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## Revue of Experiments with Multiple Photon Transitions in Organic Crystals

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The aim of my lecture which I have undertaken is to summarise the achievement of the most interesting experiments with multiple photon transitions in organic crystals.

Under the expression multiple-photon transition we shall mean an exchange of more than one photon between an extrinsic electromagnetic field and one atom, or, as in our case, one molecule. Moreover the transition should take place between real states of the molecule either through virtual intermediate states or directly. Photons which participate in above mentioned process can be equal or unequal.

The problem of multiple quanta transitions is not a new one. The possibility of two photon electric dipole transition through an intermediate level predicted by the theory of second order perturbation was considered for the first time by Goepfert-Mayer [1] in 1931.

As too selection rules, they are different than for a regular one-photon transition. A double-photon transition is allowed only between the levels of the same symmetry. Then, a double transition to a level accessible by an absorption or emission of a single photon is forbidden.

During the next years there appeared only few papers dealing with the problem [2]. They were a development and completion of Goepfert-Mayer theory.

The probabilities predicted for multiple quanta transitions are very low. As a matter of fact, the probability  $W$  of the absorption or stimulated emission is depending on the density  $u$  of the incident electromagnetic radiation. For a single photon transition a direct proportionality takes place, whereas for the multiple transition we have

$$W \sim u^k \quad (1)$$

where  $\nu$  denotes a transition frequency and  $k$  a number of photons participating in the process. Increasing the insensity of incident radiation it is possible to enhance appreciably the processes. Nevertheless a detection of multiphoton transitions in the visible region of the spectrum remained a long time impossible because of the lack of enough intense light sources.

On the contrary, for low frequencies corresponding to the microwave and radio-frequency region, obtaining of the intense radiation field makes no difficulties. Then for a long time multi-quanta transitions for inst. in double resonance and optical pumping experiments are known [3] where the multiple quanta magnetic dipole transitions between Zeeman or hyperfine structure levels were stimulated.

Extending of multiphoton transition experiments on the optical region of the spectrum became possible but after appearance of lasers. The first solid state laser, working in ruby was reported by Maiman [4, 5] in 1960 and a short time later in the next year the first successful experiment with multiphoton transition in the visible was performed. Kaiser and Garrett realized two photon absorption in  $\text{CaF}_2 \cdot \text{Eu}^{2+}$  crystal [5] using a ruby laser for excitation. The blue fluorescence about 4250 Å was the evidence of the absorption of two 6943 Å red photons leading an ion into an excited state from which it decayed to the fluorescing level. Measurements have verified the predictions of Goepfert-Mayer theory.

Appearing of lasers and a successful experiment of Kaiser and Garrett were a stimulation of numerous papers concerning our problem. Particularly two, Kleniman's [7] and Braunstein's [8] theoretical papers should be mentioned.

Kleinman starting from the Goepfert-Mayer theory has estimated the probability that an atom (or molecule) absorbs two photons each of energy  $h\nu_L$  giving an expression for relevant cross-section

$$\delta = \left( \frac{e^2}{m c^2} \right)^2 \frac{c^2}{n_a^2 \nu_L^2} F g(2\nu_L - \nu_a) \quad (2)$$

where  $\nu_a$  is the frequency of an absorption band,  $\nu_L$  is the laser pump frequency,  $g(2\nu_L - \nu_a)$  is the normalized shape factor of the absorption band,  $F$  is the incident flux in photons/cm<sup>2</sup> sec, and  $n_a$  is refractive index at  $\nu_a$ .

On the other hand, in the paper of Braunstein the theory of multiphoton excitation of an electron from the valence band to the conduction band in solids is developed.

Both Kleinman and Braunstein in their estimations take into account the possibilities of laser beams.

Generally speaking lasers became a main tool in multiple photon investigations. They offer unusually intense, collimated, monochromatic and coherent beams unattainable before. The gas lasers with regard to coherence and monochromaticity approach more closely to a perfection. However, the power output of the pulsed lasers such as ruby and  $\text{Nd}^{3+}$  glass [9] appears to be the most promising as excitation sources, and easy to understand that just they both used to be most often applied in multiple photon investigations. The energy output of a regular ruby laser with a good quality ruby rod may be assumed to be 1J. Assuming the time of emission, composed of a large number of sharp spikes, to be one msec, the power reaches about 1 kW, and the photon flux is of order of  $10^{22}$  phot/cm<sup>2</sup> sec. This last value can be still increased of two to three orders of magnitude focussing the beam by means of a lens. Even more possibilities offers a Q-switched pulsed laser [10]. "Giant Pulse" in which the whole energy is emitted in one single peak has an extremely high intensity. The peak duration in a giant pulse half intensity is about 30 nsec for a laser with a rotating prism. Recently using nonlinear absorption filters in the resonant cavity the peak duration of about 10 nsec have been obtained [11]. Assuming

like before 1J output for a giant pulse with the duration of 30 nsec the power would be  $\sim 30$  MW and the photon flux without focussing  $\sim 10^2$  phot  $\text{cm}^2/\text{sec}$ .

There are now a great number of various lasers operating on different frequencies. However taking into account the high monochromaticity of laser radiation and very narrow atomic energy levels it is not easy to fulfill exactly the condition of the energy coincidence. The report about multiphoton excitation concerning isolated atoms [12] should be admitted rather as peculiar cases. Easy to understand that the main subject of experiments with multiple photon transitions became molecules (mainly crystals). Most reports were concerned with crystals of aromatic hydrocarbons.

Towards the end of 1962 the first experiments with two-photon excitation of several polycyclic aromatic molecular crystals were reported [13]. Peticolas, Galsborough and Rieckhoff observed blue or green fluorescence emerging from the irradiated by a ruby laser, powder samples of crystalline pyrene, anthracene and 3,4 benzpyrene. The fluorescence of benzpyrene was particularly intense where as an experiment with phenanthrene was unsuccessful. The exciting beam from a regular ruby laser was focused in a region of  $10^{-6}$   $\text{cm}^3$  of the sample and a maximum photon flux reached  $3-10^{23}$  phot/ $\text{cm}^2\text{sec}$ . Measurement of the relationship between intensity of resulting fluorescence and excitation gave a square-law dependence in accordance with (1). Figure 1 shows as an example the dependence under consideration for benzpyrene in a log-log scale, with a slope of 2. The spectrum has been found to be identical with that obtained by conventional U. V. irradiation. Possible excitation by harmonics generated in the sample was ruled out. The results for anthracene and benzpyrene were in satisfactory agreement with those calculated from Kleinman's theory. Authors arrived at a conclusion that the observed fluorescence appears as a result of two-photon absorption.

