THE RELATION BETWEEN THE RAMAN SPECTRA AND THE STRUCTURE OF ORGANIC MOLECULES

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ABSTRACT

The following procedure is proposed for identifying the type of vibration in the molecule to which an observed frequency in a Raman spectrum corresponds. It is assumed that the only forces acting between the atoms in the molecule are those produced by the chemical bonds, and that there is a restoring force if the bond is stretched or if the angle which the bond makes with the other bonds on an atom is altered from the normal equilibrium value. It is also assumed that all non-polar chemical bonds have the same force constants in organic compounds. The different frequencies observed in the Raman spectra may then be considered as due solely to the variation in mass of the atoms concerned and to their space relation to each other, that is, whether they are in a straight chain, a branching chain, a ring, etc. It is possible to calculate in this way the number of Raman lines which should be observed for any compound, and the frequencies they should have. There is fair agreement with the observed spectra close enough so that the lines can be identified with different types of motion in the molecule.

INTRODUCTION

IN SPITE of the great deal of work which has been done on the Raman effect since its discovery two years ago we still lack a theory which is satisfactory for explaining at all completely the relation between the structure of organic molecules and the frequencies in the light which they scatter. The simplest explanation is that the shift in the frequency of the scattered light corresponds to a fundamental mechanical frequency in the vibrating molecule. This hypothesis has been supported by the extensive work of Dadieu and Kohlrausch1 who have measured the Raman spectra for a large number of compounds, and have pointed out a great many significant relations between Raman lines and molecular structure in their own results and those of others working in this field. For example, certain special groups in a molecule such as hydrogen bound to carbon or two carbons bound by a double bond appear to have lines of definite frequency associated with them. Moreover, the calculation of the binding force between the atoms from the values of the Raman shifts lead to such uniform values among a wide variety of compounds that it seems reasonable to suppose that the frequencies of the Raman shift must correspond very closely to fundamental frequencies in the molecule.

Now, this hypothesis would also lead us to expect a close correspondence

between the frequencies of the Raman shifts and the frequencies in infrared absorption spectra. This has not been found to be true, particularly where the infrared absorption spectra can be interpreted with some degree of assurance, as in the simplest diatomic and triatomic molecules. However, Langer and Meggers\(^2\) pointed out that in order to have such correspondence there must be a certain amount of freedom in the selection rules such as may not be found in triatomic or smaller molecules, but which may well be present in the case of molecules of more than six atoms, the class into which most organic compounds fall.

Granting that such a correspondence exists, the problem is still larger than merely finding relations between certain lines and certain characteristic groups in the molecule if we are to explain Raman spectra at all completely. Considering the mechanical nature of the vibrating system which we find in the molecule, it becomes evident that the majority of frequencies correspond to types of motion in which the whole molecule takes part rather than individual groups of two atoms. Now the problem of the dependence of frequencies on individual pairs of atoms as contrasted with the molecule as a whole is a moot question. Ellis\(^3\) and Marton\(^4\) have shown that certain band series in the infrared seem to be characteristic of pairs of molecules, and relatively independent of the structure of the molecule in which the pair is located. It appears, however, that this condition occurs only in special cases. For instance it may be due to the difference in mass of the vibrating particles. Thus in the case of hydrogen attached to carbon, we may expect the frequency \(\nu\), to be given rather closely by the equation for the harmonic oscillator

\[
\nu = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2},
\]

where \(k\) is the elastic constant of the C-H bond, and \(\mu\) the reduced mass, determined by the equation

\[
\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}
\]

where \(m_1\) is the mass of the hydrogen atom and \(m_2\) the effective mass of the rest of the molecule. Since the ratio of \(m_2\) to \(m_1\) will nearly always be greater than twelve, it may be seen that the effect of the mass or structure of the rest of the molecule on the frequency will be small. Again this effect may be due to a pair of atoms being very tightly bound to each other and loosely bound to the rest of the molecule. An example of this is the \(-\text{C} = \text{O}\) group which will be discussed later. On the other hand the majority of the frequencies will not depend on a pair of atoms, but on the nature of the molecule as a whole. This point is well brought out in Dennison’s very complete analysis of the frequencies in me-

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\(^3\) J. W. Ellis, Phys. Rev. 27, 298 (1926).
It is therefore, evident that if we are to explain the general nature of Raman spectra, we must formulate some ideas about the nature of the mechanical system in the molecule.

