DEVIATION OF THE C—H BOND IN LIQUID AND GASEOUS CHLOROMETHANE AND IODOMETHANE

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The method of $3N$ matrices has been used to solve the inverse spectral problem of vibrational spectroscopy for molecules of chloromethane, $ClCH_3$, and iodomethane, ICH_3, belonging to the liquid or gaseous phases. The deviation angles of C—H bonds have been calculated irrespective of the models of the molecular force field and the environment. A comparison of the calculated values of the shape parameter of molecular vibration modes, the parameter of anharmonicity, and the deviation angle of chemical bonds, which are characteristic of molecules belonging to different states of aggregation, has been carried out. The frequencies of characteristic vibrations of molecules and the approximation of identical parameters of anharmonicity for all vibration modes have been chosen for calculations. The formalism of a "non-full" basis of the vibration shapes has been used.

1. Introduction

The method of $3N$ matrices [1] has been developed as one of the methods for solving the inverse spectral problem of vibrational spectroscopy of molecules. Its main advantages are the applicability of the method to both isolated and condensed phase molecules, and the opportunity to evaluate a set of molecular force constants (force matrix) without introducing any assumptions concerning the molecular force field or molecular environment. The basic approximation implied in this method is the approximation of harmonicity.

Application of this method to various molecules has allowed the phenomenon of the deviation of a chemical bond [2–5] to be revealed. This phenomenon consists in that a direction of a chemical bond between two atoms deviates from the straight line that connects their nuclei. The method has also made it possible to study variations of the deviation angle when the molecules underwent the gas—liquid phase transition [6] and to estimate the effective electric charges of atoms as well as the dipole [5] or quadrupole [7] moments of molecules.

In this work, we have studied the variations of molecular parameters of chloromethane, $ClCH_3$, and iodomethane, ICH_3, in going from liquid to gas. The choice of the specified substances was connected with a significant interest in Freons, which those substances belong to. It was also of interest to find the direction of a deviation in the molecules concerned, because a deviation of the C—H bond was probable, in principle, both towards the halogen atom and inwards CH_3 group, similarly to what occurred in an ammonia molecule [5].

2. Method of Calculation

In order to calculate the set of force constants for a molecule in the form of a force matrix $\hat{V}$, we used the method of solving the inverse spectral problem of vibrational spectroscopy of molecules, namely, the method of $3N$ matrices. In the framework of this method, the force matrix $\hat{V}$ is determined as

$$\hat{V} = \hat{M}\hat{L}\hat{\omega}\tilde{\hat{L}}\hat{M}, \tag{1}$$

where $\hat{M}$ is the diagonal matrix of kinematic coefficients composed of the masses of atoms, which the molecule is made up of,

$$\hat{M} = \mathrm{diag}\{m_i\} = \mathrm{diag}\{m_\mathrm{X}, m_\mathrm{X}, m_\mathrm{X}, m_\mathrm{C}, m_\mathrm{C}, m_\mathrm{C}, m_\mathrm{H}, m_\mathrm{H}, m_\mathrm{H}, m_\mathrm{H}, m_\mathrm{H}, m_\mathrm{H}, m_\mathrm{H}, m_\mathrm{H}, m_\mathrm{H}\}, \tag{2}$$

m_H, m_C, and m_X are the atomic masses of hydrogen (H), carbon (C), and chlorine (X = Cl) or iodine (X = I), respectively, and

$$\hat{\omega} = \mathrm{diag}\{\omega_i^2\} = \mathrm{diag}\{\omega_1^2, \omega_2^2, \omega_3^2, \omega_4^2, \omega_4^2, \omega_5^2, \omega_5^2, \omega_6^2, \omega_6^2, \omega_{tx}^2, \omega_{ty}^2, \omega_{tz}^2, \omega_{rx}^2, \omega_{ry}^2, \omega_{rz}^2\} \tag{3}$$

is the diagonal matrix composed of the squared harmonic frequencies of molecular vibrations.

The twice degenerate frequencies $\omega_{4,5,6}$, which belong to the E presentation of the C_{3v} molecular symmetry group, are included twice into the matrix. The last six frequencies correspond to the vibrations that are non-eigen, namely, translational and librational ones. It should be noted that a classification of molecular vibrations as eigen (free) and non-eigen is relative to a certain extent: the concept of eigen vibrations was introduced for a free molecule, for which the translational and librational frequencies were equal to zero. Formally, all vibrations of a molecule in a condensed phase are eigen. In this work, following works [1–7], translational and librational vibrations are referred to as "non-eigen" and all others as "eigen" ones in order to preserve the analogy with free molecules and to simplify the usage of unificated terms.

