QUASILINEAR ELECTRONIC SPECTRA OF METAL DERIVATIVES OF TETRABENZOPORPHIN AND PHTHALOCYANINE

PHYSICS

1966

SovietRxiv

Abstract

Full Text

UDC 535.333

PHYSICS

Academician of the Academy of Sciences of the BSSR A. N. SEVCHENKO, K. N. SOLOV' EV,
A. T. GRADYUSHKO, S. F. SHKIRMAN

QUASILINEAR ELECTRONIC SPECTRA OF METAL DERIVATIVES OF TETRABENZOPORPHIN AND PHTHALOCYANINE

Metalloporphyrins, i.e., complex compounds of porphyrin derivatives with metals, deserve careful study as analogues of compounds of major importance for biology—chlorophyll, heme, cytochromes, and others. A spectroscopic study of chlorophyll-like molecules should provide valuable information on the electronic structure of the chlorophyll molecule, which is essential for understanding the process of photosynthesis.

The introduction of a metal atom into the center of the porphyrin ring and related structures is accompanied by sharp changes in the electronic absorption spectra and by less significant changes in the fluorescence spectra, which at room temperature remain two-banded and approximately mirror-symmetric to the two longest-wavelength absorption bands (see the review (ˆ1)). These phenomena are due, in general terms, to an increase in molecular symmetry from D_{2h} to D_{4h} upon introduction of the metal and to the influence of the nature of the metal on the intensity of the 0—0 band.

Until recently, the fine structure of the electron-vibrational spectra of porphyrins had not been studied. The use of E. V. Shpol' skii' s method of quasilinear spectra made it possible to solve this problem for a number of metal-free porphyrin derivatives (^{2}-6). However, for the only metalloporphyrin investigated —Mg-phthalocyanine—the quasilinear spectrum obtained was considerably less sharp than that of metal-free phthalocyanine (ˆ2). This circumstance, together with the complex character of the main "multiplet," hindered interpretation of the spectrum.

For the magnesium and zinc complexes of tetrabenzoporphin (TBP) and tetrabenzo-tetraazaporphin (phthalocyanine, Pc), we have succeeded in finding conditions under which the quasilinear spectra are sufficiently sharp and the main multiplet sufficiently simple to permit a vibrational analysis of the fluorescence and absorption spectra. The work of selecting conditions for obtaining quasilinear spectra of metalloporphyrins is extremely laborious and,

Figure 1

Figure 1: Figure 1

unfortunately, largely empirical. As in the case of the previously studied metal-free compounds ([4-6]), we used the method of dissolving additives to introduce the substance into a hydrocarbon matrix (*n*-octane). It turned out that the best additional solvent for the magnesium complexes studied is absolute ethanol, and for the zinc complexes, a pyridine–acetone mixture. A small addition of solution was introduced into octane immediately before freezing (the experimental temperature was 77° K). The spectra were recorded on an ISP-51 spectrograph with a UF-84 camera ($F = 800$ mm) using Infra-720 photographic plates (for TBP) and Infra-760 (for Pc). The compounds studied were prepared and purified by T. F. Kachura: Mg-TBP according to (^7, ^8) with subsequent chromatography on Al_2O_3 using an acetone–trichloroethylene mixture as developer; Mg-Pc according to (^9); and the zinc complexes from spectrally pure TBP (^5) and commercial phthalocyanine by reaction with zinc acetate in boiling pyridine.

As already mentioned, the fluorescence spectra of metalloporphyrins at room temperature consist, as a rule, of two bands with frequency-

with an interval of about 1500 cm^{-1}. Between them there is sometimes observed a less intense band, which is especially pronounced in metallophthalocyanines. The spectra of the compounds studied (Fig. 1) differ by an increased intensity of the 0–0 band, due to the removal of the quasi-forbiddenness of the long-wavelength electronic transition as a result of benzo- and aza-substitution. The absorption spectra are approximately mirror-symmetric to the fluorescence spectra, in accordance with Levshin' s law of mirror symmetry of absorption and emission spectra, but the frequency interval between the absorption bands in the TBP complexes is smaller than in the fluorescence spectra, while in the PC complexes it is somewhat larger.

