EFFECTIVE CROSS SECTIONS OF TWO-PHOTON ABSORPTION IN ORGANIC MOLECULES

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We have determined the effective cross sections of two-photon absorption for organic molecules of different symmetries: anthracene, acridine, and 3-aminophthalimide, and compared the absorption of anthracene in solution and in crystal form.

For molecules with an inversion center, the transitions that are allowed in the single-photon approximation should be forbidden in the two-photon one. In this connection, it is of interest to compare the two-photon absorption for a molecule with symmetry center - anthracene - and for molecules of lower symmetry.

The two-photon absorption was determined from the intensity of the luminescence induced by a ruby laser. Unlike in other investigations, the two-photon and single-photon excitation intensities were compared directly. This has made it possible to eliminate corrections for the photomultiplier sensitivity, luminescence light gathering, and luminescence quantum yield. A Q-switched laser (rotating prism) of low power was used (up to 10 MW/cm^2 = 3 x 10^{25} photons/cm^{2}sec) to avoid various extraneous effects. The excitation was with an unfocused beam, thereby ensuring practically constant energy density along the laser beam in the investigated substance. The single-photon excitation was by means of a flash lamp with filters transmitting a narrow region near λ = 347 nm, corresponding to double the ruby-laser frequency. In the case of single-photon excitation the absorption was complete, since the investigated substances had high absorption coefficients (5 x 10^4 cm^{-1} for anthracene at 347 nm). The produced luminescence was received by the same photomultiplier. The laser and flash lamp energies were determined with a calorimeter. When the laser was used for excitation, part of the light was diverted to a second photomultiplier to monitor the magnitude of the excited pulse. The luminescence pulses obtained by single-photon and two-photon excitation were compared with an oscilloscope. This yielded the magnitude of the two-photon absorption under the assumption that the single-photon abosrption is complete.

The intensity of the two-photon-excitation luminescence was measured for different laser-beam energies. The energy was varied by attenuation with calibrated filters. This made it possible to check the quadratic dependence of the luminescene intensity on the laser power.

At our values of laser power the absorption was weak, and it can be assumed that the luminescence intensity per cm of laser beam is proportional to the absorption coefficient in cm^{-1}. The absorption of the investigated solutions (in ethyl alcohol) with concentration of approximately 10^{-3} M/l was ~10^{-7} cm^{-1}, and that of the anthracene crystal (1 cm thick) reached 0.02 cm^{-1}.

Substance	10^{50} cm^{4}sec
Anthracene, crystal	25
Anthracene, solution	3.5
Acridine, solution	2
3-aminophtalimide, solution	2

The table lists the obtained values of δ (cm^{4}sec/photon-molecule), equal to the ratio of the effective cross sections σ (cm^2) to the flux F (photons/cm^{2}sec), i.e., quantities no longer dependent on the power.

As seen from the table, the effective cross sections of two-photon absorption are very close for the three investigated molecules. This indicates that the symmetry of a complex molecule does not influence the probability of two-photon absorption. The values of δ for the anthracene crystal exceeded by several times those for the solution. We assumed that this was due to the influence of the crystal surface on the luminescence yield in the case of single-photon excitation. The reduced yield of single-photon excitation obtained in our method of measurement yielded too high a value of the two-photon absorption. However, a control experiment with a cleaned surface did not confirm this assumption. The value obtained for δ for an anthracene solution was higher than indicated earlier [1], even with allowance for the possible error (by a factor $\sim$2) in the determination of the laser energy density.

An estimate of the two-photon absorption coefficient for allowed transitions can be obtained, following Kleinman's paper [2], using the formula

$$\delta = \frac{\sigma}{F} = (e^2/mc^2)^2 \frac{f_1 f_2 \overline{\cos^2 \vartheta_1 \cos^2 \vartheta_2}}{cn^2 \overline{\nu}^2 \overline{\Delta \nu}^2},$$

where f_1 and f_2 are the oscillator strengths for transitions in the intermediate state, ϑ_1 and ϑ_2 are the angles between the light-wave vector and the dipole moment of these transitions, and $\overline{\Delta \nu}$ (in cm^{-1}) is the half-width of the absorption band. Putting $f_1 = f_2 = 1$ and $\overline{\Delta \nu} \sim 5000$ cm^{-1}, we obtain $\delta \sim 10^{-49}$ cm^{4}sec. The values of δ measured by us agree with this estimate in order of magnitude.

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

CAUSES OF FORMATION OF A RADIATION PEAK BEHIND A SHOCK WAVE IN A NONEQUILIBRIUM GAS

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A number of recent papers [1,2] report experimental observation of a radiation peak behind a shock wave. Radiation from a nonequilibrium relaxing gas greatly exceeds the radiation level after equilibrium is reached. Attempts to explain this phenomenon were not successful. We show here that the causes of the radiation peak are: (i) nonequilibrium state