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THEORY OF VIBRATIONS OF TETRA-ATOMIC SYMMETRIC BENT MOLECULES

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Abstract. In this contribution we submit a theory of vibrations of a tetra-atomic symmetric bent molecule *ABBA* in *cis*-conformation. Compared to the previous calculations, where some approximations have been made, now we gave a more rigorous version. For the molecule studied we have calculated frequencies of all five vibrations. Among them three vibrations, *ax1, ay1*, and *sy1*, are normal or nearly normal. The longitudinal vibrations are of two types: $(\rightarrow\leftarrow\ \rightarrow\leftarrow)$ and $(\rightarrow\rightarrow\ \leftarrow\leftarrow)$.

1. Introduction

Structure of molecules and macromolecules manifest themselves in vibration spectra. Modern physics, chemistry, and biology widely use the vibration spectra for solving numerous and diverse problems which refer to the study of molecule and macromolecule structure and its changing in physical, chemical and biological processes. Molecule vibrations play a crucial role in relaxation phenomena, in kinetics of chemical reactions, in self-organization of polymers and biopolymers with the resulting formation of a particular structure [1]. For this reason the theory of molecule vibrations is of fundamental importance for condensed matter physics, molecular physics, biology, and even for nanotechnology.

Vibration frequencies of molecules and macromolecules, after the dissociation energy and the energy of chemical bonds, are the most important constants of these substances [2]. One of the most reliable and precise methods for the experimental determination of eigen frequencies of molecules and macromolecules are infrared spectroscopy and Raman spectroscopy. To analyze the vibration spectra of complex molecules, which are very complicated, we must be able to establish purely theoretically characteristic vibrations of atomic groups incorporated in one or another molecule. Such vibrations depend very little on the presence of other atomic groups.

By the purely theoretical approach to molecule vibrations we understand any analytical solution obtained in the framework of mechanics or another science without using semi-empirical potential functions with a lot of parameters, usually elastic constants, which are necessary for a numerical solution and which number exceeds, usually significantly, the number of atoms in a molecule. The appearance of excess parameters had led to endless discussion about the correctness of parameter choice instead of developing new approaches, e.g. electronic theory of molecule vibrations was created with the purpose to gain better insight into the nature of those vibrations [3]. Careful analysis of this situation has been given in [4]. Unfortunately, the majority of researchers prefer calculating instead of thinking. Probably for this reason, the purely analytical theory was created, at this moment, only for triatomic molecules in the framework of mechanics [2, 5] and relatively recently by the combination of mechanics and the bond-charge theory which takes into account electronic degrees of freedom [3]. The mechanical theory has become a classical one and was incorporated into text-books long ago [2, 5]. The new theory enhances the possibilities for studying properties of molecules significantly. In particular, it gives a unified approach to vibrations and rotations of molecule and macromolecules [6]. Nevertheless it is not worth leaving the classical mechanical theory out of scientific reckoning. As before, it remains the basis for classification of vibrations.

We have developed the theory of molecule vibrations in the frame work of classical mechanical approach for tetra-atomic linear symmetric molecules [7] and for tetra-atomic bent symmetric molecules [8]. However, in the last case, due to some approximations one of vibrations was lost. In this contribution we give a revised and more complete version of the calculations done in [8] without the previous approximations.

2. Target setting

Consider a tetra-atomic bent symmetric molecule *ABBA*. Let in an equilibrium position the molecule has the *cis*–form of a symmetric bent chain with the valence angles θ, the equilibrium distance between atoms A and B being equal to a_1 and between atoms B, respectively a_2 (Fig. 1).

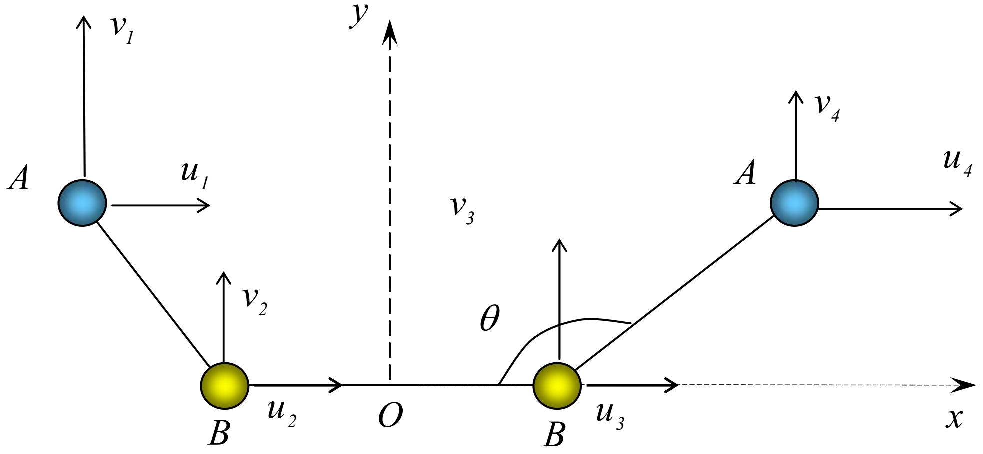

Fig. 1. Displacements of atoms in a tetra-atomic symmetric bent molecule.

