On the study of $XY_2$ ($m_y \ll m_x$) plane molecules

O.N. Ulenikov*, S.N. Yurchenko, R.N. Tolchenov

Laboratory of Molecular Spectroscopy, Physics Department, Tomsk State University, Tomsk 634050, Russian Federation

Received 11 April 1996; accepted 23 July 1996

Abstract

The 'expanded local mode approach' derived in Ref. [1] (Ulenikov et al., Spectrochim. Acta Part A, 52 (1996) 1829) is modified in an appropriate way for the analysis of $XY_2$ ($C_{2v}$) molecules having an arbitrary value of the equilibrium interbond angle $2\phi_0$. It is shown that the conditions considered allow one to estimate with good enough accuracy the harmonic frequencies (quadratic force field parameters) of a molecule on the basis of experimental information on pure rotational spectra only. © 1997 Elsevier Science B.V.

Keywords: Centrifugal parameters; Local modes; Harmonic frequencies

1. Introduction

In Ref. [1] we have shown that for $XY_2$ ($C_{2v}$ symmetry) molecules with a value of the equilibrium interbond angle $2\phi_0$ near to $\pi/2$ and $m_y/m_x \ll 1$ (we will further denote $m_y \equiv m$, $m_x \equiv M$), analysis of the properties of $I_{Nz1}$ transformation provides the possibility to improve on results of the local mode approach formerly given in the spectroscopic literature and to derive new relations, e.g., between centrifugal distortion parameters (for more details, see Ref. [1]). In this case, the main idea of Ref. [1] was an analytical determination and analyzing of the ambiguous parameter $\sin \gamma$, which the $I_{Nz1}$ transformation coefficients depend on, in a simple form. In turn, that gave us the possibility to obtain simple relations between the $\zeta_{2\mu}$ and $a^{\phi^{\mu}}_{2\mu}$ parameters and, as a consequence, between different spectroscopic parameters.

It should be mentioned here that the condition $2\phi_0 = \pi/2$ restricts the number of molecules to which the results of Ref. [1] can be applied. In this respect it would be interesting to apply the procedure used in Ref. [1] to a more general situation.

* Corresponding author. E-mail: Ulenikov@phys.tsu.tomsk.su

1 The first systematic study of the rotational energy level structure of $XY_2$ ($C_{2v}$) molecules in the strict local mode limit was made by Halonen and Robiette in Ref. [2]. They assumed (a) that mass $M$ of the central nucleus $X$ is far greater than the masses $m$ of the nuclei $Y$, and in the limit $(m/M) = 0$, (b) that the equilibrium angle $2\phi_0 = \pi/2$, and (c) that deforming motion is totally absent in a molecule, and in the potential function $V$ only changes of valence bond lengths $\Delta r_i$ ($i = 2,3$) are taken into account (in this case $f_{\mu} = f_{\mu} = f_{\mu} = 0$). In Ref. [1] we have retained conditions (a) and (b), but rejected conditions (c).
with arbitrary value of the interbond angle $2\alpha_\epsilon$ and to look at the consequences of such a consideration for some spectroscopic problems.

Thus, in Section 2 an approach is considered that allows the possibility of determining the ambiguous parameter $\sin \gamma$ for any value of equilibrium interbond angle $2\alpha_\epsilon$ under the condition $m/M \ll 1$. Section 3 presents formulas obtained under the above conditions for the Coriolis $\xi_{3 \mu}$ and $\alpha_{3 \mu}$ parameters. In Section 4 centrifugal distortion parameters, which are obtained as a result of the above approximation, are considered. And in Section 5 a procedure is discussed which allows one to estimate with good enough accuracy the harmonic frequencies (quadratic force field parameters) of a molecule on the basis of experimental information on pure rotational spectra only.

2. Potential function and determination of $\sin \gamma$ parameter

As was mentioned in Ref. [1], in the general case the Coriolis $\xi_{3 \mu}$ and vibration–rotation $\alpha_{3 \mu}$ parameters of an $XY_2$ (C$_2v$) molecule have the following form:

$$\xi_{13} = \xi_{31} = -\frac{I_{xx}}{I_{yy}} \sin \gamma + \frac{I_{zz}}{I_{yy}} \cos \gamma,$$

and

$$\xi_{23} = \xi_{32} = -\frac{I_{xx}}{I_{yy}} \cos \gamma + \frac{I_{zz}}{I_{yy}} \sin \gamma,$$  

