Functional Materials 11, No.1 (2004)

Chemical bonds deviation in NH_3, PH_3, AsH_3, and SbH_3 molecules

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Force matrices for PH_3, AsH_3 and SbH_3 molecules have been computed. Approximation for two anharmonic parameters separately for stretching and bending vibrations is used. Form parameters for the investigated molecules are obtained. X–H bond deviation angles are calculated to be 3.9°, 5.3°, and 5.4°, respectively. Negative values for anharmonic parameters are obtained in some cases. This may be caused by deflection of potential energy curve from parabola toward the dependence of higher degree.

Рассчитаны силовые матрицы молекул PH_3, AsH_3, SbH_3. Использована аппроксимация с двумя параметрами ангармонизма, отдельно для валентных и деформационных колебаний. Для исследованных молекул получены параметры форм колебаний. Углы девиации X–H связей равны соответственно 3,9°, 5,3°, 5,4°. В некоторых случаях получены отрицательные значения для ангармонических параметров, что может быть обусловлено отклонением зависимости потенциальной энергии от параболической в сторону более высокой степенной зависимости.

In previous works [1, 2], a method was designed for solving the inverse spectral problem of vibrational spectroscopy for NH_3 molecule. In those papers, the form parameters, effective atomic charges and dipole moment for NH_3 molecule have been obtained. This method referred to as the method of $3N$ matrix one [3] has an advantage as compared to other computing methods, that is, the independence of the force field models. As to NH_3 molecule, the method, first of all, was used for harmonic frequencies [1]. In this way, a force field model that was used to obtain this frequencies, was implicitly included into final results. The next step was to develop a method for experimental frequencies. This was done by introducing the anharmonic parameters as additional ones (to the form parameters) of the method [2]. The influence of frequency doubling was also analyzed. Just for NH_3 molecule, the inversion doubling is the highest. It was stated that for more massive molecule, better calculated results can be obtained. For this reason, the inversion doubling is not actual for the chosen molecules because of their heavy masses.

The main task in the inverse spectral problem is to construct the form matrix containing information on vibration forms (on atomic displacements at each vibration). In this work, a new way of constructing the basic form matrix is presented: the forms of degenerated vibrations are not stated but calculated. In such a way, a reduced number of parameters and degeneration is taken into account automatically. The method is used to obtain force matrixes and, then, chemical bonds deviation angles [1,2] in the series of molecules NH_3, PH_3, AsH_3, SbH_3. This makes it possible to study comparatively the molecular parameters. The presented method is designed for XH_3 molecules (X means N, P, As, Sb) but it can be used for any molecule or complex of the XY_3 chemical structure and C_{3v} symmetry.

In the harmonic approximation, the inverse spectral problem of vibrational spectroscopy gives as a final result the force matrix of the investigated system [3]:

$$V = ML\omega^2 L^T M. \qquad (1)$$

In (1), all multipliers are the $3N \times 3N$ matrices where N is the number of elements in the system (atoms in the molecule). This feature is reflected in the method name — the method of $3N$ matrices [1-3]. In this work, only molecules are investigated, so all explanations will be referred to molecules as systems and atoms as their elements. For short, let X mean one of N, P, As, Sb.

M is a diagonal matrix of atomic masses:

$$M = \mathrm{diag}\{m_X, m_X, m_X, m_H, m_H, m_H, m_H, m_H, m_H, m_H, m_H, m_H, m_H\}, \quad (2)$$

where m_X is the X atom mass, m_H is the H atom mass. ω^2 is a diagonal matrix of squared frequencies of molecule vibrations:

$$\omega^2 = \mathrm{diag}\{\omega_1^2, \omega_2^2, \omega_3^2, \omega_3^2, \omega_4^2, \omega_4^2, \omega_{tx}^2, \omega_{ty}^2, \omega_{tz}^2, \omega_{rx}^2, \omega_{ry}^2, \omega_{rz}^2\}. \quad (3)$$

In general, an XH_3 molecule has 12 vibrations which squared frequencies form the ω^2 matrix: $\omega_{1,2}$ is a full-symmetric eigenvibrations, $\omega_{3,4}$ is a twice-degenerated eigenvibration (due to degenerations, these frequencies are included in ω^2 twice), $\omega_{tx,\ ty,\ tz}$ are the frequencies of translations along X, Y and Z axis, respectively, $\omega_{rx,\ ry,\ rz}$ are the frequencies of rotations (librations) about X, Y and Z axis respectively. The last six vibrations (translations and librations) are non-eigen ones that are caused by environment. Including into calculations the frequencies of non-eigen vibrations makes it possible to analyze influence of environment, for example, lattice field or effective field in liquids. Frequencies of non-eigen vibrations are equal to zero for molecules in gaseous phase, where they are considered to be free.

