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The calculation of the vibrational spectrum of methylfurazan and dimethylfurazan molecules in coordinates X_δ^0

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Abstract

In the framework of the density functional theory methods (DFT) in the valence-split basis with the correlation functional of Lee, Yang and Parr, are famous acronym B3LYP 6-311++G(3df,3pd), two molecules methylfurazan and dimethylfurazan were calculated. The force field of molecules in equilibrium geometry is determined. Then, the resulting force coefficients of the Cartesian coordinate system were translated into the coordinates of X_δ^0. In these coordinates, each of the bond vectors of the molecule is represented in its own rectangular coordinate system. The sum of the diagonal elements forms the so-called generalized force coefficient of each bonds. This makes it possible to compare the power coefficients of different molecules and evaluate the effect of molecular structure on the "rigidity of bonds". Such an approach was proposed by L.S. Mayants and G. B. Schaltuper for the purpose of the correct solution of the spectral problem for objects with any combination of atoms (these are molecules with covalent bonds, various complexes, complex supramolecular formations, etc.), while maintaining the "chemical visibility" of the results.

So for molecules methyfurazan determined that the generalized force coefficients of bonds C=N, N-O and C-H in the molecule is, respectively, 18.5366 mdyn/Å, 15.5121 mdyn/Å and 6.8250 mdyn/Å (average values) obtained with the B3LYP/6-311++G(3df,3pd) in the coordinates X_δ^0. For the dimethylfurazan molecule, it is obtained that the generalized binding force constants C=N, N-O and C-H (mean values for C-H) are 18.4430 mdyn/Å, 15.3478 mdyn/Å and 6.7566 mdyn/Å, respectively.

The resulting force field of molecules allowed to solve the so-called spectral problem and to find the frequencies and forms of normal vibrations in the harmonic approximation (for the considered molecules).

For molecules methylfurazan found the most intense band with the value at 919 cm^{-1}. It can be attributed to the symmetric vibration of two bonds C=N and C=C of the furazan ring. Next in intensity vibration has a wave number 1079 cm^{-1} and corresponds to the movement of atoms N and O in opposite directions. At the same time, there is still a valence vibration for the C-C ring coupling. The hydrogen atoms of the methyl group move in concert. In General, this vibration is related to the asymmetric for C=N and N-O bonds of ring (from the methyl group) and the rocking vibration for $-CH_3$ group. Next, in descending order of intensity is the vibration of 1025 cm^{-1}. It can be attributed to the symmetrical vibration of the two bonds N-O and C-C in the ring.

For molecules dimethylfurazan found the most intense band with the value at 1073 cm^{-1}. This band can be attributed to the symmetric valence vibrations of the N-O bonds of the furazan ring. The next band intensity has a value of 1494 cm^{-1}. It can be interpreted as the valence vibration of the C-C bond of the furazan ring together with the deformation vibrations in the methyl group.

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