(1)

and

$$a_1^{x\gamma} = 2I_{xx}^{1/2} \cos \gamma, \quad a_2^{x\gamma} = 2I_{xx}^{1/2} \sin \gamma,$$

$$a_2^{x\gamma} = 2I_{xx}^{1/2} \sin \gamma, \quad a_2^{x\gamma} = -2I_{zz}^{1/2} \cos \gamma,$$

$$a_1^{y\gamma} = 2I_{yy}^{1/2} \xi_{23}, \quad a_2^{y\gamma} = -2I_{yy}^{1/2} \xi_{13},$$

$$a_2^{z\gamma} = a_3^{z\gamma} = -2 \left(\frac{I_{xx}I_{zz}}{I_{yy}}\right)^{1/2}.$$

(2)

In this case, $\sin \gamma$ is an ambiguous parameter which can be obtained from the condition

$$W_{12} \equiv \left(\frac{\partial^2 V}{\partial q_1 \partial q_2}\right)_q = 0,$$

(3)

where the quadratic part $V_{(2)}$ of the potential function has the form

$$V_{(2)} = \frac{1}{2} f_{rr}(\Delta \epsilon_2 + \Delta \epsilon_3) + f_{rr} \Delta \epsilon_2 \Delta r_3 + \frac{1}{2} f_{xz}(r_\epsilon \Delta \alpha)^2$$

$$+ f_{rr} (\Delta \epsilon_2 + \Delta \epsilon_3) r_\epsilon \Delta \alpha.$$

(4)

As was shown in Ref. [1], Eq. (3) can be exactly transformed to a form convenient for further analysis:

$$A \cos 2\gamma - B \sin 2\gamma,$$

(5)

where

$$\left(\frac{M}{2m + M}\right)^{1/2} \left(\frac{A}{\sin 2\alpha_\epsilon}\right) = f_{rr} + f_{rr} - 2f_{xx} + 4f_{rr} \cos 2\alpha_\epsilon,$$

(6)

and

$$BM = (f_{rr} + f_{rr})(M \sin^2 \alpha_\epsilon - (2m + M) \cos^2 \alpha_\epsilon)$$

$$+ \frac{2f_{xx}}{\sin^2 2\alpha_\epsilon} - (2m + M) \cos^2 \alpha_\epsilon (1 - \cos 2\alpha_\epsilon)^2$$

$$+ \frac{2f_{xx}}{\sin 2\alpha_\epsilon} - (2m + M) \cos^2 \alpha_\epsilon (1 - \cos 2\alpha_\epsilon)^2.$$

(7)

It should be mentioned that Eq. (7) can be exactly transformed to a simpler form:

$$B = (-f_{rr} - f_{rr} + 2f_{xx}) \cos 2\alpha_\epsilon + 2f_{rr} \sin 2\alpha_\epsilon$$

$$+ \frac{2m}{M} (-2f_{xx} \sin^2 \alpha_\epsilon - (f_{rr} + f_{rr}) \cos^2 \alpha_\epsilon$$

$$+ 2f_{rr} \sin^2 \alpha_\epsilon \sin 2\alpha_\epsilon).$$

(8)

Now, (1) if one assumes that all three conditions (a), (b) and (c) of footnote 1 are fulfilled, then the results of the Strict Local Mode Approach can be obtained at once; (2) if one assumes that conditions (a) and (b) are fulfilled (condition (c) is not fulfilled), then the results and relations of the Expanded Local Mode Approach will be obtained [1].

Now let us analyze the situation where only the condition $m/M \ll 1$ is fulfilled. Moreover, in the further discussion let us keep only terms which

---

1 It should be mentioned that Eq. (18) of Ref. [1] is a simple consequence of Eq. (5) of the present paper.
are proportional to \((m/M)^n\), and omit terms which are proportional \((m/M)^n\) with \(n > 1\). In this case, Eq. (5) can be transformed to the following form:

\[
\cos 2\alpha_c \sin 2\gamma = -\cos 2\gamma + O(m/M),
\]

where

\[
O(m/M) = \frac{4f_{\rho z} \cos^2 \alpha_c + \sin^2 \alpha_c - m}{\sin 2\alpha_c M}
\]

In fact, in obtaining Eq. (9) it was taken into account that for molecules of the considered type the conditions \(f_{\rho z}/f_{rr} \ll 1\), \(f_{\rho z}/f_{rr} \ll 1\) and \(f_{rr}/f_{rr} \ll 1\) are valid (at least, there are many molecules of the type with \(m/M \ll 1\) which satisfy these conditions). In this case, after substituting Eqs. (6) and (8) into Eq. (5) and omitting terms proportional to \((m/M)^n\) (with \(n > 1\)), one will simply obtain Eq. (9).

