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SYMMETRY OF THE VIBRATIONAL STATES AND ELECTRONIC π-ORBITALS IN A BENZENE MOLECULE C6H6. THE FINE STRUCTURE OF SPIN-DEPENDENT SPLITTING [1]

Analytical expressions and vector images have been constructed for all patterns of the normal vibrations, including doubly degenerate ones, of a benzene molecule C_6H_6 using the projection operator on the matrix elements of irreducible representations of the point symmetry group $6/mmm$ (D_{6h}). The characters of representations corresponding to the symmetry of both the electronic π-orbitals in a benzene molecule (without taking the electron spin into account) and the projective representations of its spinor π'-orbitals are found. The representations of the spinor π'-orbitals of a benzene molecule C_6H_6 belong to the projective class K_1 and describe the fine structure of spin-dependent splitting of the degenerate spinless π-orbitals, which are revealed for the first time.

K e y w o r d s: benzene, vector and spinor representations of symmetry groups, normal-vibration patterns, classes of symmetry-group projective representations, electronic states, spin-dependent splitting.

1. Introduction

The benzene molecule C_6H_6 is a basic molecule for aromatic hydrocarbons. Its elements of symmetry compose the point group $6/mmm$ (D_{6h}), which is the maximum symmetry group for sp^2-hybridized structures with unsaturated covalent π-bonds. A large number of works (see, e.g., works [1–5]) are devoted to the study of vibrational spectra and normal-vibration patterns of both the benzene molecule and its derivatives. However, the available calculation results obtained for the patterns of doubly degenerate vibrational modes of the benzene molecule contain errors and lots of inconsistencies.

The method of group-theoretic analysis most clearly reveals the symmetric properties of the spatial structure of the molecular quantum states. The quantum-mechanical projection-operator technique makes it possible to determine the representations according to which the vibrational excitations of molecules can be classified, in particular, those of the benzene molecule, which are considered in this work in detail. With the help of this technique, one can determine the patterns of normal molecular vibrations and find projective representations corresponding to the π-electronic states of the molecule without taking and taking the electron spin into account. Taken all together, this means the fulfillment of the symmetrization procedure of the linear combinations of atomic orbits (LCAO) method for the molecule and the execution of an additional analysis concerning the electron-spin influence on the energy spectrum of the molecular π-orbitals from the symmetry positions.

The results of the symmetry analysis obtained in this work for the electronic states in the C_6H_6 molecule are compared with the results of quantum chemical calculations obtained for the energy spectrum of π-orbitals in this molecule.

2. Structure of a Benzene Molecule. Symmetry of Its Vibrational Modes

In Fig. 1, the structure of the benzene molecule C_6H_6 and the selected orientation of the elements of the symmetry group $6/mmm$ (D_{6h}) are shown. Hollow circles correspond to the positions of carbon atoms C, and gray ones to the positions of hydrogen atoms H. The numbers enumerate the positions of the C and H atoms.

The results of the group-theoretic analysis obtained for the normal vibrational modes of the C_6H_6 molecule are quoted in Table 1. The table gives information on the representation characters for the displacements of atoms from their equilibrium positions, the improper translational and rotational vibrations, and the proper vibrations, as well as the distributions of those representations over the irreducible vector representations and the selection rules that characterize the activity of vibrations in the Raman and infrared (IR) absorption spectra.

From Table 1, one can see that the distribution of all vibrations of the benzene molecule C_6H_6 over the irreducible representations of the $6/mmm$ (D_{6h}) group looks like

$$\Gamma_{\text{dis}} = 2A_1^+ + 2A_2^- + 2A_3^+ + 2A_3^- + 2A_4^+ +$$
$$+ 2A_4^- + 4E_1^+ + 2E_1^- + 2E_2^+ + 4E_2^-$$

or

$$\Gamma_{\text{dis}} = 2\Gamma_1^+ + 2\Gamma_2^- + 2\Gamma_3^+ + 2\Gamma_3^- + 2\Gamma_4^+ +$$
$$+ 2\Gamma_4^- + 4\Gamma_5^+ + 2\Gamma_5^- + 2\Gamma_6^+ + 4\Gamma_6^-.$$

The distribution of vibrational eigenmodes is

$$\Gamma_{\text{vib}} = 2A_1^+ + 2A_2^- + A_3^+ + A_3^- + 2A_4^+ +$$
$$+ 2A_4^- + 4E_1^+ + 2E_1^- + E_2^+ + 3E_2^-$$

or

$$\Gamma_{\text{vib}} = 2\Gamma_1^+ + 2\Gamma_2^- + \Gamma_3^+ + \Gamma_3^- + 2\Gamma_4^+ +$$
$$+ 2\Gamma_4^- + 4\Gamma_5^+ + 2\Gamma_5^- + \Gamma_6^+ + 3\Gamma_6^-,$$
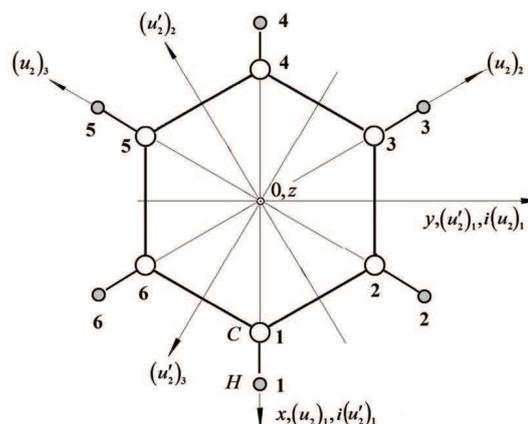
Fig. 1. Structure of the benzene molecule C_6H_6 and the orientations of the symmetry elements of the $6/mmm$ (D_{6h}) group

the distribution of induced translational vibrations is

$$\Gamma_{\text{tr}} = A_3^- + E_2^- \text{ or } \Gamma_{\text{tr}} = \Gamma_3^- + \Gamma_6^-,$$

and the distribution of induced rotational vibrations is

$$\Gamma_{\text{rot}} = A_3^+ + E_2^+ \text{ or } \Gamma_{\text{rot}} = \Gamma_3^+ + \Gamma_6^+.$$

3. Patterns of Normal Vibrations of the Benzene Molecule C_6H_6

Let us calculate the patterns of normal vibrations of the benzene molecule C_6H_6. It is easy to do in the framework of the standard projection operator method on the matrices of the irreducible representations of the $6/mmm$ (D_{6h}) group [6], which coincide with their characters in the case of one-dimensional representations.

With the help of the projection operator on the irreducible representations of the D_{6h} group, let us determine the symmetrized displacements or, which is the same, the symmetry coordinates, i.e. the invariant vector functions that are transformed according to irreducible representations of the D_{6h} group. The number of linearly independent symmetrized displacements and the number of vibrational modes are identical for each symmetry type, but the symmetrized displacements do not necessarily have to be orthogonal. At the next stage, an orthogonal system of the linear combinations of symmetrized displacements is constructed for each symmetry type, and just this system describes a pattern of normal vibrations.

