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DOUBLE PHOTON EXCITATION IN ORGANIC CRYSTALS

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Although ruby lasers[1-3] have been used for studying two-photon processes, absorption, and fluorescence in inorganic crystals,[4] no examples of two-photon processes in the broad band spectra of organic molecules have as yet been reported. We have detected two-photon excitation in a number of polycyclic aromatic molecular crystals from the 6943Å line of a ruby laser by observing the resultant blue-green (4000 to 5000Å) fluorescent bands.

The red light from one end of the ruby laser was passed through a red pass filter and focused in a region of ~10^{-6} cm^3 on a powder sample. The fluorescent light from the powder was filtered through a blue-green pass filter, which removed the laser light and then was focused on a photomultiplier. The light from the other end of the laser was picked up by a photocell monitor, and the signals from both photocells were fed through identical networks into a dual-beam oscilloscope. The background in the fluorescence signal due to stray light from the laser was <1% of the observed signal and was obtained by repeating the experiment with a suitable blank in place of the sample. A time constant was intentionally put into the phototube circuits to provide integration of the individual laser spikes. During the laser flash a maximum photon flux of 3×10^{23} photons cm^{-2} sec^{-1} was obtained in the active region for a time of 2×10^{-4} sec. The total number of fluorescent photons omitted during this time was estimated to be 5×10^7, 10^8, and 10^9 for pyrene, anthracene, and benzpyrene, respectively.

Figure 1 shows a plot of the log of the fluorescent intensity versus that of the exciting intensity for benzpyrene. The slope of 2, corresponding to a square-law relationship between intensity of fluorescence and excitation, indicates a double-quantum effect. Possible excitation of the fluorescence by harmonics of the laser light generated in the sample was ruled out experimentally. When the sample was irradiated with 3471 Å from a monochromator, the ratio of fluorescent intensity to transmitted exciting light was 400. When laser excitation was used, no 3471Å radiation could be detected. The limit of detectability was 10^{-4} compared to the fluorescent intensity. In the case of benzpyrene the fluorescent spectrum excited by the laser was measured, by placing a monochromator in front of the photomultiplier, and found to be identical to that obtained by uv irradiation[5] within the accuracy of our measurements.

All of the hydrocarbons examined (see Table I) possessed one or possibly two types of absorption bands in the uv at the double-quantum frequency (28 800 cm^{-1}) of the ruby laser. The two bands which often overlap at this wavelength are the transition $^1A\rightarrow{}^1L_a$ and the transition $^1A\rightarrow{}^1L_b$ which have been assigned for a larger number of polycyclic aromatic hydrocarbons.[6-8] Furthermore, the strongly forbidden singlet-triplet transition, $^1A\rightarrow{}^3L_a$, of anthracene lies very close to the single-quantum frequency (14 400 cm^{-1}), and this is

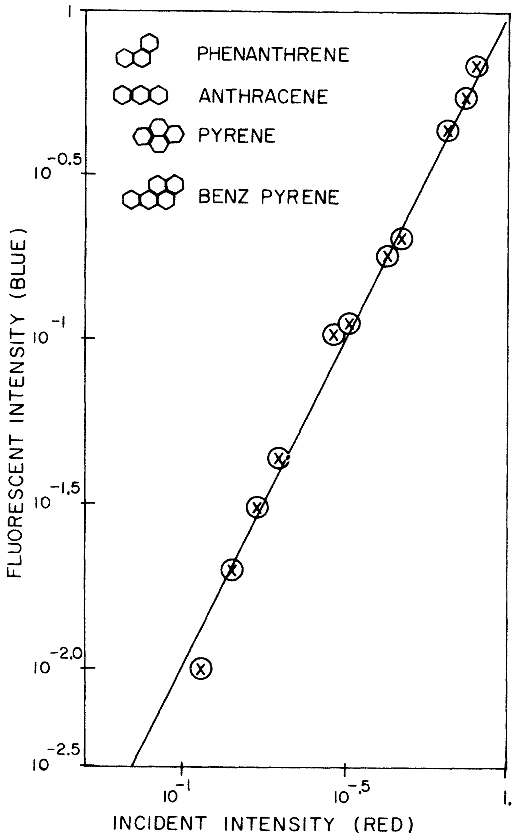

FIG. 1. Fluorescent intensity vs incident intensity for benzpyrene.