If one now looks at Eq. (10), one can see that its two parts have opposite signs, because both \(f_{\rho z}\) and \(f_{rr}\), and \(\sin 2\alpha_c\) have positive values. Moreover, as the analysis of situations in the literature shows (see, e.g., Ref. [3]) the two parts of Eq. (10) partially compensate each other. At least, one can assume that the second part \(O(m/M)\) of Eq. (9) is a small value of the order \((m/M)^n\) (with \(n > 1\)), and it can be omitted. After this assumption one will obtain a very simple relation for the ambiguous parameter \(\gamma\), namely

\[
\tan 2\gamma = -\tan 2\alpha_c.
\]

Eq. (11) now gives the possibility of obtaining the value of angle \(\gamma\) and, as a consequence, of parameter \(\sin \gamma\) which the transformation coefficients, \(l_{\text{Naio}}\) Coriolis \(\zeta_{\mu}^\alpha\) and vibration-rotation \(\alpha_{\mu}^\alpha\) parameters depend on:

\[
(\gamma + \alpha_c) = 0, \pm \pi/2, \pi.
\]

As can be seen from further analysis, the solutions \((\gamma + \alpha_c) = 0\) and \((\gamma + \alpha_c) = \pi\) are physically unreasonable, because values \((\gamma + \alpha_c) = 0\) or \(\pi\) lead to an absolute value of the \(\zeta_{13}\) parameter equal to 1. Solutions \(\pi/2\) and \(-\pi/2\) lead to one and the same result. For this reason we will further consider only \((\gamma + \alpha_c) = \pi/2\). The last leads to the following result:

\[
\sin \gamma = \cos \alpha_c \quad \text{and} \quad \cos \gamma = \sin \alpha_c.
\]

To illustrate this deduction, Table 1 presents values of parameter \(\sin \gamma\) calculated with formula (11) (Column 2) and corresponding values of \(\sin \gamma\) for the molecules \(\text{H}_2\text{O}, \text{H}_2\text{S}\) and \(\text{H}_2\text{Se}\) taken from Ref. [3] (Column 3). One can see a satisfactory correspondence (about 2-4 per cent) of the pairs of values. The second part of Table 1 presents values of \(\sin \gamma\) also for the \(\text{PH}_3, \text{CH}_2\) and \(\text{SiH}_2\) free radicals. The values of angles \(\alpha_c\) necessary for the calculations have been taken from references marked in Column 4 of Table 1. It should be mentioned here that the value of parameter \(\sin \gamma\) for a molecule can be obtained, in principle, from a known value of the Coriolis parameter \(\zeta_{\mu}^\alpha\) (see, e.g., Eq. (1) of the present paper, or the discussion in Refs. [7,8]), or from isotopic relations between the harmonic frequencies \(\nu_1\) and \(\nu_2\) of initial \(\text{YH}_2\) and deuterated \(\text{YD}_2\) species (see, e.g., Eq. (8) of Ref. [9]). However, both these methods require additional experimental data about excited vibrational states. At the same time, Eq. (11) only requires knowledge of angle \(\alpha_c\).

3. Coriolis \(\zeta_{\mu}^\alpha\), and \(\alpha_{\mu}^\alpha\) parameters

Before speaking about the \(\zeta_{\mu}^\alpha\) and \(\alpha_{\mu}^\alpha\) parameters, let us mention that for \(\text{XY}_2\) (\(C_{3v}\) symmetry) molecules the following exact relations between equilibrium moments of inertia and equilibrium rotational constants are fulfilled:

