SEXTIC CENTRIFUGAL DISTORTION CONSTANTS IN THE LOCAL MODE APPROACH

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The problem of calculation of the sextic centrifugal distortion constants is considered within the framework of the "expanded local mode approach" for XY_2 (C_{2v}), XY_3 (C_{3v}), and XY_4 (T_d) molecules with relatively heavy X nucleus. Some conditions imposed on the structure and dynamic characteristics of molecules of this type allow significantly simpler derivation of analytical expressions for parameters of the effective rotational Hamiltonian. The simple expressions can be thus obtained for the sextic centrifugal constants. As an illustration, the corresponding values of the centrifugal constants are calculated using these expressions for such molecules as H_2Se, H_2S, AsH_3, SbH_3, CH_4, SiH_4, *and* GeH_4. *The correspondence between the calculated and experimental values is demonstrated.*

INTRODUCTION

Fast progress of microwave and infrared spectroscopy in the last decades allowed calculation of some (or even all) sextic centrifugal distortion constants for different polyatomic molecules. At the same time, derivation of analytical formulas expressing the sextic constants through the molecular constants requires at least the fourth order of the perturbation theory to be considered, what is too complicated and extremely laborious process. Besides, the result is very cumbersome and hard-to-analyze. However, there are strong grounds for believing that for some molecules (for example, for molecules of the XY_N type with relatively heavy X nucleus, see Ref. 1) the corresponding expressions for the sextic centrifugal constants can be significantly simplified using the local mode approach actively developed in recent years. As an example, we can note the well-known results of this approach as applied to derivation of the relations, including nontrivial ones, between different spectroscopic characteristics of molecules, in particular, between quadratic centrifugal distortion constants for XY_2 (Ref. 2) and XY_3 (Ref. 3) molecules. The restrictions imposed on the molecules of this type are the following:

1) the mass ratio between Y and X atoms is a small value tending to zero in the limit;

2) for XY_2 and XY_3 molecules the equilibrium angle between the valency bonds is close to 90°;

3) the contribution from valency oscillations into the potential function of a molecule is far greater than that from deformation oscillations.

The use of these conditions in this work allowed us to obtain a number of interesting relations between the sextic centrifugal distortion constants for XY_2, XY_3, and XY_4 molecules.

XY_2 MOLECULE OF THE C_{2v} SYMMETRY

Within the framework of the model considered, it becomes much simpler to calculate the parameters entering into the rotational–vibrational molecular Hamiltonian, because such parameters as $a_\lambda^{\alpha\beta}$, rotational constants B_α, rotational–vibrational and Coriolis constants $\zeta_{\lambda\mu}^{\alpha}$, centrifugal quadratic constants $\tau_{\alpha\beta\gamma\delta}$, and potential constants $k_{\lambda\mu\nu}$, the functions of which are the sextic centrifugal constants, comply with the following simple relations (see Ref. 2):

$$B_x^e = B_z^e = 2B_y^e \equiv B_e; \tag{1a}$$

$$a_1^{xx} = a_1^{zz} = a_2^{xx} = -\,a_2^{zz} = -\,a_3^{xz} = -\,a_3^{zx}, \tag{1b}$$

$$a_1^{yy} = 2a_1^{xx},\ a_2^{yy} = 0; \tag{1c}$$

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

$$\tau'_{xxxx} = \tau'_{zzzz} = -\,8\,\frac{B_e^3}{\omega^2}\left(1 + \frac{1}{\theta^2}\right), \tag{1e}$$

$$\tau'_{xxzz} = -\,8\,\frac{B_e^3}{\omega^2}\left(3 - \frac{1}{\theta^2}\right), \tag{1f}$$

$$\tau'_{xxyy} = \tau'_{zzyy} = 2\tau'_{yyyy} = -\,4\,\frac{B_e^3}{\omega^2}\,; \tag{1g}$$

$$\omega_1 = \omega_3 \equiv \omega,\quad k_{133} = 3k_{111}; \tag{2a}$$

$$k_{111} = -\,\frac{1}{6B_e}\sqrt{\frac{\omega}{B_e}}\,(3B_e^2 + \omega\,\alpha_1^x), \tag{2b}$$

