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ON SECOND-ORDER ANHARMONIC CONSTANTS FOR XY_2 MOLECULES IN THE LOCAL-MODE APPROACH

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Expressions relating the second-order anharmonic constants for the XY_2 *molecules* (C_{2v} *symmetry) are obtained using the local-mode approach. These are used to calculate the harmonic frequencies and anharmonic parameters for the* H_2Se *molecule.*

INTRODUCTION

The choice of physically valid models for objects under study is an issue of importance for the solution of inverse spectroscopic problems. This could be considered one of the basic points, as the usage of incorrect models might lead not only to quantitative but qualitative errors as well. A search for pinpointing ways to attract supplementary *a priori* information (in particular, those to establish additional relations between the parameters characterizing different molecular systems) is, therefore, one of the matters to be given special attention when handling inverse spectroscopic problems.

This information could be contributed, for instance, through consideration of characteristics of the molecule studied, in particular, by taking into account special features of the shape of the potential function, the nuclear masses ratio, etc. One of the approaches being intensively developed recently is the local-mode method, which found its application in the XY_N molecules with a relatively heavy nucleus X (see review [1]). For molecules such as XY_2, XY_3, and XY_4, it has been possible to formulate an appropriate mathematical model for describing the potential function, which allowed one, firstly, to obtain simple transformation coefficients that are independent of the shape of the potential function and, secondly, to arrive at relations between such spectroscopic parameters of a molecule as the parameters $a_\lambda^{\alpha\beta}$, the Coriolis parameters $\zeta_{\mu\nu}^{\alpha}$, the rovibrational parameters α_μ^{β}, the vibrational parameters $x_{\mu\nu}$, and the centrifugal and other second-order parameters of perturbation theory (PT). These relations permit one to substantially reduce the number of parameters necessary for a correct solution of the inverse spectroscopic problem and thereby simplify it, which is of special significance in the analysis of high-resolution spectra of highly excited vibrational bands. It should be noted, however, that the constantly growing requirements on the accuracy of the analysis make the usage of solely the above spectroscopic parameters insufficient for an adequate theoretical description of the real spectra. In this connection, the present work is aimed at considering the problem of extending the scope of application of the local-mode approach to the spectroscopic parameters belonging to the fourth order of PT, namely: determination of the relationship between the vibrational parameters $y_{\lambda\mu\nu}$ and the Darling–Dennison resonance parameter $\gamma_\lambda^{D\text{-}D}$ for molecules of the XY_2-type.

LOCAL-MODE METHOD FOR XY_2- TYPE MOLECULES

It is noteworthy that in the general case derivation of a direct relation between the vibrational parameters $y_{\lambda\mu\nu}$ and the structural and dynamical constants of a molecule is a complex and effort-consuming process. Moreover, the resulting relation is cumbersome, which in the majority of cases rules out the possibility of its further use. The analysis, however, shows that this can be avoided through the use of the following approximations for the fourth-order PT calculations corresponding to the local-mode model:

1) the central X-nucleus mass, M, is much larger than that of the Y-nuclei, m;

2) the equilibrium bond angle $2\alpha_e$ approaches $\pi/2$;

3) the interaction between the stretching and bending modes can be neglected in the quadratic part of the potential function

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$$V = \frac{1}{2} f_{rr}\left(\Delta r_2^2 + \Delta r_3^2\right) + f_{rr'}\Delta r_2 \Delta r_3 + \frac{1}{2} f_{\alpha\alpha}\left(r_e \Delta\alpha\right)^2 \ldots . \tag{1}$$

In the above approximation, the calculation is considerably simplified inasmuch as such parameters as $a_\lambda^{\alpha\beta}$, rotational B_α^e, rovibrational Coriolis parameters $\zeta_{\lambda\mu}^\alpha$, and the potential parameters $\varphi_{\lambda\mu\eta}$ satisfy the following simple relations (see [2]):

$$\begin{gathered} a_1^{xx} = a_1^{zz} = a_2^{xx} = -a_2^{zz} = -a_3^{xz} = -a_3^{zx} = \frac{a_1^{yy}}{2}, \quad a_2^{yy} = 0 ; \\ B_x^e = B_z^e = 2B_y^e \equiv B_e ; \\ \zeta_{13}^y = -\zeta_{31}^y = 0, \quad \zeta_{23}^y = -\zeta_{31}^y = 1 ; \\ \varphi_{111} = \varphi_{133} = 6k_{111}, \quad \omega_1 = \omega_3 \equiv \omega . \end{gathered} \tag{2}$$

