On isotopic effect in XH_2 (C_{2v}) molecules with arbitrary value of equilibrium angle α_e: $XH_2 \to XHD$

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Some manifestations of the effect of isotopic substitution reducing the symmetry of a molecule are considered as applied to triatomic molecules XH_2 (C_{2v}) with an arbitrary value of the equilibrium angle α_e.

The knowledge of relations between some or other spectroscopic parameters of molecules proves to be useful in solution of various practical problems of high-resolution molecular spectroscopy. Among wide variety of such relations, isotopic relations occupy a particular place, because they allow the spectroscopic properties of isotopically substituted molecules to be predicted based on the properties of the "parent" molecule.

In Ref. 1, the known information was generalized and the theory of isotopic substitution was developed as applied to arbitrary multiatomic molecules. However, it turned out that simple and convenient isotopic relations can be obtained within the framework of the developed theory only in the case that heavy enough nuclei are substituted ($|(m'_N - m_N)/m_N| \ll 1$) or in the case that the symmetry of a molecule does not change after substitution. For a great number of molecules interesting from the spectroscopic point of view (in the first turn, molecules containing hydrogen atoms), the results obtained in Ref. 1 proved to be inapplicable to a great degree.

In Refs. 2–5, the above-mentioned problem was partially solved for XH_2 (C_{2v}) molecules based on the advanced local-mode model developed earlier.[6] For the case of $XH_2 \to XHD$ isotopic substitution, numerous simple relations were obtained for different spectroscopic parameters. These relations have demonstrated their high predicting capability in analysis of actual high-resolution spectra. However, it should be noted that the significant restriction of the model used in Refs. 2–5 is the requirement that the equilibrium angle $2\alpha_e$ between the X–H bonds be close to 90°.

In this paper, we present the results of the similar study aimed at derivation of possible isotopic relations for a molecule with an arbitrary equilibrium angle $2\alpha_e$. Here we assume that

1) the H/X mass ratio is small enough and tends to zero;

2) the interaction between bending and stretching modes in the square part of the intramolecular potential function is weak ($f_{r\alpha}/f_{rr}$ is small). This condition is fulfilled with a good accuracy for the known molecules of this type.

If the above conditions hold, then it can be readily shown that the following relations are valid for the XH_2 molecule:

$$B_x^{\mathrm{e}} = \frac{B^{\mathrm{e}}}{2\sin^2\alpha_{\mathrm{e}}}\,,\quad B_z^{\mathrm{e}} = \frac{B^{\mathrm{e}}}{2\cos^2\alpha_{\mathrm{e}}}\,,\quad 2B_y^{\mathrm{e}} = B^{\mathrm{e}}\,; \tag{1}$$

$$\zeta_{13}^y = \zeta_{31}^y = 0\,,\quad \zeta_{23}^y = -\zeta_{32}^y = 1\,; \tag{2}$$

$$\begin{gathered}\frac{a_1^{xx}}{\sin^2\alpha_{\mathrm{e}}} = \frac{a_1^{zz}}{\cos^2\alpha_{\mathrm{e}}} = \frac{a_2^{xx}}{\cos\alpha_{\mathrm{e}}\sin\alpha_{\mathrm{e}}} = -\frac{a_2^{zz}}{\cos\alpha_{\mathrm{e}}\sin\alpha_{\mathrm{e}}} = \\ = \frac{a_2^{xz}}{\cos\alpha_{\mathrm{e}}\sin\alpha_{\mathrm{e}}} = -\frac{a_1^{yy}}{2};\quad a_2^{yy} = 0,\end{gathered} \tag{3}$$

where B_α^{e} are equilibrium rotational constants; $\zeta_{\lambda\mu}^{\alpha}$ and $a_\lambda^{\alpha\beta}$ are the Coriolis and rotational-vibrational coefficients of the parent molecule (it should be noted that Eqs. (1)–(3) are derived on the assumption $m_{\mathrm{H}}/m_{\mathrm{X}} \ll 1$).