Denote by M_A , M_B , M_B , M_A the masses of the atoms and by $\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3$ $\mathbf{u}_4$ their displacements from equilibrium positions. Suppose, as before [7], that interatomic forces both stretching the bounds and bending the angle between bonds are of a short-range character. The forces acting between the nearest neighbors are central. Let k_1 , k_2 , k_1 be their elastic constants. The forces changing the valence angles θ, whose vertices are occupied by the second and the third atom, are of noncentral character. Let k_θ be their elastic constant. The valence angle and elastic constants are input parameters. Hence we will study the vibrations of this tetra-atomic molecule in the framework of a four–parameter model.

3. Geometric constraints and new coordinates

In the same way as before [7], we exclude translation motion of the molecule along the axes x and y putting the total linear momentum of the molecule equal to zero. It means that the inertia center of the molecule is immobile so the following relation takes place

$$\sum M_i \boldsymbol{u}_i = 0 .$$

In our case this leads to appearance of the geometric constraints of atomic displacements what look like

$$M_A\,(u_1 + u_4) + M_B\,(u_2 + u_3) = 0 ,$$

$$M_A\,(v_1 + v_4) + M_B\,(v_2 + v_3) = 0 .$$

Introduce the new coordinates

$$q_{ax1} = u_1 + u_4 , \qquad q_{ax2} = u_2 + u_3 ,$$

$$q_{sx1} = u_4 - u_1 , \qquad q_{sx2} = u_3 - u_2 ,$$

$$q_{ay1} = v_1 + v_4 , \qquad q_{ay2} = v_2 + v_3 ,$$

$$q_{sy1} = v_4 - v_1 , \qquad q_{sy2} = v_3 - v_2 .$$

At that the geometric constraints take the form

$$q_{ax2} = -\frac{M_A}{M_B}\, q_{ax1} \;, \qquad q_{ay2} = -\frac{M_A}{M_B}\, q_{ay1} \;.$$

To exclude rotation of the molecule, one needs to assume that its total angular momentum is zero. For small vibrations this condition takes the form [7]

$$\sum M_i \left[\boldsymbol{r}_{i0}, \boldsymbol{u}_i\right] = 0 ,$$

where $\boldsymbol{r}_{i0}$ is the radius vector of the immobile equilibrium location of i atom.

Let us project the displacement of atom *4* on the direction normal to the line *OA* (Fig.2).

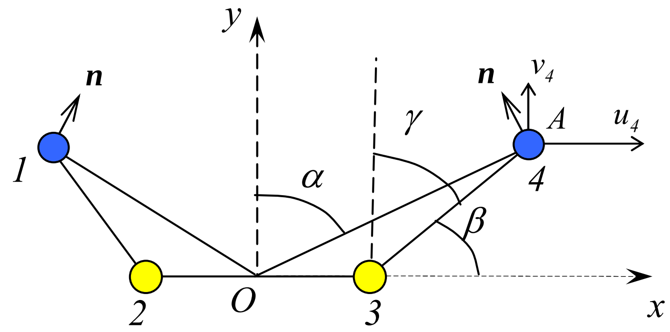

Fig. 2. Angles in a bent tetra-atomic symmetric molecule used in calculation.

This gives the displacement producing the rotation $\Delta\theta_4$ of the molecule around the axis z going through the origin of coordinates

$$b\,(\Delta\theta_4) = v_4 \sin\,\alpha - u_4 \cos\alpha\ .$$

Here

$$\tan\alpha = \frac{\sin\beta}{(a_2 / 2\,a_1) + \cos\beta}\,, \qquad \beta = \pi - \theta\,,$$

$$b = OA\,, \qquad b^2 = \frac{a_2^2}{4} + a_1\,a_2 + a_1^2\,.$$

The displacement producing the rotation $\Delta\theta_1$ of the molecule in opposite direction can be obtained by the action of rotation $C_2(\,y\,)$ on $b\,(\Delta\theta_4\,)$,

$$b\,(\Delta\theta_1) = C_2\,(\,y\,)\ b\,(\Delta\theta_3) = v_1 \sin\,\alpha + u_1 \cos\alpha\ .$$

If the rotation does not take place, then

$$M_A\ b\,(\Delta\theta_1) + M_B\ \frac{a_2}{2}\ v_2 = M_A\ b\,(\Delta\theta_4) + M_B\ \frac{a_2}{2}\ v_3\,,$$

or

$$M_A\,b\,\big[(v_1 - v_4)\sin\,\alpha + (u_1 + u_4)\cos\alpha\big] = M_B\ \frac{a_2}{2}\,(v_3 - v_2)\,.$$

Therefore

$$v_3 - v_2 = \frac{M_A}{M_B}\,\frac{2\,b}{a_2}\,\big[(v_1 - v_4)\sin\,\alpha + (u_1 + u_4)\cos\alpha\big].$$

In the new coordinates

$$q_{sy2} = \frac{M_A}{M_B}\,\frac{2\,b}{a_2}\Big(\,q_{ax1} \cos\,\alpha - q_{sy1} \sin\,\alpha\,\Big).$$

Thus three coordinates, namely $q_{ax2}, q_{ay2}, q_{sy2}$, are superfluous.