Intermolecular bonds that arise when the substance becomes liquid manifest themselves through a variation of the characteristic vibration frequency and the appearance of non-eigen vibrations with nonzero frequencies. Inasmuch, when considering molecules in the liquid state, the frequencies of their non-eigen vibrations are small in comparison with those of eigen ones, the former may be neglected when studying the modification of the latter. The eligibility of such an approximation is enhanced by the fact that it is used the squared frequencies in calculations.

To calculate the harmonic frequencies ω_i from experimental values of ν_i, we used the formula [3–9]

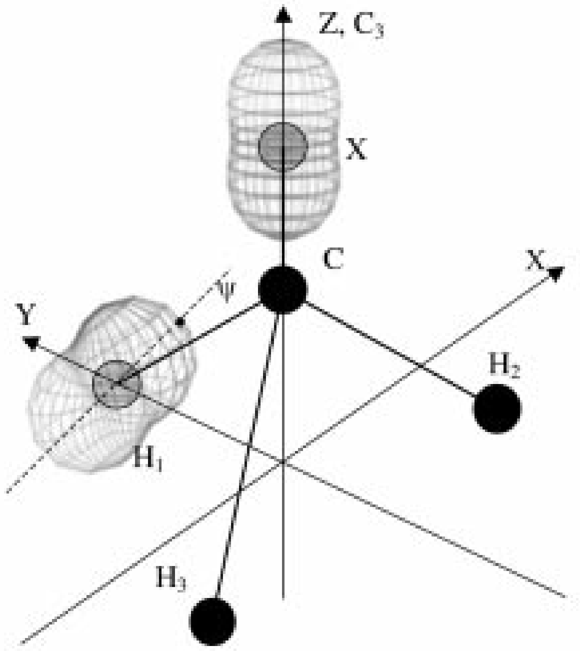
$$\omega_i = \nu_i\left(1 + u\nu_i\right), \tag{4}$$

where u is the parameter of anharmonicity. In the general case, each vibration of the molecule should be characterized by its own parameter of anharmonicity u_i. However, in the model force fields [9–13], the obtained values of the parameters of anharmonicity did not differ strongly (by no more than a factor of two) for various vibrations. If an individual parameter of anharmonicity had been used for each vibration, the number of parameters using in the framework of this method would have exceeded the number of initial data (vibration frequencies), which would have resulted in the ambiguity of solutions of the problem. In order that the set of the parameters of anharmonicity to be smaller ($1 < u_i < 9$), all vibrations should be split into several groups, which does not seem substantiated for the selected molecules. Therefore, the approximation of identical parameters of anharmonicity for all vibration modes has been used: $u_1 = u_2 = \ldots = u$.

The *a priori* determination of the parameter u, without any assumption concerning the form of a molecular force field, seems to be impossible. To preserve the robustness of the method with respect to the form of the force field, the parameter of anharmonicity u was introduced as a mathematical parameter of the method and was to be determined together with other parameters. In so doing, the matrix $\hat{\omega}$ was introduced as a one-parameter set $\hat{\omega}(u)$.

The matrix of vibration shapes $\hat{L}$ in Eq. (1) defines a displacement of each atom of the molecule at every vibration, and $\widetilde{\hat{L}}$ is the transposed matrix. The unambiguous determination of the mode shapes of molecular vibrations is possible only in the case where no more than one vibration of the molecule corresponds to every irreducible representation of the molecular symmetry group [1]. The shapes of different vibration modes that belong to the same irreducible representation of the symmetry group cannot be deduced from the symmetry considerations, because any linear combination of shapes that belong to the same irreducible representation also belongs to this representation.

