Isotopic substitution theory for molecules meeting the local mode approximation

G.A. Onopenko

Tomsk State University

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Some nontrivial results allowing the molecular and/or spectroscopic parameters of isotopic modifications of different-type polyatomic molecules to be related are reviewed. The results were obtained based on compilation of the extended local mode approach and the general theory of isotopic substitution.

The information about the isotopic dependence of spectroscopic and molecular parameters of polyatomic molecules is of particular importance for solution of numerous practical problems in high-resolution rotational-vibrational spectroscopy. The need in establishing isotopic relations between spectroscopic parameters was noted by many authors (see, for example, Refs. 1, 2 and bibliography therein), because such relations would allow one to predict the structure of excited states for isotopic modifications of different molecules, to analyze their weak, still unstudied bands, and so on. This paper is devoted to the theory of isotopic substitution developed for XH_2 and XH_3 molecules, in particular, of H_2O, H_2S, PH_3, and others that are of interest for atmospheric optics.

It should be noted that the general isotopic substitution theory developed earlier[3] works well only in the case of substitution of heavy nuclei such that $|(m'_N - m_N)/m_N| \ll 1$ or the substitutions of light nuclei that do not change the symmetry of a molecule. In the case that, for example, hydrogen nuclei are substituted or the molecular symmetry changes, the results given by this theory are either too cumbersome or hard-to-obtain. At the same time, the efficient spectroscopic methods dealing just with molecules including light nuclei are the local mode method developed in the mid-80s and its modification – the extended local mode method.[4–9] In this paper, the extended local mode approximation means the study of molecules meeting the following three conditions:

1) the atomic mass ratio m_H/M_X is small;

2) the equilibrium angle between the bonds X–H–X is close to $\pi/2$;

3) the interaction of stretching vibrations with bending ones is neglected in the potential function (the parameter $f_{r\alpha}$ is small).

It is an important circumstance that the knowledge of molecular constants is a key point in both the general isotopic substitution theory[3] and in the extended local mode method.[4–9] Consequently, the possibility of obtaining these constants within the framework of the local mode approximation in a simple form for the main isotopic modification allows one to hope for the possibility of their determination in a simple form for other isotopic modifications as well.

Thus, to find the relationships between spectroscopic constants of isotopically substituted molecules, we should remember the conditions, the molecular constants $l_{N\alpha\lambda}$ (and, consequently, ambiguity parameters $\sin\gamma_i$) should meet[10]:

Eckart conditions

$$\sum_N m_N^{1/2} l_{N\alpha\lambda} = 0, \qquad (1)$$

$$\sum_N m_N^{1/2} (l_{N\alpha\lambda} r^e_{N\beta} - l_{N\beta\lambda} r^e_{N\alpha}) = 0, \qquad (2)$$

normalization conditions

$$\sum_{N\alpha} l_{N\alpha\lambda}\, l_{N\alpha\mu} = \delta_{\lambda\mu}, \ \lambda \neq \mu \qquad (3)$$

conditions for second derivatives of the potential function with respect to normal coordinates

$$W_{\lambda\mu} \equiv (\partial^2 V / \partial q_\lambda \partial q_\mu) = 0, \ \lambda \neq \mu. \qquad (4)$$

It should be noted that the number of constants $l_{N\alpha\lambda}$ is equal to the number of equations (1)–(4), from which they can be determined. However, in practice the symmetry properties of a molecule are usually used in place of Eqs. (4). These properties give the relationships between the $l_{N\alpha\lambda}$ parameters, which are then used in Eqs. (1)–(3). The left-hand sides of the Eqs. (4), in this case, are identically equal to zero, and the total number of non-zero equation (4) determines the corresponding number of the $l_{N\alpha\lambda}$ constants, which are declared to be the empirical parameters $\sin\gamma_i$, through which all other $l_{N\alpha\lambda}$ constants are expressed.

Summarizing the above-said, it can be mentioned that the problem on the properties of the ambiguity parameters $\sin\gamma_i$ should be solved through analytical solution of Eqs. (4). In the simplest situations (XH_2 molecules of C_{2v} symmetry and XH_3 molecules of C_{3v} symmetry), investigations into this field are described in Refs. 7–9. Under conditions meeting the local mode

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approximation, simple results were obtained for the ambiguity parameters of the considered molecules:

(a) for XH_2 molecules of C_{2v} symmetry

$$\sin^2\gamma = 1,\ \gamma = \pm\left(\frac{\pi}{4} + n\frac{\pi}{2}\right),\ \text{where } n = 0, \pm1, \pm2, \ldots, \quad (5)$$

(b) for XH_3 molecules of C_{3v} symmetry

$$\sqrt{2}\cos\gamma = \sin\gamma \quad \text{or} \quad \sqrt{2}\sin\gamma = -\cos\gamma, \quad (6)$$

$$\sqrt{2}\sin\delta = 4\cos\delta \quad \text{or} \quad \sqrt{2}\cos\delta = -4\sin\delta. \quad (7)$$

Based on this, extremely simple relationships between $l_{N\alpha\lambda}$ were found. In particular, for the XH_2 (C_{2v}) molecule it was obtained[7] that

$$l_{2z1} = -l_{3z1} = -l_{2x1} = -l_{3x1} = l_{2z2} = -l_{3z2} = l_{2x2} = l_{3x2} = -l_{2z3} = -l_{3z3} = l_{2z3} = -l_{3x3} = 1/2, \quad (8)$$

$$l_{Ny\lambda} = 0 \text{ and } l_{1\alpha\lambda} = 0. \quad (9)$$

The above reasoning, it its turn, gives a lot of earlier unknown information, for example, about numerous relationships between different molecular and/or spectroscopic parameters for some types of molecules meeting the conditions of the local mode method.[8,9] The above approach was used for further development of the extended local mode method, namely, for the development of the theory of isotopic substitution in molecules including hydrogen atoms and meeting the local mode approximation.

As was emphasized above, the general results of the extended local mode method can be easily obtained based on analysis of the $l_{N\alpha\lambda}$ constants. Consequently, in studying properties of isotopomers, we should first determine the corresponding parameters of the substituted molecule. As was shown in Ref. 3, in the general case the $l_{K\gamma\lambda}$ constants of the substituted molecule can be presented in the form

$$l'_{K\gamma\lambda} = \sum_{\alpha\mu} K^e_{\alpha\gamma}\left(\frac{m_N}{m'_N}\right)^{1/2} l_{K\alpha\mu}\,\beta_{\lambda\mu}. \quad (10)$$

The indices N, K, L here denote the atoms of a molecule; the primed parameters correspond to the substituted molecule; the indices α, β, γ, δ denote x, y or z components of a vector parameter; λ, μ, ν number the normal vibrational coordinates; m_N and m'_N are, respectively, the nuclei mass of the initial and substituted molecules. The parameters $K^e_{\alpha\gamma}$ (the superscript «e» corresponds to the equilibrium nuclei configuration) are elements of the matrix determining rotation of the molecular coordinate system at transition from the initial modification to the isotopically substituted one. The parameters $\beta_{\lambda\mu}$ are the elements of the matrix inverse to the matrix $\{\alpha_{\lambda\mu}\}$, with the latter determining the transition from the normal coordinates of the initial molecule to the substituted molecule. The matrix elements $\alpha_{\lambda\mu}$ are determined by the equations[3]:

$$\sum_{\nu}\alpha_{\lambda\nu}\,\alpha_{\mu\nu} = A_{\lambda\mu} = \sum_{N\alpha}\left(\frac{m_N}{m'_N}\right) l_{N\alpha\lambda}\,l_{N\alpha\mu},$$
$$\sum_{\nu} A_{\lambda\nu}W_{\nu}\alpha_{\nu\mu} = \alpha_{\lambda\mu}W'_{\mu}, \quad (11)$$

leading to the secular equation $\det(AW - W') = 0$, where A is the matrix with the elements $A_{\lambda\nu}$; W and W' are the diagonal matrices with the elements $W_{\lambda\nu} = \omega^2_{\lambda}\,\delta_{\lambda\nu}$ and $W'_{\lambda\nu} = \omega'^2_{\lambda}\,\delta_{\lambda\nu}$, correspondingly; ω_{λ} and ω'_{λ} are the harmonic frequencies of the initial and isotopically substituted configurations. The parameters $K^e_{\alpha\gamma}$ are determined from the conditions

$$\sum_{\alpha} K^e_{\alpha\beta}\,K^e_{\alpha\gamma} = \sum_{\alpha} K^e_{\beta\alpha}\,K^e_{\gamma\alpha} = \delta_{\beta\gamma}, \quad (12)$$

$$\sum_{\beta} J^e_{\alpha\beta}\,K^e_{\beta\gamma} = I'^e_{\gamma\gamma}\,K^e_{\alpha\gamma}, \quad (13)$$

where $I'^e_{\gamma\gamma}$ are equilibrium moments of inertia of the isotopically substituted molecule, and $J^e_{\alpha\beta}$ are determined by the equations:

$$J^e_{\alpha\beta} = \sum_{\gamma\delta\chi}\varepsilon_{\alpha\gamma\chi}\,\varepsilon_{\beta\delta\chi}\,j^e_{\gamma\delta},$$
$$j^e_{\gamma\delta} = j^e_{\delta\gamma} = \sum_{N} m'_N r^e_{N\gamma} r^e_{N\delta} - \sum_{K} m'_K r^e_{K\gamma}\sum_{L} m'_L r^e_{L\delta} \Big/ \sum_{N} m'_N. \quad (14)$$

Here $r^e_{N\alpha}$ are the Cartesian coordinates determining the equilibrium configuration of the initial molecule in the molecular coordinate system. It is seen that $K^e_{\alpha\gamma}$ can also be considered as eigenvectors of the inertia tensor $J^e_{\alpha\beta}$ with the eigenvalues $I'^e_{\gamma\gamma}$.

For further analysis, it is important to know the isotopic relationships between the anharmonic parameters[3]:

$$k'_{\lambda'\mu'\nu'} = \sum_{\lambda\le\mu\le\nu}\sum_{(\lambda',\mu',\nu')}\left(\frac{\omega_{\lambda}\omega_{\mu}\omega_{\nu}}{\omega'_{\lambda}\omega'_{\mu}\omega'_{\nu}}\right)^{1/2} \times k_{\lambda\mu\nu}\alpha_{\lambda\lambda'}\alpha_{\mu\mu'}\alpha_{\nu\nu'} + \left(\frac{\hbar}{2\pi c}\right)^{1/2}\sum_{i}\sum_{(\lambda',\mu'\nu')}\frac{\omega_i^2}{(\omega'_{\lambda}\omega'_{\mu}\omega'_{\nu})^{1/2}}\alpha_{i\lambda'}\alpha^{i}_{\mu'\nu'}. \quad (15)$$

All parameters of Eq. (15), except for $\alpha^{i}_{\mu'\nu'}$, are defined above, the $k_{\lambda\ldots\mu}$ parameters are anharmonic force constants corresponding to the dimensionless normal coordinates. The parameters $\alpha^{i}_{\mu'\nu'}$ are also known, but they are expressed through much complicated functions of molecular parameters, which are omitted here (the corresponding equations can be found in Refs. 2 and 3). The signs $\sum_{\lambda',\mu',\nu'}$ and $\sum_{\lambda',\mu'\nu'}$ denote summation over all

permutations of different indices from the set λ′ μ′ ν′ (in this case the condition $\mu' \le \nu'$ is fulfilled for the indices not separated by comma).

