



Nanostructural impurity centers of organic molecules in Shpolsky matrices: appearance in quasi-linear luminescence spectra.

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Introduction. Motivations

Phenomenon of quasi-linear luminescence spectra of complex organic molecules in solutions of n-paraffins at low temperatures, which was called the Shpolsky effect, was first observed in [1]. Later, these spectra have been found out to possess a multiplet structure with a different number of components, which are observed in the form of the similar band series located from each other at a distance of 10-100 cm⁻¹ along the entire electronic vibrational spectrum.

The multiplet structure was associated with the formation of different types of impurity centers, which were individual molecules that were in "different physical conditions" (or "different local fields") in polycrystalline solutions n-paraffins. At the same time, the model of the impurity center was not specified. The physical causes of a number of characteristic regularities in the structure of multiplets were not discussed, in particular, the doublet character of the spectra of the vast majority of studied aromatic molecules.

This work proposes a new approach to the explanation of the Shpolsky effect, based on the symmetry properties of the impurity molecule and the crystal matrix. It allows determining the number of components in the multiplet and modeling the structure of the impurity center, which is not taken into account in the previous interpretation.

Experimental results. Discussion

The analysis of the experimental results shows that the impurity molecules that were used to obtain a quasi-linear structure in the luminescence and absorption spectra are in most cases derived from the molecules of highly symmetrical aromatic compounds (naphthalene, anthracene, pyrene, etc.).

Table. Spectral characteristics of solid solutions of various molecules in n-hexane (* - for a solution in n-octane)

	Substance	ν_{01} , cm ⁻¹	ν_{02} , cm ⁻¹	$\Delta\nu$
1	Naphthalene	31162	31220	58
2	Pyrene	26860	26918	58
3	Diphenylene oxide	32959	33048	89
4	Diphenylene sulfide	30441	30367	74
5	1,5-dichloronaphthalene	30722	30826	104
6	2,6-dichloronaphthalene	30349	30432	83
7	2-fluoronaphthalene	31426	31446	20
8	Acenaphthene	31143	31191	48
9	Stilben*	29691	29922	231
10	1-methyl-3,4- besphenanthrene	26434	26497	63
11	2-methyl-3,4- besphenanthrene	26427	26574	147
12	8-methyl-3,4- besphenanthrene	26434	26610	176
13	Chrysen	27747	27777	30
14	1-methylpyrene	26817	26845	28
15	3-methylpyrene	26666	26688	22

All positions occupied by atoms in the structure of highly symmetrical molecules are divided into classes of equivalent positions. Therefore, when atoms which are located in equivalent positions in a symmetrical molecule are replaced by atoms (groups of atoms) of other chemical elements, a new chemical compound is formed, which can have several "optical isomers" with lower symmetry. In particular, the 2-fluoronaphthalene molecule has 4 isomers, as the fluorine atom replaces the hydrogen atom in one of the 4 possible equivalent positions in the naphthalene molecule: 2, 3, 6, and 7 (Fig. 1). If the 2-fluoronaphthalene molecule is placed in the unit cell of the n-hexane crystal in the general position (a crystal and an impurity do not have common symmetry elements), then all 4 equivalent positions of the free molecule in the crystal become non-equivalent, which corresponds to the formation of 4 impurity centers of different types. If the substitution takes place with preservation of the inversion center I of n-hexane crystal and the naphthalene nucleus of 2-fluoronaphthalene, then the formation of only two impurity centers of different types is possible, since equivalence is preserved only for positions 2, 6 and positions 3, 7. This explains the doublet in the luminescence spectra of 2-fluoronaphthalene in n-hexane.

