

Formation of supramolecular structures in organic solvents*

Ivan Yu. Kalagaev[‡] and Iosif I. Grinvald

Department of Chemistry, Nizhny Novgorod State Technical University, Minin st. 24, Nizhny Novgorod, 603950, Russia

Abstracts: The unusual interactions in organic liquids such as methane derivatives, arenes, and alkanes by the infrared (IR) method were revealed. The transformations of molecular shapes, arising from nonclassical hydrogen and dihydrogen bonds, as well as water factor provide the existence of supramolecular structures in organic fluids. The interpretation of the obtained results in terms of the quantum-chemical calculations has been suggested.

Keywords: hydrogen bonding; infrared; liquid phases; molecular rearrangements; organic solvents.

INTRODUCTION

The mechanism of interactions in organic fluids is still not quite clear [1]. The formation of the condensed phase in general is interpreted as the action of relatively weak van der Waals or dispersive forces, arising between temporary dipoles [2]. The hydrogen or dihydrogen bond can also be considered as a providing factor in the formation of the liquid state [3].

A direct experimental definition of the structural parameters for organic liquids such as X-ray and neutron-scattering diffraction even in cases of the simplest systems cannot determine completely the characteristics of the molecular volume position [1f,4]. The most current data of these methods [4a,5] allow a description of the internal structure, but do not give any detailed information about the intermolecular arrangement. The results of the methylene chloride study by X-ray scattering diffraction, combined with the dynamic simulation (DS) calculations, may be presented as a good example of such a situation [4a]. The two interactions $C\cdots Cl$ and $Cl\cdots Cl$ only contribute to the total intermolecular radial distribution extracted from the experiment. In terms of these data, the possibility of hydrogen bond formation was not considered, meanwhile this one can play a distinctive role in the phase arrangement of the mentioned compound. Furthermore, the first peak of X-ray distribution function has a complex counter near 2 Å, which may mean the nonequivalence of CCl bonds. In the case of the neutron-scattering diffraction, the situation is even more ambiguous than for the X-ray study. It is not possible to resolve the different interactions in the total radial distribution function, especially for deuterated patterns [4c].

The works devoted to the theoretical treatment of the liquid state include either the quantum-chemical calculation (HF, DFT, etc.) [6] or the effective potential study (DS, RISM, MC, etc.) [1a,g,4a,6c,7]. The quantum-chemical calculations describe the distribution of electronic density in isolated molecules and aggregates, containing a restricted number of molecules, therefore this method can-

Pure Appl. Chem.* **85, 1–305 (2013). A collection of invited papers based on presentations at the 32nd International Conference on Solution Chemistry (ICSC-32), La Grande Motte, France, 28 August–2 September 2011.

[‡]Corresponding author

not perform the condensed state as a system of a thick packed bulk. As a consequence of this problem, a number of important liquid properties stay beyond consideration.

In terms of the dynamic simulation study (DS, RISM) or Monte Carlo (MC) method, one can reproduce the volume arrangement of a big molecular ensemble. However, in this theoretical procedure the effective potential describes the intermolecular action via van der Waals or dispersive forces only. By this approximation, it cannot be imagined why such a weak coupling holds the system in a condensed equilibrium state.

In the traditional version it is impossible to understand a number of facts, the basics of which can be formulated as follows:

- In weak charged systems, for example, alkanes, the boiling temperature, in other words the destruction energy of the phase, can be higher than in polar compounds or in systems with the hydrogen bond [1b].
- It cannot be imagined why weak interactions with energy less than 2 kcal/mol may provide a molecular arrangement in the liquid state [8].
- The interaction of dipoles in organic fluids should have a certain orientation, however, the molecules in liquids do not have any anisotropy [1a].

These considerations lead to the conclusion that our knowledge about the structure of organic liquids is not complete. In this paper we have presented the results for the series of typical organic fluids such as methane derivatives, liquid arenes, and alkanes, obtained by Fourier transform infrared (FTIR) spectroscopy and interpreted by the quantum-chemical methods. In the framework of the three effects, which can be the factors of liquid-state stabilization, the following are performed: (1) the conversion of initial molecule and coexistence of a few shapes in liquid phase; (2) the arising of hydrogen and dihydrogen bonds in the cases when the traditional approach rejects such binding; and (3) the formation of the water complexes involved in the structure of organic solvents.

RESULTS AND DISCUSSION

The IR spectra of organic liquids in the middle- and high-frequency region have “additional” bands that cannot be expected by the normal coordinate’s analysis [9]. The observed spectral phenomenon was interpreted as the display of the anharmonicity [10]. Such a version was formed a long time ago and has changed a little so far. The theory of vibrational spectra has initially considered the molecules in an isolated state, i.e., in the gas phase. Meanwhile, many organic compounds have low pressure of vapors and, therefore, weak spectra of gases even in a vacuumed cell [10c]. This situation has led to the addition for the interpretation of internal vibrations of the bands in the spectra of liquid or solid samples. However, in this case some bands were extra. Since every frequency can be worse or better performed either as the line combination of a few other observed frequencies or as a n -multiple repetition of one frequency, the “additional” bands have been assigned to the combination bands or overtones [10b]. In general, as the procedure of the differentiation between fundamental and anharmonic components does not have any strong rules and was made basically by intuition [10a–c,e], the other variants of assignment have the right to exist.

Conversion of molecular structure in liquid methane halides

In this section, we have reasonably demonstrated by FTIR and density functional theory (DFT) study for several typical organic liquids that the bands, which were interpreted as a manifestation of the anharmonicity, may be caused by the appearance of unusual structures in the condensed phase.

The IR spectra of haloform shapes (CX_3H), having the C_{3v} geometry, should show two types of vibrations: HCX bending in the 1400–1000 cm^{-1} region and CX stretching in the 800–400 cm^{-1} range [10c]. In reality, there are a few bands in the 1600–1000 cm^{-1} region that almost do not change their

positions in the spectra of CHCl_3 and CDCl_3 (Fig. 1, the left-hand side, bands **a**). Therefore, these bands cannot correspond to hydrogen vibrations. The absence of these bands in the gas phase is confirmed in [11]. For bromoform (CHBr_3), similar bands in the $1600\text{--}1200\text{ cm}^{-1}$ range (Fig. 1, the left-hand side, **b**) were observed, but unlike the spectra of chloroform, one of the bands is considerably weaker. They were not found in the gas-phase spectra of this compound either [12]. The attribution of the discussed absorption to anharmonic components can be questioned, because this explanation for the very heavy bromine to an even greater degree than for the chlorine atom does not have any physical sense. Therefore, the detected bands were assigned to the manifestation of CX stretching in the structures, differing from the initial (C_{3v}) shape.

