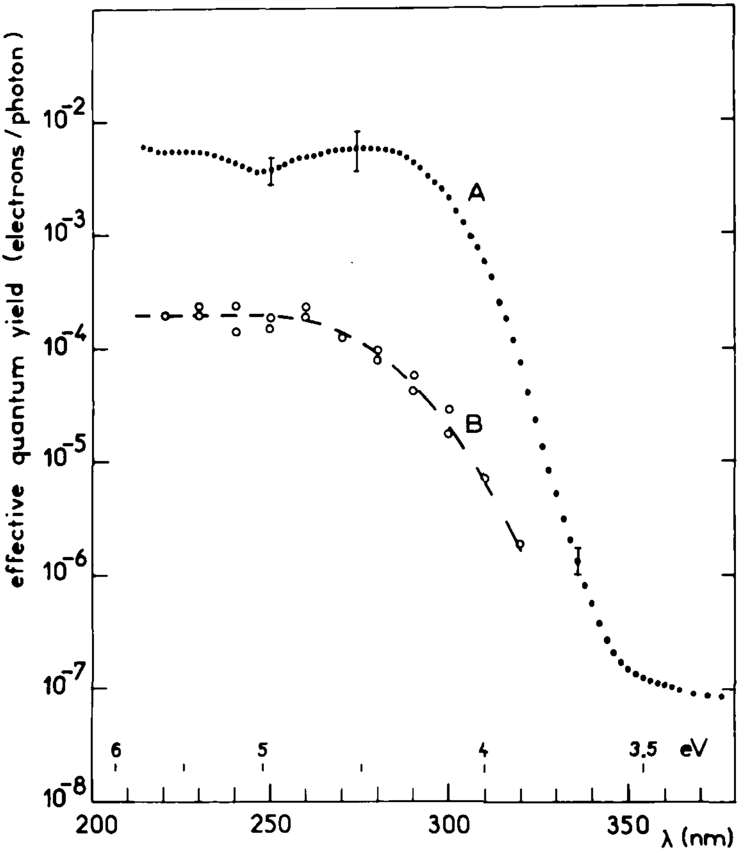

FIGURE 1 Spectral dependences of the photogeneration efficiency for sandwich (A) and surface-type (B) samples of iodoform. Efficiences for the sandwich-type sample are given in measured charge carriers/incident photon at 10^4 V/cm for a positive polarity of the irradiated electrode. No correction factors are applied. Results for the surface-type sample are given in arbitrary units.

Photocurrent—voltage dependences have been measured for illumination with different wavelengths of the exciting light. A typical dependence is given in Figure 4. The photocurrent increases linearly with the square of the applied voltage which is typical of a space-charge-limited current.[24] In some samples, for the highest voltages used in this study, there were occasionally indications of a saturation-like behavior of the photocurrent which would indicate that the current may be close to the value limited by the generation rate. In most cases, however, the observed voltage dependence suggests that the photocurrent is limited not only by the photogeneration efficiency but also by the effects of the space charge which is undoubtedly formed in the vicinity of the irradiated electrode and by bulk trapping of charge carriers.