Concerning the researched molecules, the condition of unequivocal determination of mode shapes is not fulfilled: three full-symmetric vibrations belong to the representation A_1 of the molecular symmetry group, while other six eigen vibrations to the representation E. Only the shape of the librational vibration ω_{rz} satisfies the indicated condition. Therefore, the matrix of the



An XCH_3 molecule, a coordinate system, the sequence of atoms, and schematic plots of the potential energy variation at displacements of X and H_1 atoms

basic shapes L_0 was constructed *a priori*, taking into account the symmetry and convenience considerations. The matrix of real mode shapes was introduced as a multiparameter set $\hat{L}(\{p_{ij}\})$, where each parameter p_{ij} (shape parameter) was responsible for a linear combination of the i-th and j-th shapes in agreement with the formalism [1–6, 8]:

$$\begin{pmatrix} L_i \\ L_j \end{pmatrix} = \begin{pmatrix} \cos p_{ij} & \sin p_{ij} \\ -\sin p_{ij} & \cos p_{ij} \end{pmatrix} \begin{pmatrix} L_i^0 \\ L_j^0 \end{pmatrix}, \qquad (5)$$

where L_i is the vector of atom displacement at the i-th vibration (actually, it is the i-th column of the matrix $\hat{L}$) and L_i^0 is the vector of the basic shape.

The introduction of the basic mode shapes required to establish the coordinate system of the molecule and the sequence of the account of atoms in matrices. For the calculations, a Cartesian coordinate system was used (see the figure): the axis Z coincided with the axis of symmetry C_3 of the molecule and the axis Y traversed one of the hydrogen atoms (H_1). The sequence of the atom account was X—C—H_1—H_2—H_3. The matrix of the basic shapes in the selected coordinate system and with the indicated sequence of atoms was presented in work [8].

While constructing the shapes of non-full symmetric vibrations that correspond to the representation E, we used [8] the fact that the representation E of the group C_{3V} is expanded as the sum $E = A + B$ of irreducible representations of the subgroup $C_S(E, \sigma^{YZ})$. It corresponds to the fact that one of the two mode shapes of each degenerate vibration has the plane σ^{YZ} as an element of symmetry, keeping the symmetry subgroup C_S (namely, corresponding to the representation A of this subgroup); the other mode shape is antisymmetric with respect to the indicated plane.

Three shape parameters are needed to form all the possible linear combinations of full-symmetric vibrations (the representation A_1 of the group C_{3V}), and six more parameters to form other six combinations (the representation E). Therefore, if the degeneration of vibrations is not taken into account, nine shape parameters are necessary for the shape "mixing" to be described completely. So, if the degeneration is taken into account, the shape matrix is defined as a set of six shape parameters: $p_1 = p_{12}$, $p_2 = p_{23}$, $p_3 = p_{13}$, $p_4 = p_{46} = p_{57}$, $p_5 = p_{68} = p_{69}$, and $p_6 = p_{48} = p_{59}$. The double subscripts of the parameters correspond to the column numbers of the matrix, when being substituted into Eq. (5).

To calculate the mode shapes of degenerate vibrations, we used the following procedure. Two orthogonal shapes were constructed for each shape obtained after "mixing" of the pair of vibrations possessing the same symmetry; degeneration was fulfilled making use of the shape parameter. The construction of the orthogonal shapes was carried out according to the following scheme. At the first stage, for the shape with the vector $\vec{L}$, two shapes $\vec{L}_1$ and $\vec{L}_2$ that correspond to a molecule rotated around the axis of C_3 symmetry by the angle $\varphi = +120$ or $-120°$, respectively, were determined. This means that the molecule was transformed using the operations of symmetry C_3 and C_3^{-1}:

$$\vec{L}_1 = \hat{C}_\varphi \vec{L}, \quad \vec{L}_2 = \hat{C}_\varphi^{-1} \vec{L}, \qquad (6)$$

where $\hat{C}_\varphi$ is the matrix of rotation of the molecule around the axis Z by the angle $\varphi = 120°$, which takes into account the rearrangement of atoms and the variation of the directions of coordinate axes. The matrix C_3^{-1} corresponds to a rotation of the molecule by the angle $\varphi = -120°$. The matrix $\hat{C}_\varphi$ can be presented in the block form

$$\hat{C}_\varphi = \begin{pmatrix} \hat{c}_\varphi & 0 & 0 & 0 & 0 \\ 0 & \hat{c}_\varphi & 0 & 0 & 0 \\ 0 & 0 & 0 & \hat{c}_\varphi & 0 \\ 0 & 0 & 0 & 0 & \hat{c}_\varphi \\ 0 & 0 & \hat{c}_\varphi & 0 & 0 \end{pmatrix}, \qquad (7)$$

where

$$\hat{c}_\varphi = \begin{pmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}. \qquad (8)$$

At the second stage, a new shape $\vec{L}'$ was constructed using the shapes $\vec{L}_1$ and $\vec{L}_2$ (see Eq. (6)) as their normalized difference:

$$\vec{L}' = \frac{\vec{L}_1 - \vec{L}_2}{\sqrt{2(1-\tilde{\vec{L}}\hat{M}\hat{C}_\varphi\vec{L})}}. \qquad (9)$$

The mode shape $\vec{L}'$ is orthogonal to the initial mode shape $\vec{L}$.

