LUMINESCENCE OF CHLOROPHYLL

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Abstract

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LUMINESCENCE OF CHLOROPHYLL UNDER EXCITATION BY A RUBY LASER

When complex molecules are excited in the second (short-wavelength) band of the absorption spectrum, it is known that rapid deactivation of the molecule (internal conversion) occurs from the level S_2^* (the second excited singlet level) to the first level S_1^*, from which emission of the fluorescence spectrum takes place. This circumstance produces, in the condensed phase, an independence of the emission spectrum from the wavelength of the exciting light over a large extent of the absorption spectrum (1, 2). However, from the level S_2^*, as from the level S_1^*, intercombination conversion to the fundamental triplet level is above all possible, $S_1^* \rightsquigarrow T_0$, $S_2^* \rightsquigarrow T_0$ (3); in addition, nonradiative deactivation of the molecule with its transfer to the ground level S_0 (internal conversion) is possible, and in some cases energy transfer from the second excited level S_2^* (4, 6) and (5)—see, however, (23)—(external conversion). Moreover, at high excited levels, intersection with potential curves (surfaces) may lead to predissociation or stereoisomerization. All these factors may lead, in the condensed phase, to a dependence of the quantum yield on the wavelength of the exciting light (7). The radiative transition $S_2^* \to S_0$ is known as an anomaly only for azulene and its derivatives (8), and also for diphenylene (9), which do not give the usual fluorescence from the first excited singlet level S_1^*. Grabowski (10) first evaluated the possibility of observing fluorescence in the transition from the second excited singlet level S_2^* to the ground S_0. The quantum yield in such a process should, by this estimate, be approximately equal to $5 \cdot 10^{-5}$ in the presence of normal fluorescence $S_1^* \to S_0$ with a quantum yield of the order of unity.

The experiments described below were carried out with the aim of experimentally detecting emission in the transition from the second excited singlet level S_2^* of the molecule to the ground one. McClain' s attempt (11) to detect such emission proved unsuccessful. It is quite clear that special conditions are necessary for observing such a weak phenomenon. The energy difference between the levels $S_2^* - S_1^*$ is usually small, and the possible weak emission from the level S_2^* will be substantially weakened as a result of its overlap by the first singlet-singlet absorption band (self-filtering action). Therefore tetrapyrrole pigments (chlorophyll and its analogs—phthalocyanines) were chosen, since, owing to the large energy interval $S_2^* - S_1^* = 500$ cm^{-1} between the levels and the narrowness of

Fig. 1

Figure 1: Fig. 1

the absorption bands, the expected emission band from the second excited level will overlap only weakly with the first singlet-singlet absorption band. However, if intense direct excitation is applied within the limits of the second singlet-singlet absorption band, parasitic scattered light will inevitably arise, masking the desired emission. Therefore, to excite up to the second level S_2, use was made of a phenomenon that occurs in polyacene crystals ([12]) and their solutions ([13]) under the action of the powerful radiation of a ruby laser.

The radiation of the ruby laser "Razdan" K-4-2, with a pulse energy of 1 J, operating in a periodic regime at a frequency of 2 Hz, was focused on the object by a lens through an KS-17 light filter. The luminescence of the object was isolated with a ZMR-3 mirror monochromator (linear dispersion in the region studied: 20 mμ/mm). The photon-counting method was used to record the luminescence spectrum. The photoelectric recording circuit was assembled from standard units: a wide-band amplifier with a discriminator, a counting-rate meter, and an electronic potentiometer. To improve the accuracy of the measurements, radiation at certain wavelengths was also recorded over equal time intervals by counting the number of photons with an PP-8 scaling device. As the light receiver we used an FEU-64 photomultiplier, cooled with liquid-nitrogen vapor and powered by a standard high-voltage stabilizer.

The objects of the study were solutions of chlorophyll a ($5 \cdot 10^{-3}$ M), methylchlorophyllide ($5 \cdot 10^{-3}$ M), magnesium phthalocyanine (10^{-4} M) in ethanol, chlorophyllin ($5 \cdot 10^{-3}$ M) in methyl alcohol, and also metal-free phthalocyanine (10^{-4} M) in dioxane. The solutions were in glass cuvettes 3 mm thick, and observations were made perpendicular to the exciting light. The ZMR-3 monochromator in combination with crossed light filters—SZS-22 of 5 mm thickness in front of the monochromator slit and KS-17 of 7 mm thickness in front of the source (laser)—created conditions that practically completely eliminated the parasitic scattered light of the source.

