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UDC 539.193, 539.194

INFLUENCE OF A DEFORMATION OF NH₃ MOLECULE ON A DEVIATION OF THE CHEMICAL BOND N–H

Additional information about the force matrix of an ammonia molecule within the framework of studying the influence of molecule's deformation on the chemical bond deviation is obtained. The elastic constants of the central forces between chemically unbound atoms of hydrogen, which are usually neglected in the valence force field model, are calculated. The deformation forces the deviation curve to become non-symmetric, changes the deviation angles, and shifts the equilibrium positions of other atoms. It is found that if the geometry of a molecule is unchanged, molecule's rotation leads to such change in the force matrix that its eigenvalues remain constant.

K e y w o r d s: chemical bonds, chemical bond deviation, vibrational spectroscopy.

1. Introduction

The idea that the directions of the chemical bond between the atoms of nitrogen and hydrogen in an ammonia molecule do not coincide with the segments connecting the nuclei of molecule's atoms has been proposed, to our best knowledge, in [1]. This phenomenon was referred to as chemical bond deviation, and the corresponding angle is called the chemical bond deviation angle.

Such result was obtained by solving the inverse problem of vibrational spectroscopy using a relatively new method [2] of $3N$-matrices. The distinctive characteristic of this method, reflected in its name, is that it operates matrices of order $3N$, where N is the number of atoms in the molecule. This method is unique for the following reasons. First, it does not use any presuppositions about the character of molecule's force field. Second, it can be used both in case of free molecules and in that of condensed state molecules. The influence of the environment is taken into account by, among other things, using the frequencies of translational and librational (rotational) non-natural vibrations of the molecule.

A similar approach taking the non-natural normal vibrations into account was used in solving the inverse spectral problem for water in the liquid state [3–8]. The obtained value of deviation angle correlated well with the experimental neutronographic data on the hydrogen bond bending in water in the condensed state. Since the chemical bond deviation phenomenon is present in both free molecules and in molecules in the condensed state, it allows one to interpret the bending of hydrogen bonds in water as a special case of a more fundamental phenomenon of chemical bond deviation.

The research shows that the deviation phenomenon is present in a number of other molecules such as H_2S [9], NO_2^- [10], H_2Se, H_2Te [11, 12], $ClCH_3$, ICH_3 [13], and SO_2 [14].

The deviation phenomenon points toward the notion that the valence-force field model, first introduced by Niels Bjerrum [15], corresponds to the true force field of a molecule only to a certain extent. The existence of a non-zero deviation angle can be thought of as an "addition" of a central-force field to the valence-force field. Another direct support for this claim can be found in A.S. Davydov's words about ammonia molecules: "a somewhat higher value of the theoretically predicted angle of 90° can be eas-
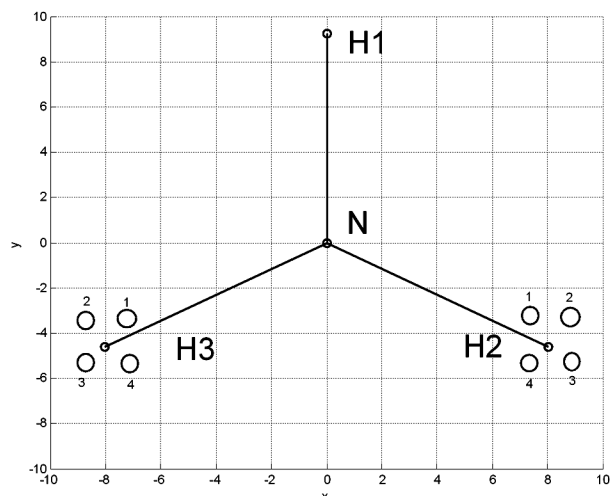
Fig. 1. Location of hydrogen atoms H1, H2, and H3 in the xy plane relative to the coordinate axes. Four consecutive deformations of the ammonia molecule due to displacements of H2 and H3 atoms are numbered and labeled "o"

ily explained by the mutual repulsion of hydrogen atoms" [16].