4. Kinetic energy

The kinetic energy of the molecule is

$$E_{kin}(\dot{\boldsymbol{u}}_1, \dot{\boldsymbol{u}}_2, \dot{\boldsymbol{u}}_3, \dot{\boldsymbol{u}}_4) = \frac{M_A}{2}\left(\dot{\boldsymbol{u}}_1^{\,2} + \dot{\boldsymbol{u}}_4^{\,2}\right) + \frac{M_B}{2}\left(\dot{\boldsymbol{u}}_2^{\,2} + \dot{\boldsymbol{u}}_3^{\,2}\right)$$

$$= \frac{M_A}{2}\left(\dot{u}_1^2 + \dot{u}_4^2 + \dot{v}_1^2 + \dot{v}_4^2\right) + \frac{M_B}{2}\left(\dot{u}_2^2 + \dot{u}_3^2 + \dot{v}_2^2 + \dot{v}_3^2\right).$$

Write down the kinetic energy in the new coordinates. Since

$$u_1^2 + u_4^2 = \frac{1}{2}(q_{ax1}^2 + q_{sx1}^2) \,, \qquad u_2^2 + u_3^2 = \frac{1}{2}(q_{ax2}^2 + q_{sx2}^2) \,,$$

$$v_1^2 + v_4^2 = \frac{1}{2}(q_{ay1}^2 + q_{sy1}^2), \qquad v_2^2 + v_3^2 = \frac{1}{2}(q_{ay2}^2 + q_{sy2}^2),$$

we have

$$E_{kin} = \frac{M_A}{4}\left(\dot{q}_{ax1}^2 + \dot{q}_{sx1}^2 + \dot{q}_{ay1}^2 + \dot{q}_{sy1}^2\right) + \frac{M_B}{4}\left(\dot{q}_{ax2}^2 + \dot{q}_{sx2}^2 + \dot{q}_{ay2}^2 + \dot{q}_{sy2}^2\right).$$

Eliminate the superfluous coordinates

$$q_{ax2} = -\frac{M_A}{M_B}\, q_{ax1} \,, \qquad q_{ay2} = -\frac{M_A}{M_B}\, q_{ay1}$$

Because of

$$q_{ax2}^2 = \left(\frac{M_A}{M_B}\right)^2 q_{ax1}^2 \,, \qquad q_{ay2}^2 = \left(\frac{M_A}{M_B}\right)^2 q_{ay1}^2 \,,$$

the second term takes the form

$$\frac{M_A^2}{4M_B}\left(\dot{q}_{ax1}^2 + \dot{q}_{ay1}^2\right) + \frac{M_B}{4}\left(\dot{q}_{sx2}^2 + \dot{q}_{sy2}^2\right).$$

As a result, we have

$$E_{kin} = \frac{M_A}{4}\left[\left(1 + \frac{M_A}{M_B}\right)\left(\dot{q}_{ax1}^2 + \dot{q}_{ay1}^2\right) + \left(\dot{q}_{sx1}^2 + \dot{q}_{sy1}^2\right)\right] + \frac{M_B}{4}\left(\dot{q}_{sx2}^2 + \dot{q}_{sy2}^2\right) .$$

Now eliminate the superfluous coordinate

$$q_{sy2} = \frac{M_A}{M_B}\,\frac{2b}{a_2}\left(q_{ax1}\cos\alpha - q_{sy1}\sin\alpha\right).$$

Because of

$$q_{sy2}^2 = \left(\frac{M_A}{M_B}\right)^2 \left(\frac{2b}{a_2}\right)^2 \left(q_{ax1}^2 \cos^2\alpha + q_{sy1}^2 \sin^2\alpha - 2\, q_{ax1}\, q_{sy1} \cos\alpha \,\sin\alpha\right),$$

the second term takes the form

$$\frac{M_B}{4}\,\dot{q}_{sx2}^2+\frac{M_A^2}{M_B}\left(\frac{b}{a_2}\right)^2\left(\dot{q}_{ax1}^2\cos^2\alpha+\dot{q}_{sy1}^2\sin^2\alpha-\dot{q}_{ax1}\,\dot{q}_{sy1}\sin 2\alpha\right)$$

Finally we obtain

$$E_{kin}=\frac{M_A}{4}\left[\left(1+\frac{M_A}{M_B}\right)\left(\dot{q}_{ax1}^2+\dot{q}_{ay1}^2\right)+\left(\dot{q}_{sx1}^2+\dot{q}_{sy1}^2\right)\right]$$
$$+\frac{M_B}{4}\,\dot{q}_{sx2}^2+\frac{M_A^2}{M_B}\left(\frac{b}{a_2}\right)^2\left(\dot{q}_{ax1}^2\cos^2\alpha+\dot{q}_{sy1}^2\sin^2\alpha-\dot{q}_{ax1}\,\dot{q}_{sy1}\sin 2\alpha\right) .$$

