

Thematic section: Quantum-Chemical Research.

Subsection: Physical Organic Chemistry.

Full Paper

The Reference Object Identifier – ROI-jbc-A/21-1-1-3

The Digital Object Identifier – DOI: 10.37952/ROI-jbc-A/21-1-1-3

Received 18 January 2021; Accepted 20 January 2021

The calculation of the vibrational spectrum of F₃CNO₂, F₂C(NO₂)₂ and FC(NO₂)₃ molecules in coordinates X_δ⁰

Alexander V. Belik,*⁺ and Albina R. Gayfulina

*Faculty of Chemical Technology and Computing Chemistry. Chelyabinsk State
University. Kashyrynych Br. St, 129. Chelyabinsk, 454001. Russia.*

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

*Supervising author; ⁺Corresponding author

Keywords: trifluoronitroethane, difluorodinitromethane, fluorotrinitromethane, generalized force constants, coordinates X_δ⁰, 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), three molecules trifluoronitroethane, difluorodinitromethane and fluorotrinitromethane 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_δ⁰. 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 trifluoronitroethane determined that the generalized force coefficients of bonds C-F, C-N and N-O in the molecule is, respectively, 9.1324 mdyn/Å, 5.4022 mdyn/Å and 13.3059 mdyn/Å (average values) obtained with the B3LYP/6-311++G(3df,3pd) in the coordinates X_δ⁰. For the difluorodinitromethane molecule, it is obtained that the generalized binding force constants C-F, C-N and N-O (average values) are 9.3025 mdyn/Å, 5.3066 mdyn/Å and 13.3694 mdyn/Å, respectively. For the fluorotrinitro-methane molecule, it is obtained that the generalized binding force constants C-F, C-N and N-O (average values) are 9.6010 mdyn/Å, 5.1676 mdyn/Å and 13.4389 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 trifluoronitroethane found the most intense band with the value at 1680 cm^{-1} . It can be attributed to the antisymmetric vibration of two bonds NO.

For molecules difluorodinitromethane found the most intense band with the value at 1668 cm^{-1} . This band can be attributed to the antisymmetric valence vibrations of the N-O bonds.

For molecules fluorotrinitromethane found the most intense band with the value at 1693 cm^{-1} . This band can be attributed to the antisymmetric valence vibrations of the N-O bonds.

For citation: Alexander V. Belik, Albina R. Gayfulina. The calculation of the vibrational spectrum of F_3CNO_2 , $\text{F}_2\text{C}(\text{NO}_2)_2$ and $\text{FC}(\text{NO}_2)_3$ molecules in coordinates X_8^0 . *Butlerov Communications A*. **2021**. Vol.1. No.1. Id.3. DOI: 10.37952/ROI-jbc-A/21-1-1-3

References

- [1] S.S. Novikov, G.A. Shvehgeimer, V.V. Sevost'yanova, V.A. Shlyapochnikov. Chemistry of aliphatic and alicyclic nitrocompounds. *Moscow: Chemistry*. **1974**. 416p. (Russian)
- [2] A.V. Pankratov. Chemistry of nitrogen fluorides. *Moscow: Chemistry*. **1973**. 264p. (Russian)
- [3] S.M. Igumnov, E.V. Igumnova. Synthesis of fluororganic compounds. Part 1. *Moscow: "PiM-Invest"*. **2010**. 215p. (Russian)
- [4] M.V. Volkenstein, L.A. Gribov, M.A. Eliashevich, B.I. Stepanov. Vibrations of molecules. *Moscow: Nauka*. **1972**. 699p. (Russian)
- [5] V. Kon. Electronic structure of matter – wave functions and density functionals. *Journal of applied physics* (Nobel lectures in chemistry – 1998). **2002**. Vol.172. No.3. P.336-348. (Russian)
- [6] 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.
- [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. Theoretical estimation of the force field of tetrafluorohydrazine. *Butlerov Communications*. **2013**. Vol.34. No.4. P.90-94. ROI-jbc-01/13-34-4-90
- [9] A.V. Belik. New aspects of computation chemistry: monograph. *Chelyabinsk: Polygraph – Master*. **2015**. 200p. (Russian)
- [10] 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
- [11] 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)
- [12] L.S. Mayants, G.B. Shaltuper. General methods of analysing molecular vibrations. *J. Mol. Struct.* **1975**. Vol.24. P.409-431.
- [13] A.V. Belik. Modern elements computational chemistry: monograph. *Chelyabinsk: Publishing House of Chelyabinsk. State University*. **2013**. 161p. (Classical University).
- [14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, et al. Gaussian 09, Revision A.02. Wallingford: Gaussian, Inc. **2009**.
- [15] E.V. Butyrskaya. Computational chemistry: basic theory and work with programs Gaussian and Gauss View. *Moscow: SOLON-PRESS*. **2011**. 224p. (Russian)
- [16] Alexander V. Belik, Albina R. Gayfulina. The calculation of the vibrational spectrum of F_3CNO_2 , $\text{F}_2\text{C}(\text{NO}_2)_2$ and $\text{FC}(\text{NO}_2)_3$ molecules in coordinates X_8^0 . *Butlerov Communications*. **2021**. Vol.65. No.1. P.32-40. DOI: 10.37952/ROI-jbc-01/21-65-1-32 (Russian)