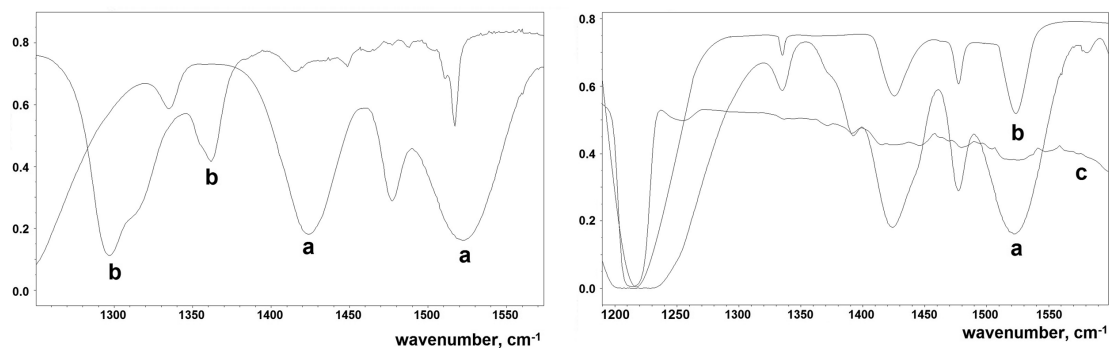
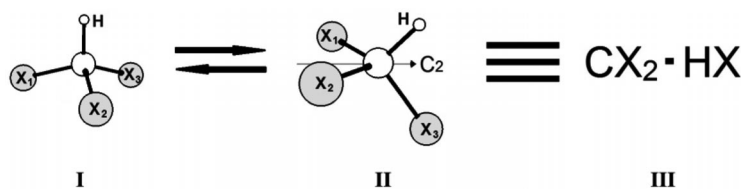


Fig. 1 FTIR spectra of chloroform (bands **a**) and bromoform (bands **b**) in the $1600\text{--}1200\text{ cm}^{-1}$ region (the left-hand side). FTIR spectra of CHCl_3 (the right-hand side): **a** - the liquid sample at room temperature; **b** - the film deposited at 14 K; **c** - the film heated up to 120 K and cooled again to 14 K.

The low-temperature FTIR spectra of haloforms give to some extent the evidence of the suggested interpretation: we have found in the spectra of CHX_3 films deposited on the NaCl window at 14 K the same bands as in the spectra of a liquid sample. At film heating up to 120 K and cooling it back to 14 K, the bands disappear (Fig. 1, the right-hand side, **c**). One can reasonably presume that such behavior of the IR picture is connected with the conversion of less stable structures at this manipulation.

The DFT calculations of chloroform indicate the possibility of transformation of the initial structure (**I**) in biplane shape (**II**) (Scheme 1). The energy barrier of transition for chloroform is less than 4 kcal/mol. Two halogen atoms positioned in the XCX plane (Scheme 1, structure **II**) have positive charges (Table 1). For bromoform, both structures have closer energies of electronic states (the barrier is lower than 2 kcal/mol). All charges of halogen atoms in bromoform are positive, unlike chloroform (Table 1).



Scheme 1 The transformation of initial C_{3v} shape (**I**) into C_i structure (**II**) for haloforms.

Table 1 Atomic charges in initial (C_{3V}) and transformed (C_{2V}) shapes of haloforms (the indexes of X atoms are given in Scheme 1).

Haloform	C	H	X ₁	X ₂	X ₃
CHCl ₃ (C_{3V})	-0.01	0.05	-0.02	-0.02	-0.02
CHCl ₃ (C_{2V})	-0.09	0.08	0.02	0.02	-0.03
CHBr ₃ (C_{3V})	-0.26	0.13	0.04	0.04	0.04
CHBr ₃ (C_{2V})	-0.27	0.13	0.05	0.05	0.03

It is known that carben dihalides stabilize owing to the shift of the halogen electron pair to the p -orbital of carbon, as a result the two resonance structures with positive charged halogen atoms can arise [13]. Thus, the obtained data allow one to perform the biplane structure (Scheme 1, structure **II**) as the complex of the hydrogen halide HX and carben dihalide CX₂ (Scheme 1, structure **III**). These structures can be considered as an initial point of future molecular transformations in liquid state.

The assignment of vibrations for methylene halides in C_{2V} shape is similar to C_{3V} structures in haloforms [10c,e]. At the same time, the FTIR spectra for all CH₂X₂ halides have additional bands in the 1600–1200 cm⁻¹ region, which are weakly sensitive to deuteration of the initial patterns (Fig. 2). The gas-phase spectra do not give the mentioned absorption [14–16]. As the anharmonic factor for very heavy bromine and especially iodine atoms should be negligible, we have assigned these bands to molecular vibrational modes of the transformed shapes, arising in the liquid phase.

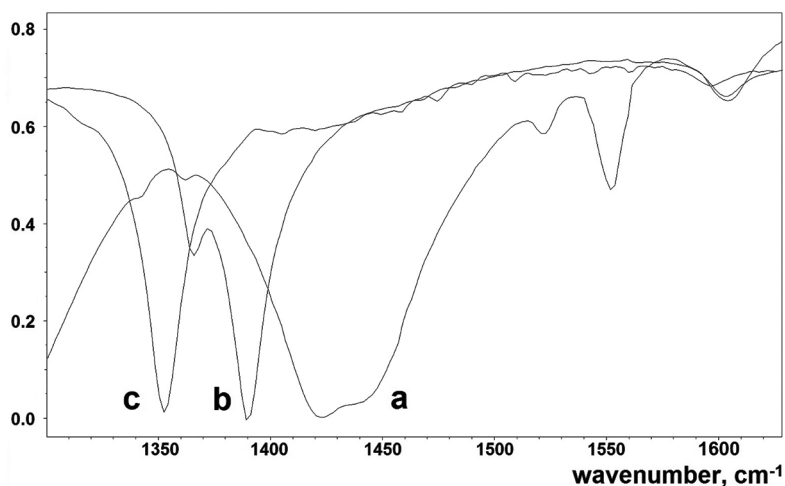
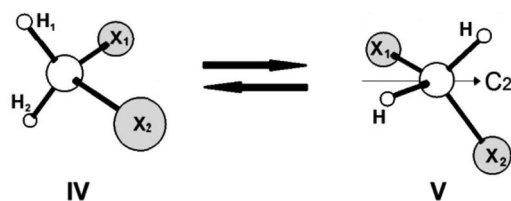


Fig. 2 FTIR spectra for methylene halides in the 1600–1200 cm⁻¹ range: **a** - CH₂Cl₂; **b** - CH₂Br₂; **c** - CH₂I₂.

The quantum-chemical calculations for CH₂Cl₂, CH₂Br₂ were carried out by DFT method (B3LYP/6-311G++(2d,2p)) and for CH₂I₂ by MP4(SDQ). They predict a small barrier (0.2–3 kcal/mol) for the conversion of the shape with C_{2V} geometry in C_i symmetry structure (Scheme 2, structures **IV**, **V**). The charge distribution in methylene halides (CH₂X₂) defines the different design of their spectra (Fig. 2) [17]. The shape **V** can be taken as an intermediate of carben halide and hydrogen halide (CHX·HX), able to transform in other structures.



