

VIBRATION-ROTATION HAMILTONIAN OF ZXY₃ AND XY₃ MOLECULES OF C_{3V} SYMMETRY

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The dependence of all the values comprising an exact vibration-rotation Hamiltonian on the structural and dynamic parameters of a molecule is obtained in an explicit form for the axially symmetric molecules of ZXY₃ and XY₃ type.

Knowledge of a correct vibration-rotation Hamiltonian of a molecule is very important for solving almost any problem of vibration-rotation spectroscopy of molecules. In the general case for a normal (i.e., nonlinear with the vibrations of only small amplitude) molecule such a Hamiltonian is well known¹⁻³:

$$\begin{aligned} \frac{H}{hc} = & \frac{1}{2} \sum_{\lambda} \omega_{\lambda} (p_{\lambda}^2 + q_{\lambda}^2) + \\ & + \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} (J_{\alpha} - G_{\alpha}) (J_{\beta} - G_{\beta}) + \\ & + \frac{h^2}{32 \pi^2} \sum_{\alpha} \mu_{\alpha\alpha} + \sum_{\lambda\mu\nu} k_{\lambda\mu\nu} q_{\lambda} q_{\mu} q_{\nu} + \\ & + \sum_{\lambda\mu\nu\xi} k_{\lambda\mu\nu\xi} q_{\lambda} q_{\mu} q_{\nu} q_{\xi} + \dots \end{aligned} \quad (1)$$

In Eq. (1) ω_{λ} and $k_{\lambda\dots\nu}$ are the harmonic frequencies and anharmonicity constants; J_{α} and G_{α} are the operators of the components of the total and vibrational angular momenta, respectively; the third term in Eq. (1) is a small operator depending on vibrational coordinates q_{λ} , which is a small addition to the potential function and, as a rule, it is not considered; G_{α} and $\mu_{\alpha\alpha}$ can be represented as

$$G_{\alpha} = \sum_{\lambda\mu} \zeta_{\lambda\mu}^{\alpha} [(\omega_{\mu}/\omega_{\lambda})^{1/2} q_{\lambda} p_{\mu} - (\omega_{\lambda}/\omega_{\mu})^{1/2} q_{\mu} p_{\lambda}]; \quad (2)$$

$$\begin{aligned} \frac{1}{2} \mu_{\alpha\beta} = & \frac{1}{2} \left(\mu_{\alpha\beta}^e + \sum_{\alpha\beta\lambda} \mu_{\alpha\beta}^{\lambda} q_{\lambda} + \sum_{\alpha\beta\lambda\mu} \mu_{\alpha\beta}^{\lambda\mu} q_{\lambda} q_{\mu} + \dots \right) = \\ = & B_{\alpha}^e \delta_{\alpha\beta} - \sqrt{2} \sum_{\lambda} \frac{B_{\alpha}^e B_{\beta}^e}{\omega_{\lambda}^{1/2}} \left(\frac{8\pi^2 c}{h} \right)^{1/2} a_{\lambda}^{\alpha\beta} q_{\lambda} + \\ & + \frac{3}{2} \sum_{\gamma\lambda\mu} \left(\frac{B_{\alpha}^e B_{\beta}^e B_{\gamma}^e}{\omega_{\lambda}^{1/2} \omega_{\mu}^{1/2}} \right) \frac{8\pi^2 c}{h} a_{\lambda}^{\alpha\gamma} a_{\mu}^{\gamma\beta} q_{\lambda} q_{\mu} + \dots \end{aligned} \quad (3)$$

In this case the equilibrium rotational constants B_{α}^e , the Coriolis constants $\zeta_{\lambda\mu}^{\alpha}$, and the parameters $a_{\lambda}^{\alpha\beta}$ depend only on the parameters of equilibrium configuration of the molecule $r_{N\alpha}^e$, which can be expressed via the

equilibrium bond lengths and the angles between them, nuclear masses, and transformation coefficients $l_{N\alpha\lambda}$:

$$\zeta_{\lambda\mu}^{\alpha} = \sum_N (l_{N\beta\lambda} l_{N\gamma\mu} - l_{N\gamma\lambda} l_{N\beta\mu}); \quad (4)$$

$$a_{\lambda}^{\alpha\alpha} = 2 \sum_N m_N^{1/2} (l_{N\beta\lambda} r_{N\beta}^e + l_{N\gamma\lambda} r_{N\gamma}^e); \quad (5)$$

$$a_{\lambda}^{\alpha\beta} = -2 \sum_N m_N^{1/2} l_{N\alpha\lambda} r_{N\beta}^e, \quad \alpha \neq \beta; \quad (6)$$

$$\begin{aligned} B_{\alpha}^e = & (h/8\pi^2 c) (I_{\alpha\alpha}^e)^{-1} = \\ = & (h/8\pi^2 c) \left\{ \sum_N m_N [(r_{N\beta}^e)^2 + (r_{N\gamma}^e)^2] \right\}^{-1}. \end{aligned} \quad (7)$$

