The vibration spectrum and molecular configuration of 1:4-dioxane

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The symmetry properties and selection rules for the normal vibrations of 1:4-dioxane have been derived for all possible symmetries of the molecule. The numbers of frequencies observed in the infra-red spectrum of the vapour and Raman spectrum of the liquid are shown to be inconsistent with structures of low symmetry. While the number of observed Raman frequencies do not distinguish between the ‘chair’ and planar configurations, the number of observed infra-red frequencies slightly favours the ‘chair’ structure. The twelve vibration frequencies of the ring have been calculated for the ‘chair’ structure using a simple valency force field with four force constants. Seven of the calculated frequencies agree with the observed frequencies to within 1%, and two frequencies agree to within 3 to 4%. Of the three remaining frequencies, two are active in the infra-red spectrum but are too low to be observed with prism spectrometers, while the third is active in the Raman spectrum but has not been experimentally observed. These three frequencies, however, agree satisfactorily with the corresponding assignments for cyclohexane. The stretching constants of the C-C and C-O bonds, viz. $3.7 \times 10^3$ and $4.45 \times 10^3$ dynes/cm., were found to be the same as for cyclohexane and dimethyl ether respectively.

INTRODUCTION

In an earlier communication (Ramsay & Sutherland 1947) the physical evidence for the structure of the cyclohexane molecule was shown to favour a ‘chair’ configuration, and a satisfactory interpretation of the ring frequencies of the molecule was obtained by applying a simple valency force field. In this paper the results of a similar investigation of the structure of the dioxane molecule are presented.

The five possible ring structures for the dioxane molecule are (i) a planar configuration with symmetry $D_{2h}$, (ii) a ‘chair’ or trans-configuration with symmetry $C_{2v}$, (iii) a symmetrical ‘boat’ or cis-configuration with symmetry $C_{2v}$, (iv) an unsymmetrical ‘boat’ or cis-configuration with symmetry $C_{2}$, (v) an irregular configuration with no symmetry elements.

![Figure 1](http://rspa.royalsocietypublishing.org/) O, oxygen atom

X-ray data for the structure of the dioxane molecule appear to be lacking, but the electron diffraction data of Sutton & Brockway (1935) showed that the molecule exists predominantly in the ‘chair’ form. Assuming all the carbon-bond angles to be tetrahedral and the C-C bond length to be 1.54 A, they obtained values of $1.46 \pm 0.04$ A for the C-O bond length and $110 \pm 5^\circ$ for the oxygen-bond angle.

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The dipole moment of dioxane has been measured by several workers. The early measurements of Sängwald & Weissberger (1929), Williams (1930), Smyth & Walls (1931), Hunter & Partington (1933) and Böseken, Tellegen & Henriques (1935), gave values ranging from 0 to 0.45 D which, however, were indistinguishable from zero by the methods used. Schwingel & Greene (1934) showed that the total molecular polarization of dioxane vapour was independent of temperature, indicating a zero dipole moment for the molecule, but these results were not confirmed by Kubo (1936). Later measurements by Vaughan (1939), using the liquid, however, confirmed the conclusions of Schwingel & Greene (1934). Hence the dioxane molecule must exist predominantly in the highly symmetrical planar or ‘chair’ configurations, and the less symmetrical structures, if present, must exist in very small proportions.

The different symmetries of the above structures enable them to be distinguished further by the different numbers of fundamental vibration frequencies active in the infra-red and Raman spectra and by differences in the states of polarization of the Raman lines. This spectroscopic evidence for the configuration of the dioxane molecule is discussed in the following sections. An attempt is then made to calculate the vibration frequencies of the dioxane ring using a simple valency force field and hence derive information concerning the strengths of the C-C and C-O bonds in the molecule.

Experimental

The infra-red absorption of dioxane between 1500 and 700 cm.\(^{-1}\) in the vapour and in the liquid was measured using a Hilger D209 double-beam spectrometer with a rock-salt prism. The dioxane was dried over sodium and distilled through a Fenske column, the constant-boiling middle fraction being used. The vapour absorption was measured using a 25 cm. cell with rock-salt windows. Liquid dioxane was contained in a small side bulb, the vapour pressure in the cell being determined by the temperature of the bulb. To prevent condensation of dioxane vapour on the rock-salt windows, the cell was heated electrically and maintained at a higher temperature than the bulb. The absorption curves for different pressures of dioxane vapour are given in figure 2 and the frequencies are listed in table 1. Pressures up to 200 mm. Hg were investigated, but the only additional band which began to appear was a very weak 740 cm.\(^{-1}\) frequency.

