ON THE NATURE OF MULTIPLETS IN QUASILINEAR SPECTRA OF ORGANIC MOLECULES

PHYSICS

1968

SovietRxiv

Abstract

Full Text

UDC 535.37

PHYSICS

R. I. PERSONOV, O. N. KOROTAEV

ON THE NATURE OF MULTIPLETS IN QUASILINEAR SPECTRA OF ORGANIC MOLECULES

(Presented by Academician Ya. B. Zel' dovich, 24 VI 1968)

1. A characteristic feature of the quasilinear spectra of complex molecules, obtained in frozen crystalline *n*-paraffin solutions by the method of E. V. Shpol' skii (^{1}), is their "multiplet" structure. At present the generally accepted point of view (see, for example, ($^{1-4}$)) is that the "multiplets" in quasilinear spectra are due to the presence in the crystal matrix of several types of spatially separated emitting centers. Owing to the slight differences in the conditions in which different types of centers are found, the positions of their electronic levels differ somewhat, and the corresponding vibronic progressions prove to be shifted on the wavelength scale, which leads to a multiplet pattern of the spectrum.* This interpretation is confirmed in studies of the dependence of the character of multiplets on the method of preparing the sample (^{2}), on the concentration of impurity molecules (^{6}), and in studies of luminescence-excitation spectra for individual components of the multiplet (^{4}).

However, in our opinion, a number of facts are difficult to reconcile with the assumption that multiplets are caused only by the existence of different emitting centers in the *n*-paraffin crystal. Among such facts one should first of all include the very great complexity of the multiplets observed in spectra at 4° K. Thus, for example, in the spectrum of 3,4,6,7-dibenzpyrene at 4° K, multiplets containing as many as 22 components are observed (^{7}). It is also difficult, for example, to reconcile with the hypothesis of different centers the presence, in the spectra of a number of molecules in the region of the O—O transition, of nonresonance lines ($^{7-9}$), and the substantial difference in the character of multiplets in the spectra of related compounds having identical geometrical dimensions and shape, in one and the same solvent (phthalocyanines (^{9,10})).

In connection with the above, we carried out special studies of quasilinear spectra, and especially of the region of the O—O transition, of a number of compounds of the porphyrin class at 4° K. The choice of these compounds for this type of investigation is due, on the one hand, to the fact that already at 77° K some of them ($^{8-11}$) display very complex multiplets in their spectra; on the

Figure 1: Fluorescence spectra and long-wavelength absorption regions of phthalocyanines in *n*-decane at 4°K

Figure 1: Figure 1: Fluorescence spectra and long-wavelength absorption regions of phthalocyanines in *n*-decane at 4°K

other hand, these compounds absorb in the red region of the spectrum, which makes it possible to use, for excitation of fluorescence, the almost monochromatic radiation of a helium–neon laser and to compare the structure of the spectra under excitation by a laser and by ordinary sources. The present communication gives the results of a study of the spectra of three phthalocyanines: free phthalocyanine H_2-PhC and its magnesium and zinc complexes Mg-PhC and Zn-PhC.

---

[*] The question of how the conditions corresponding to different types of centers differ has not yet been clarified. Suggestions have been made concerning different orientations of impurity molecules in the *n*-paraffin crystal ([5]), the connection between the multiplet structure of the spectra and the existence of polymorphic forms of *n*-paraffins and the possible presence in them of rotational isomers ([1]), etc.

To the article by R. I. Personov and O. N. Korotaev, p. 815

Fig. 1. Fluorescence spectra (*a, b, c*) and long-wavelength absorption regions (a', b', c') of phthalocyanines in *n*-decane at 4°K (fluorescence was excited by the 6328 Å laser line)

2. In view of the very poor solubility of Mg- and Zn-PhTC in *n*-paraffins, these preparations were first dissolved in octyl alcohol, and then their solutions were introduced into *n*-decane in the form of a small additive (1 : 10). The solutions under study were poured into a spatula-shaped cuvette (1 to 3 mm thick), frozen in nitrogen, and then quickly transferred to a cryostat with liquid helium.

Fluorescence was excited by the 6328 Å line of an OKG-12 helium–neon laser or by the light of a DRSh-1000 mercury lamp with an SZS-9 filter (transmission region 3500–6000 Å). In studying the absorption spectra, the radiation source was a 500 W motion-picture projection incandescent lamp. To eliminate the fluorescence excited by the incandescent lamp and distorting the absorption spectrum in the region of the O–O transition, a red filter (KS-15) was placed between the lamp and the sample when this region was investigated. The spectra were photographed on an ISP-67 spectrograph with a camera $F = 1500$ mm (dispersion 16 Å/mm at 6500 Å), and in a number of cases were recorded photoelectrically on the same instrument by means of an attachment assembled on the basis of an FEU-38 photomultiplier. The wavelengths of the spectral lines were determined with an accuracy of 0.5–1 Å.

