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Vibrations of Symmetrical Tetratomic Molecules

JENNY E. ROSENTHAL, *Chemistry Department, Columbia University*

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The general method for obtaining the vibration frequencies of any symmetrical molecule is outlined, and the results of its application to the tetratomic case are given. The frequencies are derived for the most general force field consistent with geometrical symmetry and also for a more specific case based on a simplified model. It is shown that the assumption of the rigidity of the bonds requires two different forces perpendicular to the lines of bond. The coplanar tetratomic and the collinear triatomic molecules are found to be the only ones of a number of molecules investigated so far, where an unambiguous determination of the physical force constants is possible. In the general case, no very definite meaning can, apparently, be attached to terms like "magnitude of bond constant."

THE general procedure for obtaining the normal vibration frequencies of a molecule of any type of symmetry, with the minimum amount of calculations and without the use of group theory, may be summarized briefly in the following manner.[1] We write the expression for the kinetic energy T in terms of the displacements of the various atoms from their equilibrium positions. The potential energy, V, a function of the mutual displacements of the atoms, is written in terms of these variables as the most general quadratic form consistent with geometrical symmetry. (For small vibrations there is a linear connection between the mutual displacements of the atoms and their displacements from the positions of equilibrium.) As the next step, new variables, linear combinations of the original displacements, are introduced and both T and V are transformed to them, the usual assumptions of the conservation of the linear and angular momenta are taken into account when the transformation on T is performed. The normal vibration frequencies, ω, or rather $\lambda=4\pi^2\omega^2$, are then obtained as the roots of $|\lambda T-V|=0$. For n degrees of internal freedom, the expansion of this nth order determinant will give rise to an equation in λ of the nth degree. For molecules with some kind of symmetry, this nth degree equation may usually be resolved into a number of component equations of lesser degree. In this case, it is possible, by a proper choice of variables, to resolve the original determinant immediately into a product of determinants of lesser order. This proper choice of variables is, to some extent, a matter of guess-work in each particular case, but, they are usually indicated by the symmetry of the geometrical configuration. A fairly detailed treatment illustrating the procedure outlined here has been given for the symmetrical tetrahedral pentatomic molecules.[2] Some of the results of its application to tetratomic molecules of the type YX_3 have also been previously reported.[3, 4] A complete discussion of the vibration frequencies and isotopic shifts of tetratomic molecules, both of the pyramidal and coplanar types, will now be given together with a discussion of various intramolecular forces and of the physical meaning of the results.

Denoting, as usual, the positions of the three X atoms by A_1, A_2, A_3 and that of the Y atom by A_4, we let

$$A_4A_i=r_i=r^0+\delta r_i;\quad A_iA_j=q_{ij}=q^0+\delta q_{ij};$$

$$A_iA_4A_j=2\Omega_{ij}=2(\Omega^0+\delta\Omega_{ij});\quad (i,j=1,2,3);$$

(the superscript 0 refers to the equilibrium configuration). The δr_i and δq_{ij} are the mutual displacements of the particles. z^0 denotes the height of the pyramid and $g=z^0/q^0$,

$$r^{02}=z^{02}+\tfrac{1}{3}q^{02}=\tfrac{1}{3}q^{02}(1+3g^2).$$

We introduce:

$$x+\tfrac{1}{3}u=(\delta r_2-\delta r_3)(r^0/q^0);\quad u=\delta q_{12}-\delta q_{13};$$

$$y+\tfrac{1}{3}t=(2/\surd 3)[\tfrac{1}{2}(\delta r_2+\delta r_3)-\delta r_1](r^0/q^0);$$

$$t=-(2/\surd 3)[\tfrac{1}{2}(\delta q_{12}+\delta q_{13})-\delta q_{23}];$$

$$3gz+w/\surd 3=(\delta r_1+\delta r_2+\delta r_3)(r^0/q^0);$$

$$w=(\delta q_{12}+\delta q_{13}+\delta q_{23})/\surd 3. \qquad (1)$$

x, y and z may be shown to be the displacements

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[1] A group-theoretical method giving qualitative but not quantitative results has been given by E. Bright Wilson, Jr., J. Chem. Phys. **2**, 432 (1934).

[2] J. E. Rosenthal, Phys. Rev. **45**, 538 (1934).