$$k_{122} = \sqrt{\omega B_e}/(2\theta)\,(1 - 2\theta^2). \tag{2c}$$

Using these relations in the expressions from Ref. 4, we can obtain

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$$H_J = \frac{B_e^5}{\omega^4}\left[\frac{9}{2} + \frac{8}{\theta^2} + \frac{8}{\theta^4} - \frac{3}{4}\frac{\omega\alpha_1^x}{B_e^2}\right], \tag{3a}$$

$$H_{JK} = \frac{B_e^5}{\omega^4}\left[\frac{207}{4} - \frac{18}{\theta^2} - \frac{56}{\theta^4} - \frac{95}{12}\frac{\omega\alpha_1^x}{B_e^2}\right], \tag{3b}$$

$$H_{KJ} = \frac{B_e^5}{3\omega^4}\left[-\frac{469}{2} - \frac{64}{\theta^2} + \frac{226}{\theta^4} + \frac{80}{3}\frac{\omega\alpha_1^x}{B_e^2}\right], \tag{3c}$$

$$H_K = \frac{B_e^5}{3\omega^4}\left[\frac{359}{4} + \frac{142}{\theta^2} - \frac{34}{\theta^4} - \frac{14}{3}\frac{\omega\alpha_1^x}{B_e^2}\right]; \tag{3d}$$

$$h_J = \frac{B_e^5}{\omega^4}\left[\frac{7}{4} + \frac{4}{\theta^2} + \frac{4}{\theta^4} - \frac{7}{24}\frac{\omega\alpha_1^x}{B_e^2}\right], \tag{3e}$$

$$h_{JK} = \frac{B_e^5}{\omega^4}\left[\frac{443}{16} - \frac{1}{2\theta^2} - \frac{23}{\theta^4} - \frac{13}{3}\frac{\omega\alpha_1^x}{B_e^2}\right], \tag{3f}$$

$$h_K = \frac{B_e^5}{3\omega^4}\left[\frac{349}{16} + \frac{13}{2\theta^2} + \frac{94}{\theta^4} - \frac{7}{3}\frac{\omega\alpha_1^x}{B_e^2}\right]. \tag{3g}$$

Here θ is the semiempirical parameter; B_e is the equilibrium rotational constant (for details see Ref. 2); α_1^x is the rotational–vibrational spectroscopic constant (Eqs. (3) may use, for example, its experimental value). The expressions derived for the sextic centrifugal distortion constants have a more complicated form than the similar expressions for quadratic centrifugal constants (see Ref. 2). This fact reflects the higher order of the perturbation theory used in derivation of Eqs. (3).

The expressions (3) allow sufficiently correct prediction of values of the sextic centrifugal constants under conditions of minimum available information. As an illustration, the first and fourth columns of Table I give the results of numerical calculation of the parameters H_J, H_{JK}, H_{KJ}, H_K, h_J, h_{JK}, and h_K based on Eqs. (3) for the H_2Se and H_2S molecules, respectively. The presented below values of the parameters were used as initial data in the calculations.

[H_2Se] The value $B_x^e = 7.727$ cm^{-1} was taken as the equilibrium rotational constant B_e according to Eq. (1a); $\omega = 2438.5$ cm^{-1} was taken as an arithmetic mean of the harmonic frequencies ω_1 and ω_3; $\theta = 0.4277$ (all the values are borrowed from Ref. 2); and the rotational–vibrational parameter $\alpha_1^x = 0.1072$ cm^{-1} was taken from:

[H_2S] $B_e = B_x^e = 9.0181$ cm^{-1} (Ref. 6); $\omega = 2727.5$ cm^{-1}; $\theta = 0.4447$ (Ref. 7); $\alpha_1^x = 0.1237$ cm^{-1} (Ref. 2).

