
doi:

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THEORETICAL AND EXPERIMENTAL RESEARCHES OF METHANOL CLUSTERS IN LOW-TEMPERATURE MATRICES

PACS 31.15.A-, 61.25.Em,
63.50.-x

Molecular vibrational spectra of methanol in argon and nitrogen matrices have been studied. Since methanol belongs to a class of substances with hydrogen bonds, there is a possibility of forming molecular associations and clusters with various numbers of molecules. IR spectra of methanol in Ar and N₂ matrices experimentally obtained in the temperature range from 10 to 50 K are compared with the results of computer simulation using the ab initio Car–Parrinello molecular dynamics (CPMD) method. The results obtained for small clusters in model calculations demonstrate a good correlation with experimental data for various matrices at the corresponding temperatures.

Keywords: spectroscopy, cluster structure, methanol, matrix isolation.

1. Introduction

The application of molecular vibrational spectroscopy methods in modern experimental physics makes it possible, on the one hand, to solve various problems of the applied character and, on the other hand, to study the structure of multiatomic molecules, nature and character of intermolecular interactions, internal structures of various compounds, and their dynamics [1]. Hence, there appears an opportunity to analyze variations in the internal structure of substances near their phase transition points. However, the experimental researches of involved dynamic processes running in multimolecular systems in the framework of such disciplines as biophysics, immunology, and

medicine are associated with certain difficulties. The latter results from objective factors, which include the variety of possible configurations of a system, the metastability at phase transition points, etc.

In this connection, together with experimental researches, a large role is played by molecular simulation methods, in particular, the computer-assisted molecular dynamics (MD) as one of the most powerful calculation techniques used to study and to solve complex problems in the mentioned domains. Modern tendencies in development of computer facilities make it possible to resolve problems of the algorithmic realization of available MD simulation methods. MD methods form a basis of modern computation biology. Owing to their development and application, there appeared a capability of the sequencing of a human genome. The application of computer-assisted simulation methods allows the quantitative analysis of the

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ISSN 2071-0186. Ukr. J. Phys. 2015. Vol. 60, No. 11

dynamics of nucleic acids and immunologic interactions to be carried out [2]. In particular, MD methods can be used to describe the formation (assembling) of the spatial structure of proteins, which governs their functioning in certain cases. In some works [3, 4], the results of calculations concerning the dynamics of condensed systems (the cluster structure of liquids and the nucleation phenomena in them) were reported. This is especially challenging for our researches.

Water is one of the major components of physiologic fluids. However, its anomalous properties such as the temperature dependences of isobaric heat capacity and isobaric compressibility, as well as other thermodynamic properties that considerably differ from the properties of other non-associated fluids, strongly complicate its study. The specific features of water properties are related to the presence of intermolecular hydrogen bonds, which govern the aggregation (clustering) of water in the condensed phase. Researches of water clustering processes with the help of vibrational spectroscopy are complicated owing to the presence of two hydrogen atoms bound to the oxygen atom in the molecule. For this reason, while studying the intermolecular hydrogen bond, it is expedient to use simpler model objects. As such convenient model objects, there can be molecules of monohydroxy alcohols, in particular, methanol as the nearest analog of water. From the viewpoint of the computer simulation, methanol is convenient, because it belongs to the simplest alcohols (it is the first in the homologous series of monohydroxy alcohols) and consists of a rather small number of atoms, which makes it possible to reduce the time and computer capacities required in theoretical calculations [5, 6].

The computer-assisted molecular dynamics is one of the most powerful methods used to simulate physical and biological systems [7, 8]. It is used in a wide range of simulation problems: from the calculation of classical trajectories of separate atoms to the research of the dynamics of the interaction between particles in condensed systems. In addition, owing to their high spatial and temporal resolutions, MD methods can provide information about the processes on the atomic and molecular scales and within the time interval of about several nanoseconds [9]. Due to the development of modern computation facilities, there appears a capability to simulate the dynamics of systems consisting of a large number of molecules (from

tens of thousands to millions) with regard for various sets of conditions and parameters that simulate the physical experiment.

While studying the processes, in which covalent bonds are destroyed, the methods of classical molecular dynamics are used simultaneously with the methods of quantum chemistry [10]. In this work, the results of molecular dynamic researches of a methanol molecule carried out in the framework of the density functional theory (DFT) are reported. The work itself was aimed at studying the structure of methanol isolated in low-temperature matrices and at comparing the experimentally obtained IR spectra with the results of a computer MD simulation of the structures concerned. Hydrogen bonds in such compounds are responsible for the appearance of a specific interaction between the molecules, the energy of which considerably exceeds that of ordinary van der Waals interaction and is only an order of magnitude lower than the energy of strong chemical bonds. It is this interaction that stimulates separate molecules to associate into groups to form molecular clusters.

