

AN APPROXIMATION METHOD FOR EVALUATING CENTRIFUGAL DISTORTION CONSTANTS IN XH_2 BENT SYMMETRIC MOLECULES

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It is shown that the condition τ_{xxxx} being a minimum with respect to F_{12} corresponds to setting $L_{21} = 0$ in XY_2 bent symmetric molecules. Expressions for the $\tau_{\alpha\beta\gamma\delta}$ elements under this condition involve only the molecular geometry, atomic masses and fundamental vibrational frequencies. The $\tau_{\alpha\beta\gamma\delta}$ elements calculated within this approximation compare favourably with the experimental values for hydride molecules.

The centrifugal distortion constants $\tau_{\alpha\beta\gamma\delta}$ in molecules are related to quantities $t_{\alpha\beta\gamma\delta}$ through [1]

$$t_{\alpha\beta\gamma\delta} = -2I_{\alpha\alpha}^e I_{\beta\beta}^e I_{\gamma\gamma}^e I_{\delta\delta}^e \tau_{\alpha\beta\gamma\delta} \quad (1)$$

Here $\alpha, \beta, \gamma, \delta = x, y$ or z and $I_{xx}^e, I_{yy}^e, I_{zz}^e$ are the principal moments of inertia at equilibrium. In a modified method given by Cyvin [2-4] to calculate these constants, the $t_{\alpha\beta\gamma\delta}$ elements are given by the matrix relation

$$t = \tilde{T}_s G^{-1} F^{-1} G^{-1} T_s \quad (2)$$

The elements of the T_s matrix can be calculated for a given molecular model from the equilibrium position vector and Wilson's S vectors. G^{-1} and F are the kinetic energy and force constant matrices respectively [5]. Use of the T_s matrix given by Cyvin [3] for the XY_2 bent symmetric molecular type, in eq. (2) yields

$$t_{xxxx} = \frac{8R^2}{\Lambda_1 \Lambda_2 |G|} (G_{22}^2 F_{22} + G_{12}^2 F_{11} + 2G_{12} G_{22} F_{12}) \quad (3)$$

Here, R refers to the X-Y bond length. Λ_i are obtained from the vibration frequencies [5] and form elements of a diagonal matrix Λ .

The sum of the roots of the secular equation $|\mathbf{GF} - \Lambda\mathbf{E}| = 0$ in the 2×2 case is [5]

$$\Lambda_1 + \Lambda_2 = G_{11} F_{11} + G_{22} F_{22} + 2G_{12} F_{12} \quad (4)$$

Substituting for F_{22} from eq. (4) into eq. (3) and then differentiating with respect to F_{12} gives

$$dt_{xxxx}/dF_{12} = -(8R^2/\Lambda_1 \Lambda_2) dF_{11}/dF_{12} \quad (5)$$

It is well known that F_{11} is a maximum with respect to F_{12} when $L_{21} = 0$ [6-8] and that $(F_{11})_{\max}$ corresponds to almost the "correct" force field for hydride molecules [9]. Together with these results, eq. (5) leads to the conclusion that the t_{xxxx} element attains a minimum when $L_{21} = 0$ and that $(t_{xxxx})_{\min}$ would correspond very closely to its true value.

Expressions for the $t_{\alpha\beta\gamma\delta}$ elements have been evaluated by employing the F_{ij} elements at $L_{21} = 0$ [7] in eq. (2) and are given below:

$$t_{xxxx} = A \Lambda_1^{-1},$$

$$t_{yyyy} = A \Lambda_1^{-1} \cos^4(\alpha/2)$$

$$+ B[C + 2^{3/2} G_{12} \cos^2(\alpha/2)] \Lambda_1^{-1} + D \Lambda_2^{-1},$$

Table 1

Centrifugal distortion constants corresponding to $(\tau_{xxxx})_{\min}$ compared with their experimental values for H₂O, H₂S and H₂Se

Molecule (xxxx)	(yyyy)	(zzzz)	(xxyy)	(xxzz)	(yyzz)	Ref. for data	
H ₂ O	-0.00104 (-0.00107 ± 0.00027)	-0.09281 (-0.1084 ± 0.0012)	-0.009212 (-0.0083 ± 0.0012)	-0.002975 (-0.00491)	-0.00158 (-0.00108)	0.001936 (0.01985)	[10]
H ₂ S	-7.94 (-8.03)	-241.9 (-247.56)	-145.6 (-151.25)	-17.6	-14.84	123.7 (123.66)	[11]
H ₂ Se	5.057	-140.49 (-141.8 ± 0.9)	119.0 (121.977)	-9.988	9.317	87.38 (90.036)	[12]

a) For H₂S and H₂Se the results given are the $\tau_{\alpha\beta\gamma\delta}$ elements (in MHz) while for H₂O the results given are the $T_{\alpha\beta\gamma\delta}$ elements (in cm⁻¹) so as to enable direct comparison with the experimental values, given within brackets. The two sets of constants are related [3] by $T_{\alpha\beta\gamma\delta} = (h^3/16\pi^4 c) \tau_{\alpha\beta\gamma\delta}$.

$$t_{zzzz} = A \Lambda_1^{-1} \sin^4(\alpha/2) + B[C - 2^{3/2} G_{12} \sin^2(\alpha/2)] \Lambda_1^{-1} + D \Lambda_2^{-1},$$

$$t_{xxyy} = A \Lambda_1^{-1} \cos^2(\alpha/2) + 2^{1/2} B G_{12} \Lambda_1^{-1},$$

$$t_{xxzz} = A \Lambda_1^{-1} \sin^2(\alpha/2) - 2^{1/2} B G_{12} \Lambda_1^{-1},$$

$$t_{yyzz} = (A/4) \Lambda_1^{-1} \sin^2 \alpha - B(C + 2^{1/2} G_{12} \cos \alpha) \Lambda_1^{-1} - D \Lambda_2^{-1},$$

$$t_{yzyz} = (2R^2/G_{33}) \sin^2 \alpha \Lambda_3^{-1}.$$

Here α denotes the YXY angle, $A = 8R^2 G_{22}/|G|$, $B = 4R^2 \sin \alpha/|G|$, $C = G_{12}^2 \sin \alpha/G_{22}$ and $D = 4R^2 \sin^2 \alpha/G_{22}$.

The expressions involve only the molecular geometry, atomic masses and the fundamental vibrational frequencies. The $\tau_{\alpha\beta\gamma\delta}$ elements can now be calculated from the $t_{\alpha\beta\gamma\delta}$ elements using eq. (1). Since the $\tau_{\alpha\beta\gamma\delta}$ elements are directly related to the $t_{\alpha\beta\gamma\delta}$ elements through the principal moments of inertia of the molecule, the present results indicate that the minimisation of τ_{xxxx} corresponds to $L_{21} = 0$ and this, in turn, provides an excellent criterion for evaluating the centrifugal distortion constants in bent symmetric hydride molecules. The results of calculations using these expressions are compared with the actual experimental values of the centrifugal distortion constants for a

few XH₂ molecules and are listed in table 1.

It is worth noting that the present method will be of definite advantage to the microwave spectroscopist since the method yields values of centrifugal distortion constants very near the actual ones without recourse to a detailed force field analysis.

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