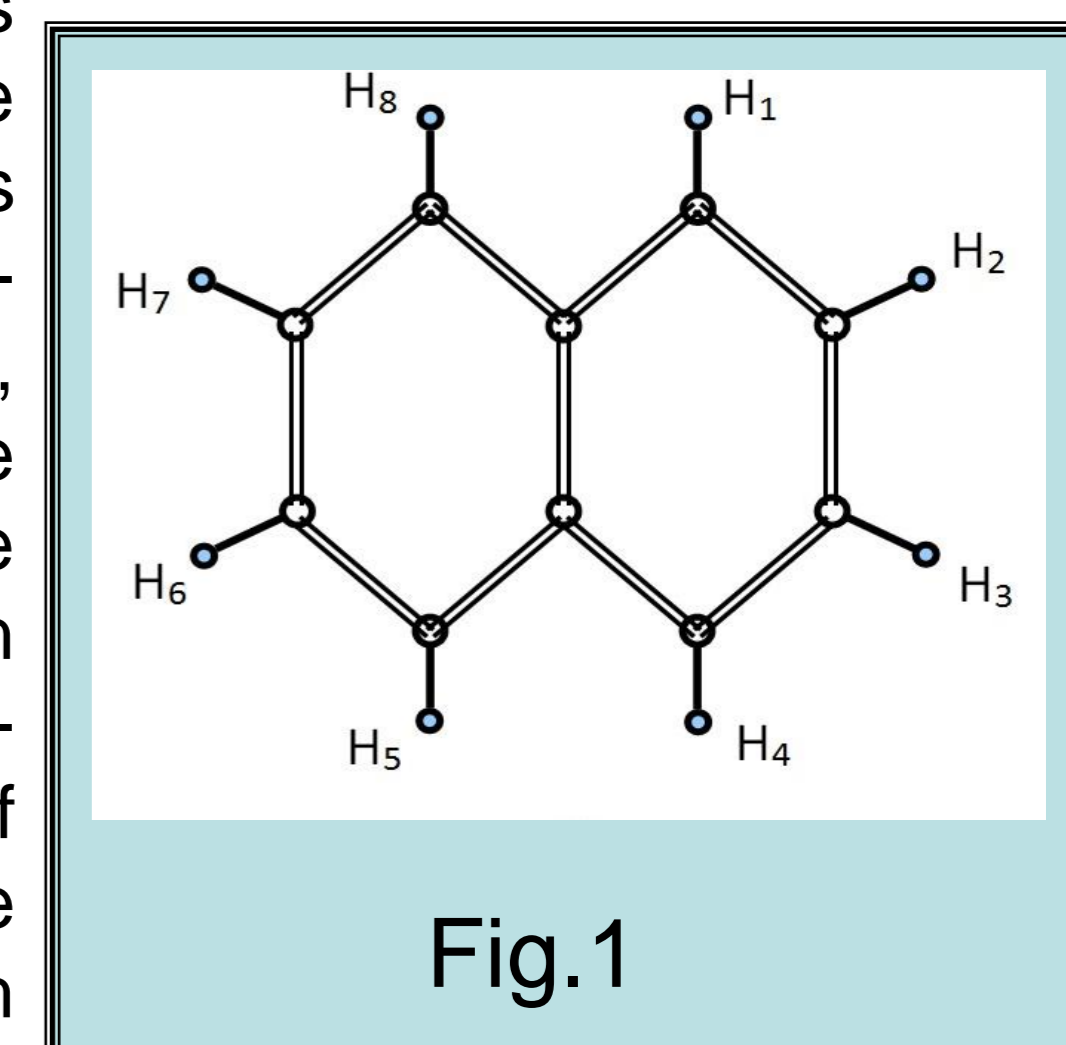


Fig.1

Different orientations, different positions of molecules are created by sequential replacement of equivalent hydrogen atoms in the free naphthalene molecule by substituent atoms (fluorine atoms), the coordinates of the naphthalene nucleus atoms do not change. Thus, based on these considerations, it becomes possible to determine the structure of each impurity center and find the number of impurity centers of different types [2].

The procedure for determining the number of impurity centers m is the following:

Determination of the optical isomers n_m for the given impurity. The 2-fluoronaphthalene molecule has 4 optical isomers (2, 3, 6, 7 positions).