Few months later, there appeared the next publications confirming the report quoted above [14, 15]. Singh and Stoicheff in NRC observed blue fluorescence of

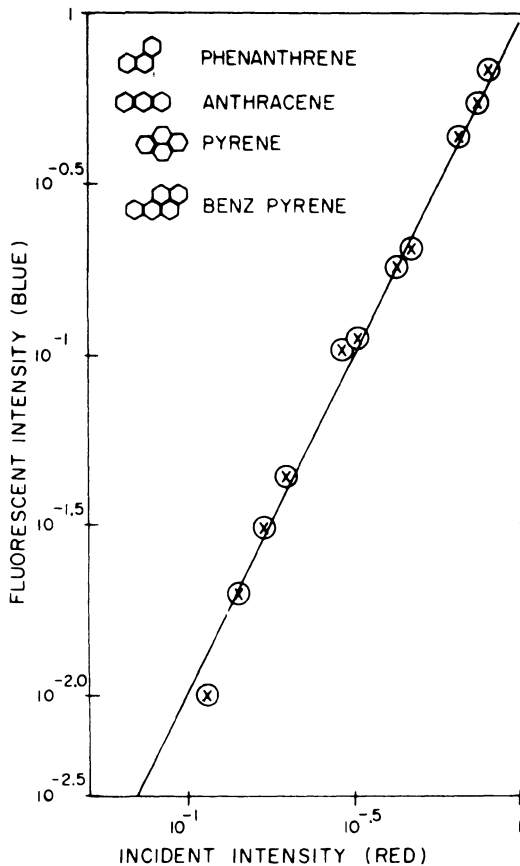


Fig. 1. Fluorescence intensity versus incident intensity for benzpyrene. After [13].

anthracene monocrystals excited as before by a ruby laser. Fig. 2 shows their experimental arrangement. Fluorescence intensity varied as the square of that of the laser beam. The same dependence has been found both for thin and thick crystals, at 77°K as well as 300°K. The discussed few different interpretations and arrived at the conclusion as follows.

Excitation by the second harmonic radiation generated in the irradiated crystal should be excluded because the crystal as well as the molecule has a center of symmetry [16]. The stepwise absorption through an intermediate stationary state (triplet level

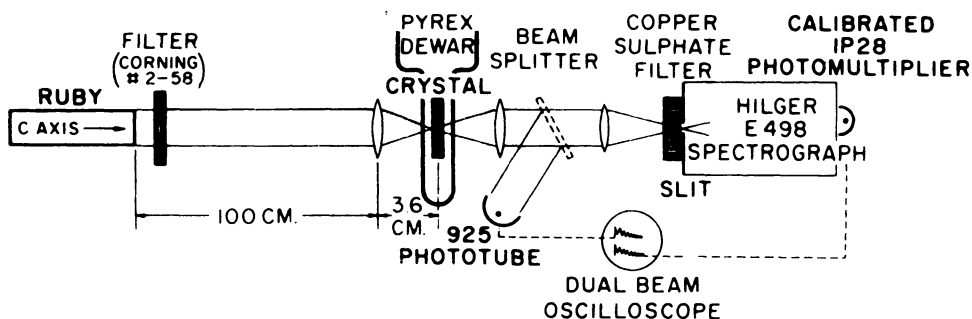


Fig. 2. Experimental arrangement. After [15].

$^3B_{2u}$  at  $\sim 14,800 \text{ cm}^{-1}$ ) rather should not be taken into account. They have tried looking for the  $^1A_g \rightarrow ^3B_{2u}$  forbidden absorption at the laser wavelength using a long (4.7 cm) crystal without result. The most probable interpretation is assuming the simultaneous absorption of two photons through an intermediate virtual state. In connection with the theoretical requirement that the double transition could take place amongst levels with the same parity ( $g \leftrightarrow g, u \leftrightarrow u$ ) authors have assumed the existence of an electronic level  $^1B_g$  or  $^1A_g$  at  $28,800 \pm 5,000 \text{ cm}^{-1}$  although no excited states  $g$  have been yet found there. A few weeks later the paper of Kepler, Caris, Avakian and Abramson [17] concerning the same problem has been given to press. This last report brought on a large discussion.

During the similar experiments with anthracene crystals they have detected the delayed fluorescence after the laser pulse ended. After them the excited singlet level giving rise to the fluorescence is populated not by a double photon absorption but through bimolecular annihilation of triplet excitons [18] generated directly by the one-photon absorption of laser red light. Square dependence of the fluorescence intensity on the excitation in the first period of the decay is self evident taking into account the bimolecular character of the process. Energy coincidence for a single photon absorption of the laser light (1.79 eV) with triplet excitons (1.8 eV) [19] is after authors satisfactory. Delayed fluorescence could be measured till 40 msec after the end of excitation and decayed at first as  $\frac{1}{t^2}$  passing gradually to be in accordance with an exponential law (Fig. 3).

The concentration of triplet excitons  $n$  is determined by the equation

$$\frac{dn}{dt} = \alpha I - \beta n - \gamma n^2 \quad (3)$$

where  $\alpha I$  represents generation of triplet excitons,  $\beta = \frac{1}{\tau}$  and  $\tau$  is the triplet excitons lifetime, and  $\gamma$  is the triplet-triplet interaction constant. The intensity of the delayed fluorescence is proportional to  $\frac{1}{2} \gamma n^2$  taking into account two triplet excitons are needed for one singlet exciton creation.

Using the experimental data they have estimated the values of constants in the equation (3) to be  $\alpha = 10^{-5} \text{ cm}^{-1}$ ,  $\beta = 10^{-4} \text{ sec}^{-1}$ , and  $\gamma = 10^{-11} \text{ cm}^3/\text{sec}^{-1}$ . The value of  $\gamma$  is of the same order as that previously reported [20].

Moreover in June appeared the next paper of the same authors in which they have shown that the population of the triplet level could be obtained also through a single photon transition with a conventional incoherent light source. The light from an 850 Wdc. Xe arc passing through a monochromator was sufficient source of excitation. The intensity of the delayed fluorescence could be measured as a function of the exciting wavelength. That experimental technique enabled the investigation of triplet levels structure and obtaining the results consistent with former data [21].

They have estimated also the constant  $\gamma$  and found the value  $4 \times 10^{-11} \text{ cm}^3\text{sec}^{-1}$  in good agreement with the former laser experiment.

As it is seen the existence of blue fluorescence of anthracene crystals excited by a red laser light has found two controversial interpretations, one as a two photon absorption giving rise of a molecule to the fluorescence state, and the other as a result of one photon excitation followed by a triplet-triplet annihilation process.

In the meantime there appeared interesting paper of Adelman and Verber [22] which reported two-photon excitation experiment in a charge transfer complex of naphthalene and tetrachlorophthalic anhydride single crystal. The charge transfer

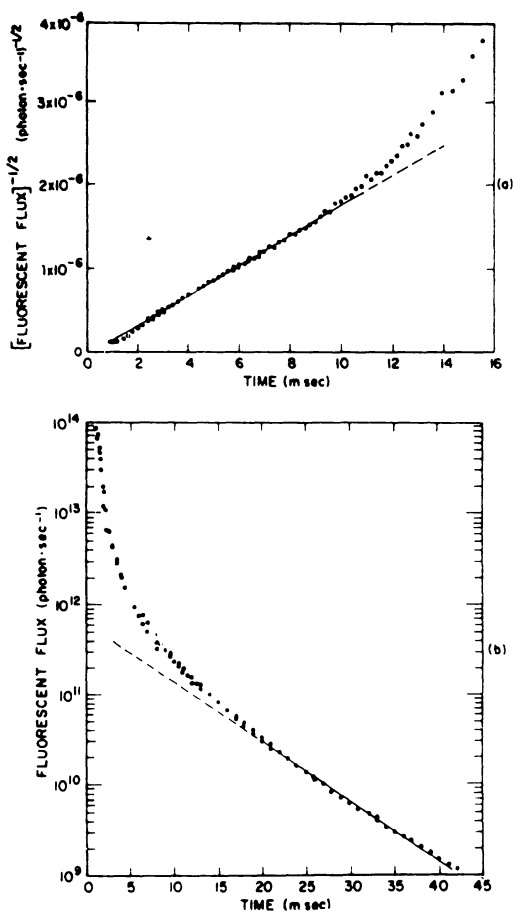


Fig. 3. Time dependence of the delayed fluorescence. The upper graph shows, that around the time of laser shutoff the fluorescence varies inversely with the square root of time. The lower graph shows, that at later times the fluorescence decays exponentially. After [17]

absorption band lies above  $22\,700\text{ cm}^{-1}$  peaking at  $27\,500\text{ cm}^{-1}$ . The naphthalene first triplet level is much higher in frequency than  $14\,400\text{ cm}^{-1}$ , consequently the crystal is transparent for a laser light and a direct single photon excitation could not take place. Fig 4 shows the relative energy levels.

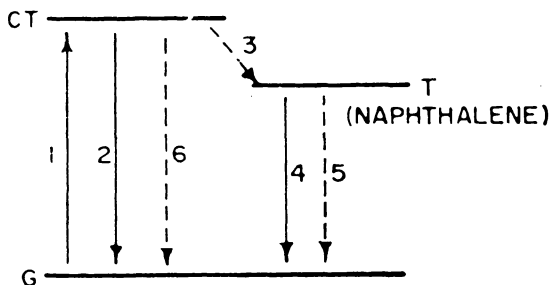


Fig. 4. Pertinent energy levels for the charge transfer complex. Dashed lines indicate nonradiative transitions. Absorption is shown as 1, fluorescence and phosphorescence by 2 and 4 respectively, and intersystem crossing by 3. After [22]

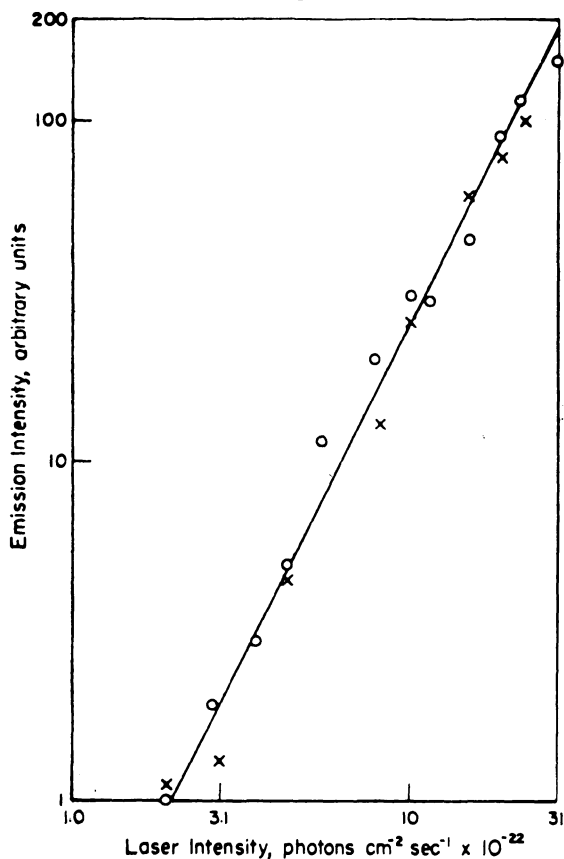


Fig. 5. Log-log plot of emission as a function of laser intensity. Phosphorescence indicated by crosses and fluorescence by circles. The solid line has a slope of 2. After [22].

Authors were using in their experiment both laser excitation or UV from a Xe flash tube and have measured the fluorescence as well as phosphorescence. The fluorescence and phosphorescence intensities with laser excitation showed the square law dependence on the incident photon flux indicating to a double-photon way of absorption (Fig 5). The laser photon flux on the sample was  $3.1 \times 10^{23}$  phot/cm<sup>2</sup>sec. They have measured also the ratio of the phosphorescence to fluorescence for both laser and UV excitation obtaining the same results.

Experiment showed that for both way of excitation all the processes observed were a consequence of the two-photon charge-transfer state excitation. The controversion which rose up about the interpretation of the anthracene fluorescence induced by a ruby laser stimulated wide discussion during 1963 and 1964 followed by a number of papers.