Table 1. **Characters of the single-valued irreducible representations of the 6/mmm (D₆ₕ) group, classification of normal vibrational modes of the benzene molecule over the symmetry types, and their activity (the selection rules) in the Raman and IR absorption spectra**

$6/mmm\,(D_{6h})$		e	$2c_3$	$3u_2$	c_2	$2c_6$	$3u'_2$	i	$2ic_3$	$3iu_2$	ic_2	$2ic_6$	$3iu'_2$	n_{dis}	n_{tr}	n_{rot}	n_{vib}	Selection
Γ_1^+	A_1^+	1	1	1	1	1	1	1	1	1	1	1	1	2	0	0	2	$\alpha_{zz},\ \alpha_{xx}+\alpha_{yy};\ ia$
Γ_1^-	A_1^-	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	0	0	0	0	$v;\ ia$
Γ_2^+	A_2^+	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1	0	0	0	0	$v;\ ia$
Γ_2^-	A_2^-	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1	2	0	0	2	$v;\ ia$
Γ_3^+	A_3^+	1	1	-1	1	1	-1	1	1	-1	1	1	-1	2	0	1	1	$v;\ ia$
Γ_3^-	A_3^-	1	1	-1	1	1	-1	-1	-1	1	-1	-1	1	2	1	0	1	$\mu_z;\ ia$
Γ_4^+	A_4^+	1	1	-1	-1	-1	1	1	1	-1	-1	-1	1	2	0	0	2	$v;\ ia$
Γ_4^-	A_4^-	1	1	-1	-1	-1	1	-1	-1	1	1	1	-1	2	0	0	2	$v;\ ia$
Γ_5^+	E_1^+	2	-1	0	2	-1	0	2	-1	0	2	-1	0	4	0	0	4	$\alpha_{xx}-\alpha_{yy},\ \alpha_{xy};\ ia$
Γ_5^-	E_1^-	2	-1	0	2	-1	0	-2	1	0	-2	1	0	2	0	0	2	$v;\ ia$
Γ_6^+	E_2^+	2	-1	0	-2	1	0	2	-1	0	-2	1	0	2	0	1	1	$\alpha_{zx},\ \alpha_{zy};\ ia$
Γ_6^-	E_2^-	2	-1	0	-2	1	0	-2	1	0	2	-1	0	4	1	0	3	$\mu_x,\ \mu_y;\ v$
$\chi\Gamma_{\mathrm{dis}}$		36	0	-4	0	0	0	0	0	0	12	0	4					
$\chi\Gamma_{\mathrm{tr}}$		3	0	-1	-1	2	-1	-3	0	1	1	-2	1					
$\chi\Gamma_{\mathrm{rot}}$		3	0	-1	-1	2	-1	3	0	-1	-1	2	-1					
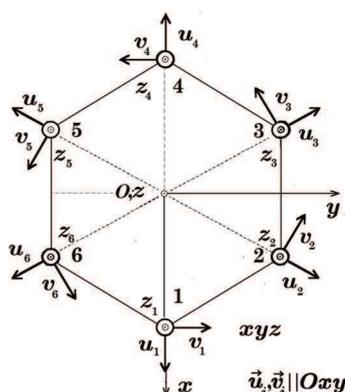
Fig. 2. Generating basis in the form of a combined coordinate system for determining the patterns of nondegenerate normal vibrations of the benzene molecule

The benzene molecule C_6H_6 includes atoms of only two chemical elements, carbon C and hydrogen H. As one can see from Fig. 1, the symmetry of their arrangement and the selected enumeration of the atoms of each chemical element are absolutely identical. Therefore, the analytical expressions for their symmetrized displacements will be qualitatively identical for the vibrational modes of the same symmetry types except, in the general case, for the displacement amplitudes.

For instance, for the vibrations of the benzene molecule belonging to the nondegenerate symmetry types, there are only two symmetrized displacements (two symmetry coordinates) $S_1(C)$ and $S_2(H)$ with the same analytical expression for each vibration type. They differ from each other only by the atoms belonging to that or another chemical element. In this case, normal vibrational modes are composed of their symmetric and antisymmetric combinations. In other words, there are two vibrational modes of the benzene molecule for each symmetry type of nondegenerate vibrations. They are defined as follows:

$$Q_1 = \frac{1}{\sqrt{2}}\left[S_1(C) + S_2(H)\right]$$

and

$$Q_2 = \frac{1}{\sqrt{2}}\left[S_1(C) - S_2(H)\right].$$

3.1. Patterns of nondegenerate normal vibrations of the benzene molecule

To obtain analytical expressions for the patterns of nondegenerate normal vibrations of the benzene molecule, it is convenient to describe the displacements of atoms making use of a generating basis in the form of a combined coordinate system. It is created by shifting each C or H atom in the directions

of the orthogonal unit vectors $\mathbf{z}_i$, $\mathbf{u}_i$, and $\mathbf{v}_i$, where $(\mathbf{u}_i, \mathbf{v}_i) \parallel Oxy$, which form orthogonal right-hand coordinate subsystems with the same directions of the unit vectors $\mathbf{z}_i$ along the axis Oz for each i-th atom. The total orthogonality of the combined system of atomic displacements is determined by an additional orthogonality condition with respect to the atomic numbers.

In Fig. 2, such a generating basis is exhibited in the form of a combined coordinate system for the displacements of carbon atoms (as an example). Let us introduce a similar combined coordinate system to describe the displacements of hydrogen atoms, where the unit vectors of the coordinate displacements of the i-th hydrogen atom are co-directed with the unit vectors of the coordinate displacements of the i-th carbon atom. For the benzene molecule C_6H_6, the patterns of nondegenerate normal vibrations are described by the following analytical expressions:
for the A_1^+ symmetry,

$$Q_1^{A_1^+} = \frac{1}{2\sqrt{3}}(\mathbf{u}_1^C + \mathbf{u}_2^C + \mathbf{u}_3^C + \mathbf{u}_4^C + \mathbf{u}_5^C + \mathbf{u}_6^C +$$
$$+ \mathbf{u}_1^H + \mathbf{u}_2^H + \mathbf{u}_3^H + \mathbf{u}_4^H + \mathbf{u}_5^H + \mathbf{u}_6^H),$$

$$Q_2^{A_1^+} = \frac{1}{2\sqrt{3}}(\mathbf{u}_1^C + \mathbf{u}_2^C + \mathbf{u}_3^C + \mathbf{u}_4^C + \mathbf{u}_5^C + \mathbf{u}_6^C -$$
$$- \mathbf{u}_1^H - \mathbf{u}_2^H - \mathbf{u}_3^H - \mathbf{u}_4^H - \mathbf{u}_5^H - \mathbf{u}_6^H),$$

for the A_2^- symmetry,

$$Q_1^{A_2^-} = \frac{1}{2\sqrt{3}}(\mathbf{u}_1^C - \mathbf{u}_2^C + \mathbf{u}_3^C - \mathbf{u}_4^C + \mathbf{u}_5^C - \mathbf{u}_6^C +$$
$$+ \mathbf{u}_1^H - \mathbf{u}_2^H + \mathbf{u}_3^H - \mathbf{u}_4^H + \mathbf{u}_5^H - \mathbf{u}_6^H),$$

$$Q_2^{A_2^-} = \frac{1}{2\sqrt{3}}(\mathbf{u}_1^C - \mathbf{u}_2^C + \mathbf{u}_3^C - \mathbf{u}_4^C + \mathbf{u}_5^C - \mathbf{u}_6^C -$$
$$- \mathbf{u}_1^H + \mathbf{u}_2^H - \mathbf{u}_3^H + \mathbf{u}_4^H - \mathbf{u}_5^H + \mathbf{u}_6^H),$$

for the A_3^+ symmetry,

$$Q_1^{A_3^+} = \frac{1}{2\sqrt{3}}(\mathbf{v}_1^C + \mathbf{v}_2^C + \mathbf{v}_3^C + \mathbf{v}_4^C + \mathbf{v}_5^C + \mathbf{v}_6^C +$$
$$+ \mathbf{v}_1^H + \mathbf{v}_2^H + \mathbf{v}_3^H + \mathbf{v}_4^H + \mathbf{v}_5^H + \mathbf{v}_6^H),$$

$$Q_2^{A_3^+} = \frac{1}{2\sqrt{3}}(\mathbf{v}_1^C + \mathbf{v}_2^C + \mathbf{v}_3^C + \mathbf{v}_4^C + \mathbf{v}_5^C + \mathbf{v}_6^C -$$
$$- \mathbf{v}_1^H - \mathbf{v}_2^H - \mathbf{v}_3^H - \mathbf{v}_4^H - \mathbf{v}_5^H - \mathbf{v}_6^H),$$