2. Experiment and MD Simulations

The model calculations, the results of which are reported in this work, were carried out using the Car-Parrinello MD method, DFT/B3LYP functional, potential, and basis set of plane waves. The calculations were executed for a cubic box 15 Å in dimensions. The dynamics step was 0.2 fs, and the trajectory length 100–200 ps. The model spectra were compared with experimentally registered Fourier-transform spectra of IR absorption by matrix-isolated methanol [11–14].

Liquid Fluka methanol with a purity degree higher than 99.9% was additionally purified from water molecules by holding the specimens on a molecular sieve for 48 h. Then, the mixture of gaseous methanol with Ar or N₂ taken in the ratio 1:1000 was deposited as a matrix on a CsI window at a rate of 4 mmol/h and a temperature of 10 K. The IR absorption spectra were registered with a resolution of 1 cm⁻¹ in a frequency interval of 500–5000 cm⁻¹ on a Fourier-transform IR spectrometer Bruker IFS 113 at various temperatures of a matrix.

In Fig. 1, the spectra of methanol in the interval of valent vibrations of a hydroxyl group (3100–3800 cm⁻¹) measured at temperatures of 30, 40, and 50 K of the argon matrix, as well as a model spectrum calculated following the method described

above, are shown. The presented data testify that the band transforms with the temperature. The spectrum registered at 30 K contains a pronounced band corresponding to monomer vibrations. On the other hand, this band is absent from the spectrum measured at 40 K. The asymmetry of the band obtained at 50 K, which is observed on its high-frequency side, testifies to the presence of methanol tri- and tetramers in the argon matrix at this temperature [11–14]. At the same time, no bands are observed that would correspond to free vibrations of the O–H group at the given temperature.

The maximum in the model spectrum corresponds to the formation of clusters composed of 3–4 molecules in the simulation box. A considerable width of the model band (about 30 cm^{-1}) correlates with cluster dissociation times in alcohols (about 350 fs), which were determined using the direct methods of femtosecond spectroscopy.

The analysis of the shapes and the relative arrangement of bands in the indicated spectral intervals testifies that the shape and the position of the calculated band in the MD spectrum correlates with the shape of the band given by matrix-isolated methanol at a temperature of 50 K both in the frequency intervals of O–H (Fig. 1) and C–O vibrations (Fig. 2). According to the results of works [11–14] and taking the box size used in the MD simulation (15 Å) into account, the number of molecules in the methanol clusters can be assumed not to exceed 3 to 4.

From Fig. 2, one can see that the model spectrum is qualitatively similar to the methanol spectrum in the argon matrix at a temperature of 40 K. At the same time, it strongly differs from the experimental spectrum registered at a matrix temperature of 50 K. It is known [11–14] that the bands corresponding to small (1–3 molecules) methanol clusters disappear from the spectrum of matrix-isolated methanol at a temperature of 50 K. At the same time, the intensity of the bands corresponding to clusters with 5–6 molecules increases.

The obtained width of the model spectrum testifies that the MD method makes allowance for a finite time of the cluster existence in the simulation box. It is of interest that the widths of model bands correlate with those of vibrational bands in the matrix experiment.

It is worth noting that, at low temperatures, the C–O band has a well-pronounced structure induced by clusters with a small number of molecules. It is easy

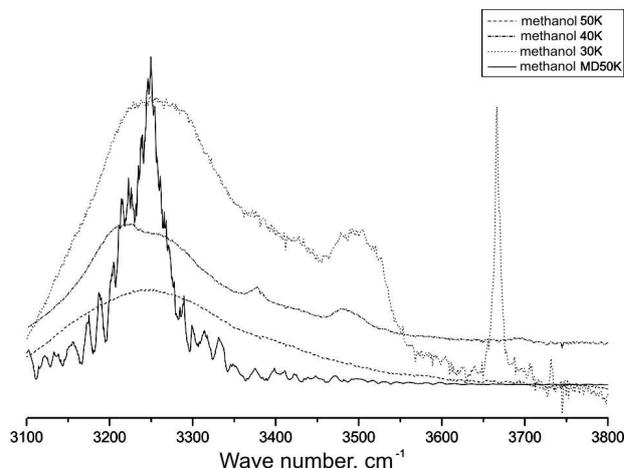


Fig. 1. Comparison of the MD simulation spectrum of methanol isolated in the argon matrix with the corresponding experimental IR spectra measured at various temperatures in the interval of O–H valence vibrations

