

Two-Photon Absorption in Anthracene

Koji CHIHARA*, Motoi HYODO, Toshiya SHIOTANI and Akira SADO

Department of Chemistry, Faculty of Science, Kanazawa University

(Received May 30, 1972)

Abstract We observed the two-photon absorption in anthracene crystal by using a ruby laser as a light source. The absorption cross section per molecule was estimated as $\sigma = 10^{-52} \sim 10^{-53} \text{ cm}^4 \text{ sec photon}^{-1}$.

With the present availability intense monochromatic source of radiation utilizing optical masers, many types of the multipole photon absorption processes in gases¹⁻³⁾, liquids⁴⁾, and solids⁵⁻⁷⁾ have been investigated. In intense radiation fields, Maxwell's equations for a dielectric medium are no longer linear. Two-photon absorption is a nonlinear phenomenon in which two photons are simultaneously absorbed in an electronic transition, energy being conserved only between the electronic system and the two photons.

The two-photon absorption spectrum should contain as much informations about a system as does the ordinary single-photon absorption, because the selection rules are different (even-parity transitions for two-photon absorption *versus* odd-parity transitions for single-photon absorption). Then the two methods of the investigation are complementary rather than identical. The change in the selection rules may be readily rationalized by considering the electromagnetic interaction potential for a charged particles, which is given by⁸⁾

$$H' = -\frac{e}{mc} \mathbf{P} \cdot \mathbf{A} + \left(\frac{e^2}{2mc^2} \right) \mathbf{A}^2$$

where \mathbf{A} is the vector potential of the radiation field and \mathbf{P} the momentum operator. Two-photon transitions can take place in first order by means of \mathbf{A}^2 term or in second order by the $(\mathbf{P} \cdot \mathbf{A})$ ⁹⁾ term. As the contribution of the \mathbf{A}^2 term to the

*Present address; Research Institute of Applied Electricity, Hokkaido University, Sapporo, Hokkaido.

two-photon transitions is negligible small, the $(P \cdot A)$ term induces two-photon excitations *via* intermediate states so that the parity is conserved in the electronic transition¹⁰⁾.

We have investigated the generation of the blue fluorescent light around $\lambda_b = 4500 \text{ \AA}$ by illuminating an anthracene single crystal with red light $\lambda_r = 6943 \text{ \AA}$, of a ruby laser. The anthracene crystal exhibits the strong absorption between 30000 cm^{-1} and 25000 cm^{-1} . Excitation of the anthracene crystal with light absorbed in this wavelength range gives rise to a brilliant blue fluorescence (band width *ca.* 800 \AA) which originates at the levels around 4500 \AA and terminates at the ground state.

We have performed the following experiments. The anthracene single crystal of 0.5 cm thickness was mounted in front of the entrance slit of a quartz spectroscope, and the light beam of a ruby laser (0.65 joules output) was focussed onto the sample. The red filter was mounted between the laser and the anthracene in order to eliminate the possibility that the blue range of the stream radiation from the flash lamp reaches the sample. The fluorescence of the crystal was photographed by using the spectrograph. In Fig. 1, a picture (lower) of the output spectrum is presented which

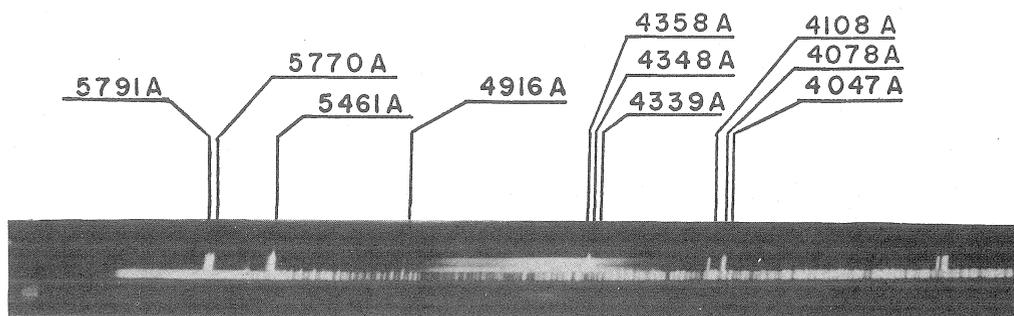


Fig. 1. The fluorescent spectra of anthracene induced by laser beam (lower) and Hg arc lamp (upper).
The center of the photograph is Fe arc spectrum.

was obtained by three flashes ($200 \mu \text{ sec}$) of the red light. The bright spot at 6943 \AA results from the incident laser light. Of particular interest is the observation of the light around 4500 \AA , which is characteristic for the blue fluorescence of the anthracene. This fact is explicit from the upper spectrum induced by Hg arc lamp.

