

Some manifestations of the effect of isotopic substitution in axially symmetric XH_3 (C_{3v}) molecules: $\text{XH}_3 - \text{XH}_2\text{D}$

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For axially symmetric XH_3 (C_{3v}) molecules, manifestation of the effect of isotopic substitution followed by reduction of the molecule's symmetry is considered.

Simple isotopic relations for triatomic XH_2 molecules (symmetry C_{2v}) meeting the local-mode approximation and their isotopic species XHD (C_i) and XD_2 (C_{2v}) were derived by us earlier.¹⁻⁴ These relations agree well with the results of analysis of experimental rotational-vibrational spectra of D_2Se , HDSe , D_2S , and HDS . As a continuation, this work is devoted to analysis of the similar problem for the substitution XH_3 (C_{3v}) - XH_2D (C_s) in axially symmetric tetrahedral molecules meeting the conditions:

(a) the atomic mass ratio $m_{\text{H}}/M_{\text{X}}$ is small;

(b) the equilibrium value of the angle $\text{H} - \text{X} - \text{H}$ is close to $\pi/2$;

(c) the frequencies of stretching vibrations are roughly equal to each other and far larger than those of bending vibrations (i.e., the parameters f_{rr} , $f_{r'}$, $f_{\alpha\alpha}$, and $f_{\alpha\beta}$ are nonzero, and $f_{r\alpha} = f_{r\beta} = 0$).

The molecule PH_3 meets all these conditions rather well.

From general physical principles it is clear that the parameters of different isotopic species must be related, because the species differ only in atomic masses. As was discussed in Ref. 5, from the mathematical point of view, the possibility of obtaining such relations is based on the fact that the constants $l_{N\alpha\mu}$ and $l'_{N\gamma\lambda}$ of the initial and substituted molecules are related to each other as:

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

The subscript N indicates the number of an atom; the parameters $K_{\alpha\gamma}^e$ (the superscript e shows that the parameters corresponds to the equilibrium configuration of the molecule) are elements of the matrix that determines rotation of the fixed molecular coordinate system after isotopic substitution. The parameters $\beta_{\lambda\mu}$ are elements of the matrix inverse to the matrix $\{\alpha_{\lambda\mu}\}$ of transition from the normal vibrational coordinates of the initial molecule to the normal vibrational coordinates of the isotopic specie. The matrix elements of $\alpha_{\lambda\mu}$ are determined as (for detail see Ref. 5):

$$\sum_{\nu} \alpha_{\lambda\nu} \alpha_{\mu\nu} = A_{\lambda\mu} = \sum_{N\alpha} \left(\frac{m_N}{m'_N} \right) l_{N\alpha\lambda} l_{N\alpha\mu}. \quad (2)$$

The parameters $K_{\alpha\gamma}^e$ can be found from the condition of orthogonality of the substituted molecule

$$\sum_{\alpha} K_{\alpha\beta}^e K_{\alpha\gamma}^e = \sum_{\alpha} K_{\beta\alpha}^e K_{\gamma\alpha}^e = \delta_{\beta\gamma} \quad (3)$$

and the equations

$$\sum_{\beta} J_{\alpha\beta}^e K_{\beta\gamma}^e = I'_{\gamma\gamma} K_{\alpha\gamma}^e, \quad (4)$$

where $I'_{\gamma\gamma}$ are equilibrium moments of inertia of the substituted molecule, and $J_{\alpha\beta}^e$ are determined as

$$J_{\alpha\beta}^e = \sum_{\gamma\delta\zeta} \varepsilon_{\alpha\gamma\zeta} \varepsilon_{\beta\delta\zeta} j_{\gamma\delta}^e, \quad (5)$$

$$j_{\gamma\delta}^e = j_{\delta\gamma}^e = \sum_N m'_N r'_{N\gamma} r'_{N\delta} - \frac{\sum_K m'_K r'_{K\gamma} \sum_L m'_L r'_{L\delta}}{\sum_N m'_N}. \quad (6)$$

Here $r'_{N\alpha}$ are Cartesian coordinates determining the equilibrium positions of nuclei about the molecule-fixed coordinate system.