for the A_3^- symmetry,

$$Q_1^{A_3^-}(z - \text{tr.}) = \frac{1}{2\sqrt{3}}(\mathbf{z}_1^C + \mathbf{z}_2^C + \mathbf{z}_3^C + \mathbf{z}_4^C + \mathbf{z}_5^C + \mathbf{z}_6^C +$$
$$+ \mathbf{z}_1^H + \mathbf{z}_2^H + \mathbf{z}_3^H + \mathbf{z}_4^H + \mathbf{z}_5^H + \mathbf{z}_6^H),$$

$$Q_2^{A_3^-} = \frac{1}{2\sqrt{3}}(\mathbf{z}_1^C + \mathbf{z}_2^C + \mathbf{z}_3^C + \mathbf{z}_4^C + \mathbf{z}_5^C + \mathbf{z}_6^C -$$
$$- \mathbf{z}_1^H - \mathbf{z}_2^H - \mathbf{z}_3^H - \mathbf{z}_4^H - \mathbf{z}_5^H - \mathbf{z}_6^H),$$

for the A_4^+ symmetry,

$$Q_1^{A_4^+} = \frac{1}{2\sqrt{3}}(\mathbf{z}_1^C - \mathbf{z}_2^C + \mathbf{z}_3^C - \mathbf{z}_4^C + \mathbf{z}_5^C - \mathbf{z}_6^C +$$
$$+ \mathbf{z}_1^H - \mathbf{z}_2^H + \mathbf{z}_3^H - \mathbf{z}_4^H + \mathbf{z}_5^H - \mathbf{z}_6^H),$$

$$Q_2^{A_4^+} = \frac{1}{2\sqrt{3}}(\mathbf{z}_1^C - \mathbf{z}_2^C + \mathbf{z}_3^C - \mathbf{z}_4^C + \mathbf{z}_5^C - \mathbf{z}_6^C -$$
$$- \mathbf{z}_1^H + \mathbf{z}_2^H - \mathbf{z}_3^H + \mathbf{z}_4^H - \mathbf{z}_5^H + \mathbf{z}_6^H),$$

and for the A_4^- symmetry,

$$Q_1^{A_4^-} = \frac{1}{2\sqrt{3}}(\mathbf{v}_1^C - \mathbf{v}_2^C + \mathbf{v}_3^C - \mathbf{v}_4^C + \mathbf{v}_5^C - \mathbf{v}_6^C +$$
$$+ \mathbf{v}_1^H - \mathbf{v}_2^H + \mathbf{v}_3^H - \mathbf{v}_4^H + \mathbf{v}_5^H - \mathbf{v}_6^H),$$

$$Q_2^{A_4^-} = \frac{1}{2\sqrt{3}}(\mathbf{v}_1^C - \mathbf{v}_2^C + \mathbf{v}_3^C - \mathbf{v}_4^C + \mathbf{v}_5^C - \mathbf{v}_6^C -$$
$$- \mathbf{v}_1^H + \mathbf{v}_2^H - \mathbf{v}_3^H + \mathbf{v}_4^H - \mathbf{v}_5^H + \mathbf{v}_6^H).$$

The patterns of nondegenerate normal vibrations of the benzene molecule corresponding to their analytical expressions are shown in Fig. 3.

3.2. Patterns of doubly degenerate normal vibrations of the benzene molecule

To find the patterns of doubly degenerate normal vibrations of the benzene molecule, we used the matrices of two-dimensional irreducible representations that were written in the same Cartesian coordinate system for all symmetry elements of the $6/mmm$ (D_{6h}) group. The sets of corresponding matrices for the two-dimensional irreducible representations of the $6/mmm$ (D_{6h}) group for various symmetry types are quoted in Table 2.

When constructing the patterns of doubly degenerate normal vibrations of the benzene molecule, the symmetrized displacements (symmetry coordinates) can be determined only for carbon atoms, as was done for the nondegenerate normal vibrations. As was
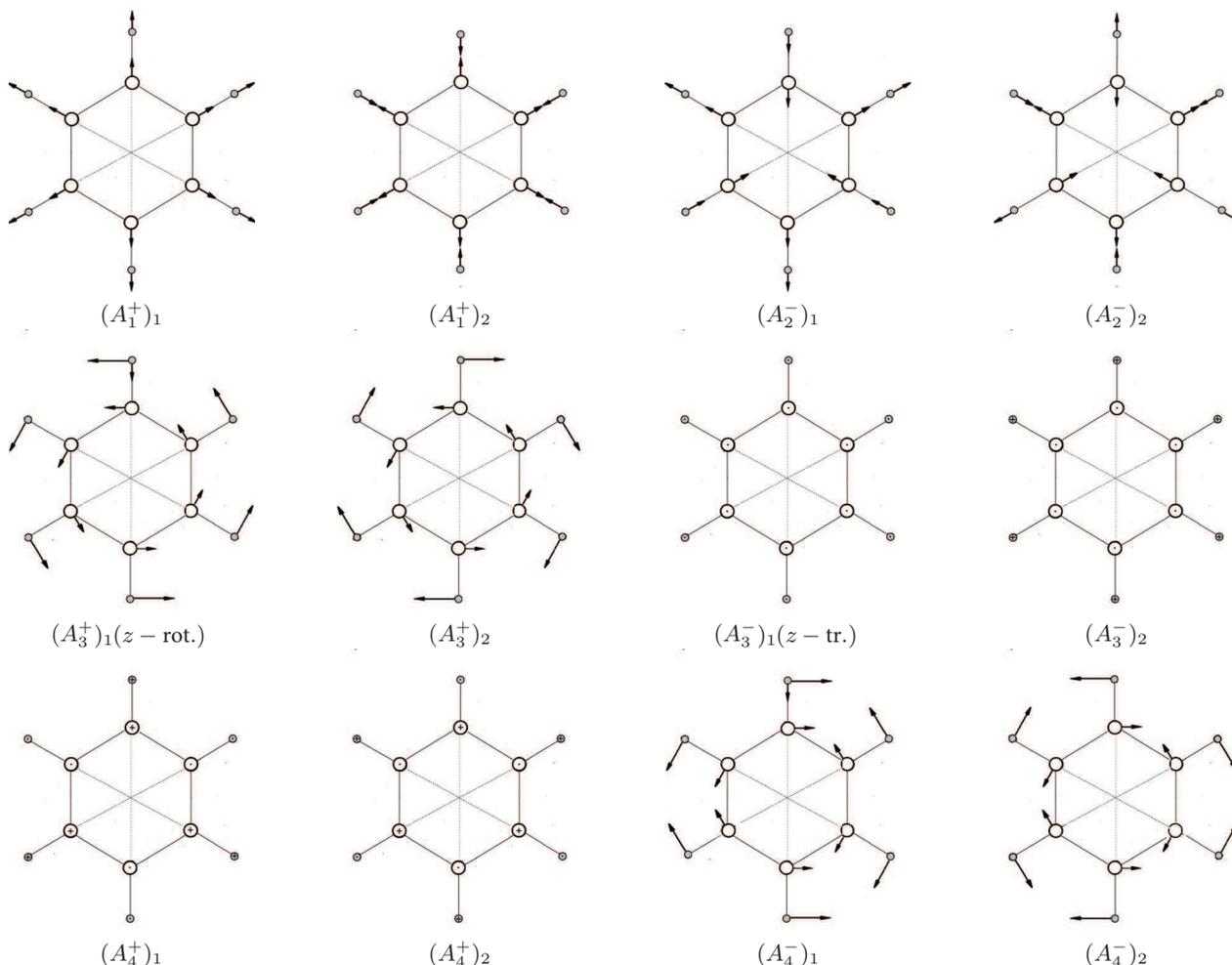
Fig. 3. Patterns of nondegenerate vibrations of the benzene molecule C_6H_6

shown above, the analytical expressions for the symmetrized displacements and the patterns of normal vibrations of the hydrogen and carbon atoms are identical. When creating the symmetrized displacements and the patterns of normal vibrations of the benzene molecule for each symmetry type, they will be added two times to the displacements and the patterns of normal vibrations of carbon atoms: at first in cophase, and then in antiphase.