In Eqs. (4)–(7) $\alpha \neq \beta \neq \gamma$. The equilibrium parameters $r_{N\alpha}^e$ can be determined from the relationships

$$\sum_N m_N r_{N\alpha}^e = 0, \quad \sum_N m_N r_{N\alpha}^e r_{N\beta}^e = 0 \quad \text{for } \alpha \neq \beta. \quad (8)$$

To determine the constants $l_{N\alpha\lambda}$, one should use the Eckart conditions

$$\sum_N m_N^{1/2} l_{N\alpha\lambda} = 0, \quad (9)$$

$$\sum_N m_N^{1/2} (l_{N\alpha\lambda} r_{N\beta}^e - l_{N\beta\lambda} r_{N\alpha}^e) = 0 \quad (10)$$

and the conditions of orthogonality

$$\sum_{N\alpha} l_{N\alpha\lambda} l_{N\alpha\mu} = \delta_{\lambda\mu}, \quad (11)$$

as well as the conditions for second derivatives of the potential function

$$W_{\lambda\mu} \equiv (\partial^2 V / \partial q_{\lambda} \partial q_{\mu})_{q=0} = 0. \quad (12)$$

However, since in the general case the potential function is unknown, it is appropriate to use the symmetry properties of a molecule. Then, if the vibrational coordinates q_{λ} and q_{μ} are transformed by different irreducible representations of the molecule symmetry group, the relations (12) are fulfilled identically. However, if q_{λ} and q_{μ} have the same symmetry, the symmetry properties cannot already be

used for deriving the relationships of Eq. (12) type. As a consequence, the values of $l_{N\alpha\lambda}$ can be determined only as functions of some arbitrary parameters. One can show that in the general case the number of these parameters is equal to the number of different pairs of vibrational coordinates of the same symmetry.

Since in practical applications the form of all the parameters entering into the Hamiltonian or, as minimum, the possible relationships between them should be known, in this paper the problem has been formulated to determine the parameters in Eqs. (2)–(7) for a comprehensive investigation interesting from the standpoint of analysis of different intramolecular effects and interactions in the class of molecules of ZXY_3 type of C_{3V} symmetry.

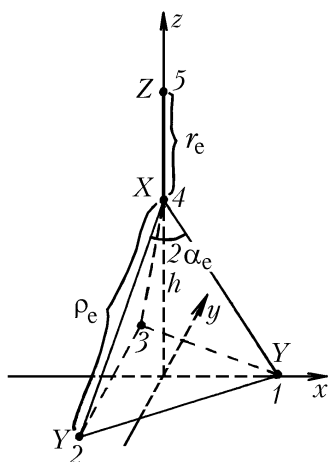


FIG.1. Positions of axes and nuclei of ZXY_3 molecule of C_{3V} symmetry.

Having recognized that all the values entering into Eqs. (2)–(7) are the functions of the parameters $l_{N\alpha\lambda}$ and $r_{N\alpha}^e$, first of all, it is necessary to determine these parameters from Eqs. (8)–(11) and symmetry properties of the molecule. Solution of Eq. (8) (see the positions of nuclei and coordinate axes in the figure) gives:

$$r_{4x}^e = r_{5x}^e = 0, \quad r_{1x}^e = -2r_{2x}^e = -2r_{3x}^e = 2\rho_e \sin\alpha_e / \sqrt{3}, \quad (13)$$

$$r_{4y}^e = r_{5y}^e = 0, \quad r_{1y}^e = 0, \quad r_{3y}^e = -r_{2y}^e = \rho_e \sin\alpha_e, \quad (14)$$

$$r_{4z}^e = \frac{3mh - M_5 r_e}{M_4 + M_5 + 3m}, \quad r_{5z}^e = \frac{M_4 r_e + 3m(r_e + h)}{M_4 + M_5 + 3m}, \quad (15)$$