[3] E. O. Salant and J. E. Rosenthal, Phys. Rev. **42**, 812 (1932).

[4] J. E. Rosenthal, Phys. Rev. **45**, 426 (1934).

of the Y atom from its equilibrium position; x and y are parallel to the plane of the X atoms and z is perpendicular to it. With the six arbitrary constants permitted by the geometrical symmetry,[5] the potential energy, V, is written as:[6]

$$V(x,y,z,u,t,w)=\tfrac{1}{2}[A(x^2+y^2)+Bz^2+Cw^2 \\ +D(u^2+t^2)+2E(xu+yt)+2Fzw]. \qquad (2)$$

If the three X atoms have the same mass: $m_1=m_2=m_3=m$ (i.e., if we disregard isotope effects) and if M is the mass of the Y atom, the corresponding expression for the kinetic energy is

$$T=\tfrac{1}{2}m[3\mu(\dot{x}^2+\dot{y}^2)/b+3\mu\dot{z}^2+\tfrac{1}{3}(\dot{u}^2+\dot{t}^2+\dot{w}^2)], \qquad (3)$$

where $\mu=M/(M+3m)$ and $b=1+6\mu g^2$.

The frequencies are then given by

$$\left.\begin{aligned}&[m^2\lambda^2{}_{(xu),\,(yt)}-m\lambda(\tfrac{1}{3}Ab/\mu+3D)\\ &\qquad +(b/\mu)(AD-E^2)]^2=0,\\ &m^2\lambda^2{}_{(zw)}-m\lambda(\tfrac{1}{3}B/\mu+3C)+(BC-F^2)/\mu=0.\end{aligned}\right\} \qquad (4)$$

The subscripts attached to λ indicate to what variables, hence to what types of motion, these frequencies correspond. With this notation it is immediately evident that the vibrations of the electric moment are parallel to the symmetry axis of the molecule for the two single frequencies represented by $\omega_{(zw)}$ and perpendicular to it for the two double frequencies.

In the case where one of the X atoms is replaced by its isotope X^* so that $m_1=m+\Delta m$, while $m_2=m_3=m$, the kinetic energy becomes:

$$\begin{aligned}T=&\tfrac{1}{2}m[b(1-\kappa)-\mu\kappa]^{-1}[3\mu(1-\kappa)\dot{x}^2\\ &+\tfrac{1}{3}(b-\mu\kappa)\dot{u}^2-2\mu\kappa\dot{u}\dot{x}]+\tfrac{1}{2}m[b'(1-2\kappa-\mu\kappa)]^{-1}\\ &\times\{3\mu(1-2\kappa)(1-\mu\kappa)\dot{y}^2+3\mu[b'(1-2\kappa)-2\mu\kappa^2]\dot{z}^2\\ &+\tfrac{1}{3}[b'(1-\kappa-\mu\kappa)-\mu\kappa^2(b-1)](\dot{t}^2+\dot{w}^2)\\ &+2[\mu\kappa(1-\mu\kappa)\dot{y}(\dot{t}-\dot{w})-6\kappa(1-2\kappa)g\mu^2\dot{y}\dot{z}\sqrt{3}\\ &-2\kappa^2\mu^2g\dot{z}(\dot{t}-\dot{w})\sqrt{3}-\tfrac{1}{3}\kappa(b'-\mu\kappa b+\mu\kappa)\dot{t}\dot{w}]\}; \qquad (3')\end{aligned}$$

where $b'=b(1-2\kappa)+2\kappa-\mu\kappa$. The corresponding frequencies are given by:

$$m^2\lambda^2-m\lambda[\tfrac{1}{3}A(b/\mu-\kappa)+3D(1-\kappa)+2\kappa E] \\ +[(1-\kappa)b/\mu-\kappa](AD-E^2)=0, \qquad (4')$$

$$m^4\lambda^4{}_{(ytzw)}-P_1m^3\lambda^3+P_2m^2\lambda^2-P_3m\lambda+P_4=0,$$

where:

$$P_1=[\tfrac{1}{3}Ab'/\mu+3(1-\kappa)D-2\kappa E] \\ +[\tfrac{1}{3}(1-\mu\kappa)B/\mu+3C(1-\kappa)];$$