3. In Fig. 1 (see insert to p. 824) the fluorescence spectra and the long-wavelength absorption region of three phthalocyanines at 4°K are presented. These spectra differ from the spectra at 77°K $^{(8-11)}$ by a considerably smaller line width and by the resolution of individual bands into groups of lines, as a result of which the number of lines observed in the spectrum approximately doubled (in the liquid spectra we measured 80-100 lines) *. The presence of complex multiplets is characteristic of all the spectra studied. In the region of the O-O transition the multiplets in each of the spectra number about 20 lines. Throughout the entire spectrum one can also trace multiplets corresponding to the group of the most intense lines of the O-O multiplet. Thus, for example, in the fluorescence spectrum of H_2-PhTC doublets are especially clearly manifested (with $\Delta\nu = 20$ cm^{-1}); in the spectrum of Mg-PhTC, quartets; and in Zn-PhTC, quintets (Fig. 1).

It is of interest to compare the fluorescence spectra under excitation by the light of a mercury lamp and by a laser. A preliminary study of the absorption spectra at 4°K showed that, whereas in the absorption spectrum of Zn-PhTC there is a 6329 Å line, close in wavelength to the laser radiation line (6328 Å), in the absorption spectra of H_2-PhTC and Mg-PhTC such lines are absent. Therefore it might have been expected that, upon irradiation with laser light, only the fluorescence of Zn-PhTC would be effectively excited, and that, in accordance with the hypothesis of different centers, single lines corresponding to the emission of the excited center would appear in its spectrum instead of multiplets. However, in all cases laser excitation proves to be considerably more effective than lamp excitation (the exposures under laser excitation are reduced by approximately an order of magnitude), while the character of the multiplets and of the entire spectrum as a whole is basically the same as under excitation by lamp light **. The explanation of this lies in the fact that, as the investigations showed, in all three compounds the narrow absorption maxima in the region of the 6328 Å laser line are situated on a sufficiently intense diffuse background (band), in which excitation of fluorescence also takes place. This indicates that that the impurity centers responsible for quasi-line spectra also possess, in addition, diffuse absorption.

* A separate paper will be devoted to a detailed analysis of the vibrational structure of these spectra at 4°K.

** In Mg- and Zn-PhTC, on going from lamp excitation to laser excitation, an insignificant redistribution of the intensities in the multiplet takes place. It is observed more distinctly in Zn-PhTC: the first lines of the quintets 6662, 6978, 7011 Å, etc., become somewhat enhanced. However, this redistribution cannot be understood from the standpoint of the hypothesis of different centers. The 6329 Å line in the absorption spectrum of Zn-PhTC, as vibrational analysis of the spectrum has shown, does not belong to the sequence beginning with the origin line 6662 Å (Fig. 1).

Fig. 2. Photoelectric recording of part of the principal multiplet of the fluorescence spectrum of Zn-PhTC in n-decane at $T = 4^\circ$ K (a) and $T = 77^\circ$ K (b)

Figure 2: Fig. 2. Photoelectric recording of part of the principal multiplet of the fluorescence spectrum of Zn-PhTC in n-decane at $T = 4^\circ$ K (a) and $T = 77^\circ$ K (b)

In connection with the main question touched upon in the present work, it was of special interest to compare in detail the principal multiplets in the fluorescence and absorption spectra in the spectra studied. Such a comparison immediately reveals a characteristic feature in the absorption spectra of Mg- and Zn-PhTC: in the principal multiplets of the absorption spectrum there are intense lines that give rise to the corresponding electronic-vibrational sequences, but have no analogs in the fluorescence spectrum. Such nonresonant intense lines are the 6659 Å line in the absorption spectrum of Mg-PhTC and the 6638 Å line in the absorption spectrum of Zn-PhTC. (Alongside the indicated intense lines in the region of the 0—0 transition in the absorption and fluorescence spectra there is also a number of weaker nonresonant lines, the nature of which requires further investigation.) From the standpoint of ideas about the existence of different emitting centers in the *n*-paraffin crystal, it must be assumed that those centers to which these nonresonant intense absorption lines and the corresponding electronic-vibrational sequences correspond either do not luminesce (at 4° K), or transfer the excitation energy to other centers whose electronic levels are located somewhat lower.

