DEVIATION OF CHEMICAL BOND C–H IN A DEFORMED METHANE MOLECULE

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The force matrix for the methane molecule has been calculated making no *a priori* assumptions concerning the force field character. The calculations have been carried out in the framework of a relatively new $3N$-matrix method and using experimental frequencies for the normal vibrations of CH_4, CD_4, and CT_4 molecules. The deviation of the valence-force field from a real molecular force field has been calculated, and the "additive" of the central force field was found to be about 11%. The deviation of C–H chemical bound, which accompanies a certain preliminary deformation of the molecule, is a manifestation of the central-force field "additive" to the valence-force field.

A deviation of the chemical bond between atoms X and Y consists in that the direction of the interatomic bond and the straight line connecting the nuclei of those atoms do not coincide. The deviation angle is an angle between those two directions.

The explicit conclusion on the existence of the deviation phenomenon, in particular, the deviation of the O–H bond in a water molecule, was drawn for the first time in work [1]. The term "deviation", which is usually applied to characterize a deviation of one direction from another, was proposed in work [2], where some manifestation features of this phenomenon have been studied for water molecules in the condensed state. According to the results of works [1–3], the deviation angle is about 2° for a free water molecule and grows to 7.5° for a water molecule in the liquid state. As was indicated in work [3], this result correlates with the results of neutron diffraction researches, according to which a "bend" of hydrogen bonds, i.e. their deviation from a direct line by an angle of about 10°, is observed in a condensed medium.

The deviation phenomenon was found in work [1], when solving the inverse spectral problem of vibrational spectroscopy using the $3N$-matrix method [4]. This method was proposed in 1985, and it can be considered to be rather new in comparison with the standard approximation of valence-force field, which has been known since 1904. Unlike many others, the $3N$-matrix method, first, does not require any *a priori* assumptions concerning the character of the molecular force field, and, second, it can be applied to molecules irrespective of whether they are free or in a condensed medium. When solving the inverse spectral problem taking advantage of this method, the frequencies of normal vibrations of isotope-substituted modifications of a molecule with the same symmetry are used as the initial data. Just this circumstance allows the force matrix of a molecule to be calculated without any *a priori* assumptions concerning the configuration of the molecular force field. Therefore, the results obtained in this work should be considered as experimental. They can be used as reference ones for the sake of comparison with the results of theoretical calculations of the molecular force field, e.g., making use of quantum-mechanical methods.

The physical origins of a chemical bond deviation were discussed in work [1]. If the approximation of central-force field would be valid for a water molecule, then, provided that the H–H and O–H bonds are equivalent, the chemical bond direction would coincide with the direction of a bisector between them.

In another limiting case where the model of valence-force field is realized completely, the deviation would be equal to zero. The actual direction of the chemical bond, which is characterized by a nonzero deviation angle, can be considered as an "additive" of the central-force field to the valence-force one.

It is worth noting that the ideas, which implicitly point to the deviation phenomenon, were put forward rather long ago. As an example, we cite A.S. Davydov's statement [5] concerning, in essence, a certain "additive" of the central-force field to the valence-force one: "A somewhat larger angle value in comparison with the theoretical one of 90° can be easily explained by a mutual repulsion of hydrogen atoms". Though the cited statement concerned the molecule of ammonia, it can be extended to include the water molecule as well.

Further researches in this branch revealed the deviation of a chemical bond in other molecules which belong to symmetry groups C_{2v} [6–10] and C_{3v} [11–14]. The fact that the deviation angle differs from zero for every studied molecule can be regarded as a confirmation that a noticeable "additive" of the central-force field to the valence-force one is rather a widespread phenomenon.

The application of the elaborated technique to the analysis of noncentral impurities in crystals [15–17] can be considered as a probable further development of this approach. To date, the activity in this direction is hampered by the absence of required experimental data.

Information given above on the manifestation scope of the central-force-field "additive" allows one to suppose that it can also be present in other molecules belonging to groups with higher symmetry, in particular, in the CH_4 molecule which belongs to group T_d. Attention drawn to studying the vibration spectra of this molecule stems from a lot of factors. Methane-filled cells are used for the stabilization of a laser lasing frequency [18]. The main method for monitoring the methane content in the terrestrial atmosphere, which gives an appreciable contribution to the greenhouse effect, is an optical one [19]. Precision spectroscopic researches of methane are also carried out to solve some astrophysical problems [20].

The solution of the inverse spectral problem of vibrational spectroscopy for a methane molecule making use of the $3N$-matrix method can assist in the solution of another problem. In work [21], the splitting of ν_2-vibration was revealed experimentally. This fact was discussed in monographies [22, 23], but, to our knowledge, there is no exhaustive explanation of this phenomenon yet.

The first attempt to apply the $3N$-matrix method to a CH_4 molecule was made in work [4]. However, the calculations were carried out making use of zero-point frequencies for normal vibrations, which were obtained in the framework of the valence-force field model. Since the choice of the force field model affects the values of zero-point frequencies, the results of work [4] cannot be considered as completely independent. In this connection, it is expedient to carry on calculations by applying the $3N$-matrix method and without involving any data obtained in the framework of any force field model.

The application of the $3N$-matrix method to the solution of the inverse spectral problem of vibrational spectroscopy dealing with a methane molecule allows one to determine a 15 × 15 force matrix which can implicitly include both the valence-force field model and the "additive" given by the central-force field model. However, even provided that the "additive" is large, the deviation would not manifest itself so strongly as it can be observed for molecules with C_{2v} and C_{3v} symmetries. It is a result of the high symmetry of a CH_4 molecule. One may expect that a purposeful reduction of the molecular symmetry owing to some deformation will be accompanied by a manifestation of a certain chemical bond deviation.

All the remarks made above were taken into account in this work. Our calculations were based on experimental data. No *a priori* assumptions were used concerning the character of the molecular force field.

For the calculation of the force matrix, we use the formula

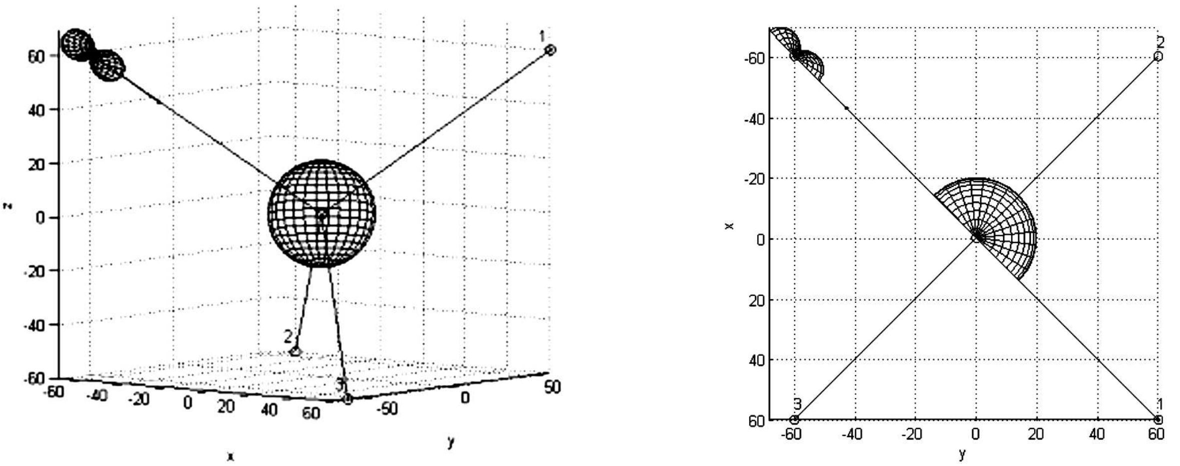
$$\hat{V} = \hat{M}\hat{L}\hat{\omega}\hat{\tilde{L}}\hat{M}, \tag{1}$$

where $\hat{V}$ is the force matrix of the molecule, $\hat{M}$ is the diagonal matrix of atomic masses, $\hat{L}$ is the matrix of normal vibration shapes, and $\hat{\omega}$ is the matrix of squared zero-point normal vibration frequencies [4].

Since Eq. (1) includes the squares of zero-point characteristic vibration frequencies, the correction of experimental frequencies for anharmonicity was executed, similarly to what was done in works [1–3], using the formula

$$\omega_{i0} = \omega_{ie}(1 + u_i\omega_{ie}), \tag{2}$$

where ω_{i0} and ω_{ie} are the zero-point and experimental frequencies, respectively, and u_i is the anharmonicity constant. The subscript $i = (1, 2, 3, 4)$ enumerates the characteristic frequencies of normal vibrations of a methane molecule. Owing to the high symmetry of the latter, the matrix $\hat{V}$ is composed of nine nonzero elements different by the absolute value. The analytical form of the matrix $\hat{V}$ as a function of the shape parameter and the zero-point vibration frequencies is given in work [4]. When determining the shape parameters and the anharmonicity factors, a condition was used that the force matrix of the molecule is independent of the isotope modification. Since the anharmonicity factors depend only on the characteristics of the molecular force field, they can also be adopted identical for different isotopic shapes of the molecule. We looked for such values of the anharmonicity factors and the shape parameters



a

b

Fig. 1. Energy diagrams for hydrogen and carbon atoms in a nondeformed methane molecule. Side (*a*) and top (*b*) views

