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The Moles of Vibration of Butane and Pentane. "Free Rotation" about Carbon-Carbon Bonds and a New Type of Stereoisomerism¹

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The Hamiltonian function for a chain of four carbon atoms with the simple valence force system potential energy is transformed by successive changes of variables to such a form that the wave equation is nearly separable into five harmonic oscillator equations and a sixth equation governing the internal rotation. This rotation equation has been solved numerically for twelve different rotational levels of the nonvibrating molecule, some of which actually correspond to rotations, others to a torsional oscillation of restricted amplitude about either the *cis* or the *trans* position. The remaining terms in the wave equation are treated as a perturbation; the first-order perturbation

energy is less than 1 cm^{-1} for all moderately low vibrational states. There are thus two isomeric forms of butane with plane carbon skeletons, and a third form in which the two ethyl groups are rotating about the central carbon-carbon bond. The vibration frequencies for the three possible plane forms of a five-carbon chain have been calculated. When the frequencies of C_2 , C_3 , C_4 and C_5 are calculated with the same two force constants throughout, and by taking account of the two plane forms of C_4 and the three of C_5 , results are obtained in fair statistical agreement with observed Raman and infrared lines.

INTRODUCTION

VERY little work has been done on the motions of molecules which are capable of internal rotations. Nielsen³ has studied a generalization of the symmetrical top, one with an extra degree of torsional freedom about the symmetry axis, and LaCoste⁴ has treated the spherical top with four symmetric tetrahedrally arranged gyroscopes. These investigations of models of ethane and tetramethylmethane, respectively, both deal with the interaction between external and internal rotation for nonvibrating molecules. The present paper is an attempt to consider the interaction of the internal rotation with vibration. This interaction will be relatively small for the foregoing molecules; for saturated hydrocarbons with a chain of four or more carbon atoms, the internal rotation changes the shape of the carbon skeleton, and a relatively large interaction results. Because of the considerable difference in mass between carbon and hydrogen atoms, there is little interaction between C-H and C-C vibrations, and useful results probably can be obtained by treating the carbon skeleton alone. In addition to neglect of the hydrogen atoms, and

treatment only of states in which the total angular momentum of the molecule is zero, it is necessary to use the simplest possible valence-force potential function

$$V = (k/2) \sum_i \overline{\Delta d_i}^2 + (b/2) \sum_j d^2 \overline{\Delta \theta_j}^2, \quad (1)$$

where d_i and θ_j are the bond lengths and bond angles; d , the equilibrium bond length, has been introduced in the second term to make k and b dimensionally homogeneous. With these three simplifications, it becomes possible to give a fairly complete solution of the problem.

For completeness, we give the results for C_2 and C_3 based on the foregoing assumptions. In terms of λ defined by

$$\nu = (1/2\pi)\lambda^{1/2} \quad (2)$$

they are

$$C_2: \lambda = 2k/m, \quad (3)$$

$$C_3: \lambda = (7/3)(k/m), \quad (4)$$

$$\lambda = (5/3)(k/m) + (16/15)(b/m) + (288/125)(b^2/km) + \dots, \quad (5)$$

$$\lambda = (18/5)(b/m) - (288/125)(b^2/km) + \dots, \quad (6)$$

the last two values being roots of

$$\lambda^2 - (5k + 14b)(\lambda/3m) + 6bk/m^2 = 0. \quad (7)$$

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³ Nielsen, Phys. Rev. 40, 445 (1932).

⁴ LaCoste, Phys. Rev. 46, 718 (1934).

HAMILTONIAN FOR THE C_4 CHAIN

The coordinates in which the potential energy is written are shown in Fig. 1. It is desirable to make the substitutions

$$d_1 + d_3 = d\epsilon_1, \quad d_2 = d\epsilon_2, \quad d_1 - d_3 = d\epsilon_3, \quad (8)$$

$$\theta_1 + \theta_2 = \eta_1, \quad \theta_1 - \theta_2 = \eta_2. \quad (9)$$

The kinetic energy is most easily obtained from auxiliary Cartesian coordinates referred to the center of gravity as origin, thus excluding translational energy. It is not feasible to exclude rotational energy of the whole molecule as can be done in simpler problems by using an auxiliary system which rotates with the molecule. The method used here should be generally useful for polyatomic molecules of low symmetry. We

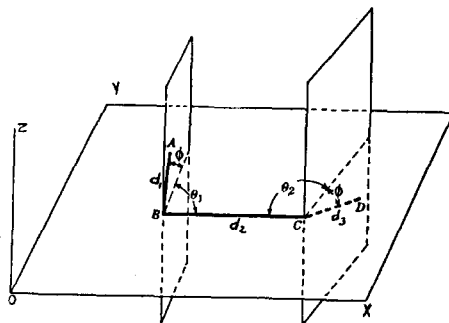


FIG. 1.

first calculate the kinetic energy of vibration plus rotation

$$T' = (m/2) \sum_{i=1}^4 (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) = (md^2/2) [(9 - 4\gamma^2)\dot{\epsilon}_1^2/18 + \dot{\epsilon}_1\dot{\epsilon}_2/3 + 2^{1/2}\gamma^2\dot{\epsilon}_1\dot{\eta}_1/9 + 8\gamma\delta\dot{\epsilon}_1\dot{\phi}/9 + \dot{\epsilon}_2^2 + 2^{3/2}\dot{\epsilon}_2\dot{\eta}_1 + (6 - \gamma^2)\dot{\eta}_1^2/12 - 2^{3/2}\gamma\delta\dot{\eta}_1\dot{\phi}/9 + 8(1 - \gamma^2)\dot{\phi}^2/9] + (md^2/2) [(9 + 8\gamma^2)\dot{\epsilon}_3^2/36 - 2^{1/2}\gamma^2\dot{\epsilon}_3\dot{\eta}_2/9 + (4 + \gamma^2)\dot{\eta}_2^2/36], \quad (10)$$

where

$$\gamma = \cos \varphi, \quad \delta = \sin \varphi. \quad (11)$$

This expression is not exact, having been obtained by putting $d_1 = d_2 = d_3 = d$ and $\theta_1 = \theta_2 = \cos^{-1}(-1/3)$ wherever functions of these variables occur as coefficients in \dot{x}_i , \dot{y}_i and \dot{z}_i , in accordance with the usual custom in treating small vibrations. No similar substitution is possible for φ , and as a result the quadratic form for T' does not have constant coefficients. The error introduced at this stage could be reduced by the perturbation-theory methods recently used by Bonner⁵ for the water molecule, but this refinement would be wasted in the present crude treatment.