Fig. 1. 1 —anomalous luminescence of methylchlorophyllide (conc. 10^{-3} M in ethanol) under laser excitation (694.3 mμ); 2 —absorption spectrum of methylchlorophyllide; 3 —triplet-triplet absorption of methylchlorophyllide ([22])

In solutions of chlorophyll a, chlorophyllin, and methylchlorophyllide, a blue-green luminescence is clearly visible to the eye along the path of the laser beam. The spectrum of this luminescence at 290° K is a band at 430-510 mμ with a maximum at 480 mμ (Fig. 1), shifted to the long-wavelength side relative to the Soret band (430 mμ) of the absorption spectrum. The observed band may be attributed to the expected radiative transition from the S_2^* level to the ground level S_0.

On the other hand, this band can be interpreted as triplet-triplet emission (tran-

Fig. 2. Diagram of energy levels and transitions in methyl chlorophyllide. Energy values are given in reciprocal centimeters; radiative transitions (straight arrows) are given in millimicrons.

Figure 2: Fig. 2. Diagram of energy levels and transitions in methyl chlorophyllide. Energy values are given in reciprocal centimeters; radiative transitions (straight arrows) are given in millimicrons.

sition $T_1^* \to T_0$), analogous to that observed in an electric discharge through naphthalene vapor (^{14}), and also upon photoexcitation of a frozen triphenylene solution (^{15}).

However, this process is unlikely, since the excitation energy of two photons in the laser radiation (29000 cm^{-1}) is insufficient to transfer the molecule into the state T_1^*, from which triplet-triplet emission is possible.

Four processes may be envisaged that cause excitation of the molecule to the high level S_2^* upon absorption of photons of lower energy:

1. Addition of two photons of a powerful pulse through an intermediate virtual level (^{12,16}).
2. Two-photon excitation through the first excited singlet state during its lifetime of $2 \cdot 10^{-9}$ sec, measured in Ref. (^{17}).
3. Accumulation, under a powerful pulse, of a high concentration of triplet molecules, followed by triplet-triplet annihilation (^{18,19}).

In the latter variant, when the energies of two triplet molecules of chlorophyll and its analogs are combined, the transfer of one of them to the second excited singlet level is energetically allowed, as follows from the diagram in Fig. 2.

It should be noted that, under the same experimental conditions, in a solution of the fluorescing magnesium phthalocyanine and metal-free phthalocyanine it was not possible to observe, in the path of the laser beam, any emission in the spectral region close to the second singlet absorption band. This result casts doubt on the possibility of excitation of chlorophyll, chlorophyllin, and methyl chlorophyllide by mechanisms 1 and 2, since the energy of two photons supplied to the phthalocyanine molecule in such processes (29 000 cm^{-1}) was sufficient to transfer it to the excited state.

Fig. 2. Diagram of energy levels and transitions in methyl chlorophyllide. Energy values are given in reciprocal centimeters; radiative transitions (straight arrows) are given in millimicrons.

If variant 3 is valid, the observed emission is delayed fluorescence, which should have a lifetime on the order of 10^{-4} sec. When a solution of methyl chlorophyllide and others is cooled to 77°K, with formation of a glassy medium, the luminescence described above is not observed upon laser excitation, which does not contradict the assumption of an addition of the energies of two triplet molecules.

Indeed, under these conditions diffusion is eliminated and, consequently, triplet-triplet annihilation is hindered, which leads to a drop in the intensity of the delayed fluorescence. It should be noted that deoxygenation of the solutions in vacuum does not affect the intensity of the emission.

Interpretation according to mechanism 3 explains the absence of the expected emission in phthalocyanines, since in the latter, presumably as in copper phthalocyanine, the triplet level lies energetically lower ([20–22]) than in chlorophyll, and the energy supplied to the phthalocyanine molecule during triplet-triplet annihilation is insufficient to transfer it to the S_2^* level.

Finally, for chlorophyll it is in principle possible to reach the level by absorption of a second photon by the triplet molecule (total energy $25\,000\ \mathrm{cm}^{-1}$), with violation of the prohibition of the intercombination optical transition. We therefore consider this process less probable.

The possibility that emission arises as a result of the formation, under such powerful light exposure, of short-lived radical or ion-radical forms in a reversible reaction with the solvent, with emission upon their recombination, is unlikely, since, as mentioned above, no emission is observed for phthalocyanines—analogs of chlorophyll in photochemical behavior.

Interpretation 3 is contradicted, however, by the absence of an effect of dissolved oxygen, known to be a strong deactivator of triplet molecules.

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Note: Figure translations are in progress. See original paper for figures.