<table>
<thead>
<tr>
<th>Molecule</th>
<th>1</th>
<th>2 (\sin \gamma) (our)</th>
<th>3 (\sin \gamma)</th>
<th>4 Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{O})</td>
<td>0.6122</td>
<td>0.5913</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{S})</td>
<td>0.6934</td>
<td>0.6670</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{Se})</td>
<td>0.7014</td>
<td>0.6797</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_2) ((^1\text{A}_1))</td>
<td>0.6526</td>
<td>0.6590</td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td>(\text{CH}_2) ((^3\text{B}_1))</td>
<td>0.3190</td>
<td>0.3190</td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td>(\text{SiH}_2) ((^3\text{X}_1))</td>
<td>0.6947</td>
<td>0.6947</td>
<td>[5]</td>
<td></td>
</tr>
<tr>
<td>(\text{SiH}_2) ((^1\text{A}_1))</td>
<td>0.4772</td>
<td>0.4772</td>
<td>[5]</td>
<td></td>
</tr>
<tr>
<td>(\text{PH}_2) ((^3\text{B}_1))</td>
<td>0.6972</td>
<td>0.6972</td>
<td>[6]</td>
<td></td>
</tr>
<tr>
<td>(\text{PH}_2) ((^1\text{A}_1))</td>
<td>0.4840</td>
<td>0.4840</td>
<td>[6]</td>
<td></td>
</tr>
</tbody>
</table>
I' - \frac{I_x}{\sin^2 \alpha} = \frac{I_x}{M \cos^2 \alpha} - I_y' = \frac{M + 2m}{2m \sin^2 \alpha} = 2 \pi \mu^2 e
\equiv I_e (14)

and

B_e \sin^2 \alpha = \frac{B_e M}{M + 2m} = \frac{B_e M}{M + 2m} \equiv B_e / 2
\equiv B_e
(15)

where

B_e = \frac{\hbar}{4 \pi c} \sqrt{m r_c^2}.

After this remark, by using Eq. (13) in Eq. (1) one can obtain

\zeta_1 = \zeta_1 = - \frac{\sin 2 \alpha}{2M}, \quad \zeta_2 = \zeta_2 = \frac{\sin 2 \alpha}{2M} = 1;
(16)

and

a_{i}^{2 \alpha} = \frac{a_{i}^{2 \alpha}}{\sin^2 \alpha} \cdot \sin \alpha \cos \alpha = (1 + \frac{m}{M}) \frac{a_{i}^{2 \alpha}}{\cos^2 \alpha}\n= \left(1 - \frac{m}{M} \right) \frac{a_{i}^{2 \alpha}}{\sin \alpha \cos \alpha} = \left(1 + \frac{m}{M} \right) \frac{a_{i}^{2 \alpha}}{\cos^2 \alpha}\n= \left(1 + \frac{m}{M} \right) \frac{a_{i}^{2 \alpha}}{\sin \alpha \cos \alpha} = 2 \sqrt{I_e}.
\frac{a_{i}^{2 \alpha}}{M} = m \sin 2 \alpha \sqrt{I_e}.
(17)

In Eqs. (16) and (17), as in Eq. (9), we omitted terms proportional to \((m/M)^n\) \((n > 1)\).

4. Quartic centrifugal distortion constants

It is well known (see, e.g., Ref. [10]) that quartic centrifugal distortion coefficients \(\tau_{\mu \beta \rho \delta}\) in the general case have the following form:

\tau_{\mu \beta \rho \delta} = \sum_{\sigma} \frac{\mu_{\mu \beta} \mu_{\rho \delta}}{2 \alpha_{\sigma}} \phi_{\sigma},
\tau_{xx} = \frac{2 B_e^3}{\sin^6 \alpha} \left(\frac{\sin^2 \alpha}{\omega_1^2} + \frac{\cos^2 \alpha}{\omega_2^2}\right),
\tau_{zz} = \frac{2 B_e^3}{\cos^6 \alpha} \left(\frac{\sin^2 \alpha}{\omega_1^2} + \frac{\cos^2 \alpha}{\omega_2^2}\right) \left(1 + \frac{6m}{M}\right),
\tau_{yy} = \frac{2 B_e^3}{\omega_1^2} \left(1 + \frac{6m}{M} \cos^2 \alpha\right),
\tau_{xxz} = \frac{2 B_e^3}{\sin^2 \alpha \cos^2 \alpha} \left(\frac{1}{\omega_1^2} - \frac{1}{\omega_2^2}\right) \left(1 + \frac{3m}{M}\right),
\tau_{xyy} = \frac{2 B_e^3}{\sin^2 \alpha \cos^2 \alpha} \left(1 + \frac{3m}{M} \cos^2 \alpha\right) \left(1 + \frac{m}{\omega_2^2} \cos^2 \alpha\right),
\tau_{zyy} = \frac{2 B_e^3}{\cos^2 \alpha} \left(1 + \frac{3m}{M} \cos^2 \alpha\right) \left(1 + \frac{m}{\omega_2^2} \cos^2 \alpha\right),
\tau_{xzz} = \frac{2 B_e^3}{\omega_1^2} \left(1 + \frac{m}{\omega_2^2} \cos^2 \alpha\right),
(19)