Scheme 2 The transformation of C_{2v} shape (**IV**) into C_i structure (**V**) for methylene halides.

The IR spectrum of methyl iodide in the CH stretching region ($3100\text{--}2800\text{ cm}^{-1}$) shows three bands (3051 , 2947 , and 2828 cm^{-1}) one of which (2828 cm^{-1}) is split (Fig. 3, the left-hand side, bands **a**), whereas the selection rules for C_{3v} symmetry allow only two bands (A_1 - and E-species). In gas-phase spectra, two of the mentioned bands were detected [18]. All these three bands have a strong isotopic shift in CD_3I (2292 , 2140 , 2062 cm^{-1} , respectively), the average isotopic ratio ($\nu_{\text{H}}/\nu_{\text{D}}$) is 1.36 (theoretical value ~ 1.41 [10]). Besides two of the discussed bands disappear at low temperature and the other remains (Fig. 3, the left-hand side, **a**, **b**). Therefore, the assignment of peaks at 2863 to overtone and at 2842 cm^{-1} (here 2828 cm^{-1}) to a combination band suggested in [19] is ambiguous.

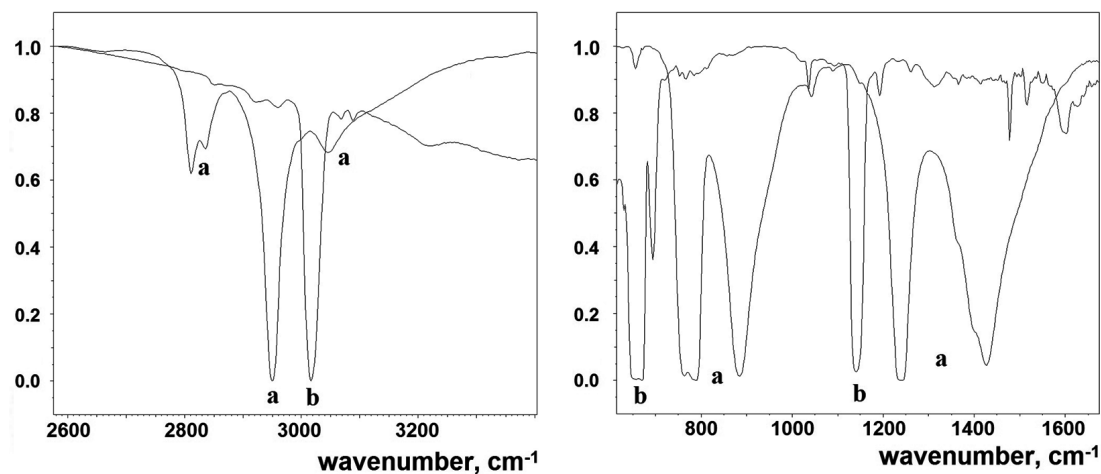


Fig. 3 FTIR spectrum of CH_3I in the $3400\text{--}2600\text{ cm}^{-1}$ region (the left-hand side): **a** - recorded at room temperature in the liquid phase (NaCl cell 0.1 mm); **b** - recorded for the solid film after deposition on the cooled NaCl window at 14 K. FTIR spectrum of CH_3I in $1600\text{--}600\text{ cm}^{-1}$ region (the right-hand side): **a** - recorded at room temperature in liquid phase (NaCl cell 0.1 mm); **b** - recorded for the solid film after deposition on the cooled NaCl window at 14 K.

The reasonable interpretation of this spectral picture can be founded on the presumption that CH_3I in liquid phase exists in two molecular shapes: with the almost planar CH_3 -fragment and with the pyramidal one. Since the first shape corresponds to D_{3h} symmetry, for this structure one IR band only is active, meanwhile the vibrations of the pyramidal CH_3 -fragment (C_{3v} symmetry) give two CH stretching bands (A_1 - and E-species) [17a]. As a result, we should observe three bands in the spectrum, as it is shown in reality.

In the middle IR region ($1600\text{--}600\text{ cm}^{-1}$), the spectral picture is also a compilation of two kinds of bands, differing in behavior at room and low temperature: the bands 1428 , 885 cm^{-1} disappear in the low-temperature spectra, whereas the bands 1237 , 774 cm^{-1} reproduce in both spectra and shift to 1140 , 664 cm^{-1} at 14 K (Fig. 3, the right-hand side, **a**, **b**).

The quantum-chemical study at MP4(SDQ) level of the theory demonstrates the relatively high barrier of molecular transformation for isolated CH_3I into a planar structure, approximately 32 kcal/mol. However, for the cluster shape, consisting of three oriented along the axes of I-C-I molecules, the energy of the barrier decreases up to 18 kcal/mol. Taking into consideration that such a barrier is quite low for the liquid phase [1b], we can assume that this molecule in condensed state can transform to a shape with an almost planar CH_3 fragment.

Thus, we can conclude that for methane halides the observed FTIR spectra are the manifestation of the existence of transformed structures in liquid phase along with usual shapes.

Hydrogen and dihydrogen bonds

The traditional opinion formulates that the hydrogen bond for organic compounds can arise as a rule for oxygen–hydrogen and nitrogen–hydrogen interaction [1a,b,3g]. The formation of a dihydrogen bond needs the existence of oppositely charged hydrogen atoms [3a]. Nevertheless, for many organic liquids containing hydrogen atoms, in the high-frequency region (higher than 2000 cm^{-1}), where the H-stretching vibrations locate, “additional” bands are observed [9]. Although for the H-modes the anharmonic factor is essential, just in this case we can reliably identify the fundamental modes from the anharmonic components by the IR spectra of deuterated patterns. That follows from the basic laws of the vibrational spectra theory: the frequency of harmonic oscillator (ν) should depend on the atomic mass (m), namely, $\nu \sim m^{-1/2}$. This relation predicts the ratio ($\nu_{\text{H}}/\nu_{\text{D}}$) for hydrogen vibrations approximately equal to $2^{1/2}$ [10c].

Hereby, we present the IR data for such typical organic fluids, as haloforms CX_3H ($\text{X} = \text{Cl}, \text{Br}$), methylene halides CH_2X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), benzene and its monosubstituted derivatives as well as for n -hexane, n -heptane, and n -octane, for which the traditional approach rejects the existence of hydrogen or dihydrogen bonds.

Methane halides

In the IR spectra of methane halides, the bands in $2300\text{--}2000\text{ cm}^{-1}$ region, having strong and similar to CH vibrations in CH_n fragment isotopic shift, were observed (Table 2). Their frequencies depend on the halogen masses analogically to the tendency for hydrogen halides [10e].

Table 2 The bands (cm^{-1}) in the $2400\text{--}2000\text{ cm}^{-1}$ region and their isotopic shift in methane halides.