The $XH_2 \to XHD$ isotopic substitution

Consider now the derivation of isotopic relations between different parameters of molecules in the case of $XH_2 \to XHD$ isotopic substitution. As was noted above, the first step in the investigation of substituted molecules is determination of the $l'_{N\alpha\lambda}$ constants. Unlike the initial molecule, the most important task for which was to determine the ambiguity parameter $\sin\gamma_i$, in the case of the isotopically substituted molecule there is no need in such analysis (which is a rather complicated problem), because Eq. (10) allows the $l'_{N\alpha\lambda}$ constants of the isotopically substituted molecule to be obtained directly from the already known $l_{N\alpha\lambda}$ constants of the main modification. In the case of a plane XH_2 molecule of C_{2v} symmetry for both the rigorous and extended local mode approximation, the sought constants have quite a simple form given by Eqs. (8) and (9).

To use Eq. (10), we should also know the coefficients $\beta_{\lambda\mu}$, but for their determination, we should first solve the system of equations (11), that is, determine the harmonic frequencies ω'_λ of the substituted molecule, as well as the coefficients $\alpha_{\lambda\mu}$ from the harmonic frequencies and the $l_{N\alpha\lambda}$ constants of the main modification. Within the framework of the local mode model, the harmonic frequencies ω_1 and ω_3 of the main molecule meet the following equality $\omega_1 = \omega_3 \equiv \omega$ (Ref. 7). Assume also that the atom H substituted by D has the number 2 (that is, $m'_1 = M$; $m'_2 = 2m$; $m'_3 = m$; $M \equiv M_X$, $m \equiv m_H$). Solution of Eq. (11) gives the following results:

$$\omega'_1 = \frac{1}{\sqrt{2}}\,\omega, \quad \omega'_2 = \frac{\sqrt{3}}{2}\,\omega_2, \quad \omega'_3 = \omega \tag{16}$$

for the harmonic frequencies and

$$\alpha_{11} = -\alpha_{31} = \pm\frac{1}{2}, \quad \alpha_{33} = \alpha_{13} = \pm\frac{1}{\sqrt{2}},$$
$$\alpha_{12} = \alpha_{21} = \alpha_{23} = \alpha_{32} = 0, \quad \alpha_{22} = \pm\frac{\sqrt{3}}{2} \tag{17}$$

for the matrix $\{\alpha_{\lambda\mu}\}$. The coefficients $\beta_{\lambda\mu}$ can be determined as

$$\beta_{11} = -\beta_{13} = \pm 1, \quad \beta_{33} = \beta_{31} = \pm\frac{1}{\sqrt{2}},$$
$$\beta_{12} = \beta_{21} = \beta_{23} = \beta_{32} = 0, \quad \beta_{22} = \pm\frac{2}{\sqrt{3}}. \tag{18}$$

As to $K^e_{\alpha\beta}$ obtained from solution of Eqs. (12)–(14), it can be easily shown that, because of the symmetry properties of the molecule considered, the matrix $\{K^e_{\alpha\beta}\}$ has the form

$$\begin{pmatrix} \cos\chi & 0 & \sin\chi \\ 0 & 1 & 0 \\ -\sin\chi & 0 & \cos\chi \end{pmatrix}, \tag{19}$$

where $\cot 2\chi = -4m/M$. It should be noted that, in spite of the presence of the factor 4 in the equation for $\cot 2\chi$, the angle 2χ is close to $-\pi/2$, if the condition $m/M \ll 1$ is fulfilled. Thus, we have the following nonzero elements of the matrix $\{K^e_{\alpha\beta}\}$:

$$K^e_{xx} = -K^e_{xz} = K^e_{zx} = K^e_{zz} = 1/\sqrt{2}; \quad K^e_{yy} = 1. \tag{20}$$

Under these conditions, solution of Eqs. (12) leads to the following equilibrium moments of the inertia for the substituted molecule:

$$I'^e_{xx} = 2I_e; \quad I'^e_{yy} = 3I_e; \quad I'^e_{zz} = I_e, \tag{21}$$

where $I^e = m\rho_e^2 = I^e_{zz} = I^e_{xx} = 1/2I^e_{yy}$ are the equilibrium moments of inertia for the initial molecule; ρ_e is the equilibrium bond length. Thus, we get the following relationships for the equilibrium rotational constants B'^e_α:

$$2B'^e_x = B_e; \; 3B'^e_y = B_e; \; 2B'^e_z = B_e. \tag{22}$$

Finally, after substituting Eqs. (8), (18), and (20) in Eq. (10), we obtain, for the $l'_{N\alpha\lambda}$ constants of the substituted molecule, that:

$$l'_{2z1} = -1, \quad l'_{3x3} = 1,$$
$$l'_{2x2} = -1/\sqrt{3}, \quad l'_{3z2} = \sqrt{2}/\sqrt{3}. \tag{23}$$

All other $l'_{N\alpha\lambda}$ constants are zero.

Knowledge of the $l'_{N\alpha\lambda}$ parameters allows us to derive simple equations for the Coriolis $\zeta'^{\alpha}_{\lambda\mu}$ and vibrational-rotational $a'^{\alpha\beta}_\lambda$ constants that determine different spectroscopic parameters. In particular, the equations for $\zeta'^{\alpha}_{\lambda\mu}$ in the general case have the form[2]

$$\zeta'^{\alpha}_{\lambda\mu} = \sum_{\beta\gamma} \varepsilon_{\alpha\beta\gamma} \sum_N l'_{N\beta\lambda} l'_{N\gamma\mu}, \tag{24}$$

but become extremely simple at substitution of Eqs. (23):

$$\zeta'^{y}_{12} = 1/\sqrt{3}, \quad \zeta'^{y}_{23} = \sqrt{2}/\sqrt{3}. \tag{25}$$

Similarly, substituting equations for the constants in the general equations for the vibrational-rotational parameters $a'^{\alpha\beta}_\lambda$ (Ref. 2):

$$a'^{\alpha\beta}_\lambda = 2\sum_{\gamma\delta\chi} \varepsilon_{\alpha\gamma\chi}\, \varepsilon_{\beta\delta\chi} \sum_N m'^{\,1/2}_N r'^e_{N\gamma}\, l'_{N\delta\lambda}, \tag{26}$$

we obtain quite simple results:

$$a_1'^{xx} = a_1'^{yy} = 2\sqrt{2}\, I_e^{1/2},\ \ a_2'^{xz} = a_2'^{zx} = -(2\sqrt{2}/\sqrt{3})\, I_e^{1/2},$$
$$a_3'^{yy} = a_3'^{zz} = 2\, I_e^{1/2}. \qquad (27)$$

Nonzero equilibrium atom coordinates $r'^e_{N\alpha}$ in the substituted molecule have the form

$$r'^e_{2z} = r'^e_{3x} = \rho_e, \qquad (28)$$

what follows from the isotopic relationships[3]

$$r'^e_{N\gamma} = \sum_\beta K^0_{\beta\gamma} \left\{ r^e_{N\beta} - \frac{\sum_K (m'_K - m_K) r^e_{K\beta}}{\sum_L m'_L} \right\}, \qquad (29)$$

where $r^e_{N\gamma}$ are the equilibrium atom coordinates of the initial molecule XH_2.

It is known that the parameters of the effective Hamiltonian can be expressed as functions of fundamental characteristics of the molecule. Since the latter are found with the use of the above isotopic relationships, it is not difficult to determine the spectroscopic constants for a substituted molecule as functions of the fundamental parameters of the basic molecule. Their following comparison with similar equations for the main modification and with each other yields various relationships between spectroscopic parameters of the main and substituted modifications.

Up to the terms of the order of κ^4 with respect to the vibrational energies, the effective rotational constants B'^v_β are determined by the equation[11]:

$$B'^v_\beta = B'^e_\beta - \sum_\lambda \alpha'^\beta_\lambda \left(v_\lambda + \frac{1}{2} \right), \qquad (30)$$

where v is a set of vibrational quantum numbers, and B'^e_β are determined above by Eq. (22).

The vibrational-rotational spectroscopic constants α'^β_λ can be obtained from the general equation for asymmetric-top molecules.[11] In the absence of resonances, the equation for α'^β_λ has the form

$$-\alpha^\beta_k = \frac{2(B^e_\beta)^2}{\omega_k} \left\{ \frac{3}{4} \sum_\gamma \frac{(a_k^{\beta\gamma})^2}{I^e_{\gamma\gamma}} + 6\pi \left(\frac{c}{h} \right)^{1/2} k_{kkk} a_l^{\beta\beta} \frac{1}{\omega_k^{1/2}} + \right.$$
$$\left. + 2\pi \left(\frac{c}{h} \right)^{1/2} \sum_l k_{kkl} a_l^{\beta\beta} \frac{\omega_k}{\omega_l^{3/2}} + \sum_l (\zeta^\beta_{kl})^2 \frac{3\omega_k^2 + \omega_l^2}{\omega_k^2 - \omega_l^2} \right\}. \qquad (31)$$

In the presence of Fermi resonance[11,12] between the vibrational states l and k ($\omega_l \approx 2\omega_k$), the corresponding term with k_{kkl} should be excluded from Eq. (31).

As a result, it becomes possible to determine the number of very simple, earlier unknown isotopic relations between the parameters α'^β_λ describing the interactions between vibration and rotation:

$$\alpha'^z_3 = \alpha^x_3 + \alpha^z_3;\ \ \alpha'^z_1 = \alpha'^x_3 = 0;\ \ \alpha'^x_1 = \frac{1}{2\sqrt{2}} (\alpha^x_1 + \alpha^z_1);$$

$$\frac{9\sqrt{2}}{8}\, \alpha'^y_1 = \alpha^y_1 - \frac{B_e^2}{\omega} \frac{2\theta^2}{2 - 3\theta^2};$$

$$\frac{9}{4}\, \alpha'^y_3 = \alpha^y_3 - \frac{B_e^2}{\omega} \left\{ \frac{4\theta^2}{4 - 3\theta^2} - \frac{2\theta^2}{1 - \theta^2} \right\};$$

$$\alpha'^x_2 = \frac{1}{12\sqrt{3}} \frac{7 - 3\theta^2}{2 - \theta^2} (\alpha^x_2 + \alpha^z_2); \qquad (32)$$

$$\alpha'^z_2 = \frac{1}{3\sqrt{3}} \frac{5 - 3\theta^2}{2 - \theta^2} (\alpha^x_2 + \alpha^z_2);$$

$$\alpha'^y_2 = \alpha^y_2 \frac{4}{9\sqrt{3}} \frac{1 - \theta^2}{(2 - 3\theta^2)(4 - 3\theta^2)} \times$$
$$\times \left\{ 9(3 - \theta^2) - \frac{41}{3 - \theta^2} \right\}.$$

In Eqs. (32), θ is the known parameter of the main isotopic modification of the molecule XH_2. On the one hand, the parameter θ can be calculated based on the ratio of harmonic frequencies ω and ω_2 (in this case, ω is taken as the average value of the frequencies ω_1 and ω_3, $\theta = \omega/\omega_2$). On the other hand, it can be considered as a semiempirical parameter determined from the centrifugal distortion constants.