We thus believe that such terms as "N–H bond length", "angle between N–H bonds," or "N–H bond direction" should be viewed as approximations, since their use intrinsically implies the absence of a deviation. Hence, the current paper operates such terms as "edge N–H" or "face N–H1–H2," *etc.*

The further research of the deviation phenomenon and the factors that influence its magnitude such as, for instance, a deformation of the molecule, is deemed desirable for the following reasons. The very existence of the chemical bond deviation phenomenon contributes to the development of ideas about the peculiarities of the chemical bonds in polyatomic molecules. Such peculiarities cannot be adequately discussed in the valence-force field discourse. In addition, as shown in [17], the study of the effect of a deformation of the molecule on the deviation of the chemical bond provides additional information about the force field of this molecule.

The chemical bond deviation is an experimentally supported fact since it has been determined as a result of the processing of experimental data. In [18], the existence of the chemical bond deviation was confirmed by *ab initio* calculations.

When comparing the results of computation with experimental data, most authors confine themselves to comparing the calculated values of normal vibrations with experimental values. Such comparison has a limited value as the same set of normal vibrations corresponds to a one-parameter set of force matrices. The direct comparison of the elements of these matrices can hardly be an effective method of identifying the true matrix. We believe that the comparison of the values of normal vibrations should be accompanied by the comparison of the theoretical and experimental values of chemical a bond deviation. It is also worth noting that the results of the computations should be compared with only such experimental data, whose processing is not based on the presuppositions of the force field character.

Such criterion is met by the $3N$ matrices method, even though certain approximations are used in this method as well. In particular, the zero frequencies of normal vibrations that have been obtained through the use of certain force field models were used in [1]. As this could influence the results of calculations, the further research was adjusted to tackle this problem in [19–21]. According to [21], a deviation angle for the N–H chemical bond constitutes 2.09° in the harmonic approximation.

2. Method

The present paper utilizes the force matrix found in [21]. Elements of the ammonia molecule force matrix $\widehat{V}$ are shown in Table 1 (top rows). The orientation of the coordinate system and the numbering of hydrogen atoms in the molecule are shown in Fig. 1.

It is taken that the "direction of a chemical bond" is the direction corresponding to the maximum of the gradient of the potential energy describing a displacement of the hydrogen atom from its equilibrium position. In order to determine the direction of the chemical bond, the potential energy of the molecule as a function of (for instance) the H1 atom displacement in the yz plane should be calculated in accordance with

$$V_0(\varphi) = \frac{1}{2}\tilde{v}_0(\varphi)\widehat{V}v_0(\varphi), \qquad (1a)$$

where $V_{i,j}$ are force matrix elements $\widehat{V} = \|V_{i,j}\|$, indices have range $1 \leq i, j \leq 12$, values of x_1, x_2, x_3 correspond to displacements x, y, z from the equilibrium positions of the nitrogen atom, x_4, x_5, x_6 correspond to analogous displacements of the H1 hydrogen atom, *etc.*

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Table 1. **Force matrix $\widehat{V} \times 10^{-6}$ of NH$_3$ molecule (top rows) and $\widehat{V}_r \times 10^{-6}$ (bottom rows, in bold font)**