Or in another form

$$E_{kin}=\frac{M_A}{4}\left(1+\frac{M_A}{M_B}\right)\dot{q}_{ay1}^2+\frac{M_A}{4}\,\dot{q}_{sx1}^2+\frac{M_B}{4}\,\dot{q}_{sx2}^2$$
$$+\frac{M_A}{4}\left\{\left[\left(1+\frac{M_A}{M_B}\right)+\frac{M_A}{M_B}\left(\frac{2b}{a_2}\right)^2\cos^2\alpha\right]\dot{q}_{ax1}^2\right\}+\frac{M_A}{4}\left\{\left[1+\frac{M_A}{M_B}\left(\frac{2b}{a_2}\right)^2\sin^2\alpha\right]\dot{q}_{sy1}^2\right\}$$
$$-\frac{M_A^2}{M_B}\left(\frac{b}{a_2}\right)^2\sin 2\alpha\,(\dot{q}_{ax1}\,\dot{q}_{sy1})$$

5. Potential energy

The potential energy of the molecule consists of three parts

$$U(\boldsymbol{u}_1,\boldsymbol{u}_2,\boldsymbol{u}_3\ \boldsymbol{u}_4)=U_1+U_2+U_3 ,$$

where

$$U_1=\frac{k_1}{2}\left[(\Delta l_1)^2+(\Delta l_3)^2\right],\ U_2=\frac{k_2}{2}(\Delta l_2)^2, \qquad U_3=\frac{k_\theta}{2}a^2\left[(\Delta\theta_2)^2+(\Delta\theta_3)^2\right].$$

Here Δl_1 , Δl_2 and Δl_3 are the length changes of the interatomic bonds *AB, BB,* and *BA*, respectively, $\Delta\theta$ is the deviation of the valence angle from its equilibrium value θ during deformation vibrations, $2a=a_1+a_2$.

We can find the value $\Delta\,l_3$ projecting the vector $\boldsymbol{u}_4-\boldsymbol{u}_3$ on the direction *BA*,

$$\Delta\,l_3=(u_4-u_3)\sin\gamma+(v_4-v_3)\cos\gamma ,$$

where $\gamma=\theta-\pi/2$. From this it follows that

$$(\Delta l_3)^2=(u_4-u_3)^2\sin^2\gamma+(v_4-v_3)^2\cos^2\gamma+2(u_4-u_3)(v_4-v_3)\sin\gamma\,\cos\gamma .$$

Acting by the rotation $C_2(y)$ on $(\Delta l_3)^2$, we find $(\Delta l_1)^2$

$$(\Delta l_1)^2 = (u_1 - u_2)^2 \sin^2 \gamma + (v_1 - v_2)^2 \cos^2 \gamma - 2(u_1 - u_2)(v_1 - v_2) \sin \gamma \cos \gamma .$$

The sum of these two last expressions is

$$(\Delta l_1)^2 + (\Delta l_3)^2 = \left[(u_1 - u_2)^2 + (u_4 - u_3)^2\right] \sin^2 \gamma + \left[(v_1 - v_2)^2 + (v_4 - v_3)^2\right] \cos^2 \gamma$$

$$+ 2\left[(u_4 - u_3)(v_4 - v_3) - (u_1 - u_2)(v_1 - v_2)\right] \sin \gamma \cos \gamma .$$

Since

$$(u_1 - u_2)^2 + (u_4 - u_3)^2 = u_1^2 + u_4^2 + u_2^2 + u_3^2 - 2(u_1 u_2 + u_3 u_4),$$

$$(v_1 - v_2)^2 + (v_4 - v_3)^2 = v_1^2 + v_4^2 + v_2^2 + v_3^2 - 2(v_1 v_2 + v_3 v_4),$$

$$u_1 = \tfrac{1}{2}(q_{ax1} - q_{sx1}), \qquad u_2 = \tfrac{1}{2}(q_{ax2} - q_{sx2}),$$

$$u_3 = \tfrac{1}{2}(q_{ax2} + q_{sx2}), \qquad u_4 = \tfrac{1}{2}(q_{ax1} + q_{sx1}),$$

$$u_1 u_2 = \tfrac{1}{4}(q_{ax1} - q_{sx1})(q_{ax2} - q_{sx2}), \qquad u_3 u_4 = \tfrac{1}{4}(q_{ax2} + q_{sx2})(q_{ax1} + q_{sx1}),$$

$$u_1 u_2 + u_3 u_4 = \tfrac{1}{2}(q_{a1} q_{a2} + q_{s1} q_{s2}), \qquad u_2 u_3 = \tfrac{1}{4}(q_{ax2}^2 - q_{sx2}^2),$$

and analogous formulas are valid for the components v_i, we have

$$\begin{aligned} U_1 = {} & \frac{k_1}{4}\left(q_{ax1}^2 + q_{sx1}^2 + q_{ax2}^2 + q_{sx2}^2 - 2 q_{ax1} q_{ax2} - 2 q_{sx1} q_{sx2}\right) \sin^2 \gamma \\ & + \frac{k_1}{4}\left(q_{ay1}^2 + q_{sy1}^2 + q_{ay2}^2 + q_{sy2}^2 - 2 q_{ay1} q_{ay2} - 2 q_{sy1} q_{sy2}\right) \cos^2 \gamma \end{aligned} .$$

Let us eliminate the superfluous coordinates

$$q_{ax2} = -\frac{M_A}{M_B} q_{ax1}, \qquad q_{ay2} = -\frac{M_A}{M_B} q_{ay1}$$

Because of

$$q_{ax2}^2 = \left(\frac{M_A}{M_B}\right)^2 q_{ax1}^2, \qquad q_{ay2}^2 = \left(\frac{M_A}{M_B}\right)^2 q_{ay1}^2,$$

we have

$$U_1 = \frac{k_1}{4}\left(q_{ax1}^2 + q_{sx1}^2 + \left(\frac{M_A}{M_B}\right)^2 q_{ax1}^2 + q_{sx2}^2 + 2\frac{M_A}{M_B} q_{ax1}^2 - 2 q_{sx1} q_{sx2} \right) \sin^2 \gamma +$$

$$+\frac{k_1}{4}\left(q_{ay1}^2+q_{sy1}^2+\left(\frac{M_A}{M_B}\right)^2 q_{ay1}^2+q_{sy2}^2+2\frac{M_A}{M_B}q_{ay1}^2-2q_{sy1}q_{sy2} \right)\cos^2\gamma \ .$$

Now eliminate the superfluous coordinate

$$q_{sy2}=\frac{M_A}{M_B}\frac{2b}{a_2}\left(q_{ax1}\cos\alpha-q_{sy1}\sin\alpha \right).$$

Because of

$$q_{sy2}^2=\left(\frac{M_A}{M_B}\right)^2\left(\frac{2b}{a_2}\right)^2\left(q_{ax1}^2\cos^2\alpha+q_{sy1}^2\sin^2\alpha-2\,q_{ax1}q_{sy1}\cos\alpha\ \sin\alpha\right),$$

we obtain

$$U_1=\frac{k_1}{4}\left[\left(1+\frac{M_A}{M_B}\right)^2\sin^2\gamma+\frac{M_A^2}{M_B^2}\frac{4b^2}{a_2^2}\cos^2\alpha\cos^2\gamma\right]q_{ax1}^2+\frac{k_1}{4}\sin^2\gamma\, q_{sx1}^2+\frac{k_1}{4}\sin^2\gamma\, q_{sx2}^2$$
$$-\frac{k_1}{4}\sin^2\gamma\, 2q_{sx1}q_{sx2}+\frac{k_1}{4}\cos^2\gamma\left[\left(1+\frac{M_A}{M_B}\right)^2\right]q_{ay1}^2+\frac{k_1}{4}\cos^2\gamma\left[\left(1+\sin\alpha\frac{M_A}{M_B}\frac{2b}{a_2}\right)^2\right]q_{sy1}^2$$
$$-\frac{k_1}{4}\frac{M_A}{M_B}\frac{2b}{a_2}2\cos\alpha\cos^2\gamma\left[1+\sin\alpha\frac{M_A}{M_B}\frac{2b}{a_2}\right]q_{ax1}q_{sy1}$$

The next term is the potential energy U_2. Here

$$(\Delta l_2)^2=(u_3-u_2)^2+(v_3-v_2)^2=q_{sx2}^2+q_{sy2}^2$$

and we have

$$U_2=\frac{k_2}{2}(\Delta l_2)^2=\frac{k_2}{2}(q_{sx2}^2+q_{sy2}^2)$$

Again let us eliminate the superfluous coordinate

$$q_{sy2}=\frac{M_A}{M_B}\frac{2b}{a_2}\left(q_{ax1}\cos\alpha-q_{sy1}\sin\alpha \right).$$

Because of

$$q_{sy2}^2=\left(\frac{M_A}{M_B}\right)^2\left(\frac{2b}{a_2}\right)^2\left(q_{ax1}^2\cos^2\alpha+q_{sy1}^2\sin^2\alpha-2\,q_{ax1}q_{sy1}\cos\alpha\ \sin\alpha\right),$$

we obtain

$$U_2 = \frac{k_2}{2} (q_{sx2}^2 + \left(\frac{M_A}{M_B} \right)^2 \left(\frac{2b}{a_2} \right)^2 \left(q_{ax1}^2 \cos^2 \alpha + q_{sy1}^2 \sin^2 \alpha - 2\, q_{ax1} q_{sy1} \cos\alpha \; \sin\alpha \right))$$

Now find the change of the angle *BBA* for the bent molecule. For this purpose, project the vector $\boldsymbol{u}_4 - \boldsymbol{u}_3$ on the direction normal to *BA*. Then we have

$$\Delta\theta_3 = \frac{1}{a} \left[(v_4 - v_3) \sin\gamma - (u_4 - u_3) \cos\gamma \right].$$

The angle change $\Delta\theta_1$ can be found by acting the rotation $C_2(y)$ on $\Delta\theta_3$

$$\Delta\theta_1 = C_2(y)\, \Delta\theta_3 = \frac{1}{a} \left[(v_1 - v_2) \sin\gamma + (u_1 - u_2) \cos\gamma \right] .$$

Therefore

$$a^2 \Delta\theta_1^2 = (v_1 - v_2)^2 \sin^2\gamma + (u_1 - u_2)^2 \cos^2\gamma + 2(u_1 - u_2)(v_1 - v_2) \sin\gamma \; \cos\gamma ,$$

$$a^2 \Delta\theta_3^2 = (v_4 - v_3)^2 \sin^2\gamma + (u_4 - u_3)^2 \cos^2\gamma - 2(u_4 - u_3)(v_4 - v_3) \sin\gamma \; \cos\gamma .$$