The general equation for parameters α^β_λ, besides $a'^{\alpha\beta}_\lambda$, B'^e_β, ω'_λ, and ζ'^β_{kl}, includes also the cubic anharmonic constants $k'_{\lambda\mu\nu}$ connected with the corresponding parameters $k_{\lambda\mu\nu}$ (15) of the initial molecule XH_2. As to the latter, here we used a simpler model[7] in which only the constants k_{111}, k_{133}, and k_{122} of the initial molecule are nonzero. Based on this assumption, the nonzero $k'_{\lambda\mu\nu}$ parameters determined, in the general case, by Eq. (15) can be reduced to the following form:

$$k'_{111} = \frac{k_{111}}{\sqrt[4]{2}};\ k'_{333} = \sqrt{2}\, k_{111};$$

$$k'_{122} = \frac{\sqrt[4]{2}\sqrt{3}}{9} \frac{1 - 3\theta^2}{1 - 2\theta^2} k_{122};$$

$$k'_{322} = \frac{2\sqrt{6}}{9} \frac{2 - 3\theta^2}{1 - 2\theta^2} k_{122}. \qquad (33)$$

These equations were used in derivation of Eqs. (32). As was shown in Ref. 7, $k^2_{122} = (B^e\omega)^{1/2}/2\theta) \times (1 - 2\theta^2)$, and k_{111} remains a parameter determined from the vibrational-rotational constants $a^{\alpha\beta}_\lambda$ of the initial molecule.

The relationships (32), on the one hand, relate the α' parameters of the XHD molecule to each other and, on the other hand, they show how the α parameters of the initial XH_2 molecule are connected with those of

the XHD modifications, thus enabling us to estimate the spectroscopic constants of the substituted molecule from the corresponding parameters of the initial molecule. To illustrate their correctness, column 2 of Table 1 presents the values of the α' parameters for the HDS molecule as calculated by Eq. (32). The calculations involved the values of the α_λ^β parameters of the H_2S molecule from Ref. 7 (they are given in column 4). The value $\omega = 2727.6$ cm^{-1} was determined as an average of ω_1 and ω_3 taken from Ref. 13; the parameter $\theta = 0.4411$ was borrowed from Ref. 7; the parameter $B^e = 9.444$ cm^{-1} was calculated as $B^e = h/8\pi^2 cm\rho_e^2$, where $\rho_e = 1.336$ Å was also taken from Ref. 13. Column 3 of Table 1 presents the experimental (that is, obtained from the experimental data[14]) parameters $\alpha_\lambda'^\beta$ of the HDS molecule. Columns 5–7 give the corresponding values for the molecules HDSe and H_2Se. The parameters $\theta = 0.4276$ and $B^e = 7.727$ cm^{-1} were taken from Ref. 7. The parameters α_1^β and α_3^β in column 6 of the Table 1 were determined by processing the experimental data, whose analysis is given in Ref. 15 (ν_1 and ν_3 of HDSe), and the coefficients α_2^β were taken from Ref. 16. As can be seen from the comparison of columns 2 and 3, 5 and 6, the calculated results agree well with the experimental data.

Using simple relations (27) for $a_\lambda'^{\alpha\beta}$ parameters, we can obtain interesting and useful relationships between squared centrifugal distortion constants. The latter are the coefficients $\tau'_{\alpha\beta\gamma\delta}$ at the operators $J_\alpha J_\beta J_\gamma J_\delta$ in the effective rotational Hamiltonian.[17] It is known[11] that $\tau'_{\alpha\beta\gamma\delta}$ can be written in the form

$$\tau'_{\alpha\beta\gamma\delta} = -\frac{1}{2}\sum_\lambda \frac{\mu'^\lambda_{\alpha\beta}\,\mu'^\lambda_{\gamma\delta}}{\omega'_\lambda}, \qquad (34)$$

where

$$\mu'^\lambda_{\alpha\beta} = 2\sqrt{2}\left(\frac{4\pi c}{\hbar}\right)^{1/2}\frac{B'^e_\alpha B'^e_\beta}{\omega'_\lambda}\,a'^{\alpha\beta}_\lambda\,. \qquad (35)$$

Having substituted Eq. (35) in Eq. (34) and taking into account the relationships found between the parameters entering into these equations, we obtain the following nonzero values of $\tau'_{\alpha\beta\gamma\delta}$:

$$\tau'_{xxxx} = -4\frac{B_e^3}{\omega^2}\,,\quad \tau'_{xxyy} = -\frac{16}{9}\frac{B_e^3}{\omega^2}\,,$$

$$\tau'_{yyyy} = -\frac{80}{81}\frac{B_e^3}{\omega^2}\,,\quad \tau'_{yyzz} = -\frac{4}{9}\frac{B_e^3}{\omega^2}\,, \qquad (36)$$

$$\tau'_{zzzz} = -16\frac{B_e^3}{\omega^2}\,,\quad \tau'_{xzxz} = -\frac{32}{9}\frac{B_e^3}{\omega^2\,\theta^2}\,.$$

As is known,[11] the Watson Hamiltonian can be written in different forms using the method of contact transformations. Let us write the rotational Hamiltonian in the cylindrical form:

$$H_{\rm rot} = \left\{\tilde B_{200}J^2 + \tilde B_{020}J_z^2 + \tilde T_{400}(J^2)^2 + \tilde T_{220}J^2J_z^2 + \tilde T_{040}J_z^4\right\} + \frac{1}{2}\left[(\tilde B_{002} + \tilde T_{202}J^2 + \tilde T_{022}J_z^2),(J_+^2 + J_-^2)\right]_+ + \tilde T_{004}(J_+^4 + J_-^4). \qquad (37)$$

In Eq. (37) $[A, B]_+ = AB + BA$ is the anticommutator; J^2 is the square of the total angular momentum operator, and $J_\pm = J_x \pm iJ_y$. The indices of the coefficients denote the power of the operators J^2, J_z^2, and $J_\pm$, respectively. The relation of the parameters $\tilde B$ and $\tilde T$ to the fundamental molecular constants and the transformation parameter of the Hamiltonian can be found in Ref. 11. The so-called asymmetric top reduction (or A-reduction) made by Watson[18] is based on removing, from Eq. (37), of the last term containing the matrix elements with $|\Delta k| > 2$:

$$H_{\rm rot}^{(A)} = \sum_\alpha B_\alpha^{(A)}J_\alpha^2 - \Delta_J(J^2)^2 - \Delta_{JK}J^2J_z^2 - \Delta_K J_z^4 - \frac{1}{2}\left[(\delta_J J^2 + \delta_K J_z^2),(J_+^2 + J_-^2)\right]_+ + \ldots\,. \qquad (38)$$

Table 1. Vibrational-rotational parameters α_λ^β of the HDS and HDSe molecules, in cm^{-1}

Parameter	HDS_{cal}	HDS_{exp} [a]	H_2S (Ref. 7)	$HDSe_{cal}$	$HDSe_{exp}$ [b]	H_2Se (Ref. 33)
α_1^z	0.0000	0.0106	0.1596	0.0000	0.0037	0.1158
α_1^x	0.1002	0.1026	0.1237	0.0794	0.0794	0.1086
α_1^y	0.0382	0.0393	0.0698	0.0318	0.0313	0.0568
α_2^z	−0.2675	−0.2752	−0.3619	−0.1949	−0.2030	−0.2413
α_2^x	−0.0972	−0.0924	−0.2063	−0.0706	−0.0720	−0.1721
α_2^y	0.0281	0.0345	0.0619	0.0208	0.0252	0.0461
α_3^z	0.2967	0.2875	0.2178	0.2284	0.2247	0.1565
α_3^x	0.0000	−0.0003	0.0789	0.0000	0.0003	0.0719
α_3^y	0.0279	0.0292	0.0544	0.0210	0.0233	0.0416

[a] The values are calculated based on the data from Refs. 14 and 19. [b] α_1^β and α_3^β are calculated based on the data from Ref. 15, α_2^β are calculated based on the data from Ref. 16.

The parameters $\tau'_{\alpha\beta\gamma\delta}$ from Eq. (36), in their turn, can be used to obtain equations for the centrifugal distortion constants Δ'_J, Δ'_{JK}, Δ'_K, δ'_J, and δ'_K (Refs. 11–18) entering into the reduced rotational Hamiltonian (38). In this case, we can obtain:

(a) relationships determining the parameters Δ'_J, Δ'_{JK}, Δ'_K, δ'_J, and δ'_K of the XHD molecule as functions of B^e, ω, and θ of the initial XH_2 molecule:

$$\Delta'_J = \frac{B_e^3}{\omega}\frac{5}{8}; \quad \Delta'_{JK} = -\frac{B_e^3}{\omega^2}\left\{\frac{95}{72} - \frac{16}{9}\theta^{-2}\right\};$$

$$\Delta'_K = \frac{B_e^3}{\omega^2}\left\{\frac{55}{12} - \frac{16}{9}\theta^{-2}\right\};$$

$$\delta'_J = \frac{B_e^3}{\omega^2}\frac{3}{16}; \quad \delta'_K = \frac{B_e^3}{\omega^2}\left\{\frac{7}{18} + \frac{8}{9}\theta^{-2}\right\}; \qquad (39)$$

(b) direct relationships between the centrifugal distortion parameters of the XHD molecule:

$$3\Delta'_J = 10\delta'_J, \qquad (40)$$

$$2\delta'_K - \Delta'_{JK} = \frac{151}{45}\Delta'_J = \frac{302}{27}\delta'_J, \qquad (41)$$

$$2\delta'_K + \Delta'_K = \frac{128}{15}\Delta'_J = \frac{256}{9}\delta'_J. \qquad (42)$$

To illustrate the correctness of obtained relationships (39), column 2 of Table 2 presents the results of theoretical prediction for the HDS molecule. The initial values of the constants B^e, ω, and θ were the same as in Table 1, and the values of the centrifugal distortion parameters of the H_2S molecule were taken from Ref. 19 (they are given in column 4 of Table 2). For a comparison, column 3 gives the experimental values of HDS molecule parameters borrowed from Ref. 14.

studies of actual spectra or in solving other problems. In particular, the values of $\alpha_\lambda^{\prime\beta}$ were used for calculation of a synthetic spectrum of some bands of the HDSe and HDS molecules.[15,30,31]

As to the relationships between the centrifugal distortion parameters (calculated data are given for the ground vibrational state) of the HDS molecule, the experimental data from Ref. 14 give us the following values for Eqs. (40)–(42): 2.62 cm^{-1} for the left-hand side of Eq. (40) and 2.84 cm^{-1} for its right-hand side; 3.41 cm^{-1} for the left-hand side of Eq. (41), 2.92 and 3.18 cm^{-1} for the central and right-hand sides; 9.20, 7.42, and 8.09 cm^{-1} for the left-hand, central, and right-hand sides of Eq. (42).