The absorption of liquid dioxane was measured using a rock-salt cell of thickness 0.01 mm. The frequencies agreed well with those observed in the vapour but were slightly displaced to lower frequencies. By comparing the absorptions of the liquid and the vapour it is seen that the 1042 and 1066 cm.\(^{-1}\) frequencies in the spectrum of the latter are \(P\) and \(R\) branches of a band with a strong central \(Q\) branch at 1054 cm.\(^{-1}\). Similarly, the vapour bands at 1450 and 1461 cm.\(^{-1}\) are due to rotational contour of a single band. The 880 and 889 cm.\(^{-1}\) frequencies in the vapour spectrum, however, are distinct vibrational frequencies corresponding to the two frequencies at 874 and 887 cm.\(^{-1}\) in the liquid spectrum. By increasing the absorption path of the liquid to 0.25 mm. four additional weak frequencies were observed, viz. 1020,
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753, 735 and 711 cm$^{-1}$. The 735 cm$^{-1}$ band corresponds to the 740 cm$^{-1}$ frequency observed in the vapour spectrum at higher pressures. That these bands were not due to small traces of impurities was confirmed by using an independent sample of dioxane when the frequencies again appeared with equal intensity.

![Graph showing absorption peaks at different frequencies.

Figure 2. Vapour: (a) pressure 30 mm. Hg, temp. 30°C; (b) pressure ~ 3 mm. Hg, temp. 20°C; (c) pressure 200 mm. Hg, temp. 100°C. Liquid: (d) 0.01 mm. cell; (e) 0.25 mm. cell.

The frequencies listed in table 1 agree to ± 3 cm$^{-1}$ with the earlier measurements of McKinney, Leberknight & Warner (1937). These authors, however, did not observe the weak bands between 700 and 800 cm$^{-1}$ and did not record the 1327 cm$^{-1}$ vapour band as a separate frequency though their curves show a shoulder in this position. They investigated the region 2.27 to 3.72 μ with a prism-grating spectrometer of high resolving power and found four frequencies in the spectrum of the liquid. These frequencies were also observed in the vapour spectrum where they all showed a $P$, $Q$, $R$ structure with a strong central $Q$ branch. These frequencies were confirmed by Fox & Martin (1938) and are included in table 1.

No data are available for the Raman frequencies of dioxane in the vapour, but the Raman frequencies in the liquid have been reported by several authors. The values quoted in table 1 are taken from a summary by Kahovec & Kohlrusnau (1937) of all earlier measurements.

**Symmetry properties**

The dioxane molecule possesses $3 \times 14 - 6 = 36$ normal modes of vibration which may, to a first approximation, be described as 8 C-H stretching vibrations, 4 H-C-H bending vibrations, 12 $\delta$CH$\delta$ rocking and twisting vibrations, 6 C-O and C-C stretching vibrations and 6 C-O-C and O-C-C bending vibrations. The frequency ranges in which these various types of vibration may be expected to appear is
known from a study of simpler molecules. The symmetry classes of the normal vibrations may be derived by the methods of group theory for the various symmetries of the dioxane ring. These are given in table 2 together with the infra-red and Raman selection rules and the polarization properties of the Raman lines.

The different structures may now be distinguished by the different numbers of fundamentals allowed in the infra-red and Raman spectra. These are summarized in table 3 and compared with the numbers of observed frequencies.

It is seen that the less symmetrical structures could only be permitted by postulating that several of the frequencies had not been observed. In view of the care taken to find weak bands in the infra-red spectrum, this explanation is unlikely. Moreover, only occasional coincidences are observed between the experimental infra-red and Raman frequencies indicating that the selection rules are mutually
Table 2. Symmetry classes of normal vibrations

<table>
<thead>
<tr>
<th>type of vibration and frequency range (cm(^{-1}))</th>
<th>irregular</th>
<th>unsym. boat, (C_2_v)</th>
<th>sym. boat, (C_2_v)</th>
<th>chair, (C_2_h)</th>
<th>planar, (D_3h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 C-H stretching 2800 to 3000</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>4 H-C-H bending 1350 to 1500</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>12 CH(_{3}) rocking and twisting 750 to 1350</td>
<td>12</td>
<td>6</td>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>6 C-C and C-O stretching 750 to 1350</td>
<td>6</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>6 O-C-C and C-O-C bending &lt;750</td>
<td>6</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

IR, infra-red active; \(R\), Raman active; \(D\), depolarized line; \(P\), polarized line.