In turn, the well-known relations (51) from Ref. [11] allow one to connect the \(\tau_{\mu \beta \rho \delta}\) parameters from Eq. (20) with \(\Delta_{K}, \Delta_{JK}, \Delta_{J}, \delta_{K}\) and \(\delta_{J}\) parameters determined from experimental data. As a consequence, any experimentally determined \(\Delta_{K}, \Delta_{JK}, \Delta_{J}, \delta_{K}\) or \(\delta_{J}\) parameter can be expressed as a simple function of the harmonic frequencies \(\omega_1, \omega_2, \omega_3\), of \(B_e\) and \(\sin \alpha\). To illustrate this, Table 2 presents results of calculations of centrifugal distortion parameters for one of the most inconvenient molecules from the viewpoint of theoretical predictions, H,O, on the basis of Eq. (20) and, for comparison, values of the same parameters obtained from experimental data (when we speak of the inconvenience of the H,O molecule for theoretical predictions we mean the presence of such effects as strong resonance interactions and anomalously large bending effects which can strongly perturb both the picture of the spectrum.
and, as a consequence, the values of some parameters). In this case, the experimental values of the centrifugal parameters and the value of the $B_e$ parameter necessary for the calculations were taken from Ref. [12], harmonic frequencies $\omega_1$ from Ref. [13], and the value of equilibrium angle $\chi_e$ from Ref. [3]. One can see a satisfactory enough correspondence between the experimental and predicted values of the $A_{JK}$, $A_j$, and $\delta_j$ parameters. Some discrepancies between predicted and expected values of the $A_K$ and $\delta_K$ parameters can be explained by the presence in the $H_2O$ molecule of bending effects, which were not taken into account in Eq. (20).

The same Table 2 also presents results of estimates of the centrifugal parameters for the $H_2S$, $H_2Se$ and $D_2O$ molecules (harmonic frequencies necessary for the calculations were taken from Refs. [3], [13–15]). It is seen that even for the $D_2O$ molecule (ratio $m/M = 1/8$) the results of predictions are correct enough.

### Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Calc. $10^4$ cm$^{-1}$</th>
<th>Exp. $10^4$ cm$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{JK}$</td>
<td>-53.79</td>
<td>-57.66</td>
<td>[12]</td>
</tr>
<tr>
<td>$A_j$</td>
<td>12.158</td>
<td>12.489</td>
<td></td>
</tr>
<tr>
<td>$\delta_j$</td>
<td>4.900</td>
<td>5.084</td>
<td></td>
</tr>
<tr>
<td>$A_K$</td>
<td>257.27</td>
<td>325.20</td>
<td></td>
</tr>
<tr>
<td>$\delta_K$</td>
<td>4.70</td>
<td>13.01</td>
<td></td>
</tr>
<tr>
<td>$D_2O$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{JK}$</td>
<td>-13.426</td>
<td>-15.359</td>
<td>[16]</td>
</tr>
<tr>
<td>$A_j$</td>
<td>2.915</td>
<td>3.096</td>
<td></td>
</tr>
<tr>
<td>$\delta_j$</td>
<td>1.137</td>
<td>1.221</td>
<td></td>
</tr>
<tr>
<td>$A_K$</td>
<td>73.691</td>
<td>92.457</td>
<td></td>
</tr>
<tr>
<td>$\delta_K$</td>
<td>1.724</td>
<td>3.658</td>
<td></td>
</tr>
<tr>
<td>$H_2S$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{JK}$</td>
<td>-21.283</td>
<td>-22.803</td>
<td>[17]</td>
</tr>
<tr>
<td>$A_j$</td>
<td>6.239</td>
<td>6.526</td>
<td></td>
</tr>
<tr>
<td>$\delta_j$</td>
<td>2.816</td>
<td>2.955</td>
<td></td>
</tr>
<tr>
<td>$A_K$</td>
<td>32.670</td>
<td>37.033</td>
<td></td>
</tr>
<tr>
<td>$\delta_K$</td>
<td>-1.812</td>
<td>-1.326</td>
<td></td>
</tr>
<tr>
<td>$H_2Se$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{JK}$</td>
<td>-17.328</td>
<td>-18.491</td>
<td>[18]</td>
</tr>
<tr>
<td>$A_j$</td>
<td>5.041</td>
<td>5.283</td>
<td></td>
</tr>
<tr>
<td>$\delta_j$</td>
<td>2.392</td>
<td>2.425</td>
<td></td>
</tr>
<tr>
<td>$A_K$</td>
<td>23.084</td>
<td>26.368</td>
<td></td>
</tr>
<tr>
<td>$\delta_K$</td>
<td>-2.092</td>
<td>-1.833</td>
<td></td>
</tr>
</tbody>
</table>