Before discussing the anharmonic parameters $x_{\lambda\mu}$ and the resonance parameters F and D (Fermi and Darling–Dennison resonances, respectively), let us consider the fourth-order anharmonic constants. Six parameters of all entering into the potential function of the XH_2 molecule (k_{1111}, k_{1133}, k_{3333}, k_{1122}, k_{1223}, and k_{2233}) are nonzero within the framework of the extended local mode approximation (for details see Ref. 7). In this case, the general equations[3] lead to the following values of nonzero $k'_{\lambda\mu\nu\chi}$ parameters for the XHD molecule:

$$k'_{1111} = k_{1111}, \quad k'_{1133} = 0, \quad k'_{2233} = \frac{8\sqrt{3}}{9}k_{2233},$$

$$k'_{2222} = \frac{2}{9}k_{2222}\frac{17 - 36\theta^2}{3 - 8\theta^2}, \quad k'_{1223} = \frac{\sqrt[4]{8}}{3\sqrt{3}}B_e\,\theta,$$

$$k'_{122} = \frac{\sqrt{6}}{9}k_{1122} + \frac{5\sqrt{6}}{36}B_e\,\theta, \quad k'_{333} = 2k_{1111}. \qquad (43)$$

In the general case, the anharmonic constants for an asymmetric top molecule have the following form[2]:

Table 2. Centrifugal distortion parameters of the ground vibrational state of the HDS and HDSe molecules, in cm^{-1}

Parameter	HDS_{cal}	HDS_{exp}	H_2S (Ref. 19)	$HDSe_{cal}$	$HDSe_{exp}$	H_2Se (Ref. 33)
$\Delta_J \cdot 10^4$	0.71	0.87	6.53	0.48	0.57	5.29
$\Delta_{JK} \cdot 10^4$	8.85	9.56	−22.8	6.49	7.43	−18.49
$\Delta_K \cdot 10^4$	−5.16	−3.77	37.03	−3.97	−4.08	26.37
$\delta_J \cdot 10^4$	0.21	0.28	2.96	0.15	0.18	2.43
$\delta_K \cdot 10^4$	5.61	6.49	−1.33	4.05	4.76	−1.83

Columns 5–7 of Table 2 present the centrifugal distortion parameters for the HDSe molecule along with the experimental values taken from Ref. 20.

As can be seen, the calculated results for the HDS and HDSe molecules in many cases differ from the experimental data (see columns 2 and 3, 5 and 6). However, it should be kept in mind that the centrifugal distortion parameters presented in columns 2 and 5 were calculated based only on the information about the main isotopic modifications of the H_2S and H_2Se molecules. From this point of view, the results obtained can be considered satisfactory. Consequently, it should be expected that using Eqs. (39) we could predict the values to be used as the initial approximation in the

$$x_{kk} = \phi_{kkkk}/16 - \sum_m \phi_{kkm}^2/(8\omega_m) -$$

$$- \sum_m \phi_{kkm}^2[(2\omega_k + \omega_m)^{-1} - (2\omega_k - \omega_m)^{-1}]/32,$$

$$x_{kl} = \phi_{kkll}/4 - \sum_m \phi_{kkm}\phi_{mll}/(4\omega_m) -$$

$$- \sum_m \phi_{klm}^2[(\omega_k + \omega_l + \omega_m)^{-1} + (\omega_k - \omega_l + \omega_m)^{-1} +$$

$$+ (-\omega_k + \omega_l + \omega_m)^{-1} - (\omega_k + \omega_l - \omega_m)^{-1}]/8 +$$

$$+ \sum_\alpha B_\alpha^e(\zeta_{kl}^\alpha)^2[(\omega_k/\omega_l) + (\omega_l/\omega_k)]. \qquad (44)$$

Here $\phi_{\lambda\lambda\lambda} = 6k_{\lambda\lambda\lambda}$; $\phi_{\lambda\mu\mu} = 2k_{\lambda\mu\mu}$, $\lambda \neq \mu$; $\phi_{\lambda\mu\nu} = k_{\lambda\mu\nu}$, $\lambda \neq \mu \neq \nu$. In Eq. (44), the parameters that become extremely large in the case of Fermi resonance $\omega_m \approx 2\omega_k$ or the resonance $\omega_m \approx \omega_k + \omega_l$ are separated explicitly. If such resonances are taken into account, the corresponding terms should be excluded from Eq. (44).

Using then Eqs. (15), (33), and (43) in the general equations (44), for the anharmonic parameters $x_{\lambda\mu}$ and the Fermi resonance parameters $F_{\mu\mu}$ we have:

$$x'_{11} = \frac{1}{2}x'_{33} = x_{11}, \qquad x'_{13} = 0,$$

$$x'_{22} = \frac{2}{9}\frac{(17 - 36\theta^2)}{(3 - 8\theta^2)}x_{22} + \tau_{22}(\theta), \tag{45}$$

$$x'_{12} = \frac{2}{3\sqrt{6}}x_{12} + \tau_{12}(\theta), \qquad x'_{23} = \frac{8}{3\sqrt{3}}x_{23} + \tau_{23}(\theta),$$

$$F_{\mu\mu} = \frac{1}{2\sqrt{2}}k'_{\lambda\mu\mu}. \tag{46}$$

The following designations have been used in Eqs. (45):

$$\tau_{22}(\theta) = \frac{B_e}{72\theta^2}\left\{\frac{(17 - 36\theta^2)(1 - 2\theta^2)^2}{1 - 4\theta^2} - \right.$$

$$\left. - 4\frac{(1 - 2\theta^2)(2 - 3\theta^2)^2}{1 - 3\theta^2} - \frac{(1 - 4\theta^2)(1 - 3\theta^2)^2}{1 - 6\theta^2}\right\};$$

$$\tau_{12}(\theta) = -\frac{1}{6\sqrt{6}}\frac{\omega\theta}{B_e}\alpha_3^z + \frac{2}{3\sqrt{6}}\frac{B_e}{\theta} \times \tag{47}$$

$$\times \left\{\frac{1}{3} + \theta^2 - \frac{(1 - 2\theta^2)^2}{2(1 - 4\theta^2)} + \frac{(1 - 3\theta^2)^2}{6(1 - 6\theta^2)}\right\};$$

$$\tau_{23}(\theta) = \frac{1}{3\sqrt{3}}\frac{\omega\theta}{B_e}\alpha_3^z + \frac{2}{9\sqrt{3}}\frac{B_e}{\theta}\left\{\frac{(2 - 3\theta^2)^2}{1 - 3\theta^2} - 4\right\}.$$

As to the Darling–Dennison resonance interaction, it is weak in the considered cases because of large absolute frequency difference $\omega_\lambda - \omega_\mu$. It should be noted that both of the stretching modes q_1 and q_3 in the XH_2 molecule are characterized by the simultaneous motion of the atoms 2 and 3 ($l_{N\alpha\lambda s}$ constants for these atoms are nonzero and close in value), while in the substituted XHD molecule only the 1–2 bond is excited at the q'_1 vibration and only the 1–3 mode at the q'_3 vibration. As a consequence, excitation of one of the two stretching modes in the XH_2 molecule necessarily leads to excitation of the another mode. It follows, in particular, from the fact that x_{13} and F_{D-D} have large absolute values. In the case of the XHD molecule, we have $x'_{13} = 0$ and the weak Darling–Dennison resonance. All the above-said allows us to conclude that, in this case, excitation of one of the vibrational stretching modes leads to a very weak (zero in the local mode approximation) excitation of the another mode. Excitation of one of the stretching modes can be obtained only due to coupling of both modes to the deformation mode, what follows from the presence of nonzero x'_{12} and x'_{12} parameters in Eqs. (45).

Column 2 of Table 3 gives the values of the parameters for the HDS molecule as calculated by Eqs. (45). The initial values of the x-parameters for the H_2S molecule were taken from Ref. 13 (for convenience, they are given in column 4). Column 3 presents the corresponding *ab initio* values from Ref. 21. From a comparison of columns 2 and 3, one can see a satisfactory agreement between the results.

Table 3. Anharmonic parameters of the HDS molecule, cm^{-1}

Parameter	HDS_{cal}	$HDS_{ab\ initio}$ (Ref. 21)	H_2S (Ref. 13)
x_{11}	−25.1	−28.6	−25.09
x_{22}	−5.2	−4.8	−5.72
x_{33}	−50.2	−55.5	−24.00
x_{12}	−10.1	−11.7	−19.69
x_{13}	0.0	−1.3	−94.68
x_{23}	−24.9	−21.8	−21.09

The $XH_3 \rightarrow XH_2D$ and $XH_3 \rightarrow XHD_2$ isotopic substitution

Using the procedure described above for the $XH_2 \rightarrow XHD$ substitution, we can obtain the molecular parameters for the isotopic modifications XH_2D (C_s) and XHD_2 (C_s) as functions of the parameters of the initial molecule XH_3 (C_{3v}). In this case, we consider both of the isotopic modifications of the XH_3 molecule in parallel.

The equilibrium configurations for the main and two substituted molecules are given in Table 4, and for the XHD_2 molecule the coordinate system is additionally turned around the axis $x = y = z$ through the angle $\pi/3$ or, in other words, cyclic permutation of the indices $x \rightarrow y \rightarrow z \rightarrow x$ is performed in order to direct the axis OZ along the smallest moment of inertia (in both cases, we have a quasisymmetric top).

Table 4. Parameters of equilibrium configuration of pyramidal tetratomic molecule in a local mode approximation[a]

Parameter	XH_3	XH_2D	XHD_2
r^e_{1x}	$\rho_e\sqrt{2}/\sqrt{3}$	0	0
r^e_{1y}	0	0	0
r^e_{1z}	$-\rho_e/\sqrt{3}$	$-\rho_e$	ρ_e
r^e_{2x}	$-\rho_e/\sqrt{6}$	$-\rho_e/\sqrt{2}$	$-\rho_e/\sqrt{2}$
r^e_{2y}	$-\rho_e/\sqrt{2}$	$-\rho_e/\sqrt{2}$	$-\rho_e/\sqrt{2}$
r^e_{2z}	$-\rho_e/\sqrt{3}$	0	0
r^e_{3x}	$-\rho_e/\sqrt{6}$	$-\rho_e/\sqrt{2}$	$\rho_e/\sqrt{2}$
r^e_{3y}	$\rho_e/\sqrt{2}$	$\rho_e/\sqrt{2}$	$-\rho_e/\sqrt{2}$
r^e_{3z}	$-\rho_e/\sqrt{3}$	0	0

[a] $r^e_{3z} = 0$ because $m/M = 0$.

The equilibrium rotational constants B'^{e}_{β} in this case are determined by the following equations:

(a) for XH_2D

$$B'^{e}_{x} = B'^{e}_{y} = \frac{2}{3} B_e; \quad B'^{e}_{z} = B_e; \tag{48}$$

(b) for XHD_2

$$B'^{e}_{x} = B'^{e}_{y} = \frac{2}{3} B_e; \quad 2B'^{e}_{z} = B_e, \tag{49}$$

where B_e is the equilibrium rotational constant of the XH_3 molecule in the local mode approximation and $B^{e}_{x} = B^{e}_{y} = B^{e}_{z} = B_e$.

Consider now the vibrational-rotational parameters $\alpha'^{\beta}_{\lambda}$. The general equation for them, in the case of the asymmetric top molecule, is given by Eq. (31). The terms of this equation can be easily found. Actually, the constants B'^{e}_{β} are presented in Eqs. (48) and (49). The harmonic frequencies can be determined from Eqs. (11). Using the initial information, namely, $\omega_1 = \omega_3 = \omega$, $\omega_2 = \omega_4 = \omega\theta$ ($l_{N\alpha\lambda s}$ parameters of the XH_3 molecule are given in Table 5), we obtain:

(a) for the XH_2D molecule:

$$\omega'_1 = \omega'_5 = \sqrt{2}\ \omega'_2 = \omega,$$
$$\sqrt{3}/2\ \omega'_3 = \omega'_4 = \omega'_6 = \sqrt{3}/2\ \omega\theta; \tag{50}$$

(b) for the XHD_2 molecule:

$$\omega'_1 = \omega'_5 = \sqrt{2}\ \omega'_2 = \sqrt{2}\ \omega'_5 = \omega,$$
$$\sqrt{2}\ \omega'_3 = \omega'_4 = \omega'_6 = \sqrt{3}/2\ \omega\theta. \tag{51}$$

The corresponding $l_{N\alpha\lambda s}$-parameters are given in Tables 6 and 7.

Now let us pass to the Coriolis $\zeta'^{\beta}_{\lambda\mu}$ and vibrational-rotational $a'^{\alpha\beta}_{\lambda}$ constants of the substituted molecules. Using the data from Tables 6 and 7 we obtain, from the general equations (24) and (26), that:

(a) for the XH_2D modification:

$$a'^{xx}_1 = a'^{yy}_1/2 = a'^{zz}_1 = -\,a'^{xx}_3 = a'^{zz}_3 = -\,a'^{xz}_5 =$$
$$= -\,a'^{zx}_5 = a'^{xx}_2/2 = a'^{yy}_2/2 = \left(\frac{h}{8\pi^2 c B_e}\right)^{1/2}, \tag{52}$$

$$a'^{yz}_4 = a'^{zy}_4 = a'^{xy}_6 = a'^{yx}_6 = -\,(2/\sqrt{3})\left(\frac{h}{8\pi^2 c B_e}\right)^{1/2};$$

$$\zeta'^{x}_{14} = -\,\zeta'^{x}_{24} = -\,\zeta'^{x}_{34} = \zeta'^{x}_{56} = -\,\zeta'^{z}_{16} = \zeta'^{z}_{26} =$$
$$= -\,\zeta'^{z}_{36} = \zeta'^{z}_{45} = -\,1/\sqrt{3}, \tag{53}$$
$$\zeta'^{y}_{35} = -\,1, \quad \zeta'^{y}_{46} = 1/3;$$

(b) for XHD_2

$$a'^{xx}_1 = a'^{yy}_1 = a'^{xx}_2 = a'^{zz}_1/2 = a'^{xy}_5 =$$
$$= a'^{yx}_5 = \left(\frac{h}{8\pi^2 c B_e}\right)^{1/2},$$
$$-\,a'^{xx}_3/\sqrt{2} = a'^{yy}_3/\sqrt{2} = -\sqrt{3}\ a'^{zy}_6/2 = \tag{54}$$
$$= -\sqrt{3}\ a'^{zy}_6/2 = \sqrt{3}\ a'^{xz}_4 = \sqrt{3}\ a'^{zx}_4 = \left(\frac{h}{8\pi^2 c B_e}\right)^{1/2};$$

Table 5. $l_{N\alpha\lambda s}$ parameters of XY_3 molecule in the rigorous local mode approximation

N	α	λ	s	$l_{N\alpha\lambda s}$	N	α	λ	s	$l_{N\alpha\lambda s}$	N	α	λ	s	$l_{N\alpha\lambda s}$
1	x	1		$-(2)^{1/2}/3$	1	x	2		$1/3$	1	x	3	1	$2/3$
2	x	1		$-(2)^{1/2}/6$	2	x	2		$-1/6$	2	x	3	1	$1/6$
3	x	1		$-(2)^{1/2}/6$	3	x	2		$-1/6$	3	x	3	1	$1/6$
1	y	1		0	1	y	2		0	1	y	3	1	0
2	y	1		$-1/(6)^{1/2}$	2	y	2		$-1/2(3)^{1/2}$	2	y	3	1	$1/2(3)^{1/2}$
3	y	1		$1/(6)^{1/2}$	3	y	2		$1/2(3)^{1/2}$	3	y	3	1	$-1/2(3)^{1/2}$
1	z	1		$-1/3$	1	z	2		$(2)^{1/2}/3$	1	z	3	1	$-(2)^{1/2}/3$
2	z	1		$-1/3$	2	z	2		$(2)^{1/2}/3$	2	z	3	1	$1/3(2)^{1/2}$
3	z	1		$-1/3$	3	z	2		$(2)^{1/2}/3$	3	z	3	1	$1/3(2)^{1/2}$
1	x	3	2	0	1	x	4	1	$1/3(2)^{1/2}$	1	x	4	2	0
2	x	3	2	$1/2(3)^{1/2}$	2	x	4	1	$-(2)^{1/2}/3$	2	x	4	2	$1/(6)^{1/2}$
3	x	3	2	$-1/2(3)^{1/2}$	3	x	4	1	$-(2)^{1/2}/3$	3	x	4	2	$-1/(6)^{1/2}$
1	y	3	2	0	1	y	4	1	0	1	y	4	2	$1/(2)^{1/2}$
2	y	3	2	$1/2$	2	y	4	1	$1/(6)^{1/2}$	2	y	4	2	0
3	y	3	2	$1/2$	3	y	4	1	$-1/(6)^{1/2}$	3	y	4	2	0
1	z	3	2	0	1	z	4	1	$1/3$	1	z	4	2	0
2	z	3	2	$1/(6)^{1/2}$	2	z	4	1	$-1/6$	2	z	4	2	$-1/2(3)^{1/2}$
3	z	3	2	$-1/(6)^{1/2}$	3	z	4	1	$-1/6$	3	z	4	2	$1/2(3)^{1/2}$

$$\zeta'^{y}_{14}/2 = -\zeta'^{y}_{24} = -\zeta'^{y}_{34} = -\zeta'^{y}_{56} = \zeta'^{x}_{16}/2 = -\zeta'^{x}_{26} = \zeta'^{x}_{36} = -\zeta'^{x}_{54} = -1/\sqrt{6}, \quad \zeta'^{z}_{35} = -1, \quad \zeta'^{z}_{46} = -2/3. \tag{55}$$

Table 6. $l_{N\alpha\lambda}$ parameters of XH_2D molecule in the local mode approximation

N	α	λ	$l_{N\alpha\lambda}$	N	α	λ	$l_{N\alpha\lambda}$	N	α	λ	$l_{N\alpha\lambda}$
1	x	1	0	1	x	2	0	1	x	3	0
2	x	1	$-1/2$	2	x	2	0	2	x	3	$1/2$
3	x	1	$-1/2$	3	x	2	0	3	x	3	$1/2$
1	y	1	0	1	y	2	0	1	y	3	0
2	y	1	$-1/2$	2	y	2	0	2	y	3	$-1/2$
3	y	1	$1/2$	3	y	2	0	3	y	3	$1/2$
1	z	1	0	1	z	2	-1	1	z	3	0
2	z	1	0	2	z	2	0	2	z	3	0
3	z	1	0	3	z	2	0	3	z	3	0
1	x	4	$1/(3)^{1/2}$	1	x	5	0	1	x	6	0
2	x	4	0	2	x	5	$1/2$	2	x	6	0
3	x	4	0	3	x	5	$-1/2$	3	x	6	0
1	y	4	0	1	y	5	0	1	y	6	$-1/(3)^{1/2}$
2	y	4	0	2	y	5	$1/2$	2	y	6	0
3	y	4	0	3	y	5	$1/2$	3	y	6	0
1	z	4	0	1	z	5	0	1	z	6	0
2	z	4	$1/(3)^{1/2}$	2	z	5	0	2	z	6	$-1/(3)^{1/2}$
3	z	4	$1/(3)^{1/2}$	3	z	5	0	3	z	6	$-1/(3)^{1/2}$

* $l_{4\alpha\lambda} = 0$ because $m/M = 0$, $f_{rr'} = 0$, $f_{r\alpha} = 0$, $f_{r\beta} = 0$.

Table 7. $l_{N\alpha\lambda}$ parameters of XHD_2 molecule in the local mode approximation

N	α	λ	$l_{N\alpha\lambda}$	N	α	λ	$l_{N\alpha\lambda}$	N	α	λ	$l_{N\alpha\lambda}$
1	x	1	0	1	x	2	0	1	x	3	0
2	x	1	0	2	x	2	$-1/2$	2	x	3	$-1/2$
3	x	1	0	3	x	2	$1/2$	3	x	3	$1/2$
1	y	1	0	1	y	2	0	1	y	3	0
2	y	1	0	2	y	2	$-1/2$	2	y	3	$1/2$
3	y	1	0	3	y	2	$-1/2$	3	y	3	$1/2$
1	z	1	1	1	z	2	0	1	z	3	0
2	z	1	0	2	z	2	0	2	z	3	0
3	z	1	0	3	z	2	0	3	z	3	0
1	x	4	$(2/3)^{1/2}$	1	x	5	0	1	x	6	0
2	x	4	0	2	x	5	$1/2$	2	x	6	0
3	x	4	0	3	x	5	$1/2$	3	x	6	0
1	y	4	0	1	y	5	0	1	y	6	$(2/3)^{1/2}$
2	y	4	0	2	y	5	$1/2$	2	y	6	0
3	y	4	0	3	y	5	$-1/2$	3	y	6	0
1	z	4	0	1	z	5	0	1	z	6	0
2	z	4	$1/(6)^{1/2}$	2	z	5	0	2	z	6	$-1/(6)^{1/2}$
3	z	4	$-1/(6)^{1/2}$	3	z	5	0	3	z	6	$-1/(6)^{1/2}$

* $l_{4\alpha\lambda} = 0$ because $m/M = 0$, $f_{rr'} = 0$, $f_{r\alpha} = 0$, $f_{r\beta} = 0$.

