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EFFECT OF DEUTERATION ON QUASILINE ELECTRONIC-VIBRATIONAL SPECTRA OF PHTHALOCYANINE

S. F. Shkirman,[a] **N. A. Sokolov,**[b] **V. K. Konstantinova,**[b] **and K. N. Solov'ev**[a*]

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Quasiline electronic-vibrational spectra of fluorescence and absorption (excitation of fluorescence in selective recording) of the molecules of phthalocyanine deuterated around the periphery of benzene rings (H_2Phc-d_{16}) and the center of the macrocycle (D_2Phc) are obtained. The vibrational frequencies of the ground state are almost insensitive to this deuteration (except for vibrations with the participation of angular deformations). In excitation spectra, changes in deuteration are more pronounced due to the effects of nonadiabatic vibronic interaction of the vibrational sublevels of the S_1 state and of the purely electronic level S_2.

Keywords: *phthalocyanine, deutero derivative, quasiline spectrum, frequency of normal vibration, electronic-vibrational interaction.*

The spectroscopy of phthalocyanine-type molecules continues to attract the attention of researchers in view of the numerous practical applications of phthalocyanines (many of which are industrial dyes) and their structural affinity to biologically important tetrapyrrole pigments such as porphyrins and metalloporphyrins. The metal-free phthalocyanine (H_2Phc) is one of the first three tetrapyrroles (together with dimethyl ether of protoporphyrin IX and Mg-phthalocyanine) for which quasiline spectra (QLS) of fluorescence were obtained [1]. Thereafter, the characteristics of the quasiline spectra of fluorescence and absorption of H_2Phc were investigated in [2–9].

A detailed interpretation of vibronic quasiline spectra of H_2Phc is difficult because of its complicated molecular structure. For the solution of such problems by comparing experimentally determined vibrational frequencies with the data of calculation of normal vibrations, it would be most advantageous to have information on the influence of isotopic substitution and, first of all, of deuteration on experimental spectra.

In this work, we present the results of studying the quasiline fluorescence and absorption (fluorescence excitation) spectra of two deutero derivatives of H_2Phc:

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[*] To whom correspondence should be addressed.

[a]Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus, 70 F. Skorina Ave., Minsk, 220072, Belarus; e-mail: llum@imaph.bas-net.by; [b]Belarusian State University, Minsk, Belarus.
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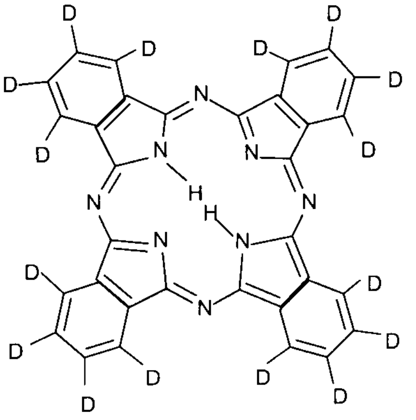
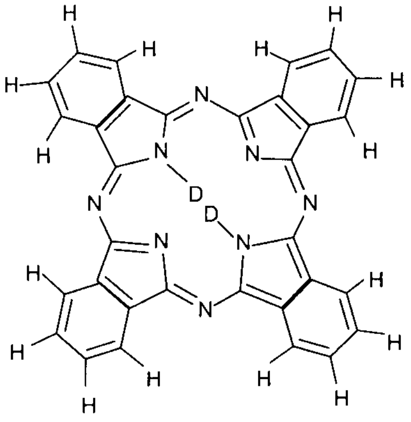
H_2Phc-d_{16}



D_2Phc



in *n*-octane matrices at 77 K.