Fig. 1. Absorption and fluorescence spectra of Mg-phthalocyanine (solid curves) and Zn-tetrabenzoporphin (dashed curves) at room temperature

In frozen octane solutions, the spectra described split into a series of quasilines; moreover, the first band corresponds to an intense principal multiplet and a group of weak vibrational satellites with small frequencies (which justifies the name 0–0 band), while the second and intermediate bands correspond to groups of lines, indicating the complex character of these bands (see Fig. 2). Under the conditions we selected, only two components of the principal multiplet possess appreciable intensity, one of them being much more intense than the other, so that the quasilinear spectrum appears as consisting of singlets (except for Mg-TBP). The absorption spectra begin with a principal "multiplet," resonantly coinciding with the principal "multiplet" of fluorescence, and likewise consist practically of singlets, with the exception of Zn-TBP, where the absorption

Quasi-line fluorescence spectra

Figure 2: Quasi-line fluorescence spectra

spectrum has a "doublet" structure. The reason for the latter is unclear; it may be connected with the presence of two forms differently solvated by the solvent additives—pyridine and acetone.

On the basis of the data obtained, a vibrational analysis was carried out and the frequencies of the normal vibrations active in the electronic spectra of the compounds studied were determined. The results of the analysis of the fluorescence spectra, i.e., the frequencies of the ground state, are summarized in Table 1, where data are also presented for metal-free TBP ([5]) and PC ([3]).

Comparison of the spectra of the metal derivatives with the spectra of the free bases makes it possible to draw a number of conclusions. First, the general character of the vibrational structure changes little upon introduction of the metal: the frequencies change only slightly, by no more than 50 cm^{-1}; the same normal vibrations are the most active in the spectrum. However, for some vibrations the activity changes appreciably upon introduction of the metal. Secondly, it is possible to correlate the majority of frequencies in both types of compounds—TBP and PC—with the exception of the most active frequencies in the interval 1500-1600 cm^{-1}. Thirdly, the changes of the corresponding vibrations in the series free base—magnesium—zinc are analogous for TBP and PC, which confirms the kinship of the indicated vibrations and points to a similar influence of the metal atom on the dynamics of the molecule in both cases. Fourthly, most vibrations can be assigned to two types: the first type is characterized by an increase in frequency upon introduction of magnesium, the second by a decrease in frequency upon introduction of magnesium; in both cases, on going from magnesium to zinc the frequencies increase. The first type includes, mainly, low frequencies, and the second includes frequencies above 1000 cm^{-1}. It may be supposed

Fig. 2. Quasi-line fluorescence spectra at 77° K in *n*-octane: *a* —Mg-phthalocyanine, *b* —Zn-phthalocyanine, *c* —Mg-tetrabenzoporphin, *d* — Zn-tetrabenzoporphin.

Table 1*

TBP ([5]), ν, cm^{-1}	Int.	TBP, ν, cm^{-1}	Int.	Mg-TBP, ν, cm^{-1}	Int.	Zn-TBP, ν, cm^{-1}	Int.	Mg-PC, ν, cm^{-1}	Int.	Mg-PC, ν, cm^{-1}	Int.	Zn-PC, ν, cm^{-1}	Int.	PC ([8]), ν, cm^{-1}	Int.	PC, ν, cm^{-1}	Int.
118	med.	130	very weak	137	very weak	138	very weak	148	very weak	139	med.						
127	med.	160	extr. weak	153	very weak	182	weak	173	extr. weak	184	weak						