Table 3. Numbers of active fundamentals

<table>
<thead>
<tr>
<th>2800 to 3000 cm(^{-1})</th>
<th>1350 to 1500 cm(^{-1})</th>
<th>750 to 1350 cm(^{-1})</th>
<th>&lt;750 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(IR)</td>
<td>(R)</td>
<td>(IR)</td>
</tr>
<tr>
<td>irregular</td>
<td>8</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>unsym. boat</td>
<td>8</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>sym. boat</td>
<td>6</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>chair</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>planar</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>observed</td>
<td>4</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

exclusive and that the molecule possesses a centre of symmetry. Hence it is necessary only to distinguish between the ‘chair’ and planar configurations. The numbers of Raman active fundamentals are the same for the two structures and hence fail to differentiate between them. The structures could be distinguished by the different polarization properties of the Raman lines, but no satisfactory measurements are available. The structures may be distinguished, however, by the numbers of fundamentals active in the infra-red spectrum. In the region 2800 to 3000 \text{cm}^{-1} four well-defined bands have been observed in the spectrum of the vapour in agreement with the number allowed by the ‘chair’ structure. The two frequencies observed between 1350 and 1500 \text{cm}^{-1} agree with the number allowed by both the ‘chair’ and planar configurations and hence do not distinguish between them. In the region 750 to 1350 \text{cm}^{-1} of the vapour spectrum eight separate vibrational frequencies have been observed, though one of these frequencies, viz. 1327 \text{cm}^{-1}, appeared only as a weak unresolved shoulder. Two additional bands, viz. 1020 and 753 \text{cm}^{-1}, appeared in the spectrum of the liquid, but these may be due to violation of the selection rules which is well known in the liquid state. Indeed, the former frequency may correspond to the strong Raman frequency at 1014 \text{cm}^{-1}. Hence the number of frequencies observed in this region does not distinguish conclusively between the two structures. The lack of experimental data below 750 \text{cm}^{-1} prevents a comparison in this region.
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Thus although the numbers of infra-red and Raman-active fundamentals are not consistent with structures of low symmetry, unless present in small amounts which escape spectroscopic detection, the evidence does not differentiate conclusively between the ‘chair’ and planar configurations. The appearance of four well-defined infra-red bands in the region 2800 to 3000 cm$^{-1}$, however, favours the ‘chair’ structure.

Valency force treatment

The vibration equations for the ‘chair’ configuration of the dioxane molecule have been obtained using the vector method developed by Eliashevich (1940). The dioxane molecule was treated as a system of six mass points, $i, j, k, l, m, n$, situated at the vertices of a puckered hexagon (figure 3). All the bond angles $\gamma$ were assumed to be tetrahedral (109° 28') in agreement with the electron diffraction data. Applying a simple valency force field to the molecule, the potential energy $V$ was expressed by the equation

$$V = \frac{1}{2} \sum_{ij} k_{ij} q_{ij}^2 + \frac{1}{2} \sum_i c_i \alpha_i^2,$$

where $q_{ij} =$ change in the bond length $s_{ij}$ and $\alpha_i =$ change in the bond angle $\gamma_i$.

![Figure 3](http://rspa.royalsocietypublishing.org/)

**Figure 3.** $m_a, m_b$, masses of the O atom and CH$_2$ group respectively. $s_a, s_b$, lengths of the C-O and C-C bonds. $k_a, k_b$, stretching constants of the C-O and C-C bonds. $c_a, c_b$, deformation constants of the C-O-C and O-C-C bond angles.

The equations of motion, viz. $\ddot{q}_{ij}$ and $\ddot{\alpha}_i$, were then derived by the methods of Eliashevich (1940). Substituting

$$q_{ij} = (q_{ij})_0 e^{ibt} \quad \text{and} \quad \alpha_i = (\alpha_i)_0 e^{ibt},$$

equations in $v^2$ were obtained whose roots determined the normal vibration frequencies of the molecule. These equations were considerably simplified by a knowledge of the symmetry co-ordinates of the normal vibrations which were derived by the methods of group theory as follows.