There is the publication of Peticolas and Rieckhoff [23] where they vigorously attacked the stand of Kepler, Caris, Avakian and Abramson. They have repeated the experiment with anthracene powder using an oscilloscope with a short time constant of  $0.1\ \mu\text{sec}$ . Fig 6 represents the oscilloscope

oscilloscope

oscilloscope

graphs. Each spike of laser light with about  $1 \mu\text{sec}$  duration corresponds to fluorescence signal of the same shape. No evidence of the delayed fluorescence which after Kepler et al. should have the lifetime of miliseconds order. Moreover Kepler has affirmed that whole fluorescence observed had an origin in triplet-triplet annihilation.

Besides, Peticolas and Rieckhoff have investigated by the same manner two-photon excitation of benzpyrene in a diluted solution of  $\alpha$ -methyl naphthalene. No evidence of delayed fluorescence and no dependence of the fluorescence lifetime on concentration have been found.

Analogous results they obtained with a solid solution of anthracene in phenanthrene. The fluorescence lifetime is shorter than a microsecond and its intensity is proportional to the anthracene concentration. They agreed with a suggestion of Stoicheff and Singh concerning the existence of  $^1B_g$  or  $^1A_g$  anthracene state at twice laser frequency.

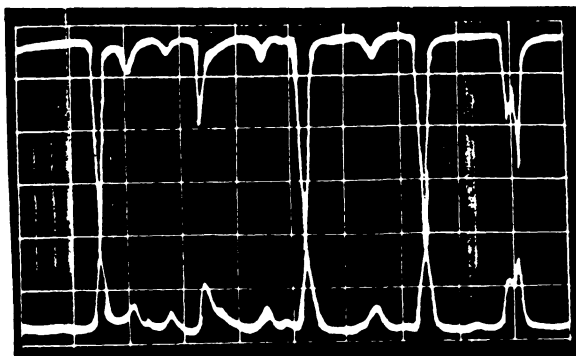


Fig. 6. Upper trace (negative polarity signal): fluorescence in anthracene. Lower trace (positive polarity signal): laser output. Time scale:  $4 \mu\text{sec}$  per cm. After [23].

The delayed fluorescence, of course, could be expected but its intensity should be negligible compared with that of the fluorescence excited by two-photon process.

In the same year there appeared a very interesting paper of Hall, Jennings and McClintock [24]. They arrived to a conclusion that both two-photon absorption and triplet-triplet annihilation processes were present and easy to separate each other with regard to different time dependences. It is worth emphasizing that they have used for the first time the giant pulse laser for excitation. Q-switched ruby laser with a rotating prism delivered giant pulses of 3 megawatts power what enabled to obtain a photon flux of order  $10^{24}$  phot/cm<sup>2</sup>sec.

Resulting fluorescence consisted of two components. One was the fast fluorescence and the second delayed fluorescence with lifetimes 26 nsec and 17.2 msec correspondingly. First of them fulfilling the square dependence on the exciting photon flux was the true fluorescence involved by two-photon process.

The delayed fluorescence was observed and measured like the former on the oscilloscope graphs but the photomultiplier was gated on  $10 \mu\text{sec}$  after the intense fast fluorescence signal to avoid overloading. It decayed as  $\frac{1}{t^2}$  for short times and afterwards exponentially in agreement with the Kepler equation (3). Authors have estimated the constants in that equation obtaining values of  $\alpha$  and  $\gamma$  approximate to those of Kepler:  $\alpha = 8.6 \times 10^{-6} \text{ cm}^{-1}$  and  $\gamma = 5.5 \times 10^{-11} \text{ cm}^3\text{sec}^{-1}$ . However, the value of  $\beta$  was appreciably different.

Silver and Zahlan [25] considering the results of Hall experiments suggested that



the fast and delayed fluorescence should differ from each other by intensity dependences. The population of anthracene triplet level apart of the direct single-photon excitation undoubtedly is carried mainly through the radiationless transitions from two-photon excited fluorescent singlet level. Therefore having regard to the fact that the delayed fluorescence arises as a result of bimolecular triplet excitons interaction and annihilation rather a fourth power intensity dependence of the delayed fluorescence should be observed.

Basing upon the value of the intersystem crossing rate constant given by McGlynn [26] authors have estimated the laser flux about  $10^{26}$  phot  $\text{cm}^2\text{sec}$  required to obtain the fourth power dependence. Reversely, from delayed fluorescence measurements it is possible to determine directly the intersystem crossing constant.

The same authors reported [27] a successful experiment with two-photon absorption of anthracene crystals using uncoherent light from a 75 J Xe flash. They observed both for fast and delayed fluorescence a square dependence on the excitation. That result agreed with their former statement because the incident flux was much smaller than required for obtaining the fourth power relation ( $10^{23}$  phot  $\text{cm}^2\text{sec}$ ).

In January 1965 appeared the paper of Singh, Jones, Siebrand, Stoicheff and Schneider [28] containing an assembly of very interesting experiments performed in NRC laboratories, concerning two-photon excitation of anthracene single crystal. Authors in their experiments used a Q-switched ruby laser with giant pulses, of 1–10 MW and  $\sim 30$  nsec duration. For a long lived component investigation served a rotating sector disc arrangement to cut off the exciting red light pulse. For the excitation, apart of  $14400 \text{ cm}^{-1}$  — primary laser frequency they used  $28800 \text{ cm}^{-1}$  — second harmonic radiation generated in ADP as well as  $12800 \text{ cm}^{-1}$  and  $17500 \text{ cm}^{-1}$  — frequencies shifted by a stimulated Raman effect in liquid oxygen.

Their kinetic considerations brought about equations as follows:

$$\frac{dx}{dt} = -\alpha x + \frac{1}{2} \gamma y^2 \quad (4a)$$

$$\frac{dy}{dt} = Kx - n\gamma y^2 - \beta y \quad (4b)$$

where  $x$  denotes exciton concentration of excited singlet level ( $^1B_{2u}$ ) and  $y$  that of the triplet level ( $^3B_{2u}$ ).  $\alpha$  is the unimolecular decay constant,  $\frac{1}{2} \gamma$  is the rate constant of singlet creation via triplet-triplet annihilation.  $K$  is the rate constant of triplet level population via radiationless  $^1B_{2u} - ^3B_{2u}$  processes  $\beta$  is triplet decay constant (radiationless deactivation and phosphorescence),  $n\gamma$  is triplet-triplet annihilation rate constant,  $n$  is the factor depending on the nature of the annihilation process assumed to be equal unity if the annihilation process leads to singlet excitation only.