17.75 **17.75**	0 **0**	0 **0**	−5.91 **−5.91**	3.80 **3.78**	0 **0/37**	−9.21 **−9.21**	−1.90 **−2.30**	4.16 **3.95**	−2.62 **−2.62**	−1.90 **−1.47**	−4.16 **−4.33**
0 **0**	17.75 **17.63**	0 **1.19**	3.80 **3.78**	−5.91 **−6.65**	4.81 **4.33**	−1.90 **−2.15**	−2.62 **−2.23**	−2.40 **−2.43**	−1.90 **−1.63**	−9.21 **−8.75**	−2.40 **−3.09**
0 **0**	0 **1.19**	5.68 **5.80**	0 **0.37**	2.98 **2.50**	−1.89 **−1.15**	2.58 **2.38**	−1.49 **−1.52**	−1.89 **−2.28**	−2.58 **−2.7**	−1.49 **−2.1**	−1.89 **−2.3**
−5.91 **−5.91**	3.80 **3.78**	0 **0.37**	4.17 **4.17**	−2.53 **−2.62**	1.03 **0.77**	1.97 **1.97**	1.27 **1.45**	−1.90 **−1.76**	−0.22 **−0.22**	−2.54 **−2.61**	0.87 **0.61**
3.80 **3.78**	−5.91 **−6.65**	2.98 **2.50**	−2.53 **−2.62**	8.07 **8.52**	−2.59 **−1.93**	0.83 **0.96**	−2.17 **−2.20**	0.69 **0.48**	−2.10 **−2.12**	0.02 **0.328**	−1.08 **−1.05**
0 **0.37**	4.81 **4.33**	−1.89 **−11.15**	1.03 **0.77**	−2.59 **−1.93**	1.93 **1.47**	−1.37 **−1.28**	−0.21 **−0.43**	−0.02 **0.01**	0.34 **0.13**	−1.99 **−1.96**	−0.02 **−0.32**
−9.21 **−9.21**	−1.90 **−2.15**	2.58 **2.38**	1.97 **1.97**	0.83 **0.96**	−1.37 **−1.28**	9.29 **9.29**	−0.41 **−0.14**	−2.76 **−2.79**	−2.05 **−2.05**	1.48 **1.32**	1.55 **1.69**
−1.90 **−2.30**	−2.62 **−2.23**	−1.49 **−1.52**	1.27 **1.45**	−2.17 **−2.20**	−0.21 **−0.43**	−0.41 **−0.14**	2.95 **2.86**	0.40 **0.49**	1.04 **0.99**	1.84 **1.57**	1.29 **1.45**
4.16 **3.95**	−2.40 **−2.43**	−1.89 **−2.28**	−1.90 **−1.76**	0.69 **0.48**	−0.02 **0.001**	−2.76 **−2.79**	0.40 **0.49**	1.93 **2.025**	0.50 **0.60**	1.29 **1.45**	-0.02 **0.25**
−2.62 **−2.62**	−1.90 **−1.63**	−2.58 **−2.76**	−0.22 **−0.22**	−2.10 **−2.12**	0.34 **0.13**	−2.05 **−2.05**	1.04 **0.99**	0.50 **0.60**	4.90 **4.90**	2.95 **2.76**	1.73 **2.02**
−1.90 **−1.47**	−9.21 **−8.75**	−1.49 **−2.18**	−2.54 **−2.61**	0.02 **0.32**	−1.99 **−1.96**	1.48 **1.32**	1.84 **1.57**	1.29 **1.45**	2.95 **2.76**	7.34 **6.85**	2.19 **2.68**
−4.16 **−4.33**	−2.40 **−3.09**	−1.89 **−2.35**	0.87 **0.61**	−1.08 **−1.05**	−0.02 **−0.32**	1.55 **1.69**	1.29 **1.45**	-0.02 **0.25**	1.73 **2.02**	2.19 **2.68**	1.93 **2.42**

In order to compute the above-mentioned $V(\phi)$, we assume that, among displacements x_i, only two are non-zero. They are $x_5 = y(\phi) = d_0 \cos(\phi)$ and $x_6 = z(\phi) = d_0 \sin(\phi)$, where ϕ is an angle between the H1 atom displacement direction and the y axis, and d_0 is the magnitude of this displacement.

If the traditional matrix-vector approach is used, formula (1a) can be written as

$$V_0(\phi) = \frac{1}{2}\tilde{v}_0(\phi)\widehat{V}v_0(\phi). \tag{1b}$$

In (1b), symbol $v_0(\phi)$ corresponds to the 12-component displacement vector. With regard for the H1 atom displacements from equilibrium, this vector can be written as

$$\tilde{v}_0(\phi) = [0\ 0\ 0\ 0\ y(\phi)\ z(\phi)\ 0\ 0\ 0\ 0\ 0\ 0], \tag{2}$$

where the tilde designates the transposition operation.