Let us construct the patterns of doubly degenerate normal vibrations of the benzene molecule C_6H_6. For this purpose, as was noted above, it is enough to construct the patterns of doubly degenerate normal vibrations only for the atoms of either of the chemical elements that form the benzene molecule, e.g., the carbons.

Let us begin by constructing the patterns for doubly degenerate normal vibrations of the carbon atoms with the E_1^+ symmetry. One of the generating coordinates, the displacement $(x_1^C)'$, generates the symmetrized displacement

$$(S_{1,1}^C)_{1\alpha}^{E_1^+} = \frac{1}{\sqrt{6}}\left(2x_1^C - \frac{1}{2}x_2^C - \frac{\sqrt{3}}{2}y_2^C + \frac{1}{2}x_3^C - \frac{\sqrt{3}}{2}y_3^C - \right.$$
$$\left. - 2x_4^C + \frac{1}{2}x_5^C + \frac{\sqrt{3}}{2}y_5^C - \frac{1}{2}x_6^C + \frac{\sqrt{3}}{2}y_6^C\right),$$

when applying the projection operator to elements of the matrices $D_{11}^{E_1^+}$ (they are elements of the matrices of the two-dimensional irreducible representation E_1^+, which are given in Table 2), and the symmetrized

Table 2. **Matrices of the two-dimensional irreducible representations of the $6/mmm$ (D_{6h}) group**

	e	c_3	c_3^2	$(u_2)_1$	$(u_2)_2$	$(u_2)_3$
E_1^+	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$
E_1^-	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$
E_2^+	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$
E_2^-	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$

	c_2	c_6^5	c_6	$(u_2')_1$	$(u_2')_2$	$(u_2')_3$
E_1^+	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$
E_1^-	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$
E_2^+	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$
E_2^-	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$

	i	ic_3	ic_3^2	$i(u_2)_1$	$i(u_2)_2$	$i(u_2)_3$
E_1^+	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$
E_1^-	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$
E_2^+	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$
E_2^-	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$

	ic_2	ic_6^5	ic_6	$i(u_2')_1$	$i(u_2')_2$	$i(u_2')_3$
E_1^+	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$
E_1^-	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$
E_2^+	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$
E_2^-	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$

$(S_{1,1}^C)_{1\alpha}^{E_1^+}$ $(S_{2,1}^C)_{1\beta}^{E_1^+}$

$(S_{1,2}^C)_{2\alpha}^{E_1^+}$ $(S_{2,2}^C)_{2\beta}^{E_1^+}$

a

$(Q_{1\alpha}^C)^{E_1^+}$ $(Q_{1\beta}^C)^{E_1^+}$

$(Q_{2\alpha}^C)^{E_1^+}$ $(Q_{2\beta}^C)^{E_1^+}$

b

Fig. 4. Symmetrized displacements (*a*) and patterns of doubly degenerate normal vibrations (*b*) of the E_2^- symmetry in the benzene molecule

displacement

$$(S_{2,1}^{\mathrm{C}})_{1\beta}^{E_1^+} = \frac{1}{2}\left(-\frac{1}{2}x_2^{\mathrm{C}} - \frac{\sqrt{3}}{2}y_2^{\mathrm{C}} - \frac{1}{2}x_3^{\mathrm{C}} + \frac{\sqrt{3}}{2}y_3^{\mathrm{C}} + \frac{1}{2}x_5^{\mathrm{C}} + \right.$$

$$\left. + \frac{\sqrt{3}}{2}y_5^{\mathrm{C}} + \frac{1}{2}x_6^{\mathrm{C}} - \frac{\sqrt{3}}{2}y_6^{\mathrm{C}}\right),$$

when projecting on elements of the matrices $D_{12}^{E_1^+}$. The other generating coordinate, the displacement $(y_1^{\mathrm{C}})'$, generates the symmetrized displacement

$$(S_{1,2}^{\mathrm{C}})_{2\alpha}^{E_1^+} = \frac{1}{2}\left(-\frac{\sqrt{3}}{2}x_2^{\mathrm{C}} + \frac{1}{2}y_2^{\mathrm{C}} + \frac{\sqrt{3}}{2}x_3^{\mathrm{C}} + \frac{1}{2}y_3^{\mathrm{C}} + \frac{\sqrt{3}}{2}x_5^{\mathrm{C}} - \right.$$

$$\left. - \frac{1}{2}y_5^{\mathrm{C}} - \frac{\sqrt{3}}{2}x_6^{\mathrm{C}} - \frac{1}{2}y_6^{\mathrm{C}}\right),$$

when projecting on elements of the matrices $D_{21}^{E_1^+}$, and the symmetrized displacement

$$(S_{2,2}^{\mathrm{C}})_{2\beta}^{E_1^+} = \frac{1}{\sqrt{6}}\left(2y_1^{\mathrm{C}} + \frac{\sqrt{3}}{2}x_2^{\mathrm{C}} - \frac{1}{2}y_2^{\mathrm{C}} + \frac{\sqrt{3}}{2}x_3^{\mathrm{C}} + \frac{1}{2}y_3^{\mathrm{C}} - \right.$$

$$\left. - 2y_4^{\mathrm{C}} - \frac{\sqrt{3}}{2}x_5^{\mathrm{C}} + \frac{1}{2}y_5^{\mathrm{C}} - \frac{\sqrt{3}}{2}x_6^{\mathrm{C}} - \frac{1}{2}y_6^{\mathrm{C}}\right).$$

when projecting on elements of the matrices $D_{22}^{E_1^+}$.

The vector images of the above-indicated symmetrized displacements of the symmetry E_1^+ are illustrated in Fig. 4, *a*. It is easy to see that the components of the doubly degenerate normal vibrational modes of the benzene molecule with the symmetry E_1^+, which are formed by the atoms of only one of the chemical elements, e.g., carbon, are as follows:

$$(Q_{1\alpha}^{\mathrm{C}})^{E_1^+} = \frac{1}{\sqrt{2}}[(S_{1,1}^{\mathrm{C}})_{1\alpha}^{E_1^+} + (S_{1,2}^{\mathrm{C}})_{2\alpha}^{E_1^+}] =$$

$$= \frac{1}{\sqrt{6}}(x_1^{\mathrm{C}} - x_2^{\mathrm{C}} + x_3^{\mathrm{C}} - x_4^{\mathrm{C}} + x_5^{\mathrm{C}} - x_6^{\mathrm{C}}),$$

$$(Q_{1\beta}^{\mathrm{C}})^{E_1^+} = \frac{1}{\sqrt{2}}[(S_{2,1}^{\mathrm{C}})_{1\beta}^{E_1^+} + (S_{2,2}^{\mathrm{C}})_{2\beta}^{E_1^+}] =$$

$$= \frac{1}{\sqrt{6}}(y_1^{\mathrm{C}} - y_2^{\mathrm{C}} + y_3^{\mathrm{C}} - y_4^{\mathrm{C}} + y_5^{\mathrm{C}} - y_6^{\mathrm{C}}),$$

$$(Q_{2\alpha}^{\mathrm{C}})^{E_1^+} = \frac{1}{\sqrt{2}}[(S_{1,1}^{\mathrm{C}})_{1\alpha}^{E_1^+} - (S_{1,2}^{\mathrm{C}})_{2\alpha}^{E_1^+}] =$$

$$= \frac{1}{\sqrt{6}}(2x_1^{\mathrm{C}} + x_2^{\mathrm{C}} - \sqrt{3}y_2^{\mathrm{C}} - x_3^{\mathrm{C}} - \sqrt{3}y_3^{\mathrm{C}} -$$

$$- 2x_4^{\mathrm{C}} - x_5^{\mathrm{C}} + \sqrt{3}y_5^{\mathrm{C}} + x_6^{\mathrm{C}} + \sqrt{3}y_6^{\mathrm{C}}),$$

$$(Q_{2\beta}^{\mathrm{C}})^{E_1^+} = \frac{1}{\sqrt{2}}[(S_{1,1}^{\mathrm{C}})_{1\beta}^{E_1^+} - (S_{1,2}^{\mathrm{C}})_{2\beta}^{E_1^+}] =$$

$$= \frac{1}{\sqrt{6}}(-2y_1^{\mathrm{C}} - \sqrt{3}x_2^{\mathrm{C}} - y_2^{\mathrm{C}} - \sqrt{3}x_3^{\mathrm{C}} + y_3^{\mathrm{C}} +$$

$$+ 2y_4^{\mathrm{C}} + \sqrt{3}x_5^{\mathrm{C}} + y_5^{\mathrm{C}} + \sqrt{3}x_6^{\mathrm{C}} - y_6^{\mathrm{C}}).$$

The vector images of the carbon components of the patterns for doubly degenerate normal vibrations of the symmetry E_1^+ are depicted in Fig. 4, *b*.