The further usage of Eq. (1) in ordinary equations of the rotation-vibration theory (see, for example, Refs. 6-7) allows deriving isotopic relations for any spectroscopic parameters of the isotopically substituted molecule. However, it should be noted that the equations (1) are generally rather complicated for practical applications, and the parameters in the right-hand side of Eq. (1) can be determined only numerically. This is mostly caused by the fact that the constants $l_{N\alpha\lambda}$ of the initial molecule have a complex form.

At the same time, in Ref. 8 it was shown that the constants $l_{N\alpha\lambda}$ of the initial molecule have a very simple form (for convenience they are given in Table 1), if some XH_3 molecule of symmetry C_{3v} meets the conditions (a)-(c).

Table 1. Constants $l_{N\alpha\lambda}$ for XY_3 molecule in local-mode approximation *

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

* All constants $l_{4\alpha\lambda s}$ are zero.

In this case, we can expect that similar simple relations can be derived from the general equations (1) for the isotopic specie as well.

Let us consider the situation that only one atom H is replaced by the atom D. In this case, the use of the conditions (a)–(c) (Fig. 1) in the general equations (2)–(6) gives the following simple nonzero values for the coefficients $K_{\alpha\gamma}^e$ and $K_{\lambda\mu}^e$:

$$K_{xx}^e = \frac{1}{\sqrt{3}}, \quad K_{xz}^e = -K_{zx}^e = \sqrt{\frac{2}{3}}, \quad (7)$$

$$K_{zz}^e = \frac{1}{\sqrt{3}}, \quad K_{yy}^e = 1;$$

$$\beta_{11} = \sqrt{\frac{2}{3}}, \quad \beta_{21} = \sqrt{\frac{2}{3}}, \quad \beta_{13_1} = -\frac{1}{\sqrt{3}},$$

$$\beta_{23_1} = \frac{2}{\sqrt{3}}, \quad \beta_{53_2} = 1, \quad (8)$$

$$\beta_{32} = \frac{1}{\sqrt{3}}, \quad \beta_{42} = \frac{2\sqrt{2}}{3}, \quad \beta_{34_1} = -\sqrt{\frac{2}{3}},$$

$$\beta_{44_1} = \frac{2}{3}, \quad \beta_{64_2} = \frac{2}{\sqrt{3}}.$$

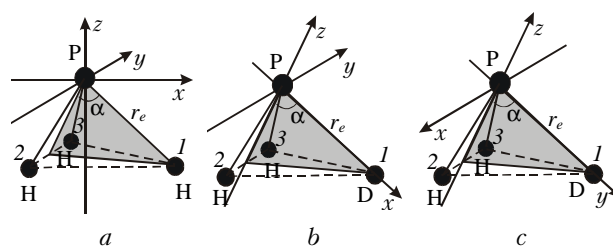


Fig. 1

If we now substitute these results and the values of the constants $l_{N\alpha\lambda}$ of the initial XH_3 molecule from Table 1 to the general equation (1), then we obtain very simple results for the constants $l'_{N\alpha\lambda}$ of the isotopic specie XH_2D . It should be noted that equations (7) describe rotation of the axes of the molecular coordinate system from the configuration shown in Fig. 1a to the configuration shown in Fig. 1b. At the same time, as was already discussed in Ref. 9, for the molecule PH_2D the coordinate axes should be oriented as shown in Fig. 1c. This means that the subscripts α of the constants $l'_{N\alpha\lambda}$ should be re-denoted in accordance with the direction of axes in Fig. 1c. The obtained values of the constants $l'_{N\alpha\lambda}$ are given in Table 2.