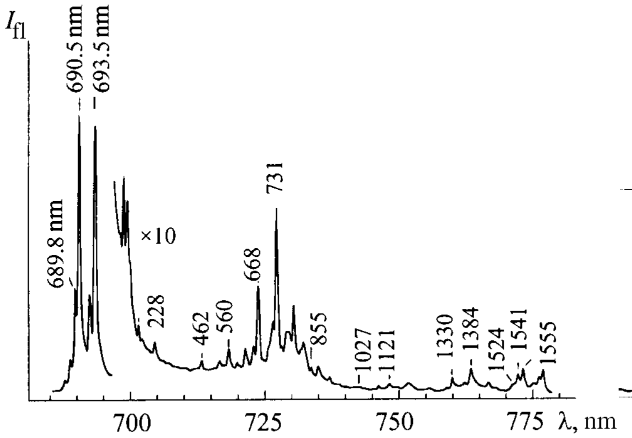
Synthesis of H_2Phc-d_{16} was made via the sodium complex of phthalonitrile-d_4. The latter was prepared in five stages from *o*-xylol-d_4, which in turn was obtained by deuteration of *o*-xylol in D_2SO_4–D_2O at 20°C by a modified technique [10]. The synthesis of Na_2Phc-d_{16} was made by interaction of phthalonitrile-d_4 with sodium amylate (a solution of metallic sodium in *n*-amyl alcohol) at 138–140°C. The treatment of Na_2Phc-d_{16} with an aqueous solution of H_2SO_4 (dilution 1:2 by volume) at 0°C for 2 h with stirring gave H_2Phc-d_{16}. For purification purposes, the product was redeposited from concentrated H_2SO_4 at 0°C. The center of the molecule was deuterated (production of D_2Phc) by introducing several drops of CD_3OD into a prepared *n*-octane solution of H_2Phc.

The quasiline spectrum was recorded on a spectrometric setup (described in [11]) with two monochromators. The quasiline spectra of fluorescence were measured on excitation by total radiation in the 360–600-nm region. The quasiline spectra of fluorescence excitation were recorded in selective recording of the intense components of the head "multiplet."

The quasiline spectrum of the fluorescence of H_2Phc-d_{16} is presented in Fig. 1. The head "multiplet" consists of the four most intense components. However, we can separate two major quasilines at 690.53 nm (14,482 cm^{-1}) and 693.49 nm (14,420 cm^{-1}). The relative intensity of their "satellites" at 689.81 and 692.46 nm depends respectively on the means of preparation of a sample, and it decreases sharply when the sample is subjected to slow freezing. We will denote the type of center ("site") with ν_{00} = 14,482 cm^{-1} by 1, that with ν_{00} = 14,420 cm^{-1} by 2, and the "satellites" by 1′ and 2′ (see Fig. 1). The fluorescence excitation spectra of the same object for sites 1 and 2 are shown in Fig. 2.

The results of vibration analysis of the obtained quasiline spectra of H_2PhC-d_{16} are listed in Table 1. As is seen, there are marked differences in the vibrational structure of the fluorescence spectra of H_2Phc and H_2Phc-d_{16} (our data for H_2Phc agree well with the data of [1–3, 7]). Thus, the frequency of the vibration (most active in the fluorescence spectrum) of an H_2Phc molecule in the ground state (S_0) 683 cm^{-1} is decreased to 668 cm^{-1}, whereas the frequencies of the vibrations of H_2Phc 1141 and 1355 cm^{-1} are decreased to 1121 and 1330 cm^{-1}, respectively. Conversely, the group of frequencies in the 1500–1550-cm^{-1} region virtually does not change on deuteration of benzene rings. New vibrational frequencies 126, 818, and 855 cm^{-1} appear in the spectrum of H_2Phc-d_{16}. To interpret the isotopic shifts observed, we will carry out calculation of normal vibrations.

Let us focus our attention on the quasiline fluorescence excitation spectrum of impurity centers 1 and 2 of H_2Phc-d_{16}. Earlier [4], an interesting feature was revealed in H_2Phc. If, for the shortwave site 1 in the excitation spectrum, one broadened quasiline corresponds to the purely electronic transition $S_2 \leftarrow S_0$, then there is a "doublet" for site 2. This splitting is explained in [4] (see also [12]) by quantum-mechanical inter-