For the purposes of illustration, the calculated results are compared not only with the corresponding experimental data[5,6] (given in the third and sixth columns of Table I), but also with the values of the centrifugal constants calculated without use of the local mode approach, by the exact expressions of the perturbation theory[4] (given in the second and fifth columns). Such an analysis allows more adequate evaluation of the approximations used, because it excludes the influence of the models, which invoke, first, analysis of experimental data (effective rotational Hamiltonian) and, second, construction of perturbation series.

TABLE I. Sextic centrifugal parameters of the H_2Se *and* H_2S *molecules,* 10^{-6} cm^{-1}.

Parameter	H_2Se			H_2S		
	LM	Exact expressions	Experiment	LM	Exact expressions	Experiment
H_J	0.2205	0.1965	0.216541	0.2660	0.2259	0.27098
H_{JK}	− 1.365	− 1.231	− 1.24626	− 1.624	− 1.458	− 1.5329
H_{KJ}	1.635	1.392	1.284898	1.919	1.457	1.2592
H_K	− 0.04900	0.2655	0.449608	− 0.0300	0.9943	1.3811
h_J	0.1102	0.09815	0.107858	0.1328	0.1128	0.13541
h_{JK}	− 0.5309	− 0.4707	− 0.406704	− 0.6273	− 0.5399	− 0.48509
h_K	0.7421	0.7433	0.78668	0.8813	1.004	1.229

As expected, the predictions of the sextic centrifugal distortion constants of the ground vibrational state based on the expanded local mode approach are wholly satisfactory.

In fact, they are no worse than the predictions for the quadratic parameters made in the same approximations. This fact is illustrated by Table II, which presents the results for the quadratic constants calculated on the basis of expressions from Ref. 2 (the "expanded local mode approach") with the use of the same data as for the parameters H_J, H_{JK}, H_{KJ}, H_K, h_J, h_{JK}, and h_K.

TABLE II. Quadratic centrifugal parameters of the H_2Se *and* H_2S *molecules,* 10^{-3} cm^{-1}.

	H_2Se		H_2S	
	Calc.	Exp.	Calc.	Exp.
Δ_J	0.5211	0.5283	0.6218	0.652598
Δ_{JK}	− 1.791	− 1.849	− 2.0739	− 2.28026
Δ_K	2.273	2.6368	2.6465	3.7326
δ_J	0.2411	0.2425	0.28626	0.295517
δ_K	− 0.2495	− 0.1833	− 0.27676	− 0.132618

XY$_3$ MOLECULE OF THE *C*$_{3v}$ SYMMETRY

Let us remind the principal approximations of the model used as applied to XY_3 molecules[3]:

1) the mass M of the X-nucleus is far greater than the mass m of the Y-nucleus;

2) the equilibrium value of the angle between the bonds $2\alpha_e$ is close to $\pi/2$;

3) the interaction between the valency and deformation modes can be neglected in the quadratic part of the potential function:

$$V = \frac{1}{2} f_{rr} (\Delta r_1^2 + \Delta r_2^2 + \Delta r_3^2) +$$

$$+ f_{rr'} (\Delta r_1 \, \Delta r_2 + \Delta r_1 \, \Delta r_3 + \Delta r_2 \, \Delta r_3) +$$

$$+ \frac{1}{2} f_{\alpha\alpha} \, r_e^2 \, (\Delta\alpha_{12}^2 + \Delta\alpha_{13}^2 + \Delta\alpha_{23}^2) + \ldots \; . \tag{4}$$

It can be shown (see Ref. 3) that within the framework of these approximations the following relations, needed for calculation of the sextic centrifugal distortion constants, are valid:

$$a_1^{xx} = a_1^{yy} = a_1^{zz} = 2\sqrt{6I_e}/3, \tag{5a}$$

$$a_{31}^{xz} = a_{32}^{yz} = -\sqrt{2}\, a_{31}^{xx} = \sqrt{2}\, a_{31}^{yy} = \sqrt{2}\, a_{32}^{xy} = \sqrt{6I_e}/3, \tag{5b}$$