$$r_{1z}^e = r_{2z}^e = r_{3z}^e = -\frac{M_4 h + M_5(r_e + h)}{M_4 + M_5 + 3m}; \quad (16)$$

$$h = \rho_e \left\{ 1 - \frac{4}{3} \sin^2\alpha_e \right\}^{1/2}. \quad (17)$$

As a consequence, the equilibrium moments of inertia I_{α}^e are of the form:

$$I_x^e = I_y^e = (3m + M_4 + M_5)^{-2} \{ 3m[M_4 h + M_5(r_e + h)]^2 + M_4(3mh - M_5 r_e)^2 + M_5[M_4 r_e + 3m(r_e + h)]^2 \} + 2m\rho_e^2 \sin^2\alpha_e; \quad (18)$$

$$I_z^e = 4m\rho_e^2 \sin^2\alpha_e. \quad (19)$$

Solution of Eqs. (9)–(11) gives the following relationships for $l_{N\alpha\lambda}$ parameters:

a) for $\lambda = 1, 2, 3$ (nondegenerate vibrations):

$$l_{3y\lambda} = -l_{2y\lambda} = -\sqrt{3} l_{2x\lambda} = -\sqrt{3} l_{3x\lambda} = \sqrt{3} l_{1x\lambda} / 2 = l_{\lambda}^{(1)} / 2, \quad (20)$$

$$l_{4x\lambda} = l_{5x\lambda} = 0,$$

$$l_{4y\lambda} = l_{5y\lambda} = l_{1y\lambda} = 0, \quad (21)$$

$$l_{4z\lambda} = l_{\lambda}^{(3)}, \quad l_{1z\lambda} = l_{2z\lambda} = l_{3z\lambda} = l_{\lambda}^{(2)}, \quad (22)$$

$$l_{5z\lambda} = -\left(\frac{M_4}{M_5}\right)^{1/2} l_{\lambda}^{(3)} - 3\left(\frac{m}{M_5}\right)^{1/2} l_{\lambda}^{(2)}. \quad (23)$$

Besides, the following relationships must hold:

$$l_{\lambda}^{(1)} l_{\mu}^{(1)} + 3\left(\frac{M_5 + 3m}{M_5}\right) l_{\lambda}^{(2)} l_{\mu}^{(2)} + \left(\frac{M_4 + M_5}{M_5}\right) l_{\lambda}^{(3)} l_{\mu}^{(3)} + \frac{3\sqrt{mM_4}}{M_5} (l_{\lambda}^{(3)} l_{\mu}^{(2)} + l_{\lambda}^{(2)} l_{\mu}^{(3)}) = \delta_{\lambda\mu}, \quad (24)$$

where $\lambda, \mu = 1, 2, 3$. Equations (20)–(24) define the parameters $l_{N\alpha\lambda}$ as functions of three parameters, which can be determined from the conditions (12).

(b) for $\lambda = 4, 5, 6$ (degenerate vibrations):

$$l_{1y\lambda_1} = l_{4y\lambda_1} = l_{5y\lambda_1} = 0, \quad l_{1x\lambda_2} = l_{4x\lambda_2} = l_{5x\lambda_2} = 0,$$

$$l_{4z\lambda_1} = l_{5z\lambda_1} = l_{1z\lambda_2} = l_{4z\lambda_2} = l_{5z\lambda_2} = 0, \quad (25)$$

$$l_{2x\lambda_1} = l_{3x\lambda_1}, \quad (26)$$

$$l_{1y\lambda_2} = \frac{1}{3} (4 l_{2x\lambda_1} - l_{1x\lambda_1}), \quad (27)$$

$$l_{2x\lambda_2} = l_{2y\lambda_1} = -l_{3y\lambda_1} = -l_{3x\lambda_2} = \frac{1}{\sqrt{3}} (l_{1x\lambda_1} - l_{2x\lambda_1}), \quad (28)$$

$$l_{3y\lambda_2} = l_{2y\lambda_2} = \frac{1}{3} (2 l_{1x\lambda_1} + l_{2x\lambda_1}), \quad (29)$$

$$l_{2z\lambda_2} = -l_{3z\lambda_2} = \sqrt{3} l_{2z\lambda_1} = \sqrt{3} l_{3z\lambda_1} = -\frac{\sqrt{3}}{2} l_{1z\lambda_1} = \frac{1}{2} \frac{r_{1z}^e}{r_{2y}^e} (l_{1x\lambda_1} + 2 l_{2x\lambda_1}) + \frac{1}{2} \left(\frac{M_4}{m}\right)^{1/2} \frac{r_{4z}^e}{r_{2y}^e} l_{4x\lambda_1} + \frac{1}{2} \left(\frac{M_5}{m}\right)^{1/2} \frac{r_{5z}^e}{r_{2y}^e} l_{5x\lambda_1}, \quad (30)$$

$$l_{4x\lambda_1} = l_{4y\lambda_2}, \quad l_{5x\lambda_1} = l_{5y\lambda_2}. \quad (31)$$

The relevant conditions of orthonormality should be added to Eqs. (25)–(31).