$$\begin{aligned}P_2=&[\tfrac{1}{3}(1-\mu\kappa)B/\mu+3C(1-\kappa)][\tfrac{1}{3}Ab'/\mu\\ &+3(1-\kappa)D-2\kappa E]+(1/\mu-\kappa)(1-\kappa)(BC-F^2)\\ &+(b'/\mu)(1-\kappa)(AD-E^2)-\kappa^2[(4/3)g^2AB\\ &+AC+AD-E^2+4gF(A+3E)/\sqrt{3}\\ &+9CD+6CE];\end{aligned}$$

$$\begin{aligned}P_3=&(b'/\mu)(1-\kappa)(AD-E^2)[\tfrac{1}{3}(1-\mu\kappa)B/\mu\\ &+3C(1-\kappa)]+(1/\mu)(1-\kappa)(1-\mu\kappa)(BC-F^2)\\ &\times[\tfrac{1}{3}Ab'/\mu+3D(1-\kappa)-2\kappa E]-(\kappa^2/\mu)\\ &\times\{(AD-E^2)[\tfrac{1}{3}B(b'+b-1)+3C(b'+2\mu)\\ &+4\mu gF\sqrt{3}]+(BC-F^2)[\tfrac{1}{3}A(b'+b-1)\\ &+3(1-\mu\kappa)D+2(1-\mu\kappa)E]\};\end{aligned}$$

$$\begin{aligned}P_4=&(b'/\mu^2)(1-2\kappa-\mu\kappa)(AD-E^2)(BC-F^2)\\ &=(b'/\mu^2)[(1-\kappa)^2(1-\mu\kappa)\\ &-\kappa^2(1+2\mu-\mu\kappa)](AD-E^2)(BC-F^2).\end{aligned}$$

We may now try to correlate the very general, arbitrary constants A, B, C, D, E and F with certain force constants f_1, f_2, etc., which would be postulated on the basis of a simple physical model of the molecule. We would expect that for YX_3 the potential energy for small vibrations around an equilibrium configuration could be expanded in the form:

$$\begin{aligned}V=&V^0+(\partial V/\partial q)^0(\delta q_{12}+\delta q_{13}+\delta q_{23})\\ &+(\partial V/\partial r)^0(\delta r_1+\delta r_2+\delta r_3)\\ &+\tfrac{1}{2}(\partial^2V/\partial r^2)^0(\delta r_1{}^2+\delta r_2{}^2+\delta r_3{}^2)\\ &+\tfrac{1}{2}(\partial^2V/\partial q^2)^0(\delta q_{12}{}^2+\delta q_{13}{}^2+\delta q_{23}{}^2)+W, \qquad (5)\end{aligned}$$

where W represents the potential energy due to the rigidity of the bonds, i.e., due to restoring forces perpendicular to the lines of bond.[7, 8, 9]

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[5] J. B. Howard and E. Bright Wilson, Jr., J. Chem. Phys. **2**, 630 (1934), confirm this result previously given in reference 3 in 1932.

[6] The constant C used here is identical with C' of reference 4.

[7] Cf. the potential energy assumed for the pentatomic molecule by H. C. Urey and C. A. Bradley, Jr., Phys. Rev. **38**, 1969 (1931).

[8] A different expression for the potential energy of the pyramidal molecule based on chemical considerations has been given in reference 5.

[9] D. M. Dennison, Phil. Mag. **1**, 195 (1926), has considered the case: $W=0$.

These perpendicular forces are of two kinds: there are forces proportional to the change in angle between any two bond lines;[10] in addition there is a force proportional to the change in trihedral angle at the top of the pyramid. In the coplanar case the first force is in the plane of the X atoms, while the second one is perpendicular to it. Denoting the trihedral angle by $2S$ and the force constants (multiplied by suitable factors which simplify calculations) by f_4 and f_2, we obtain:

$$W=\tfrac{1}{2}\{[f_4(1+12g^2)(1+3g^2)]r^{02}(\delta\Omega_{12}{}^2+\delta\Omega_{13}{}^2+\delta\Omega_{23}{}^2)+[(1/9)(1+12g^2)^2f_2](r^0\delta S)^2\}. \quad (6)$$

It may be shown that in the case of the pentatomic molecule the two forces are identical.[11]