The polar graph of (1), referred to as a deviation loop, is shown in Fig. 2. In the harmonic approximation, as suggested by (1), the deviation loop is a symmetric curve. The maximum of the loop for a smaller magnitude of the angle ϕ corresponds to a compression of the edge N–H. The direction of the maximum
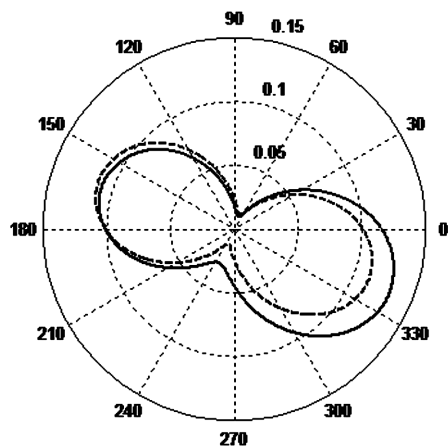
Fig. 2. Deviation loops of an undeformed ammonia molecule (dotted line) and a deformed molecule (solid line) for deformation "2"
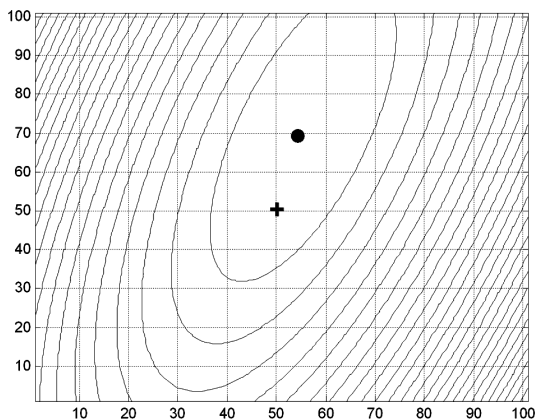

Fig. 3. Contours of constant values of the atom H1 energy in the plane of symmetry of a deformed ammonia molecule. Signs "+" and "o" mark the equilibrium positions of the atom H1 in undeformed and deformed molecules, respectively. The deformation corresponds to position "2" of atoms H2 and H3 in Fig. 1

thus gives the direction of the chemical bond, which does not correspond to the segment connecting N and H. The second maximum corresponds to a stretching of the N–H edge. Due to the symmetry of the loop, the deviation angles are the same for compression and stretching.

As mentioned above, the non-zero magnitude of a deviation angle can be explained by the central repulsive forces between hydrogen atoms. In an attempt to illustrate the action of these forces better, the calculation of the deviation loop of the molecule in a

deformed molecule is carried out. The deformation is carried out by means of displacements of H2 and H3 atoms in such way that the molecule remains symmetric with respect to the plane yz. The four displacements, whose effect was studied, are shown in Fig. 1. The deformations labeled "1" and "3" correspond to the compression and the stretching of edges H1–H2 and H1–H3, the angle between which remains unchanged. The deformations labeled "2" and "4" correspond to an increase and a decrease of the angle between edges H1–H2 and H2–H3, the length between them being unchanged.

The displacement vector of atoms H2 and H3 from their equilibrium positions in case of a deformation is given by

$$\tilde{v}_i(\psi_i) = [0\ 0\ 0\ 0\ 0\ 0\ x(\psi_i)\ y(\psi_i)\ 0\ -x(\psi_i)\ y(\psi_i)\ 0]$$

Deformations 1 through 4 can be described by angles $\psi_i = 120°,\ 30°,\ -60°,\ -150°$ such that $x(\psi_i) = d\cos\psi_i,\ y(\psi_i) = d\sin\psi_i$, where d is the magnitude of deformational displacement.

The deviation loop of the deformed molecule is given by

$$V_{0i}(\varphi,\psi_i) = \frac{1}{2}\tilde{v}_{0i}(\varphi,\psi_i)\widehat{V}\,v_{0i}(\varphi,\psi_i) - V_i(\psi_i), \qquad (3)$$

where

$$V_i(\psi_i) = \frac{1}{2}\tilde{v}_i(\psi_i)\widehat{V}\,v_i(\psi_i),$$
$$\tilde{v}_{0i}(\varphi,\psi_i) = \tilde{v}_0(\varphi) + \tilde{v}_i(\psi_i). \qquad (4)$$

The expression $V_i(\psi_i) = \frac{1}{2}\tilde{v}_i(\psi_i)\widehat{V}\,v_i(\psi_i)$ corresponds to the energy due to molecule's deformation given by vector (3). The energy $V_i(\psi_i)$ contained in (4) does not influence the position of the deviation loop maximum, since it maintains a constant value for each type of the deformation. The inclusion of this physical quantity into (4) is equivalent to a change in the origin for the energy $V_{0i}(\phi,\psi_i)$.

Figure 2 shows the deviation loop of the deformed molecule in case of deformation "2". The loop is visibly non-symmetric. The domineering maximum corresponds to an increase of the distance between the hydrogen and nitrogen atoms, the deviation angles for compression and stretching being different. Similar changes occur for all other deformations. Table 2 summarizes the changes noticed.

It is important that the differences between deviation loop graphs are not just cosmetic. In case

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Table 2. **Chemical bond deviation angles of bond N–H1 for compression and stretching in case of four different deformations. Displacement of H2 and H3 atoms constitutes 30% of the N–H edge length**

	Undeformed	Deformation type			
		"1"	"2"	"3"	"4"
Compression	2.09	4.95	5.02	−1.19	−0.52
Stretching	2.09	−1.19	−0.52	4.95	5.02
Δy	0	0.010	0.004	−0.010	−0.004
ΔZ	0	0.019	0.019	−0.019	−0.019
Dominating maximum	none	smaller φ	larger φ	larger φ	smaller φ

of an undeformed molecule, the maximum of the loop points, indeed, in the direction of the chemical bond. In case of a deformed molecule, however, such statement is not quite true. Due to the deformation, the equilibrium position of atom H1 changes. The above-mentioned displacement is shown in Fig. 3. The center of the square corresponds to the initial equilibrium position of H1 in case of an undeformed molecule. The new equilibrium position of H1 atom after the deformation is denoted by "o" in the figure.

With the help of Fig. 3, the domineering maximum of the deviation loop in Fig. 2 can be explained. To plot it, (4) uses vector (5), which takes displacement (2) (that depends on ϕ) of atom H1 into account, as well as the constant displacements of atoms H2 and H3. The displacements of atom H1 correspond to the displacements from the center of the square (Fig. 3). The direction from the center of the square to the closest point on the ellipse determines the direction of the domineering maximum in the deviation loop in Fig. 2. Similar conclusions are justified for other types of deformation. Table 2 shows the new equilibrium positions of atom H1 for four types of deformation.

Summarizing the data shown in Table 2, the following conclusion can be made. Approaching edge H2–H3 toward the molecule's symmetry axis by means of a parallel transposition in the plane xy leads to the upward shift in the equilibrium position of H1 ($\Delta z > > 0$). One can conceive it as atom H1 moving along a "trough" due to the repulsion from edge H2–H3. The change in the z coordinate is accompanied by a change in the y coordinate. The recession of edge H2–H3 from molecule's symmetry axis is accompanied by a shift of H1 atom in the opposite direction.

Apart from the four cases of deformation discussed earlier, the fifth type was considered as well. It was a deformation, with respect to which the new position of atom H1 could be predicted without calculations. Such deformation is shown in Fig. 4. It corresponds to the rotation of face N–H2–H3 by the angle $\varphi = 0.1$ rad around an axis parallel to the axis x and passing though molecule's center of mass. The new equilibrium position of atom H1 must shift in the same way as an atom in an undeformed molecule that has been rotated by such angle.

The displacement vector for the atoms of face N–H2–H3 in this case can be given as

$$\tilde{\boldsymbol{v}}_d = [0 \; y_0 \; 0 \; 0 \; 0 \; 0 \; 0 \; y_2 \; z_2 \; 0 \; y_3 \; z_3],$$

where $y_0 = l_0\phi$, l_0 is the distance to the axis of rotation passing through the center of mass to the atom N, $y_2 = y_3 = l\phi\sin\theta$, $z_2 = z_3 = l\phi\cos\theta$ l is the distance between the center of mass to atom H1, and θ is the angle between the axis z and the H1 atom shift direction.

Thus, the new equilibrium positions of atoms in an ammonia molecule can be given by the vector

$$\tilde{\boldsymbol{v}}_r = [0 \; y_0 \; 0 \; 0 \; y_1 \; z_1 0 \; y_2 \; z_2 \; 0 \; y_3 \; z_3], \tag{5}$$

which corresponds to a rotation of the undeformed molecule by the angle φ.

After such rotation operation applied to the molecule, the deviation loop was calculated for atom H1, by using

$$V_{0r}(\varphi) = \frac{1}{2}\tilde{\boldsymbol{v}}_{0r}(\varphi)\widehat{V}\boldsymbol{v}_{0r}(\varphi), \tag{6}$$

where

$$\tilde{\boldsymbol{v}}_{0r}(\varphi) = \tilde{\boldsymbol{v}}_0(\varphi) + \tilde{\boldsymbol{v}}_r. \tag{7}$$
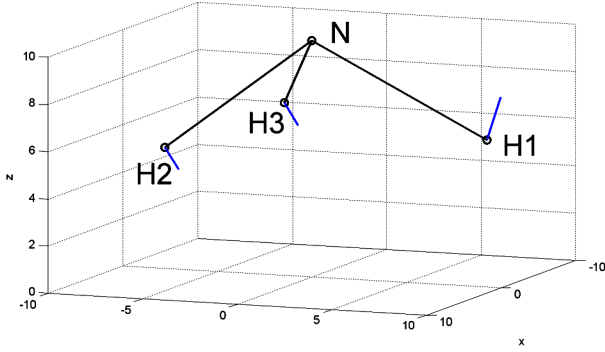
Fig. 4. Deformation of a molecule is given by the displacement vectors of H2 and H3 atoms parallel to the plane yz. Displacements of H2 and H3 correspond to the rotation of face N–H1–H2 around the x axis by 0.1 rad. The calculated vector of H1 atom displacement into a new equilibrium position corresponds to the rotation of the molecule by 0.1 rad around the x axis

The rotation considered did not change the position of atoms with respect to each other; the shift in equilibrium positions was taken into account by means of vector (5). It would appear that the deviation loop would have to rotate with the molecule by an angle φ. However, the deviation loop plotted with the help of (6) is the same as one found with (1), as seen in Fig. 5 (left). This result, at first glance, seems unexpected.

Such result is due to the following. Vector (5) corresponds to one of the forms of non-natural vibrations. For a free molecule, displacement (5) does not lead to a change in the potential energy. Hence, vector (7) gives the same magnitudes of energy as vector (2), and the deviation loop (6) traces along loop (1).

The operation of rotation by a given angle is known to be equivalent to the rotation of the coordinate system by the same angle in the opposite direction. The matrices given in the initial system of coordinates are transformed by the similarity transformation.

Elements of the force matrix $\widehat{V}$ are determined in the system of coordinates corresponding to Fig. 1. In this case, the axis z is directed along the third degree axis of symmetry. The rotation of the system of coordinates around the axis x violates this condition. Hence, the matrix $\widehat{V}$ does not correspond to the new orientation of the system of coordinates. The new system of coordinates requires the matrix $\widehat{V}_r$ such that the following similarity transformation is true:

$$\widehat{V}_r = \widehat{C}_r \widehat{V} \widehat{C}_r^{-1}, \tag{8}$$

where

$$\widehat{C}_r = \begin{bmatrix} \widehat{c}_\phi & \widehat{0} & \widehat{0} & \widehat{0} \\ \widehat{0} & \widehat{c}_\phi & \widehat{0} & \widehat{0} \\ \widehat{0} & \widehat{0} & \widehat{c}_\phi & \widehat{0} \\ \widehat{0} & \widehat{0} & \widehat{0} & \widehat{c}_\phi \end{bmatrix},$$

$$\widehat{c}_\phi = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\phi & \sin\phi \\ 0 & -\sin\phi & \cos\phi \end{bmatrix},$$

and $\widehat{0}$ is a 3×3 zero matrix.