Their simplified solution leads to following results.

For very short times values ( $t \sim \alpha^{-1} \sim 30$  nsec)  $\frac{1}{2} \gamma y^2 \ll \alpha x$  and from (4a) we have  $\frac{dx}{dt} = -\alpha x$  and then

$$x = x_0 \exp(-\alpha t) \quad (5)$$

where  $x_0$  is the singlet exciton concentration just after laser pulse.

For long times ( $t \gg 30$  nsec) we have approximated expression

$$x = \frac{\gamma}{2\alpha} y^2 \quad (6)$$

and

$$y = \beta y_0 [(\gamma' y_0 + \beta) \exp(\beta t) - \gamma' y_0] \quad (7)$$

where

$$\gamma' = \gamma \left( n - \frac{K}{2\alpha} \right) \quad (8)$$

and  $y_0$  is the initial concentration of triplet excitons.

For the long times compared with the triplet lifetime ( $t \gg \beta^{-1}$ ) we have approximated relation

$$x = \frac{\gamma}{2\alpha} [\beta y_0 (\gamma' y_0 + \beta)]^2 \exp(-2\beta t) \quad (9)$$

For intermediate times ( $\alpha^{-1} \ll t \ll \beta^{-1}$ ) we obtain

$$x = \frac{\gamma}{2\alpha} \{y_0 [(\gamma' y_0 + \beta) t]\}^2 \quad (10)$$

Taking into account that the intensity of the delayed fluorescence  $I_{DF} = \alpha x$ , after reformations we can obtain the linear function

$$(I_{DF})^{-\frac{1}{2}} = f(t)$$

with the slope

$$\begin{aligned} S &\equiv \frac{d}{dt} (I_{DF})^{\frac{1}{2}} = \\ &= (2\gamma)^{\frac{1}{2}} \left( n - \frac{K}{2\alpha} \right) + \frac{\beta}{(I_{DF})^{\frac{1}{2}}} \end{aligned} \quad (11)$$

where  $I_{DF}$  is the fluorescence intensity extrapolated by means of Eq 10 to  $t = 0$ . The constants values can be determined from suitable experimental curves.

The fast fluorescence was observed using the excitation with light beams of  $14\,400\text{ cm}^{-1}$  and  $12\,800\text{ cm}^{-1}$ . The square depend-

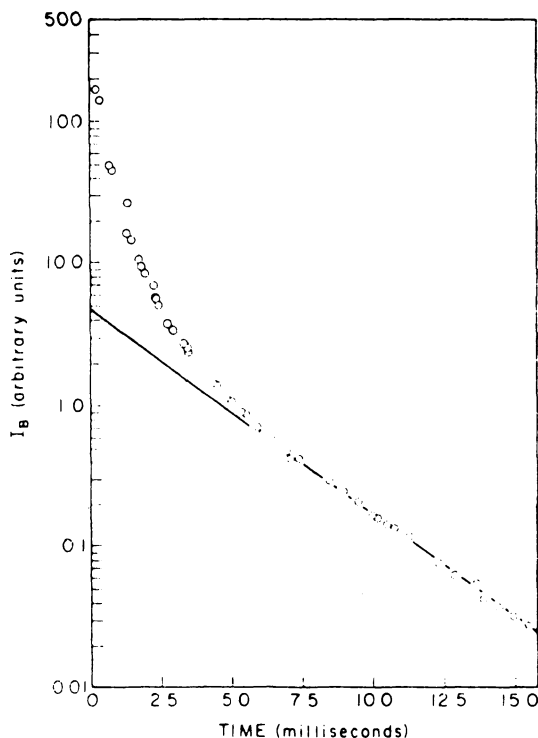


Fig. 7. Time dependence of the delayed fluorescence. The graph shows that at time  $\sim 5$  msec the fluorescence decays exponentially. After [28].

ence testified that two-photon excitation took place at both frequencies ( $28\,800\text{ cm}^{-1}$  and  $25\,600\text{ cm}^{-1}$ ) and led into vibronic levels of  $A_g$  or  $B_g$  symmetry of the  $B_{2u}$  electronic state. The decay of the fast fluorescence was exponential with agreement with Eq. 5 and a lifetime was  $\alpha^{-1} = 3.0 \times 10^{-8}\text{ sec}$ .

As too delayed fluorescence it decayed until  $t = 4\text{ msec}$  as  $t^{-2}$  and for long times exponentially in accordance with Eq. 10 and Eq. 9 (Fig 7). The triplet lifetime seemed

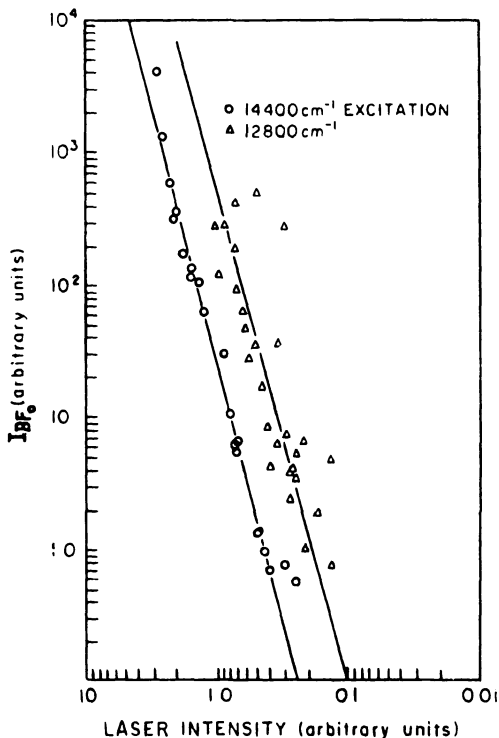


Fig. 8. Dependence of the delayed fluorescence intensity  $IDF_0$  on laser power  $L_L$ , for high-intensity  $14400\text{ cm}^{-1}$  and low-intensity  $12800\text{ cm}^{-1}$  radiation. The graph shows that  $IDF_0 \sim I_R^4$  under these conditions. For the  $14400\text{ cm}^{-1}$  excitation, one  $IDF_0$  unit corresponds to  $4 \times 10^{14}\text{ cm}^{-3}\text{ sec}^{-1}$ , one laser intensity unit to  $\sim 10^{27}\text{ cm}^{-2}\text{ sec}^{-1}$ . Both factors are considerably smaller for the  $12800\text{ cm}^{-1}$  excitation.

to increase with purification of anthracene and for purest samples a value of  $18\text{ msec}$  has been found. The measurements of delayed fluorescence intensity as a function of exciting flux were an essential part of the investigation.