Formulae (6)—(9) allowed the shapes of degenerate vibrations to be obtained without knowing their analytical forms. Formally, this means that the 4-th and 6-th columns in the basic shape matrix can be simply obliterated, taking into account that those columns were determined completely by the 3-rd and 5-th ones, respectively. In this case, the preservation of shape symmetry (the preservation of the subgroup C_S) and the equality of frequencies of degenerate vibrations were taken into account automatically. Such an approach made it possible to avoid complexities that arose while constructing the complete basis of mode shape vectors and to use the "non-full" one $\hat{L}'_0$:

$$\hat{L}'_0 = \begin{pmatrix}
0 & 0 & 0 & 0 & - & 0 & - & 0 & - & g & 0 & 0 & 0 & r_A & 0 \\
0 & 0 & 0 & 0 & - & s_A & - & t_A & - & 0 & g & 0 & -r_A & 0 & 0 \\
a & j_A & 0 & 0 & - & 0 & - & 0 & - & 0 & 0 & g & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & - & 0 & - & 0 & - & g & 0 & 0 & 0 & r_B & 0 \\
0 & 0 & 0 & 0 & - & -s_B & - & t_B & - & 0 & g & 0 & -r_B & 0 & 0 \\
a & -j_B & 0 & 0 & - & 0 & - & 0 & - & 0 & 0 & g & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & - & 0 & - & 0 & - & g & 0 & 0 & 0 & -r_C & -c \\
0 & 0 & c & c & - & s_C & - & t_C & - & 0 & g & 0 & r_C & 0 & 0 \\
-b & 0 & 0 & 0 & - & 0 & - & 2w & - & 0 & 0 & g & 2r_{CX} & 0 & 0 \\
0 & 0 & c\sqrt{3}/2 & -c\sqrt{3}/2 & - & 0 & - & 0 & - & g & 0 & 0 & 0 & -r_C & c/2 \\
0 & 0 & -c/2 & -c/2 & - & s_C & - & t_C & - & 0 & g & 0 & r_C & 0 & c\sqrt{3}/2 \\
-b & 0 & 0 & 0 & - & 0 & - & -w & - & 0 & 0 & g & -r_{CX} & -r_{CY} & 0 \\
0 & 0 & -c\sqrt{3}/2 & c\sqrt{3}/2 & - & 0 & - & 0 & - & g & 0 & 0 & 0 & -r_C & c/2 \\
0 & 0 & -c/2 & -c/2 & - & s_C & - & t_C & - & 0 & g & 0 & r_C & 0 & -c\sqrt{3}/2 \\
-b & 0 & 0 & 0 & - & 0 & - & -w & - & 0 & 0 & g & -r_{CX} & r_{CY} & 0
\end{pmatrix}. \qquad (10)$$

Here

$$a = \sqrt{\frac{3m_\mathrm{H}}{M\,(m_\mathrm{X}+m_\mathrm{C})}}, \quad b = a\frac{m_\mathrm{X}+m_\mathrm{C}}{3m_\mathrm{H}},$$

$$c = \frac{1}{\sqrt{3m_\mathrm{H}}}, \quad g = \frac{1}{\sqrt{M}}, \quad j = \sqrt{\frac{m_\mathrm{C}/m_\mathrm{X}}{m_\mathrm{C}+m_\mathrm{X}}},$$