Compounds	CH_2Cl_2	CD_2Cl_2	CH_2Br_2	CH_2I_2	CHCl_3	CDCl_3	CHBr_3
ν, cm^{-1}	2305	1753	2182	2056	2400 2334 sh.	1790 1815 sh.	2242
$\nu_{\text{H}}/\nu_{\text{D}}$		1.31				1.34 1.34	

As the discussed, bands locate in the same spectral region like the ones of the hydrogen vibrations in nitromethane, acid hydrates ($\text{HBr}\cdot n\text{H}_2\text{O}$), and some other compounds with the bound proton [10e], we can consider this absorption as a manifestation of ($\text{C}\cdots\text{H}\cdots\text{X}\cdots$) intermolecular binding, arising in liquid methane halides.

In the high IR region ($4500\text{--}3600\text{ cm}^{-1}$), we have found the bands ($\nu_1\text{--}\nu_4$), performed in Table 3, having isotopic H/D shift close to the one of the CH stretching and bending vibrations in CH_n fragment.

Table 3 The bands (cm^{-1}) in high-frequency regions and their isotopic shift for methane halides.

Compound	ν_1	ν_2	ν_3	ν_4
CH_2Cl_2	4454	4253, 4197	3945	3759, 3694
CD_2Cl_2	3342	3158, 3124	3011	2913, 2877
CH_2Br_2	4441	4142, 4050	3863	3638, 3560
CH_2I_2	4352	4063, 3922	3748	3528, 3460
$\nu_{\text{H}}/\nu_{\text{D}}$	1.33	1.35, 1.34	1.31	1.29, 1.28
CHCl_3	–	4216	–	3624, 3620
CDCl_3	–	3156	–	2986, 2903
CHBr_3	–	4137	–	3582, 3521
$\nu_{\text{H}}/\nu_{\text{D}}$	–	1.34	–	1.21, 1.25

Since in the presented region there is one suitable analogue for interpretation only, namely, the stretching in H_2 molecule ($4200\text{--}4100\text{ cm}^{-1}$) [10e], we have assigned the detected bands to intermolecular dihydrogen bond stretching. Thick packing in the condensed phase causes a strong interaction of hydrogen atoms in the neighboring molecules and can lead to the formation of the dihydrogen fragment.

Arenes

Another example of the unusual self-association in organic liquids is benzene. For the planar structure of this compound (D_{6h} symmetry) one active CH stretching vibration in IR spectrum (E_{1u} -species) is allowed. However, the IR spectra in the CH stretching region demonstrate three bands (Fig. 4). In the gas-phase spectra, there is one band only [21].

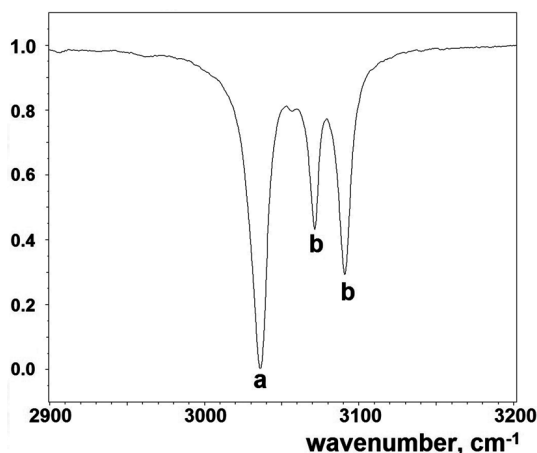


Fig. 4 FTIR bands of liquid benzene in CH-stretching region at room temperature.

This spectral picture can be interpreted as the manifestation of two molecular shapes, existing in liquid phase: initial planar (D_{6h} symmetry, band **a** in Fig. 4) and nonplanar (C_{3v} symmetry, bands **b** in Fig. 4) formed at the bending of CH bonds from the carbon cycle. To the last structure, two active CH stretching vibrations (A_1 - and E-species), corresponding to the C_{nv} symmetry group, can be assigned.

At the same time in the middle IR region two extra bands at 1952, 1814 cm^{-1} are found (Table 4), which cannot be assigned to the known internal vibration modes [10,21]. These bands have a strong isotopic shift, close to one for the CH vibration of aromatic ring [21]. The bands were not found in the gas-phase spectra [21].

Table 4 The “additional” bands (cm^{-1}) in the middle IR region for the aromatic systems and their isotopic ratio $\nu_{\text{H}}/\nu_{\text{D}}$ (given in brackets).

C_6H_6	C_6D_6	$\text{C}_6\text{H}_5\text{CH}_3$	$\text{C}_6\text{D}_5\text{CD}_3$	$\text{C}_6\text{H}_5\text{Br}$	$\text{C}_6\text{D}_5\text{Br}$	$\text{C}_6\text{H}_5\text{NO}_2$	$\text{C}_6\text{D}_5\text{NO}_2$
1962	1617 (1.21)	1942 1858	1492 (1.30) 1435 (1.29)	1962, 1942 1881, 1863	1505 (1.30) _{av} 1400 (1.34) _{av}	1951, 1883 1852	
1814	1456 (1.25)	1804 1732	1321 (1.36) 1272, 1245 (1.38) _{av}	1788 1732	1280 (1.35)	1837 1735, 1745	1268, 1249 (1.38) _{av}

The spectra of substituted benzenes give some evidence of our version: instead of two bands (in the spectra of benzene) these bands demonstrate a few components (Table 4). Such a spectral picture may be caused by the nonequivalence of hydrogen atoms in different position in the carbon ring (*ortho*-, *meta*-, and *para*-positions). Since the probability of π -bonding for all hydrogen atoms is approximately equal, we can explain such a spectral effect by the arising of different hydrogen π -interaction owing to the nonequivalence of hydrogen atoms in substituted benzenes.

The quantum-chemical calculations predict the possibility of π -cluster formation for benzene even in the gas phase [22]. Two molecular shapes, having a low transition barrier, can exist: the shape with T-configuration and the one with parallel disposition of aromatic rings (Fig. 5, structures **VI** and **VII**, respectively). On this ground, we have assigned the bands listed in Table 4 to stretching of π -bonded hydrogen atoms bent on the angle α from the carbon cycle in structures with parallel or T-deposited aromatic rings.

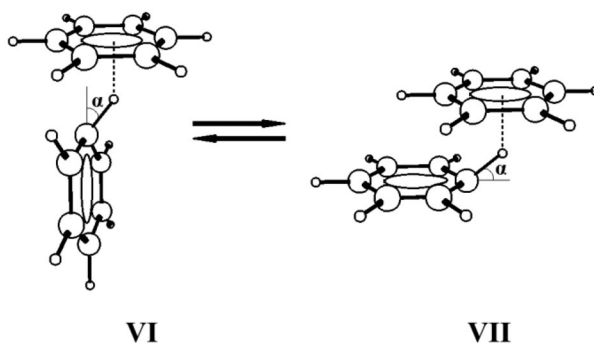


Fig. 5 T-configuration (**VI**) and parallel disposition of aromatic rings (**VII**) in benzene dimers.