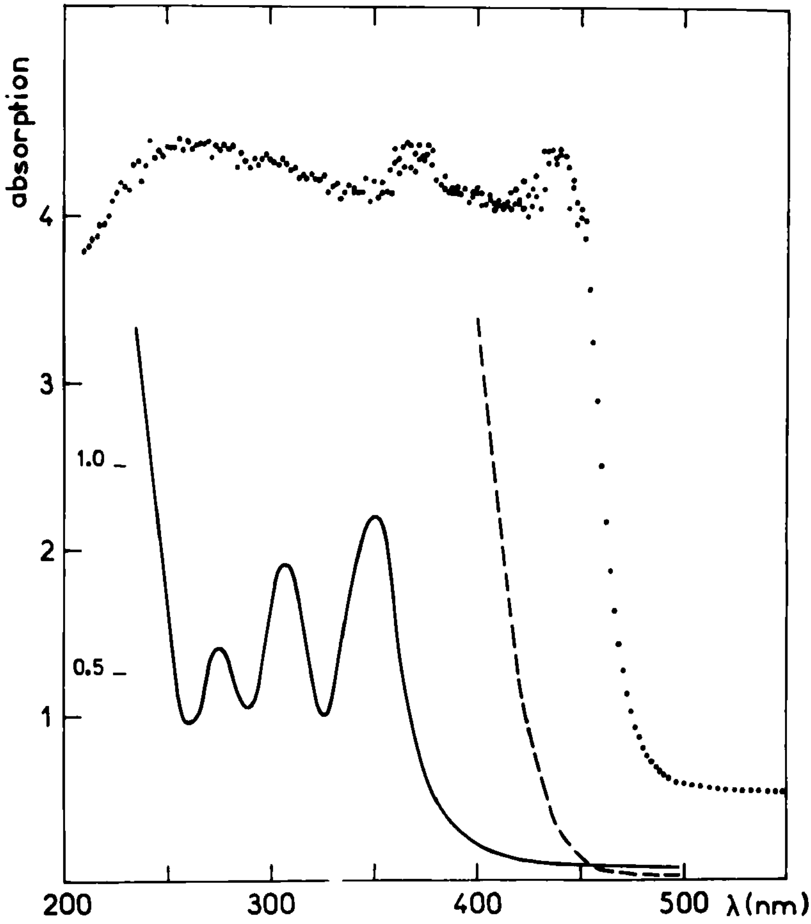

FIGURE 2 Unpolarized absorption spectra obtained for an iodoform crystal (dots) the light beam being parallel to the sixfold axis, and for *n*-heptane solutions: full line—2.45 × 10^{-4} M, dashed line—1.07 × 10^{-2} M.

It is necessary to mention that, although photocurrents in sandwich structures could be observed for both positively and negatively biased front electrode, negative photocurrents were three orders of magnitude lower than positive photocurrents. Assuming the current-voltage dependence to be given by the Child's law

$$J = \tfrac{9}{8}\, \mu_{eff}\, \epsilon\, \epsilon_o \frac{V^2}{L^3} \qquad (1)$$

one can calculate the effective mobility of carriers μ_{eff} provided the photogeneration efficiency is high enough to make the reservoir of carriers at the illum-

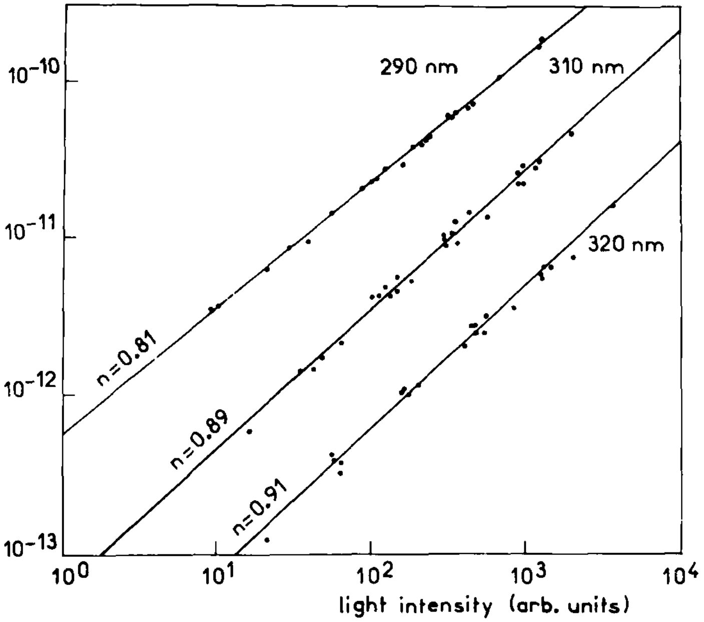

FIGURE 3 Light intensity dependences of the hole photocurrent measured for the wavelengths marked in the figure. Least-square values of the slopes are also given.

inated electrode to be practically infinite. Taking $\epsilon = 3.11$ (square of the refractive index of iodoform in the *c* direction [25]) and the current density J and sample thickness L from experimental data one calculates the effective mobility of holes as 1.3×10^{-6} cm^2/Vs. The appropriate calculation of electron mobility gives still lower numbers. The mobility of holes measured in the *c* direction employing a pulse technique amounts to *ca.* 0.2 cm^2/Vs.[14] An apparent explanation of this disagreement is the existence of bulk trapping which may effectively reduce the steady-state value of the mobility of holes, and, even more so, that of electrons. Indeed, rapid trapping of electrons was observed,[14] whereas pulse photocurrent signals of holes were only slightly modified by trapping. Nonetheless, while trapping is the obvious factor diminishing the value of the steady-state current, the assumption of the infinite reservoir of charges at the illuminated electrode is far from realistic. It may be concluded that the differences between the theoretical trap-free values of the space-charge-limited current which may be calculated from Eq. (1) and the measured current densities arise from both the trapping effects and the fact that the current is not really space-charge limited but rather space-charge perturbed.