$$a_2^{xx} = a_2^{yy} = -\, a_2^{zz}/2 = -\sqrt{3I_e}/3, \tag{5c}$$

$$a_{41}^{xx} = -\, a_{41}^{yy} = -a_{42}^{xy} = \sqrt{2}\, a_{41}^{xz} = \sqrt{2}\, a_{42}^{yz} = -\sqrt{6I_e}/3; \tag{5d}$$

$$\zeta_{1,31}^{y} = \zeta_{1,32}^{x} = \zeta_{1,41}^{y} = \zeta_{1,42}^{x} = 0;$$

$$\sqrt{2}\, \zeta_{2,31}^{y} = -\sqrt{2}\, \zeta_{2,32}^{x} = 1, \tag{6a}$$

$$2\zeta_{2,41}^{y} = -\, 2\, \zeta_{2,42}^{x} = -\, 1;\; 2\zeta_{41,42}^{z} = -\, 1,\; \zeta_{31,32}^{z} = 0, \tag{6b}$$

$$\sqrt{2}\, \zeta_{31,42}^{z} = \sqrt{2}\, \zeta_{41,32}^{z} = -\, 1,$$

$$2\zeta_{31,42}^{x} = 2\zeta_{32,41}^{x} = 2\zeta_{31,41}^{y} = -\, 2\zeta_{32,42}^{y} = -\, 1; \tag{6c}$$

$$k_{122} = \sqrt{3\omega\, B_e}/(3\theta)\, (1 - 2\theta^2), \tag{7a}$$

$$k_{222} = -\sqrt{6\omega\theta\, B_e}/6, \tag{7b}$$

$$k_{133} = 3k_{111}, \tag{7c}$$

$$k_{333} = (\sqrt{2}/2)\, k_{111}, \tag{7d}$$

$$k_{234} = k_{122}, \tag{7e}$$

$$k_{144} = k_{122}, \tag{7f}$$

$$k_{344} = -\, (\sqrt{2}/4)\, k_{122}, \tag{7g}$$

$$k_{244} = -\, (3/2)\, k_{222}, \tag{7h}$$

$$k_{444} = -\, (\sqrt{2}/2)\, k_{222}, \tag{7i}$$

where

$$I_e \equiv I_{xx}^e = I_{yy}^e = I_{zz}^e = 2\, m r_e^2;\; \omega_3 = \omega_1 \equiv \omega. \tag{8}$$

Under these conditions, the expressions for the sextic centrifugal parameters are the following:

$$H_J = \frac{8B_e^5}{9\omega^4}\left[19 + \frac{16}{\theta^2} + \frac{5}{\theta^4} - \frac{11}{4}\frac{\omega\alpha_1^x}{B_e^2}\right], \tag{9a}$$

$$H_{JK} = \frac{16B_e^5}{3\omega^4}\left[7 - \frac{1}{\theta^2} - \frac{8}{\theta^4} - \frac{1}{2}\frac{\omega\alpha_1^x}{B_e^2}\right], \tag{9b}$$

$$H_{KJ} = \frac{8B_e^5}{3\omega^4}\left[-\, 23 + \frac{32}{\theta^2} - \frac{1}{\theta^4} + \frac{3}{4}\frac{\omega\alpha_1^x}{B_e^2}\right], \tag{9c}$$

$$H_K = \frac{32B_e^5}{3\omega^4}\left[2 - \frac{4}{\theta^2} + \frac{1}{\theta^4} + \frac{1}{8}\frac{\omega\alpha_1^x}{B_e^2}\right]. \tag{9d}$$

As an illustration, Table III gives the results for the centrifugal distortion constants of AsH_3 and SbH_3 calculated with the use of the expressions derived. All the data needed for calculation, as well as the experimental values of the centrifugal parameters, are borrowed from Ref. 8.

[AsH_3] $B_e = B_x^e = 3.7516$ cm^{-1}; $\omega = 2196.0$ cm^{-1} as an arithmetic mean of the harmonic frequencies ω_1 and ω_3; $\theta = 0.4415$; the rotational–vibrational parameter $\alpha_1^x = 0.037725$ cm^{-1}.