Alkanes

In the spectra of *n*-hexane, *n*-heptane, *n*-octane, we have revealed a group of bands in the high-frequency region (3800–3400 cm^{-1}) (they are labeled **a** in Fig. 6). The bands are not shown in the gas-phase spectra [23]. The complicated configuration of this absorption and its strong isotopic H/D shift in full deuterated pattern (the bands **b** in Fig. 6), similar to the isotopic shift of internal CH-stretching vibrations (the average isotopic ratio $\nu_{\text{H}}/\nu_{\text{D}}$ is 1.31 and 1.34, respectively), justify the assignment of these bands to the vibrations of dihydrogen bond in liquid saturated hydrocarbons.

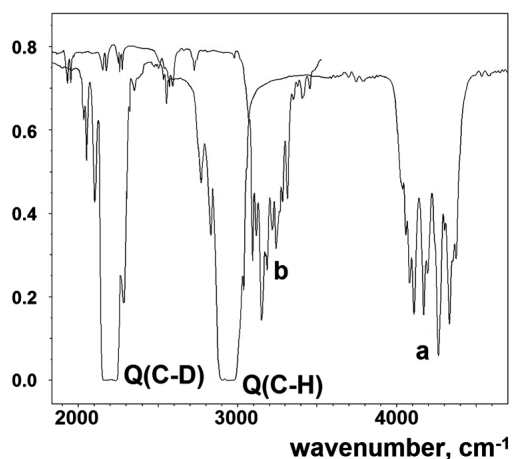


Fig. 6 IR spectra of hexane (**a**) and its full deuterated analogue (**b**) in the 4500–2000 cm^{-1} region (NaCl liquid cell 0.1 mm).

The existence of dihydrogen bonds for alkanes looks especially unexpected, since the hydrogen atoms are weakly activated here and should be at first sight equally charged. Nevertheless, for these compounds the hydrogen interaction, leading to the conformational isomerism, is known [1b]. As the diatomic distances for such an interaction are comparable with the intermolecular ones in the liquid state [1a,b,3a,g,24], we can assume that the thick packing of molecules in the condensed phase can cause the appearance of intermolecular dihydrogen binding.

Water involved in molecular arrangement of organic liquids

The behavior of water in an organic medium is a very important phenomenon, which attracts much attention due to the possibility of different types of interactions [25]. The organic compound-water systems have been extensively examined by many authors [1b,26,27]. Common knowledge explains the nature of water binding with organic molecules by weak van der Waals or dispersive forces. The known IR data show that for the dissolved water intermediates the stretching vibrations locate in typical H_2O absorption region (3400–3700 cm^{-1}) [27,28]. In the quoted literature, the possibility of complex formation for organic molecules with water clusters and hydroxonium cation in particular was not considered. Meanwhile, the mentioned water-transformed shapes are revealed even in the gas phase [26b], therefore, they should have been included in the study of the aggregated shapes.

We have observed in the high frequencies region for nitromethane the bands of two types (bands **a** and **b** in Fig. 7, the left-hand side). The first of them have an expected (H/D) shift (they are labeled **a**), but the others are weakly sensitive to deuteration (they are labeled **b**). These bands cannot be the display of impurity as the recorded spectra remain at distillation and for the pattern of a different origin. There is not any suitable unit (non-sensitive to deuteration of CH_3 group in initial molecule), having vibrations in the discussed region. At the inputting into the system of heavy water, the new weak bands at 2118 and 1992 cm^{-1} were found (sample preparation and preliminary IR data obtained at room temperature are described in [29]). The calculated isotopic ratios for these bands ($\nu_{\text{H}}/\nu_{\text{D}}$), being 1.38 and 1.39 respectively, are in good agreement with the theoretical value. In low-temperature spectra, recorded after deposition on the cooled (14 K) NaCl window, the relation of band intensities considerably changes in contrast to the absorbance in other regions (Fig. 7, the left-hand side). Such a behavior of the revealed bands means the existence of two different mixed components. In the presented spectral range there is no suitable analogue for the interpretation, except water stretching. That is why the con-

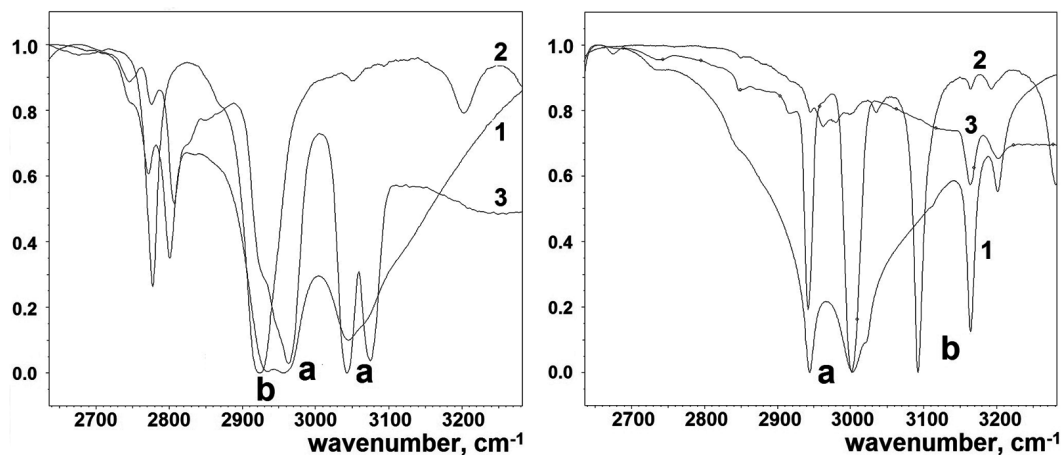


Fig. 7 The IR bands in the 3300–2600 cm^{-1} spectral range: for liquid CH_3NO_2 (1), CD_3NO_2 (2), (the thicknesses of NaCl cell is 0.1 mm) and CH_3NO_2 film (3), deposited on the cooled (14 K) NaCl window (the left-hand side); for liquid CH_3CN (1), CD_3CN (2) (the thickness of NaCl cell was 0.1 mm) and CH_3CN film (3), deposited on the cooled (14 K) NaCl window (the right-hand side).

sidered absorbance (the bands **b** in Fig. 7) can be assigned to the stretching in complexes of bound water.

For acetonitrile as well as for nitromethane we have detected in the high-frequency region the bands, which are sensitive to deuteration (they are labeled **a** in Fig. 7, the right-hand side) and the ones, having small isotopic shift at H/D substitution (they are labeled **b** in Fig. 7, the right-hand side). These bands change their relevant intensities in spectra, recorded after deposition on the cooled (14 K) NaCl window (Fig. 7, the right-hand side). Thus, we can assign the found bands as well as for nitromethane to water stretching in adducts. In both cases, the bands do not have a dependence on the water concentration and remain after vacuum distillation under basic. It should be noted that one band for nitromethane (3586 cm^{-1}) and two bands for acetonitrile (3635 , 3540 cm^{-1}) in the typical OH-stretching region were observed.

The FTIR spectra of nitromethane and its CD_3 -analogue in the middle IR region (2000 – 1100 cm^{-1}) are presented in Fig. 8, the left-hand side. The band 1377 cm^{-1} (room temperature), having an expected isotopic H/D shift assigns to the mixed vibration [$\alpha\text{HCH} + \text{Q}(\text{CN})$] [30]. At the same time, the found double band with maximums at 1404 and 1425 cm^{-1} weakly shifts at deuteration. Since the mixed [$\alpha\text{HCH} + \text{Q}(\text{CN})$] vibration should be sensitive to the deuteration, we have assigned the mentioned double band to the vibrations of non-initial component, namely, to the bending of bound water.

For the acetonitrile, the band 1375 cm^{-1} (Fig. 8, the right-hand side), having a strong isotopic shift, assigns to the [$\alpha\text{HCH} + \text{Q}(\text{CC})$] vibration [31]. The stretching vibration $\text{Q}(\text{CC})$ is strongly mixed in the form with CH_3 -bending and should have quite a strong isotopic shift [10c,31]. However, the twin band with maximums at 1445 , 1420 cm^{-1} shifts considerably less than might be expected. From this point of view, this band may be associated with the bending vibration of the water molecule in a complex with the organic solvent.

We could not find bands that might be assigned to the bending of bound D_2O . The problem is that the supposed region of D_2O bending is overlapped by strong bands of organic solvents. However, another interpretation will depend on the following reason: two pairs of bands (1425 , 1404 cm^{-1} for nitromethane and 1445 , 1420 cm^{-1} for acetonitrile) are closely located, meanwhile, the vibrations in nitromethane, which should have no isotopic shift, cannot copy the position and counter of the analogical bands in acetonitrile.

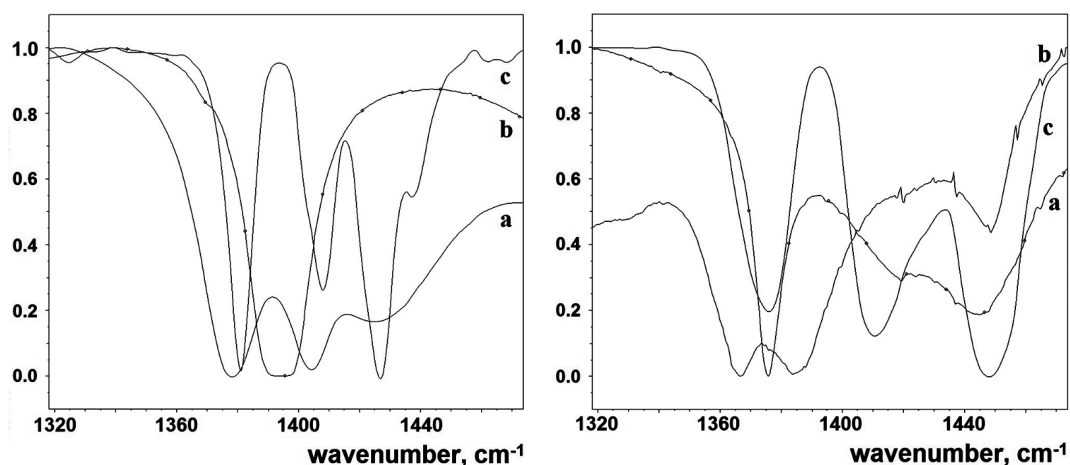
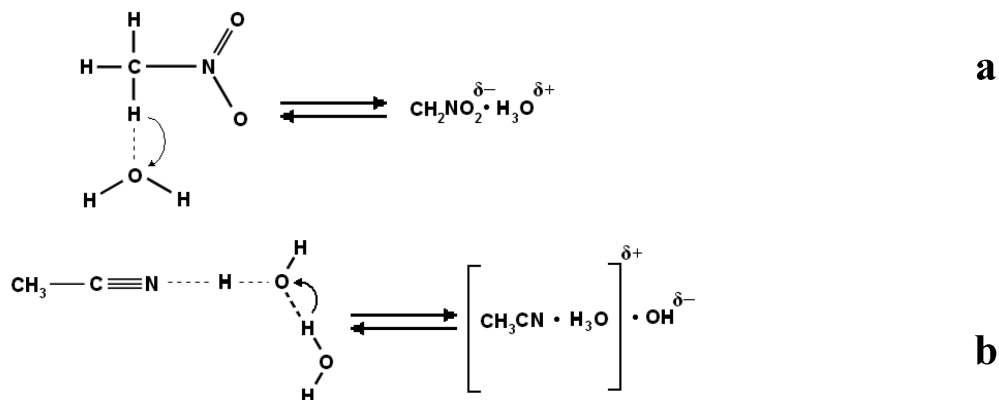


Fig. 8 FTIR spectra in the middle IR region: for nitromethane (a) and nitromethane- d_3 (b), recorded at room temperature and the spectra recorded at 14 K (c), the left-hand side; for acetonitrile (a) and acetonitrile- d_3 (b), recorded at room temperature and the spectra recorded for the film, deposited at 14 K (c), the right-hand side.

In the recent work, we have tried to give insight into the electronic structure of these unusual intermediates by DFT calculations. The main results indicate the formation of not only weakly bounded H_2O complexes, but also the transformation of these complexes in more stable H_3O^+ adducts. In the case of nitromethane, the H_2O molecule is bound with the organic fragment via the hydrogen atom of the methyl group (Scheme 3, a). It simplifies the formation of the H_3O^+ complex, owing to the transfer of the hydrogen atom from the methyl group to the water molecule.

The calculations for acetonitrile do not predict the formation of complexes between the hydrogen atom of the methyl group and water fragment. However, according to the computational study the hydrogen atom of water can shift to the nitrogen atom of the CN-group in the complex. This interme-



Scheme 3 The formation and conversion in the water intermediates: **a** - for nitromethane, **b** - for acetonitrile.

diates is the source of the further hydrogen migration of other H_2O molecules with formation of H_3O^+ adducts (Scheme 3, b).

Thereby, we conclude that water molecules may be involved in the supramolecular structure of organic solvents in consequence of hydrogen transfer and play an important role in the molecular arrangement of organic liquids.

CONCLUSION

One may reasonably doubt that the nature of the thick packing and high stability of the liquid phase can be provided in general by the very weak van der Waals or dispersive forces only. As we have shown, the liquid state is a supramolecular system, forming due to the complicated molecular interactions. The main interactions can be formulated as follows:

- The balance of different molecular shapes of one initial compound leads to partial spending of the input energy for the transformation between these structures and therefore the energy of the phase destruction decreases.
- The hydrogen and dihydrogen bonds in the condensed phase can appear even in cases when the traditional approach rejects the formation of these bonds. These bonds probably arise owing to the thick packing in condensed phase.
- Water may be incorporated into the molecular structure of organic liquids like in biological systems (proteins, ferments, etc.) [32].