Comparing these expressions with

$$(\Delta l_1)^2 = (u_1 - u_2)^2 \sin^2\gamma + (v_1 - v_2)^2 \cos^2\gamma - 2(u_1 - u_2)(v_1 - v_2) \sin\gamma \; \cos\gamma ,$$

$$(\Delta l_3)^2 = (u_4 - u_3)^2 \sin^2\gamma + (v_4 - v_3)^2 \cos^2\gamma + 2(u_4 - u_3)(v_4 - v_3) \sin\gamma \; \cos\gamma ,$$

and the potential energies

$$U_3 = \frac{k_\theta}{2} a^2 \left[(\Delta\theta_2)^2 + (\Delta\theta_3)^2 \right] \qquad U_1 = \frac{k_1}{2} \left[(\Delta l_1)^2 + (\Delta l_3)^2 \right],$$

with each other, we can write right away

$$U_3 = \frac{k_\theta}{4} \left[\left(1 + \frac{M_A}{M_B} \right)^2 \cos^2\gamma + \frac{M_A^2}{M_B^2} \frac{4b^2}{a_2^2} \cos^2\alpha \sin^2\gamma \right] q_{ax1}^2 + \frac{k_\theta}{4} \cos^2\gamma\, q_{sx1}^2 + \frac{k_\theta}{4} \cos^2\gamma\, q_{sx2}^2$$
$$- \frac{k_\theta}{4} \cos^2\gamma\, 2\, q_{sx1} q_{sx2} + \frac{k_\theta}{4} \sin^2\gamma \left[\left(1 + \frac{M_A}{M_B} \right)^2 \right] q_{ay1}^2 + \frac{k_\theta}{4} \sin^2\gamma \left[\left(1 + \sin\alpha \frac{M_A}{M_B} \frac{2b}{a_2} \right)^2 \right] q_{sy1}^2$$
$$- \frac{k_\theta}{4} \frac{M_A}{M_B} \frac{2b}{a_2} 2 \cos\alpha \sin^2\gamma \left[1 + \sin\alpha \frac{M_A}{M_B} \frac{2b}{a_2} \right] q_{ax1} q_{sy1}$$

6. Lagrange function and normal coordinates

Combining all the previous results obtained, we obtain the Lagrange function

$$
\begin{aligned}
L = {} & \frac{M_A}{4}\left(1+\frac{M_A}{M_B}\right)\dot{q}_{ay1}^2 + \frac{M_A}{4}\dot{q}_{sx1}^2 + \frac{M_B}{4}\dot{q}_{sx2}^2 \\
& + \frac{M_A}{4}\left\{\left[\left(1+\frac{M_A}{M_B}\right)+\frac{M_A}{M_B}\left(\frac{2b}{a_2}\right)^2\cos^2\alpha\right]\dot{q}_{ax1}^2\right\} + \frac{M_A}{4}\left\{\left[1+\frac{M_A}{M_B}\left(\frac{2b}{a_2}\right)^2\sin^2\alpha\right]\dot{q}_{sy1}^2\right\} \\
& - \frac{M_A^2}{M_B}\left(\frac{b}{a_2}\right)^2\sin 2\alpha\,(\dot{q}_{ax1}\,\dot{q}_{sy1}) - \frac{k_1}{4}\left[\left(1+\frac{M_A}{M_B}\right)^2\sin^2\gamma + \frac{M_A^2}{M_B^2}\frac{4b^2}{a_2^2}\cos^2\alpha\cos^2\gamma\right]q_{ax1}^2 \\
& - \frac{k_1}{4}\sin^2\gamma\, q_{sx1}^2 - \frac{k_1}{4}\sin^2\gamma\, q_{sx2}^2 + \frac{k_1}{4}\sin^2\gamma\, 2\,q_{sx1}\,q_{sx2} - \frac{k_1}{4}\cos^2\gamma\left[\left(1+\frac{M_A}{M_B}\right)^2\right]q_{ay1}^2 \\
& - \frac{k_1}{4}\cos^2\gamma\left[\left(1+\sin\alpha\frac{M_A}{M_B}\frac{2b}{a_2}\right)^2\right]q_{sy1}^2 + \frac{k_1}{4}\frac{M_A}{M_B}\frac{2b}{a_2}2\cos\alpha\cos^2\gamma\left[1+\sin\alpha\frac{M_A}{M_B}\frac{2b}{a_2}\right]q_{ax1}\,q_{sy1} \\
& - \frac{k_2}{2}\left(q_{sx2}^2 + \left(\frac{M_A}{M_B}\right)^2\left(\frac{2b}{a_2}\right)^2\left(q_{ax1}^2\cos^2\alpha + q_{sy1}^2\sin^2\alpha - 2\,q_{ax1}\,q_{sy1}\cos\alpha\,\sin\alpha\right)\right) \\
& - \frac{k_\theta}{4}\left[\left(1+\frac{M_A}{M_B}\right)^2\cos^2\gamma + \frac{M_A^2}{M_B^2}\frac{4b^2}{a_2^2}\cos^2\alpha\sin^2\gamma\right]q_{ax1}^2 - \frac{k_\theta}{4}\cos^2\gamma\, q_{sx1}^2 - \frac{k_\theta}{4}\cos^2\gamma\, q_{sx2}^2 \\
& + \frac{k_\theta}{4}\cos^2\gamma\, 2\,q_{sx1}\,q_{sx2} - \frac{k_\theta}{4}\sin^2\gamma\left[\left(1+\frac{M_A}{M_B}\right)^2\right]q_{ay1}^2 - \frac{k_\theta}{4}\sin^2\gamma\left[\left(1+\sin\alpha\frac{M_A}{M_B}\frac{2b}{a_2}\right)^2\right]q_{sy1}^2 \\
& + \frac{k_\theta}{4}\frac{M_A}{M_B}\frac{2b}{a_2}2\cos\alpha\sin^2\gamma\left[1+\sin\alpha\frac{M_A}{M_B}\frac{2b}{a_2}\right]q_{ax1}\,q_{sy1}
\end{aligned}
$$

