ROLE OF INTERMOLECULAR INTERACTIONS IN FORMATION OF MOLECULAR CLUSTERS OF NITROMETHANE AND ITS SOLUTIONS

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INTRODUCTION

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The clustering phenomena and structural peculiarities of partially ordered liquids are of great interest in the scientific community. **The aim of the research** is to establish the mechanisms of formation of molecular clusters in vital biological objects in a condensed state with a hydrogen bond, as well as to develop new methods for studying molecular clusters and their interaction with the radiation field.

The object of the research is molecules that differ in shape and polar properties, and their molecular clusters formed by hydrogen bonds.

This work is devoted to the study of molecular clusters of liquid nitromethane and its solutions. As is known, the Raman spectrum of liquid nitromethane is complex and this complexity is explained by the formation of molecular clusters. Due to its high dissolving ability, DMF is widely used in scientific research as a solvent and a substance that forms aggregates with nanomaterials. In various industries, pharmaceuticals, and medicine it is used as a universal solvent.

Nitromethane is one of the molecules with a large dipole moment (3.54 D), so there is a possibility of dipole aggregation, but ab initio calculations have shown that there is an intermolecular hydrogen bond. This is especially observed for the structure of the dimeric cluster of nitromethane. This conclusion is confirmed by the results of charge redistribution during the formation of molecular clusters, as well as experimental results of the study of liquid nitromethane in solutions with chloroform and hexane.

PURPOSES

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- to establish the mechanisms of formation of molecular clusters in nitromethane in a condensed state with a hydrogen bond and the most general regularities of intermolecular interaction, as well as the development of new methods for studying molecular clusters and their interaction with the radiation field;
- to detect and systematize spectroscopic manifestations in the Raman spectra of the structure of molecular clusters with intermolecular and intramolecular bonds;
- to determine, using ab initio calculation methods, the optimal geometric structure, electron density distribution, spectral and energy parameters of molecular clusters in nitromethane;
- to establish the most energetically favorable structures for isolated nitromethane molecules and their molecular clusters;
- to establish the physical foundations of clustering, spatial distribution and interaction of clusters with each other in a condensed state.

EXPERIMENTAL

Raman spectroscopy was used. The spectra were recorded on a diffraction spectrometer DFS-52. The Source was argon laser LGN-503, λ = 488.0 nm, power ~ 1 W, $\Delta\nu$ = 1.8 cm^{-1}. Errors in determining the relative position of the maxima and the half-width of the bands were $\pm$ 0.3 $см^{-1}$

CALCULATIONS

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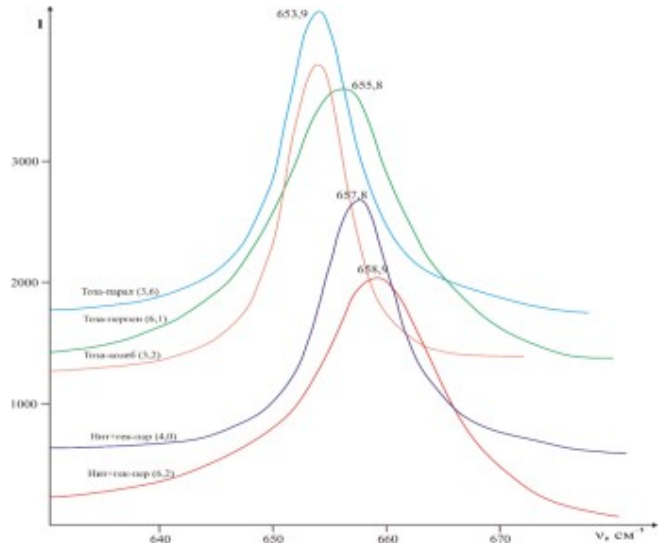
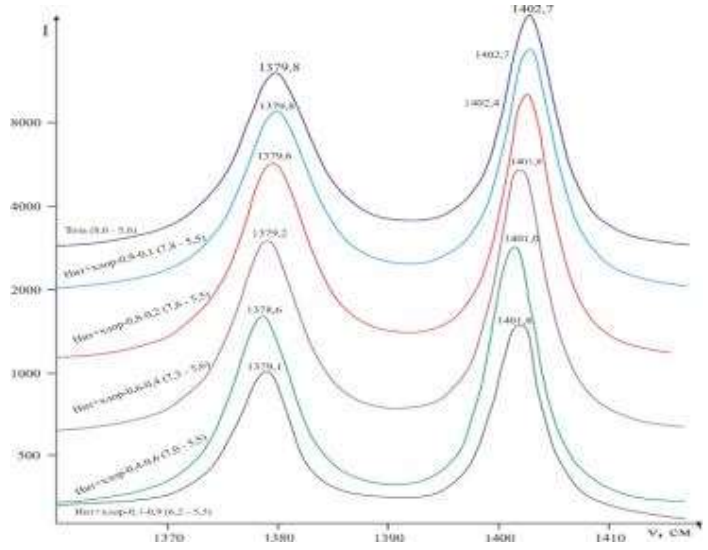
Quantum-chemical simulation we use the density functional theory with choice of interaction potential in approximation B3LYP and basis 6-31G(d,p). All density functional theory calculations were carried out using the Gaussian 03 suite software. Quantum-chemical simulation of possible cluster structure of liquid water and corresponding spectra of Raman scattering. Ab initio calculations were carried out in the B3LYP approximation with a set of Gaussian functions 6-31G++(d, p).