Calculation of the equivalent position n_k for the same impurity in the n-paraffin crystal. Crystals of n-paraffins (n-hexane, n-heptane, n-octane) belong to low-symmetry space groups of symmetry C_i , with two symmetry elements, most often E and i. The symmetry operations of these groups determine the number of equivalent positions for the impurity in the crystal n_k . In the case of 2-fluoronaphthalene:

$$\begin{array}{llll} E(2) \rightarrow 2 & E(3) \rightarrow 3 & E(6) \rightarrow 6 & E(7) \rightarrow 7 \\ i(2) \rightarrow 6 & i(3) \rightarrow 7 & i(6) \rightarrow 2 & i(7) \rightarrow 3 \end{array}$$

One can see that two equivalent positions are formed in the crystal, and $n_k = 2$.

The number of impurity centers of different types m is equal to the ratio n_m/n_k . And for 2-fluoronaphthalene in n-hexane, we obtain $m = n_m/n_k = 4/2 = 2$. Indeed, experimentally, the fluorescence spectrum of 2-fluoronaphthalene in n-hexane is characterized by two series of identical bands, observed with initial peaks at $\nu_{01} = 31426 \text{ cm}^{-1}$ and $\nu_{02} = 31446 \text{ cm}^{-1}$.

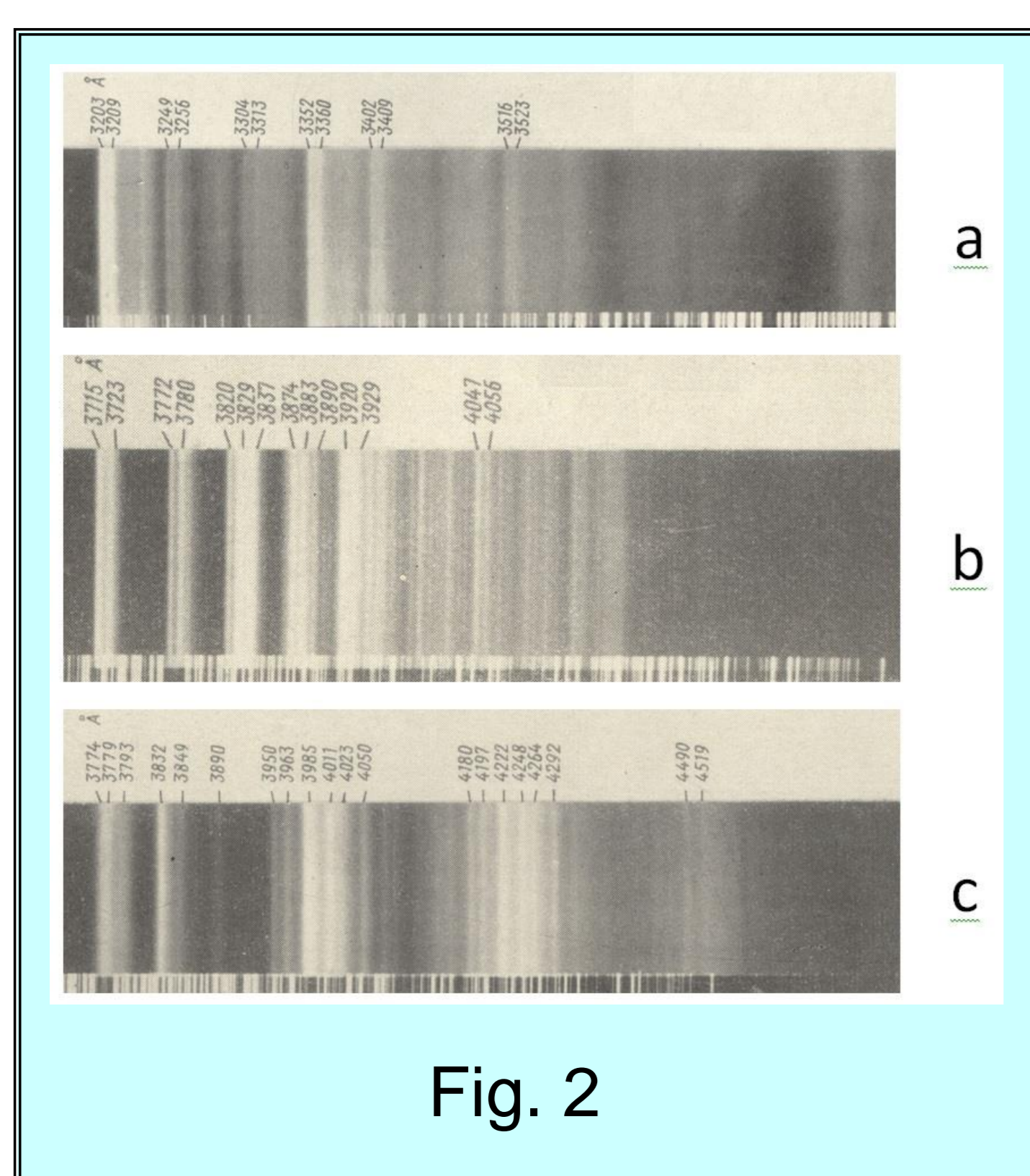


Fig. 2

Considering the highly symmetrical molecules such as naphthalene, anthracene, pyrene (Fig. 2 a, b, c), their spectra in n-paraffins are turned out to be also doublet.