Now, let us proceed to the construction of a patterns for doubly degenerate normal vibrations of carbon atoms in the benzene molecule with the symmetries E_1^- and E_2^+. Each carbon atom of the benzene molecule forms only one symmetric displacement with the components α and β for doubly degenerate normal vibrations of the symmetries E_1^- and E_2^+. Therefore, the analytical expressions for the symmetrized displacements with the components α and β for the symmetries E_1^- and E_2^+ coincide with the analytical expressions for the components α and β of their patterns for doubly degenerate normal vibrations. They look like as follows:

• for the E_1^- symmetry,

$$\left(Q_\alpha^C\right)^{E_1^-} = \left(S_{1,2}^C\right)_\alpha^{E_1^-} = \frac{1}{2}(\mathbf{z}_2^C - \mathbf{z}_3^C + \mathbf{z}_5^C - \mathbf{z}_6^C)$$

(obtained by projecting the generating coordinate, the displacement $(z_1^C)'$, on the elements of the matrix $D_{21}^{E_1^-}$) and

$$\left(Q_\beta^C\right)^{E_1^-} = \left(S_{2,2}^C\right)_\beta^{E_1^-} =$$
$$= \frac{1}{\sqrt{6}}(2\mathbf{z}_1^C - \mathbf{z}_2^C - \mathbf{z}_3^C + 2\mathbf{z}_4^C - \mathbf{z}_5^C - \mathbf{z}_6^C)$$

(obtained by projecting the generating coordinate, the displacement $(z_1^C)'$, on the elements of the matrix $D_{22}^{E_1^-}$);

• and for the E_2^+ symmetry,

$$\left(Q_\alpha^C\right)^{E_2^+} (x{-}\text{rot.}) = \frac{1}{2}(-\mathbf{z}_2^C - \mathbf{z}_3^C + \mathbf{z}_5^C + \mathbf{z}_6^C)$$

(obtained by projecting the generating coordinate, the displacement $(z_1^C)'$, on the elements of the matrix $D_{21}^{E_2^+}$) and

$$\left(Q_\beta^C\right)^{E_2^+} (y{-}\text{rot.}) = \frac{1}{\sqrt{6}}(2\mathbf{z}_1^C + \mathbf{z}_2^C - \mathbf{z}_3^C - 2\mathbf{z}_4^C -$$
$$- \mathbf{z}_5^C + \mathbf{z}_6^C)$$

(obtained by projecting the generating coordinate, the displacement $(z_1^C)'$, on the elements of the matrix $D_{22}^{E_2^+}$).

The vector images of the carbon components of the patterns for doubly degenerate normal vibrations of

$$(Q_\alpha^C)^{E_1^-} \qquad (Q_\beta^C)^{E_1^-}$$

$$(Q_\alpha^C)^{E_2^+}(x-\text{rot.}) \qquad (Q_\beta^C)^{E_2^+}(y-\text{rot.})$$
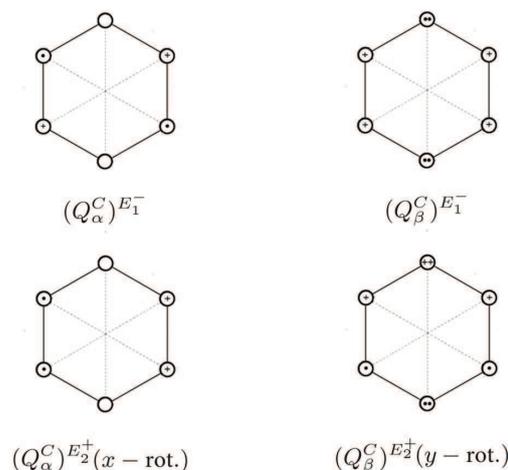
Fig. 5. Patterns of doubly degenerate normal vibrations of the E_1^- (top panel) and E_2^+ (bottom panel) symmetries in the benzene molecule

the benzene molecule with the symmetries E_1^- and E_2^+ are shown in Fig. 5 (panel *a* for the vibrations of the symmetry E_1^-, and panel *b* for the vibrations of the symmetry E_2^+). The components of the patterns for the doubly degenerate normal vibrations of the benzene molecule of the symmetries E_1^- and E_2^+ are the sums and the differences of the patternss for the doubly degenerate normal vibrations of the carbon and hydrogen atoms, which possess identical analytical expressions.

Now let us determine the patterns for the doubly degenerate normal vibrations of the carbon atoms in the benzene molecule with the symmetry E_2^-. One of the generating coordinates, the displacement $(x_1^C)'$, generates the symmetrized displacements

$$\left(S_{1,1}^C\right)_{1\alpha}^{E_2^-} = \frac{1}{\sqrt{6}}\bigg(2x_1^C + \frac{1}{2}x_2^C + \frac{\sqrt{3}}{2}y_2^C + \frac{1}{2}x_3^C -$$
$$- \frac{\sqrt{3}}{2}y_3^C + 2x_4^C + \frac{1}{2}x_5^C + \frac{\sqrt{3}}{2}y_5^C + \frac{1}{2}x_6^C - \frac{\sqrt{3}}{2}y_6^C\bigg),$$

when applying the projection operator to the elements of the matrices $D_{11}^{E_2^-}$ (they are elements of the matrices of the two-dimensional irreducible representation E_2^-, which are given in Table 2), and the symmetrized displacement

$$\left(S_{2,1}^C\right)_{1\beta}^{E_2^-} = \frac{1}{2}\bigg(\frac{1}{2}x_2^C + \frac{\sqrt{3}}{2}y_2^C - \frac{1}{2}x_3^C + \frac{\sqrt{3}}{2}y_3^C +$$
$$+ \frac{1}{2}x_5^C + \frac{\sqrt{3}}{2}y_5^C - \frac{1}{2}x_6^C + \frac{\sqrt{3}}{2}y_6^C\bigg),$$

$(S_{1,1}^{C})_{1\alpha}^{E_2^-}$ $(S_{2,1}^{C})_{1\beta}^{E_2^-}$

$(S_{1,2}^{C})_{2\alpha}^{E_2^-}$ $(S_{2,2}^{C})_{2\beta}^{E_2^-}$

a

$(Q_{1\alpha}^{C})^{E_2^-}(x-\text{tr.})$ $(Q_{1\beta}^{C})^{E_2^-}(y-\text{tr.})$