Elements of $\widehat{V}_r$ found using (8) are shown in Table 1 (bottom rows). One can see that the matrices $\widehat{V}$ and $\widehat{V}_r$ are different, despite both of them describe the undeformed molecule of ammonia.

The deviation loop calculated with the matrix $\widehat{V}_r$ using

$$V_r(\varphi) = \frac{1}{2}\tilde{v}_0(\varphi)\widehat{V}_r v_0(\varphi),$$

is shown in Fig. 5 (right). The shape of the loop is visibly unchanged. Compared to the original deviation loop, its axis of symmetry is rotated by an angle ϕ, as foreseen.

3. Results and Their Discussion

According to the data shown in Table 2, approaching edge H2–H3 to the axis of symmetry pushes atom H1 out of its previous equilibrium position. This fact, along with the non-zero magnitude of deviation angle, points to the existence of the central forces of repulsion between hydrogen atoms. Keeping that in mind, the elastic constants, corresponding to the forces acting between N–H and H–H pairs, can be estimated.

To do so, the following approximation is used. Consider an expression for the ammonia molecule energy in case of a small decrease of length N–H1 due to a displacement of H1 along edge N–H1

$$V_1 = \frac{1}{2}\left(k_1 l_{01}^2 + k_2 l_{12}^2 + k_2 l_{13}^2\right) \tag{9}$$

and an expression corresponding to the equal contraction of the lengths of three edges N–H1, N–H2, and N–H3

$$V_3 = \frac{1}{2}\left(3k_1 l_{01}^2 + k_2 l_{12}^2 + k_2 l_{13}^2 + k_2 l_{23}^2\right). \tag{10}$$

In these expressions, k_1 and k_2 are the elastic constants which, according to this model, characterize
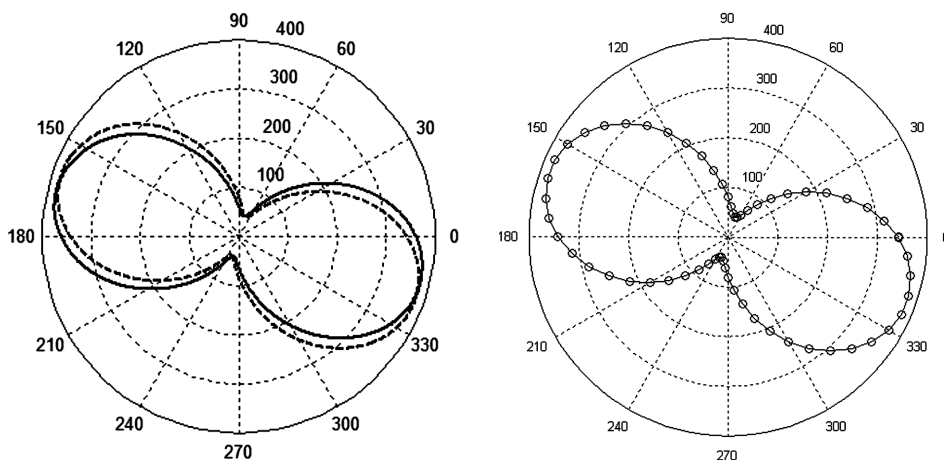
Fig. 5. Left: Deviation loop for atom H1 in case of an undeformed atom (solid line) and in case of a molecule rotated by 0.1 rad around the x axis (labeled as "o") both plotted using the matrix $\widehat{V}$. Right: deviation loop for atom H1 in case of an undeformed atom (dotted line, graph plotted using the matrix $\widehat{V}$) and in case of a molecule rotated by 0.1 rad around the x axis (solid line, graph plotted using the matrix $\widehat{V}_r$)

the forces acting, accordingly, between atoms N–H and H–H, whereas l_{ik} is a change in distances between atoms. Index "0" corresponds to the atom of nitrogen.

Evidently, for $k_2 = 0$, the ratio $V_3/V_1 = 3$. The force matrix used to evaluate such ratio gives $V_3/V_1 = 4.12$. With respect to the latter, the ratio of elastic constants was found to be $k_2/k_1 = 0.46$.