The symmetry operations which leave the ‘chair’ configuration of the dioxane molecule unchanged are

(a) The identity operation, $I$.
(b) Rotation of $\pm \pi$ about the twofold axis, $C_2(z)$.
(c) Reflexion across the plane of symmetry perpendicular to the twofold axis, $\sigma_h(xy)$.
(d) Inversion about the centre, $i$.

The symmetry properties of the various classes of vibration with respect to these symmetry operations are given in table 4.
Table 4. Symmetry properties of normal vibrations

<table>
<thead>
<tr>
<th>class</th>
<th>$I$</th>
<th>$c_d(z)$</th>
<th>$\sigma_h(xy)$</th>
<th>$i$</th>
<th>selection rules</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>$R$</td>
</tr>
<tr>
<td>$A_u$</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>$IR$</td>
</tr>
<tr>
<td>$B_g$</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>$R$</td>
</tr>
<tr>
<td>$B_u$</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>$IR$</td>
</tr>
</tbody>
</table>

+ symmetrical; - antisymmetrical.

The geometric forms of the normal vibrations were obtained using these symmetry relations and the property that all the normal vibrations must be mutually orthogonal. These are given in figure 4.

![Figure 4](image)

The symmetry co-ordinates were obtained by expressing these vibrations in terms of $q$ and $\alpha$ and are given in figure 5.

![Figure 5](image)
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By substituting these symmetry co-ordinates into the equations for \( \tilde{q}_{ij} \) and \( \tilde{\alpha}_i \) the vibration equations were obtained. It is convenient here to introduce the following abbreviations:

\[
c = \cos \gamma, \quad s = \sin \gamma, \quad M = \frac{1}{m_a} + \frac{1}{m_b},
\]

\[
L_1 = \frac{1}{m_a s_a^3}, \quad L_2 = \frac{1}{m_b s_b^3}, \quad L_3 = \frac{1}{m_b s_a s_b}, \quad L_4 = \frac{1}{m_b s_a s_b},
\]

\[
M_1 = 2s_a^2 L_2 , \quad M_2 = \frac{1}{2} c M_1 , \quad M_3 = -s L_1 s_a ,
\]

\[
M_4 = -s L_2 s_a , \quad M_5 = M + c L_4 s_a , \quad M_6 = M - c L_1 s_a,
\]

\[
M_7 = -\frac{1}{2} s (L_1 + L_4) s_a, \quad M_8 = \frac{1}{2} s (L_1 - L_4) s_a, \quad M_9 = M_7 - s L_4 s_a,
\]

\[
M_{10} = M_8 - s L_4 s_a, \quad M_{11} = 2(1 - c) L_1 + 2 L_2 ,
\]

\[
M_{12} = (2L_1 + L_2 + L_3) + \frac{1}{2} c (L_1 - 2 L_4), \quad M_{13} = -\frac{1}{2} (L_1 + L_2 + 2 L_4 - c L_1), \quad M_{14} = M_{12} - (2 + c) L_1 ,
\]

\[
M_{15} = M_{13} + (2 + c) L_4, \quad M_{16} = M_{14} + 2(L_3 - c L_4), \quad M_{17} = M_{16} + (2 + c) L_1 .
\]

The vibration equations may then be expressed in the determinant form as follows:

Class \( A_g \):

\[
\begin{vmatrix}
(k_a M_5 - \nu^2), & k_b M_2, & c_a M_3, & c_b M_8 \\
2k_a M_2, & (k_b M_1 - \nu^2), & -c_a M_4, & 2c_b M_4 \\
2k_a M_3, & -k_b M_4, & (c_a M_11 - \nu^2), & 2c_b M_15 \\
k_a M_6, & k_b M_4, & c_a M_15, & (c_b M_12 - \nu^2)
\end{vmatrix} = 0.
\]

Class \( A_u \):

\[
\begin{vmatrix}
(k_a M_6 - \nu^2), & k_b M_2, & c_b M_7 \\
2k_a M_3, & (k_b M_1 - \nu^2), & 2c_b M_4 \\
k_a M_7, & k_b M_4, & (c_b M_14 - \nu^2)
\end{vmatrix} = 0.
\]

Class \( B_g \):

\[
\begin{vmatrix}
(k_a M_6 - \nu^2), & c_b M_9 \\
k_a M_6, & (c_b M_16 - \nu^2)
\end{vmatrix} = 0.
\]