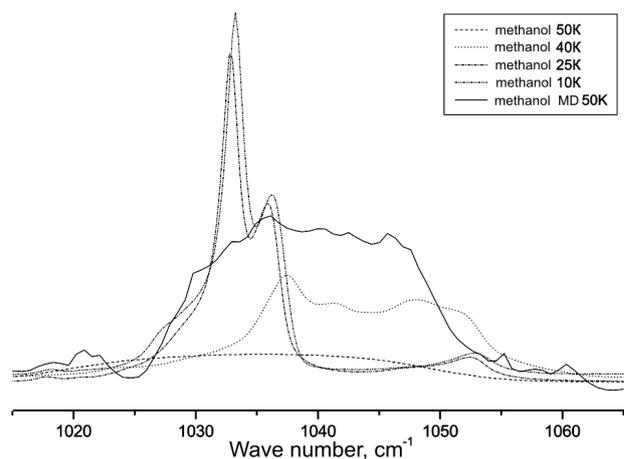


Fig. 2. Comparison of the MD simulation spectrum of methanol isolated in the argon matrix with the corresponding experimental IR spectra measured at various temperatures in the interval of C–O valence vibrations

to notice that the temperature elevation gives rise to a substantial modification in the shape of the C–O band: its pronounced structure disappears, which results from the increase in the dimensions of pores in the matrix and, accordingly, the appearance of clusters with a considerable number of molecules besides the small ones (monomers and dimers). Hence, the comparative analysis of the model and experimental spectra verifies that the MD method involves the presence of clusters with various dimensions at a rather high qualitative level.

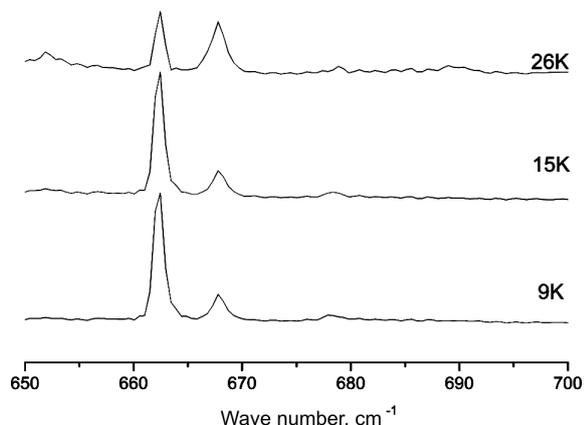


Fig. 3. Spectra of methanol in the nitrogen matrix at various temperatures

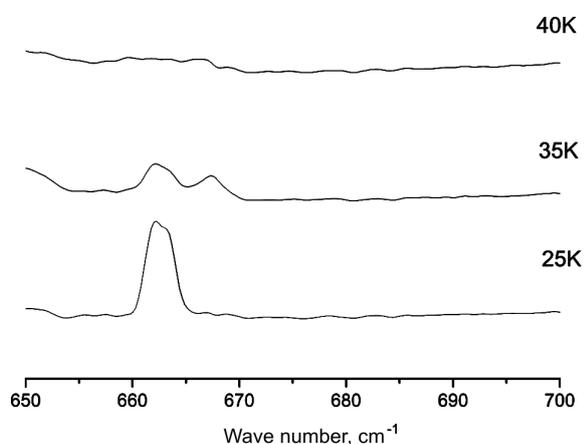


Fig. 4. Spectra of methanol in the argon matrix at various temperatures

As a rule, the peculiarities of the clustering in methanol are analyzed, by using the transformations of vibrational bands that correspond to isolated molecules. In methanol, these are the bands of O–H and C–O vibrations. At the same time, the clustering leads to the formation of aggregates and, hence, to the appearance of new vibrational bands, which are not inherent to isolated molecules. Such bands appear in the methanol spectra in both the argon and nitrogen matrices.

In Figs. 3 and 4, the low-frequency intervals of methanol spectra registered in the nitrogen (at temperatures of 9, 15, and 26 K) and argon (at temperatures of 25, 35, and 40 K) matrices, respectively, are exhibited. The qualitative analysis reveals the existence of dimers. At the same time, as the temperature

of the matrix and, accordingly, the size of voids in the matrix grow, the change of the band intensity ratio testifies to the emergence of a considerable number of larger clusters.