Depending on the model used and the accepted initial values, the calculated constants were found to be different. In particular, if $k_2 = 0$, then (9) gives $k_1 = 5.3$ dyn/Å, whereas (10) gives $k_1 = 7.3$ dyn/Å. The mean value is close to $k_1 = 6.5$ dyn/Å found in [15, p. 165]. If the ratio is taken as $k_2/k_1 = 0.46$, then (9) and (10) give $k_1 = 3.3$ dyn/Å and $k_2 = 1.5$ dyn/Å.

Although the obtained value of $k_2/k_1 = 0.46$ for the ratio of constants is, probably, too high, an estimate dictated by the choice of the model and a non-zero deviation angle point to the necessity to consider the central forces acting between hydrogen atoms. A relatively small magnitude of deviation angle suggests that the domineering model in this case is, indeed, the valence-force field one.

The obtained ratio of elastic constants k_2/k_1 depends on the chosen model, which, of course, uses approximations. Nevertheless, this result and the non-zero value for deviation angle indicate a significant role of the central forces acting between hydrogen atoms in an ammonia molecule.

Interestingly, the matrices $\widehat{V}$ and $\widehat{V}_r$ (table 1) differ significantly from each other. The difference between matrices is due to the difference in the reference frame orientations used. Consequently, the following inequality stands: $\frac{\partial V}{\partial \varphi} \neq 0$. As the matrix $\widehat{V}$ is contained in expression (1) for the potential energy V, it implies that the Lagrangian $L = T - V$ depends on the parameter φ or the angle of reference frame rotation. Formally, this can be expressed as $\frac{\partial L}{\partial \varphi} \neq 0$.

This circumstance affects one of the fundamental tenets, on which the law of conservation of angular momentum is based. One of the provisions for the conservation law stipulates that the Lagrangian function in the isotropic space must be invariant to the small rotation of the reference frame.

However, another provision stipulates that the Lagrange function that corresponds to normal vibrations of a molecule is not invariant with respect to operations, which do not belong to molecule's symmetry group [22]. The direct calculations carried out in this paper support the second provision. The contradiction between the first and second provisions can be resolved in view of the comment on the vibrational angular momentum, according to which "this momentum ... does not conserve" [22]. Indeed, for the Lagrange function corresponding to the vibrations of a polyatomic molecule, the inequality $\frac{\partial L}{\partial \varphi} \neq 0$ holds, which results in that the vibrational angular momentum is not conserved.

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ВПЛИВ ДЕФОРМАЦІЇ МОЛЕКУЛИ NH₃
НА ДЕВІАЦІЮ ХІМІЧНОГО ЗВ'ЯЗКУ N–H

Р е з ю м е

Отримана додаткова інформація про силову матриці молекули аміаку під час дослідження впливу деформації молекули на девіацію хімічного зв'язку. Оцінено константи пружності центральних сил, що діють між хімічно незв'язаними атомами водню, якими зазвичай нехтують в моделі валентно-силового поля. Деформація молекули супроводжується появою асиметричності в петлі девіації, зміною кутів девіації та зміщенням положення рівноваги інших атомів. Встановлено, що поворот молекули при збереженні її геометричних параметрів приводить до зміни силової матриці. Шпур силової матриці і її власні значення при цьому не змінюються.

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ВЛИЯНИЕ ДЕФОРМАЦИИ МОЛЕКУЛЫ NH₃
НА ДЕВИАЦИЮ ХИМИЧЕСКОЙ СВЯЗИ N–H

Р е з ю м е

Получена дополнительная информация о силовой матрице молекулы аммиака при исследовании влияния деформации молекулы на девиацию химической связи. Оценены константы упругости центральных сил, действующих между химически несвязанными атомами водорода, которыми обычно пренебрегают в модели валентно-силового поля. Деформация молекулы сопровождается появлением асимметричности в петле девиации, изменением углов девиации и смещением положения равновесия остальных атомов. Установлено, что поворот молекулы при сохранении ее геометрических параметров приводит к изменению силовой матрицы. Шпур силовой матрицы и ее собственные значения при этом не изменяются.