Class \( B_u \):

\[
\begin{vmatrix}
(k_a M_5 - \nu^2), & c_a M_3, & c_b M_10 \\
2k_a M_3, & (c_a M_11 - \nu^2), & 2c_b M_13 \\
k_a M_{10}, & c_a M_{13}, & (c_b M_{17} - \nu^2)
\end{vmatrix} = 0.
\]

These equations were checked by putting \( m_a = m_b = m, \ s_a = s_b = s, \ k_a = k_b = k \) and \( c_a = c_b = c \), when it was found that the equations reduced to the earlier equations for cyclohexane (Ramsay & Sutherland 1947) in the following manner:

<table>
<thead>
<tr>
<th>dioxane</th>
<th>cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g )</td>
<td>( A_{1u}, E_{1u} )</td>
</tr>
<tr>
<td>( A_u )</td>
<td>( A_{1u}, E_{1u} )</td>
</tr>
<tr>
<td>( B_g )</td>
<td>( A_{2g}, E_{1u} )</td>
</tr>
<tr>
<td>( B_u )</td>
<td>( A_{2u}, E_{1u} )</td>
</tr>
</tbody>
</table>
ASSIGNMENT OF FREQUENCIES

Before attempting to evaluate the vibration equations it is helpful to consider the evidence which can be derived from the states of polarization of the Raman lines, the contours of the infra-red bands and the corresponding assignments for cyclohexane. Unfortunately, no satisfactory polarization measurements are available to assist the assignment of the Raman frequencies, but it is almost certain that the intense Raman line at 835 cm.\(^{-1}\) is the totally symmetrical class \(A_g\) 'breathing' frequency (cf. the strong cyclohexane frequency at 802 cm.\(^{-1}\)). Since the dioxane frequency is slightly greater than the cyclohexane frequency despite an increase in the mass of the molecule, this would imply that the stretching constant of the C-O bond is greater than the C-C value for cyclohexane. The doubly degenerate class \(E_{1g}\) Raman line at 426 cm.\(^{-1}\) in cyclohexane is split into two component lines at 430 and 454 cm.\(^{-1}\) in the Raman spectrum of tetrahydropyran (Kahovec & Kohlrausch 1937). This splitting in the case of dioxane probably corresponds to the observed Raman lines at 432 and 485 cm.\(^{-1}\). Again, the increase in frequency from cyclohexane to dioxane suggests that the deformation constant for the C-O-C bond angle is somewhat greater than the C-C-C value for cyclohexane. Since the class \(E_{1g}\) vibrations for cyclohexane split into class \(A_g\) and class \(B_g\) vibrations for dioxane, and, moreover, since the latter vibrations are not dependent on the value of the C-O-C deformation constant, the 432 cm.\(^{-1}\) frequency may be assigned to class \(B_g\) and the 485 cm.\(^{-1}\) frequency to class \(A_g\).

The contours of the infra-red bands may be derived from a knowledge of the principal moments of inertia of the dioxane molecule. Taking the lengths of the C-C, C-O and C-H bonds as 1.54, 1.46 and 1.09 A respectively and all the bond angles as tetrahedral in agreement with the electron diffraction data (Sutton & Brockway 1937), the principal moments of inertia of the 'chair' structure are

\[
I_A = 172 \times 10^{-40} \text{g.cm}^2, \quad I_B = 183 \times 10^{-40} \text{g.cm}^2, \quad I_C = 314 \times 10^{-40} \text{g.cm}^2.
\]

The molecule thus approximates to a symmetric top. According to Gerhard & Dennison (1933), vibrations involving changes of electric moment parallel to the greatest axis of inertia should give bands with \(P\), \(Q\) and \(R\) branches. Using the mean value of \(I_A\) and \(I_B\) for the least moment of inertia, the \(P-R\) separation was calculated using the doublet formula of these authors and found to be 24 cm.\(^{-1}\) at 30° C. The contours of the perpendicular bands were obtained by reference to the curves of Gerhard & Dennison (1933) for different values of \(\beta = A/C - 1\). For dioxane \(\beta = -0.436\), hence the perpendicular bands should also show a \(P\), \(Q\), \(R\) structure, the \(Q\) branch, however, being less prominent than for the parallel bands and the doublet separation being somewhat smaller.