T a b l e 1. Experimental and zero-point frequencies of normal vibrations for various isotopic modifications of the methane molecule calculated by the $3N$-matrix ($3N$) and valence-force field (VFF) methods

i	ω_e (cm^{-1})			$\omega_{0,(\mathrm{VFF})}$ (cm^{-1})			$\omega_{0,(3N)}$ (cm^{-1})			$\delta = \frac{\omega_{0,(\mathrm{VFF})}-\omega_{0,(3N)}}{\omega_{0,(3N)}}$ (%)		
	CH_4	CD_4	CT_4	CH_4	CD_4	CT_4	CH_4	CD_4	CT_4	CH_4	CD_4	CT_4
1	2916.5	2108.5	1738	3143	2224	1817	3152	2232	1822	−0.3	−0.34	−0.25
2	1533.6	1092.6	896	1573	1113	910	1574	1113	910	-0.03	0.01	0.04
3	3018.9	2259.9	1937	3154	2333	1990	3192	2357	2008	−1.2	−1.0	−0.9
4	1305.9	996	858	1357	1027	880	1343	1018	874	1.0	0.9	0.66

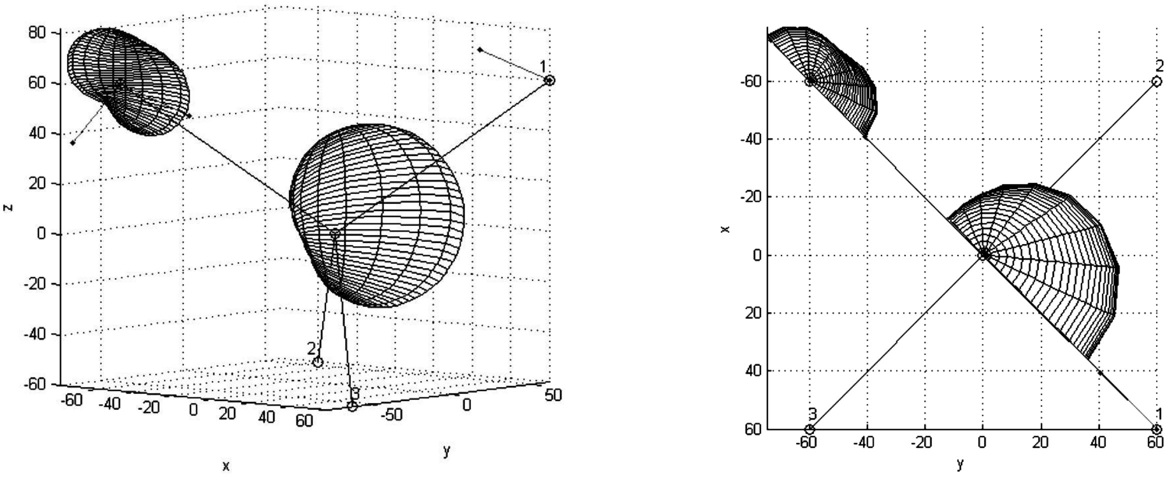
that the difference between the elements of force matrices for different isotope modifications of the methane molecule would be minimal. Formally, the problem was to find a minimum of the function of seven parameters

$$f(u_1, u_2, u_3, u_4, \psi_H, \psi_D, \psi_T) = \sum_{j=1}^{3}\sum_{i=1}^{9} A_{ij}, \qquad (3)$$

where $A_{i,1} = \left(\frac{V_i^H - V_i^D}{V_i^H + V_i^D}\right)^2$, $A_{i,2} = \left(\frac{V_i^H - V_i^T}{V_i^H + V_i^T}\right)^2$, $A_{i,3} = \left(\frac{V_i^T - V_i^D}{V_i^T + V_i^D}\right)^2$, and V_i^H, V_i^D, and V_i^T are the nonzero elements of force matrices for CH_4, CD_4, and CT_4, respectively. To solve this problem, the steepest descent method was applied. As the initial approximation, we used the results of calculations obtained in the approximation, when all anharmonicity factors were considered to be identical. Ultimately, we found the absolute minimum of function (3) with the following parameters: $\psi_H = 0.1554$, $\psi_D = 0.0765$, $\psi_T = 0.0104$, $u_1 = 2.768 \times 10^{-5}$ cm, $u_2 = 1.697 \times 10^{-5}$ cm, $u_3 = 1.897 \times 10^{-5}$ cm, and $u_4 = 2.197 \times 10^{-5}$ cm. These results were used to calculate the zero-point frequencies of the molecules. In Table 1, the experimental and zero-point frequencies of molecular vibrations calculated following different techniques are listed. One can see that there is an appreciable difference between the corresponding values of zero-point frequencies, the quantitative estimation of which is presented in the last three columns of Table 1.