In a second experiment, we have observed the dependence of the fluorescent intensity on the incident light intensity. The basic experimental design is shown in Fig. 2. The fluorescence induced by the laser light is detected by the photomultiplier (R-136) and the incident light intensity is monitored by the photodiode (L. S. D. 39A). The signals of the photodiode and the photomultiplier were displayed simultaneously on a dual beam synchroscope. Load resistor in photomultiplier circuit (detector) was $100 \text{ K}\Omega$ and imposed on 900 V . In order to smooth out the spikes of the fluorescence corresponding to the ruby laser we placed the condenser $0.001 \mu\text{F}$ in parallel with the

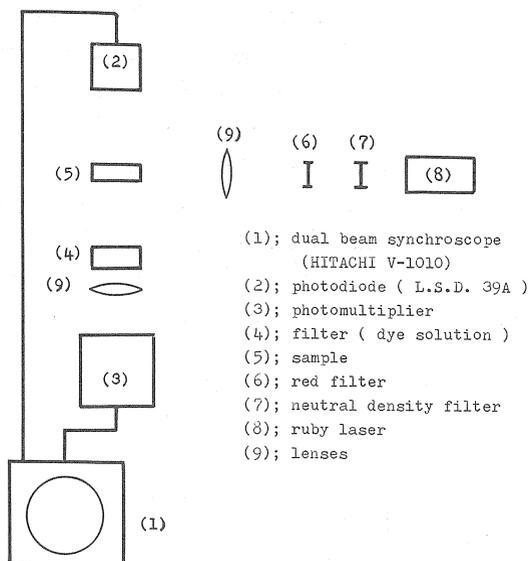


Fig. 2. A schematic diagram of the experimental arrangement.

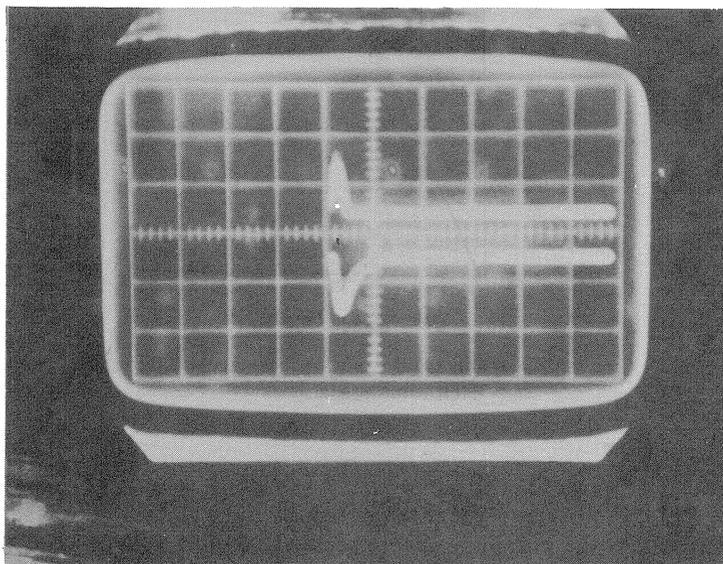


Fig. 3. The traces of the fluorescence intensity and the excitation intensity.

The upper trace is the signal from the laser monitor.

