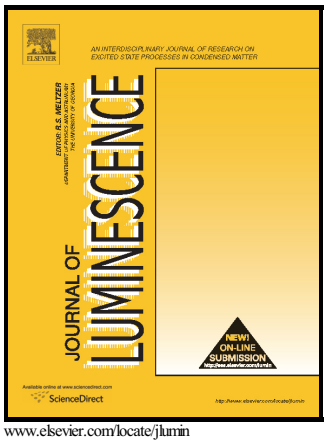

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N.D. Curmei, G.V. Klishevich, V.I. Melnik, A.G. Tereshchenko

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SIGNIFICANCE OF SYMMETRY IN THE FORMATION OF IMPURITY CENTERS IN MOLECULAR CRYSTALS

N.D. Curmei*, G.V. Klishevich, V.I. Melnik, A.G. Tereshchenko

Institute of Physics, National Academy of Sciences of Ukraine, 46 Nauki prosp., Kyiv, 03039 Ukraine.

Abstract

On the basis of the assumption concerning the symmetric properties of the free aromatic hydrocarbon molecules and those placed in host crystalline lattice cell, the analysis of the multiplet structure of the optical spectra of impurity centers of some the monosubstituted naphthalenes in naphthalene crystal was performed. The low-temperature fluorescence and absorption spectra of the 2-fluoronaphthalene, 2-chloronaphthalene, and 2-naphthol in crystalline naphthalene have been studied at 4.2 K. The results of the symmetry group theoretical analysis of the spectra multiplet structure are suggested with experimental data. The developed approach was also applied for the analysis of the multiplet structure in optical spectra of rapidly frozen solutions of 3,4-benzpyrene, porphin and its derivative in normal alkanes.

1. Introduction

Recent publications report on the studies of the fluorescence spectra of the organic compounds by using selective laser spectroscopy with of luminescence microscopy, which made it possible to obtain a fine structure of the broadened fluorescence bands [1-5]. On the other hand, the fluorescence spectra of mixed molecular crystals also show a multiplet structure due to formation of several impurity centers [6-10]. Most of the compounds used as impurities in these papers are derived from highly symmetrical polycyclic aromatic hydrocarbon molecules (naphthalene, anthracene, pyrene, etc.). In these molecules their hydrogen atoms can be easily substituted with heteroatoms giving rise to an entire class of substituted aromatics. Upon substitution of equivalent atoms present in the highly symmetrical molecules the isomeric molecules are formed. For example, if in naphthalene molecule one hydrogen atom is substituted with heteroatom in one of the four equivalent positions 2, 3, 6, and 7 (Fig. 1, left), this results in the formation of four isomeric molecules.

The purpose of this research is to analyze the multiplet structure of the optical spectra of impurity molecules in a host crystal based on possible types of impurity centers predicted from the group theoretical analysis of their symmetry properties. As the subjects of the research, we have selected three mono-substituted naphthalenes, 2-fluoronaphthalene, 2-chloronaphthalene, and 2-naphthol, in naphthalene crystal.

The naphthalene molecule belongs to the D_{2h} point symmetry group with 8 symmetry elements. Under an action of a symmetry operation, a hydrogen atom from position 2 moves to the other equivalent position as follows:

$E(H_2) \rightarrow H_2$
$\sigma_{xy}(H_2) \rightarrow H_2$ } $K = 2$ H_2

$C^y_2(H_2) \rightarrow H_7$
$\sigma_{yz}(H_2) \rightarrow H_7$ } $K = 2$ H_7

$C^z_2(H_2) \rightarrow H_6$
$i(H_2) \rightarrow H_6$ } $K = 2$ H_6

$n = 4$

$N = K \cdot n$

$$n = \frac{N}{K}$$

$H_2, H_3, H_6, H_7 – (n = 4)$

n – the number of equivalent positions of the H atom in naphtalene molecule

* Corresponding author, e-mail: Curmei_ND@ukr.net, tel.: +(038)-044-525-98-60, fax.: +(038)-044-525-15-89