Observed multiplicity of the spectra can be related to the distribution character of electrons over the orbitals of the ground state in the studied impurity molecules.

The molecule of naphthalene is considered as an example for analysis. The optical spectra of a naphthalene molecule are associated with the electronic transitions of p_z -electrons located in the molecular orbitals of the molecule. All the 10 p_z -electrons are distributed over 5 molecular π -orbitals. The last fifth filled orbit belongs to the irreducible representation a_u of the symmetry group D_{2h} . The electronic wave function of this orbital is a linear combination of 8 atomic p_z -orbitals of carbon and has the following form:

$$\Psi(a_u) = C_1(\varphi_1 - \varphi_4 + \varphi_5 - \varphi_8) + C_2(\varphi_2 - \varphi_3 + \varphi_6 - \varphi_7),$$

where $C_1 = 0.4253$ and $C_2 = 0.2629$.

Fig. 3 shows an approximate schematic distribution of the electron density in this orbital. Analysis of the presented distribution reveals that the positive wave functions $\varphi_1, \varphi_2, \varphi_5$ and φ_6 determine the electron density maxima on carbon atoms located in positions 1,2 and 5,6 of the naphthalene molecule. On the other hand, under the action of the symmetry operations of the D_{2h} point group, the carbon atoms in positions 1,2 and 5,6 remain in place four times and change to equivalent ones four times, in positions 8,7 and 4,3.

