Quantum chemical calculations of the vibrational spectrum of aliphatic nitro compounds. Cluster analysis of torsion oscillations

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Abstract. The data of theoretical analysis of vibrational spectra in the long-wave range of different isomers of methyl nitrite, methyl, ethyl, n-propyl nitrate, as well as the electron density distribution obtained within the B3LYP Density Functional Theory method with the 6-31G(d) basis set are presented. The cluster analysis of charge distribution on carbon, oxygen, nitrogen atoms and torsion oscillation frequencies in the range of 10-400 cm\textsuperscript{-1} is carried out.

1. Introduction
Quantum chemical calculations are widely used to study the structure, molecular spectra, and reactivity of organic compounds The use of these methods are of considerable interest for the calculation of vibrational spectra of nitrogen-containing compounds which are widely used in various industries, as a component of high-energy substances. Earlier, the vibrational spectra and the structure of a number of aliphatic nitro compounds were studied using quantum chemical calculation within the B3LYP Density Functional Theory method with the 6-31G(d) basis set. As a result, energetically most favorable conformers, as well as the spectral characteristics of the structure and conformational states of molecules were discovered [1-6]. As is known, a long-wave IR spectroscopy is an ideal method for studying the intramolecular and intermolecular displacements, under conditions when the danger of chemical decomposition is practically absent [7].

In our work, the statistical processing and cluster analysis of torsion oscillation frequencies in the long-wave IR spectral range (10-400 cm \textsuperscript{-1}) are carried out of the following nitro compounds: cis - (C) and \textit{trans} (T)-isomer of methyl nitrite (MNI), \textit{trans}- isomer of methyl nitrate (MNA), \textit{trans} - and gauche (G) -isomer of ethyl nitrate (ETN), as well as a series of isomers (TG, TT, GG, GG') of n-propyl nitrate (PNA). According to the earlier studies [3,4,6] the distinguished conformers are the most energy-efficient.
Special attention is paid to the analysis of torsion oscillations – $\tau_{CO}$ and $\tau_{NO}$ with frequencies in the range of $10$-$400$ cm$^{-1}$.

For the calculations we applied a widely used method of *Density Functional Theory* B3LYP with the 6-31G(d)-basis, which allows to achieve high accuracy of calculations of both thermodynamic functions and spectral characteristics.

2. Calculations

All calculations within the *Density Functional Theory* (DFT) were performed using the *Gaussian 03*- software package [8]. For DFT, Becker's three parameter exchange functional was used in combination with the Lee-Yang-Parr correlation functional (B3LYP) [9,10]. The standard 6-31G (d) basis was applied. The agreement obtained stationary points and minimum potential energy is checked by calculating the Hessian matrices and analysis of the absence of imaginary frequencies. To correct systematic errors due to the limited size of the basis set of functions, force constants were multiplied by the correction scaling factors.

Conversion of force constants calculated in Cartesian coordinates to internal coordinates and its scaling were performed using the program [11].

Statistical processing of torsion oscillation frequencies and electron density distribution on atoms was carried out using the standard program of Stat Graphics Plus 5.0. The following cluster analysis options were used: method-Nearest Neighbor, Squared Euclidean.

3. Results and discussion. The influence of the electronic density distribution on the C, O and N-atoms on the $\tau_{CO}$ and $\tau_{NO}$ torsion oscillation frequencies

The torsion oscillations onset is associated with the presence of a potential barrier that inhibits free rotation around the chemical bond CO and NO.

The values of the barriers and the frequency of torsion oscillations are sensitive to the intramolecular effect determined by the chemical structure and the conformational state of the molecules. In particular, the electronic nature of the relationship between the groups of CH$_3$ and NO (MNI), CH$_3$ and NO$_2$ (MNA), CH$_2$ and NO$_2$ (ETN, PNA), as well as the distribution of $q$ charges on C, O, N atoms of these groups, will determine the height of the barrier of rotation, hence the torsion frequency.

Cluster analysis of the calculated $\tau_{CO}$ and $\tau_{NO}$ frequencies and $q$ charge distribution on the C, O and N atoms is shown in Figure 1. The first cluster is formed from the spectral and electronic data of the cis- and trans- isomer of MNI, the second cluster – from the trans-isomer of MNA, while the third one is composed from spectral and electronic data of ETN isomers, as well as the considered series of PNA isomers.

It is noteworthy that the low frequencies of $\tau_{CO}$ in the range of 70-120 cm$^{-1}$ are typical for compounds with a high electronegativity of the O-atom and a low electronegativity of the C-atom, i.e. compounds forming cluster 3 (ETN and PNA).

At the same time, higher $\tau_{NO}$ frequencies in the range of 220-380 cm$^{-1}$ are typical for the methyl nitrite isomers with the lowest positive charge of the N atom, i.e. compounds that make up cluster 1.

The obtained correlations between the charge distribution on the C, O, N atoms and the $\tau_{CO}$ and $\tau_{NO}$ oscillation frequencies of the simplest considered representatives of the series of aliphatic nitro compounds will help further while interpretation of more complex nitrogen-containing macromolecules.
Figure 1.
Cluster analysis of torsion oscillations of $\tau\text{CO}$, $\tau\text{NO}$ and distribution of electric $q$ charge on the C, O, N atoms in a series of rotating isomers of aliphatic nitro compounds.
1 cluster - methyl nitrite,
2 cluster - methyl nitrate,
3 cluster - ethyl, propyl nitrate
($q$ - in electron units, frequency CO and NO - in cm$^{-1}$)

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