EXPERIMENTAL AND COMPUTATIONAL TECHNIQUE

For recording of IR spectra, the commercial materials with 99.9 % purity have been used. The measurement by Fourier spectrophotometer FSM 1202 and NaCl cells with the constant thickness 0.1 and 0.2 mm was carried out. For the low-temperature experiment, the standard technique of closed-cycle refrigerator ARS model CSE-202A has been applied.

The quantum-chemical calculations were carried out by the DFT method at the B3LYP/6-311++G(2d, 2p) level and MP theory at the MP4(SDQ) level [6a]. In the calculations of interaction energy, the Boys–Bernardi counterpoise (CP) technique was employed [33a]. All the located minima were subjected to the subsequent frequency calculation in order to validate the stationary point type and made the zero-point energy (ZPE) correction to the binding energy [33b]. The Gaussian 03 program [34], licensed in the Nizhny Novgorod Lobachevsky State University, was used. These results were obtained with the assistance of Prof. S. K. Ignatov and Associate Prof. A. G. Razuvaev.

REFERENCES

1. (a) A. Gavezzotti. *Molecular Aggregation: Structure Analysis and Molecular Simulation of Crystals and Liquids*, pp. 3–326, Oxford University Press, Oxford (2009); (b) M. B. Smith, J. March. *March's Advanced Organic Chemistry, Reactions, Mechanism, and Structure*, 6th ed., pp. 425–1559, John Wiley, New York (2007); (c) M. W. Evans. *J. Mol. Liq.* **25**, 211 (1983); (d) Sh.-I. Ikawa, M. Ito, T. Fukuda, M. Kimura. *J. Mol. Liq.* **32**, 219 (1986); (e) F. J. Bermejo, F. J. Mompeán, J. Santoro, D. C. Steytler, J. C. Dore. *J. Mol. Liq.* **33**, 183 (1987); (f) J. Teixeira, M.-C. Bellissent-Funel, S.-H. Chen. *J. Mol. Liq.* **48**, 111 (1991); (g) S. Hayaki, H. Sato, S. Sakaki. *J. Mol. Liq.* **147**, 9 (1991).
2. (a) I. Z. Fisher. *Statistical Theory of Liquids*, pp. 5–20, Chicago University Press, Chicago (1964); (b) T. W. G. Solomons, C. B. Fryle. *Organic Chemistry*, 9th ed., p. 143, John Wiley, New York (2008).

3. (a) V. I. Bakhmutov. *Dihydrogen Bonds*, pp. 9–148, John Wiley, New York (2008); (b) S. M. Melikova, K. S. Rutkowski, P. Rodziewicz, A. Koll. *J. Mol. Struct.* **2**, 645 (2003); (c) P. Hobza. *Ann. Rep. Progr. Chem.* **100**, 3 (2004); (d) T. Ratajczyk, I. Czerski, K. Kamienska-Trela, S. Szymanski, J. Wojcik. *Angew. Chem., Int. Ed.* **8**, 44 (2005); (e) J. Taubitz, U. Lüning, J. Grottemeyer. *Chem. Commun.* **21**, 2400 (2004); (f) S. Keinan, M. A. Ratner, T. J. Marks. *Chem. Mater.* **10**, 16 (2004); (g) L. Sobczyk, S. J. Grabowski, T. M. Krygowski. *Chem. Rev.* **105**, 3513 (2005); (h) F. Franks. *Water: A Comprehensive Treatise*, pp. 43–46, Plenum Press, New York (1972); (i) M. Benoit, D. Marx, M. Parinello. *Nature* **392**, 258 (1998); (j) V. S. Bryantsev, B. P. Hay. *J. Am. Chem. Soc.* **127**, 8282 (2005); (k) G. N. Merrill, S. P. Webb. *J. Phys. Chem. A* **108**, 833 (2004); (l) B. P. Hay, M. Gutowski, D. A. Dixon, J. Garza, R. Vargas, B. A. Moyer. *J. Am. Chem. Soc.* **126**, 7925 (2004).
4. (a) S. Bálint, I. Bakó, T. Grósz, T. Megyes. *J. Mol. Liq.* **136**, 257 (2007); (b) P. Georgiou, J. Vincent, M. Andersson, A. B. Wöhri, P. Gourdon, J. Poulsen, J. Davidsson, R. Neutze. *J. Chem. Phys.* **124**, 234507 (2006); (c) W. G. Jung, M. D. Zeidler, P. Chieux. *Mol. Phys.* **68**, 473 (1989).
5. T. Megyes, S. Bálint, T. Grósz, T. Radnai, I. Bakó. *J. Chem. Phys.* **126**, 164507 (2007).
6. (a) V. I. Baranovsky. *Quantum Mechanics and Quantum Chemistry*, pp. 161–263, Academy, Moscow (2008); (b) Y. C. Park, J. S. Lee. *J. Phys. Chem. A* **110**, 5091 (2006); (c) H. Torii. *J. Mol. Liq.* **119**, 31 (2005); (d) C. Canepa. *J. Chem. Phys.* **115**, 7592 (2001); (e) W. Wang, A. Tian, N.-B. Wong. *J. Phys. Chem. A* **109**, 8035 (2005); (f) F. H. Tikhvatullin, B. G. Hudayberdiev, A. Jumabaev, H. A. Hushvaktov, A. A. Absanov. *J. Mol. Liq.* **155**, 67 (2010); (g) F. H. Tikhvatullin, A. Jumabaev, H. Hushvaktov, A. Absanov, A. Shaymanov. *J. Raman Spectrosc.* **38**, 1633 (2007); (h) S. Ten-no, F. Hirata, S. Kato. *J. Chem. Phys.* **100**, 7443 (1994); (i) H. Sato, F. Hirata, S. Kato. *J. Chem. Phys.* **105**, 1546 (1996).
7. P. Jedlovsky. *J. Chem. Phys.* **107**, 562 (1997).
8. P. E. S. Wormer, A. van der Avoird. *Chem. Rev.* **100**, 4109 (2000).
9. (a) I. I. Greenwald, I. Yu. Kalagaev. *J. Chem. Chem. Eng.* **8**, 759 (2011); (b) I. I. Grinvald, G. A. Domrachev, I. Yu. Kalagaev. *Dokl. Phys. Chem.* **440**, 168 (2011).
10. (a) D. W. Mayo, F. A. Miller, R. W. Hannah. *Course Notes on the Interpretation of Infrared and Raman Spectra*, pp. 1–33, John Wiley, New York (2003); (b) A. L. Smith. *Applied Infrared Spectroscopy: Fundamentals, Techniques and Analytical Problem-Solving*, pp. 151–153, John Wiley, New York (1982); (c) L. M. Sverdlov, M. A. Kovner, E. P. Krainov. *Vibrational Spectra of Polyatomic Molecules*, pp. 57–421, Nauka, Moscow (1970); (d) T. Chakraborty, S. N. Rai. *Spectrochim. Acta A* **65**, 406 (2006); (e) K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., pp. 114–115, John Wiley, New York (1991).
11. (a) J. Morcillo, J. Hevrans, J. F. Biarge. *Spectrochim. Acta* **15**, 110 (1959); (b) J. A. Wiggins, E. R. Shull, D. H. Rank. *J. Chem. Phys.* **21**, 1368 (1953); (c) I. Madigan, F. Cleveland, W. Boyer, R. Bornstein. *Phys. Rev.* **77**, 740 (1950); (d) J. Morcillo, J. F. Biarge, J. M. Heredia, A. Mediu. *J. Mol. Struct.* **3**, 77 (1969).
12. (a) A. P. Lindsay, P. N. Shatz. *Spectrochim. Acta* **20**, 1421 (1964); (b) S. Ferrigle, F. Cleveland, W. Boyer, R. Bernstein. *J. Chem. Phys.* **18**, 1073 (1950).
13. D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand. *Chem. Rev.* **100**, 39 (2000).
14. (a) B. F. Palma, E. A. Piotrovski, S. Sundaram, F. F. Cleveland. *J. Mol. Spectrosc.* **13**, 119 (1964); (b) T. Shimanouchi, I. Suzuki. *J. Mol. Spectrosc.* **8**, 222 (1962).
15. (a) J. M. Dowling, A. G. Meister. *J. Chem. Phys.* **22**, 1042 (1954); (b) R. S. Dennen, E. A. Piotrovski, F. F. Cleveland. *J. Chem. Phys.* **49**, 4385 (1968).
16. (a) N. L. Singh, I. W. Straley. *J. Chem. Phys.* **25**, 490 (1956); (b) W. C. Mallard, I. W. Straley. *J. Chem. Phys.* **27**, 877 (1957).
17. (a) M. V. Volkenstein, L. A. Gribov, M. A. Elyashevish, B. I. Stepanov. *Vibrations of Molecules*, 2nd ed., p. 29, Nauka, Moscow (1972); (b) B. S. Averbukh. *J. Mol. Spectrosc.* **107**, 144 (1984).