It remained only to consider one type of parameters in Eq. (31), namely, anharmonic force constants $k'_{\lambda\mu\nu}$. In the general case, corresponding equations are rather complicated. But, using the known k-parameters of the initial molecule (with only the force constant f_{rrr} kept in the cubic part of the potential function written in the natural coordinates), we obtain the following nonzero values of $k'_{\lambda\mu\nu}$:

(a) for XH_2D

$$k'_{111} = k'_{155} = \sqrt[4]{2}\, k'_{222} = 3\sqrt{6}\, k'_{111},$$

$$k'_{133} = (1/\sqrt{2})\sqrt{B_e\,\omega}\;\theta^{-1}(1-2\theta^2) = \sqrt{3/2}\, k_{122},$$

$$k'_{144} = k'_{456} = k'_{166} = (2\sqrt{2}/3\sqrt{3})(B_e\omega)^{1/2}\theta^{-1}(2-3\theta^2),$$

$$k'_{244} = k'_{266} = (\sqrt{2}\sqrt[4]{2}/3\sqrt{3})(B_e\omega)^{1/2}\theta^{-1}(1-3\theta^2),$$

$$k'_{344} = -k'_{366} = (-7\sqrt{2}/3\sqrt{3})(B_e\omega\theta)^{1/2}; \tag{56}$$

(b) for XHD_2

$$k'_{111}/2 = \sqrt[4]{2}\, k'_{222} = \sqrt[4]{2}\, k'_{255} = 3\sqrt{3}\, k_{111},$$

$$k'_{233} = (1/2\sqrt[4]{2})(B_e\omega)^{1/2}\theta^{-1}(1-2\theta^2) = (\sqrt{3}/2\sqrt[4]{2})\, k_{122},$$

$$k'_{144} = k'_{166} = (4/3\sqrt{3})(B_e\omega)^{1/2}\theta^{-1}(2-3\theta^2),$$

$$k'_{244} = k'_{456} = k'_{266} = (\sqrt[4]{2}/3\sqrt{3})(B_e\omega)^{1/2}\theta^{-1}(1-3\theta^2),$$

$$k'_{344} = -k'_{366} = (-7\sqrt[4]{2}/3\sqrt{3})(B_e\omega\theta)^{1/2}. \tag{57}$$

In the case of Coriolis resonance ($\omega_l \approx \omega_k$), the last term including ζ'^{β}_{kl} in Eq. (31) should be replaced by[11]:

$$-(\zeta^{\beta}_{kl})^2 (B^2_{\beta}/\omega)(\omega_k - \omega_l)^2 [\omega_l(\omega_k - \omega_l)]^{-1}. \tag{58}$$

Then the corresponding resonance blocks of the effective rotational operator for the states $|v\rangle = |v_k\ v_l\rangle$ and $|\tilde{v}\rangle = |v_k + 1\ v_l - 1\rangle$ take the form[12]:

$$H_{v\tilde{v}} = (v_k+1)^{1/2} v_l^{1/2}\{iC_{\beta}J_{\beta} + C_{\alpha\beta}(J_{\alpha}J_{\beta} + J_{\beta}J_{\alpha} + \ldots)\}, \tag{59}$$

$$H_{\tilde{v}v} = (v_k+1)^{1/2} v_l^{1/2}\{-iC_{\beta} + C_{\alpha\beta}(J_{\alpha}J_{\beta} + J_{\beta}J_{\alpha} + \ldots)\},$$

where

$$C_{\beta} = \zeta^{\beta}_{kl} B_{\beta}[(\omega_l/\omega_k)^{1/2} + (\omega_k/\omega_l)^{1/2}], \tag{60}$$

and the parameter $C_{\alpha\beta} = d^{\alpha\beta}/2$ is determined by the equation similar to Eq. (31) (Ref. 6).

It should be noted that the contribution coming from the term (58) is negligibly small as compared with other contributions:

$$\left| (\zeta^{\beta}_{kl})^2 \frac{B^2_{\beta}}{\omega} \frac{(\omega_k - \omega_l)^2}{\omega_l(\omega_k + \omega_l)} \frac{1}{\alpha^{\beta}_k} \right| \approx 0.01. \tag{61}$$

At the same time, if we use Eq. (31) ignoring the Coriolis resonance, that is, leave the last term in parenthesis unchanged, then its contribution is larger than the contributions coming from other terms, and this can lead to incorrect values of the α parameters.

Thus, for the substituted XH_2D molecule we have:
(a) for the parameters of the stretching vibrations

$$\alpha'^{x}_1 = \alpha'^{y}_1 = \alpha'^{x}_5 = \alpha'^{y}_5 = -\frac{1}{2}d^{xy}_{15} =$$
$$= -\frac{4}{3}\frac{B_e^2}{\omega}\left\{1+\sqrt{3}\frac{k_{111}}{(B_e\omega)^{1/2}}\right\} - \frac{8}{9}\frac{B_e}{\omega}\frac{4\theta^2}{4-3\theta^2},$$
$$\alpha'^{z}_1 = -\frac{6B_e^2}{\omega}\left\{1+\sqrt{3}\frac{k_{111}}{(B_e\omega)^{1/2}}\right\},$$
$$\alpha'^{z}_5 = -\frac{6B_e^2}{\omega}\left\{1+\sqrt{3}\frac{k_{111}}{(B_e\omega)^{1/2}}\right\} - \frac{2B_e^2}{\omega}\frac{4\theta^2}{1-\theta^2}, \quad (62)$$
$$\alpha'^{x}_2 = \alpha'^{y}_2 = -\frac{8\sqrt{2}}{3}\frac{B_e^2}{\omega}\left\{1+\sqrt{3}\frac{k_{111}}{(B_e\omega)^{1/2}}\right\} -$$
$$-\frac{8\sqrt{2}}{9}\frac{B_e^2}{\omega}\frac{4\theta^2}{2-3\theta^2}, \alpha'^{z}_2 = 0;$$

(b) for the parameters of deformation vibrations (the term (58) is excluded because of its smallness)

$$\alpha'^{x}_3 = \alpha'^{z}_3 = \frac{8}{9}\frac{B_e^2}{\theta\omega}(\theta^2 - 1 + 2c), \quad \alpha'^{y}_3 = \frac{4B_e^2}{\theta\omega}\theta^2\frac{3-\theta^2}{1-\theta^2},$$
$$\alpha'^{x}_4 = \alpha'^{z}_6 = \frac{4}{27\sqrt{3}}\frac{B_e^2}{\theta\omega}\{42\theta^2 - 23 + 9c/2\} +$$
$$+\frac{16}{27\sqrt{3}}\frac{B_e^2}{\theta\omega}\left(\frac{4+9\theta^2}{4-3\theta^2} + \frac{2+9\theta^2}{2-3\theta^2}\right),$$
$$\alpha'^{z}_4 = \alpha'^{x}_6 = \frac{28}{9\sqrt{3}}\frac{B_e^2}{\theta\omega}(2\theta^2 - 1 + 3c/14) +$$
$$+\frac{16}{27\sqrt{3}}\frac{B_e^2}{\theta\omega}\frac{4+9\theta^2}{4-3\theta^2}, \quad (63)$$
$$\alpha'^{y}_4 = \alpha'^{y}_6 = \frac{4}{9\sqrt{3}}\frac{B_e^2}{\theta\omega}(3\theta^2 - 4 + 9c/4);$$
$$d'^{xy}_{46} = \frac{16}{9\sqrt{3}}\frac{2B_e^2}{\omega}\theta^{-1}\left\{-1+\frac{1}{6}(2-3\theta^2) + \frac{4\theta^2}{3\theta^2-4} + \frac{2\theta^2}{3\theta^2-2}\right\},$$
$$d'^{xz}_{34} = d'^{yz}_{36} = -\left(\frac{2}{\sqrt{3}}\right)^{5/2}\frac{2B_e^2}{\omega}\left\{\frac{17-3\sqrt{3}}{6\sqrt{3}(\sqrt{3}-1)} + \frac{2+\sqrt{3}}{4\theta^{-2}-3}\right\}.$$

Here B_e, $\omega = 1/2(\omega_1 + \omega_3)$, and $\theta = 1/2(\theta_2 + \theta_4)$, $\theta_2 = \omega_2/\omega$, $\theta_4 = \omega_4/\omega$ are the parameters of the initial molecule, as well as the parameter k_{111}.

Similar results were obtained for the XHD_2 molecule as well:

(a) for the parameters of the stretching vibrations

$$\alpha'^{x}_2 = \alpha'^{y}_2 = \alpha'^{x}_5 = \alpha'^{y}_5 = -\frac{1}{2}d^{xy}_{25} =$$
$$= -\frac{4\sqrt{2}}{3}\frac{B_e^2}{\omega}\left\{1+\sqrt{3}\frac{k_{111}}{(B_e\omega)^{1/2}}\right\} - \frac{4\sqrt{2}}{9}\frac{B_e^2}{\omega}\frac{4\theta^2}{2-3\theta^2},$$
$$\alpha'^{z}_2 = -\frac{3\sqrt{2}}{2}\frac{B_e^2}{\omega}\left\{1+\sqrt{3}\frac{k_{111}}{(B_e\omega)^{1/2}}\right\}, \quad (64)$$
$$\alpha'^{z}_5 = \alpha'^{z}_2 - \frac{\sqrt{2}}{2}\frac{B_e}{\omega}\frac{4\theta^2}{1-\theta^2},$$
$$\alpha'^{x}_1 = \alpha'^{y}_1 = -\frac{8}{3}\frac{B_e}{\omega}\left\{1+\sqrt{3}\frac{k_{111}}{(B_e\omega)^{1/2}}\right\} - \frac{16}{9}\frac{B_e}{\omega}\frac{4\theta^2}{4-3\theta^2},$$
$$\alpha'^{z}_1 = 0;$$