Usually $M_A << M_B$, as in hydrogen peroxide H_2O_2 . The Lagrange function contains the terms of different order of smallness: of order M_A and of order M_A^2/M_B. Eliminating small quantities of order M_A^2/M_B, one is able to separate out three functions which relate to normal and nearly normal vibrations

$$
\begin{aligned}
L\,(a\,x1) = {} & \frac{M_A}{4}\left(1+\frac{M_A}{M_B}+\frac{M_A}{M_B}\frac{4b^2}{a_2^2}\cos^2\alpha\right)\dot{q}_{ax1}^2 \\
& - \frac{k_1}{4}\left(\left(1+\frac{M_A}{M_B}\right)^2\sin^2\gamma + \frac{M_A^2}{M_B^2}\frac{4b^2}{a_2^2}\cos^2\alpha\cos^2\gamma\right)q_{ax1}^2 \\
& - \frac{k_2}{2}\frac{M_A^2}{M_B^2}\frac{4b^2}{a_2^2}\cos^2\alpha\, q_{ax1}^2 - \frac{k_\theta}{4}\left(\left(1+\frac{M_A}{M_B}\right)^2\cos^2\gamma + \frac{M_A^2}{M_B^2}\frac{4b^2}{a_2^2}\cos^2\alpha\sin^2\gamma\right)q_{ax1}^2
\end{aligned}
$$

$$L\,(a\,y1) = \frac{M_A}{4}\left(1+\frac{M_A}{M_B}\right)\dot{q}^2_{a\,y1} - \frac{1}{4}\left(1+\frac{M_A}{M_B}\right)^2\left(\,k_1\cos^2\gamma + k_\theta\sin^2\gamma\right)q^2_{a\,y1}$$

$$L\,(sy1) = \frac{M_A}{4}\left(1+\frac{M_A}{M_B}\,\frac{4b^2}{a_2^2}\sin^2\alpha\right)\dot{q}^2_{sy1} - \frac{1}{4}\left(1+\sin\alpha\,\frac{M_A}{M_B}\,\frac{2b}{a_2}\right)^2\left(k_1\cos^2\gamma + k_\theta\sin^2\gamma\right)q^2_{sy1}$$
$$-\frac{k_2}{2}\,\frac{M_A^2}{M_B^2}\,\frac{4b^2}{a_2^2}\sin^2\alpha\,q^2_{sy1}$$

The frequencies of these vibrations are equal to

$$\omega^2_{a\,x1} = \frac{k_1\left(\left(1+\frac{M_A}{M_B}\right)^2\sin^2\gamma + \frac{M_A^2}{M_B^2}\,\frac{4b^2}{a_2^2}\cos^2\alpha\cos^2\gamma\right) + 2k_2\,\frac{M_A^2}{M_B^2}\,\frac{4b^2}{a_2^2}\cos^2\alpha}{M_A\left(1+\frac{M_A}{M_B}+\frac{M_A}{M_B}\,\frac{4b^2}{a_2^2}\cos^2\alpha\right)}$$
$$+\frac{k_\theta\left(\left(1+\frac{M_A}{M_B}\right)^2\cos^2\gamma + \frac{M_A^2}{M_B^2}\,\frac{4b^2}{a_2^2}\cos^2\alpha\sin^2\gamma\right)}{M_A\left(1+\frac{M_A}{M_B}+\frac{M_A}{M_B}\,\frac{4b^2}{a_2^2}\cos^2\alpha\right)}$$

$$\omega^2_{a\,y1} = \frac{M_B}{M_A\left(M_B+M_A\right)}\left(1+\frac{M_A}{M_B}\right)^2\left(\,k_1\cos^2\gamma + k_\theta\sin^2\gamma\right)$$

$$\omega^2_{sy1} = \frac{\left(1+\sin\alpha\,\frac{M_A}{M_B}\,\frac{2b}{a_2}\right)^2\left(k_1\cos^2\gamma + k_\theta\sin^2\gamma\right) - 2k_2\,\frac{M_A^2}{M_B^2}\,\frac{4b^2}{a_2^2}\sin^2\alpha}{M_A\left(1+\frac{M_A}{M_B}\,\frac{4b^2}{a_2^2}\sin^2\alpha\right)}$$