If now we substitute Eqs. (1)–(3) into the ordinary equations of the rotational-vibrational theory, for example, from Refs. 7 and 8, then after some transformations we obtain the following simple relations for the parent molecule:

$$\alpha_1^x \sin^4\alpha_{\mathrm{e}} + \alpha_1^z \cos^4\alpha_{\mathrm{e}} = \alpha_1^y\,, \tag{4}$$

$$\alpha_3^x \sin^4\alpha_{\mathrm{e}} + \alpha_3^z \cos^4\alpha_{\mathrm{e}} = \alpha_1^y + \frac{2B_{\mathrm{e}}^2}{\omega}\,\frac{1}{1-\theta^2}\,, \tag{5}$$

$$\alpha_3^y = \alpha_1^y - \frac{2B_{\mathrm{e}}^2}{\omega}\,\frac{\theta^2}{1-\theta^2}\,, \tag{6}$$

$$\alpha_2^y = \frac{2B_{\mathrm{e}}^2}{\omega}\,\frac{(3-\theta^2)\theta}{(1-\theta^2)}\,, \tag{7}$$

$$\alpha_2^x \sin^4\alpha_{\mathrm{e}} + \alpha_2^z \cos^4\alpha_{\mathrm{e}} = \frac{B_{\mathrm{e}}^2}{\omega\theta}(\theta^2 - 2)\,. \tag{8}$$

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Here $\omega = (\omega_1 + \omega_3)/2$; θ is an empiric parameter. To illustrate the correctness of the obtained equations (4)–(8), Table 1 presents the results calculated with them for the H_2O molecule, in which the equilibrium angle $2\alpha_e$ is about 104.5° (see Ref. 12) (i.e., it differs markedly from 90°). In the calculations, we used the following values for the parameters entering into Eqs. (4)–(8):

$$\omega = 3887.59\ \text{cm}^{-1};\ \theta = 0.4237;$$

$$B_e = \frac{\hbar}{4\pi c m r_e^2} = 18.402\ \text{cm}^{-1}.$$

Table 1. Relations (4)–(8) between rotational-vibrational parameters of the H_2O molecule, cm^{-1}

Equation	Left-hand side	Right-hand side
(4)	0.191	0.173
(5)	0.208	0.211
(6)	0.139	0.135
(7)	−0.351	−0.374
(8)	0.149	0.127

As is seen from Table 1, the used model gives a sufficiently correct result for the parent molecule. This gives promise that for the isotopically substituted (deuterated) modifications of the molecule it is also possible to derive sufficiently simple and correct relations between spectroscopic (in the considered case, rotational-vibrational $a_\lambda^{\alpha\beta}$) parameters.

Table 2. Constants $l_{N\alpha\lambda}$ for the HDO molecule

$l'_{N\alpha\lambda}$	Value	$l'_{N\alpha\lambda}$	Value
l'_{1x2}	$\sqrt{2/3}\sin(\alpha_e + \chi)$	l'_{1x3}	$\cos(\alpha_e + \chi)$
l'_{1z3}	$-\sin(\alpha_e + \chi)$	l'_{1z2}	$-\sqrt{2/3}\cos(\alpha_e + \chi)$
l'_{2x2}	$\sqrt{1/3}\sin(\alpha_e - \chi)$	l'_{2x1}	$-\cos(\alpha_e - \chi)$
l'_{2z1}	$\sin(\alpha_e - \chi)$	l'_{2z2}	$\sqrt{1/3}\cos(\alpha_e - \chi)$

Let us consider here the most complex case of isotopic substitution $XH_2 \to XHD$, in which the symmetry of the molecule changes. Using the procedure described in Refs. 2–5, we can show that if the equilibrium angle $2\alpha_e$ differs from $\pi/2$, then for the substituted molecule XHD the coefficients $l'_{N\alpha\lambda}$ have the form shown in Table 2, and for the parameters $\zeta_{\lambda\mu}^{\alpha}$ and $a_\lambda^{\alpha\beta}$ we have

$$\zeta_{12}^{\prime y} = -\zeta_{21}^{\prime y} = \frac{\sqrt{3}}{3};\ \zeta_{23}^{\prime y} = -\zeta_{32}^{\prime y} = \frac{\sqrt{2}}{\sqrt{3}}; \tag{9}$$

$$a_1^{\prime yy} = 2\sqrt{2I_e};\quad a_1^{\prime zz} = \sqrt{2I_e}\,[1 + \cos 2(\alpha - \chi)]; \tag{10}$$

$$\begin{gathered} a_1^{\prime xx} = \sqrt{2I_e}\,[1 - \cos 2(\alpha - \chi)]; \\ a_1^{\prime xz} = a_1^{\prime zx} = \sqrt{2I_e}\,\sin 2(\alpha - \chi); \end{gathered} \tag{11}$$

$$a_2^{\prime xx} = -a_2^{\prime zz} = \frac{\sqrt{2I_e}}{\sqrt{3}}[\sin 2(\alpha + \chi) + \sin 2(\alpha - \chi)]; \tag{12}$$

$$a_2^{\prime xz} = a_2^{\prime zx} = -\frac{\sqrt{2I_e}}{\sqrt{3}}[\cos 2(\alpha + \chi) + \cos 2(\alpha - \chi)]; \tag{13}$$

$$a_3^{\prime xx} = \sqrt{I_e}\,[1 - \cos 2(\alpha + \chi)]; \tag{14}$$

$$a_3^{\prime xz} = a_3^{\prime zx} = -\sqrt{I_e}\,\sin 2(\alpha + \chi); \tag{15}$$

$$a_3^{\prime yy} = 2\sqrt{I_e};\quad a_3^{\prime zz} = \sqrt{I_e}\,[1 + \cos 2(\alpha + \chi)], \tag{16}$$

where $\operatorname{cotan}2\chi = 3\operatorname{cotan}2\alpha_e$. If we use Eqs. (9)–(16) in ordinary equations of the rotational-vibrational theory[7,8] and then compare with the corresponding results (4)–(8) for the parent modification, then we can derive rather simple isotopic relations:

$$\begin{gathered} \alpha_1^{\prime x} = -\frac{\sqrt{2}}{8}\Big[(\alpha_1^x + \alpha_3^x)(1 - \eta)\eta - 8\alpha_1^y(1 - 3\eta^2) - \\ -(\alpha_1^z + \alpha_3^z)(1 + \eta)\eta\Big]; \end{gathered} \tag{17}$$

$$\alpha_1^{\prime y} = \frac{4\sqrt{2}}{9}\alpha_1^y - \frac{8\sqrt{2}B_e^2\theta^2}{9\omega(2 - 3\theta^2)};$$

$$\alpha_1^{\prime z} + 4\alpha_1^{\prime x} = 4\sqrt{2}\alpha_1^y(1 - 2\eta^2); \tag{18}$$

$$\begin{gathered} \alpha_2^{\prime x} = -\frac{\sqrt{3}}{2}\alpha_2^x\eta(1 - 2\eta) - \\ -\frac{\sqrt{3}B_e^2}{9\omega\theta}\Big[7 + 18\eta - 19\eta^2 - \theta^2(3 + 9\eta - 6\eta^2)\Big]; \end{gathered} \tag{19}$$

$$\alpha_2^{\prime y} = \frac{8\sqrt{3}}{9}\,\frac{B_e^2\theta}{\omega}\,\frac{(8 - 12\theta^2 + 3\theta^4)}{(8 - 18\theta^2 + 9\theta^4)}; \tag{20}$$

$$\begin{gathered} \alpha_2^{\prime z} = 2\sqrt{3}\alpha_1^x\eta(1 - 2\eta) - \\ -\frac{4\sqrt{3}B_e^2}{9\omega\theta}\Big[5 - 18\eta + 25\eta^2 - 3\theta^2(1 - 3\eta + 4\eta^2)\Big]; \end{gathered} \tag{21}$$

$$\begin{gathered} \alpha_3^{\prime x} - \sqrt{2}\alpha_1^{\prime x} = -2\alpha_1^y(1 - 5\eta^2), \\ \alpha_3^{\prime y} = \frac{4}{9}\left[\alpha_1^y - \frac{4B_e^2\theta^2}{\omega(4 - 3\theta^2)}\right]; \end{gathered} \tag{22}$$

$$\alpha_3^{\prime z} + 4\sqrt{2}\alpha_1^{\prime x} = 12\alpha_1^y(1 - 2\eta^2). \tag{23}$$

In Eqs. (17)–(23), as well as in Eqs. (9)–(16), the primed parameters correspond to the XHD molecule and non-primed parameters correspond to the parent XH_2 molecule; η denotes $\cos 2\alpha_e$. Table 3 presents the results calculated with the derived equations and, for comparison, the values of the corresponding "experimental" parameters from Refs. 9–11.

It should be noted that Eqs. (17)–(23) have been derived on the assumption that the parameter η ($\eta = -0.25$ for the H_2O molecule) is although nonzero, but much less than unity. So it is reasonable to restrict the series expansions of the parameters in terms of η to the second degree. At the same time, Eqs. (9)–(16) can be used to obtain the analogs of Eqs. (17)–(23) in the more general form (without expansion in terms of η). However, it should be kept in mind that the result will be more cumbersome than Eqs. (17)–(23).

Table 3. Rotational-vibrational parameters of the H_2O molecule, cm^{-1}

Parameter	Experiment[9–11]	Calc.
$\alpha_1'^x$	0.1781	0.182
$\alpha_1'^y$	0.1021	0.113
$\alpha_1'^z$	0.3180	0.267
$\alpha_2'^x$	−0.1337	−0.101
$\alpha_2'^y$	0.0842	0.067
$\alpha_2'^z$	−1.4558	−1.372
$\alpha_3'^x$	0.0119	−0.019
$\alpha_3'^y$	0.0776	0.082
$\alpha_3'^z$	1.0372	1.084

To illustrate the considered approach, below we present the obtained relations that allow the quartic centrifugal distortion constants of the HDX molecule to be estimated based on the known parameters of the parent H_2X molecule:

$$\Delta_J' = \frac{B_e^3}{\omega^2}\left(\frac{5}{8} + \frac{1-3\theta^2}{\theta^2}\eta^2\right), \tag{24}$$

$$\Delta_{JK}' = \frac{B_e^3}{9\omega^2\theta^2}\left[\frac{(96-53\theta^2)}{6} - (227-305\theta^2)\eta^2\right], \tag{25}$$

$$\Delta_K' = -\frac{B_e^3}{9\omega^2\theta^2}\left[\frac{(144-353\theta^2)}{9} - 2(253-139\theta^2)\eta^2\right]; \tag{26}$$

$$\delta_J' = \frac{B_e^3}{2\omega^2}\left(\frac{3}{8} + \frac{1-3\theta^2}{\theta^2}\eta^2\right), \tag{27}$$

$$\delta_K' = \frac{B_e^3}{9\omega^2\theta^2}\left[\frac{(144-371\theta^2)}{18} - (73-139\theta^2)\eta^2\right]. \tag{28}$$

Table 4 illustrates the applicability of the obtained results.

Table 4. Centrifugal distortion parameters for the HDO molecule, in cm^{-1}

Parameter	Experiment[9]	Calc.
Δ_J	0.000361	0.000324
Δ_{JK}	0.0011	0.0009
Δ_K	0.0125	0.005
δ_J	0.00012	0.00011
δ_K	0.0021	0.0022

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References

1. A.D. Bykov, Yu.S. Makushkin, and O.N. Ulenikov, *Isotopic Substitution in Multiatomic Molecules* (Nauka, Novosibirsk, 1985).
2. O.N. Ulenikov, G.A. Onopenko, I.M. Olekhnovitch, S. Alanko, V.-M. Horneman, M. Koivusaari, and R. Anttila, J. Mol. Spectrosc. **189**, 74–82 (1998).
3. O.N. Ulenikov, E.A. Ditenberg, I.M. Olekhnovitch, S. Alanko, M. Koivusaari, and R. Anttila, J. Mol. Spectrosc. **191**, 239–247 (1998).
4. O.N. Ulenikov, G.A. Onopenko, N.E. Tyabaeva, H. Burger, and W. Jerzembeck, J. Mol. Spectrosc. **197**, 100–113 (1999).
5. O.N. Ulenikov, G.A. Onopenko, N.E. Tyabaeva, H. Burger, and W. Jerzembeck, J. Mol. Spectrosc. **198**, 27–39 (1999).
6. O.N. Ulenikov, R.N. Tolchenov, and Qing-shi Zhu, Spectrochim. Acta **A52**, 1829–1841 (1996).
7. H.H. Nielsen, Rev. Mod. Phys. **23**, 90–135 (1951).
8. D. Papoušek and M.R. Aliev, *Molecular Vibrational-Rotational Spectra* (Elsevier, Amsterdam–Oxford–New York, 1982).
9. V.D. Gupta, R. Sethi, K.K. Biswas, and V. Dixit, J. Phys. B: Mol. Phys. **15**, 4541 (1982).
10. A. Perrin, J.-M. Flaud, and C. Camy-Peyret, J. Mol. Spectrosc. **112**, 153 (1985).
11. R.A. Toth, V.D. Gupta, and J.W. Brault, Appl. Opt. **21**, 3337 (1982).
12. L.M. Sverdlov, M.A. Kovner, and E.P. Krainov, *Vibrational Spectra of Multiatomic Molecules* (Nauka, Moscow, 1970).