The next step is to determine the external rotational energy of the whole molecule, which must be subtracted from (10). The moments of inertia are

$$A = m \sum (y_i^2 + z_i^2) = (md^2/9)(16 - 8\gamma^2); \quad B = m \sum (x_i^2 + z_i^2) = (md^2/9)(33 - 16\gamma^2); \quad (12)$$

$$C = m \sum (x_i^2 + y_i^2) = (md^2/9)(17 + 8\gamma^2)$$

and there is one nonvanishing product of inertia

$$E = (10/9)2^{1/2}md^2\delta. \quad (13)$$

The angular momenta about the Cartesian axes are

$$M_x = (md^2/9)[4\gamma\delta\dot{\epsilon}_3 - 2^{1/2}\gamma\delta\dot{\eta}_2], \quad M_y = (md^2/9)[3 \cdot 2^{1/2}\delta(\dot{\epsilon}_1 - 2\dot{\epsilon}_2) - (21/2)\delta\dot{\eta}_1 + 5 \cdot 2^{1/2}\gamma\dot{\phi}], \quad (14)$$

$$M_z = (md^2/9)[-4 \cdot 2^{1/2}\gamma\dot{\epsilon}_3 + (13/2)\gamma\dot{\eta}_2].$$

It is shown in the Appendix that the rotational energy is

$$T_{\text{rot}} = \frac{1}{2} [M_y^2/B + (CM_x^2 + 2EM_xM_z + AM_z^2)/(AC - E^2)]. \quad (15)$$

When this rotational energy is subtracted, the kinetic energy of vibration is found to be

⁵ Bonner, Phys. Rev. **46**, 458 (1934).

$$\begin{aligned}
T = & [md^2/(297-144\gamma^2)][(261/4-60\gamma^2+16\gamma^4)\dot{\epsilon}_1\dot{\epsilon}_2+(171/2-60\gamma^2)\dot{\epsilon}_1\dot{\epsilon}_3+2^{1/2}(63/2-15\gamma^2-8\gamma^4)\dot{\epsilon}_1\dot{\eta}_1 \\
& +\gamma\delta(72-64\gamma^2)\dot{\epsilon}_1\dot{\phi}+(225/2-36\gamma^2)\dot{\epsilon}_2^2+2^{1/2}(36+15\gamma^2)\dot{\epsilon}_2\dot{\eta}_1+120\gamma\delta\dot{\epsilon}_2\dot{\phi}+(153/8+15\gamma^2+2\gamma^4)\dot{\eta}_1^2 \\
& +2^{1/2}\gamma\delta(72+16\gamma^2)\dot{\eta}_1\dot{\phi}+(132-32\gamma^2-64\gamma^4)\dot{\phi}^2]+[m/(72+192\gamma^2-64\gamma^4)][(9+24\gamma^2)\dot{\epsilon}_3^2 \\
& +12\cdot 2^{1/2}\gamma^2\dot{\epsilon}_3\dot{\eta}_3+9\dot{\eta}_3^2]. \quad (16)
\end{aligned}$$

The potential energy in these coordinates is

$$V=[(k\overline{\Delta\epsilon_1^2}/4+k\overline{\Delta\epsilon_2^2}/2+b\overline{\Delta\eta_1^2}/4)+(k\overline{\Delta\epsilon_3^2}/4+b\overline{\Delta\eta_2^2}/4)]d^2. \quad (17)$$

If γ were not a function of φ , one would now find by straightforward calculation in the usual way that the frequencies were $(1/2\pi)\lambda^{1/2}$ where the λ were roots of

$$\lambda^2-[2k+(2/3)(3+8\gamma^2)b](\lambda/m)+(4/9)(9+24\gamma^2-8\gamma^4)(bk/m^2)=0 \quad (18)$$

and

$$\begin{aligned}
\lambda^4-[4k+(22-16\gamma^2)b/3]\lambda^3/m+[34k^2/9+(8/9)(27-16\gamma^2-4\gamma^4)bk]\lambda^2/m^2 \\
-(4/9)(33-8\gamma^2-16\gamma^4)bk^2\lambda/m^3=0. \quad (19)
\end{aligned}$$

These roots may be expressed conveniently as power series in b/k , which is about 0.1; they then become

$$\lambda_1=2k/m+(16/9)\gamma^4b/m+(16/9)\gamma^4[1+(8/3)\gamma^2-(8/9)\gamma^4]b^2/km+\dots, \quad (20)$$

and

$$\lambda_2=2[1+(8/3)\gamma^2-(8/9)\gamma^4]b/m-(16/9)\gamma^4[1+(8/3)\gamma^2-(8/9)\gamma^4]b^2/km+\dots$$

$$\begin{aligned}
\lambda_3 &= (2+2^{1/2}/3)k/m+(4/51)[(22-28\gamma^2+12\gamma^4)-2^{1/2}(15-16\gamma^2+2\gamma^4)]b/m+\dots, \\
\lambda_4 &= (2-2^{1/2}/3)k/m+(4/51)[(22-28\gamma^2+12\gamma^4)+2^{1/2}(15-16\gamma^2+2\gamma^4)]b/m+\dots, \\
\lambda_5 &= (2/17)(33-8\gamma^2-16\gamma^4)b/m-(16/4913)(33-8\gamma^2-16\gamma^4)(81-100\gamma^2+38\gamma^4)b^2/km+\dots, \\
\lambda_6 &= 0.
\end{aligned} \quad (21)$$

The linear transformation which would reduce (16) and (17) to

$$T=(md^2/2)\left\{\sum_{i=1}^5\dot{u}_i^2+\frac{8}{9}\frac{33-8\gamma^2-16\gamma^4}{33-16\gamma^2}\dot{u}_6^2\right\}, \quad (22)$$

$$V=(md^2/2)\sum_{i=1}^5\lambda_i u_i^2 \quad (23)$$

is

$$\Delta\epsilon_3=-2u_1+(4/9)2^{1/2}\gamma^2(9+24\gamma^2-8\gamma^4)^{1/2}(b/k)u_2, \quad (24a)$$

$$\Delta\eta_2=(4/3)2^{1/2}\gamma^2u_1+(2/3)(9+24\gamma^2-8\gamma^4)^{1/2}u_2, \quad (24b)$$

$$\Delta\epsilon_1=(2+2^{1/2}/3)^{1/2}u_3+(2-2^{1/2}/3)^{1/2}u_4+(4/17)(7-6\gamma^2)[(2/17)(33-8\gamma^2-16\gamma^4)]^{1/2}(b/k)u_6, \quad (24c)$$