(b) for the parameters of the deformation vibrations (the contribution of the type (58) is omitted)

$$\alpha'^{x}_3 = \alpha'^{y}_3 = -\frac{2\sqrt{2}}{3}\frac{2B_e^2}{\omega\theta}, \quad \alpha'^{z}_3 = \frac{1}{2\sqrt{2}}\frac{2B_e^2}{\omega\theta}\frac{1+3\theta^2}{1-\theta^2},$$
$$\alpha'^{z}_4 = \alpha'^{y}_6 = -\frac{1}{2\sqrt{2}}\frac{2B_e^2}{\omega\theta}\left\{1+\frac{1}{3}(1-3\theta^2)\right\},$$
$$\alpha'^{y}_4 = \alpha'^{x}_6 = -\frac{8}{9\sqrt{3}}\frac{2B_e^2}{\omega\theta}\times$$
$$\times\left\{\frac{1}{3}+\frac{1}{3}(2-3\theta^2) + \frac{1}{6}(1-3\theta^2) + \frac{2\theta^2}{3\theta^2-2} + \frac{8\theta^2}{3\theta^2-4}\right\},$$
$$\alpha'^{x}_4 = \alpha'^{y}_6 = -\frac{8}{9\sqrt{3}}\frac{2B_e^2}{\omega\theta}\times$$
$$\times\left\{-\frac{1}{3}+\frac{1}{3}(2-3\theta^2) + \frac{1}{6}(1-3\theta^2) + \frac{2\theta^2}{3\theta^2-2}\right\}; \quad (65)$$
$$d'^{xy}_{46} = \frac{16}{9\sqrt{3}}\frac{2B_e^2}{\omega\theta}\left\{-1+\frac{1}{6}(1-3\theta^2) + \frac{4\theta^2}{3\theta^2-4} + \frac{2\theta^2}{3\theta^2-2}\right\},$$
$$d'^{xz}_{34} = d'^{yz}_{36} = \left(\frac{8}{5}\right)^{5/4}\frac{B_e^2}{\omega\theta}\left\{\frac{13-6\sqrt{6}}{3\sqrt{6}(\sqrt{6}-1)} - \frac{1}{2}\frac{2+\sqrt{6}}{2\theta^{-2}-3}\right\}.$$

Taking into account that for the initial molecule[6]

$$\alpha^{z}_1 = -4\frac{B_e}{\omega}\left\{1+\sqrt{3}\frac{k_{111}}{(B_e\omega)^{1/2}}\right\},$$

we can derive the relationships between the α parameters of the initial molecule and its isotopic modifications:

(a) for the XH_2D molecule we have:

$$\alpha'^{x}_1 = \alpha'^{y}_1 = \alpha'^{x}_5 = \alpha'^{y}_5 = -\frac{1}{2}d^{xy}_{15} = \frac{1}{3}B_e\alpha^{z}_1 - \frac{8}{9}\frac{B_e}{\omega}\frac{4\theta^2}{4-3\theta^2},$$
$$\alpha'^{z}_1 = \frac{3B_e}{2}\alpha^{z}_1, \quad \alpha'^{z}_5 = \frac{3B_e}{2}\alpha^{z}_1 - \frac{2B_e^2}{\omega}\frac{4\theta^2}{1-\theta^2},$$
$$\alpha'^{x}_2 = \alpha'^{y}_2 = \frac{2\sqrt{2}}{3}B_e\alpha^{z}_1 - \frac{8\sqrt{2}}{9}\frac{B_e^2}{\omega}\frac{4\theta^2}{2-3\theta^2}, \quad \alpha'^{z}_2 = 0; \quad (66)$$

(b) for the XHD_2 molecule:

$$\alpha_2'^x = \alpha_2'^y = \alpha_5'^x = \alpha_5'^y = -\frac{1}{2} d_{25}^{xy} =$$

$$= \frac{\sqrt{2}}{3} B_e \alpha_1^z - \frac{4\sqrt{2}}{9} \frac{B_e^2}{\omega} \frac{4\theta^2}{2-3\theta^2},$$

$$\alpha_2'^z = 6\sqrt{2} B_e \alpha_1^z, \quad \alpha_5'^z = \alpha_2'^z - \frac{\sqrt{2}}{2} \frac{B_e}{\omega} \frac{4\theta^2}{1-\theta^2}, \qquad (67)$$

$$\alpha_1'^x = \alpha_1'^y = \frac{2}{3} B_e \alpha_1^z - \frac{16}{9} \frac{B_e}{\omega} \frac{4\theta^2}{4-3\theta^2}, \quad \alpha_1'^z = 0.$$

In Eqs. (63) and (65), not all terms are gathered in order to make the comparison simpler. In particular, it is obvious that the summation rule for the parameters of the degenerated deformation vibrational states of both isotopomers takes the form

$$\alpha_4'^x(XH_2D) + \alpha_4'^y(XH_2D) + \frac{4}{9}\alpha_4'^z(XH_2D) =$$

$$= \alpha_6'^x(XH_2D) + \alpha_6'^y(XH_2D) + \frac{4}{9}\alpha_6'^z(XH_2D) =$$

$$= \alpha_4'^x(XHD_2) + \alpha_4'^y(XHD_2) + \frac{16}{9}\alpha_4'^z(XHD_2) =$$

$$= \alpha_6'^x(XHD_2) + \alpha_6'^y(XHD_2) + \frac{16}{9}\alpha_6'^z(XHD_2), \qquad (68)$$

and the direct relationships between the parameters $\alpha_3'^\beta$ have the form

$$\alpha_3'^x(XH_2D) = \alpha_3'^y(XH_2D) = \frac{1}{2\sqrt{2}}\alpha_3'^x(XHD_2) =$$

$$= \frac{1}{2\sqrt{2}}\alpha_3'^y(XHD_2),$$

$$\alpha_3'^z(XH_2D) = 2\sqrt{2}\,\alpha_3'^z(XH_2D). \qquad (69)$$

It should be noted that the term responsible for the Fermi resonance is omitted in the equations for $\alpha_3'^\beta$ of both of the isotopomers. According to Ref. 11, it contributes to the off-diagonal block of the effective rotational operator:

$$\langle v_k v_l \,|\, h_3 \,|\, v_k \pm 1\, v_l \mp 2 \rangle =$$

$$= \frac{1}{2\sqrt{2}} k_{kll}[(v_k + \frac{1}{2} \pm \frac{1}{2})(v_l + \frac{1}{2} \mp \frac{1}{2})(v_l + \frac{1}{2} \mp \frac{3}{2})]^{1/2}. \qquad (70)$$

In this case, the corrections to the coefficients at the operator q^2J^2 are on the order of κ with respect to the α-parameters. But because the errors of calculations within the local mode approximation, as is seen from the comparison with the experimental data (for example, in Table 1), are just about several percent, there is no need to consider these corrections in this case.

As to the relationships between the parameters of the stretching vibrations for the substituted and main molecules, from comparison of Eqs. (62) and (64) taking into account that

$$\alpha_1^z = \alpha_1^x = \sqrt{2}\alpha_{13}^{xx} = -\alpha_{13}^{xz} = -\frac{4B_e^2}{\omega} - \left(\frac{2B_e^2}{\omega}\right)^{3/2}\sqrt{6}k_{111},$$

we can easily obtain

$$\alpha_1'^x(XH_2D) = \frac{1}{2}\alpha_1'^x(XHD_2) =$$

$$= \frac{1}{3}\alpha_1^z(XH_3) - \frac{8}{9}\frac{B_e^2}{\omega}\frac{4\theta^2}{4-3\theta^2},$$

$$\alpha_2'^x(XH_2D) = 2\alpha_2'^x(XHD_2) =$$

$$= \frac{2\sqrt{2}}{3}\alpha_1^z(XH_3) - \frac{8\sqrt{2}}{9}\frac{B_e^2}{\omega}\frac{4\theta^2}{2-3\theta^2}, \qquad (71)$$

$$\alpha_1'^z(XH_2D) = 2\sqrt{2}\,\alpha_2'^z(XHD_2) = \frac{3}{2}\alpha_1^z(XH_3),$$

$$\alpha_2'^z(XH_2D) = \alpha_1'^z(XHD_2) = 0,$$

$$\alpha_5'^z(XH_2D) = 2\sqrt{2}\,\alpha_5'^z(XHD_2) =$$

$$= \frac{3}{2}\alpha_1^z(XH_3) - \frac{2B_e^2}{\omega}\frac{4\theta^2}{1-\theta^2}.$$

Experimental spectra for asymmetric isotopomers of XH_3 molecules are poorly studied. On the other hand, the isotopic relationships obtained allow prediction of spectroscopic parameters for such isotopic modifications from already known parameters of the main molecule. Table 8 presents the α parameters calculated by the above equations for the asymmetric isotopomers of the AsH_3 and SbH_3 molecules.

Table 8. Vibrational-rotational parameters $\alpha_\lambda'^\beta$ of asymmetric isotopomers of the AsH_3 and SbH_3 molecules, in cm^{-1}

λ	β	AsH_2D	$AsHD_2$	SbH_2D	$SbHD_2$
1	*x*	0.0112	0.0224	0.0079	0.0158
1	*y*	0.0122	0.0224	0.0079	0.0158
1	*z*	0.0566	0.0000	0.0393	0.0000
2	*x*	0.0310	0.0155	0.0220	0.0110
2	*y*	0.0310	0.0155	0.0220	0.0110
2	*z*	0.0000	0.0200	0.0000	0.0139
3	*x*	−0.0100	−0.0283	−0.0072	−0.0204
3	*y*	−0.0100	−0.0283	−0.0072	−0.0204
3	*z*	0.0588	0.0208	0.0401	0.0142
4	*x*	−0.0036	0.0010	−0.0031	0.0002
4	*y*	0.0074	−0.0023	0.0040	−0.0026
4	*z*	−0.0510	−0.0121	−0.0372	−0.0088
5	*x*	0.0112	0.0155	0.0079	0.0110
5	*y*	0.0112	0.0155	0.0079	0.0110
5	*z*	0.0438	0.0155	0.0315	0.0110
6	*x*	0.0074	−0.0023	0.0040	−0.0026
6	*y*	−0.0036	0.0010	−0.0031	0.0002
6	*z*	−0.0510	−0.0121	−0.0372	−0.0088

In this case, the equilibrium rotational constants have the values given in Table 9. The data from Refs. 22–26 were taken as the initial ones. It should also be mentioned that the above isotopic relationships were used to study IR spectra of the PH_2D molecule.[32]

Table 9. Equilibrium rotational parameters of asymmetric isotopomers of the AsH_3 and SbH_3 molecules, in cm^{-1}

Parameter	AsH_2D	$AsHD_2$	SbH_2D	$SbHD_2$
B_z^e	3.80	1.90	2.97	1.49
B_x^e	2.53	2.53	1.98	1.98
B_y^e	2.53	2.53	1.98	1.98