7. Lagrange function and longitudinal vibrations

Consider the remainder of the Lagrange function

$$L\left(s\,x1,\,s\,x2\right) = \frac{M_A}{4}\,\dot{q}^2_{sx1} + \frac{M_B}{4}\,\dot{q}^2_{sx2} - \frac{k_2}{2}\,q^2_{sx2}$$
$$-\frac{1}{4}\left(\,k_1\sin^2\gamma + k_\theta\cos^2\gamma\right)\left(q^2_{sx1} + q^2_{sx2} - 2\,q_{sx1}\,q_{sx2}\right)\quad .$$

According to the general formula

$$\frac{d}{dt}\left(\frac{\partial E_{kin}}{\partial\dot{q}_n}\right) + \frac{\partial U}{\partial q_n} = 0\,,$$

find the equations of motion

$$\left.\begin{aligned} M_A\,\ddot{q}_{sx1}+\left(k_1\sin^2\gamma+k_\theta\cos^2\gamma\right)q_{sx1}-\left(k_1\sin^2\gamma+k_\theta\cos^2\gamma\right)\,q_{sx2}=0 \\ M_B\,\ddot{q}_{sx2}+\left(2k_2+k_1\sin^2\gamma+k_\theta\cos^2\gamma\right)\,q_{sx2}-\left(k_1\sin^2\gamma+k_\theta\cos^2\gamma\right)\,q_{sx1}=0 \end{aligned}\right\} .$$

Denote the combinations of elastic and geometric constants in the following way

$$k_1\,sin^2\,\gamma+k_\theta\,cos^2\,\gamma=k_A \qquad 2\,k_2+k_1\,sin^2\,\gamma+k_\theta\,cos^2\,\gamma=k_B\,.$$

As is customary, we seek the solution of this system of linear homogeneous differential equations with constant coefficients in the form

$$q_{sx1}=A_1e^{i\omega t}\,, \qquad q_{sx2}=A_2e^{i\omega t}\,,$$

where A_1, A_2 are some constants. Substitution of these functions in the equation system and cancellation by the term $e^{i\omega t}$ gives the system of linear homogeneous algebraic equations for the constants

$$\left.\begin{aligned} (-M_A\,\omega^2+k_A\,)\,A_1-\,k_A\,A_2=0 \\ -k_A\,A_1+\left(-M_B\,\omega^2+k_B\right)\,A_2=0 \end{aligned}\right\} .$$

In order to have solutions not equal to zero, the system determinant should be zero

$$\begin{vmatrix} \omega^2-\dfrac{k_A}{M_A} & -\,\dfrac{k_A}{M_A} \\ \dfrac{k_A}{M_B} & \omega^2-\dfrac{k_B}{M_B} \end{vmatrix}=0\ .$$

Therefore

$$\omega^4-\omega^2\left(\frac{k_A}{M_A}+\frac{k_B}{M_B}\right)+\frac{k_A\,k_B}{M_A\,M_B}=0\,.$$

The equation has two roots

$$\omega_\pm^2=\frac{1}{2}\left\{\left(\frac{k_A}{M_A}+\frac{k_B}{M_B}\right)\pm\sqrt{\left(\frac{k_A}{M_A}+\frac{k_B}{M_B}\right)^2-\frac{k_A\,k_B}{M_A\,M_B}}\right\},$$

which define the frequencies of longitudinal vibrations. Since at that $q_{ax1} = 0$, i.e. $u_4 = -u_1$, and

$$M_A(u_1 + u_4) + M_B(u_2 + u_3) = 0,$$

we have $u_3 = -u_2$.
These conditions give the vibrations of two types

$$(\rightarrow \leftarrow \; \rightarrow \leftarrow) \qquad (\rightarrow \rightarrow \; \leftarrow \leftarrow).$$

8. Conclusion

We have developed the theory of molecule vibrations in the frame work of classical mechanical approach for tetra-atomic symmetric bent molecules. Compared to the previous calculations, where some approximations have been made [8], now we gave a revised and more complete version. As a result, we have found the frequencies of all five vibrations. In particular, the new symmetrical vibration along the direction normal to the longitudinal axis of the molecule is found. Besides the frequencies of normal and nearly normal vibrations differ from the values earlier obtained. At the same time, the frequencies of longitudinal vibrations did not change. This means that the vertical displacement of internal, usually more heavy atoms, do not influence on the longitudinal vibrations.

References

[1] A.I. Melker // *Proc. SPIE* **6597** (2007) 6597-01.
[2] V.N. Kondratiev, *Structure of Atoms and Molecules* (Fizmatgiz, Moscow, 1959), in Russian.
[3] A.I. Melker, M.A. Vorobyeva // *Proc. SPIE* **6253** (2006) 625305.
[4] A.I. Melker, M.A. Vorobyeva // *Reviews on Advanced Materials Science* **20** (2009) 14.
[5] L.D. Landau, E.M. Lifshitz, *Mechanis* (Nauka, Moscow, 1988), in Russian.
[6] A.I. Melker, M.A. Krupina // *Materials Physics and Mechanics* **9** (2010) 20.
[7] M.A. Vorobyeva, A.I. Melker // *Proc. SPIE* **6253** (2006) 625304.
[8] A.I. Melker, M.A. Vorobyeva // *Proc. SPIE* **6597** (2007) 659708.