[SbH_3] $B_e = B_x^e = 2.9697$ cm^{-1}; $\omega_1 = 1951.5$ cm^{-1}; $\theta = 0.4179$; $\alpha_1^x = 0.02619$ cm^{-1}.

The comparison of the parameters presented in Table III shows that the expressions of the "expanded local mode approach" give the results at least no worse than those calculated by "exact" expressions of the rotational–vibrational theory.

TABLE III. Sextic centrifugal parameters of AsH_3 *and* SbH_3 *molecules,* 10^{-8} cm^{-1}.

	AsH_3			SbH_3		
	LM	Exact expressions	Experiment	LM	Exact expressions	Experiment
H_J	0.6805	0.7059	0.6817	0.3979	0.4222	0.37
H_{JK}	− 1.118	− 1.566	− 1.207	− 1.6819	− 0.8593	− 0.63
H_{KJ}	1.145	1.347	0.53	0.6172	0.6183	0.2
H_K	0.3441	0.2750	0.6740	0.2316	0.2894	0.44

XY_4 MOLECULE OF THE T_d SYMMETRY

For the spherical top XY_4 molecules we can say that the following relations are valid in the expanded local mode approximation:

$$a_1^{xx} = a_1^{yy} = a_1^{zz} = 2\sqrt{2I_e/3}\ , \tag{10a}$$

$$a_{2a}^{xx} = a_{2a}^{yy} = -\frac{1}{2}a_{2a}^{zz} = \sqrt{\frac{1}{3}}\,a_{2b}^{xx} = -\sqrt{\frac{1}{3}}\,a_{2b}^{yy} = -\sqrt{\frac{I_e}{3}}\,, \tag{10b}$$

$$a_{3x}^{yz} = a_{3x}^{zy} = a_{3y}^{xz} = a_{3y}^{zx} = a_{3z}^{xy} = a_{3z}^{yx} = -\sqrt{2I_e/3}\ , \tag{10c}$$

$$a_{4x}^{yz} = a_{4x}^{zy} = a_{4y}^{xz} = a_{4y}^{zx} = a_{4z}^{xy} = a_{4z}^{yx} = \sqrt{I_e/3}\ ; \tag{10d}$$

$$\zeta_{2a3x}^{x} = -\zeta_{2a3y}^{y} = -\sqrt{2}\,\zeta_{2a4x}^{x} = \sqrt{2}\,\zeta_{2a4y}^{y} = \sqrt{2}/2, \tag{11a}$$

$$\zeta_{2b3x}^{x} = \zeta_{2b3y}^{y} = -\zeta_{2b3z}^{z}/2 = -\sqrt{2}\,\zeta_{2b4x}^{x} =$$
$$= -\sqrt{2}\,\zeta_{2b4y}^{y} = \sqrt{2}\,\zeta_{2b4z}^{z}/2 = -\sqrt{6}/6, \tag{11b}$$

$$\zeta_{3x4y}^{z} = -\zeta_{3x4z}^{y} = -\zeta_{3y4x}^{z} = \zeta_{3y4z}^{x} =$$
$$= \zeta_{3z4x}^{y} = -\zeta_{3z4y}^{x} = \sqrt{2}/2, \tag{11c}$$

$$\zeta_{4x4y}^{z} = -\zeta_{4x4z}^{y} = \zeta_{4y4z}^{x} = \frac{1}{2}\ ; \tag{11d}$$

$$\tau'_{xxxx} = \tau'_{yyyy} = \tau'_{zzzz} = -\frac{16B_e^3}{3\omega^2}\left[2 - \frac{1}{\theta^2}\right], \tag{12a}$$

$$\tau'_{xxyy} = \tau'_{xxzz} = \tau'_{yyzz} = -\frac{4B_e^3}{3\omega^2}\left[4 - \frac{1}{\theta^2}\right], \tag{12b}$$

$$k_{133} = 3k_{111},\ k_{333} = k_{111}, \tag{13}$$

where

$$I_e \equiv I_{xx}^e = I_{yy}^e = I_{zz}^e = (8/3)\ mr_e^2;\ B_e = \hbar/(4\pi\ c\ I_e);$$

$$\omega_3 = \omega_1 \equiv \omega;\quad \omega_2 = \sqrt{\frac{3}{2}}\,\omega_4.$$