TBP ([5]), ν, cm^{-1}	TBP, int.	Mg-TBP, ν, cm^{-1}	Mg-TBP, int.	Zn-TBP, ν, cm^{-1}	Zn-TBP, int.	Mg-PC, ν, cm^{-1}	Mg-PC, int.	Zn-PC, ν, cm^{-1}	Zn-PC, int.	PC ([8]), ν, cm^{-1}	PC, int.
218	int.	238	very weak	244	very weak	244	very weak	270	very weak	235	weak
351	extr. weak	366	extr. weak	–		354	extr. weak	344	extr. weak	–	
480	extr. weak	485	weak	486	weak	485	med.	484	med.	488	weak
510	extr. weak	519	extr. weak	512	extr. weak	561	extr. weak	–		546	weak
566	extr. weak	586	extr. weak	–		588	weak	590	med.	572	med.
629	extr. weak	643	very weak	–		611	extr. weak	611	extr. weak	–	
698	int.	701	med.	703	med.	683	int.	682	int.	684	int.
723	med.	738	med.	740	med.	748	int.	749	int.	726	int.
801	med.	829	med.	827	weak	830	med.	834	weak	801	int.
–		–		–		950	weak	949	weak	1009	weak
1018	extr. weak	1011	extr. weak	1025	extr. weak	1011	extr. weak	1018	extr. weak	1028	very weak
1045	extr. weak	1068	extr. weak	1066	extr. weak	1113	very weak	1107	very weak	1085	weak
1125	extr. weak	1124	extr. weak	1123	very weak	1144	med.	1144	med.	1143	int.
1156	extr. weak	1154	extr. weak	1159	weak	–		–		–	
1223	med.	–		1205	extr. weak	1188	weak	1181	very weak	1188	med.
1250	med.	1245	med.	1253	med.	1222	weak	1225	weak	1233	very weak
–		–		–		1308	very weak	1308	very weak	1318	weak
1331	med.	1331	med.	1335	int.	1347	med.	1346	int.	1348	int.
1418	extr. weak	–		–		1424	extr. weak	1433	extr. weak	1404	weak
1451	extr. weak	1444	very weak	1456	weak	1444	extr. weak	1455	extr. weak	1455	med.
–		–		–		1513	int.	1514	int.	1517	med.
1526	extr. weak	1530	extr. weak	1531	very weak	1562	very weak	–		–	
1596	int.	1556	int.	1570	med.	1582	int.	1540	med.	1555	int.
1624	int.	1612	int.	1624	int.	–		–		–	

TBP (^{5}), ν, cm^{-1}	int.	Mg-TBP, ν, cm^{-1}	int.	Mg-TBP, ν, cm^{-1}	int.	Zn-TBP, ν, cm^{-1}	int.	Zn-TBP, ν, cm^{-1}	int.	Mg-PC, ν, cm^{-1}	int.	Mg-PC, ν, cm^{-1}	int.	Zn-PC, ν, cm^{-1}	int.	Zn-PC, ν, cm^{-1}	int.	PC (^{8}), ν, cm^{-1}	int.	PC, ν, cm^{-1}	int.
										1651 = 1513+138	weak										

* Conventional designations: TBP—tetrabenzoporphin, PC—phthalocyanine; int.—intense, med.—medium intensity, weak—weak, very weak—very weak, extr. weak—extremely weak (estimate of the intensities of the corresponding quasi-lines).

It may be assumed that the first type is due to stabilization of the macrocycle upon introduction of a metal as a result of the conjugation effect, which increases in connection with the rise in symmetry from D_{2h} to D_{4h}, while the second type is due to the superposition on this effect of a stronger effect associated with the disappearance of the repulsion of the two central hydrogen atoms upon introduction of the me-

Table 2

Mg-TBP, ν, cm^{-1}	Mg-TBP, int.	Zn-TBP, ν, cm^{-1}	Zn-TBP, int.	Mg-PC, ν, cm^{-1}	Mg-PC, int.	Zn-PC, ν, cm^{-1}	Zn-PC, int.
–		133	very weak	138	extr. weak	123	very weak
160	extr. weak	–		177	med.	170	
220	very weak	240	very weak	243	very weak	268	very weak
362	extr. weak	–		–		–	
483	very weak	479	weak	481	med.	483	weak
–		–		540	extr. weak	–	
584	extr. weak	–		584	weak	580	med.
643	very weak	–		607	weak	–	
697	med.	694	int.	679	int.	676	int.
740	very weak	723	weak	747	int.	740	med.
817	med.	820	med.	805	med.	840	med.
–		–		939	med.	942	weak