$$\Delta\epsilon_2=(1+2^{1/2}/6)^{1/2}u_3+(1-2^{1/2}/6)^{1/2}u_4+(4/17)(4-\gamma^2)[(2/17)(33-8\gamma^2-16\gamma^4)]^{1/2}(b/k)u_5, \quad (24d)$$

$$\begin{aligned}
\Delta\eta_1 &= [(4-2^{5/2})+2^{5/2}\gamma^2][(1/17)(1-2^{1/2}/6)]^{1/2}u_3 \\
&+ [- (4+2^{5/2})+2^{5/2}\gamma^2][(1/17)(1+2^{1/2}/6)]^{1/2}u_4+[(4/17)(33-8\gamma^2-16\gamma^4)]^{1/2}u_5, \quad (24e)
\end{aligned}$$

$$\begin{aligned}
\varphi &= \gamma\delta[(1/17)(1-2^{1/2}/6)]^{1/2}u_3+\gamma\delta[(1/17)(1+2^{1/2}/6)]^{1/2}u_4 \\
&+ 2\gamma\delta(9+2\gamma^2)[(17/2)(33-8\gamma^2-16\gamma^4)]^{-1/2}u_6+u_6, \quad (24f)
\end{aligned}$$

where every coefficient is merely the leading term of a power series in b/k . The substitution (24) does still lead to (22) and (23), even though γ is a function of the old variable φ , but of course the old variables have not been completely eliminated. We note, however, that u_6 is the only one of the new variables which is not associated with a small amplitude vibration. We can therefore express γ explicitly by means of power series in the u_i

$$\gamma = \cos u_6 \left[1 + \sum_{i,j=3}^5 a_{ij} u_i u_j + \cdots \right] + \sin u_6 \left[\sum_{i=3}^5 b_i u_i + \cdots \right]. \quad (25)$$

The coefficients a_{ij} , b_i , etc., could be evaluated by substitution of (25) into (24); when (25) is substituted into (22) and (23), however, one sees that the b_i occur only in terms of at least the third degree, and the a_{ij} in terms of at least the fourth degree. Since third-degree terms have been neglected from the beginning in both T and V , we continue to neglect them here and adopt the new definition

$$\gamma = \cos u_6. \quad (26)$$

In terms of the momenta, (22) becomes

$$T = (1/2md^2) \left[\sum_{i=1}^5 p_i^2 + \frac{9}{8} \frac{33 - 16\gamma^2}{33 - 8\gamma^2 - 16\gamma^4} p_6^2 \right]. \quad (27)$$

We have now obtained the Hamiltonian in a form for which the variables are nearly separated.

WAVE-MECHANICAL TREATMENT OF THE C_4 CHAIN

Writing the wave equation by the method of Condon and Morse⁶ and making the substitutions

$$u_i = (h/2\pi)^{1/2} (m k d^4)^{-1/2} v_i, \quad i = 1, 2, 3, 4, 5; \quad u_6 = v_6, \quad (1/2\pi)(k/m)^{1/2} = v_0, \quad \lambda_i = (k/m) \rho_i \quad (28)$$

we obtain

$$\sum_{i=1}^5 \frac{\partial^2 \psi}{\partial v_i^2} + A \frac{\partial^2 \psi}{\partial v_6^2} + B \frac{\partial \psi}{\partial v_6} + \left(\frac{2W}{h v_0} - \sum_{i=1}^5 \rho_i v_i^2 \right) \psi = 0, \quad (29)$$

where

$$A = (9h/32\pi^2 m d^2 v_0) (33 - 16\gamma^2) / (33 - 8\gamma^2 - 16\gamma^4), \quad (30)$$

$$B = (27h/4\pi^2 m d^2 v_0) \gamma \delta (33 - 132\gamma^2 + 32\gamma^4) / (33 - 8\gamma^2 - 16\gamma^4)^2.$$

We shall solve this equation by a perturbation method. Let

$$\partial^2 \psi_i / \partial v_i^2 + (2W_i / h v_0 - \rho_i v_i^2) \psi_i = 0, \quad i = 1, 2, 3, 4, 5, \quad (31)$$

$$A \partial^2 \psi_6 / \partial v_6^2 + B \partial \psi_6 / \partial v_6 + (2/h v_0) (W_6 - \sum_{i=1}^5 W_i) \psi_6 = 0. \quad (32)$$

Since the ρ_i in (31) are functions of γ and therefore of v_6 , the W_i are also functions of v_6 , and thus play the role of a potential energy in (32). It is then easily seen that

$$\psi_0 = \psi_1 \psi_2 \psi_3 \psi_4 \psi_5 \psi_6 \quad (33)$$

satisfies

$$\sum_{i=1}^5 \frac{\partial^2 \psi_0}{\partial v_i^2} + A \frac{\partial^2 \psi_0}{\partial v_6^2} + B \frac{\partial \psi_0}{\partial v_6} + \left[\frac{2W_6}{h v_0} - \sum_{i=1}^5 \rho_i v_i^2 + V^1 \right] \psi_0 = 0, \quad (34)$$

where

$$-V^1 = A \sum_{i=1}^5 \frac{1}{\psi_i} \frac{\partial^2 \psi_i}{\partial v_i^2} + 2A \frac{1}{\psi_6} \frac{\partial \psi_6}{\partial v_6} \sum_{i=1}^5 \frac{1}{\psi_i} \frac{\partial \psi_i}{\partial v_6} + 2A \sum_{i=j+1}^5 \frac{1}{\psi_i} \frac{\partial \psi_i}{\partial v_6} \frac{1}{\psi_j} \frac{\partial \psi_j}{\partial v_6} + B \sum_{i=1}^5 \frac{1}{\psi_i} \frac{\partial \psi_i}{\partial v_6}. \quad (35)$$

⁶ Condon and Morse, *Quantum Mechanics*, McGraw-Hill, 1929, p. 15.

Then if ψ_0 is taken as the zeroth-order solution of (29), the perturbation potential is evidently V^1 , and the first-order perturbation energy is

$$2W^1/h\nu_0 = \int_{v_6} \int_{v_5} \int_{v_4} \int_{v_3} \int_{v_2} \int_{v_1} \psi_0^2 V^1 d\tau. \quad (36)$$

Now since

$$\int_{-\infty}^{\infty} \psi_i^2 dv_i = 1 \quad (37)$$

we find by differentiation with respect to v_6

$$\int_{-\infty}^{\infty} \psi_i \frac{\partial^2 \psi_i}{\partial v_6^2} dv_i = - \left(\frac{d\rho_i}{dv_6} \right)^2 \int_{-\infty}^{\infty} \left(\frac{\partial \psi_i}{\partial \rho_i} \right)^2 dv_i = - \frac{n_i^2 + n_i + 1}{32\rho_i^2} \left(\frac{d\rho_i}{dv_6} \right)^2 \quad (i=1, 2, 3, 4, 5), \quad (38)$$

where the last result makes use of the fact that the ψ_i are normalized solutions of (31) and therefore are

$$\psi_i = \rho_i^{1/8} \pi^{-1/4} (2^{n_i} n_i!)^{-1/2} \exp(-2^{-1} \rho_i^{1/2} v_i^2) II_{n_i}(\rho_i^{1/4} v_i) \quad (i=1 \cdots 5) \quad (39)$$

and uses also various well-known properties of the Hermitian polynomials. Most of the terms in (36) vanish and the first-order perturbation energy reduces to

$$\frac{2W^1}{h\nu_0} = - \int_0^{2\pi} \frac{A\psi_6^2}{32} \sum_{i=1}^5 (n_i^2 + n_i + 1) \rho_i^{-2} \left(\frac{d\rho_i}{dv_6} \right)^2 dv_6. \quad (40)$$

The zeroth-order energy, of course, is

$$2W^0/h\nu_0 = 2W_6/h\nu_0. \quad (41)$$

This is as far as the analytic solution can be carried; (32) is not amenable to anything except numerical solution. Fig. 2 and Table I show the dependence of the $\rho_i^{1/2}$ upon φ , calculated numerically from (18) and (19) for the case $b/k=0.1$, and also the composite $(1/2)\sum_{i=1}^5 \rho_i^{1/2}$, which is the potential energy term for (32) when all five vibrational quantum numbers are zero. This curve has a period of π , and is symmetric about $\varphi=0, \pi/2, \pi \cdots$. The differential terms in (32) likewise are seen to be symmetric about $\varphi=0, \pi/2, \pi \cdots$. The internal configuration of the atoms has a period of π , but a change of 2π is required to bring the molecule back to its original position. We therefore require solu-

tions of (32) subject to the boundary condition

$$\psi_6(\varphi) = \psi_6(\varphi + 2\pi). \quad (42)$$

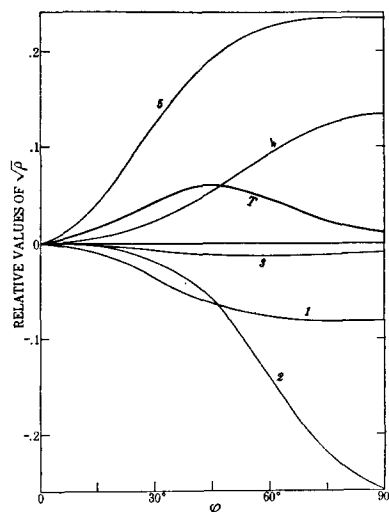


FIG. 2.

TABLE I. Values of $\rho_i^{1/2}$ for C_4 with $b/k=0.1$.

| φ | $\rho_1^{1/2}$ | $\rho_2^{1/2}$ | $\rho_3^{1/2}$ | $\rho_4^{1/2}$ | $\rho_5^{1/2}$ | $(1/2)\sum$ |
|-----------|----------------|----------------|----------------|----------------|----------------|-------------|
| 0° | 1.49550 | 0.70484 | 1.58475 | 1.26027 | 0.31667 | 2.68101 |
| 15° | 1.48503 | .70165 | 1.58275 | 1.26572 | .35853 | 2.69684 |
| 30° | 1.45968 | .68508 | 1.57800 | 1.28387 | .44148 | 2.72405 |
| 45° | 1.43385 | .64864 | 1.57347 | 1.31594 | .50908 | 2.74049 |
| 60° | 1.41888 | .56578 | 1.57215 | 1.35435 | .54231 | 2.72673 |
| 75° | 1.41453 | .48458 | 1.57433 | 1.38417 | .55061 | 2.70411 |
| 90° | 1.41421 | .44721 | 1.57607 | 1.39496 | .55084 | 2.69164 |

TABLE II. Rotational eigenfunctions.

| φ | V, cm^{-1} | 0SS | 2SA | 2AS | 4SS | 4AA | 6SA | 6AS | 8AA | 8SS | 12AA | 16AA | 20AA |
|-----------------------|---------------------|----------|----------|---------|----------|---------|----------|---------|---------|--------|--------|--------|--------|
| 0° | 0.000 | 2.330213 | 2.330308 | 0.00000 | -0.03222 | 0.00000 | -0.12917 | 0.00000 | 0.0000 | -0.634 | 0.000 | 0.000 | 0.000 |
| 3° | 3.77 | 2.303053 | 2.303147 | .00217 | -.03171 | .22343 | -.12548 | .42040 | .3677 | -.610 | .295 | .481 | .584 |
| 6° | 1.486 | 2.222462 | 2.222551 | .00431 | -.03013 | .43731 | -.11357 | .82077 | .7179 | -.532 | .567 | .893 | 1.042 |
| 9° | 3.283 | 2.091441 | 2.091524 | .00642 | -.02749 | .63155 | -.09364 | 1.18004 | 1.0327 | -.403 | .787 | 1.175 | 1.277 |
| 12° | 5.688 | 1.915922 | 1.915995 | .00850 | -.02387 | .79615 | -.06654 | 1.48082 | 1.2937 | -.230 | .931 | 1.277 | 1.220 |
| 15° | 8.601 | 1.705351 | 1.705412 | .01054 | -.01943 | .92225 | -.03314 | 1.70481 | 1.4848 | -.024 | .977 | 1.170 | .861 |
| 18° | 11.891 | 1.472545 | 1.472592 | .01259 | -.01426 | 1.00383 | .00495 | 1.84017 | 1.5948 | .202 | .914 | .856 | .267 |
| 21° | 15.425 | 1.232386 | 1.232418 | .01476 | -.00854 | 1.03933 | .04608 | 1.88352 | 1.6200 | .428 | .741 | .378 | -.428 |
| 24° | 19.048 | 0.999585 | 0.999601 | .01721 | -.00235 | 1.03255 | .08872 | 1.84184 | 1.5660 | .641 | .473 | -.190 | -1.047 |
| 27° | 22.614 | .786517 | .786514 | .02024 | .00431 | .99219 | .13194 | 1.72956 | 1.4466 | .827 | .137 | -.753 | -1.420 |
| 30° | 25.974 | .601576 | .601554 | .02427 | .01160 | .93014 | .17589 | 1.56996 | 1.2802 | .980 | -.233 | -1.215 | -1.436 |
| 33° | 28.991 | .448620 | .448574 | .02983 | .02012 | .85940 | .22170 | 1.38437 | 1.0864 | 1.098 | -.605 | -1.504 | -1.079 |
| 36° | 31.548 | .327469 | .327392 | .03782 | .03050 | .79209 | .27177 | 1.19324 | .8820 | 1.188 | -.948 | -1.579 | -.442 |
| 39° | 33.543 | .235073 | .234957 | .04936 | .04394 | .73830 | .32951 | 1.01202 | .6789 | 1.256 | -1.243 | -1.434 | .319 |
| 42° | 34.903 | .165842 | .165666 | .06609 | .06213 | .70564 | .39930 | .84933 | .4834 | 1.312 | -1.470 | -1.097 | 1.010 |
| 45° | 35.579 | .117781 | .117523 | .09024 | .08735 | .69949 | .48596 | .71274 | .2963 | 1.362 | -1.626 | -.621 | 1.457 |
| 48° | 35.555 | .083247 | .082872 | .12483 | .12273 | .72331 | .59443 | .59960 | .1151 | 1.410 | -1.705 | -.068 | 1.549 |
| 51° | 34.840 | .059342 | .058798 | .17376 | .17224 | .77900 | .72904 | .50738 | -.0650 | 1.556 | -1.700 | .487 | 1.268 |
| 54° | 33.478 | .043014 | .042230 | .24187 | .24076 | .86661 | .89248 | .43204 | -.2486 | 1.493 | -1.592 | .971 | .686 |
| 57° | 31.535 | .031998 | .030873 | .33473 | .33391 | .98363 | 1.08419 | .36844 | -.4388 | 1.510 | -1.400 | 1.314 | -.049 |
| 60° | 29.106 | .024675 | .023077 | .45810 | .45751 | 1.12385 | 1.29854 | .31156 | -.6348 | 1.493 | -1.097 | 1.456 | -.754 |
| 63° | 26.303 | .019918 | .017682 | .61702 | .61659 | 1.27606 | 1.52299 | .25682 | -.8307 | 1.422 | -.700 | 1.363 | -1.245 |
| 66° | 23.256 | .016950 | .013881 | .81441 | .81412 | 1.42317 | 1.73694 | .20031 | -.10143 | 1.281 | -.235 | 1.034 | -1.390 |
| 69° | 20.109 | .015239 | .011118 | 1.04940 | 1.04923 | 1.54234 | 1.91180 | .13996 | -.1675 | 1.057 | .254 | .513 | -1.144 |
| 72° | 17.000 | .014406 | .009005 | 1.31572 | 1.31565 | 1.60686 | 2.01348 | .07508 | -.12668 | .748 | .706 | -.108 | -.569 |
| 75° | 14.079 | .014168 | .007276 | 1.60060 | 1.60062 | 1.58998 | 2.00755 | .00711 | -.12894 | .369 | 1.054 | -.700 | .175 |
| 78° | 11.479 | .014300 | .005749 | 1.88487 | 1.88497 | 1.47023 | 1.86630 | -.06041 | -1.2158 | -.048 | 1.232 | -1.127 | .864 |
| 81° | 9.320 | .014618 | .004306 | 2.14455 | 2.14471 | 1.23733 | 1.57642 | -.12219 | -1.0369 | -.456 | 1.199 | -1.276 | 1.270 |
| 84° | 7.704 | .014967 | .002882 | 2.35406 | 2.35427 | .89684 | 1.14540 | -.17225 | -.7580 | -.803 | .951 | -1.100 | 1.239 |
| 87° | 6.698 | .015228 | .001474 | 2.49050 | 2.49074 | .47175 | .60331 | -.20551 | -.4006 | -1.036 | .525 | -.636 | .764 |
| 90° | 6.360 | .015324 | .000000 | 2.53787 | 2.53812 | .00000 | .00000 | -.21606 | .0000 | -1.118 | .000 | .000 | .000 |
| W_e, cm^{-1} | | 8.8865 | 8.8866 | 13.8952 | 13.8962 | 27.01 | 27.54 | 28.03 | 28.81 | 35.98 | 45.4 | 61.0 | 82.9 |

These solutions will be either symmetric or anti-symmetric at $\varphi=0$ and at $\varphi=\pi/2$, independently; there are thus four symmetry types, which will be designated SS, SA, AS and AA. Several solutions of each type have been computed by the numerical method of Kimball and Shortley,⁷ using an interval of 3° . In these solutions we have taken $(1/2\pi)(k/m)^{1/2}=698 \text{ cm}^{-1}$ and then have replaced $\sum W_i$ by the simpler expression

$$1878.8[(1+0.154392\gamma^2-0.162276\gamma^4)^{1/2}-0.996050] \text{ cm}^{-1}, \quad (43)$$

which is not greatly different from it; the process of solution uses only numerical values in any case, but the use of (43) avoids having to find the roots of (18) and (19) for 31 values of γ . The calculated eigenfunctions and eigenvalues are presented in Table II and Fig. 3; the second column of Table II gives values of the potential energy term (43). The main quantum number characterizing each solution has been taken to be the number of nodes in a period 0 to 2π ; the symmetry type is shown as a subscript.

A number of points related to these solutions

are worth attention. The lowest level is a very narrow doublet, lying 8.89 cm^{-1} above the potential curve at $\varphi=0$, with a separation of about $1 \times 10^{-4} \text{ cm}^{-1}$, the 0_{SS} level being lower than 2_{SA} ; the eigenfunctions for these two states fall off very rapidly as φ increases from 0° ; if $\varphi=45^\circ$ is taken as the dividing line, the probability of finding the molecule in the *trans* position is only 8×10^{-4} for 0_{SS} and 7×10^{-4} for 2_{SA} . The second level is again a narrow doublet, 7.54 cm^{-1} above the potential curve at $\varphi=90^\circ$; 2_{AS} is $10 \times 10^{-4} \text{ cm}^{-1}$ below 4_{SS} ; this is

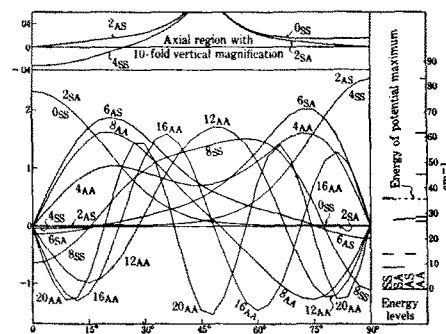


FIG. 3. Rotational eigenfunctions and eigenvalues.

⁷ Kimball and Shortley, Phys. Rev. **45**, 815 (1934).

definitely a *trans* state, with a probability of only 5×10^{-4} for the molecule to be found in the *cis* form. 6_{AB} is *cis* and 6_{BA} *trans*; these levels are still quite definitely *vibrational* in character, and have approximately three times the energy of the lowest *cis* and *trans* levels. It is to be expected that 4_{AA} and 8_{AA} will form doublets with these levels; since the latter two levels are of nearly the same energy, however, their would-be doublets, which are of the same symmetry type, can perturb each other. This is seen to occur, and neither 4_{AA} nor 8_{AA} can be characterized as either *cis* or *trans*, although they have far too little energy to execute classical rotations. All higher levels are actually rotating; 8_{BS} barely exceeds the energy of the potential maximum, and hence the eigenfunction is largest in the perpendicular region near $\varphi = \pi/4$. The higher levels execute relatively free rotation.

It is now possible to return to (40) and compute the first-order perturbation energy. It is easily found that for 0_{BS} and 2_{BA} , $W^1 = -0.04 \text{ cm}^{-1}$, while for 2_{AS} and 4_{BS} , $W^1 = -0.01 \text{ cm}^{-1}$. All the other rotational levels of the non-vibrating molecule will have values of this order, the maximum possible being -0.07 cm^{-1} . Thus if the first-order perturbation energy is a reliable criterion, which of course may not be the case, the wave equation is for all practical purposes to

be considered separated in the form (29). For higher values of the vibrational quantum numbers, particularly of n_2 and n_5 , the perturbation energy will be larger, but it can never exceed $-0.07(n^2 + n + 1) \text{ cm}^{-1}$ where n is the largest of the five n_i . This is of the order of 10^{-2} of the anharmonic term for most vibrations and is thus a negligible contribution to the absolute positions of the levels. The change in relative separations of the rotation levels is somewhat more significant, but scarcely serious for moderate values of the quantum numbers.

The form of the pseudo-potential energy curve $\sum W_i$ will be different for each vibrational state. High values of n_1 and n_2 tend to deepen the *trans* minimum and obliterate the *cis* one, while n_4 and n_5 have the reverse effect; values of n_3 of 8 or more would give a shallow minimum near 60° . It is particularly important to note that every set of n_i consisting of four 0's and one 1 gives minima at both the *cis* and the *trans* position, and hence probably has both *cis* and *trans* levels. There should accordingly be absorption bands and Raman lines corresponding to the five frequencies of each of the two plane structures, that is, near 1106, 1100, 1044, 987, 974, 879, 492, 385, 312 and 221 cm^{-1} .

It is possible to make the first-order perturbation energy vanish, by taking

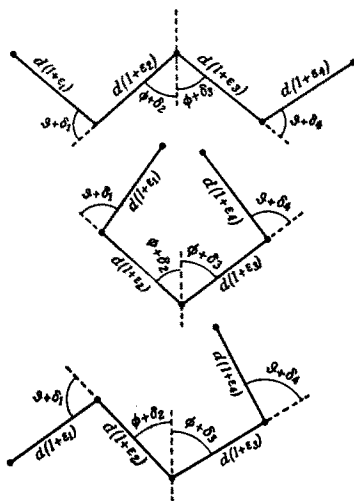
$$A \frac{\partial^2 \psi_6}{\partial v_6^2} + B \frac{\partial \psi_6}{\partial v_6} + \frac{2}{h\nu_0} \left\{ W_6 - \sum_{i=1}^5 \left[W_i + \frac{n_i^2 + n_i + 1}{32} \frac{A}{\rho_i^2} \left(\frac{\partial \rho_i}{\partial v_6} \right)^2 \right] \right\} \psi_6 = 0 \quad (44)$$

instead of (31). This might be desirable if the calculation were to be carried to the second order, but for the present purposes it seemed better to use the obvious form (31) and get a first-order energy which one might hope would give some indication of the accuracy actually obtained.

FREQUENCIES OF PLANE FORMS OF C_6

A treatment of the five-carbon chain which attempted as much as has been done for C_4 would be hopelessly difficult. Here there are seven vibrational and two rotational coordinates, and no partial separation into symmetric and

antisymmetric coordinates is possible. One would have to expand a ninth order determinant to find the seventh degree equation in λ which determined the frequencies as functions of the two angles and then solve numerically a two-dimensional wave equation to study the rotational motion. It seems likely from the work on C_4 , however, that for C_5 also the plane structures will be of outstanding importance, and the vibration frequencies therefore have been calculated for them. There are three such plane structures for C_6 , as may be seen in Fig. 4. Two of them, a W and a pentagon, have a symmetry axis, and hence give normal modes of

FIG. 4. Coordinates for three plane forms of C_4 .

vibration which are either symmetric or anti-symmetric; the third form, a dipper, has no helpful symmetry properties, and leads to an unfactored seventh degree determinant. Since the method of calculation is perfectly straightforward, we give only the Hamiltonians and the expanded secular equations. The kinetic energy terms in the Hamiltonian will be useful for a possible subsequent calculation with a more general potential energy.

The original coordinates are shown in Fig. 4. We make the substitutions

$$\begin{aligned} \delta_3 + \delta_2 &= \eta_1, & \delta_3 - \delta_2 &= \eta_2, \\ \delta_4 + \delta_1 &= \eta_3, & \delta_4 - \delta_1 &= \eta_4, \\ \epsilon_3 + \epsilon_2 &= \sigma_1, & \epsilon_3 - \epsilon_2 &= \sigma_2, \\ \epsilon_4 + \epsilon_1 &= \sigma_3, & \epsilon_4 - \epsilon_1 &= \sigma_4. \end{aligned} \quad (45)$$