**The Nature of the Mechanical System in the Molecule**

There appear to be a few simple postulates which give us a basis for a qualitative explanation of Raman spectra. They may be summarized as follows:

1. The frequencies of the Raman shifts correspond to characteristic fundamental mechanical frequencies in the molecule.
2. The masses in this vibrating mechanical system are the nuclei arranged in space as indicated by the x-ray studies of crystal structure and by the deductions from organic chemistry.
3. The forces under which these masses vibrate may to a first approximation be considered as acting along the lines associated with the chemical valence bonds. They can be characterized by two elastic constants, one of which, the stretching constant, gives the restoring force when two atoms are pulled apart unit distance from their equilibrium position in the molecule. The other, the bending constant, gives the restoring force when the angle is altered between the bonds joining a central atom to two other atoms.
4. The amplitude of vibration will be so small compared with the equilibrium distance between the atoms that the variation of the force with distance will obey Hooke's law.
5. The elastic constants for any type of bond are independent of the structure of the molecule in which it occurs, if there are no neighboring dipoles.

The reasonableness of the first postulate, at least for the cases we are considering, seems to be granted by those who have carried on the work in this field up to the present time. The second is self-evident. The third will perhaps seem more reasonable to those who have studied molecules from the chemical point of view than to those who are more familiar with their physical aspects. Nearly every chemist feels that the structural formulas of organic chemistry have met with such broad success in correlating chemical facts that the implications behind them must be given great weight. These formulas are based primarily on the assumption of the constancy of valence, one for hydrogen, two for oxygen, three for nitrogen and four for carbon; and on the hypothesis that the structure of a group or radical may remain unchanged throughout a complicated series of chemical reactions involving other parts of the molecule. In explaining the infrared spectra of methane Dennison postulated forces acting between the hydrogens which were stronger than the forces joining the hydrogens to the carbon. It might be possible to reconcile the existence of such forces with the behaviour of atoms in organic molecules, but it is certainly much simpler to think of the invariance of structure during chemical transformations as due to forces which act in the place where we have pictured the bond.

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If, however, we are to confine the forces which determine the structure of the molecule to the lines associated with chemical bonds we must say something more about the nature of the force than merely calling it attraction or repulsion. For example, there is considerable evidence that a long chain of atoms has a certain tendency to stay straight, and that there is resistance to bending. This idea has been made use of in organic chemistry by postulating that the normal position for the four valences around the carbon atom is at the tetrahedral angle. It is found that when closed rings of less than five carbon atoms are made, where the angle between the valences is less than 109°, there is instability and a tendency for the ring to break. This was pointed out by Baeyer in his "strain theory" of the organic ring compounds. It has also been evident from the observations on the specific heats of organic compounds that there must be thermal vibrations which involve bending of the molecule. This has been pointed out by E. O. Salant* and by the author† who attempted a calculation of the force constants from specific heat data.‡ Ellis has suggested that the 6.2μ band attributed to the C-H group is due to this type of vibration. In a diatomic molecule this characteristic of the forces would not of course come into play since the motion of the two atoms would have to be merely toward and away from each other in order to preserve the conservation of momentum. However, in a triatomic molecule we can expect a type of motion in which there is a variation of the angle between the lines joining the two outside atoms to the central atom, and in such a case it is possible to define the forces acting in terms of the increased separation of the atoms, stretching, and of the variation of the angle, bending.

The justification of the fourth postulate may be seen in a calculation of the energy of most of these compounds at room temperature. It is found that for nearly all types of motion the molecules are in the zero vibrational level. The transition which causes the Raman shift appears to be from the zero to the first vibrational state in nearly all cases. For vibrations of this amplitude we may expect the forces to obey Hooke's law, and we can therefore expect that the motion will be that of a harmonic oscillator. The frequency will be related to the force and mass by Eq. (1).

The fifth postulate states that the strength of the bond for small amplitudes of vibration depends only on the two atoms which it connects, and is relatively independent of the structure of the rest of the molecule. The strongest support for this lies in the constancy of the characteristic frequencies for such bonds as C—H, C=C, and C=0 throughout extensive series of compounds. This has been clearly demonstrated in the results of a number of authors, particularly Dadieu and Kohlrausch. In fact it had been rec-

‡ D. H. Andrews, