SYMMETRY OF GENERALIZED MEAN-SQUARE VIBRATION AMPLITUDES AND THEIR EFFECT ON MEAN AND EQUILIBRIUM BOND LENGTHS IN BENZENE, PYRIDINE, AND N-OXYPYRIDINE

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Symmetry properties of generalized mean-square vibration amplitudes for plane six-membered rings belonging to the \( C_{2v} \) and \( D_{3h} \) symmetry groups are investigated. Corrections to average and equilibrium interatomic distances in benzene, pyridine, and \( N \)-oxypyridine are calculated. The character of the corrections in the series of these molecules and their deuterosubstituted analogs is investigated.

Key words: generalized mean-square vibration amplitudes, symmetry, corrections to average and equilibrium bond lengths, benzene, pyridine, deuterosubstituted derivatives.

In modern methods of evaluation of molecular structure, one should discriminate between equilibrium parameters and various average values of these parameters. In estimating equilibrium bond lengths from experimental data, values of generalized mean-square vibration amplitudes (GEMSVAs), characterizing changes in interatomic distances in higher-order approximations, are essential.

In the theory of molecular vibrations, one calculates on the basis of GEMSVAs the average parallel amplitude \( l \) and the coefficient \( K \) of perpendicular amplitudes defined by the relationships

\[
l = \frac{\langle \Delta z^2 \rangle^{1/2}}{2}, \quad K = \frac{\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle}{2R},
\]

where \( \Delta z \) is the change in the bond length, \( \Delta x \) and \( \Delta y \) are displacements in the plane perpendicular to the bond, and \( R \) is the interatomic distance.

Interatomic distances evaluated electronographically are refined using the quantities \( l \) and \( K \). These quantities enter into expressions for evaluation of average \( R^E \) and equilibrium \( R^E \) interatomic distances from experimentally measured distances \( R^m \) corresponding to peak maxima on the radial-distribution curve [1]:

\[
R_{ij}^E = R_{ij}^m + \frac{l_{ij}^2}{R_{ij}^m}, \quad R_{ij}^E = R_{ij}^m + \langle \frac{l_{ij}^2}{R_{ij}^m} \rangle - K_{ij} - \langle \Delta z_{ij} \rangle,
\]

where \( \langle \Delta z_{ij} \rangle \) is the first-order term due to anharmonicity.

The objective of the present work is to investigate the symmetry of the GEMSA of interatomic distances, calculate corrections to average \( \Delta R^E \) and equilibrium \( \Delta R^E \) lengths

\[
\Delta R_{ij}^E = l_{ij}^2/R_{ij}^m, \quad \Delta R_{ij}^E = l_{ij}^2/R_{ij}^m - K_{ij}
\]
for pairs of bonded and unbonded atoms in benzene, pyridine, N-oxypyridine, and their deuterosubstituted analogs, and investigate the character of variation of $\Delta R^2$ and $\Delta R^2$ in the series of the molecules under consideration.

GEMSVA symmetry. By definition [1], GEMSVAs of the $n$-th bond are

$$\langle \Delta \alpha_n \Delta \beta_n \rangle, \quad \alpha, \beta = x, y, z,$$

where $\Delta \alpha_n$ are defined by Eq. (1).

Investigations of symmetry properties were carried out as follows [2]: 1) the inherent symmetry $\Gamma_n$ of the $n$-th bond was determined; 2) the behavior of the bond displacements $\Delta \alpha_n$ under the symmetry operations of the representation $\Gamma_n$ was considered, and the representation of displacements $\Gamma_{\Delta \alpha_n}$ was determined; 3) the representation of the product (4) was determined as

$$\Gamma_{\Delta \alpha_n \Delta \beta_m} = \Gamma_{\Delta \alpha_n \Gamma_{\Delta \beta_m}}.$$

For plane molecules (Fig. 1), mixed products of in-plane and out-of-plane displacements are as follows:

$$\langle \Delta x \Delta y \rangle = \langle \Delta y \Delta y \rangle = 0.$$

Mixed products for in-plane displacements $\langle \Delta z \Delta z \rangle$ are nonzero when products of $\Gamma_{\Delta z}$ and $\Gamma_{\Delta z}$ contain a common symmetry type. This is a sufficient but not a necessary condition.

Pyridine and N-oxypyridine belong to the $C_{2v}$ symmetry group (Fig. 1). The entire multitude of bonds in these molecules can be divided into the three types.

Type I. Bonds having inherent $C_{2v}$ symmetry:

$$N_1 \ldots C_4, N_1 \ldots H_{10}, C_4 \ldots H_{10}, N_1 \ldots O_7.$$

Type II. Bonds having inherent $C_{2v}$ symmetry:

$$C_2 \ldots C_6, C_3 \ldots C_5, H_8 \ldots H_1, H_9 \ldots H_{11}.$$

Type III. Bonds having inherent $C_{2v}$ symmetry. All other bonds not included in types I and II are referred to this type.

Within the limits of each of the symmetry types, all displacements are identical. Therefore, the bonds entering into each of the types can be called equivalent with respect to symmetry of displacements.

Table 1 presents an analysis of properties of the GEMSVA symmetry for the symmetry group $C_{2v}$. A similar consideration of properties of the displacement symmetry has been carried out for the benzene molecule,