The form matrix L defines the displacements of atoms for all vibrations. Non-eigen vibration forms should be included in this matrix even for free molecules. The L matrix is defined uniquely only if each irreducible representation of symmetry group corresponds to the only one eigenvibration. Such a situation is possible for molecules containing small number of atoms. The above-mentioned molecules exhibit character of vibrations $\chi_{vib} = 2A + 2E$, where A and E — irreducible representations of C_{3v} symmetry group. So, vibration forms cannot be defined exactly. Forms that correspond to one representation can be "mixed", i.e., any linear combination of forms corresponds to the same irreducible representation, too. Due to this fact, the matrix of basic forms L_0 is constructed. Vibration forms in this matrix are built taking into account consideration of symmetry. The form parameters [1-3] ψ_{ij} are introduced to the "mixed" i and j vibration forms to define the real forms of vibrations:

$$\begin{pmatrix} \mathbf{L}_i \\ \mathbf{L}_j \end{pmatrix} = \begin{pmatrix} \cos\psi_{ij} & \sin\psi_{ij} \\ -\sin_{ij} & \cos_{ij} \end{pmatrix} \begin{pmatrix} \mathbf{L}_{0i} \\ \mathbf{L}_{0j} \end{pmatrix}. \quad (4)$$

In (4), $\mathbf{L}_i$ and $\mathbf{L}_{0i}$ are the vectors of real and basic forms that correspond to one representation of symmetry group; mathematically, they are the i-th columns of L and L_0 matrixes. In previous works [1, 2], degeneration of vibrations was taken into account by additional form parameter which made the degenerated forms "mixed". Actually, this parameter was introduced to equalize the frequencies of degenerated vibrations. Due to condition of form orthogonality and vibration degeneration, the "mixed" pair of degenerated forms defines other pair uniquely. This makes it possible to reduce the number of form parameters. If we have one form of degenerated vibration $\mathbf{L}$, we construct two forms $\mathbf{L}_{1,2}$ that correspond to the molecule rotated on angles $\varphi = 120°$ (by multiplying with the C_φ matrix):

$$c_\varphi = \begin{bmatrix}
\cos\varphi & \sin\varphi & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-\sin\varphi & \cos\varphi & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \cos\varphi & \sin\varphi & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\sin\varphi & \cos\varphi & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cos\varphi & \sin\varphi & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\sin\varphi & \cos\varphi & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & \cos\varphi & \sin\varphi & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -\sin\varphi & \cos\varphi & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}, \quad (5)$$

and $\varphi = -120°$ (by multiplying with the C_φ^{-1} matrix):

$$\mathbf{L}_1 = C_\varphi \mathbf{L}, \quad \mathbf{L}_2 = C_\varphi^{-1} \mathbf{L}. \quad (6)$$

Then we define the second form $\mathbf{L}'$ as normalized substitution for two obtained forms:

$$\mathbf{L}' = \frac{\mathbf{L}_1 - \mathbf{L}_2}{\left(2(1 - \tilde{\mathbf{L}} M C_\varphi \mathbf{L})\right)^{1/2}}. \quad (7)$$

In (6) and (7), C_φ is the matrix of molecule rotation (5) which includes removal of atoms and change of coordinate axis direction.

The matrix L_0 has the form:

$$L_0 = \begin{bmatrix} 0 & 0 & 0 & -t_A & -g & 0 & 0 & 0 & \frac{e}{\delta} & 0 \\ 0 & 0 & 0 & -0 & -0 & g & 0 & -\frac{e}{\delta} & 0 & 0 \\ a & 0 & 0 & -0 & -0 & 0 & g & 0 & 0 & 0 \\ 0 & 0 & 0 & -t_B & -g & 0 & 0 & 0 & -\frac{d}{\delta} & -c \\ 0 & c & c & -0 & -0 & g & 0 & \frac{d}{\delta} & 0 & 0 \\ -b & 0 & 0 & -0 & -0 & 0 & g & \frac{2l}{\delta} & 0 & 0 \\ 0 & c\frac{\sqrt{3}}{2} & -c\frac{\sqrt{3}}{2} & -t_B & -g & 0 & 0 & 0 & -\frac{d}{\delta} & \frac{c}{2} \\ 0 & -\frac{c}{2} & -\frac{c}{2} & -0 & -0 & g & 0 & \frac{d}{\delta} & 0 & c\frac{\sqrt{3}}{2} \\ -b & 0 & 0 & -w & -0 & 0 & g & -\frac{l}{\delta} & -l\frac{\sqrt{3}}{\delta} & 0 \\ 0 & -c\frac{\sqrt{3}}{2} & c\frac{\sqrt{3}}{2} & -t_B & -g & 0 & 0 & 0 & -\frac{d}{\delta} & \frac{c}{2} \\ 0 & -\frac{c}{2} & -\frac{c}{2} & -0 & -0 & g & 0 & \frac{d}{\delta} & 0 & -c\frac{\sqrt{3}}{2} \\ -b & 0 & 0 & --w & -0 & 0 & g & -\frac{l}{\delta} & l\frac{\sqrt{3}}{\delta} & 0 \end{bmatrix}, \quad (8)$$

where

$$a = \frac{\sqrt{3m_{\mathrm{H}}}}{m_{\mathrm{X}}M},\ b = \frac{\sqrt{m_{\mathrm{X}}}}{3m_{\mathrm{H}}M},\quad c = \frac{1}{\sqrt{3m_{\mathrm{H}}}},\quad g = \frac{1}{\sqrt{M}},$$

$M = m_{\mathrm{X}} + 3m_{\mathrm{H}}$, $\beta = \arcsin\left(\frac{2\sin\frac{\alpha}{2}}{\sqrt{3}}\right)$, α is an angle between two X–H bonds

$$t_A = \frac{1}{\sqrt{m_{\mathrm{X}}(1 + \frac{m_{\mathrm{X}}}{3m_{\mathrm{H}}}\frac{1+\cos^2\beta}{\sin^2\beta})}} \quad (9)$$

$$t_B = -\frac{m_{\mathrm{X}}}{3m_{\mathrm{H}}}t_A,\quad w = \frac{m_{\mathrm{X}}\mathrm{ctg}\beta}{m_{\mathrm{H}}\sqrt{3}}t_A,$$

$$d = \frac{m_{\mathrm{X}}\cos\beta}{M},\ e = \cos\beta - d,\ l = \frac{\sin\frac{\alpha}{2}}{\sqrt{3}} = \frac{\sin\beta}{2},$$

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

In the L_0 matrix (8), each column is responsible for one possible vibration form. These forms could not be realized for real vibrations but they create the orthogonal basis in which any vibration could be represented as a combination of basic forms. Such decomposition in basic forms and the form mixing (4) are not the same: any molecular motion can be represented as combination of every basic forms. A vibration with definite frequency ω only can be represented as a combination of forms that corresponds to one irreducible representation of symmetry group.

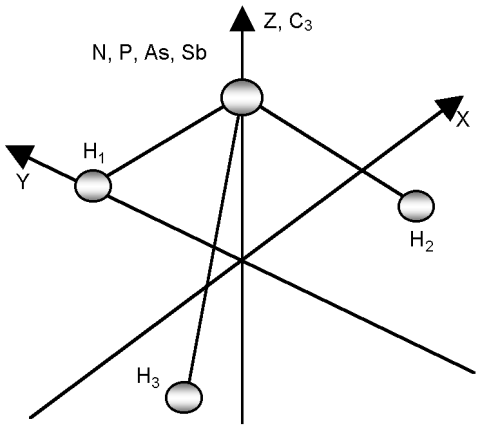

Fig. 1. Coordinate system of molecule and atoms sequence.

In the first and second columns of the matrix (8), the basic forms of two full-symmetric vibrations (ω_1 and ω_2) are located. To "mix" them, one should introduce the form parameter from (4) ψ_{12} ($i = 1$, $j = 2$). The 3-th and 5-th columns correspond to the vibrations with frequencies ω_3 and ω_4. To "mix" those, ψ_{35} is used. The 4-th and 6-th columns are defined by the 3-th and 5-th columns after their mixing in accordance with (6, 7).

To construct the form matrices (L and L_0) and vectors of atomic displacement, it is necessary to define, first, the coordinate system of molecule and, second, sequence of the atoms (the order of their appearance in matrices or vectors).

The coordinate system of the molecule [1, 2] is as follows: Z coincides with C^3 and passes through the central atom (N, P, As, or Sb), Y passes through one of H atoms (Fig. 1).

