

Zero-field line splitting in the fluorescence spectra of complex molecules

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Zero-field splitting of the triplet level ($0.095 \pm 0.005 \text{ cm}^{-1}$) has been observed for the first time ever in the phosphorescence spectrum of a complex molecule (coronene) and registered. New possibilities of investigating the parameters of the T_1 state by optical methods are indicated.

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1. It is known that molecules of organic compounds have, besides the singlet electronic levels S_n , also excited triplet levels T_n . The lowest triplet level T_1 is metastable and plays a most important role in the conversion and transmission of electron-excitation energy. Optical transitions $T_1 \rightarrow S_0$ are responsible for phosphorescence.

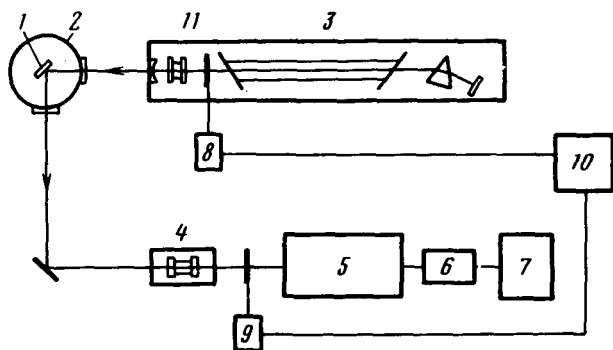


FIG. 1. Experimental setup: 1—sample; 2—optical helium cryostat; 3—argon laser; 4—pressure-scanned Fabry-Perot interferometer; 5—DFS-12 spectrometer; 6—FEU-79 photomultiplier; 7—photon-counting system; 8,9—electromagnetic shutters; 10—electronic shutter-control system; 11—frequency selector (interferometer).

The threefold degeneracy of the triplet level of a molecule is lifted, strictly speaking, even in the absence of an external magnetic field, owing to the spin-spin and spin-orbit interactions and to the influence of the surrounding crystal field.^[1] In complex organic molecules, the decisive role is played by spin-spin dipole interaction. The splitting of the spin sublevels in a zero field is characterized by the parameters D and E [the ZFS parameters, Fig. 3(a)]. The ZFS parameters (which are the principal parameters in the theory of triplet states of molecules) are quite small, usually 0.01 – 0.1 cm^{-1} . These parameters are experimentally determined by EPR methods. In optical phosphorescence spectra, zero-field splitting has never been observed, since the band widths in these spectra are larger by several orders of magnitude than the indicated values.

In our previous studies^[2,3] and in a number of subsequent ones it is shown that at low temperatures the spectral bands of many organic molecules in solution are in the main inhomogeneously broadened. Methods of eliminating this broadening from fluorescence,^[2-4] phosphorescence,^[5] and absorption spectra^[6] have been developed for monochromatic excitation.

In the present paper, using laser excitation, we have registered and measured experimentally, for the first time ever, zero-field splitting of a triplet level in the optical phosphorescence spectrum. We present here the first results obtained for coronene in butyl bromide, and point out new possibilities of determining the characteristics of triplet states of complex molecules from optical spectra.

2. The experimental setup (Fig. 1) included a spectrometer with a high-sensitivity photon counter crossed with a pressure-scanned Fabry-Perot interferometer. (Working gas—air; dispersion region— 0.312 cm^{-1} ; sharpness coefficient > 12). The phosphorescence was excited with an argon laser ($\lambda = 5145.3$ \AA) in the region of the $0-0$ transition $T_1 \leftarrow S_0$.¹¹ An interferometer placed in the resonator laser made it possible to reduce the lasing line width to 0.01 cm^{-1} (at a power 0.6 W). The instrumental

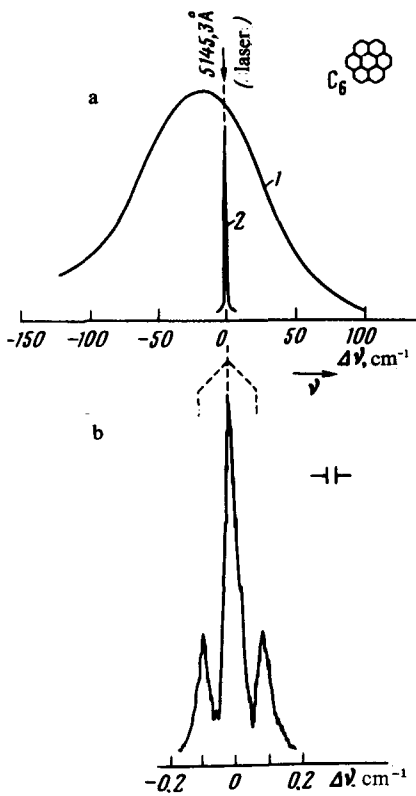


FIG. 2. Band of 0-0 transition in the phosphorescence spectrum of coronene in butyl bromide at 4.2 K; a) under ordinary $S_1 \leftarrow S_0$ excitation $\lambda_{\text{Hg}} = 313$ and 365 nm (curve 1) and 365 nm (curve 1) and monochromatic excitation with an argon laser (curve 2). DFS-12 spectrometer. b) Interferometric recording of the 0-0 line following excitation with an argon laser (with line width $\approx 0.01 \text{ cm}^{-1}$).

resolution (convolution of the instrumental function of the scanning interferometer with the contour of the exciting line) was $0.027 \pm 0.003 \text{ cm}^{-1}$.