It is known[9] that the sextic centrifugal constants are parameters of the operator

$$H_6 = H(J^2)^3 + H_{4t}\,J^2\,\Omega_4 + H_{6t}\,\Omega_6,$$

where

$$\Omega_4 = -10\,(J_x^4 + J_y^4 + J_z^4) + 6\,(J^2)^2 - 2J^2;$$

$$\Omega_6 = \frac{77}{2}\,(J_x^6 + J_y^6 + J_z^6) - \frac{35}{2}\,(J_x^4 + J_y^4 + J_z^4)\,(3J^2 - 7) +$$
$$+ 15\,(J^2)^3 - \frac{135}{2}\,(J^2)^2 + 19\,J^2.$$

The use of the local mode approximation gives in this case

$$H = \frac{64B_e^5}{35\omega^4}\left[\frac{32}{3} + \frac{31}{3}\frac{1}{\theta^2} + \frac{47}{48}\frac{1}{\theta^4} - \frac{3}{2}\frac{\omega\alpha_1}{B_e^2}\right], \tag{14a}$$

$$H_{4t} = \frac{2B_e^5}{55\omega^4}\left[\frac{128}{3} - \frac{76}{3}\frac{1}{\theta^2} - 19\,\frac{1}{\theta^4} - 6\,\frac{\omega\alpha_1}{B_e^2}\right], \tag{14b}$$

$$H_{6t} = \frac{4B_e^5}{77\omega^4}\left[\frac{160}{9} - 24\,\frac{1}{\theta^2} + 15\,\frac{1}{\theta^4} + \frac{16}{9}\frac{\omega\alpha_1}{B_e^2}\right]. \tag{14c}$$

To illustrate the usefulness of the relations derived, Table IV presents the predictions for the centrifugal parameters H, H_{4t}, and H_{6t} calculated by Eqs. (14) for the molecules CH_4, SiH_4, and GeH_4 along with the corresponding experimental values. The following initial data were used in calculations:

[CH_4] $B_e = 5.16096$ cm^{-1}; $\omega = 3025.5$ cm^{-1}; $\theta = 0.5231$; $\alpha_1 = 0.0388$ cm^{-1} (Ref. 10);

[SiH_4] $B_e = 2.859065$ cm^{-1}; $\omega = 2194.85$ cm^{-1}; $\theta = 0.4448$; $\alpha_1 = 0.0179$ cm^{-1} (Refs. 11 – 15);

[GeH_4] $B_e = 2.6969$ cm^{-1}; $\omega = 2110.86$ cm^{-1}; $\theta = 0.4428$; $\alpha_1 = 0.018$ cm^{-1} (Refs. 11, 13, 14, 16, and 17).

The comparison of theoretical and experimental data given in Table IV shows quite satisfactory agreement not only for relatively "heavy" GeH_4 and SiH_4 molecules, but for the "light" CH_4 molecule as well.

TABLE IV. Sextic centrifugal parameters of the CH_4, SiH_4 , *and* GeH_4 *molecules,* 10^{-8} cm^{-1}.

Parameter	Calc.	Exp.
	CH_4	
H	0.44	0.46
H_{4t}	– 0.052	– 0.057
H_{6t}	0.031	0.037
	SiH_4	
H	0.12	–
H_{4t}	– 0.018	– 0.020
H_{6t}	0.012	0.009
	GeH_4	
H	0.11	0.13
H_{4t}	– 0.016	– 0.018
H_{6t}	0.011	0.010

The results of prediction of the sextic centrifugal distortion parameters, as well as the quadratic ones, and other spectroscopic constants are quite satisfactory, what demonstrates a good potential of the "expanded local mode approach" (see Refs. 2, 5, and 18) both for qualitative and correct quantitative estimates of molecular properties and rovibrational spectra.

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