$M = m_\mathrm{X} + m_\mathrm{C} + 3m_\mathrm{H}$,

$\beta = \arcsin\left(2\sin\frac{\alpha}{2}/\sqrt{3}\right)$ is the angle between the axis Z and the direction C—H$_1$, α is the angle H$_1$—C—H$_2$, $z' = \frac{(m_\mathrm{X}+m_\mathrm{C})l_\mathrm{CH}\cos\beta + m_\mathrm{X}l_\mathrm{XC}}{M}$ is the z-coordinate of the center of mass of the molecule, $l_\mathrm{C-H}$ and $l_\mathrm{X-C}$ are the distances C—H$_1$ and X—C, respectively,

$$e = l_\mathrm{XC} + l_\mathrm{CH}\cos\beta - z', \quad d = z', \quad f = e - l_\mathrm{XC},$$

$$h = l_\mathrm{CH}\sin\frac{\alpha}{2}, \quad l = \frac{l_\mathrm{CH}}{2}\sin\beta = \frac{h}{\sqrt{3}}, \qquad (11)$$

$$\delta = \sqrt{m_\mathrm{X}e^2 + m_\mathrm{C}f^2 + 3m_\mathrm{H}\,(d^2+2l^2)},$$

$$\delta_S = \sqrt{\frac{3m_{\mathrm{H}}m_{\mathrm{C}}m_{\mathrm{X}}}{3m_{\mathrm{H}}m_{\mathrm{C}}(f+d)^2+3m_{\mathrm{H}}m_{\mathrm{X}}(d+e)^2+m_{\mathrm{X}}m_{\mathrm{C}}l_{\mathrm{FC}}^2}}:$$

$$s_A=(f+d)\frac{\delta_S}{m_{\mathrm{X}}},\quad s_B=(d+e)\frac{\delta_S}{m_{\mathrm{C}}},\quad s_C=l_{\mathrm{XC}}\frac{\delta_S}{3m_{\mathrm{H}}},$$

$$r_A=\frac{e}{\delta},\quad r_B=\frac{f}{\delta},\quad r_C=\frac{d}{\delta},\quad r_{\mathrm{CX}}=\frac{l}{\delta},\quad r_{CY}=\frac{h}{\delta}$$

$$\delta_t=\Big\{6m_{\mathrm{X}}m_{\mathrm{C}}m_{\mathrm{H}}/[m_{\mathrm{X}}m_{\mathrm{C}}(d(s_A+s_B)+e(s_B+s_C)+ +f(s_A-s_C))^2+2l^2(m_{\mathrm{X}}m_{\mathrm{C}}(s_A+s_B)^2+3m_{\mathrm{X}}m_{\mathrm{H}}(s_A- -s_C)^2+3m_{\mathrm{C}}m_{\mathrm{H}}(s_B+s_C)^2)]\Big\}^{1/2},$$

$$t_A=\frac{\delta_t}{m_{\mathrm{X}}}l\left(s_B+s_C\right),\quad t_B=\frac{\delta_t}{m_{\mathrm{C}}}l\left(s_A-s_C\right),$$

$$t_C=-\frac{\delta_t}{3m_{\mathrm{H}}}l\left(s_A+s_B\right),$$

$$w=\frac{\delta_t}{6m_{\mathrm{H}}}\left(d\left(s_A+s_B\right)+e\left(s_B+s_C\right)+f\left(s_A-s_C\right)\right).$$

The aforesaid yields that the force matrix of the molecule $\hat{V}(\{p\},u)$ depends on seven parameters: six shape parameters and the parameter of anharmonicity. To obtain the numerical values of those parameters, we used the data on the vibrational spectra of two isotope modifications of each molecule. In the framework of the approximation which considers the force constants of chemical bonds formed by isotope modifications of identical atoms to be equal [1–7], we used the force matrix calculated with regard for the spectrum of a molecule XCH_3 to find the vibrational spectrum of a molecule XCD_3, D being a deuteron,

$$\left\{\omega_{\mathrm{D}}^2\right\}=\text{eigenvalues}\left(\hat{M}_{\mathrm{D}}^{-1}\hat{V}\left(\{p\},u\right)\right). \tag{12}$$

Here, $\hat{M}_{\mathrm{D}}$ is the diagonal mass matrix of a molecule XCD_3. Formally, Eq. (12) means that we seek a solution of the direct spectral problem for a molecule XCD_3, basing upon the results of solving the inverse spectral problem for a molecule XCH_3. It should be noted that the spectra of arbitrary isotope modifications of the molecule can be used for calculations. The choice of the specified modifications was connected, first, with the preservation of the isotope modification symmetry, i.e. with the simplified frequency relation; secondly, with a more extended body of the available information concerning vibrations of just those modifications [9–12]; and, thirdly, with a simplified procedure of inverse calculations (the force matrix was calculated using the XCD_3 spectrum, and the force matrix was used afterwards to calculate the XCD_3 spectrum), which are necessary for monitoring the stability of the solutions obtained.