18. (a) A. S. Dickson, I. M. Mills, B. Crawford. *J. Chem. Phys.* **27**, 445 (1957); (b) F. A. Anderson. *Advances in Molecular Spectroscopy*, Vol. 2, p. 739, Oxford (1962); (c) J. Morcillo, L. J. Zamorano, J. M. V. Heredia. *Spectrochim. Acta* **22**, 1969 (1966); (d) R. G. Brown, T. H. Edwards. *J. Chem. Phys.* **37**, 1029 (1962); (e) T. J. Barnett, T. H. Edwards. *J. Mol. Spectrosc.* **23**, 302 (1967); (f) Y. Morino, J. Naramura, S. Yamamoto. *J. Mol. Spectrosc.* **22**, 34 (1967); (g) R. J. Popplewell, H. W. Thompson. *Spectrochim. Acta, Part A* **25**, 287 (1969).
19. J. L. Duncan, A. M. Ferguson, S. Mathews. *J. Chem. Phys.* **91**, 783 (1989).
20. (a) D. M. Gates. *J. Chem. Phys.* **17**, 393 (1949); (b) H. W. Schrotter, H. J. Bernstein. *J. Mol. Spectrosc.* **12**, 1 (1964); (c) M. T. Khatmullina, A. S. Krauze, L. V. Ryabchuk. *J. Struct. Chem.* **48**, 569 (2007).
21. (a) H. Spendig, D. Whiffen. *Proc. R. Soc. London, Ser. A* **238**, 245 (1956); (b) G. Varsanyi. *Vibrational Spectra of Benzene Derivatives*, p. 216, Academic Press, New York (1969); (c) F. A. Miller, B. L. Crawford. *J. Chem. Phys.* **14**, 292 (1956); (d) F. Langenbucher, R. Mecke. *Spectrochim. Acta* **21**, 1287 (1965); (e) P. C. Painter, J. L. Koenig. *Spectrochim. Acta, Part A* **33**, 1019 (1977).
22. Y. Ch. Park, J. Sh. Lee. *J. Phys. Chem. A* **110**, 5091 (2006).
23. A. G. Finkel. *Opt. Spectrosc.* **20**, 773 (1966).
24. M. V. Basilevsky, M. V. Vener. *Russ. Chem. Rev.* **72**, 1 (2003).
25. Y. Sun, H. Li, W. Liang, S. Han. *J. Phys. Chem. B* **109**, 5919 (2005).
26. (a) J. Dobrowolski, M. H. Jamroz. *J. Mol. Struct.* **293**, 147 (1993); (b) M. Baron, V. J. Kowalewski. *J. Phys. Chem. A* **110**, 7122 (2006).
27. A. V. Iogansen. *Spectrochim. Acta, Part A* **7–8**, 1585 (1999).
28. (a) D. N. Glew, N. S. Rath. *Can. J. Chem.* **49**, 837 (1971); (b) M. Besnard, Y. Danten, T. Tassaing. *J. Chem. Phys.* **113**, 3741 (2000); (c) J. P. Gallivan, D. A. Dougherty. *Org. Lett.* **1**, 103 (1999).
29. I. I. Greenwald, I. Yu. Kalagaev. *Tetrahedron Lett.* **51**, 2610 (2010).
30. (a) E. M. Popov, V. M. Shlyapochnikov. *Opt. Spectrosc.* **6**, 779 (1963); (b) T. P. Wilson. *J. Chem. Phys.* **11**, 361 (1943); (c) E. M. Popov, V. M. Shlyapochnikov. *Opt. Spectrosc.* **6**, 116 (1963).
31. (a) K. Venkateswarlu. *J. Chem. Phys.* **19**, 293 (1951); (b) D. E. Milligan, M. E. Jacos. *J. Mol. Spectrosc.* **8**, 126 (1962); (c) W. H. Fletcher, C. S. Shoup. *J. Mol. Spectrosc.* **10**, 300 (1963); (d) E. M. Popov, V. P. Roshupkin. *Opt. Spectrosc.* (issue 2, *Mol. Spectrosc.*), 116 (1963).
32. J. W. Steed, J. L. Atwood. *Supramolecular Chemistry*, Vol. 1, pp. 79–117, John Wiley, Chichester (2000).
33. (a) S. F. Boys, F. Bernardi. *Mol. Phys.* **19**, 553 (1970); (b) M. Besnard, Y. Danten, T. Tassaing. *J. Chem. Phys.* **113**, 3741 (2000).
34. Gaussian 03, Revision C.01, Gaussian, Inc., Wallingford CT (2004).