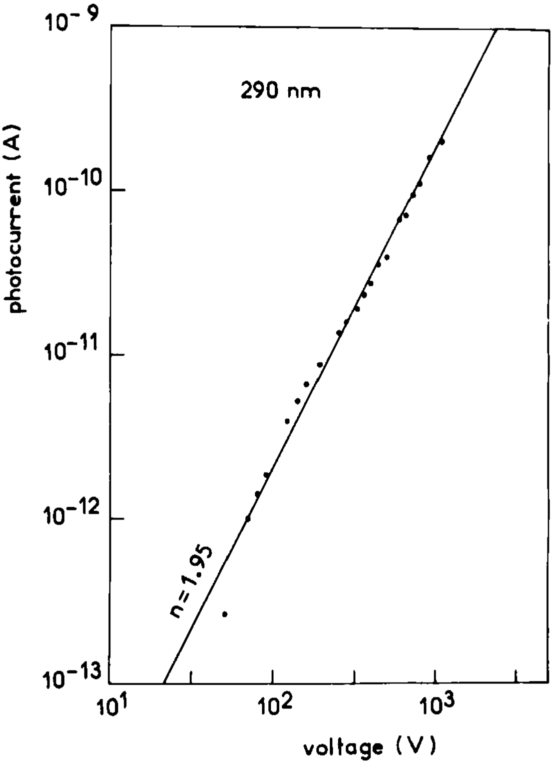

FIGURE 4 A current-voltage dependence for the hole photocurrent in a 0.6 mm thick iodoform sample irradiated with λ = 290 nm with the photon flux of 4 × 10^{13} cm^{-2} s^{-1}.

Thus, the complex nature of factors influencing the steady-state value of the photocurrent makes it impossible to accurately determine the absolute photogeneration yield i.e. the number of charge carriers produced per incident photon. One can, however, estimate a lower limit of the yield by simply taking into account values of photocurrents produced by a given photon flux. Calculations of this type give *ca.* 6 × 10^{-3} charge carriers/photon at 280 nm with the field applied being 1 × 10^4 V/cm (see Figure 1). This value is high enough to rank iodoform among the best organic photoconductors. The photogeneration quantum yield (extrapolated to the zero field) in a typical organic photoconductor—anthracene is *ca.* 10^{-4}[2,5] and higher yields reported for some organics have been obtained for relatively high electric fields. At the present time there is no way to estimate the zero field value of the photogeneration yield in iodoform, since attempts to extrapolate the value given above to the zero field using e.g. the Onsager-type relationship[2] would not be justified in view of the lack of an experimental confirmation of the applicability of this relationship.

4 The photogeneration mechanism

The experimental results presented in the preceding section, coupled with other data[13,14] are not satisfactory to provide detailed information of the mechanism of iodoform photoconduction, but they do provide a sufficient basis to interpret the observed behavior of iodoform and to suggest alternative mechanisms of the photogeneration process.

The crucial questions which have to be answered are: is the photogeneration process of surface or bulk nature, does it involve interactions of excitons with crystal defects, i.e. is it of an intrinsic or extrinsic character, and what is the spectroscopic origin of charge carriers, i.e. which crystal states serve as precursors of charge carrier pairs? An important problem which must be raised here is that of the relevance of the photochemical decomposition of iodoform, which is unambiguously present in solution or in the gas phase, to the charge carrier photogeneration process.

Lyons and Milne[5] have summarized some useful experimental criteria for distinguishing between extrinsic and intrinsic photogeneration bearing in mind the behavior of anthracene and other polycyclic aromatic hydrocarbons. In analogy, we have considered some of these criteria,[5] in relation to the results obtained for iodoform, especially with regard to the influence of the electrodes and the crystal surface, relations between electron and hole yields and relations between the absorption spectrum and the photocurrent action spectrum.