The lower trace is the signal of the fluorescence.

duration time500 sec/cm

sensitivitymonitor 1 volts/cm

detector 0.2 volts/cm

load resistor. Load resistor in the photodiode circuit (monitor) was $1\text{ K}\Omega$ and imposed on 9 V. The photodiode had also the condenser $0.001\mu\text{F}$ in order to smooth the signal. Between the sample and the photo-multiplier, the filter of the dye solution was

interposed to eliminate the scattered incident light. Therefore we could allow a direct quantitative comparison between the two signals. The traces of the signals which we obtained were shown in Fig. 3. The intensity of the exciting light was controlled by the neutral density filters. In Figure 4 the fluorescence intensity I_b obtained in the blue part of the spectrum is plotted against the signal in the red I_r , which is a direct measure of intensity of light incident on the crystal. The empirical line through our experimental points represents the quadratic relation $I_b \propto I_r^2$, which is a strong indication that we are dealing with a two-photon process. From the calibration of the photomultiplier the number of the blue fluorescent photons could be estimated to be 2×10^9 photons.

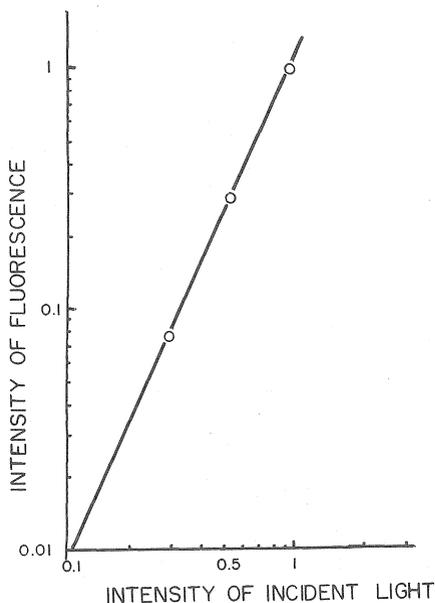


Fig. 4. The dependence of the fluorescent intensity and excitation intensity.

We believe that in our experiments the anthracene is excited by a two-photon process. Hence we are going to estimate σ which corresponds to the two-photon absorption cross section per molecule expressed in units of $\text{cm}^4 \text{ sec}$ per a photon. The estimation can be taken place by using the following equation

$$I_b = \eta \cdot n \cdot V \cdot \sigma \cdot I_r^2,$$

where V is the irradiated volume, η , the quantum yields for emission, and n , the number of the molecules per unit volume. $V = 0.001 \text{ cm}^3$, $\eta = 1$, $n = 4 \times 10^{21}$ molecules, $I_b = N_f/T = 10^{13} \text{ photons sec}^{-1}$, $T = 200 \mu \text{ sec}$, $I_r = 8 \times 10^{23} \text{ photons sec}^{-1} \text{ cm}^{-2}$, thus the σ is estimated as $\sigma = 10^{-52} \sim 10^{-53} \text{ cm}^4 \text{ sec photon}^{-1}$. This value is consistent with the results of other authors¹⁰⁾.

The authors wish to express their grateful acknowledgment to Prof. S. Aono and Mr. M. Suhara for their helpful discussions.

References

- 1) J. D. Abella, *Phys. Rev. Letters*, **9**, 453 (1962).
- 2) S. Yatsiv, *Phys. Rev. Letters*, **15**, 614 (1965).
- 3) J. L. Hall, E. J. Robinson and L. Baranscomb, *Phys. Rev. Letters*, **14**, 1013 (1965).
- 4) J. A. Gordmaine and J. A. Howe, *Phys. Rev. Letters*, **11**, 207 (1963).
- 5) W. Kaiser and C. G. B. Garrett, *Phys. Rev. Letters*, **7**, 229 (1961).
- 6) J. J. Hopfield, J. M. Worlock and K. Park, *Phys. Rev. Letters*, **11**, 414 (1963).
- 7) S. Singh and B. P. Stoicheff, *J. Chem. Phys.*, **38**, 2032 (1963).
- 8) W. Heitler, "Quantum Theory of Radiation" (Clarendon Press, Oxford, England, 1954), p. 125.
- 9) M. Goeppert-Mayer, *Ann. Physik*, **9**, 273 (1931).
- 10) J. Jortner, B. Honig and A. Szoeké, *J. Chem. Phys.*, **46** 2714 (1967); I. Webman and J. Jortner, *J. Chem. Phys.*, **50**, 2706 (1969).