

## DOUBLE-PHOTON EXCITATION OF FLUORESCENCE IN ANTHRACENE

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Recently, double-photon excitation of fluorescence, induced by a ruby laser, has been observed in anthracene crystals.<sup>1-3</sup> The fluorescent light, whose intensity has been established to vary as the square of the laser beam intensity, has been interpreted as due to two-photon absorption. Nevertheless, a quantitative interpretation of the experimental results based on the present theories of two-photon absorption<sup>4</sup> is not satisfactory. According to these theories, transitions via virtual states can take place only when (a) the initial and final levels have the same parity; (b) the separation of the energy levels is equal to the sum of quantum energy of absorbed photons. In an effort to interpret their experimental results, Singh and Stoicheff<sup>3</sup> assume that a  ${}^1B_{3g}$  band of anthracene exists with the right energy to fulfill the condition (b), although no excited states of species  $g$  have yet been identified. With this hypothesis, their calculation gives an order-of-magnitude agreement with the experimental results. In this note we wish to suggest a different interpretation of these experiments.

The nonrelativistic interaction Hamiltonian of a charged particle with an electromagnetic field is

$$\mathcal{H} = -e\phi + (e/mc)\vec{A}\cdot\vec{p} + (e^2/2mc^2)\vec{A}^2, \quad (1)$$

where the symbols have the usual meaning. We shall use perturbation theory in order to calculate the transition probability due to the last term in (1) (this term has been neglected in the theories of two-photon absorption<sup>4</sup>). Let us consider an atom or a molecule, initially in the ground state 1, which interacts with a wave packet propagating in the  $x$  direction. If we consider only the term  $(e^2/2mc^2)\vec{A}^2$  in (1), then the probability amplitude of the atom being in the final state  $f$  (whose energy is  $\hbar\omega_{fi}$  above the initial state), after the wave packet interacts with the

system, is<sup>5</sup>

$$a(\omega_{fi}) = -(ir_0/2\hbar)\langle\psi_f|\exp(ix\omega_{fi}/c)|\psi_i\rangle \times \int_0^{\omega_{fi}} \vec{A}(\omega)\cdot\vec{A}(\omega_{fi}-\omega)d\omega, \quad (2)$$

where  $\vec{A}(\omega)$  is the Fourier transform of  $\vec{A}$ , and  $r_0$  is the classical radius of electron. If the level  $f$  belongs to a continuous band,<sup>6</sup> the total transition probability to any level of the band is, of course

$$P \approx \int_{2(\omega_0-\Delta\omega)}^{2(\omega_0+\Delta\omega)} |a(\omega_{fi})|^2 d\omega_{fi}, \quad (3)$$

where  $\omega_0$  is the angular frequency, and  $\Delta\omega$  is the spectral half-width of the incident radiation. By neglecting all terms except the linear term in the expansion of the exponential in (2), we have

$$a(\omega_{fi}) = \frac{\omega_{fi} r_0}{2\hbar c} \langle\psi_f|x|\psi_i\rangle \int_0^{\omega_{fi}} \vec{A}(\omega)\cdot\vec{A}(\omega_{fi}-\omega)d\omega. \quad (2')$$

We stress the fact that in (2') no virtual states appear, and that (2') is different from zero only when the initial and final levels have different parity, as one can see by looking at the matrix element  $x(\omega_{fi}) = \langle\psi_f|x|\psi_i\rangle$ . The numerical value of  $P$  is very small when conventional light sources are used, but it can become fairly large when lasers are used.<sup>7</sup>

We shall now apply the formulas to practical cases. When coherence exists within the wave packet,

$$\int_0^{2\omega_0} \vec{A}(\omega)\cdot\vec{A}(2\omega_0-\omega)d\omega \approx \frac{c}{2\omega_0^2} I \quad (4)$$

results, where  $I$  is the total energy of the wave packet per unit area.

The above relation can be derived from  $I = 2c^{-1} \times \int \omega^2 \vec{A}^*(\omega)\cdot\vec{A}(\omega)d\omega$  for a quasimonochromatic wave packet by assuming  $\vec{A}(\omega_0 + \delta\omega) \approx \vec{A}(\omega_0 - \delta\omega)$

and both real. Moreover, if the spectral width of the bands involved in the transition is much broader than the spectral width  $2\Delta\omega$  of the laser, one obtains

$$\int_{2(\omega_0-\Delta\omega)}^{2(\omega_0+\Delta\omega)} |a(\omega_{fi})|^2 d\omega_{fi} \approx 2|a(2\omega_0)|^2 \Delta\omega. \quad (5)$$