Then for the **W**-form

$$T = (md^2/60)(22\dot{\sigma}_1^2 + 18\dot{\sigma}_1\dot{\sigma}_3 + 2^{5/2}\dot{\sigma}_1\dot{\eta}_1 - 12 \cdot 2^{1/2}\dot{\sigma}_1\dot{\eta}_3 + 13\dot{\sigma}_3^2 + 2^{7/2}\dot{\sigma}_3\dot{\eta}_1 - 2^{5/2}\dot{\sigma}_3\dot{\eta}_3 + 19\dot{\eta}_1^2 + 16\dot{\eta}_1\dot{\eta}_3 + 11\dot{\eta}_3^2) + (md^2/636)(70\dot{\sigma}_2^2 + 26\dot{\sigma}_2\dot{\sigma}_4 - 2^{5/2}\dot{\sigma}_2\dot{\eta}_4 + 91\dot{\sigma}_4^2 - 28 \cdot 2^{1/2}\dot{\sigma}_4\dot{\eta}_4 + 41\dot{\eta}_4^2); \quad (46)$$

for the pentagon form

$$T = (md^2/540)(198\dot{\sigma}_1^2 - 30\dot{\sigma}_1\dot{\sigma}_3 + 300 \cdot 2^{1/2}\dot{\sigma}_1\dot{\eta}_1 - 156 \cdot 2^{1/2}\dot{\sigma}_1\dot{\eta}_3 + 85\dot{\sigma}_3^2 - 80 \cdot 2^{1/2}\dot{\sigma}_3\dot{\eta}_1 + 20 \cdot 2^{1/2}\dot{\sigma}_3\dot{\eta}_3 + 395\dot{\eta}_1^2 - 400\dot{\eta}_1\dot{\eta}_3 + 131\dot{\eta}_3^2) + (3md^2/1012)(70\dot{\sigma}_2^2 + 58\dot{\sigma}_2\dot{\sigma}_4 - 52 \cdot 2^{1/2}\dot{\sigma}_2\dot{\eta}_4 + 59\dot{\sigma}_4^2 - 36 \cdot 2^{1/2}\dot{\sigma}_4\dot{\eta}_4 + 41\dot{\eta}_4^2); \quad (47)$$

and for the dipper

$$T = (md^2/22,860)(7414\dot{\sigma}_1^2 + 2464\dot{\sigma}_1\dot{\sigma}_2 + 4730\dot{\sigma}_1\dot{\sigma}_3 - 3184\dot{\sigma}_1\dot{\sigma}_4 + 7112 \cdot 2^{1/2}\dot{\sigma}_1\dot{\eta}_1 - 3388 \cdot 2^{1/2}\dot{\sigma}_1\dot{\eta}_3 - 1720 \cdot 2^{1/2}\dot{\sigma}_1\dot{\eta}_4 + 3766\dot{\sigma}_2^2 + 1600\dot{\sigma}_2\dot{\sigma}_3 + 658\dot{\sigma}_2\dot{\sigma}_4 + 3556 \cdot 2^{1/2}\dot{\sigma}_2\dot{\eta}_1 - 1784 \cdot 2^{1/2}\dot{\sigma}_2\dot{\eta}_3 - 2660 \cdot 2^{1/2}\dot{\sigma}_2\dot{\eta}_4 + 3985\dot{\sigma}_3^2 - 880\dot{\sigma}_3\dot{\sigma}_4 + 2540 \cdot 2^{1/2}\dot{\sigma}_3\dot{\eta}_1 - 2200 \cdot 2^{1/2}\dot{\sigma}_3\dot{\eta}_3 - 820 \cdot 2^{1/2}\dot{\sigma}_3\dot{\eta}_4 + 3991\dot{\sigma}_4^2 - 3556 \cdot 2^{1/2}\dot{\sigma}_4\dot{\eta}_1 + 524 \cdot 2^{1/2}\dot{\sigma}_4\dot{\eta}_3 + 320 \cdot 2^{1/2}\dot{\sigma}_4\dot{\eta}_4 + 11,303\dot{\eta}_1^2 - 4064\dot{\eta}_1\dot{\eta}_3 - 10,160\dot{\eta}_1\dot{\eta}_4 + 2453\dot{\eta}_4^2 + 1600\dot{\eta}_3\dot{\eta}_4 + 3935\dot{\eta}_4^2). \quad (48)$$

In each case the potential energy is

$$V = (d^2/4)(k\sigma_1^2 + k\sigma_2^2 + k\sigma_3^2 + k\sigma_4^2 + 2b\eta_1^2 + b\eta_3^2 + b\eta_4^2). \quad (49)$$

The secular equations for the **W**-form are

$$\lambda^4 - [(11/3)(k/m) + (29/3)(b/m)]\lambda^3 + [(29/9)(k^2/m^2) + (247/9)(bk/m^2) + (82/9)(b^2/m^2)]\lambda^2 - [(41/3)(bk^2/m^3) + (70/3)(b^2k/m^3)]\lambda + 10b^2k^2/m^4 = 0 \quad (50)$$

and

$$\lambda^3 - [(13/3)(k/m) + (13/3)(b/m)]\lambda^2 + [(41/9)(k^2/m^2) + (161/9)(bk/m^2)]\lambda - (53/3)(bk^2/m^3) = 0; \quad (51)$$

for the pentagon-form

$$\lambda^4 - [(11/3)(k/m) + (29/3)(b/m)]\lambda^3 + [(29/9)(k^2/m^2) + 31bk/m^2 + (82/9)(b^2/m^2)]\lambda^2 - [(73/3)(bk^2/m^3) + (566/27)(b^2k/m^3)]\lambda + 10b^2k^2/m^4 = 0 \quad (52)$$

and

$$\lambda^3 - [(13/3)(k/m) + (13/3)(b/m)]\lambda^2 + [(41/9)(k^2/m^2) + (129/9)(bk/m^2)]\lambda - (253/27)(bk^2/m^3) = 0; \quad (53)$$

and for the dipper-form

$$\begin{aligned} \lambda^7 - [8k/m + 14b/m]\lambda^6 + [(71/3)(k^2/m^2) + (928/9)(bk/m^2) + 51b^2/m^2]\lambda^5 - [(92/3)(k^3/m^3) \\ + (2486/9)(bk^2/m^3) + 344b^2k/m^3 + (1066/27)(b^3/m^3)]\lambda^4 + (1/81)[1189k^4/m^4 + 25,672bk^3/m^4 \\ + 67,303b^2k^2/m^4 + 19,664b^3k/m^4]\lambda^3 - (1/81)[10,550bk^4/m^5 + 68,156b^2k^3/m^5 + 42,838b^3k^2/m^5]\lambda^2 \\ + (1/81)[24,079b^2k^4/m^6 + 38,312b^3k^3/m^6]\lambda - (1270/9)(b^3k^4/m^7) = 0. \quad (54) \end{aligned}$$

This last equation comes from an unfactorable seven-rowed determinant which might appear impossibly laborious to expand; by suitable manipulation, however, it is possible to reduce the determinant one row at a time, always retaining somewhere a monomial term with which a row of zeros can easily be produced; the expansion in this way requires only three or four hours.

When $b/k = 0.1$ and $(1/2\pi)(k/m)^{1/2} = 698 \text{ cm}^{-1}$, the frequencies are as given in Table III.