5. Estimation of harmonic frequencies $\omega_1$ from parameters of the ground vibrational state

What has been mentioned in the above sections allows one to consider such an important problem for applications as an estimate of the harmonic frequencies of a molecule on the basis of experimental data on parameters of the ground vibrational state alone. It can be especially important for molecular objects of which the experimental recording of spectra in excited vibrational states is complicated for one or other reason. Really, if one knows the experimental values of three rotational ($A$, $B$, and $C$) and five centrifugal distortion ($A_{JK}$, $A_j$, $\delta_j$, $A_K$, and $\delta_K$) parameters of the ground vibrational state, then it is possible (1) to use the $A$, $B$, and $C$ parameters for estimation of the $B_e$ constant and equilibrium interbond angle $\chi_e$, at least in the first approximation, and then (2) to use experimental values of the centrifugal parameters and Eq. (20) of Section 4 for estimation of the three $\omega_1$ harmonic frequencies. As was mentioned above, in this case it is important that the parameter $\sin \gamma$, which cannot be determined without a number of experimental data about excited vibrational states, is not present in the formulas used.

### Table 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Calc. (cm$^{-1}$)</th>
<th>Exp. (cm$^{-1}$)</th>
<th>Diff. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega_1$</td>
<td>3880.49</td>
<td>3834.44</td>
<td>1.2</td>
</tr>
<tr>
<td>$\omega_2$</td>
<td>1606.87</td>
<td>1646.99</td>
<td>2.4</td>
</tr>
<tr>
<td>$\omega_3$</td>
<td>3882.92</td>
<td>3940.73</td>
<td>1.5</td>
</tr>
<tr>
<td>$D_2O$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega_1$</td>
<td>2736.51</td>
<td>2736.80</td>
<td>1.0</td>
</tr>
<tr>
<td>$\omega_2$</td>
<td>1159.37</td>
<td>1206.39</td>
<td>3.9</td>
</tr>
<tr>
<td>$\omega_3$</td>
<td>2943.26</td>
<td>2888.78</td>
<td>1.9</td>
</tr>
<tr>
<td>$H_2S$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega_1$</td>
<td>2699.35</td>
<td>2719.18</td>
<td>0.8</td>
</tr>
<tr>
<td>$\omega_2$</td>
<td>1181.25</td>
<td>1212.84</td>
<td>2.6</td>
</tr>
<tr>
<td>$\omega_3$</td>
<td>2736.36</td>
<td>2735.82</td>
<td>0.7</td>
</tr>
<tr>
<td>$H_2Se$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\omega_1$</td>
<td>2407.94</td>
<td>2427.65</td>
<td>0.6</td>
</tr>
<tr>
<td>$\omega_2$</td>
<td>1032.78</td>
<td>1060.94</td>
<td>2.6</td>
</tr>
<tr>
<td>$\omega_3$</td>
<td>2464.88</td>
<td>2468.66</td>
<td>0.2</td>
</tr>
</tbody>
</table>
To illustrate the validity of this, Table 3 presents values of harmonic frequencies $\omega_2$ for the molecules H$_2$O, D$_2$O, H$_2$S and H$_2$Se estimated by Eq. (20) and, for comparison, experimentally determined values of the same parameters from Refs. [3,13–15] (experimental values of the rotational and centrifugal distortion constants of the ground vibrational states of H$_2$O, D$_2$O, H$_2$S and H$_2$Se molecules were taken from Refs. [12,16–18]). In this case, since some XY$_2$ (C$_2v$) molecules possess peculiarities connected with a large amplitude bending motion, and these peculiarities first of all appear in the $A_K$ and $\delta_K$ parameters, we used in our calculations experimental values of the $A_{JK}$, $A_I$ and $\delta_J$ parameters. If one remembers that only the parameters of the ground vibrational states were used as the initial information, one can see a more than satisfactory correspondence between predicted and experimental values of the harmonic frequencies. This allows one to expect that the results of predictions for more exotic molecules, such as H$_2$Te, H$_2$Po, SiH$_2$, PH$_2$, CH$_2$, AsH$_2$, NH$_2$, H$_2$Cl and others, will be correct enough too.

Acknowledgements

This work was supported, in part, by the Russian Foundation for Fundamental Research (Pr. N95-03-08081a).

References