RESULTS

A number of low frequencies of mutual and joint vibrations appear in the Raman spectra. We have carried out an experimental study for liquid nitromethane and its solutions with hexane and chloroform. In the Raman spectra of vibrations of CNO group of nitromethane molecules, the intermolecular H-bond is clearly manifested (Fig.).From the presented spectra it can be seen that the intensity increases and the overlays will imperceptibly shift to the low-frequency side.

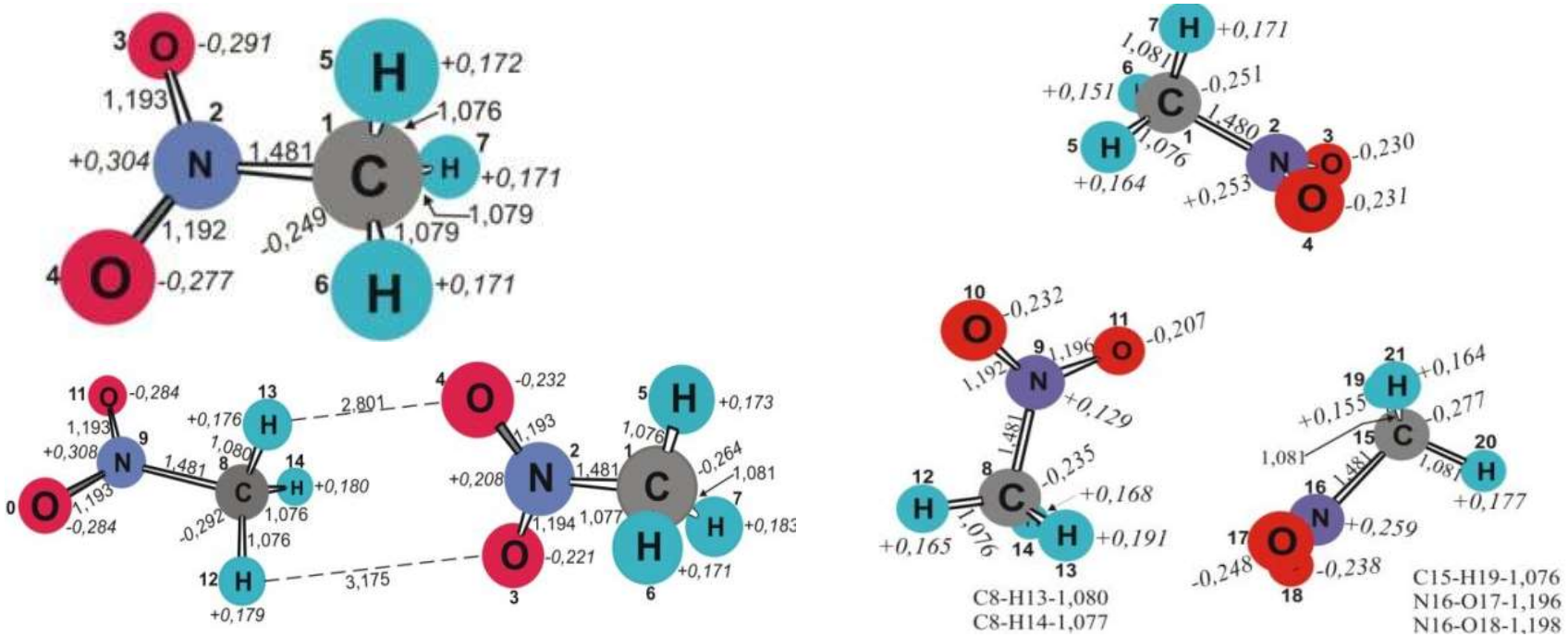


Raman spectra of the vibration band of CNO group of liquid nitromethane and its solutions with hexane