The data from Table 2 are then used for derivation of equations for various parameters (such, for example, as the Coriolis constants $\zeta_{\lambda\mu}^{\alpha}$, rotational-vibrational coefficients $a_{\lambda}^{\alpha\beta}$, and others). Below we present the obtained nonzero Coriolis constants $\zeta_{\lambda\mu}^{\alpha}$ and rotational-vibrational coefficients $a_{\lambda}^{\alpha\beta}$:

$$\zeta_{14}^x = -\zeta_{24}^x = -\zeta_{34}^x = \zeta_{56}^x = -\zeta_{16}^z = \zeta_{26}^z = -\zeta_{36}^z = \zeta_{45}^z = -1/\sqrt{3},$$

$$\zeta_{35}^y = -1, \quad \zeta_{46}^y = 1/3; \quad (9)$$

$$\alpha_1^{xx} = \alpha_1^{yy}/2 = \alpha_1^{zz} = \alpha_1^{zz}/2 =$$

$$= -\alpha_3^{xx} = \alpha_3^{zz} = -\alpha_5^{xz} = -\alpha_5^{zx} = \sqrt{2m_H r_e^2}, \quad (10)$$

$$\alpha_4^{yz} = \alpha_4^{zy} = \alpha_6^{xy} = \alpha_6^{yx} = -2\sqrt{2m_H r_e^2}/\sqrt{3}.$$

Table 2. Nonzero constants $l_{N\alpha\lambda}$ for XH_2D molecule in the local-mode approximation *

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

* All constants $l_{4\alpha\lambda}$ are zero.

Equations (9) and (10), in their turn, can be used for determination of various spectroscopic parameters. In particular, below we present the obtained isotopic relations between the rotational-vibrational coefficients $a_{\lambda}^{\alpha\beta}$ connected with the bending vibrations $\lambda = 3, 4, 5$ (in this case the model of the potential function used for the PH₂D molecule is the same as for the PH₃ molecule⁸):

$$\begin{aligned}\alpha_3^x &= \alpha_3^z = \frac{8}{9} \frac{Be^2}{\omega\theta} (\theta^2 - 1), \\ \alpha_4^x &= \alpha_6^z = \frac{4}{27\sqrt{3}} \frac{Be^2}{\omega\theta} \times \\ &\times \left\{ (42\theta^2 - 23) + \frac{16}{27\sqrt{3}} \left(\frac{4 + 9\theta^2}{4 - 3\theta^2} + \frac{2 + 9\theta^2}{2 - 3\theta^2} \right) \right\}, \\ \alpha_6^x &= \alpha_4^z = \frac{28}{9\sqrt{3}} \frac{Be^2}{\omega\theta} \left\{ (2\theta^2 - 1) + \frac{16}{27\sqrt{3}} \left(\frac{4 + 9\theta^2}{4 - 3\theta^2} \right) \right\}, \\ \alpha_3^y &= 4 \frac{Be^2}{\omega\theta} \left(\frac{3 - \theta^2}{1 - \theta^2} \right) \theta^2, \\ \alpha_4^y &= \alpha_6^y = \frac{4}{3\sqrt{3}} \frac{Be^2}{\omega\theta} (3\theta^2 - 4).\end{aligned}\quad (11)$$

Table 3. Some spectroscopic parameters for molecule PH₂D, in cm⁻¹

Parameter	Calc. by Eq. (11)	Exp. from Ref. 10
B_{43}^x	- 1.72	- 2.07
C_{46}^x	1.45	1.63
A_{36}^x	1.60	1.54
α_3^x	- 0.0145	0.0005
α_3^y	0.0460	0.0490
α_3^z	- 0.0145	0.0080
α_4^x	0.0040	0.0028
α_4^y	- 0.0437	- 0.0392
α_4^z	- 0.0085	- 0.0084
α_6^x	- 0.0085	- 0.0089
α_6^y	- 0.0437	- 0.0384
α_6^z	0.0040	0.0092

The values of the rotational-vibrational coefficients $\alpha_{\lambda}^{\alpha\beta}$ obtained from Eqs. (11) are given in the second column of Table 3. The third column gives the experimental values of these parameters from Ref. 10. One can see a good agreement between the calculated coefficients $\alpha_{\lambda}^{\alpha\beta}$ and the experimental data.

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