We introduced the error-parameter [1–6, 8]

$$\delta\left(\{p\},u\right)=\sum_{i=1}^{9}\left(1-\frac{\omega_{\mathrm{D},i}\left(\{p\},u\right)}{\omega_{\mathrm{D},i,\mathrm{exp}}}\right)^2 \tag{13}$$

between experimentally measured vibration frequencies $\omega_{\mathrm{D,exp}}$ of the molecule XCD_3, corrected with regard for the anharmonicity (4), and the frequencies $\omega_{\mathrm{D}}(\{p\},u)$ calculated by Eq. (12). The values of the parameters $(\{p\},u)$, at which δ became minimal, were considered as sought ones. The force matrix obtained after the substitution of those parameter values was the final result of the posed problem.

In the framework of the inverse spectral problem of vibrational spectroscopy of molecules, the potential energy of a molecule is introduced as a quadratic form of atomic displacements [1, 10–12, 14–18]

$$U=\frac{\tilde{\vec{x}}\cdot\hat{V}\cdot\vec{x}}{2}, \tag{14}$$

where $\vec{x}$ is a column matrix that defines displacements of atoms with respect to their positions of balance. Knowing the force matrix, one can calculate the variation of the potential energy of a molecule at trial displacements of its atoms.

Aiming at finding the deviation of chemical bonds, let us study the variation of the molecule energy caused by displacements of atom H_1 within the plane ZY. Let the atom move a distance r from the position of balance and at an angle φ with respect to the axis Y. The column matrix of such a displacement looks like

$$\tilde{\vec{x}}=\begin{pmatrix}0 & 0 & 0 & 0 & 0 & 0 & 0 & r\cos\varphi & r\sin\varphi & 0 & 0 & 0 & 0 & 0 & 0\end{pmatrix}. \tag{15}$$

Provided that the atoms are shifted in the manner described above, it is convenient [2–8] to analyze the polar plot $U(\varphi)$ of the molecular energy variation. The plot $U(\varphi)$ is symmetric and possesses two identical maxima, the positions of which differ by 180° from each other. It is evident that, at the angles that correspond to a maximum of the energy variation, the maximal force should be applied to move atom H_1. These angles define the direction of the chemical bond [2–6] between C and H_1 atoms.

In the framework of the valent force approximation, the direction of a chemical bond has to coincide with the straight line that connects the nuclei of atoms, between which this chemical bond emerges. If there exists a "contribution" of the central force field, for example, a Coulomb field, the direction of a chemical bond may deviate from the indicated line. The angle between the direction of the chemical bond and the straight line that connects the nuclei is known as the angle of a chemical bond deviation [2–6, 8]. The chemical bond itself must lie in a plane, which is defined by the axis of molecule symmetry and the straight line C–H, i.e. the C–H_1 bond must lie in the plane ZY.

3. Results and Discussion

In our calculations, we used the data summarized in Tables 1 and 2.

The problem of minimization of a function depending on many parameters has, as a rule, multiple solutions. The presence of a number of minima of the function δ considered as a set of seven parameters evidences for the existence of several solutions of the problem under study. Obviously, not all of them can be realized. Some solutions correspond to local minima of the function δ, some do not satisfy the physical conditions or approximations made. To select the required solutions from the obtained set, the following criteria were applied:

Table 1. Vibration frequencies ν (in cm^{-1}), internuclear distances r (in Å), and H—C—H angles α of molecules XCH_3 and XCD_3 belonging to the gaseous and liquid states of the substance

Quantity	$ClCh_3$		$ClCD_3$		ICH_3		ICD_3	
	gas	liquid	gas	liquid	gas	liquid	gas	liquid
ν_1	2966.2	2955	2161	2115	2969	2941	2155	2130
ν_2	1354.9	1370	1029	1018	1251.4	1241	950	938
ν_3	732.1	709	695	683	533	523	501	493
ν_4	3041.8	3036	2286	2283	3062.2	3049	2300	2285
ν_5	1454.6	1446	1058	1051	1437.8	1425	1048	1046
ν_6	1015	1016	775	769	882.5	891	660	644
r_{X-C}	1.782				2.139			
r_{C-H}	1.103				1.100			
α	110° 20′				110° 58′			