#### a) $14\,400\text{ cm}^{-1}$ excitation

The values of  $IDF_0^{-1/2}$  where  $IDF_0$  denotes the intensity of the delayed fluorescence were plotted against  $t$ . Then by extrapolation back for  $t = 0$  values of  $IDF_0$ , proportional to the triplet concentration  $y_0$  at  $t = 0$  (laser shutoff time), were found. These values of  $IDF_0$  plotted against the intensity of excitation in a log-log scale exhibited the slope between 3.3 and 3.9 (close to 4) for the strong excitation ( $\sim 10^{24}$ — $\sim 20^{27}\text{ phot/cm}^2\text{sec}$ ) (Fig 8), and for the weak excitation ( $< 10^{24}\text{ phot/cm}^2\text{sec}$ ) about 2.2 in agreement with anticipation and with the paper of Silver and Zahlan [25]. Then indeed two processes populating the triplet level compete with each other. At a strong excitation radiationless intersystem crossing transitions  $^1B_{2u} \rightarrow ^3B_{2u}$ , whereas at lower laser intensities a single-photon absorption to triplet level is predominant.

#### b) $12\,800\text{ cm}^{-1}$ excitation

That frequency is much too low to reach

#### c) $17\,500\text{ cm}^{-1}$ excitation

the triplet level but two-photon excitation to the  $^1B_{2u}$  singlet system is quite possible. Really indeed the fourth power dependence has been found. The triplet level lies at  $14\,750\text{ cm}^{-1}$  then the single-photon absorption directly to the triplet system should take place. Indeed the delayed fluorescence intensity varied as a square of excitation.

d) 28 800 cm<sup>-1</sup> excitation

This exciting frequency enables the direct single-photon absorption to <sup>1</sup>B<sub>2u</sub> singlet level. Both kinds of fluorescence should be present. Observation of the fast component was difficult because of UV exciting light presence but the delayed fluorescence with the square dependence was experimentally confirmed.

We have several times talked about the single photon direct absorption from the ground to the triplet level. However, the primary laser frequency 14 400 cm<sup>-1</sup> is somewhat lower than that of 0-0 transition. The difference is 350 cm<sup>-1</sup>. We could then anticipate that the absorption should take place from some excited vibronic level of the ground state. Authors have stated indeed the temperature dependence.

At a condition of strong excitation, as we could see above, the population of triplet level occurs rather through two-photon absorption to the excited singlet and indeed the delayed fluorescence exhibited only a slight temperature dependence. Otherwise using the lower excitation, when an one-photon absorption to the triplet level is predominant, an appreciable temperature dependence with activation energy of 350 ± 50 cm<sup>-1</sup> has been stated.

The experimental works of Stoicheff and his group elucidated to a high degree interesting phenomena observed with anthracene excited by a laser.

In the meantime there appeared two papers of rather theoretical character of Ianuzzi and Polacco [29, 30] suggesting another two-photon process. They called attention to the fact that in the Goepfert-Mayer theory in the nonrelativistic interaction Hamiltonian

$$H = H_0 + \frac{e}{mc} \vec{p} \cdot \vec{A} + \frac{e^2}{2mc^2} \vec{A} \cdot \vec{A} \quad (12)$$

where  $H$  is Hamiltonian of the isolated atom,  $\vec{A}$  is the vector potential of electromagnetic radiation, and  $\vec{p}$  is momentum operator, was generally neglected the term containing the operator  $\vec{A} \cdot \vec{A}$ . Allowance of that term leads up to double-photon transitions between the levels of opposite parity without the virtual intermediate state.

The former and the latter processes should differ each other by the polarisation of fluorescence involved. Recently Peticolas, Norris and Rieckhoff have proposed in their

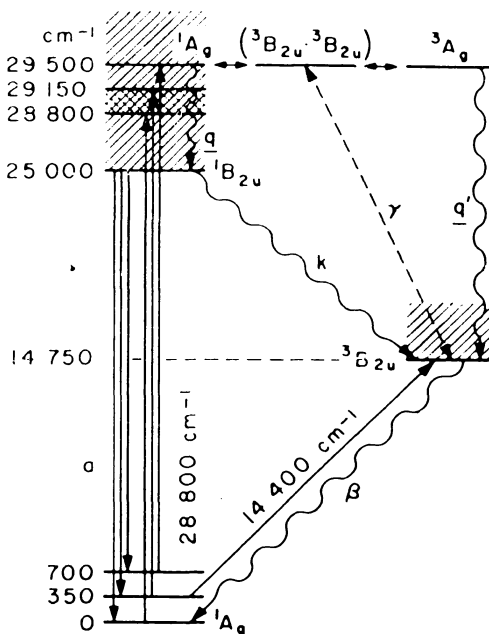


Fig. 9. Energy-level diagram of solid anthracene. Hatched regions: absorption bands. Crosshatched region: two-photon absorption band of 14 400 cm<sup>-1</sup> radiation. After [28].

paper [31] concerning the polarization effects in the two-photon excitation of anthracene that the contribution of the process suggested by Ianuzzi and Polacco is rather negligible.

We can point out that recently a number of theoretical papers were published [32, 33, 34, 35, 36] considering not only transitions through the coupling with intermediate states, but also direct transitions involved by second and higher order interaction Hamiltonians. However, probabilities of such transitions are very low.