Note that the above relations were obtained using the transformation coefficients $l_{N\alpha\lambda}$ that to the local mode approximation have simple forms:

$$\begin{gathered} l_{2z1} = -l_{3z1} = -l_{2x1} = -l_{3x1} = l_{2z2} = -l_{3z2} = l_{2x2} \\ = l_{3x2} = -l_{2z3} = -l_{3z3} = l_{2x3} = -l_{3x3} = \frac{1}{2}, \\ l_{Ny\lambda} = -0 \quad \text{and} \quad l_{1\alpha\lambda} = 0 . \end{gathered} \tag{3}$$

PARAMETERS $y_{\Lambda\mu\nu}$ AND γ_Λ IN THE LOCAL-MODE APPROXIMATION

Taking into account relations (2), one can readily understand that the rovibrational Hamiltonian of the molecule XY_2 obeying the conditions of the local-mode approximation would be written as

$$(hc)^{-1} H = \sum_{n \geq 0} H_n, \tag{4}$$

where

$$\begin{gathered} H_0 = \frac{\omega}{2}\left(p_1^2 + q_1^2 + p_3^2 + q_3^2\right), \\ H_1 = k_{111} q_1 \left(q_1^2 + 3q_3^2\right), \\ H_2 = k_{1111}\left(q_1^4 + 6q_1^2 q_3^2 + q_3^4\right) + \frac{1}{2} B_e G_y G_y, \\ H_3 = k_{11111} q_1 \left(q_1^4 + 10 q_1^2 q_3^2 + 5q_3^4\right) - \frac{B_e^{3/2}}{\sqrt{\omega}} q_1 G_y G_y, \\ H_4 = k_{111111}\left(q_1^6 + 15 q_1^4 q_3^2 + 15 q_1^2 q_3^4 + q_3^6\right) + \frac{3B_e^2}{2\omega} q_1^2 G_y G_y . \end{gathered} \tag{5}$$

At the same time, it is well known [3, 4] that the "effective" vibrational Hamiltonian of a molecule can be presented as

$$H^{\text{vib}} = \sum_{v,v'} |v\rangle\langle v| H_{vv'}, \tag{6}$$

where

$$H_{vv} = \sum_{\lambda} \omega_\lambda \left(v_\lambda + \frac{1}{2}\right) + \sum_{\lambda \le \mu} x_{\lambda\mu} \left(v_\lambda + \frac{1}{2}\right)\left(v_\mu + \frac{1}{2}\right)$$

$$+ \sum_{\lambda \le \mu \le \nu} y_{\lambda\mu\nu} \left(v_\lambda + \frac{1}{2}\right)\left(v_\mu + \frac{1}{2}\right)\left(v_\nu + \frac{1}{2}\right) + \dots ; \tag{7}$$

$$H_{vv'} = \left[F_0^{\text{D-D}} + \gamma_1\left(v_1 + \frac{1}{2} \pm 1\right) + \gamma_2\left(v_2 + \frac{1}{2}\right) + \gamma_3\left(v_3 + \frac{1}{2} \mp 1\right)\right]$$

$$\times \sqrt{\left(v_1 + \frac{1}{2} \pm \frac{1}{2}\right)\left(v_1 + \frac{1}{2} \pm \frac{3}{2}\right)\left(v_3 + \frac{1}{2} \mp \frac{1}{2}\right)\left(v_3 + \frac{1}{2} \mp \frac{3}{2}\right)} + \dots \tag{8}$$

for $|v\rangle = |v_1 v_2 v_3\rangle = |v_1 \pm 2 v_2 v_3 \mp 2\rangle$. In principle it is, therefore, clear how the spectroscopic and molecular parameters of operators (4) and (6) should be respectively related.

The dependence of the $x_{\lambda\mu}$- and $F_0^{\text{D-D}}$ constants on the initial vibrational Hamiltonian is well known (see, e.g., [3–5]). As far as the constants $y_{\lambda\mu\eta}$ and γ_λ are concerned, in order to determine their dependence on the vibrational Hamiltonian parameters one has to take the fourth order of PT into consideration, which is a rather complex task even in the local-mode approximation due to the awkwardness of calculations. In view of the latter, a software package was developed on the basis of analytical calculation systems to solve this problem.