Mg-TBP, ν, cm^{-1}	Mg-TBP, int.	Zn-TBP, ν, cm^{-1}	Zn-TBP, int.	Mg-PC, ν, cm^{-1}	Mg-PC, int.	Zn-PC, ν, cm^{-1}	Zn-PC, int.
–		–		1006	very weak	1011	extr. weak
1020	extr. weak	1025	weak	1088	extr. weak	–	
1094	very weak	1078	med.	1132	med.	1130	med.
1116	very weak	1090	med.	–		–	
1174	very weak	–		1180	weak	–	
1222	very weak	1251	int.	1225	med.	1246	weak
–		–		1295	extr. weak	1290	weak
1327	int.	1335	int.	1346	int.	1336	med.
–		–		1407	weak	–	
1437	very weak	1422	weak	–		1443	very weak
–		–		1497	very weak	1495	very weak
1514	med.	1505	int.	–		–	
–		1550	weak	1565	med.	–	
1605	weak	1595	weak	–		–	
				1628 = 1497 + 138	int.	1610 = 1495 + 123	med.
				1672 = 1497 + 177	med.	1667 = 1495 + 170	int.
						1710 = 1495 + 225	med.
						1763 = 1495 + 268	weak

···of the metal. The increase in frequencies on going from magnesium to zinc indicates the stabilizing influence of the stronger complex-forming agent.

In the first excited state, as the analysis of the absorption spectra shows, the frequencies of the normal vibrations have values close to the frequencies of the ground state (see Table 2), with some frequencies being retained to an accuracy

of 2-3 cm^{-1}, i.e., within the experimental error, while others change (as a rule, decrease) more noticeably upon electronic excitation. The intensities of the transitions change more sharply.

Our data make it possible to determine the nature of the deviations from mirror symmetry in the spectra of the compounds studied. Although at room temperature the symmetry of the frequencies is violated while the symmetry of the band intensities is satisfactory ([1]), the low-temperature quasilinear spectra show that deviations from mirror symmetry are caused not by changes in the vibrational frequencies upon electronic excitation, but by differences in the probabilities of the corresponding vibronic transitions. In the absorption of TBP metal derivatives, transitions with vibrations in the range 1000-1400 cm^{-1} are relatively more intense, whereas in the fluorescence spectrum the most active vibrations are those near 1600 cm^{-1}, which leads to a decrease in the frequency interval between the bands of the absorption spectrum at room temperature. In the absorption spectra of PC metal derivatives, the combination frequencies corresponding to excitation together with the most active vibration near 1500 cm^{-1} of small vibrational quanta (100-300 cm^{-1}) are more intense than in the fluorescence spectra; as a result, the frequency interval between the absorption bands at room temperature is larger than between the fluorescence bands.

Since the lower excited state of metalloporphyrin molecules is doubly degenerate ([1]), in the low-temperature spectra one might have expected the manifestation of the Jahn-Teller effect, i.e., splitting of the degenerate level as a consequence of the interaction of electronic and vibrational motions. We believe, however, that the doublet structure observed in the quasilinear spectra of the compounds studied is not due to the Jahn-Teller effect, since an analogous doublet structure is observed for the less symmetric free bases, where there is no degeneracy. Therefore, the increased width of the quasilines, as compared with metal-free porphyrins, should be associated with this effect; i.e., in the present case the Jahn-Teller splitting does not exceed several reciprocal centimeters.

In conclusion, the authors express their gratitude to T. F. Kachura for preparing the compounds studied.

Institute of Physics
Academy of Sciences of the BSSR

Received
24 II 1966

CITED LITERATURE

1. G. P. Gurinovich, A. N. Sevchenko, K. N. Solov' ev, *UFN*, **79**, 173 (1963).

2. F. F. Litvin, R. I. Personov, *DAN*, **136**, 798 (1961).

3. R. I. Personov, *Optics and Spectroscopy*, **15**, 61 (1963).

4. A. N. Sevchenko, K. N. Solov' ev et al., *DAN*, **153**, 1391 (1963).

5. A. N. Sevchenko, K. N. Solov' ev et al., *DAN*, **161**, 1313 (1965).

6. S. F. Shkirman, K. N. Solov' ev, *Izv. AN SSSR, ser. fiz.*, **29**, 1378 (1965).

7. P. A. Barrett, R. P. Linstead et al., *J. Chem. Soc.*, 1940, 1079.

8. K. N. Solov' ev, S. F. Shkirman, T. F. Kachura, *Izv. AN SSSR, ser. fiz.*, **27**, 767 (1963).

9. G. T. Byrne, R. P. Linstead, A. R. Lowe, *J. Chem. Soc.*, 1934, 1017.

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