

The calculation of the vibrational spectrum of methylfuran and dimethylfuran molecules in coordinates X_{δ}^0

© Alexander V. Belik,^{*,†} and Ekaterina V. Sobol

Faculty of Chemical Technology and Computing Chemistry. The Chelyabinsk State University.

Kashyrinych Br. St., 129. Chelyabinsk, 454001. Russia.

Phone: +7 (351) 799-70-66. E-mail: belik@csu.ru

^{*}Supervising author; [†]Corresponding author

Keywords: methylfuran, dimethylfuran, the generalized force constants, coordinates X_{δ}^0 , calculations DFT, vibration frequencies.

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 methylfuran and dimethylfuran 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 methylfuran determined that the generalized force coefficients of bonds C=N, N-O and C-H in the molecule is, respectively, 18.5366 mdyne/Å, 15.5121 mdyne/Å and 6.8250 mdyne/Å (average values) obtained with the B3LYP/6-311++G(3df,3pd) in the coordinates X_{δ}^0 . For the dimethylfuran 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 mdyne/Å, 15.3478 mdyne/Å and 6.7566 mdyne/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 methylfuran 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 –CH₃ 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 dimethylfuran 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.

References

- [1] L.I. Khmel'nitsky, S.S. Novikov, T.I. Godovikova. Chemistry of furoxans (Structure and synthesis). Moscow: Nauka. 1996. 383p. (russian)
- [2] L.I. Khmel'nitsky, S.S. Novikov, T.I. Godovikova. Chemistry of furoxans (Reaction and application). Moscow: Nauka. 1996. 430p. (russian)
- [3] N.N. Makhova, A.S. Kulikov. Advances in the chemistry of monocyclic amino- and nitro-furoxans. *Successes of chemistry*. 2013. Vol.82. No.11. P.1007-1033. (russian)
- [4] D.A. Pyatakov, V.M. Chernyshev. High-Energy materials on the basis of nitrogen-containing heterocycles: textbook. *Novocherkassk: South.-Grown. States polytechnic. Univ-tet*. 2013. 84p. (russian)

- [5] V. Kon. Electronic structure of matter – wave functions and density functionals. *Advances in physical Sciences* (Nobel lectures in chemistry – 1998). **2002**. Vol.172. No.3. P.336-348. (russian)
- [6] F. Jensen. Introduction to Computational Chemistry. 2nd ed. *Wiley & Sons*. **2007**. 599p.
- [7] W. Koch, M.C. Holthausen. A Chemist's Guide to Density Functional Theory 2nd ed. Weinheim: *Wiley-Vch*. **2001**. 293p.
- [8] A.V. Belik, and E.V. Sobol. Computation of vibrational spectra of furozan and nitrofurozan molecules in coordinates X_8^0 . *Butlerov Communications*. **2018**. Vol.55. No.7. P.13-21. DOI: 10.37952/ROI-jbc-01/18-55-7-13
- [9] C. Lee, W. Yang, R.G. Parr. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Journal Physical Review B*. **1988**. Vol.37. No.2. P.785-789.
- [10] A.V. Belik. New aspects of computational chemistry: monograph. *Chelyabinsk: Polygraph-Master*. **2015**. 200p. (russian)
- [11] A.V. Belik. Computation of vibrational spectra of furozan and dimethylfurozan molecules in coordinates X_8^0 with an estimation of a force fields in frameworks DFT. *Butlerov Communications*. **2015**. Vol.43. No.8. P.153-161. DOI: 10.37952/ROI-jbc-01/15-43-8-153
- [12] Belik, A.V. Computation of vibrational spectra of 4-methylfuroxane and 3-methylfuroxane molecules in coordinates X_8^0 with an estimation of a force fields in frameworks DFT. *Butlerov Communications*. **2016**. Vol.45. No.1. P.136-144. DOI: 10.37952/ROI-jbc-01/16-45-1-136
- [13] Belik, A.V. Computation of vibrational spectra of 5-methyl-4-nitrobenzofuroxane and 7-methyl-4-nitrobenzofuroxane molecules in coordinates X_8^0 with an estimation of a force fields in frameworks DFT. *Butlerov Communications*. **2016**. Vol.45. No.3. P.128-142. DOI: 10.37952/ROI-jbc-01/16-45-3-128
- [14] L.S. Mayants, G.B. Shaltuper. A new approach to the complete calculation of the vibrations of any molecule. *Dokl. USSR ACADEMY OF SCIENCES*. **1972**. No.206. P.657-660. (russian)
- [15] L.S. Mayants, G.B. Shaltuper. General methods of analysing molecular vibrations. *J. Mol. Struct.*, **1975**. Vol.24. P.409-431.
- [16] A.V. Belik. To calculation of the force coefficients of the ammonia molecule. *Bulletin of the Chelyabinsk state University. Physics*. **2011**. Vol.15. No.10. P.60-62.
- [17] A.B. Belik. Theoretical estimation of the force field of tetrafluorohydrazine. *Butlerov Communications*. **2013**. Vol.34. No.4. P.90-94. DOI: 10.37952/ROI-jbc-01/13-34-4-90
- [18] A.V. Belik. The theory and practice of calculation of vibration of molecules: textbook. *Chelyabinsk: Publishing house of Bashkir University*. **1985**. 48p. (russian)
- [19] A.V. Belik. Modern elements computational chemistry: monograph. Chelyabinsk: *publishing house of Chelyabinsk. State University*. **2013**. 161p. (Classical University). (russian)
- [20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, et al. Gaussian 09, Revision A.02. Wallingford: Gaussian, Inc. **2009**.
- [21] J.A. Joule, K. Mills. Heterocyclic Chemistry. *Moscow: Mir*. **2004**. 728p. (russian)
- [22] A.R. Katritzky, J. Lagovskaya. Chemistry of Heterocyclic Compounds. *Moscow: Foreign Literature*. **1963**. 287p. (russian)
- [23] E.V. Butyrskaya. Computational chemistry: basic theory and work with programs Gaussian and Gauss View. *Moscow: SOLON-PRESS*. **2011**. 224p. (russian)