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Polarization Dependence of Laser-Induced Fluorescence in Anthracene

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The polarization dependence of double-photon excitation of fluorescence in anthracene has been observed by using a Q-switched laser. It has been found that the fluorescence is a maximum for linearly polarized light and zero for circularly polarized light. The results agree with an earlier interpretation of double-photon excitation transitions between bands having different parity.

INTRODUCTION

A GOOD deal of work has recently been done on excitation of fluorescence in solids, particularly in anthracene, using intense radiation fields. Induced excitation of fluorescence has been observed in powdered anthracene[1] and in anthracene crystals[2,3] using—as incident light—the red light of a ruby laser ($\nu = 14\,400$ cm^{-1}).

The fluorescence, practically coincident with the laser pulse, was found proportional to the square of the incident light. The authors of these experiments interpreted the fluorescence as due to double-photon absorption. But while some[1] believe that the induced transition is the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ transition[4] (Fig. 1), others[2,3] do not agree on such an interpretation.

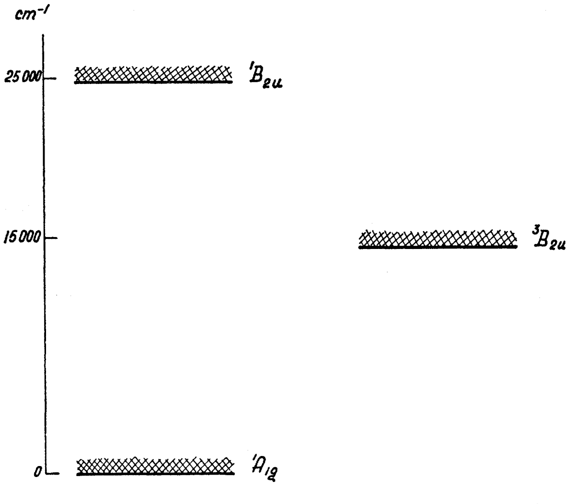

FIG. 1. Energy-level diagram of observed bands in crystalline anthracene. For ruby laser $\nu = 14\,400$ cm^{-1}.

Subsequently a delayed fluorescence (with a delay of up to 40 msec) was observed in anthracene crystals excited by the red light either of ruby lasers[5] or of conventional sources.[6] The authors excluded double-photon absorption and explained the experimental results by assuming that each of the red photons directly creates a triplet exciton (band ${}^3B_{2u}$), and these in turn interact in pairs to form singlet excitons (band ${}^1A_{2u}$) which fluoresce with a lifetime of 2.6×10^{-8} sec. The triplet excitons have a mean lifetime of 17 msec and a diffusion length[7] of about 10 μ.

Furthermore, Hall, Jennings, and McClintock[8] and Weisz, Zahlan, Silver, and Jarnagin[9] state that the red light can give rise to the simultaneous occurrence of the following effects:

(a) two-phonon processes leading to normal fluorescence;
(b) triplet excitation leading to delayed fluorescence.

THEORETICAL CONSIDERATIONS

We will consider only the two-photon processes and ordinary fluorescence.

Two-photon processes were first studied by Göppert-Mayer[10] a long time ago and more recently by Kleinman[11] and Braunstein.[12] According to these theories double-quantum transition for electric-dipole transitions can occur only if the initial and final states have the same parity. But Peticolas *et al.*[1] claim that in asymmetric molecules these selection rules will not be strictly observed and that single- and double-quantum transitions are possible to the same level by different components of the dipole operator. So they suggest,

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[1] W. L. Peticolas, J. B. Goldsborough, and K. E. Rieckhoff, Phys. Rev. Letters **10**, 43 (1963).

[2] S. Singh and B. P. Stoicheff, J. Chem. Phys. **38**, 2032 (1963).

[3] S. Singh and B. P. Stoicheff, *Proceedings of the Symposium on Optical Masers* (Brooklyn Polytechnic Press, New York, 1963), p. 385.

[4] The authors use the old notation ${}^1A \rightarrow L_a$.

[5] R. G. Kepler, J. C. Caris, P. Avakian, and E. Abramson, Phys. Rev. Letters **10**, 400 (1963).

[6] P. Avakian, E. Abramson, R. G. Kepler, and J. C. Caris, J. Chem. Phys. **39**, 1127 (1963).

[7] P. Avakian and R. E. Merrifield, Phys. Rev. Letters **13**, 541 (1964).

[8] J. L. Hall, D. A. Jennings, and R. M. McClintock, Phys. Rev. Letters **11**, 364 (1963).

[9] S. Z. Weisz, A. B. Zahlan, M. Silver, and R. C. Jarnagin, Phys. Rev. Letters **12**, 71 (1964).