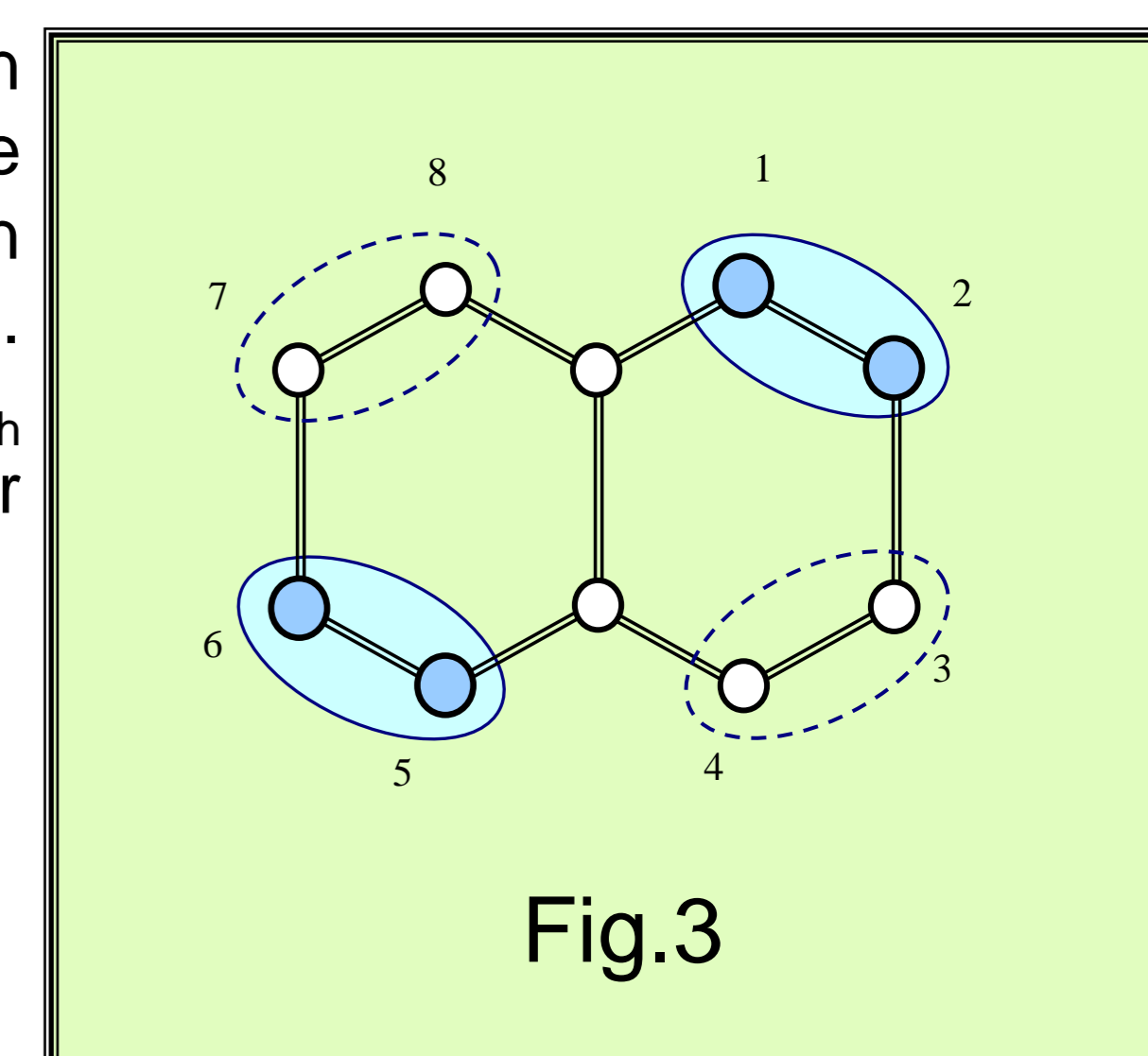


Fig.3

Consequently, the electron density maxima in a free naphthalene molecule are concentrated on carbon atoms located in two equivalent groups of carbon atoms, 1,2 and 5,6, and 3,4 and 7,8. It follows that the electronic level of the ground state in a free molecule naphthalene is doubly degenerate. The indicated degeneracy can be experimentally confirmed by the electronic spectra of single naphthalene molecules located in an electric field of lower symmetry than D_{2h} . Indeed, the low-temperature luminescence spectra of naphthalene impurity molecules in n-hexane (symmetry space group C_i with two elements E and i) are doublet over the entire electronic-vibrational spectrum (Fig. 2a). The splitting of internal molecular-electronic levels in crystalline fields can be considered as an analogue of the Bethe-splitting of degenerate atomic levels in electric fields.

[1]. E.V. Shpol'skii, A.A. Ilina, L.A. Klimova. Report of Academy of Science of the USSR, **87**, 935 (1952)

[2]. N.D. Curmei. LTP (ФНТ), Vol. **49**, № 6, 826-828 (2023)

Conclusions

1. The impurity center character of some aromatic hydrocarbon series in n-paraffin solutions has been shown to be determined by the existence of several equivalent positions for a substituent (atom or group of atoms) in a free impurity molecule, which become nonequivalent in the n-paraffin crystal. In this case, the impurity molecule replaces the n-paraffin molecule in one single way.
2. The number of possible impurity centers of different type m , formed in some organic compound solutions with n-paraffins, has been found out to be expressed by the ratio of the equivalent position number for a substituent in a free impurity molecule n_m to the same number in an n-paraffin crystal n_k : $m = n_m/n_k$.
3. An analysis of the electron density distribution over the last orbital of symmetry a_u in naphthalene molecules has showed that the electronic level of the ground state in this molecule is doubly degenerate.
4. Pronounced doublets in the luminescence spectra of naphthalene impurities in n-hexane quite reliably indicate the splitting of the degenerate electronic level of the ground state in these molecules in low-symmetry crystalline fields, which is analogous to the Bethe-splitting of degenerate atomic levels in crystalline fields.