One may have anticipated that the gold electrodes used in this work would be able to photoinject carriers into iodoform crystals when irradiated with light of suitably high energy. Although the presence of the photoinjection cannot be completely excluded in the case of the sandwich structures, the results obtained for surface electrode arrangement (see Figure 1) clearly demonstrate that photoinjection cannot account for the observed effects. Furthermore, results of measurements of transient photocurrents[13,14] indicate that the photogeneration process does not depend on the electrode nature.

The fact that the photocurrent action spectrum does not follow the absorption spectrum, especially in the longer wavelength region where no detectable photocurrent could be observed although the absorption remains very strong, virtually excludes the existence of an extrinsic photogeneration process such as occurs in anthracene.[26] That is, quenching of the lowest-lying excitonic states by bulk impurities or surface states to produce charge carriers are unimportant in iodoform. Thus, the comparison of the absorption spectrum and the photoconductivity spectrum suggests that the photogeneration is intrinsic. Though difference between the yields of electrons and holes reported in the preceding section would be in disagreement with this assumption, the values of the steady-state photocurrents are not reliable for the evaluation of primary yields of carriers due to the effects of trapping. Indeed, in pulsed measurements[14] carried out in the microsecond range the differences between magnitudes of electron and hole photocurrents were found to be less than one order of magnitude. Rapid trapping was still observed for electrons and, only slight trapping effects for holes, so probably the primary rates of production of electrons and holes are equal as it should be expected for the intrinsic photogeneration process.

To discuss the origin of charge carriers in iodoform and to evaluate mechanisms which may contribute to the photogeneration it is necessary to consider the nature of excited states of iodoform. There may be two kinds of eletronic transitions in iodine-containing aliphats: localised iodine transitions of the Rydberg type and transitions involving the promotion of an electron from the non-bonding p-orbital of iodine to the antibonding σ^* molecular orbital ($n\,\sigma^*$ transitions). It is established[27] that the Rydberg transitions take place below 200 nm, whereas iodoform absorption in the range 200—400 nm is due to four $n\,\sigma^*$ transitions.[21,28,29] Although a strong spin-orbit coupling may be predicted for iodoform and other iodine-containing compounds[30] there are no indications in the literature that spin-forbidden transitions to states bearing a triplet character may be observed in iodoform. Thus, excited states giving rise to the absorption spectrum are presumably of a singlet character.

The comparison of the photocurrent action spectrum with the absorption spectrum of iodoform shows that only absorption to higher-lying excited states may be effective as the initial step of the photogeneration. The subsequent step leading to the formation of the geminate charge carrier pair may be autoionization of the unstable exciton—the process considered to be of an importance for the photogeneration in anthracene.[31] An alternative explanation of the intrinsic photogeneration may be that suggested by Bounds and Siebrand,[9] i.e. assuming that a weak absorption by crystal CT states may be superimposed on much stronger absorption due to localised transitions. The absorption by the CT states would lead to the formation of the geminate pair directly—without the intermediate step of the formation of an unstable exciton.

It is difficult to find any experimental information which would speak in favor of either of the two mechanisms mentioned above. The analysis given in Ref. 9 is based on very precise measurements of carrier yields and the photogeneration activation energies in the threshold region performed for anthracene by Kato and Braun.[4] Unfortunately, no reliable measurements of temperature dependences of the photocurrent in iodoform have been reported. Experimental problems encountered involved peeling off of electrodes at elevated temperatures (due to a high vapor pressure of iodoform) and anomalies at lower temperatures (cf. Ref. 13). It can only be stated that the photoconductivity activation energy in the plateau region is lower than 0.1 *e*V. The position of the threshold itself may help to roughly evaluate the energy balance of the formation of charge carriers. This evaluation will depend on the photogeneration model applied (for the exciton autoionization the exciton energy may be higher than the band gap, whereas absorption to the CT states should take place at energies slightly lower than the band gap) but, in view of a low value of the activation energy, it can be anticipated that the band gap of crystalline iodoform is close to 4 *e*V. We have tried to evaluate the feasibility of this result on the basis of available literature data according to the simple relation given by Lyons[32]