[10] M. Göppert-Mayer, Ann. Physik **9**, 273 (1963).

[11] D. A. Kleinman, Phys. Rev. **125**, 87 (1962).

[12] R. Braunstein, Phys. Rev. **125**, 475 (1962).

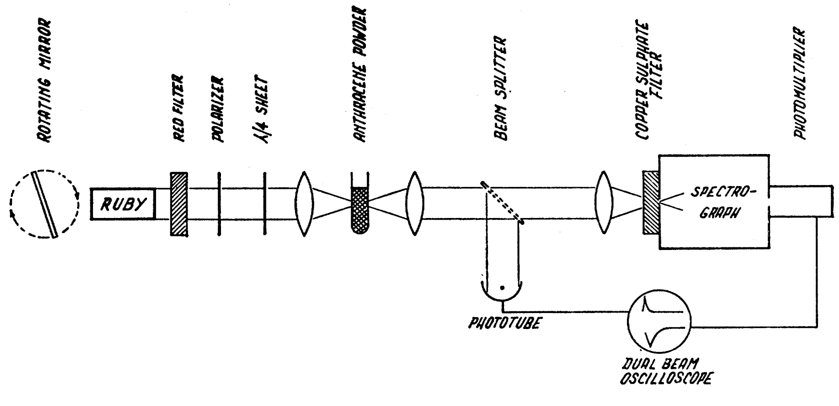

FIG. 2. Experimental arrangement.

without further explanation, that in anthracene we have the transition ${}^1A_{1g}\rightarrow{}^1A_{2u}$.

On the other hand, Singh and Stoicheff suggested, according to the Kleinman[11] formula, that the fluorescent light was due to a double-photon absorption process via virtual states between bands such as ${}^1A_{1g}\rightarrow{}^1A_g$ or ${}^1A_{1g}\rightarrow{}^1B_g$.

Actually, a lowest g level at 36 000 cm^{-1} is calculated for the free molecule of anthracene,[13] but no such state has yet been observed in solid anthracene. However, assuming the existence of a level of species g at 28 800 cm^{-1} (with more than 10% shift with respect to the calculated value for a free molecule), and a band width of 7000 cm^{-1}, Singh and Stoicheff found an order-of-magnitude agreement with the experimental results.

In a previous note[14] the authors suggested that the double-photon absorption in anthracene was due to the term $(e^2/2mc^2)\mathbf{A}^2$ in the interaction Hamiltonian:

$$H=-e\phi+\frac{e}{mc}\mathbf{A}\cdot\mathbf{p}+\frac{e^2}{2mc^2}\mathbf{A}^2, \tag{1}$$

where the symbols have the usual meaning.

The term $(e^2/2mc^2)\mathbf{A}^2$ has not been considered in the other theories of two-photon absorption. The total-transition probability due to this term for an atom or a molecule which makes transitions from the state i to the state f after having interacted with a light pulse has been found to be

$$P=\left(\frac{r_0}{2\omega_0\hbar}\right)^2 I^2|x(\omega_{fi})|^2 2\Delta\omega, \tag{2}$$

where I is the total energy for unit area of the wave packet, ω_0 and $2\Delta\omega$ are the frequency and the width of the packet respectively, $r_0=e^2/mc^2$ is the classical radius of electron, $x(\omega_{fi})=\langle\psi_f^0|x|\psi_i^0\rangle$ and is measured in cm^2 sec because of the normalization of the states f belonging to a continuous band.

Equation (2) has been obtained with the following hypotheses:

(a) The light pulse is coherent (as in the case when a Q-switched laser is used);
(b) the light is linearly polarized;
(c) the band width is much broader than the radiation width;
(d) the initial and final states have different parity (as in the case of the ${}^1A_{1g}\rightarrow{}^1A_{2u}$ transition in anthracene).

It has been shown[15] that the contribution of the interaction $(e^2/2mc^2)\mathbf{A}^2$ to the total-transition-probability amplitude for two-photon absorption is proportional to

$$\tfrac{1}{2}(\mathbf{e}_1\pm i\mathbf{e}_2)(\mathbf{e}_1\pm i\mathbf{e}_2)=0 \tag{3}$$

for circularly polarized radiation, and to

$$\mathbf{e}_1\cdot\mathbf{e}_2=1 \tag{3'}$$

for linearly polarized radiation, where $\mathbf{e}_1$ and $\mathbf{e}_2$ are two unit vectors orthogonal to each other and to the propagation vector.[16]

On the other hand, the contribution of the interaction $(e/mc)\mathbf{A}\cdot\mathbf{p}$ (this term is the one considered in the other theories) to the total transition-probability amplitude of two-photon absorption between states with the same parity is in general different from zero for both circularly polarized radiation and linearly polarized radiation.