It should be noted that the use of Eqs. (20)–(31) in the general case results in rather complicated solutions. In any case, the six parameters $l_{N\alpha\lambda}$ (three for the nondegenerate vibrations with $\lambda = 1, 2, 3$ and three for the degenerate ones with $\lambda = 4, 5, 6$) remain arbitrary.

The relationships (20)–(31) can then be used for the determination of Coriolis $\zeta_{\lambda\mu}^{\alpha}$ and vibration-rotation $a_{\lambda}^{\alpha\beta}$ parameters. One can show that after substitution of Eqs. (20)–(31) into Eqs. (4)–(6) and a series of transformations the following relations are valid:

a) for $\lambda = 1, 2, 3$:

$$a_{\lambda}^{xx} = a_{\lambda}^{yy} = \sqrt{m} (2\rho_e \sin\alpha_e l_{\lambda}^{(1)} - 6(r_e + h) l_{\lambda}^{(2)}) - 2\sqrt{M_4} r_e l_{\lambda}^{(3)}, \quad (32)$$

$$a_{\lambda}^{zz} = 4\sqrt{m} \rho_e \sin\alpha_e l_{\lambda}^{(1)}; \quad (33)$$

for $\lambda = 4, 5, 6$:

$$a_{\lambda 1}^{xx} = -a_{\lambda 1}^{yy} = -a_{\lambda 2}^{xy} = -a_{\lambda 2}^{yx} \equiv a_{\lambda}^{xx} = \frac{4}{\sqrt{3}} \sqrt{m} r_{2y}^e (l_{1x\lambda_1} - l_{2x\lambda_1}), \quad (34)$$

$$a_{\lambda 1}^{xz} = a_{\lambda 1}^{zx} = a_{\lambda 2}^{yz} = a_{\lambda 2}^{zy} \equiv a_{\lambda}^{xz} = -12\sqrt{m} r_{2x}^e l_{2z\lambda_1}; \quad (35)$$

b) for $\lambda = 1, 2, 3$ and $\mu = 4, 5, 6$:

$$\zeta_{\lambda\mu_1}^y = -\zeta_{\lambda\mu_2}^x = -\zeta_{\mu_1\lambda}^y = \zeta_{\mu_2\lambda}^x \equiv \zeta_{\lambda\mu}^x = l_{\lambda}^{(1)} \sqrt{3} l_{2z\mu_1} + l_{\lambda}^{(2)} \{l_{1x\mu_1} + 2l_{2x\mu_1} - 3(m/M_5)^{1/2} l_{5y\mu_2}\} + l_{\lambda}^{(3)} \{l_{4y\mu_2} - (M_4/M_5)^{1/2} l_{5y\mu_2}\}; \quad (36)$$

c) for $\lambda, \mu = 4, 5, 6$:

$$\zeta_{\lambda_1\mu_2}^z = -\zeta_{\lambda_2\mu_1}^z = \zeta_{\mu_1\lambda_2}^z = -\zeta_{\mu_2\lambda_1}^z \equiv \zeta_{\lambda\mu}^{(z)} = l_{4x\lambda_1} l_{4x\mu_1} + l_{5x\lambda_1} l_{5x\mu_1} - l_{1x\lambda_1} l_{1x\mu_1} + 2\{l_{1x\lambda_1} l_{2x\mu_1} + l_{2x\lambda_1} l_{1x\mu_1}\}, \quad (37)$$

$$\zeta_{\lambda_1\mu_2}^x = \zeta_{\lambda_2\mu_1}^x = -\zeta_{\mu_1\lambda_2}^x = -\zeta_{\mu_2\lambda_1}^x \equiv \zeta_{\lambda\mu}^{(x)} = \sqrt{3} \frac{r_{1z}^e}{r_{2y}^e} (l_{1x\lambda_1} l_{2x\mu_1} - l_{2x\lambda_1} l_{1x\mu_1}). \quad (38)$$

In its turn, Eqs. (32)–(38) when substituting into Eq. (1)–(3) make it possible to readily obtain the exact vibration-rotation Hamiltonian of the ZXY_3 molecule.

The following fact should be noted. If in the above considerations we set $r_e = 0$ (i.e., we assume that the positions of atoms 4 and 5 coincide, then the above-mentioned molecule is transformed into the molecule of

the type XY_3 of the C_{3V} symmetry. In this case the above relationships are transformed into the form:

$$\begin{aligned} \text{a) } r_{4x}^e &= 0, \quad r_{1x}^e = -2r_{2x}^e = -2r_{3x}^e = r_{12}/\sqrt{3}, \\ r_{4y}^e &= 0, \quad r_{1y}^e = 0, \quad r_{3y}^e = -r_{2y}^e = r_{12}/2, \\ r_{4z}^e &= h \left(\frac{3m}{M+3m} \right), \quad r_{1z}^e = r_{2z}^e = r_{3z}^e = -h \left(\frac{M}{M+3m} \right), \end{aligned} \quad (39)$$

where

$$r_{12} = 2\rho_e \sin\alpha_e; \quad h = \rho_e \left\{ 1 - \frac{4}{3} \sin^2\alpha_e \right\}^{1/2};$$

b) for $l_{N\alpha\lambda}$ ($\lambda = 1, 2$):

$$\begin{aligned} l_{3y\lambda} &= -l_{2y\lambda} = -\sqrt{3} l_{2x\lambda} = -\sqrt{3} l_{3x\lambda} = \sqrt{3} l_{1x\lambda}/2 = l_{\lambda}^{(1)}/2, \\ l_{4x\lambda} &= l_{4y\lambda} = l_{1y\lambda} = 0, \\ l_{4z\lambda} &= -3\sqrt{m/M} l_{\lambda}^{(2)}, \quad l_{1z\lambda} = l_{2z\lambda} = l_{3z\lambda} = l_{\lambda}^{(2)}. \end{aligned} \quad (40)$$

The four parameters, $l_{\lambda}^{(1)}$ and $l_{\lambda}^{(2)}$, in Eq. (40) must satisfy three conditions

$$l_{\lambda}^{(1)} l_{\mu}^{(1)} + 3 \left(\frac{M+3m}{M} \right) l_{\lambda}^{(1)} l_{\mu}^{(2)} = \delta_{\lambda\mu}, \quad (41)$$

where $\lambda, \mu = 1, 2$. The equalities (40)–(41) determine the parameters $l_{N\alpha\lambda}$ ($\lambda = 1, 2$) as functions of one arbitrary parameter.

c) for $l_{N\alpha\lambda s}$ ($\lambda = 3, 4, s = 1, 2$):

$$\begin{aligned} l_{4x\lambda_2} &= l_{1x\lambda_2} = 0, \quad l_{2x\lambda_2} = -l_{3x\lambda_2} = \sqrt{1/3} (l_{1x\lambda_1} - l_{2x\lambda_1}), \\ l_{3x\lambda_1} &= l_{2x\lambda_1}, \quad l_{4x\lambda_1} = l_{4y\lambda_2} = -\sqrt{m/M} (l_{1x\lambda_1} + 2l_{2x\lambda_1}), \\ 3l_{1y\lambda_2} &= 4l_{2x\lambda_1} - l_{1x\lambda_1}, \\ \sqrt{3} l_{2y\lambda_1} &= -\sqrt{3} l_{3y\lambda_1} = l_{1x\lambda_1} - l_{2x\lambda_1}, \\ l_{4y\lambda_1} &= l_{1y\lambda_1} = 0, \quad 3l_{2y\lambda_2} = 3l_{3y\lambda_2} = 2l_{1x\lambda_1} + l_{2x\lambda_1}, \\ l_{4z\lambda_1} &= l_{4z\lambda_2} = l_{1z\lambda_2} = 0, \\ 2l_{2z\lambda_1} &= 2l_{3z\lambda_1} = 2l_{2z\lambda_2} = -2l_{3z\lambda_2} = \\ &= -\sqrt{3} l_{1z\lambda_1} = 2h/r_{12} (l_{1x\lambda_1} - 2l_{2x\lambda_1}). \end{aligned} \quad (42)$$