Fig. 2. Photoelectric recording of part of the principal multiplet of the fluorescence spectrum of Zn-PhTC in *n*-decane at $T = 4^\circ$ K (a) and $T = 77^\circ$ K (b)

The first is improbable. The second, apparently, also falls away, since migration of energy should be very sensitive to a change in impurity concentration, whereas dilution by a factor of 5-10 of the already low-concentration ($\sim 10^{-6}$ mole/l) investigated solutions does not change the indicated spectral picture. Therefore it is natural to connect the indicated lines of the principal multiplet with one impurity center and to assume that even in one center, in the region of the first electronic transition, several closely spaced levels can exist. The absence in the fluorescence spectrum of the resonant lines 6659 Å for Mg-PhTC and 6638 Å for Zn-PhTC and of the corresponding vibrational repetitions in this case means that at 4° K the corresponding levels are practically unpopulated (at 4° K $kT \ll \Delta h\nu \sim 55$ cm^{-1}). If this is so, then one may expect that upon raising the temperature to 77° K, when $kT \sim \Delta h\nu$, owing to appreciable population of the higher levels, the corresponding short-wavelength lines will appear in the fluorescence spectrum. This in fact occurs. Special experiments showed that in the fluorescence spectrum of Zn-PhTC, upon gradual increase of the temperature of the sample from 4° to 77° K, the 6638—6641 Å* line appears and gradually increases, as does the corresponding vibrational sequence.

Figure 2 shows photoelectric recordings of part of the origin multiplet of the fluorescence spectrum of one and the same Zn-PhTC sample at two temperatures, illustrating what has been said. A similar, though less pronounced, effect is also observed for Mg-PhTC. In its fluorescence spectrum at 77°K, the short-wavelength line 6659–6662 Å and its vibrational repetitions, absent at 4°K, appear distinctly.

The experimental facts presented above indicate that at least some of the lines of complex multiplets may be associated with one and the same emitting center.

The question arises as to the origin of closely spaced levels belonging to a single center. In our case of phthalocyanines, certain hypothetical considerations may be advanced. Indeed, whereas the H_2-PhTC molecule belongs to the point symmetry group D_{2h}, the Mg- and Zn-PhTC molecules belong to the group D_{4h} (12), to which doubly degenerate electronic levels correspond. The presence in Mg- and Zn-PhTC molecules of closely spaced levels may be connected with the removal of degeneracy by symmetry. This removal of degeneracy can in principle be caused either by the action of an external crystalline field on the molecular electronic levels, or by the interaction of intramolecular electronic and vibrational motions (the Jahn—Teller effect (13)). It should also be noted that, in connection with the question of the nature of the multiplets, the new theoretical treatment of the interaction of π-electrons in a complex molecule (14), leading to a multiplet pattern of the spectrum, is of interest. However, this important and interesting problem still awaits its final solution.

The authors express their gratitude to E. V. Shpol'skii for his constant attention to and interest in their work.

Moscow State
Pedagogical Institute
named after V. I. Lenin

Received
20 VI 1968

REFERENCES

1. E. V. Shpol' skii, *UFN*, **71**, 215 (1960); **77**, 321 (1962); **80**, 255 (1963).
2. E. V. Shpol' skii, L. A. Klimova, *Optics and Spectroscopy*, **7**, 852 (1959).

---

* Upon increasing the temperature, a slight long-wavelength shift of the absorption and fluorescence spectra of Zn- and Mg-PhTC occurs. Thus, for example, the Zn-PhTC line having at 4° K a wavelength of 6638 Å has at 77° K a wavelength of 6641 Å.

3. S. Leach, *J. Phys.*, **28**, No. 5-6, 134 (1967).
4. G. M. Svishchev, *Optics and Spectroscopy*, **18**, issue 4, 614 (1965).
5. E. J. Bowen, B. Brocklehurst, *J. Chem. Soc. London*, 1955, 4320.
6. L. Pesteil, A. Ciais, *C. R.*, **242**, 528 (1959).
7. L. A. Klimova, Candidate' s dissertation, Moscow, 1963.
8. R. I. Personov, *Optics and Spectroscopy*, **15**, issue 1, 61 (1963).
9. R. I. Personov, O. N. Korotaev, *Problems of Radiophysics and Spectroscopy*, part 1, issue 3, Moscow, 1967, p. 71 (Proceedings of the Second Interuniversity Conference on Radiophysics and Spectroscopy, Moscow State Pedagogical Institute named after V. I. Lenin, 1-6 VI 1965).
10. F. Litvin, R. I. Personov, *DAN*, **136**, 798 (1961).
11. A. N. Sevchenko, K. N. Solov' ev et al., *DAN*, **169**, No. 1, 77 (1966).
12. G. P. Gurinovich, A. N. Sevchenko, K. N. Solov' ev, *UFN*, **79**, issue 2 (1963).
13. H. A. Jahn, E. Teller, *Proc. Roy. Soc. A*, **161**, 220 (1937).
14. V. Z. Kresin, *Phys. Lett.*, **24A**, 749 (1967); *DAN*, **177**, 1306 (1967).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.