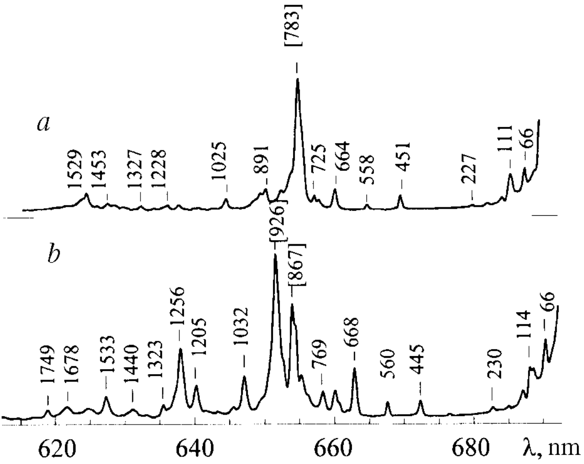


Fig. 1. Quasiline fluorescence spectrum of $H_2Phc\text{-}d_{16}$ in *n*-octane at 77 K. For the head "multiplet" the wavelengths are indicated in nm; for vibronic quasilines the frequencies of normal vibrations are given in cm^{-1} (for site 1 with λ_{00} = 690.5 nm).

Fig. 2. Quasiline fluorescence excitation spectrum of $H_2Phc\text{-}d_{16}$ in *n*-octane at 77 K (λ_{rec} = 690.5 (a) and 693.5 nm (b)). Given are the frequencies of normal vibrations (cm^{-1}) in the excited state S_1; the frequency intervals between the head quasiline and transitions with participation of the state S_2 are given in square brackets.

action of the purely electronic level S_2 with the vibrational sublevel of state S_1 (in the terminology of H. Herzberg [13] such an effect is called an electronic-vibrational analog of the Fermi resonance).

An analogous difference is also observed in $H_2Phc\text{-}d_{16}$. Site 1 (Fig. 2a) in the excitation spectrum has a very intense and somewhat broadened single quasiline that is separated from the $S_1 \leftarrow S_0$ 0–0-transition by 783 cm^{-1}. Beyond a doubt, it belongs to the 0–0-transition of $S_2 \leftarrow S_0$. Three very intense quasilines at 859, 867, and 926 cm^{-1} (the latter is the most intense one) are observed in site 2 (Fig. 2b); they are located from the 0–0-transition at a much larger distance than that given for site 1. In the quasiline spectrum of fluorescence in this region of vibrational frequencies there is a weak quasiline at 889 cm^{-1}. We may state that the S_2–S_1-interval in site 2 comes to about 900 cm^{-1} (i.e., the values of this interval in sites 1 and 2 differ markedly), and the frequency of the 0–0-transition of $S_2 \leftarrow S_0$ comes into resonance with the frequency of vibronic transition with participation of the vibration of B_{1g} symmetry, which in the state S_1 has the frequency ~880 cm^{-1} and probably corresponds to the indicated vibration in the ground state S_0. As a result, splitting by the type of the Fermi resonance occurs. We may assume that the low-frequency component of the Fermi resonance participates in an additional interaction that leads to its splitting into two frequencies.

Investigation of the fluorescence excitation quasiline spectra of sites 1′ and 2′ showed that splitting in the region of the 0–0-transition of $S_2 \leftarrow S_0$ is also typical of these sites, with splitting being insignificant for site 1′ and great for site 2′, but somewhat less than for site 2.

It is seen from Table 1 that in the remaining regions of the absorption spectrum the frequency intervals reckoned from the 0–0-transitions of $S_1 \leftarrow S_0$ of different sites agree satisfactorily with the vibrational frequencies of the ground state and among themselves. The regions 1200–1250 and 1600–1900 cm^{-1} in site 2 are an exception. In the first region we observe two intense broadened quasilines; in the second there are transitions with the participation of frequencies not typical of porphyrazines (the 1607-cm^{-1} frequency corresponds to the 1602-cm^{-1} frequency of site 1 and can belong to the valence C—C vibrations of benzene

TABLE 1. Frequencies of Normal Vibrations (in cm^{-1}) of an H_2Phc-d_{16} Molecule Active in the Fluorescence and Fluorescence Excitation Spectra