The condition of stable equilibrium for the non-vibrating molecule requires that $(\partial V/\partial q)^0=(\partial V/\partial r)^0=0$, whenever $g\neq 0$, and $(\partial V/\partial r)^0=-(\partial V/\partial q)^0\surd 3$ for $g=0$. If we let:

$$(\partial^2 V/\partial r^2)^0=(1+3g^2)f_1;\quad (\partial^2 V/\partial q^2)^0=f_3;\quad (\partial V/\partial r)^0=q^0 f_5/\surd 3, \quad (7)$$

we obtain two different sets of relations connecting A, B, etc., with the various f's for the pyramid and the coplanar case. These relations are:

$$\begin{array}{lcll}
\text{Pyramid} & & \text{Coplanar Structure} & \\
A=3(f_1+\tfrac{3}{4}f_4)/2 & & A=3(f_1+\tfrac{3}{4}f_4+f_5)/2 & \\
B=3(3g^2f_1+f_2+9g^2f_4) & & B=3(f_2+f_5) & \\
C=\tfrac{1}{3}f_1+g^2f_2+f_3+9g^4f_4 & (8) & C=\tfrac{1}{3}f_1+f_3 & (8') \\
D=\tfrac{1}{6}f_1+\tfrac{1}{2}f_3+\tfrac{1}{8}(1+6g^2)^2f_4 & & D=\tfrac{1}{6}f_1+\tfrac{1}{2}f_3+\tfrac{1}{8}f_4 & \\
E=\tfrac{1}{2}f_1-\tfrac{3}{8}(1+6g^2)f_4 & & E=\tfrac{1}{2}f_1-\tfrac{3}{8}f_4-\tfrac{1}{2}f_5 & \\
F=g(f_1-f_2-9g^2f_4)\surd 3 & & F=0 &
\end{array}$$

(If we substitute in Eqs. (4) the constants A, B, C, etc., by their values as given by (8′) and let $f_2=f_4=0$, the resulting equations reduce to those given by Menzies,[12] supporting his formulae as against those given by Nielsen.[13])

Eqs. (8) contain implicitly the two relations of linear dependence between the constants A, B, C, D, E and F:

$$\begin{aligned} &A(1+6g^2)+3E-B-(F\surd 3)/g=0,\\ &3(2D-C)+2E(1+6g^2)-F(1+3g^2)/g\surd 3-\tfrac{1}{3}B=0. \end{aligned} \quad (9)$$

They come in because the simplified model requires only four force constants for the pyramid, as compared with the six allowed by symmetry considerations. For the coplanar case, the potential energy must, for symmetry reasons, be an even function of z, so that $F=0$ independently of any special assumptions. Since in this case $f_5\neq 0$, the simplified model requires just as many constants as are allowed by symmetry considerations. Hence we can ascribe a definite physical meaning to *each* one of the general constants and determine unambiguously the values of the bond and other constants. The coplanar tetratomic and the collinear triatomic molecules seem to be the only ones of all the cases considered so far (triangular triatomic, pyramidal tetratomic, tetrahedral pentatomic configurations) where this is possible. For the other molecules, the determination of the physical force constants is dependent on the validity of expressions of the type of Eqs. (9). If experimental data (vibration frequencies, together with isotopic shifts) should show that the constants A, B, C, etc., are independent of each other, it would be necessary to postulate additional forces in order to account for the data. On the basis of a simple model, there is no obvious way of introducing these additional forces. Different assumptions could be made and corresponding to each one we would obtain a different value for the magnitude of the various forces. It is therefore questionable, whether any very definite meaning can be attached in general to terms like: "magnitude of the bond constant." But for the molecules YX_3, where the isotopic shifts are small, it is possible with four force constants to account for the data within the limits of uncertainty of the anharmonic corrections to the vibration frequencies.

In conclusion, I want to thank Professor H. C. Urey for his suggestions and interest in this problem.

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[10] F. Lechner, Wien. Bericht **141**, 633 (1932), has considered the case where this particular force is the only one present in addition to the force along the bond.

[11] In the pentatomic case we have to take $\sum_{i=1}^{4}(r^0\delta S_i)^2$ for the four pyramids formed by the Y atom and any three X atoms. This sum is equal to a constant factor times $\sum_{i,\,j=1}^{4}(r^0\delta\Omega_{ij})^2$.

[12] A. C. Menzies, Proc. Roy. Soc. **A134**, 265 (1931).

[13] H. H. Nielsen, Phys. Rev. **32**, 773 (1928).