Table 2. Atomic masses used in calculations

Atom	H	D	^{12}C	^{35}Cl	^{127}I
m, a.m.u.	1.0078	2.0141	12	34.969	126.9

1. Both "direct" and "inverse" calculations were carried out, i.e. the force matrix, which has been calculated for the molecule XCD_3, was used for evaluating the frequencies of the XCH_3 molecule. It is obvious that the obtained force matrices had to be identical, while the shape parameters, the parameter of anharmonicity, and the value of the deviation angle should not differ strongly for inverse calculations.
2. The solution had to be stable. For checking the solution stability, we studied variations of the deviation angle under small variations of the shape parameters. Unstable solutions were rejected.
3. The value of the deviation angle cannot be too large. The values of about 50° were obviously invalid. From the mathematical point of view, such a situation can be explained by a formal replacement of vibrational shapes.

After the analysis of a fluoromethane molecule following items 1—3 [8], two probable solutions of the inverse problem of spectroscopy were kept for the further consideration. Those solutions differed substantially from each other only by values of the deviation angle. Nevertheless, they did not allow us to determine the direction of deviation: inwards the CH_3 group or towards the fluorine atom. Therefore, in this work, we used the additional speculations.

4. The shape parameters, the parameter of anharmonicity, and the value of a deviation angle were expected to have close values in a series of substances similar by a chemical structure ($ClCH_3$, ICH_3) and at a transition into another state of aggregation.

The described criteria used in the analysis of solutions allowed us to obtain a single solution that satisfied all the requirements indicated above. The parameters that correspond to this solution are summarized in Table 3, together with values of the deviation angle and the parameter δ. The negative sign of the deviation angle corresponds to a deviation of the C–H bond direction towards the halogen atom (chlorine or iodine). Analogously, the solution for a fluoromethane molecule with the negative sign of the deviation angle is to be preferred [8]. If a deviation of the chemical bond direction is connected with the presence of the effective electric charges of atoms, we may assert that such a deviation evidences for that the halogen atom possesses an effective charge of the opposite sign with respect to that of the hydrogen atom.

Table 3. Shape parameters p_{ij}, the parameter of anharmonicity u, and the deviation angles ψ of C—H bonds calculated for the molecules XCH_3 and XCD_3 belonging to the gaseous and liquid states of the substance

Molecule	Parameters of the vibration mode shapes						$u \times 10^5$, cm	ψ, deg.	$\delta \times 10^4$
	completely symmetric			incompletely symmetric					
	p_{12},	p_{23},	p_{13},	p_{46},	p_{68},	p_{48},			
	rad								
$ClCH_3$(gas)	1.298	0.204	1.470	1.711	2.135	0.910	2.240	–3.0	0.15
$ClCD_3$(gas)	1.071	0.291	1.471	1.865	2.137	0.960	2.232		
$ClCH_3$(liquid)	1.365	0.117	1.472	1.802	2.027	0.969	1.124		1.8
$ClCD_3$(liquid)	1.167	0.157	1.468	1.907	2.046	0.966	1.133		
ICH_3(gas)	1.237	0.180	1.493	2.163	1.913	1.350	1.983	–3.7	0.02
ICD_3(gas)	1.056	0.157	1.431	2.254	1.955	1.340	1.984		
ICH_3(liquid)	1.254	0.104	1.422	2.423	2.076	1.301	0.234		1.4
ICD_3(liquid)	1.083	0.146	1.358	2.475	2.051	1.275	0.243		

It follows from Table 3 that only the parameter of anharmonicity underwent a substantial variation at the gas—liquid transition. Comparatively small changes of the shape parameters at the transition into the liquid state evidence for the stability of vibration mode shapes, i.e. for a relative weakness of intermolecular bonds in liquids concerned in comparison with intramolecular ones. The formation of intermolecular bonds resulted in a substantial variation of the anharmonicity parameter of vibrations, which can indicate a symmetry change of the environment field relative to the intramolecular one. The parameter of discrepancy was greater for molecules in the liquid phase. It can be connected to a smaller accuracy of the definition of molecule vibration frequencies in the liquid phase and to the influence of translations and librations, whose frequencies were not taken into account in this work.

The figure shows the polar plots of the energy $U(\varphi)$ that is acquired by the molecule owing to displacements of atoms X and H_1. The dashed line corresponds to a direction of the maximal effort for atom H_1 to be moved, and ψ is the deviation angle of the C—H bond enlarged for the sake of visualization.