$(Q_{2\alpha}^{C})^{E_2^-}$ $(Q_{2\beta}^{C})^{E_2^-}$

b
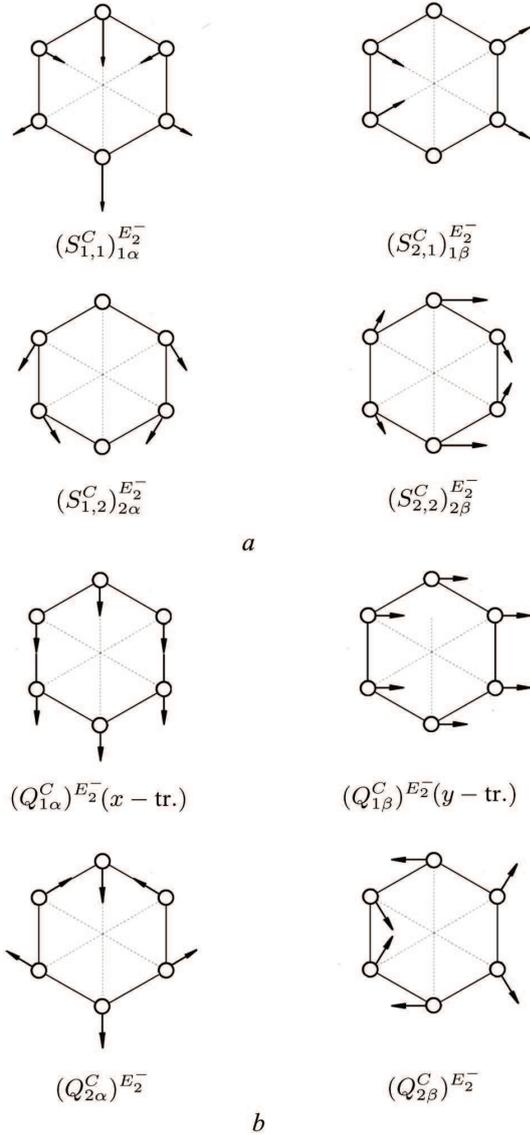
Fig. 6. Symmetrized displacements (*a*) and patterns of doubly degenerate normal vibrations (*b*) of the E_2^- symmetry in the benzene molecule

when projecting on the elements of the matrices $D_{12}^{E_2^-}$. The other generating coordinate, the displacement $(y_1^C)'$, generates the symmetrized displacement

$$(S_{1,2}^{C})_{2\alpha}^{E_2^-} = \frac{1}{2}\left(\frac{\sqrt{3}}{2}x_2^C - \frac{1}{2}y_2^C + \right.$$

$$\left. + \frac{\sqrt{3}}{2}y_3^C + \frac{1}{2}y_3^C + \frac{\sqrt{3}}{2}x_5^C - \frac{1}{2}y_5^C + \frac{\sqrt{3}}{2}x_6^C + \frac{1}{2}y_6^C\right),$$

when projecting on the elements of the matrices $D_{21}^{E_2^-}$, and the symmetrized displacement

$$(S_{2,2}^{C})_{2\beta}^{E_2^-} = \frac{1}{\sqrt{6}}\left(2y_1^C - \frac{\sqrt{3}}{2}x_2^C + \frac{1}{2}y_2^C + \frac{\sqrt{3}}{2}x_3^C + \frac{1}{2}y_3^C + \right.$$

$$\left. + 2y_4^C - \frac{\sqrt{3}}{2}x_5^C + \frac{1}{2}y_5^C + \frac{\sqrt{3}}{2}x_6^C + \frac{1}{2}y_6^C\right),$$

when projecting on the elements of the matrices $D_{22}^{E_2^-}$.

The vector images of those symmetrized displacements with the symmetry E_2^- are exhibited in Fig. 6, *a*. It is easy to see that the components of the degenerate normal vibrational modes of the benzene molecule with the symmetry E_2^-, which are formed by the atoms of only one of the chemical elements, e.g., carbon atoms, are as follows:

$$(Q_{1\alpha}^{C})^{E_2^-}(x-\text{tr.}) = \frac{1}{\sqrt{2}}[(S_{1,1}^{C})_{1\alpha}^{E_2^-} + (S_{1,2}^{C})_{2\alpha}^{E_2^-}] =$$

$$= \frac{1}{\sqrt{6}}(x_1^C + x_2^C + x_3^C + x_4^C + x_5^C + x_6^C),$$

$$(Q_{1\beta}^{C})^{E_2^-}(y-\text{tr.}) = \frac{1}{\sqrt{2}}[(S_{2,1}^{C})_{1\beta}^{E_2^-} + (S_{2,2}^{C})_{2\beta}^{E_2^-}] =$$

$$= \frac{1}{\sqrt{6}}(y_1^C + y_2^C + y_3^C + y_4^C + y_5^C + y_6^C),$$

$$(Q_{2\alpha}^{C})^{E_2^-} = \frac{1}{\sqrt{2}}[(S_{1,1}^{C})_{1\alpha}^{E_2^-} - (S_{1,2}^{C})_{2\alpha}^{E_2^-}] = \frac{1}{\sqrt{6}}(2x_1^C - x_2^C +$$

$$+ \sqrt{3}y_2^C - x_3^C - \sqrt{3}y_3^C + 2x_4^C - x_5^C + \sqrt{3}y_5^C - x_6^C - \sqrt{3}y_6^C),$$

$$(Q_{2\beta}^{C})^{E_2^-} = \frac{1}{\sqrt{2}}[(S_{2,1}^{C})_{1\beta}^{E_2^-} - (S_{2,2}^{C})_{2\beta}^{E_2^-}] =$$

$$= \frac{1}{\sqrt{6}}(-2y_1^C + \sqrt{3}x_2^C + y_2^C - \sqrt{3}x_3^C +$$

$$+ y_3^C - 2y_4^C + \sqrt{3}x_5^C + y_5^C - \sqrt{3}x_6^C + y_6^C).$$

The vector images of the carbon components of the patterns for the doubly degenerate normal vibrations of the symmetry E_2^- are shown in Fig. 6, *b*. As was said above in connection with the other symmetry types, it is easy to obtain the components of the patterns for the doubly degenerate normal vibrations of the benzene molecule with the symmetry E_2^-: they are the sums and the differences of the analytically identical components of the patterns for the doubly degenerate normal vibrations of the carbon and hydrogen atoms.

4. Symmetry and Energy Structure of the Electronic States of π-Orbitals in the Benzene Molecule C₆H₆. Fine Structure of Spin-Dependent Splitting

The symmetry of the electronic states of π-orbitals without taking and taking the electron spin into account can be determined following the method of works [7, 8], which corresponds to a practical application of the LCAO method. According to this method, the characters of the equivalence representation of π-orbitals in the benzene molecule are determined at first, i.e. the equivalence representation of the atoms possessing the electronic π-orbitals (the unsaturated covalent bonds of C atoms that arise as a result of the sp^2-hybridization of their electronic states).

Table 3 demonstrates the characters of the equivalence representation $D_{\rm eq}$ for all atoms in the benzene molecule, the representation of the polar vector $\Gamma_{\mathbf{r}}$, the representation characters for the displacements of all atoms in the benzene molecule, $\Gamma_{\rm dis} = D_{\rm eq.} \otimes \Gamma_{\mathbf{r}}$, and the equivalence representation for π-orbitals, $(D_{\rm eq})_{\rm C}$ (the equivalence representation for only carbon atoms C possessing π-orbitals). Table 3 also quotes the characters of the representation that characterizes the symmetry of π-orbital in the $6/mmm$ group (the representation of the polar vector Γ_z directed along the axis Oz) and gives, as was done in work [2], the representation characters for all π-orbitals of the benzene molecule without taking the electron spin into account (the representation $\Gamma_\pi = (D_{\rm eq})_{\rm C} \otimes \Gamma_z$).

In Table 4, the expansion of the Γ_π-representation in the irreducible vector representations of the $6/mmm$ (D_{6h}) group is presented. It is a practical procedure that implements the LCAO method without taking the electron spin into account. As one can see,

$$\Gamma_\pi = A_3^- + A_4^+ + E_1^- + E_2^+$$

or

$$\Gamma_\pi = \Gamma_3^- + \Gamma_4^+ + \Gamma_5^- + \Gamma_6^+.$$

That is, the representation of all π-orbitals is expanded in two one-dimensional representations, A_3^- (Γ_3^-) and A_4^+ (Γ_4^+), and two two-dimensional representations, E_1^- (Γ_5^-) and E_2^+ (Γ_6^+). This means that if the electron spin is not taken into account, the π-orbitals are divided into two nondegenerate or-

bitals, A_3^- and A_4^+, and two doubly degenerate ones, E_1^- and E_2^+.

It was shown in works [7, 8] (see Table 4 in work [7] and Table 1 in work [8]) that if the electron spin is taken into account, the electronic states can be classified according to the irreducible projective representations of the projective class K_1 of the $6/mmm$ (D_{6h}) group. Those representations are quoted in Table 5. The primed representation notations mean that the electron spin was taken into account.

As was done in work [7], to determine the representation of the electronic π-orbitals taking the electron spin into account (the representation of π'-orbitals), Γ_π', the formula

$$\Gamma_\pi' = (D_{\rm eq})_C \otimes \Gamma_z'$$

will be used. Here, the representation Γ_z' describing the symmetry of the π-orbital taking the electron spin into account (the spinor π'-orbital) is given by the formula

$$\Gamma_z' = \Gamma_z \otimes D_{1/2}^+,$$

where Γ_z is the irreducible representation in the $6/mmm$ (D_{6h}) group for a vector directed along the Oz-axis (this vector characterizes the symmetry of the π-orbital not taking the electron spin into account), and $D_{1/2}^+$ is the even two-dimensional (spinor) representation of the rotation group characterizing the symmetry of an electron with the total-moment quantum number $j = 1/2$.

Table 6 contains the characters of the projective representation $D_{1/2}^+$, the representations Γ_z and $(D_{\rm eq})_C$, and the projective representations Γ_z' and Γ_π'. The lower part of Table 6 demonstrates the characters of the direct products of the representations for the spinless orbitals in the benzene molecule with the representation $D_{1/2}^+$, which determines the spin (spinor) orbitals of the C₆H₆ molecule corresponding to its indicated spinless orbitals.

For instance, from Tables 5 and 6, one can see that if the electron spin is taken into account, the nondegenerate spinless orbital Γ_3^- (A_3^-) of the benzene molecule transforms into the spinor doubly degenerate orbital Γ_8^- ((E_2')$^-$), and the nondegenerate spinless orbital Γ_4^+ (A_4^+) into the doubly degenerate spin orbital Γ_7^+ ((E_1')$^+$). If the spin-orbit interaction is taken into consideration, each of the doubly de-

Table 3. **Characters of the equivalence representation of the atoms in the benzene molecule, D_{eq}, the representation of the polar vector $\Gamma_{\mathbf{r}}$, the representation of all atomic displacements in the benzene molecule, Γ_{dis}, the equivalence representation of the carbon atoms in the benzene molecule, $(D_{\text{eq}})_{\text{C}}$, the representation of the π-orbital symmetry in the $6/mmm$ group (the representation of the polar vector $\Gamma_{\boldsymbol{z}}$ directed along the Oz-axis), and the representation of the π-orbitals of the benzene molecule without talking the electron spin into account, $\Gamma_{\boldsymbol{\pi}}$**

$6/mmm$ (D_{6h})	e	$2c_3$	$3u_2$	c_2	$2c_6$	$3u'_2$	i	$2ic_3$	$3iu_2$	ic_2	$2ic_6$	$3iu'_2$
D_{eq}	12	0	4	0	0	0	0	0	0	12	0	4
$\Gamma_{\mathbf{r}}$	3	0	-1	-1	2	-1	-3	0	1	1	-2	1
$\Gamma_{\text{dis}} = D_{\text{eq}} \otimes \Gamma_{\mathbf{r}}$	36	0	-4	0	0	0	0	0	0	12	0	4
$(D_{\text{eq}})_{\text{C}}$	6	0	2	0	0	0	0	0	0	6	0	2
Γ_z	1	1	-1	1	1	-1	-1	-1	1	-1	-1	1
$\Gamma_\pi = (D_{\text{eq}})_{\text{C}} \otimes \Gamma_z$	6	0	-2	0	0	0	0	0	0	-6	0	2

Table 4. **Expansion of the representation of the π-orbitals of the benzene molecule without taking the electron spin into account (the representation of $\Gamma_{\boldsymbol{\pi}}$ on the irreducible vector representations of the $6/mmm$ (D_{6h}) group**

$6/mmm$ (D_{6h})		e	$2c_3$	$3u_2$	c_2	$2c_6$	$3u'_2$	i	$2ic_3$	$3iu_2$	ic_2	$2ic_6$	$3iu'_2$	n_{Γ_π}
Γ_1^+	A_1^+	1	1	1	1	1	1	1	1	1	1	1	1	0
Γ_1^-	A_1^-	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	0
Γ_2^+	A_2^+	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1	0
Γ_2^-	A_2^-	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1	0
Γ_3^+	A_3^+	1	1	-1	1	1	-1	1	1	-1	1	1	-1	0
Γ_3^-	A_3^-	1	1	-1	1	1	-1	-1	-1	1	-1	-1	1	1
Γ_4^+	A_4^+	1	1	-1	-1	-1	1	1	1	-1	-1	-1	1	1
Γ_4^-	A_4^-	1	1	-1	-1	-1	1	-1	-1	1	1	1	-1	0
Γ_5^+	E_1^+	2	-1	0	2	-1	0	2	-1	0	2	-1	0	0
Γ_5^-	E_1^-	2	-1	0	2	-1	0	-2	1	0	-2	1	0	1
Γ_6^+	E_2^+	2	-1	0	-2	1	0	2	-1	0	-2	1	0	1
Γ_6^-	E_2^-	2	-1	0	-2	1	0	-2	1	0	2	-1	0	0
χ_{Γ_π}		6	0	-2	0	0	0	0	0	0	-6	0	2	

Table 5. **Characters of the two-valued projective representations of the projective class K_1 of the $6/mmm$ (D_{6h}) group**

Projective class	Notation of irreducible projective representation	$6/mmm$ (D_{6h})															
		e	c_3	c_3^2	$3u_2$	c_2	c_6^5	c_6	$3u'_2$	i	ic_3	ic_3^2	$3iu_2$	ic_2	ic_6^5	ic_6	$3iu'_2$
K_1	$(\Gamma')_1^+$ (Γ_7^+) $(E'_1)^+$	2	1	-1	0	0	$\sqrt{3}$	$-\sqrt{3}$	0	2	1	-1	0	0	$\sqrt{3}$	$-\sqrt{3}$	0
	$(\Gamma')_1^-$ (Γ_7^-) $(E'_1)^-$	2	1	-1	0	0	$\sqrt{3}$	$-\sqrt{3}$	0	-2	-1	1	0	0	$-\sqrt{3}$	$\sqrt{3}$	0
	$(\Gamma')_2^+$ (Γ_8^+) $(E'_2)^+$	2	1	-1	0	0	$-\sqrt{3}$	$\sqrt{3}$	0	2	1	-1	0	0	$-\sqrt{3}$	$\sqrt{3}$	0
	$(\Gamma')_2^-$ (Γ_8^-) $(E'_2)^-$	2	1	-1	0	0	$-\sqrt{3}$	$\sqrt{3}$	0	-2	-1	1	0	0	$\sqrt{3}$	$-\sqrt{3}$	0
	$(\Gamma')_3^+$ (Γ_9^+) $(E'_3)^+$	2	-2	2	0	0	0	0	0	2	-2	2	0	0	0	0	0
	$(\Gamma')_3^-$ (Γ_9^-) $(E'_3)^-$	2	-2	2	0	0	0	0	0	-2	2	-2	0	0	0	0	0

Table 6. **Characters of the equivalence representation of atoms in the benzene molecule, D_{eq}, the representation of the polar vector Γ_{r}, the representation of all atomic displacements in the benzene molecule, Γ_{dis}, the equivalence representation of the carbon atoms in the benzene molecule, $(D_{\mathrm{eq}})_{\mathrm{C}}$, the representation of the π-orbital symmetry in the $6/mmm$ group (the representation of the polar vector Γ_z directed along the Oz-axis), and the representation of the π-orbitals of the benzene molecule without talking the electron spin into account, Γ_π**

$6/mmm\ (D_{6h})$	e	c_3	c_3^2	$3u_2$	c_2	c_6^5	c_6	$3u_2'$	i	ic_3	ic_3^2	$3iu_2$	ic_2	ic_6^5	ic_6	$3iu_2'$
Γ_z	1	1	1	-1	1	1	1	-1	-1	-1	-1	1	-1	-1	-1	1
$(D_{\mathrm{eq}})_{\mathrm{C}}$	6	0	0	2	0	0	0	0	0	0	0	0	6	0	0	2
$\Gamma_z' = \Gamma_z \otimes D_{1/2}^+$	2	1	-1	0	0	$-\sqrt{3}$	$\sqrt{3}$	0	-2	-1	1	0	0	$\sqrt{3}$	$-\sqrt{3}$	0
$\Gamma_\pi' = (D_{\mathrm{eq}})_{\mathrm{C}} \otimes \Gamma_z'$	12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\Gamma_3^-(A_3^-) \otimes D_{1/2}^+$	2	1	-1	0	0	$-\sqrt{3}$	$\sqrt{3}$	0	-2	-1	1	0	0	$\sqrt{3}$	$-\sqrt{3}$	0
$\Gamma_4^+(A_4^+) \otimes D_{1/2}^+$	2	1	-1	0	0	$\sqrt{3}$	$-\sqrt{3}$	0	2	1	-1	0	0	$\sqrt{3}$	$-\sqrt{3}$	0
$\Gamma_5^-(E_1^-) \otimes D_{1/2}^+$	4	-1	1	0	0	$\sqrt{3}$	$-\sqrt{3}$	0	-4	1	-1	0	0	$-\sqrt{3}$	$\sqrt{3}$	0
$\Gamma_6^+(E_2^+) \otimes D_{1/2}^+$	4	-1	1	0	0	$-\sqrt{3}$	$\sqrt{3}$	0	4	-1	1	0	0	$-\sqrt{3}$	$\sqrt{3}$	0

generate spinless orbitals $\Gamma_5^-(E_1^-)$ and $\Gamma_6^+(E_2^+)$ becomes split into two components, which are doubly degenerate spinor orbitals. Namely, the doubly degenerate spinless orbital $\Gamma_5^-(E_1^-)$ becomes split into two doubly degenerate spinor orbitals $\Gamma_7^-((E_1')^-)$ and $\Gamma_9^-((E_3')^-)$, and the doubly degenerate spinless orbital $\Gamma_6^+(E_2^+)$ into two doubly degenerate spinor orbitals $\Gamma_8^+((E_2')^+)$ and $\Gamma_9^+((E_3')^+)$. This result is important for the experimental studies of both the benzene molecule itself and the complexes with its participation [9].

A schematic diagram illustrating the transformations of the spinless orbitals of the C_6H_6 molecule into its spinor orbitals, as well as the corresponding manifestations of the spin-dependent fine structure and the symmetry of the spinless orbital splitting in this molecule, when the electron spin is taken into account is shown in Fig. 7. The right panels demonstrate the corresponding distribution maps of the electron wave function in a vicinity of the molecular skeleton for each spinor π'-orbital of the benzene molecule, which were calculated with the help of the Gaussian-09 software [10].

It is important to note that if the electron spin is taken into account, the energy spectrum of the π'-orbitals in the benzene molecule C_6H_6 forms all six, without exceptions, spinor orbitals that are feasible according to the symmetry of the projective class K_1 of the $6/mmm\ (D_{6h})$ group. Furthermore, each of the symmetry types in the projective class K_1 reveals itself only once in the electronic energy spectrum of the π'-orbitals of the benzene molecule.
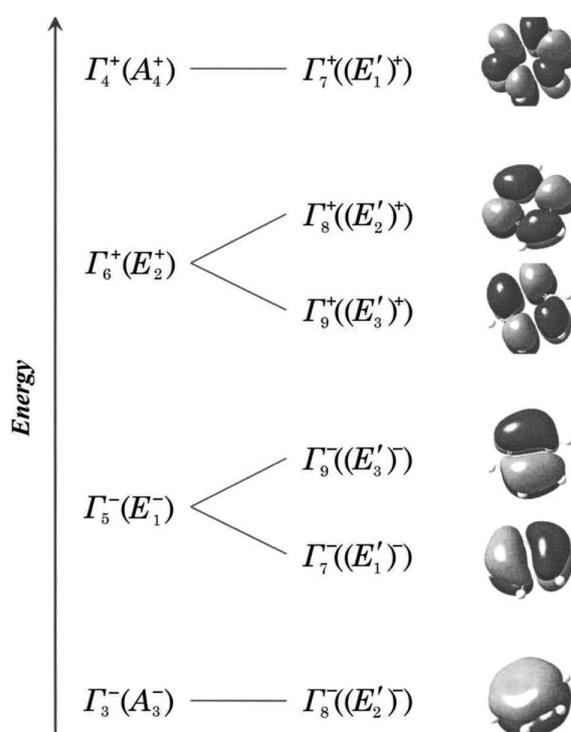
Fig. 7. Schematic diagrams of the spin-dependent splittings of the electronic π'-orbitals in the benzene molecule (left panels) and the maps of the corresponding wave functions (right panels)

According to the results of quantum chemical calculations obtained by the Gaussian-09 software [10], the magnitudes of the spin-dependent splittings equal 1–2 meV. This value agrees well with the estimates

made for the energy of the spin-orbit interaction in the carbon atoms (also about 1–2 meV) [11]. It is also of interest to attract attention to that the calculated energy distance between the binding spinor orbital $\Gamma_8^-((E_2')^-)$ and the anti-binding spinor orbital $\Gamma_7^+((E_1')^+)$ in the carbon skeleton of the benzene molecule is about 24 eV, which is close to an energy distance of about 19 eV between the valence and conduction bands at the point Γ in the Brillouin zone of single-layer graphene [12].

5. Conclusions

Making use of the quantum-mechanical projection operator, the analytical expressions and vector images for the patterns of all normal vibrations of the benzene molecule, including doubly degenerate ones, have been obtained for the first time. The characters of the equivalence representation for the carbon atoms in the benzene molecule are determined and used to calculate the representation characters of the electronic π-orbitals in the benzene molecule without taking the electron spin into account and the projective representation characters of the projective class K_1 characterizing the symmetry of the electronic π'-orbitals taking the electron spin into account. It is shown for the first time that the account for the electron spin leads to the appearance of a spin-dependent splitting in the electronic states of the benzene molecule. The magnitudes of those splittings equal about 1–2 meV because of the low spin-orbit interaction energy of the carbon atoms.

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СИМЕТРІЯ КОЛИВАЛЬНИХ
СТАНІВ ТА ЕЛЕКТРОННИХ π-ОРБІТАЛЕЙ
МОЛЕКУЛИ БЕНЗЕНУ C_6H_6. ТОНКА
СТРУКТУРА СПІНЗАЛЕЖНИХ РОЗЩЕПЛЕНЬ

Із застосуванням оператора проектування на елементи матриць незвідних представлень точкової групи симетрії $6/mmm$ (D_{6h}) молекули бензену C_6H_6 побудовано аналітичні вирази та векторні зображення форм всіх її нормальних коливань, у тому числі двократно вироджених. Знайдено характери представлень, що відповідають симетрії π-електронних орбіталей молекули бензену без урахування спіну електрона та проективних представлень її спінорних π'-орбіталей. Представлення спінорних π'-орбіталей молекули бензену C_6H_6 належать проективному класу K_1 та описують тонку структуру вперше встановлених спінзалежних при врахуванні спіну електрона розщеплень станів, вироджених без врахування спіну π-орбіталей.

Ключові слова: бензен, векторні та спінорні представлення груп симетрії, форми нормальних коливань, класи проективних представлень груп симетрії, спінзалежне розщеплення електронних станів.