Therefore, an obvious experiment to test formula (2) is the observation of the polarization dependence of the laser-induced fluorescence.

EXPERIMENT AND RESULTS

The experimental arrangement used to observe the fluorescence from anthracene powder is shown in Fig. 2. The Q-switched laser produced a total output pulse of 0.01 J. The output of the laser was focussed with a lens onto the anthracene sample, producing a

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[13] R. Pariser, J. Chem. Phys. 24, 250 (1956).

[14] M. Iannuzzi and E. Polacco, Phys. Rev. Letters **12**, 371 (1964).

[15] E. Corinaldesi and F. Strocchi, *Relativistic Wave Mechanics* (North-Holland Publishing Company, Amsterdam, 1963), p. 285.

[16] If we take $\mathbf{A}$ real and equal to $A_0[(\cos t)\mathbf{e}_1+(\sin t)\mathbf{e}_2]$, we have $\mathbf{A}^2=A_0^2=\text{const}$. Therefore, in this case also, $\langle\psi_f^0|\mathbf{A}^2|\psi_i^0\rangle=0$.

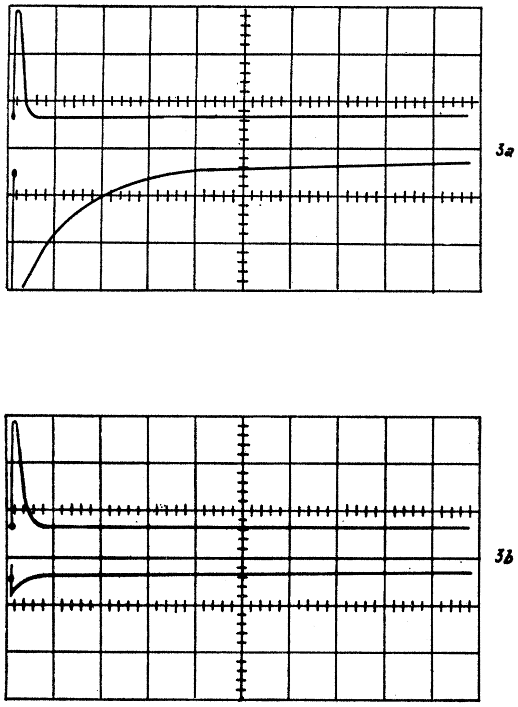

FIG. 3. Upper trace: phototube output; lower trace: photomultiplier output; sensitivity: 20 mV/cm; writing time: 2 μsec/cm. The longer time constant in the lower signal is due to the circuit. (a) Linearly polarized light; (b) nearly circularly polarized light.

spot size of approximately 2×10^{-5} cm^2. Suitable filters were used to ensure that only the 1.78-eV photons were being transmitted to the sample and that no such photons were being transmitted to the photomultiplier. A polaroid and a quarter-wavelength plate were used to obtain polarized radiation. The signal from the photomultiplier and the laser pulse from a monitoring phototube were displayed on a Tektronix 551 scope which was triggered by the phototube signal.

The experimental results in Fig. 3 indicate a strong dependence of the fluorescence on the polarization of the laser light, in agreement with the preceding discussion. The fluorescence is a maximum for linearly polarized light and zero for circularly polarized light.

DISCUSSION

In conclusion, the present experimental results seem to indicate the occurrence of double-photon absorption between states having different parity due to the term $(e^2/2mc^2)\mathbf{A}^2$.

It has now come to our notice[17] that double-photon absorption has been observed in anthracene crystals using a high-intensity flash tube. We believe that this result is not in disagreement with our theory. In fact, for a flash tube with a pulse of duration T and band width $2\Delta\omega$ we can speak of a coherence time τ, which is roughly $\tau\simeq1/\Delta\omega$. If we suppose that the light pulse is a succession of $N=T/\tau$ coherent waves we can apply for each formula (2), and so we get that

$$P'=\left(\frac{r_0}{2\omega_0\hbar}\right)^2 I^2|x(\omega_{fi})|^2\frac{2\Delta\omega}{N}. \tag{4}$$

While the coherence time of the light emitted from a flash tube is very short, $\Delta\omega$ is very large. And, as $\Delta\omega/N\simeq$const, formula (4) shows that, in this case also, two-photon absorption between states having different parity should be observable.

ACKNOWLEDGMENTS

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[17] S. Z. Weisz, A. B. Zahlan, J. Gilreath, R. C. Jarnagin, and M. Silver, J. Chem. Phys. 41, 3491 (1964).