Similar to Eq. (40), four parameters, $l_{1x\lambda_1}$ and $l_{2x\lambda_2}$ ($\lambda = 3, 4$), cannot be determined from Eq. (42), however, they must satisfy the orthogonality conditions

$$l_{1x\lambda_1}^2 + 2l_{2x\lambda_1}^2 + l_{4x\lambda_1}^2 + \frac{2}{3} (l_{1x\lambda_1} - l_{2x\lambda_1})^2 + 6l_{2z\lambda_1}^2 = 1; \quad (43)$$

$$\sum_{N\alpha} l_{N\alpha 31} l_{N\alpha 41} = 0. \quad (44)$$

As a result, only one parameter remains arbitrary.

For the equilibrium moments of inertia, Coriolis and vibration-rotation parameters, we have:

$$\text{a) } I_{xx}^e = I_{yy}^e = \frac{mM \rho_e^2}{M + 3m} \left[3 + 2 \sin^2 \alpha_e \left(\frac{3m}{M} - 1 \right) \right],$$

$$I_{zz}^e = 4m \rho_e^2 \sin^2 \alpha_e; \quad (45)$$

b) for $\lambda = 1, 2$:

$$a_{\lambda}^{xx} = a_{\lambda}^{yy} = \sqrt{m} (r_{12} l_{\lambda}^{(1)} - 6h l_{\lambda}^{(2)}), a_{\lambda}^{zz} = 2\sqrt{m} r_{12} l_{\lambda}^{(1)} \quad (46)$$

and for $\lambda = 3, 4$:

$$a_{\lambda}^{xx} = -a_{\lambda}^{yy} = -a_{\lambda 1}^{xy} = -a_{\lambda 2}^{yx} \equiv a_{\lambda}^{xx} = -2\sqrt{m} r_{12} l_{2y\lambda 1},$$

$$a_{\lambda 1}^{xz} = a_{\lambda 1}^{zx} = a_{\lambda 2}^{yz} = a_{\lambda 2}^{zy} \equiv a_{\lambda}^{xz} = +2\sqrt{3m} r_{12} l_{2z\lambda 1}; \quad (47)$$

c) for $\lambda = 1, 2$ and $\mu = 3, 4$:

$$\zeta_{\lambda\mu 1}^{xy} = -\zeta_{\lambda\mu 2}^{yx} = -\zeta_{\mu 1\lambda}^{xy} = \zeta_{\mu 2\lambda}^{yx} \equiv \zeta_{\lambda\mu}^{xy} = l_{\lambda}^{(1)} \sqrt{3} l_{2z\mu 1} +$$

$$+ l_{\lambda}^{(2)} \{l_{1y\mu 2} + 2l_{2y\mu 2} - 3\sqrt{m/M} l_{4x\mu 1}\}, \quad (48)$$

for $\lambda, \mu = 3, 4$:

$$\zeta_{\lambda 1\mu 2}^z = -\zeta_{\lambda 2\mu 1}^z = \zeta_{\mu 1\lambda 2}^z = -\zeta_{\mu 2\lambda 1}^z \equiv \zeta_{\lambda\mu}^{(z)} =$$

$$= l_{4x\lambda 1} l_{4x\mu 1} - l_{1x\lambda 1} l_{1x\mu 1} + 2 \{l_{1x\lambda 1} l_{2x\mu 1} + l_{2x\lambda 1} l_{1x\mu 1}\}, \quad (49)$$

$$\zeta_{3142}^x = -\zeta_{4231}^x = -\zeta_{4132}^x = \zeta_{3241}^x = \zeta_{3141}^y = -\zeta_{4131}^y = \zeta_{4232}^y =$$

$$= -\zeta_{3242}^y \equiv \zeta_{34}^{(x)} = (2\sqrt{3} h/r_{12}) (l_{1x31} l_{2x41} - l_{2x31} l_{1x41}). \quad (50)$$

The above relationships determine completely the vibration-rotation Hamiltonians of the molecules ZXY_3 and XY_3 of the symmetry group C_{3v} .

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REFERENCES

1. J.K.G. Watson, *Molec. Phys.* **15**, 479-490 (1968).
2. Yu.S. Makushkin and O.N. Ulenikov, *J. Mol. Spectrosc.* **68**, 1-20 (1977).
3. D. Papousek and M.R. Aliev, *Molecular Vibration-Rotation Spectra* (Elsevier Sci. Publ. Corp., Amsterdam-Oxford-New York, 1982).