The sequence of atoms is: 1) the central atom (N, P, As or Sb); 2) H_1 (at $x = 0$); 3) H_2 ($x > 0$); 4) H_3 ($x < 0$).

Being designed in harmonic approximation, the method of $3N$ matrices requires to include harmonic frequencies into (3). To obtain harmonic frequencies from experimental ones, anharmonic parameters are used. In general, the harmonic frequency ω_0 is defined from experimental frequency ω as

$$\omega_0 = \omega \cdot (1 + u \cdot \omega). \quad (10)$$

The anharmonic parameter u is a characteristic of vibration. Thus, each vibration should have the proper anharmonic parameter. But vibrations that occur in the same conditions should have the same parameter

u. In approximation that all stretching vibrations have the same potential energy and their frequencies are close to each other, all the stretching vibrations are believed to have the same anharmonic parameter u_1. The bending vibrations have u_2 parameter, by the same reasons.

$$\omega_{01} = \omega_1 \cdot (1 + u_1 \cdot \omega_1), \quad (11)$$
$$\omega_{03} = \omega_3 \cdot (1 + u_1 \cdot \omega_3),$$
$$\omega_{02} = \omega_2 \cdot (1 + u_2 \cdot \omega_2),$$
$$\omega_{04} = \omega_4 \cdot (1 + u_2 \cdot \omega_4).$$

The parameters u_1 and u_2 are entered as mathematical parameters of method to avoid the dependence from force field model. Thereby, the force matrix (1) is a four-parametric set

$$V = V(\psi_{12},\psi_{35},u_1,u_2). \quad (12)$$

Determination of these parameters requires additional information. In this work, such information on vibrational frequencies of isotopic modifications of the investigated molecules is used. The frequencies of the XD_3 molecule vibrations are calculated making use of the obtained force matrix V (1, 12) for the XH_3 molecule. The frequencies are compared with their experimental values. Harmonic frequencies of the XD_3 molecule are calculated using

$$\left\{\omega_0^2\right\}^{theor} = eigenvalues(M_{isot}^{-1}V). \quad (13)$$

Here M_{isot} is a diagonal matrix of masses of the XD_3 molecule. The harmonic frequencies ω_0^{exper} are calculated from (11) using the experimental frequencies of the XD_3 molecule. As a characteristic of difference between ω_i^{theor} and ω_i^{exper} the parameter δ is used:

$$\delta = \sum_i \left(1 - \frac{\omega_i^{theor}}{\omega_i^{exper}}\right)^2. \quad (14)$$

It is obvious that δ, like V, is a four-parametrical set $\delta = \delta(\psi_{12},\psi_{35},u_1,u_2)$. The values of these parameters can be obtained from the condition of minimum δ.

From the obtained parameters and force matrix, the X–H chemical bond deviation angle is computed. When one H atom is shifted out of the equilibrium position, the molecule obtains an excess energy. To find out the deviation for X–H bond, we can consider the shift of the H_1 for the distance r at the angle φ to Y axis in (ZY) plane. The vector of such displacement is:

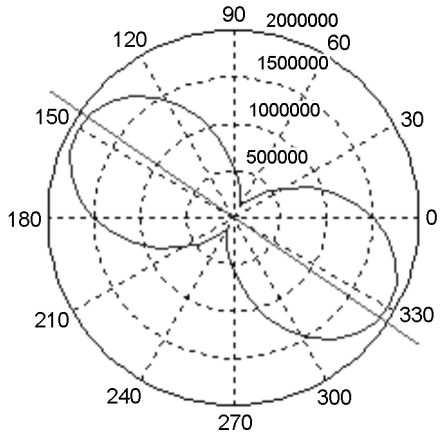

Fig. 2. Polar diagram of molecular extra energy $U(\varphi)$.

$$\mathbf{x}(\varphi) = (0\ 0\ 0\ 0\ r\cos\varphi\ r\sin\varphi\ 0\ \ 0\ 0\ 0\ 0\ 0). \quad (15)$$

The excess energy of molecule with shifted atom is described as

$$U(\varphi) = \frac{\mathbf{x}(\varphi) \cdot V \cdot \tilde{\mathbf{x}}(\varphi)}{2}. \quad (16)$$

$U(\varphi)$ for SbH_3 is plotted in polar scale in Fig. 2 as 8-like curve. Straight line corresponds to the dependence $\varphi = \alpha$. It shows the direction of the line that connects Sb and H nuclei in (ZY) plane. The angle φ_0 that maximizes $U(\varphi)$ defines the chemical bond angle. It is seen from Fig. 2 that maximum of $U(\varphi)$ does not lie in the $\varphi = \alpha$ line. This phenomenon is called "the chemical bond deviation" [1, 2]. The difference Δ between ${\varphi_0}^0$ and α ($\Delta = \varphi_0 - \alpha$) is called "the chemical bond deviation angle".

In calculations, the parameters of XH_3 and XD_3 molecules (X means P, As, Sb) from Table 1 were used [4–8]. The calculated results are summarized in Tables 2 and 3. Molecule NH_3 and N–H bond deviation were examined before [2], and main results are presented in Table 2. The method for the NH_3 molecule was provided with 3 form parameters for other basis L_0, that is why in Table 2 only the ψ_{12} value is shown which is the same in both methods for NH_3.

Chemical bond deviation results from existence of central force field. In valence force approximation, the deviation is principally impossible: the extra energy U(16) reaches maximum when H atom is shifted along the straight line connecting X and H nuclei. So the deviation angle can be a

Table 1. Vibration frequencies (ω,, cm^{-1}) and H–X–H angles (α) of molecules

Molecule	ω_1	ω_2	ω_3	ω_4	α, °	Ref.
PH_3	2448	1045	2390	1153	93.5	5
PD_3	1760	759	1720	822		
AsH_3	2209	973	2225	1012	91.6	5
AsD_3	1571	696	1582	719		
SbH_3	1988.9	795.9	1974.5	844.7	91.5	4
SbD_3	1409.4	568.5	1403.5	599.5		

Table 2. Parameters of molecules: form parameters ψ, anharmonic parameters $u \cdot 10^6$, X–H bond deviation angle Δ

Molecule	ψ_{12}	ψ_{35}	u_1	u_2	Δ, °	α, °
NH_3[1]	1.06	–	8.0	8.7	3	106.7
PH_3	0.96	2.24	2.6	−4.7	3.9	93.5
AsH_3	1.02	2.42	0.66	−5.8	5.3	91.6
SbH_3	1.16	2.19	0.67	3.0	5.4	91.5

Table 3. Harmonic vibration frequencies (ω_0, cm^{-1}) of molecules

Molecule	ω_{01}	ω02	ω03	ω04
PH_3	2463.78	1039.91	2405.04	1146.81
PD_3	1768.16	756.32	1727.79	818.85
AsH_3	2213.82	966.84	2229.89	1005.34
AsD_3	1573.44	692.85	1584.47	715.64
SbH_3	1991.56	797.81	1977.12	846.85
SbD_3	1410.73	569.48	1404.82	600.59

measure of H–H interaction. It is obvious that H–H interaction is stronger as H–X–H angle is smaller.

Thus, the smaller H–X–H angle α is, the larger is the X–H bond deviation angle Δ. Negative values of anharmonic parameters are obtained in some cases. In current calculations, anharmonic parameters are responsible for changing atomic masses in (13). Usually, they are responsible for decreasing overtone frequencies. This means that classical meaning of anharmonic parameter is connected with the form of potential energy curve at high vibrational levels. The parameters $u_{1,2}$ in present calculations are responsible for its form at ground vibrational level. Simple modeling shows that for rectangular potential well, the anharmonic parameter entered from (10) is negative, while for parabolic well, ($U(x) \sim x^2$) $u = 0$. In general, for the dependence $U(x) \sim x^\beta$, one can obtain that when $\beta < 2$, $u > 0$; for $\beta > 2$, $u < 0$; for $\beta = 2$, $u = 0$. For PH_3 and AsH_3 molecules, the potential energy curve at the ground level of the bending vibration has a form steeper than parabola.

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Девіація хімічного зв'язку в молекулах NH_3, PH_3, AsH_3, SbH_3

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Розраховано силові матриці молекул PH_3, AsH_3, SbH_3. Використано апроксимацію з двома параметрами ангармонізму, окремо для валентних і деформаційних коливань. Для досліджених молекул отримано параметри форм коливань. Кути девіації X–H зв'язків дорівнюють відповідно 3,9°, 5,3°, 5,4°. У деяких випадках отримано від'ємні значення для ангармонічних параметрів, що може бути обумовлено відхиленням залежності потенціальної енергії від параболічної у бік більш високої степеневої залежності.