From (2'), (3), (4), and (5), we have

$$P \approx \left(\frac{\gamma_0}{2\omega_0\hbar}\right)^2 I^2 |x(\omega_{fi})|^2 2\Delta\omega. \quad (6)$$

For comparison, we also write the formula of the total transition probability  $P'$  valid for one-photon absorption at  $\omega_{fi}$  with the same hypotheses as in formula (6):

$$P' = (\pi e^2 / \hbar c) I |x(\omega_{fi})|^2.$$

We can apply formulas (4) and (5) to interpret the experimental results obtained using anthracene, because coherence exists within every single laser spike<sup>8</sup> and because anthracene has a band  ${}^1B_{2\mu}$  whose parity is opposite to the parity of the ground band  ${}^1A_g$  and whose energy levels are such to permit a double photon absorption of laser light. Moreover, the spectral widths of the anthracene bands are of course much broader than the spectral width of the laser. We have not found in the papers by Peticolas, Goldsborough, and Rieckhoff,<sup>1</sup> and Singh and Stoicheff,<sup>2,3</sup> all the experimental data we need to make a rigorous calculation on the actual experiments with a ruby laser. Therefore, we shall make the calculation for the simpler case when a Q-switched laser is used. The results we obtain in this way, (6') and (7'), are only approximate but, as they are in quite reasonable agreement with the experimental results, they seem to indicate that a more rigorous calculation would lead to a good agreement. By assuming a fluorescent quantum efficiency of one, the number of fluorescent photons from a sample whose volume is  $V$  is

$$n = NPV, \quad (7)$$

where  $N$  is the number of molecules per  $\text{cm}^3$ . If we assume the following reasonable values

for a focused Q-switched laser,

$$\begin{aligned} I &= 10^{11} \text{ erg/cm}^2, \quad \omega_0 = 2.7 \times 10^{15} \text{ rad sec}^{-1}, \\ \Delta\omega &\approx 1/\Delta t \approx 5 \times 10^7 \text{ rad sec}^{-1}, \quad V = 10^{-6} \text{ cm}^3, \\ |x(\omega_{fi})|^2 &= 2 \times 10^{-33} \text{ cm}^2 \text{ sec} \end{aligned}$$

(deduced from data on cross section<sup>1</sup>), we obtain

$$P = 5 \times 10^{-6}, \quad (6')$$

$$n = 2 \times 10^{10}. \quad (7')$$

In their experiments, Peticolas, Goldsborough, and Rieckhoff, and Singh and Stoicheff, find the number of fluorescent photons to be  $10^8$  and  $10^{11}$  (within a factor of 10), respectively.

Finally, we wish to suggest that the theory proposed in this note in relation to anthracene might also be applied to the interpretation of other experimental results on two-photon transitions in solids.<sup>9</sup>

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<sup>1</sup>W. L. Peticolas, J. P. Goldsborough, and K. E. Rieckhoff, *Phys. Rev. Letters* **10**, 43 (1963).

<sup>2</sup>S. Singh and B. P. Stoicheff, *J. Phys. Chem.* **38**, 2032 (1963).

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

<sup>4</sup>M. Goepfert-Mayer, *Ann. Physik* **9**, 273 (1931); D. A. Kleinman, *Phys. Rev.* **125**, 87 (1962); R. Braunschtein, *Phys. Rev.* **125**, 475 (1962); R. Braunschtein and N. Ockman, *Phys. Rev.* **134**, A499 (1964).

<sup>5</sup>E. Corinaldesi and F. Strocchi, *Relativistic Wave Mechanics* (North-Holland Publishing Co., Amsterdam, 1963), p. 274.

<sup>6</sup>We recall that in this case completeness is expressed by the relation

$$\sum_i \psi_i^*(\vec{x}) \psi_i(\vec{x}') + \int \psi_f^*(\vec{x}) \psi_f(\vec{x}') d\omega = \delta(\vec{x} - \vec{x}').$$

<sup>7</sup>G. Fornaca, M. Iannuzzi, and E. Polacco, to be published. In this paper the transition probability resulting from the term  $\vec{A}^2$  is studied in detail.

<sup>8</sup>M. S. Lipsett and L. Mandel, *Nature* **199**, 553 (1963); L. Waszak, *Proc. IEEE* **52**, 428 (1964).

<sup>9</sup>J. J. Hopfield, J. M. Worlock, and Kwangjai Park, *Phys. Rev. Letters* **11**, 414 (1963); W. Kaiser and C. G. B. Garrett, *Phys. Rev. Letters* **7**, 229 (1961).