Raman spectra of the vibration band of CNO group of liquid nitromethane and its solutions with chloroform

RESULTS

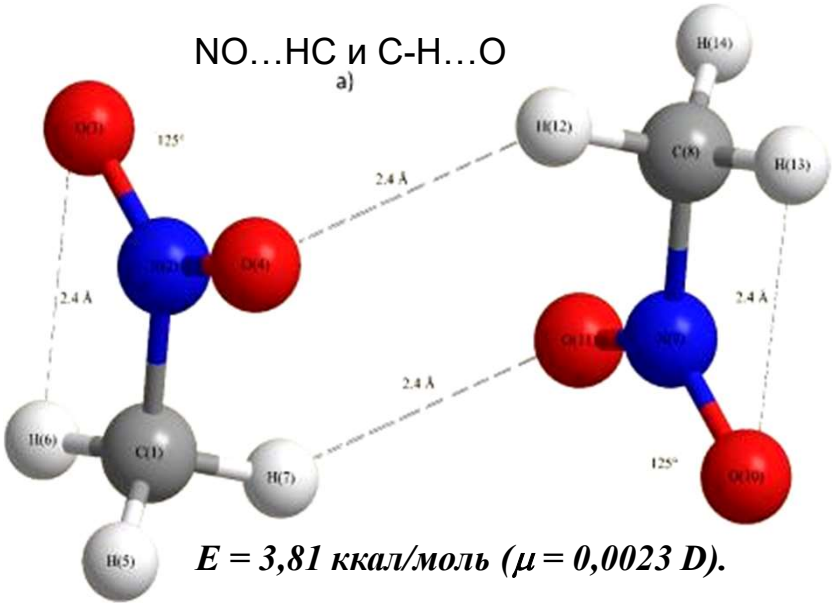


E=2,9 ккал/моль

E = 10,5 ккал/моль.

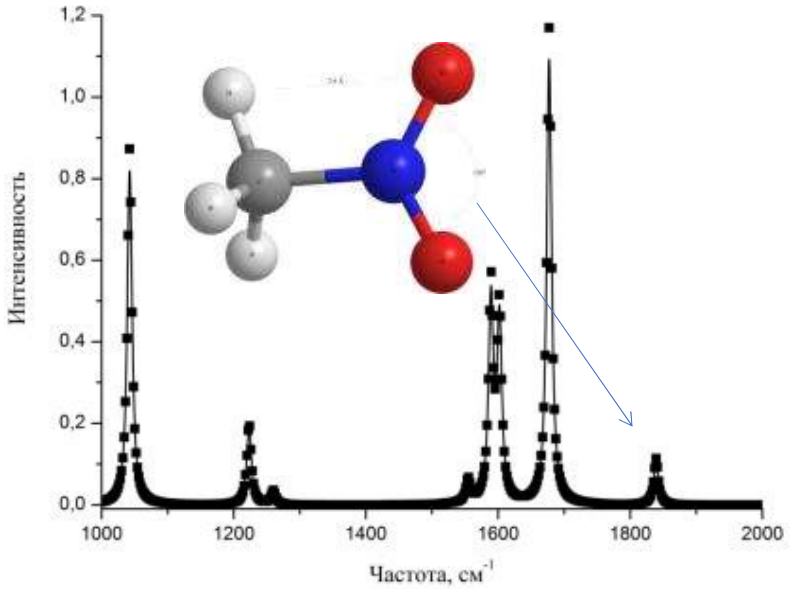
Structure of molecular clusters of nitromethane: a) monomer, b) dimer, c) trimer

RESULTS



E = 3,81 ккал/моль (μ = 0,0023 D).

Structure of a dimer cluster of nitromethane



Calculated spectra of molecular clusters of nitromethane

The main reason for aggregation is the dipole-dipole interaction, but the intermolecular hydrogen bond also makes a large contribution to the formation of molecular clusters of nitromethane. The energy of dimer formation is 3.81 kcal / mol (the dipole moment of such an aggregate is 0.0023 D). The formation of a hydrogen bond of the type NO ... HC and C-H ... O between the oxygen atom of the nitromethane molecule and the hydrogen atom of the C-H group was found, and these interactions have a significant effect on the formation of molecular clusters of nitromethane.