In most cases, the deviations do not exceed 1%, which can be regarded to a certain extent as an evidence for a relatively small "additive" made by the central-force field to the valence-force one. The values of zero-point frequencies and shape parameters of normal vibrations were used to calculate the specific values of elements in the force matrix $\hat{V}$. Table 2 gives the results of corresponding calculations which can be compared with those reported in work [4].

The known force matrix makes it possible to calculate and to plot the dependence of the molecular potential energy on the shift direction of one atom (the shift magnitude is supposed constant), provided that the positions of all other atoms are fixed in the polar coordinate system. Two such diagrams are schematically depicted in Fig. 1.



a **b**

Fig. 2. Energy diagrams for hydrogen and carbon atoms in a methane molecule preliminarily deformed by shifting atom H_1 to the left. Side (*a*) and top (*b*) views

For a hydrogen atom, the diagram looks like a dumbbell, the symmetry axis of which is oriented along the line connecting the nuclei of this atom and the carbon one. The direction, for which the energy is maximal, corresponds to the chemical bond direction. In this case, this direction coincides with that of a straight line connecting the nuclei of hydrogen and carbon atoms, i.e. there is no deviation of the C–H chemical bond for a nondeformed methane molecule, and the deviation angle is equal to zero.

The similar way of calculation was used, when plotting the energy diagram for the carbon atom. It looks like a sphere, which is associated with a high position symmetry of the carbon.

The situation changes, if the methane molecule is preliminarily deformed. In Fig. 2, the energy diagrams for hydrogen and carbon atoms in the deformed methane molecule are depicted.

The preliminary deformation of the molecule is simulated by shifting atom H_1 from its equilibrium position by a fixed distance in the direction that practically corresponds to that of the normal to the plane, in which hydrogen atoms H_1, H_2, and H_3 are located. The shift direction and magnitude are characterized by a straight-line segment directed to the left from atom H_1 in Fig. 2,*a*. The preliminary deformation of the methane molecule is so selected that only the distance between atoms H_4 and H_1 changes, whereas all other interatomic distances remain practically constant. Such a preliminary deformation gives rise to the appearance of a chemical bond deviation, which is illustrated by the energy diagram for hydrogen atom H_4 in Fig. 2,*a*. The directions of maximal and minimal energy values are marked by two straight-line segments, one of which forms an angle of about 10° with the segment that connects the hydrogen and carbon atoms. This is the deviation angle of the C–H chemical bond in a deformed methane molecule.

Two factors are responsible for a capability for the chemical bond deviation to reveal itself. First, it becomes possible owing to a reduction of the molecular symmetry resulting from a preliminary deformation. Second, the deviation can be regarded as a manifestation of the "additive" made by the central-force field of the molecule to the valence-force one.

However, the results obtained can be interpreted ambiguously. On the one hand, the situation can exist when the "additive" of the central-force field is completely absent for a nonndeformed molecule and appears only as a result of its deformation. On the other hand, the very

T a b l e 2. Shape parameters (ψ) and force matrix elements V_{ij} ($\times 10^6$ cm^{-1}) for isotopic modifications of the methane molecule

	CH_4	CD_4	CT_4	CH_4*	CD_4*	CT_4*
ψ	0.1554	0.0765	0.0104	0.143	0.063	−0.005
V_{11}	14.225	14.224	14.224	14.339	14.331	14.337
V_{14}	−3.556	−3.556	−3.556	−3.585	−3.583	−3.84
V_{15}	−2.460	−2.460	−2.461	−2.398	−2.398	−2.399
V_{44}	3.973	3.973	3.973	3.915	3.916	3.915
V_{45}	2.773	2.774	2.773	2.708	2.708	2.707
V_{47}	−0.361	−0.363	−0.361	−0.349	−0.350	−0.350
V_{48}	−0.290	−0.288	−0.291	−0.265	−0.265	−0.265
V_{49}	0.306	0.308	0.305	0.368	0.367	0.68

*Results of calculations taken from work [4] deformation of the molecule may stimulate the central-force field – which characterizes, to a certain extent, a nonndeformed molecule as well – to manifest itself.