A similar situation can be observed for methanol in the argon matrix (Fig. 4). The difference consists in that, in this case, the pore dimensions exceed those in the nitrogen matrix from the very beginning, keeping the same temperature dynamics.

To summarize, a comparison of the vibrational spectra of methanol in the argon and nitrogen matrices with the corresponding model spectra calculated with the use of the molecular dynamics method testifies that the latter allows the clustering processes of methanol molecules in the argon and nitrogen matrices to be adequately simulated. It was experimentally proved that clusters that are formed in the nitrogen and argon matrices at identical temperatures contain different numbers of methanol molecules. On this basis, we may assert that voids in nitrogen matrices more rigorously restrict the clustering of methanol molecules than voids in argon matrices do. The appearance of bands in the low-frequency interval of the vibrational spectra of matrix-isolated methanol testifies that hydrogen bonds between methanol molecules give rise to the formation of quasimolecular aggregates and the appearance of the corresponding spectrum with characteristic vibrational frequencies. Those vibrational bands are not inherent to free methanol molecules and emerge only due to the formation of aggregates. Their frequencies considerably exceed the frequencies of ordinary intermolecular vibrations in non-associated liquids.

The work was sponsored by the State Fund for Fundamental Researches (grant F54.1/008) and the Swedish Research Council (grant 348-2013-6720). Computation facilities of the joint calculation cluster of the State Scientific Institution "Institute for Single Crystals" and the Institute for Scintillation Materials of the National Academy of Sciences of Ukraine as a part of the Ukrainian National Grid were used at calculations.

1. V. Pogorelov, L. Bulavin, I. Doroshenko, O. Fesjun, and O. Veretennikov, *J. Mol. Struct.* **708**, 61 (2004).
2. M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1989).
3. F.H. Stillinger and Th.A. Weber, *Phys. Rev. B* **31**, 5262 (1985).

4. S. Ihara, S. Itoh, and J. Kitakami, *Phys. Rev. B* **58**, 10736 (1998).
5. S.L. Boyd and R.J. Boyd, *J. Chem. Theory Comput.* **7**, 54 (2007).
6. I.Yu. Doroshenko, O.I. Lizengevych, V.E. Pogorelov, and L.I. Savransky, *Ukr. J. Phys.* **49**, 540 (2004).
7. R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
8. L. Qi and S.B. Sinnott, *Nucl. Instrum. Methods B* **140**, 39 (1998).
9. N.K. Balabaev, A.G. Gritsov, and E.E. Shnol, *Dokl. Akad. Nauk SSSR* **220**, 1096 (1975).
10. S. Dapprich *et al.*, *J. Mol. Struct.* **461–462**, 1 (1999).
11. I.Yu. Doroshenko, V.E. Pogorelov, G.A. Pitsevich, and V. Shablinskas, *Cluster Structure of Liquid Alcohols: Vibrational Spectroscopy Study* (LAMBERT Acad. Publ., 2012) (in Russian).
12. V. Pogorelov, I. Doroshenko, P. Uvdal, V. Balevicius, and V. Sablinskas, *Molec. Phys.* **108**, 2165 (2010).
13. I. Doroshenko, V. Pogorelov, V. Sablinskas, and V. Balevicius, *J. Mol. Liq.* **157**, 142 (2010).
14. I.Yu. Doroshenko, *Fiz. Nizk. Temp.* **37**, 764 (2011).

Received 19.01.15.

Translated from Ukrainian by O.I. Voitenko

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ТЕОРЕТИЧНІ ТА ЕКСПЕРИМЕНТАЛЬНІ
ДОСЛІДЖЕННЯ КЛАСТЕРІВ МЕТАНОЛУ
В НИЗЬКОТЕМПЕРАТУРНИХ МАТРИЦЯХ

Резюме

На даний момент об'єктом наших досліджень є метанол в аргонових та азотних матрицях. Цей спирт належить до класу речовин з водневими зв'язками, тому існує можливість формування молекулярних асоціатів – кластерів з різною кількістю молекул в них. У цій роботі представляємо порівняння експериментально отриманих ІЧ спектрів метанолу в Ar та N₂ матрицях у температурному діапазоні від 10 до 50 К з результатами, отриманими за допомогою комп'ютерного моделювання з використанням методів *ab initio* Car–Parrinello молекулярної динаміки (CPMD). Наші результати показують, що розрахунки моделей невеликих кластерів добре корелюють з експериментальними даними у різних матрицях при відповідних температурах.