4. Conclusions

The shape parameters, the parameter of anharmonicity, and the values of the deviation angle of C—H bonds of chloromethane and iodomethane molecules have been calculated making no assumption concerning the forms of the intramolecular and environment force fields. Comparatively small changes of the shape parameters, which accompany substantial variations of the parameter of anharmonicity, evidence for a relative weakness of intermolecular bonds in the researched liquids in comparison with intramolecular ones. The direction of the chemical bond deviation, namely, towards the halogen atom, testifies to that the halogen and the hydrogen atom interact stronger with each other than two hydrogen atoms do. In other words, the center of the negative charge is shifted towards the halogen atom.

1. *Belyi M.U., Okhrimenko B.A., Yablochkov S.M.* // Izv. Vyssh. Ucheb. Zaved., Ser. Fiz. — 1987. — N 4. — P. 52 — 57.
2. *Belyi M.U., Okhrimenko B.A.* // Ukr. Fiz. Zh. — 2001. — **46**, N 4. — P. 466 — 470.
3. *Bilyi M.U., Okhrimenko B.A.* // Ibid. — N 8. — P. 825 — 828.
4. *Bilyi M.U., Gaididei G.I., Okhrimenko B.A. et al.* // Ibid. — N 12. — P. 1256 — 1261.
5. *Okhrimenko B.A., Samoilenko D.M.* // Visn. Kyiv. Nat. Univ., Ser. Fiz. — 2002. — N 4. — P. 45 — 48.
6. *Bilyi M.U., Okhrimenko B.A.* // Ukr. Fiz. Zh. — 1999. — **44**, N 3. — P. 326 — 331.
7. *Okhrimenko B.A., Samoilenko D.M.* // Ibid. — 2002. — **47**, N 4. — P. 334 — 337.
8. *Okhrimenko B.A., Samoilenko D.M.* // Funct. Mater. — 2003. — **10**, N 3. — P. 547 — 553.
9. *Sverdlov L.M., Kovner M.A., Krainov E.P.* Vibrational Spectra of Polyatomic Molecules. — Moscow: Nauka, 1970 (in Russian).
10. *Nakamoto K.* Infrared Spectra of Inorganic and Coordination Compounds. — New York: Wiley, 1963.
11. *Nakamoto K.* Infrared and Raman Spectra of Inorganic and Coordination Compounds. — New York: Wiley, 1997.
12. *Molecular* Constants of Inorganic Compounds: A Handbook / Ed. by Krasnov K.S. — Leningrad: Khimiya, 1979 (in Russian).
13. *Ramaswamy K., Swaminathan S.* //. Aust. J. Chem. — 1969. — **22**, N 2. — P. 291 — 297.
14. *Osipov O.A., Minkin V.I., Garnovsky A.D.* Handbook of Dipole Momenta. — Moscow: Vysshaya Shkola, 1971 (in Russian).

15. *Gribov L.A.* Introduction to Molecular Spectroscopy. — Moscow: Nauka, 1976 (in Russian).

16. *Herzberg G.* The Spectra and Structure of Simple Free Radicals. — Ithaca: Cornell Univ. Press, 1971.

17. *Gribov L.A., Dement'ev V.A.* Calculation Methods and Algorithms in the Theory of Vibrational Spectra of Molecules. — Moscow: Nauka, 1981 (in Russian).

18. *Gribov L.A., Dement'ev V.A.* Computer Simulation of Vibrational Spectra of Complex Compounds. — Moscow: Nauka, 1989 (in Russian).

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ДЕВІАЦІЯ С—Н-ЗВ'ЯЗКУ В РІДКОМУ ТА ГАЗОПОДІБНОМУ ХЛОРМЕТАНІ ТА ЙОДМЕТАНІ

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Резюме

Метод $3N$-матриць застосовано для розв'язання оберненої спектральної задачі коливальної молекулярної спектроскопії для молекул хлорметану $ClCH_3$ та йодметану ICH_3 в рідкому та газоподібному станах. Не залежно від моделей силового поля молекул та оточення отримано значення кутів девіації С—Н-зв'язків. Проведено порівняння отриманих параметрів форми коливань молекул, параметрів ангармонізму та кута девіації хімічних зв'язків у молекулах різного агрегатного стану. Для розрахунків вибрані частоти власних коливань молекул та наближення однакового параметра ангармонізму всіх коливань, використаний формалізм "неповного" базису форм коливань.