In this connection, it is expedient to evaluate the energy component associated with the "additive" of the central-force field in a nonndeformed molecule. For this purpose, let us consider the ratio between the energies E_1 and E_4, which are determined in different ways. Let E_1 determine the potential energy of a methane molecule in the case where the C–H distance is increased by dl owing to the shift of one H atom along the C–H line, whereas all the other atoms remain in their initial positions. The energy E_4 is defined as the energy that corresponds to the increase of all C–H distances by the same magnitude dl. In the framework of the valence-force field model, we have

$$\frac{E_{4(\mathrm{VFF})}}{E_{1(\mathrm{VFF})}} = 4. \tag{4}$$

At the same time, calculating this ratio with the help of the force matrix found in this work, we obtain

$$\frac{E_{4(\mathrm{3N})}}{E_{1(\mathrm{3N})}} = 4.2069, \tag{5}$$

which evidences for an existence of central forces between hydrogen atoms in the methane molecule. On the other hand, making use of such a force field model, where central forces in both C–H and H–H pairs are taken into consideration, we obtain

$$E_1 = \frac{k_\mathrm{C} dl^2}{2} + 3\frac{k_\mathrm{H} dl^2}{2}\cos^2\left(\frac{\pi-\beta}{2}\right), \tag{6}$$

$$E_4 = 4\frac{k_\mathrm{C} dl^2}{2} + 24\frac{k_\mathrm{H} dl^2}{2}\cos^2\left(\frac{\pi-\beta}{2}\right), \tag{7}$$

where k_C and k_H are the elastic constants that characterize C–H and H–H bonds. It is evident that, if $k_\mathrm{H} = 0$, i.e. in the absence of the H–H interaction, the second terms in Eqs. (6) and (7) equal zero, which, in turn, provides the validity of relation (4). Since, actually, relation (5) holds true, it follows that $k_\mathrm{H} \neq 0$.

On the basis of Eqs. (5)–(7), we obtain $\frac{k_\mathrm{H}}{k_\mathrm{C}} \approx 0.0273$. Whence, it follows that the second term in Eq. (7) makes a contribution of about 11% to the energy, in comparison with the first term. These estimations testify that the field calculated in the valence-force field approximation deviates from the actual force field of the methane molecule by approximately 11%. In many cases, such an accuracy of the model is considered quite satisfactory. However, for spectroscopic researches, it may turn out insufficient. Therefore, the results obtained in this work should be taken into account, when comparing the results of theoretical calculations carried out with a rather high accuracy and the experimental ones.

The unambiguous solution of the inverse spectral problem was obtained owing to our assumption that the force matrices for three isotope-substituted methane modifications with tetrahedral symmetry – $\mathrm{CH_4}$, $\mathrm{CD_4}$, and $\mathrm{CT_4}$ – are identical. This assumption allowed us to determine the molecular force matrix using only experimental vibrational spectra of those three molecules, without any other assumptions concerning the character of the force field. Therefore, the results obtained in this work should be considered as experimental ones.

Thus, in this work, the force matrix of a methane molecule has been determined in the framework of the $3N$-matrix method and making use of experimental vibration frequencies for isotopic modifications of the molecule. The deviation of the real molecular force field from that obtained in the valence-force field approximation has been evaluated. The corresponding "additive" of the central force field amounts to about 11%. A deviation of the C–H chemical bond is observed in a deformed methane molecule, when one of three hydrogen atoms is shifted in parallel to this bond. This effect is a manifestation of central interaction forces between hydrogen atoms.

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ДЕВІАЦІЯ ХІМІЧНОГО ЗВ'ЯЗКУ C–H ДЕФОРМОВАНОЇ МОЛЕКУЛИ МЕТАНУ

О.В. Матяш, Б.А. Охріменко

Резюме

Без використання попередніх припущень про характер силового поля знайдено силову матрицю молекули метану. Розрахунки виконано відносно новим методом $3N$-матриць із використанням експериментальних частот нормальних коливань молекул CH_4, CD_4 і CT_4. Встановлено ступінь відхилення реального силового поля молекули від моделі валентно-силового поля – "домішка" центрально-силового поля становить близько 11%. Одним із проявів "домішки" центрально-силового поля до валентно-силового поля є девіація хімічного зв'язку C–H при певній попередній деформації молекули.