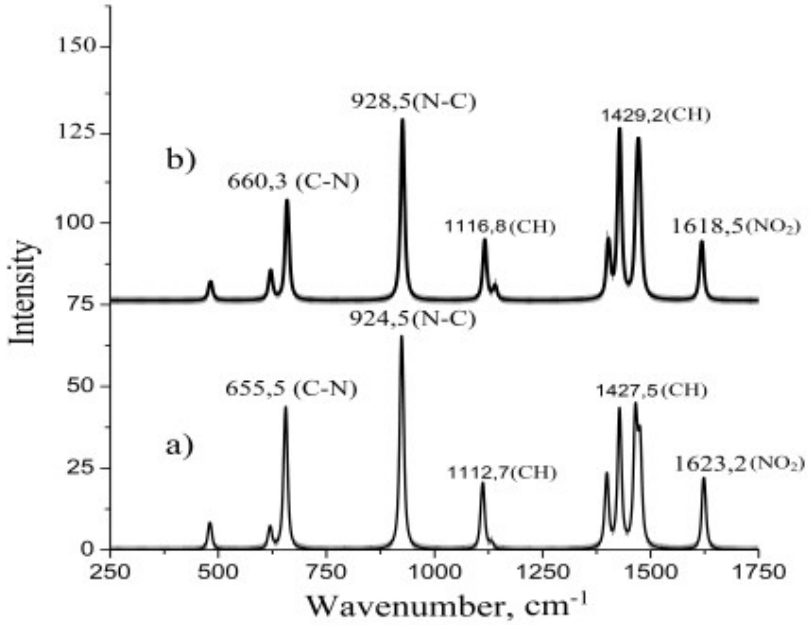
RESULTS

Redistribution of charges in the atoms of nitromethane molecules during the formation of molecular clusters

Structure	O (O_3, O_4,)	N (N_2, N_9)	O (O_{10}, O_{11})	C (C_1, C_8)	H (H_5, H6)	H (H_7,H_{12})	H (H_{13}, H_{14})
Monomer	-0,064	-0,102	-0,066	-0,344	0,176	0,200	0,200
Dimer	-0,032 -0,023	-0,188 -0,188	-0,032 -0,023	-0,378 -0,378	0,201 0,176	0,244 0,244	0,176 0,201

This conclusion is confirmed when analyzing the results of calculating the redistribution of charges (Table), as well as our experimental results of studying liquid nitromethane in solutions with chloroform.In liquid nitromethane, dimeric clusters with the orientation of molecules in a "tail" to each other, as well as trimeric clusters in the form of a closed triangle, can form. The main reason for the aggregation is the dipole-dipole interaction, but it was found by ab initio calculations that the intermolecular hydrogen bond also makes a large contribution to the formation of molecular clusters of nitromethane.

RESULTS



Raman spectra of valence vibrations of nitromethane: a) monomer and b) dimer.

Intramolecular vibrations: as expected, the bands for the dimer split into doublets with a shift towards both higher and lower frequencies. For example, the band at 3384.7 cm^{-1} (Δ=0.74) in the Raman spectra of the monomer in the dimer corresponds to two bands 3385.3 and 3392.7 cm^{-1} (both with Δ=0.75). The bands correspond to the CH vibrations of one molecule and the CH vibrations of another molecule. The monomer band with a frequency of 1042.5 cm^{-1} (Δ=0.0739) in the dimer corresponds to the bands at 1041.0 cm^{-1} (Δ=0.12) and 1042.8 cm^{-1} (Δ=0.06) , etc.

CONCLUSION

- The nitrogen atom can give four valence bonds, so it should be assumed that NO bonds are special, the charges of O atoms in the monomer are different.
- The energy of dimer formation is 3.81 kcal / mol (the dipole moment of such an aggregate is 0.0023 D). A similar value for the trimer is 10.5 kcal / mol.
- The formation of a hydrogen bond of the type NO ... HC and C-H ... O between the oxygen atom of nitromethane molecule and the hydrogen atom of C-H group was found, and these interactions have a significant effect on the formation of molecular clusters of nitromethane.
- Ab initio calculations have shown for the first time that in nitromethane in addition to dipole-dipole interactions, there are also intramolecular and intermolecular hydrogen bonds, which determine the formation of the cyclic structure of the nitromethane dimer;
- ab initio calculations taking into account experimental data give a detailed description of the energy states for characteristic and initial structures. The most energetically favorable cluster structures for nitromethane molecules and their solutions have been determined for the first time.

Thanks for attention

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