probably true for 3, 4-benzpyrene as well. Consequently, we might imagine our double-quantum transition to occur by one of three different mechanisms: $A \xrightarrow{2h\nu} {}^1L_a$; $A \xrightarrow{2h\nu} {}^1L_b$; and ${}^1A \xrightarrow{h\nu} {}^3L_a \xrightarrow{h\nu} ({}^1L_a$ or ${}^1L_b)$. The second possibility has been tentatively ruled out by our experiments on phenanthrene. Here, the ${}^1A \rightarrow {}^1L_b$ band is separated from the L_a band, and only the L_b band is located at the double-quantum transition.[6] No double excitation was observed from phenanthrene. The third possibility has been ruled out by experiments on pyrene where the triplet level lies at 16 800 cm^{-1}. Even allowing for a fairly broad triplet energy band, it appears very unlikely that excitation into this band could be effected from a 14 400-cm^{-1} excitation source. The absorption cross sections required for this process to cause an effect of the magnitude observed appear to be unrealistically large, even in the case of benzpyrene and anthracene.

Kleinman[9] gives a theory which semiquantitatively agrees with the results on a similar experiment on Eu^{++} in CaF by Kaiser and Garret.[4] For benzpyrene and anthracene, our results are also within one or two orders of magnitude of those calculated from his theory. However, there appears to be no way the theory can be used to predict the differences in effect which we have observed between different molecules.

A direct double-quantum transition to a level accessible by a single-quantum transition is generally forbidden.[10] LaPorte's rule requires a

Table I. Absorption cross section and classification for single-quantum excitation and fluorescent intensity resulting from double-quantum excitation.

Compound	Absorption cross section[a] (10^{-18} cm^2) at 28 800 cm^{-1}	Singlet-singlet bands[b] at 28 800 cm^{-1}	Fluorescence intensity (arbitrary units)
Phenanthrene	0.1	${}^1A \rightarrow {}^1L_b$	0
Pyrene	1	${}^1A \rightarrow {}^1L_a$ ${}^1A \rightarrow {}^1L_b$	1
Anthracene	3	${}^1A \rightarrow L_a$ ${}^1A \rightarrow L_b$	2
3,4 benzpyrene	50	${}^1A \rightarrow {}^1L_a$ ${}^1A \rightarrow {}^1L_b$	30

[a] The absorption cross sections are estimated from measurements in dilute solution and, thus, will not be exactly correct for the crystal.

[b] See references 6-8.

change in parity for dipole transitions. Double-quantum transitions would occur with no change in parity. In asymmetric molecules, however, these selection rules will not be strict and both single- and double-quantum transitions are possible to the same level by different components of the dipole operator.

A correlation is shown in Table I between the absorption cross sections for the $A \rightarrow {}^1L_a$ single-quantum transitions and the observed intensity of fluorescent light. We feel that this correlation of double-quantum excitation with single-quantum absorption probabilities is reasonable, since it is highly likely that there are many levels to which double-quantum transitions are allowed in the absorption bands of these complex molecules. Consequently, we suggest that such a two-quantum excitation is taking place in these molecules and that this phenomenon should be a general one for organic molecules of this type.

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ABSORPTION OF ELECTROMAGNETIC WAVES IN QUANTUM AND CLASSICAL PLASMAS*

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Recently some calculations of the absorption of electromagnetic waves in a plasma have been given. The absorption in classical plasmas has been treated with an elementary model by Dawson and Oberman[1] and by Oberman, Ron, and Dawson[2] via the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy. Reference 2 gives a complete classical derivation of the high-frequency conductivity of a plasma, taking into account properly collective effects. Another approach to the classical problem has been given by Perel' and Eliashberg[3] via a quantum-mechanical diagram technique. Although the latter approach can be systematized, most of the results are in error, because of the nonsystematic treatment of the ion role, and thus differ from the results of references 1 and 2.

The purpose of the present Letter is to give results of a systematic study of the absorption problem in *both classical* and *quantum* plasmas. We study the problem using the same temperature-dependent Green's function method as that employed in reference 2. We are, however, able to correct their procedure to give a consistent treatment of multispecies quantum and classical systems. In the classical limit complete agreement with reference 2 is obtained. Furthermore, we get an exact expression for the absorption coefficient valid for all temperatures, which covers both quantum and classical domains.

The outline of the calculation is as follows: We start from Kubo's[4] expression for the conductivity in terms of the autocorrelation function of the current operators. We then evaluate the leading asymptotic contribution to the conductivity by applying the well-known diagram technique of the temperature-dependent Green's function, taking into account the diagrams given in Fig. 1. These diagrams represent the exact contribution to the conductivity in quantum (classical) plasma, when the number of particles in the Bohr (Debye) sphere is large, the frequency is higher than the collision frequency, and the wavelength of the in-