$$E_g = I_g - A_g - 2|P| \tag{2}$$

where I_g and A_g are the gas phase ionization potential and the electron affinity, respectively and P stands for the polarization energy of an electron or a hole in the crystal (to the first approximation P can be considered equal for electrons and holes). The first ionization potential of iodoform is known to be *ca.* 9.25 *e*V,[30,33] whereas no exact values of A_g are known. The electron affinity is, however, reported to be greater than the energy of a *C—I* bond in iodoform molecule.[34] The latter value is near 2 *e*V.[35] The polarization energy being the crucial factor in the determination of the band gap can be roughly estimated to be similar to the value for anthracene, i.e. *ca.* 1.5 *e*V,[36] if one takes into account that values of molecular polarizabilities of iodoform[37] do not differ much from those for anthracene. Inserting above values into Eq. (2) yields *ca.* 4.2 *e*V as a very rough estimate of the band gap. The agreement between this estimate and the experimental value is, of course, only a weak support for the interpretations given above, in view of the uncertainties in the values of A_g and P.

Apart from the two mechanisms of photogeneration suggested above i.e. those of autoionization and absorption by CT states, one can also postulate some other mechanisms which may involve intermediate steps caused by the free radical dissociation of iodoform molecules. The photochemistry of iodoform and other alkyl halides is well described by the dissociative primary process

$$\mathrm{CHI_3} + h\nu \rightarrow \mathrm{CHI_2}\cdot + I\cdot \tag{3}$$

which takes place when alkyl halides are irradiated within the first absorption band.[27] Van den Ende *et al.*[38] have shown that when iodoform is irradiated in mesitylene solution with a 3 ns laser pulse at 347 nm, a complex of mesitylene and an iodine atom is immediately formed. The gas phase experiments[29] in which a molecular beam of iodoform was crossed by polarized UV light (300—370 nm) and products of the photodecomposition were analyzed by a mass spectrometer have shown that lower lying excited states of $\mathrm{CHI_3}$ dissociate to give iodine atom and the corresponding radical in a time period shorter than the period of a single rotation of the molecule. The quantum efficiency of the photodecomposition is practically unity,[39] and may be even greater due to free radical chain reactions occuring in the presence of iodine and oxygen.[28] However, no reports on the photodissociation of iodoform in the crystalline phase are known to the authors. Single-crystalline samples when irradiated with UV, even for a long time, do not show visually any traces of the photodecomposition taking place. Incidentally, neither do they show any radiative emission which might be attributed to the radiative decay of excited states. There may be some doubt whether photochemical reactions do take place in the solid state. As a matter of fact, a tightly packed crystal structure of iodoform hardly allows for the bulky iodine atom to dissociate apart from the diiodomethyl radical. Although it is the most likely event that the free radicals, if formed at all, will simply recombine, one can also suppose that the radicals may carry enough excess energy to further react with adjacent molecules to accomplish an electron transfer, e.g.

$$CHI_2\cdot + CHI_3 \rightarrow CHI_2^- + CHI_3^+ \tag{4}$$

The subsequent step of the reaction chain would be the recombination of the CHI_2^- ion with the iodine atom

$$CHI_2^- + I\cdot \rightarrow CHI_3^- \tag{5}$$

One can also postulate another reaction path involving an action of the iodine atom i.e.

$$I\cdot + CHI_3 \rightarrow I^- + CHI_3^+ \tag{6}$$

and

$$I^- + CHI_2\cdot \rightarrow CHI_3^- \tag{7}$$

The above reaction schemes can be, for completeness, written also with the direction of the charge transfer reverse to that assumed above. It is difficult to discuss the feasibility of the above free radical mechanisms on the basis of the available energetic data. It should be stressed that, independently of the reaction path, the net effect of the process is the formation of the charge carrier pair and thus the energy of the light quantum initiating the process (Eq. 3) must be the same as for the photogeneration process occuring through the autoionization or by a direct light absorption, i.e. close to the value of the energy gap.

Thus, the fact that formation of charge carriers does not take place with the irradiation in the long wavelength part of iodoform absorption spectrum is of no consequence for confirming or rejecting the free radical mechanism. It can be simply supposed that the excess energy of radicals formed on irradiation within this part of the spectrum is not high enough to initiate the appropriate reaction chain.

To summarize, we have offered three alternative explanations of the photogeneration process in iodoform crystals. The high quantum efficiency of the charge carrier generation makes iodoform an interesting candidate for further experimental and theoretical studies aimed at understanding of the relations between photoconductive and spectroscopic properties of organics.

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