S_0	$S_1^{(1)}$	$S_1^{(2)}$	S_0	$S_1^{(1)}$	$S_1^{(2)}$
–	66	66	–	1065	1072
–	104 sh.	109	1121	1119	1123
113	111	114	–	1139 sh.	–
126	–	–	–	1158	1161
134 sh.	135	137	1193	1190	–
182	179	181	–	–	1205 (ampl.)
228	227	230	–	1228 (br.)	–
462	451	455	–	–	1256 (ampl., br.)
560	558	560	–	1277	–
592	–	597	1330	1327	1323
652	–	–	1384	–	1379
668	664	668	–	1394	–
718 sh.	713 sh.	718 sh.	–	1424 (br.)	1425 sh. (br.)
731	725	731	1470(?)	1453 (br.)	1440 (br.)
756 sh.	–	769	–		1480 (v.w.)
818	809 sh.	817 sh.	1524	1529	1533
855	841	839 sh.	1541	1545 sh.	–
889 (v.w.)	891	902 sh.	1553		1588 sh.
–	907 sh.	–	–	–	1598
–	929 sh.	–	–	1602 (v.w.)	1607
–	–	970 sh.	–	–	1678 (br.)
–	–	980 sh.	–	–	1749
1023	1025	1032	–	–	1926

Note. Characteristics of some of the quasilines: v.w. (very weak), ampl. (amplified), br. (broadened), sh. ("shoulder").

rings). It should be noted that the appearance of a larger number of vibronic transitions in the absorption spectra in comparison with the emission spectrum can be due to the activation of the incompletely symmetrical B_{1g} vibrations in an excited state as a result of interaction of the corresponding vibronic levels with the S_2 level.

Deuteration of the center of the H_2Phc molecule has a weak effect on the quasiline spectrum of fluorescence. We managed to record only the disappearance of the quasiline with the frequency 1357 cm^{-1} and the appearance of the 990-cm^{-1} frequency in D_2Phc. Changes in the excitation spectra were more noticeable. In particular, this refers to the region of the above-considered vibronic resonance. Site 2 of H_2Phc displays a well-expressed "doublet" of quasilines offset from the 0—0-transition by 867 and 923 cm^{-1} (the latter line is more intense and somewhat broadened asymmetrically from the shortwave side). Deuteration of the center complicates the picture: two quasilines of nearly the same intensity at 889 and 904 cm^{-1} are observed, whereas the intensity of the 862-cm^{-1} quasiline is noticeably smaller than that of the corresponding 867-cm^{-1} quasiline of H_2Phc. It was noted above that H_2Phc-d_{16} also displays three intense transitions. These facts point to the complex character of vibronic interaction in the case considered, viz., to the participation of more than one vibration (it is seen from Table 1 that the data for site 1 of H_2Phc-d_{16} display two vibrations (891 and 907 cm^{-1}) in the corresponding interval).

It should be noted that in site 1 the deuteration influences the S_2–S_1 interval and the shape of the $S_2 \leftarrow S_0$ quasiline. The changes of the S_2–S_1 interval of 788, 798, and 783 cm^{-1} in H_2Phc, D_2Phc, and H_2Phc-d_{16}, respectively, exceed the experimental error (2–3 cm^{-1} for intense quasilines). These changes can be explained only by the fact that the contour of the given quasiline is the envelope of forbidden vibronic transitions and therefore the observed S_2–S_1 interval is not a true one.

In the fluorescence excitation spectra, the region in which one can await the manifestation of deformation vibrations of B_{1g} symmetry with participation of the central N—H bonds (for example, by analogy with the data for tetrabenzoporphin [14, 15] and tetraazaporphin [16]) is complex and difficult to analyze because of the vibronic interactions considered above. Nevertheless, for different sites we managed to reveal three frequencies of vibrations in the S_1 state that disappear in N-deuteration of H_2Phc: 905 and 1205 cm^{-1} (site 1) and 1110 cm^{-1} (site 2). The 869, 988, and 1006 cm^{-1} frequencies appear in this case (the data for site 1). For comparison, the 907, 1020, and 1228 cm^{-1} frequencies in tetrabenzoporphin disappear in the ground state S_0 and the 864, 993, and 1053 cm^{-1} frequencies appear. Moreover, vibrational frequencies 1361 and 1373 cm^{-1} of the state S_1 of site 1 were revealed, which disappear in deuteration of the center and may correspond to the above-noted frequency of the ground state 1357 cm^{-1} (site 2).

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