These calculations brought forth simple relations between the parameters associated with the stretching vibrations:

$$y_{133} = y_{113} = 9y_{333} = 9y_{111} = 3\gamma_1 = 3\gamma_3, \tag{9}$$

where

$$y_{111} = \frac{5}{2}k_{111111} - \frac{35k_{11111}k_{111}}{2\omega} + \frac{225k_{1111}k_{111}^2}{4\omega^2} - \frac{17k_{1111}^2}{4\omega} - \frac{705k_{111}^4}{16\omega^3}. \tag{10}$$

The uttermost simplicity of the resulting relations permits us (a) to substantially ease solution of the inverse spectroscopic problems for the XY_2-type molecules satisfying the conditions of the local-mode approximation, (b) to considerably reduce the body of experimental information needed, and (c) to reproduce and predict to a high accuracy the centers of the stretching vibration bands.

By way of illustration of a possible application of the relations obtained, we analyzed the band centers of the stretching vibrations of the molecule H_2Se. As input data use was made of 23 bands whose centers were taken elsewhere [6–14]. The second column of Table 1 lists the corresponding experimental data.

Thirteen parameters, ω_1, ω_2, ω_3, x_{11}, x_{22}, x_{33}, x_{12}, x_{13}, x_{23}, $F_0^{\text{D-D}}$, y_{111}, y_{112}, and y_{123} (including relation (9)), were used in solving the inverse spectroscopic problem by the least-squares method, with Table 2 showing the results. The third column in Table 1 displays the reproducibility of the initial experimental data for vibrational conditions except for the last two centers. These were omitted in determining the parameters of Table 2; therefore, the results cited for them in the third column of Table 1 (marked by an asterisk) can be viewed as an illustration of the predicting power of the model used.

It might be well to point out that the example cited above illustrates the predicting power of the model for data extrapolation. It is noteworthy that interpolation is much higher, which is supported by the data of the fourth column in Table 1. In this case, the parameters listed in the third column of Table 2 were obtained through analyzing the experimental values of the band centers, except for four centers: $v_1 + 3v_3$, $3v_1 + v_3$, $4v_1$, and $2v_1 + 2v_3$. The values of the latter shown in the fourth column of Table 1 (marked by an asterisk) should be taken as a prediction.

TABLE 1

Band	Band center, cm^{-1}		
	Exper.	Calc. 1	Calc. 2
ν_2	1034.171	1034.207	1034.209
$2\nu_2$	2059.956	2059.867	2059.868
ν_1	2344.363	2344.326	2344.310
ν_3	2357.654	2357.600	2357.592
$3\nu_2$	3076.930	3076.979	3076.977
$\nu_1 + \nu_2$	3361.696	3361.733	3361.729
$\nu_2 + \nu_3$	3371.793	3371.867	3371.865
$\nu_1 + 2\nu_2$	4370.608	4370.592	4370.597
$2\nu_2 + \nu_3$	4377.619	4377.587	4377.587
$2\nu_1$	4615.328	4615.339	4615.370
$\nu_1 + \nu_3$	4617.393	4617.411	4617.431
$2\nu_3$	4702.547	4702.561	4702.553
$2\nu_1 + \nu_2$	5612.711	5612.714	5612.716
$\nu_1 + \nu_2 + \nu_3$	5613.754	5613.757	5613.758
$3\nu_1$	6798.097	6798.084	6798.076
$2\nu_1 + \nu_3$	6798.208	6798.213	6798.202
$\nu_1 + 2\nu_3$	6953.427	6953.430	6953.428
$3\nu_1 + \nu_3$	8894.504	8894.508	8894.259*
$4\nu_1$	8894.504	8894.513	8894.263*
$2\nu_1 + 2\nu_3$	9140.734	9140.737	9140.737*
$\nu_1 + 3\nu_3$	9146.441	9146.442	9146.422*
$6\nu_1$	12828.030	12829.903*	12828.039
$5\nu_1 + \nu_3$	12828.030	12829.903*	12828.040

TABLE 2

Parameters	Calculation 1	Calculation 2
ω_1	2436.456(63)	2436.230(67)
ω_2	1060.283(44)	1060.244(47)
ω_3	2452.353(55)	2452.149(84)
x_{11}	–20.901(18)	–20.824(22)
x_{22}	–4.2738(78)	–4.2751(85)
x_{33}	–21.429(17)	–21.356(27)
x_{12}	–14.741(59)	–14.638(65)
x_{13}	–83.415(46)	–83.161(45)
x_{23}	–19.380(23)	–19.360(27)
$F_0^{D\text{–}D}$	–20.660(10)	–20.5977(69)
y_{111}	–0.015008(71)	–0.02039(43)
y_{112}	–0.750(22)	–0.788(26)
y_{123}	–1.120(28)	–1.154(32)

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