It is known that the coefficients $\tau'_{\alpha\beta\gamma\delta}$ at the rotational quantum number J raised to the fourth power are calculated by the general equation (34). In the case of a simple model, we have $B_x^e = B_y^e$. Thus, A-reduction cannot be used because of the difference $B_x^e - B_y^e$ in the denominators of the equations for the parameters D' of the reduced Watson Hamiltonian (38) (Ref. 11). In this case, one has to use the so-called symmetric top reduction (or S-reduction) proposed by Winnewisser[27] and Van Eijck.[28] This reduction is obtained through removal of all terms depending on J_z and including the matrix elements $|\Delta k| > 0$ from Eq. (37). The reduced Hamiltonian can be written, accurate to the fourth-power terms, as[11]:

$$H_{\text{rot}}^{(S)} = \sum_{\alpha} B_{\alpha}^{(S)} J_{\alpha}^2 - D_J (J^2)^2 - D_{JK} J^2 J_z^2 -$$

$$- D_K J_z^4 + d_1 J^2 (J_+^2 + J_-^2) + d_2 (J_+^2 + J_-^2) + \ldots, \quad (72)$$

where $J_{\pm} = J_x \pm iJ_y$. Finally, we obtain simple relationships for the parameters D':

(a) for XH_2D

$$D_J'^{H_2DX} = \frac{8}{81}\frac{B_e^3}{\omega^2\theta^2}(19\theta^2 + 1),$$

$$D_{JK}'^{H_2DX} = \frac{80}{81}\frac{B_e^3}{\omega^2\theta^2}(3 - 2\theta^2),$$

$$D_K'^{H_2DX} = \frac{4}{81}\frac{B_e^3}{\omega^2\theta^2}(83\theta^2 - 62), \quad (73)$$

$$d_2'^{H_2DX} = \frac{4}{81}\frac{B_e^3}{\omega^2\theta^2}(\theta^2 - 1), \quad d_1'^{H_2DX} = 0.$$

Using then Eqs. (73), we can find the sought parameters and compare them with each other. In this case, it is necessary to know only the semiempirical parameters θ:

$$\frac{D_J'^{H_2DX}}{19\theta^2 + 1} = \frac{D_{JK}'^{H_2DX}}{10(3 - 2\theta^2)} = \frac{2D_K'^{H_2DX}}{83\theta^2 - 62} = \frac{2d_2'^{H_2DX}}{\theta^2 - 1}; \quad (74)$$

(b) for XHD_2

$$D_J'^{HD_2X} = \frac{32}{81}\frac{B_e^3}{\omega^2\theta^2}(4\theta^2 + 1), \; D_{JK}'^{HD_2X} = \frac{16}{81}\frac{B_e^3}{\omega^2\theta^2}(6 + \theta^2),$$

$$D_K'^{HD_2X} = \frac{1}{81}\frac{B_e^3}{\omega^2\theta^2}(63\theta^2 + 128),$$

$$d_2'^{HD_2X} = \frac{16}{81}\frac{B_e^3}{\omega^2\theta^2}(\theta^2 - 1), \; d_1'^{HD_2X} = 0 \quad (75)$$

and

$$\frac{D_J'^{HD_2X}}{8\theta^2 + 2} = \frac{D_{JK}'^{HD_2X}}{6 + \theta^2} = \frac{2D_K'^{HD_2X}}{128 + 63\theta^2} = \frac{2d_2'^{HD_2X}}{\theta^2 - 1}. \quad (76)$$

The centrifugal distortion parameters calculated by these equations for asymmetric isotopomers of the AsH_3 and SbH_3 molecules are given in Table 10.

Table 10. Centrifugal distortion parameters of the ground vibrational state of asymmetric isotopomers of the AsH_3 and SbH_3 molecules, in cm^{-1}

Parameter	AsH_2D	$AsHD_2$	SbH_2D	$SbHD_2$
$D_J \cdot 10^4$	0.71	2.77	1.68	2.63
$D_{JK} \cdot 10^4$	15.1	7.18	10.2	4.76
$D_K \cdot 10^4$	−13.3	10.2	−9.12	−6.70
$d_1 \cdot 10^4$	0.00	0.00	0.00	0.00
$d_2 \cdot 10^4$	−0.23	−0.92	−0.16	−0.64

Consider then the parameters x_{kl} corresponding to the stretching vibrations. Since the three stretching coordinates are arranged so that two of them form a couple of vibrations located along the X–H (XH_2D) or X–D (XHD_2) bonds, as in the case with the XH_2 molecule, and the third one experiences a very weak (zero in the limit) effect from the first two, we have the following equations:

$$x'_{11}(XH_2D) = \frac{1}{4}x'_{15}(XH_2D) = x'_{55}(XH_2D) =$$

$$= x'_{22}(XH_2D) = 2x'_{22}(XHD_2) = 2x'_{35}(XHD_2) =$$

$$= \frac{1}{2}x'_{25}(XHD_2) = \frac{1}{2}x'_{11}(XHD_2) =$$

$$= \frac{3}{2}x_{11}(XH_3) = \frac{9}{4}\left\{k_{1111} - \frac{5}{2}\frac{k_{111}^2}{\omega}\right\}, \quad (77)$$

$$x'_{12}(XH_2D) = x'_{25}(XHD_2) = x'_{12}(XHD_2) =$$

$$= x'_{15}(XHD_2) = 0,$$

where k_{1111} is the fourth-order anharmonic constant of the potential function of the XH_3 molecule.

For the case that one index corresponds to a stretching vibration, while the other one to the deformation vibration, the relationships between the parameters take the following form:

$$x'_{13}(XH_2D) = 2x'_{23}(XHD_2) = \frac{3}{2}x_{12}(XH_3),$$

$$x'_{35}(XH_2D) = 2x'_{35}(XHD_2) = \frac{3}{2}x_{23}(XH_3) +$$
$$+\frac{B_e}{\theta}(1-3\theta^2) + \frac{3}{8}\frac{k^2_{122}}{\omega}\left(\frac{1}{2\theta+1}+\frac{1}{2\theta-1}\right),$$
$$x'_{14}(XH_2D) = x'_{16}(XH_2D) = x'_{45}(XH_2D) =$$
$$= x'_{56}(XH_2D) = \frac{1}{2}x'_{14}(XHD_2) =$$
$$= \frac{1}{2}x'_{16}(XH_2D) = \frac{B_e}{6\sqrt{3}\theta}(19\theta^2-4) +$$
$$+3\theta k_{111}\sqrt{\frac{B_e}{\omega}} + \frac{2B_e}{9\sqrt{3}\theta}\frac{(2-3\theta^2)^2}{1-3\theta^2}, \qquad (78)$$

$$x'_{24}(XH_2D) = x'_{26}(XH_2D) = 2x'_{24}(XHD_2) =$$
$$= 2x'_{45}(XHD_2) = 2x'_{26}(XHD_2) =$$
$$= 2x'_{56}(XHD_2) = \frac{5\sqrt{2}}{3\sqrt{3}}B_e\theta +$$
$$+\frac{3}{\sqrt{2}}\theta k_{111}\sqrt{\frac{B_e}{\omega}} + \frac{2B_e}{9\sqrt{6}\theta}\frac{(1-3\theta^2)^2}{1-6\theta^2},$$
$$x'_{23}(XH_2D) = x'_{13}(XHD_2) = 0.$$

And, finally, when both indices correspond to a deformation vibration, we have the following equations:

(a) for XH_2D:

$$x'_{33} = -\frac{3}{8}\frac{B_e}{\theta^2}(8\theta^2-1) - \frac{3}{4}\frac{k^2_{122}}{\omega} - \frac{3}{16}\frac{k^2_{122}}{\omega}\left\{\frac{1}{2\theta+1}-\frac{1}{2\theta-1}\right\},$$

$$x'_{44} = x'_{66} = -\frac{1}{144}\frac{B_e}{\theta^2}(233\theta^2-36) -$$
$$-\frac{1}{18}\frac{B_e}{\theta^2}\left\{(2-3\theta^2)^2\frac{1-2\theta^2}{1-3\theta^2} + \frac{1}{2}(1-3\theta^2)^2\frac{1-4\theta^2}{1-6\theta^2}\right\},$$

$$x'_{34} = x'_{36} = -\frac{1}{36\sqrt{3}}\frac{B_e}{\theta^2}(151\theta^2-24) -$$
$$-\frac{1}{3\sqrt{3}}\frac{B_e}{\theta^2}(1-2\theta^2)(2-3\theta^2), \qquad (79)$$

$$x'_{46} = -\frac{1}{54}\frac{B_e}{\theta^2}(207\theta^2-50) -$$
$$-\frac{2}{9}\frac{B_e}{\theta^2}(2-3\theta^2)^2\frac{1-2\theta^2}{1-3\theta^2} - \frac{1}{27}\frac{B_e}{\theta^2}(1-3\theta^2)^2;$$

(b) for XHD_2

$$2x'_{33} = -\frac{3}{8}\frac{B_e}{\theta^2}(8\theta^2-1) - \frac{3}{4}\frac{k^2_{122}}{\omega} - \frac{3}{16}\frac{k^2_{122}}{\omega}\left\{\frac{1}{2\theta+1}-\frac{1}{2\theta-1}\right\},$$

$$x'_{44} = x'_{66} = -\frac{1}{72}\frac{B_e}{\theta^2}(161\theta^2-33) -$$
$$-\frac{1}{9}\frac{B_e}{\theta^2}\left\{(2-3\theta^2)^2\frac{1-2\theta^2}{1-3\theta^2} + \frac{1}{8}(1-3\theta^2)^2\frac{1-4\theta^2}{1-6\theta^2}\right\} - \frac{49B_e}{120},$$

$$x'_{34} = x'_{36} = -\frac{1}{90\sqrt{6}}\frac{B_e}{\theta^2}(158\theta^2-15) -$$
$$-\frac{1}{6\sqrt{6}}\frac{B_e}{\theta^2}(1-2\theta^2)(2-3\theta^2), \qquad (80)$$

$$x'_{46} = -\frac{1}{54}\frac{B_e}{\theta^2}(102\theta^2-35) -$$
$$-\frac{4}{9}\frac{B_e}{\theta^2}(2-3\theta^2)^2\frac{1-2\theta^2}{1-3\theta^2} - \frac{1}{9}\frac{B_e}{\theta^2}(1-3\theta^2)^2.$$

The resonance term is separated explicitly in the equations for x'_{33}. This should be kept in mind, when considering the Fermi resonance $\theta \to 1/2$.

Thus, using the XH_2 and XH_3 molecules as a case study, we have demonstrated new prospects of using the results of the extended local mode approximation and the isotopic substitution theory. It should be noted that this does not exhaust the capabilities of this approach, because the theory of isotopic substitution in this case was considered based on the extended local mode approximation, whose application implies fulfillment of the conditions presented in the beginning of this paper. However, similar investigations can be conducted in the case that some of these conditions of the local mode approximation are lifted. For example, the problems of the isotopic substitution theory as applied to the XH_2 molecules with an arbitrary angle between the bonds were considered in Ref. 29.

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