Complete suppression of the scattered laser radiation that was at resonance with the registered phosphorescence line was attained by using a two-shutter phosphoroscope. One of the shutters was placed in the laser resonator and shut off the lasing during the phosphorescence registration time.

The concentration of the coronene solutions in the butyl bromide was $\approx 5 \times 10^{-4}$ mole/liter. All the measurements were made at 4.2 K.

3. Figure 2(a) (curve 1) shows the 0-0 band in the phosphorescence spectrum of coronene under ordinary $S_1 \leftarrow S_0$ excitation. Its width is $\approx 120 \text{ cm}^{-1}$. When the excitation is with a laser line $\approx 0.1 \text{ cm}^{-1}$ wide and the recording is with resolution $\approx 1 \text{ cm}^{-1}$, the band is narrowed down by two orders of magnitude [curve 2 on Fig. 2(a)] yet it remains inhomogeneously broadened, and the observed width is determined by the spectral resolution. When the laser line is narrowed down to $\approx 0.01 \text{ cm}^{-1}$ and the resolution is improved (to 0.027 cm^{-1}), the zero-field structure is clearly observed in the spectrum [Fig. 2(b)]. It is clearly seen that in the latter case, instead of a single line, the spectrum contains a "triplet". This triplet is directly connected with the zero-field scattering. Let us analyze this result in greater detail.

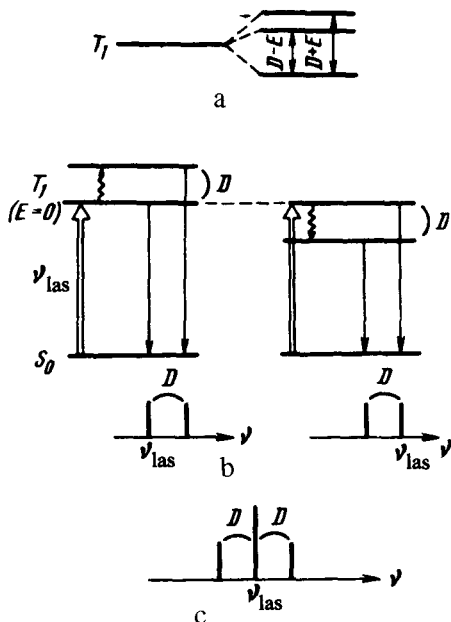


FIG. 3. a) Zero-field splitting parameters; b) levels and spectral doublets of two types of centers excited by the same laser line ($D \neq 0$, $E = 0$); c) the "triplet" produced in the spectrum.

For molecules with threefold and higher-order symmetry axes (perpendicular to the molecule plane) we have $E = 0$.^[1] The coronene molecule has a sixfold axis and its triplet level should split only into two components with $\Delta\nu = D$.^[2] Under conditions of inhomogeneous broadening, the same laser line excites centers of two types, each with its own sublevels [Fig. 3(b)]. Each type of center should give doublets in the emission spectrum. But the doublet components at the laser frequency coincide and a "triplet" is present in the spectrum [Fig. 3(c)].^[3] Obviously, the distances between its components yield directly the parameter D . In our case of coronene, measurements yielded $D = 0.095 \pm 0.005 \text{ cm}^{-1}$ (in good agreement with the 0.096 cm^{-1} obtained by EPR^[7]).

4. Interferometric recording of the 0-0 line in the phosphorescence spectrum makes it possible to estimate its homogeneous width. The observed width of the central component is $0.042 \pm 0.004 \text{ cm}^{-1}$. This yields $0.02 \pm 0.01 \text{ cm}^{-1}$ (with allowance for the instrumental contour width) for the homogeneous width of the 0-0 line.^[3]

5. Thus, the foregoing data demonstrate the possibility of directly observing zero-field splitting in optical spectra of organic molecules. To obtain more complete information it is necessary to measure, besides the frequencies of the lines, also their widths, shapes, intensities, and the corresponding temperature dependences. The optical spectra can then yield information that supplements substantially the EPR data. Thus, for example, from the relative intensity and width of the components of the zero-field scattering multiplet in the optical spectrum it is possible to determine, in principle, the following: the radiative lifetimes of the spin sublevels, the contribution made to the zero-field splitting parameters by the external crystal field (as revealed by the broadening of the hybrid components in comparison with the simple component), the spin-lattice relaxation constants, and others.

¹As shown in^[5], to eliminate the inhomogeneous broadening from the phosphorescence spectra it is necessary to produce direct excitation in the region of the forbidden T_1-S_0 transition (rather than ordinary S_1-S_0 excitation). The coefficient of absorption on this transition is very small ($\epsilon_{T_1-S_0} < 10^{-2}$ for coronene), and this is the main difficulty of experiments aimed at direct observation of the triplet state.

²Transitions with two zero-field components of the T_1 level in the phosphorescence spectrum of coronene are symmetry-forbidden.^[1] This forbiddenness is lifted, however, in butyl bromide, apparently because the symmetry of the free molecule is destroyed (D_{6h}). This is confirmed by the fact that in this solvent the symmetry-forbidden line 0-0 becomes most intense in the spectrum.^[5]

³If $E \neq 0$, the spectrum will contain "multiplets" of 7 lines.

⁴At higher concentrations, the homogeneous width of the 0-0 line increases somewhat. This may be due to the resonant interaction of the molecules in the concentrated solution.

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