The four bands in the vapour spectrum between 2800 and 3000 cm.\(^{-1}\) observed by McKinney et al. (1937), using a prism grating spectrometer, all showed \(P\), \(Q\), \(R\) structures with prominent \(Q\) branches. Since these bands may be assigned to C-H stretching vibrations, they would be expected to show predominantly parallel type
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contours. The P-R separations as measured from the curves of the above authors varied from 18 to 23 cm.\(^{-1}\) at 26°6° C in reasonable agreement with the calculated value. The three ring vibrations between 750 and 1350 cm.\(^{-1}\) in the infra-red spectrum should all give perpendicular type bands. Of the six CH\(_2\) rocking and twisting vibrations active in this region, four should give perpendicular type bands and the other two should give bands with hybrid parallel-perpendicular type contours. Hence in all there should be seven perpendicular type bands and two with hybrid contours. The only band in this region with a P, Q, R structure has well-defined Q and R peaks at 1054 and 1066 cm.\(^{-1}\), the P branch appearing as a weak shoulder at 1042 cm.\(^{-1}\). The P-R separation agrees with the value calculated for a parallel band, hence this frequency cannot be assigned to a ring vibration. It must be due to a \(\text{CH}_2\) rocking motion.

With this preliminary information a complete assignment of the ring frequencies was attempted by evaluating the vibration equations. Initially it was assumed that the stretching constant of the C-C bond and the deformation constant of the carbon bond angle were the same as for cyclohexane, viz. \(k_{\text{C-C}} = 3.7 \times 10^5\) dynes/cm. and \(c_{\text{C-C}} = 1.04 \times 10^{-11}\) dyne cm./radian. The C-O stretching constant was taken as 4.45 \(\times 10^5\) dynes/cm. and the deformation constant for the C-O-C bond angle as 1.4 \(\times 10^{-11}\) dyne cm./radian, the latter value being chosen to get agreement with the assignment of the 485 cm.\(^{-1}\) frequency to class \(A_g\). The vibration equations were then solved by means of the electrical calculating machine described by Mallock (1933), the frequencies being given in table 5.

**Table 5. Calculated and observed ring frequencies for dioxane**

<table>
<thead>
<tr>
<th>class</th>
<th>activity</th>
<th>calculated frequency (cm.(^{-1}))</th>
<th>observed frequency (cm.(^{-1}))</th>
<th>percentage difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_g)</td>
<td>Raman</td>
<td>1111</td>
<td>1111</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>834</td>
<td>835</td>
<td>-0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>488</td>
<td>485</td>
<td>+0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>390</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A_u)</td>
<td>infra-red</td>
<td>1141</td>
<td>1136</td>
<td>+0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>927</td>
<td>889 (or 880)</td>
<td>+4.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>205</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_g)</td>
<td>Raman</td>
<td>1126</td>
<td>1125</td>
<td>+0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>429</td>
<td>432</td>
<td>-0.7</td>
</tr>
<tr>
<td>(B_u)</td>
<td>infra-red</td>
<td>982</td>
<td>1020</td>
<td>-3.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>742</td>
<td>740</td>
<td>+0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>233</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The six calculated Raman frequencies were all found to lie remarkably close to observed Raman lines with the exception of the 390 cm.\(^{-1}\) frequency in class \(A_g\). This frequency agrees well with the corresponding observed frequencies for cyclohexane and tetrahydroxyran, viz. 384 and 396 cm.\(^{-1}\) respectively, and is presumably the missing Raman frequency below 700 cm.\(^{-1}\) permitted by the selection rules.
The calculated values for the infra-red frequencies, however, did not show such good agreement with experiment. The calculated frequency at 1141 cm.$^{-1}$ lies close to the intense infra-red adsorption band at 1136 cm.$^{-1}$, but the predicted frequencies at 927 and 982 cm.$^{-1}$ do not correspond so closely with observed frequencies. If the weak infra-red frequency at 1020 cm.$^{-1}$ in the spectrum of the liquid is taken as the missing fundamental permitted by the selection rules in the region 750 to 1350 cm.$^{-1}$ the most plausible assignment is this weak band to class $B_u$ and the 889 cm.$^{-1}$ (or 880 cm.$^{-1}$) frequency to class $A_u$. The 1054 cm.$^{-1}$ frequency has been eliminated as a possible ring frequency from contour considerations. The discrepancies between the calculated and observed values for these two frequencies are then of the order of 3 to 4% and are not unduly large in view of the simplified treatment of the molecule and neglect of the interactions of the hydrogen atoms.