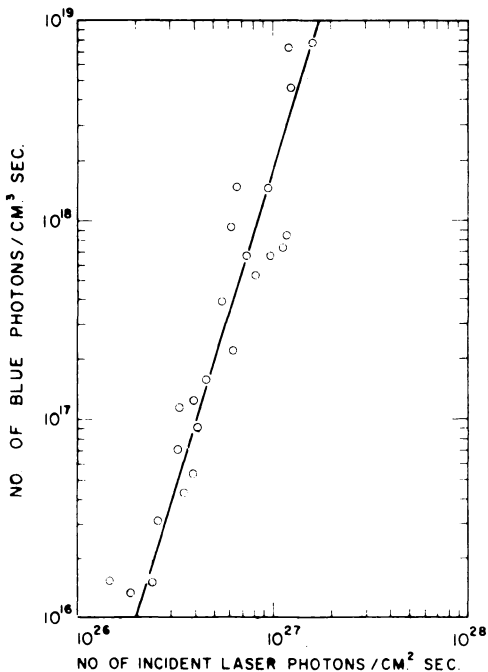


Fig. 10. Dependence of the intensity of the naphthalene fluorescence on the intensity of the ruby laser in log-log scale. Slope of 3.1 indicates the three-photon absorption. After [37].

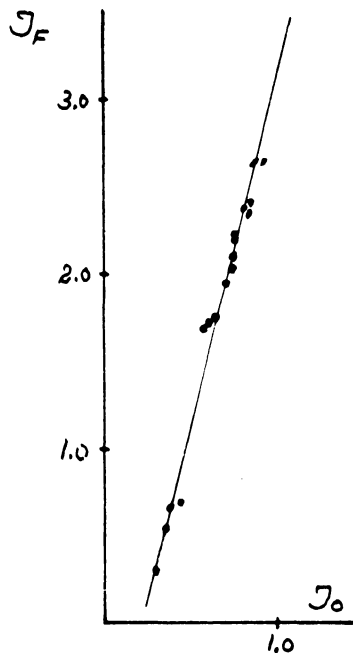


Fig. 11. Dependence of the intensity of the naphthalene fluorescence on the intensity of excitation in log-log scale. The slope is 4.

Hitherto we have dealt with the transitions in which two photons participated. I should like at present to give some attention to a report of Singh and Bradley [37] concerning an absorption of three photons.

Crystalline naphthalene has no absorption bands at either 14 400  $\text{cm}^{-1}$  nor at 28 800  $\text{cm}^{-1}$  whereas the triple ruby laser frequency at 43 200  $\text{cm}^{-1}$  is falling within a region of strong absorption. That fact makes possible looking for a three-photon excitation.

Authors used a giant pulse ruby laser with an exciting flux till  $10^{27}$  phot  $\text{cm}^2\text{sec}$ . Naphthalene single crystals few millimeters thick were irradiated normally to the a, b plane. The intensity of the resulting fluorescence was detected by a photomultiplier and measured on the oscilloscope patterns. By the similar manner was monitored the exciting light.

The measurements of the fluorescence intensity dependence on the incident flux have indicated indeed the three photon excitation. Fig. 10 shows the relevant dependence in a log log scale with a slope of 3.1, close to expected value of 3. The photographing of the fluorescence spectrum have exhibited the identity with that obtained with a conventional UV excitation. Authors have measured also the efficiency and the fluorescence lifetime which were  $\sim 10^{-10}$  and 83 nsec respectively.

According to Singh and Bradley a naphthalene molecule absorbed three red photons and after radiationless processes decayed to the first singlet Fluorescing, Level at  $31\,450\text{ cm}^{-1}$ .

Returning to the power dependence, the recent investigations (38) with laser excitation of naphthalene have given rather higher exponent values than 3. Measurements were repeated many times obtaining different exponent values. They changed from 3 to 4.5 but in the case of rather low laser intensities the slope values were close to 4 (Fig 11). The conditions of experiment were almost the same as in Singh and Bradley's except the intensity of excitation because the giant pulse laser beam incident on the sample has been used without focussing.

There are reasons to suppose that at least a part of the fluorescence is involved as a result of the triplet level population. It seems that in naphthalene crystal occur more than one process involved by the laser irradiation leading to different power dependences. The contribution of these processes depends, among others, on the intensity of excitation. However, it is too early to speak about their nature. The investigations are under way.

We have pointed out previously that the exactly definite laser frequencies are a factor limiting the number of materials investigated. Recently a new method has been developed based on the absorption of two unequal photons. This method enables to explore the complete spectrum of two-photon absorption and not only its narrow region. The sample is irradiated by a monochromatic laser beam and a continuum simultaneously. An intense laser pulse stimulates an absorption of two photons, one from each source, in accordance with the condition

$$h\nu + h\nu_L = \Delta E \quad (13)$$

where  $h\nu$  is the photon absorbed from a continuum,  $h\nu_L$  is the laser photon and  $\Delta E$  is the energy levels difference.

That method, called, two-photon spectroscopy, was used for the first time by Hopfield and Worlock [39] to explore the two-photon transitions in KJ and CsI crystals.

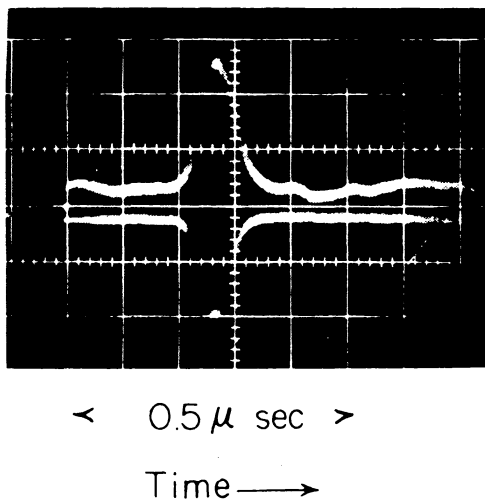


Fig. 12. Coincidence of the laser signal (lower trace) and the two-photon absorption signal (upper trace). Absorption gives rise to an upward signal on the oscilloscope. After [40].

Recently Fröhlich and Mahr applied the method described above for anthracene [40]. They used a Q-switched Nd glass laser in combination with a flash tube of very short pulse duration about 50  $\mu$ sec and a delay line to obtain the proper timing. The choice of Nd laser with  $10\,600\text{ cm}^{-1}$  wave number made impossible the two laser photons absorption. For an incident laser photon flux of  $5 \times 10^{25}$  phot/cm<sup>2</sup>sec the change of the transmission at  $\sim 31\,000\text{ cm}^{-1}$  was about 10% for a 2.5 cm crystal length (Fig 12). Varying the frequency of the flash tube polarized light, by means of a monochromator, authors obtained the whole two-photon absorption spectrum. The relative changes in transmission were different depending on the polarization of exciting light sources. For the polarization parallel to *b* crystal axis the effects were much more intense. It is in agreement with former data.