TABLE III.

| W-form | Pentagon-form | Dipper-form |
|--------|---------------|-------------|
| 1041 | 1092 | 1126 |
| 1008 | 853 | 1062 |
| 336 | 559 | 995 |
| 213 | 143 | 908 |
| 1115 | 1127 | 467 |
| 946 | 981 | 343 |
| 428 | 298 | 174 |

The first four frequencies for the **W**- and pentagon-forms belong to symmetrical, the last three to antisymmetrical, vibrations.

COMPARISON WITH EXPERIMENT

There are no data on the fine structure of absorption or of Raman lines which could be compared with the calculated torsional and low

rotational levels of the φ -motion. Such a comparison would in any case be difficult without knowledge of the selection rules, which we have not found, and without any theoretical study of the states with nonvanishing total angular momentum. Hence it is only possible to seek necessarily rough correspondences between calculated vibration frequencies and the observed spectra. The choice $b/k = 0.1$ has been found to give the best results; Fig. 5 shows the calculated frequencies for C_2 , C_3 , C_4 and C_5 , and such experimental data as are available for ethane, propane, butane and pentane.

The C—C frequency for ethane is definitely located at 993 cm^{-1} by the Raman data of Bhagavantam⁸ and Lewis and Houston.⁹ The infrared line at 838 cm^{-1} reported by Coblenz¹⁰ cannot be understood, since it seems too low to be a C—H bending frequency. The Raman data on propane are from Bhagavantam and Kohlrausch and Köppl,¹¹ the infrared from Bartolome,¹² an infrared line at 750 cm^{-1} which is tentatively identified as the harmonic of the Raman line at 373 cm^{-1} has accordingly been

⁸ Bhagavantam, Ind. J. Phys. **6**, 595 (1931).

⁹ Lewis and Houston, Phys. Rev. **44**, 903 (1933).

¹⁰ Coblenz, Carnegie Institute Publications, No. 35 (1905).

¹¹ Kohlrausch and Köppl, Zeits. f. physik. Chemie **B26**, 209 (1934).

¹² Bartolome, Zeits. f. physik. Chemie **B23**, 152 (1933).

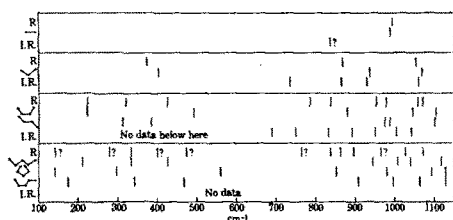


FIG. 5. Calculated and observed frequencies.

omitted from the figure. The Raman data on butane are due to Bhagavantam, Murray and Andrews¹³ and Kohlrausch and Köppl, while the infrared are from the old work of Coblentz. In the case of pentane, twelve Raman lines below 1100 cm^{-1} were reported by Ganeswan and Venkateswaran,¹⁴ a number of which have not been confirmed by the later work of Kohlrausch and Köppl and are indicated as doubtful. No infrared data are available for pentane. The calculated deformation frequencies for the pentagon form are certainly worthless due to the repulsion between the terminal CH_3 groups.

When allowance is made for the extreme approximations of the theory, and the uncertainty of the experimental data, there does seem to be a fairly satisfactory statistical agreement between the two. One may therefore feel that the frequencies calculated for still longer chains will be approximately correct and can be used to estimate specific heats and other thermodynamic properties without gross errors. It is intended to do this in the near future.

ACKNOWLEDGMENT

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APPENDIX. THE KINETIC ENERGY OF A ROTATING MOLECULE

Treatises on mechanics give the rotational energy of a rigid body in terms of moments of momentum about the principal axes. A more

general formula is derived here. Let the moments and products of inertia be

$$\begin{aligned} A &= m \sum (y^2 + z^2), & B &= m \sum (x^2 + z^2), \\ C &= m \sum (x^2 + y^2), & D &= m \sum yz, \\ E &= m \sum xz, & F &= m \sum xy, \end{aligned} \quad (55)$$

and the instantaneous moments of momentum be

$$\begin{aligned} M_x &= m \sum (yz - \dot{z}y), & M_y &= m \sum (\dot{z}x - \dot{x}z), \\ M_z &= m \sum (\dot{x}y - \dot{y}x). \end{aligned} \quad (56)$$

It is supposed that the origin of the system is fixed at the center of gravity. Transform to rotating axes by the infinitesimal rotation

$$\begin{aligned} x &= X - \epsilon_z Yt + \epsilon_y Zt, & X &= x + \epsilon_z yt - \epsilon_y zt, \\ y &= \epsilon_z Xt + Y - \epsilon_x Zt, & Y &= -\epsilon_z xt + y + \epsilon_x zt, \\ z &= -\epsilon_y Xt + \epsilon_x Yt + Z, & Z &= \epsilon_y xt - \epsilon_x yt + z, \end{aligned} \quad (57)$$

where t is at once the time and an infinitesimal parameter. Setting the moments of momentum in the new coordinate system equal to zero gives the conditions

$$\begin{aligned} A\epsilon_z - F\epsilon_y - E\epsilon_x &= -M_x, \\ -F\epsilon_x + B\epsilon_y - D\epsilon_z &= -M_y, \\ -E\epsilon_x - D\epsilon_y + C\epsilon_z &= -M_z. \end{aligned} \quad (58)$$

It is then easily shown that

$$\begin{aligned} T_{\text{rot}} &= (m/2) \sum (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \\ &\quad - (m/2) \sum (\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2) \\ &= -(1/2) (\epsilon_x M_x + \epsilon_y M_y + \epsilon_z M_z) \\ &= (1/2) [(BC - D^2) M_x^2 + (AC - E^2) M_y^2 \\ &\quad + (AB - F^2) M_z^2 + 2(CF + DE) M_x M_y \\ &\quad + 2(BE + DF) M_x M_z + 2(AD + CF) M_y M_z] \\ &\quad \times [ABC - AD^2 - BE^2 - CF^2 - 2DEF]^{-1}. \end{aligned} \quad (59)$$

When only one product of inertia, say E , is not zero, the result reduces to

$$\begin{aligned} T_{\text{rot}} &= (1/2) [M_y^2/B + (CM_x^2 + 2EM_x M_z \\ &\quad + AM_z^2)/(AC - E^2)], \end{aligned} \quad (60)$$

which is the form needed in this paper.

¹³ Murray and Andrews, J. Chem. Phys. **1**, 406 (1933).

¹⁴ Ganeswan and Venkateswaran, Ind. J. Phys. **4**, 195 (1929).