The calculated value for the class $B_u$ in-plane bending frequency agrees well with the very weak vapour band observed at 740 cm.$^{-1}$. The corresponding frequency for cyclohexane was also found to be exceptionally weak in absorption. The two out-of-plane bending frequencies predicted at 205 and 233 cm.$^{-1}$ lie beyond the range of prism spectrometers and have not been experimentally observed, but they correspond satisfactorily to a splitting of the doubly degenerate calculated frequency at 206 cm.$^{-1}$ for cyclohexane. Confirmation of these low frequencies from specific heat data has not been possible since the only existing measurements apply to the liquid state.

This completes the assignment of the ring frequencies. Of the twelve frequencies calculated, using four force constants, seven agree with the experimental frequencies to within 1%, two agree with the observed values to within 3 to 4%; while the remaining three frequencies have not yet been experimentally observed. These three frequencies, however, agree satisfactorily with the corresponding assignments for cyclohexane. In view of the simplified force field and treatment of the molecule it is doubtful if any further small changes in the force constants to attempt to improve the agreement between the observed and calculated frequencies could be regarded as significant. The only frequencies below 1200 cm.$^{-1}$ which have not been assigned are the 852 and 1014 cm.$^{-1}$ Raman lines and the 880 and 1087 cm.$^{-1}$ infra-red frequencies. These are presumably hydrogenic frequencies (cf. the cyclohexane frequencies at 864 and 1015 cm.$^{-1}$).

**Discussion of Force Constants**

It is interesting to note that the values of the stretching constant of the C-C bond and deformation constant of the carbon bond angle for dioxane are essentially the same as for cyclohexane. For the latter molecule it was shown that the C-C bond was considerably weaker than in ethane (Ramsay & Sutherland 1947), hence this weakening also persists in dioxane. It is seen from table 6 that the C-C bonds in cyclopropane and ethylene oxide also appear to be weaker than in ethane.
Values for the stretching constants of the C-O bonds in various molecules are given in Table 6.

<table>
<thead>
<tr>
<th>author</th>
<th>molecule</th>
<th>stretching constant ($\times 10^6$ dynes/cm.)</th>
<th>deformation constant ($\times 10^6$ dynes/cm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kohlrausch (1936)</td>
<td>dimethyl ether</td>
<td>4·53</td>
<td>0·34</td>
</tr>
<tr>
<td></td>
<td>methyl alcohol</td>
<td>4·99</td>
<td>0·34</td>
</tr>
<tr>
<td>Bonner (1937)</td>
<td>dimethyl ether</td>
<td>4·56</td>
<td>0·46</td>
</tr>
<tr>
<td></td>
<td>methyl alcohol</td>
<td>5·00</td>
<td>0·46</td>
</tr>
<tr>
<td></td>
<td>ethyl alcohol</td>
<td>3·80</td>
<td>0·23</td>
</tr>
<tr>
<td></td>
<td>ethylene oxide</td>
<td>3·73</td>
<td>0·44</td>
</tr>
<tr>
<td></td>
<td>cyclopropane</td>
<td>4·04</td>
<td>0·44</td>
</tr>
<tr>
<td>Stitt (1939)</td>
<td>ethane</td>
<td>3·86</td>
<td>0·084</td>
</tr>
<tr>
<td>de Hemptinne (1946)</td>
<td>methyl alcohol</td>
<td>4·50</td>
<td>0·44</td>
</tr>
<tr>
<td>Ramsay &amp; Sutherland (1947)</td>
<td>cyclohexane</td>
<td>3·7</td>
<td>0·44</td>
</tr>
<tr>
<td>present</td>
<td>dioxane</td>
<td>3·7</td>
<td>0·44</td>
</tr>
</tbody>
</table>

The C-O stretching constant for dioxane does not differ appreciably from the values obtained for the C-O bonds in dimethyl ether, ethylene oxide and ethyl alcohol. The C-O stretching constant for methyl alcohol, however, is somewhat larger. The value for this constant obtained by de Hemptinne (1946), using a detailed potential function, agrees with the earlier values of Kohlrausch (1936) and Bonner (1937) obtained by treating the molecule as a diatomic system. Hence the high value of the C-O force constant for methyl alcohol probably implies a real strengthening of the C-O bond. Little information is available on the deformation constants of oxygen bond angles, but the value for dioxane appears to be considerably larger than for dimethyl ether. While the values of the C-C and C-O stretching constants for dioxane are similar to those found for related molecules, any attempt to interpret the chemical reactivities of these bonds in terms of their force constants should be treated with caution.

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D. A. Ramsay

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