As a matter of fact, during the last years several organic crystals, from the viewpoint of the multiple photon transitions were investigated [41]. However, we have discussed only few of them limiting mainly to anthracene. The experiments with this crystal were interesting and have given the most complete informations.

The experiments with multiphoton transitions, and particularly two-photon spectroscopy became a promising tool of investigations. They permit to examine the forbidden states unaccessible by one photon transitions.

## References

- [1] M. GOEPPERT-MAYER, *Ann. Phys.* **9**, 273 (1931)
- [2] for inst.  
J. A. WHEELER, *J.O.S.A.* **37**, 813, (1947)  
V. HUGHES, L. GRABNER, *Phys. Rev.* **79**, 829 (1950)
- [3] J. M. WINTER, *Ann. Phys. (NY)* **4**, 49 (1959)
- [4] T. H. MAIMAN, *Nature* **187**, 493 (1960)
- [5] T. H. MAIMAN, R. H. HOSKINS, I. J. D'HAENES, C. K. ASAWA, V. EVTUHOV, *Phys. Rev.* **123**, 1151 (1961)
- [6] W. KAISER, C. G. B. GARRETT, *Phys. Rev. Lett.* **7**, 229 (1961)
- [7] D. A. KLEINMAN, *Phys. Rev.* **125**, 87 (1962)
- [8] R. BRAUNSTEIN, *Phys. Rev.* **175**, 475 (1962)
- [9] E. SNITZER, *Phys. Rev. Lett.* **7**, 444 (1962)
- [10] F. J. McCLUNG, RW. HELLWARTH, *J. Appl. Phys.* **33**, 828 (1962)
- [11] for. inst.  
Y. LE DUFF, P. PERETTI, R. DUPEYRAT, *Rev. Phys. Appl.* **1**, 117 (1966)
- [12] I. D. ABELLA, *Phys. Rev. Lett.* **9**, 453 (1962)
- [13] W. L. PETICOLAS, J. P. GOLDBOROUGH, K. E. RIECKHOFF, *Phys. Rev. Lett.* **10**, 43 (1963)
- [14] S. SINGH, B. P. STOICHEFF, *J. Chem. Phys.* **39**, 2032 (1963)
- [15] S. SINGH, B. P. STOICHEFF, *Proceedings of the symposium on Optical Masers. Polytechnic Institute of Brooklyn. Apr. 16-19 (1963)*
- [16] for. inst. P. A. FRANKEN, A. E. HILL, C. W. PETERS, G. WEINRICH, *Phys. Rev. Lett.* **7**, 118 (1961)
- [17] R. G. KEPLER, J. C. CARIS, P. AVAKIAN, E. ABRAMSON, *Phys. Rev. Lett.* **10**, 400 (1963)
- [18] S. CZARNECKI, *Bull. Acad. Pol. Sci.* **9**, 7, 561 (1961)  
C. A. PARKER, C. G. HATCHARD, *Proc. Roy. Soc.* **269**, 574 (1962)  
G. C. NIEMAN, G. W. ROBINSON, *J. Chem. Phys.* **37**, 2150 (1962)  
R. M. HOCHSTRASSER, *Rev. Mod. Phys.* **34**, 531 (1962)
- [19] D. S. McCLURE, in *Solid State Physics* edited by F. Seitz and D. Turnbull (Acad. Press. Inc. N. Y. 1959), Vol. 8 pl

- [20] S. CHOI, S. A. RICE, J. Chem. Phys. **38**, 366 (1963)  
M. SILVER, D. OLNESS, M. SWICORD, R. C. JARNAGIN, Phys. Rev. Lett. **10**, 12 (1963)
- [21] for. inst. M. R. PADHYE, S. P. MCGLYNN, M. KASHA, J. Chem. Phys. **24**, 588 (1956)
- [22] A. H. ADELMAN, C. M. VERBER, J. Chem. Phys. **39**, 931 (1963)
- [23] W. L. PETICOLAS, K. E. RIECKHOFF, J. Chem. Phys. **39**, 1347 (1963)
- [22] J. L. HALL, D. S. JENNINGS, M. MCCLINTOCK, Phys. Rev. Lett. **11**, 364 (1963)
- [25] M. SILVER, A. B. ZAHLAN, J. Chem. Phys. **40**, 1458 (1964)
- [26] M. KLEINERMAN, L. AZZAROGA, MCGLYNN, **Luminescence of Organic and Inorganic Materials** edited by H. P. Kallman and G. Marmor Spruch. (John Wiley and Sons N. Y. 1962, p. 207)
- [27] S. Z. WEISZ, A. B. ZAHLAN et Al., J. Chem. Phys. **41**, 3491 (1964)
- [28] S. SINGH, W. J. JONES, W. SIEBRAND, B. P. STOICHEFF, W. G. SCHNEIDER, J. Chem. Phys. **42**, 330 (1965)
- [29] M. IANUZZI, E. POLACCO, Phys. Rev. Lett. **13**, 371 (1964)
- [30] M. IANUZZI, E. POLACCO, Phys. Rev. **138**, A806 (1965)
- [31] W. L. PETICOLAS, R. NORRIS, K. E. RIECKHOFF, J. Chem. Phys. **42**, 4164 (1965)
- [32] E. EVLETH, W. L. PETICOLAS, J. Chem. Phys. **41**, 1400 (1964)
- [33] R. GUCCIONE, J. VAN KRANENDONK, Phys. Rev. Lett. **15**, 583 (1965)
- [34] S. KIELICH, Proc. Phys. Soc. **86**, 709 (1965)
- [35] S. KIELICH, Acta Phys. Pol. **27**, 913 (1965)
- [36] S. KIELICH, Acta Phys. Pol. **30**, 393 (1966)
- [37] S. SINGH, L. T. BRADLEY, Phys. Rev. Lett. **12**, 612 (1964)
- [38] S. CZARNECKI, unpublished data
- [39] J. J. HOPFIELD, J. M. WORLOCK, Phys. Rev. **137**, A1455 (1964)
- [40] D. FROHLICH, H. MAHR, Phys. Rev. Lett. **16**, 895 (1966)
- [41] For inst. D. H. MCMAHON, R. A. SOREF, A. R. FRANKLIN, Phys. Rev. Lett. **14**, 1060 (1966)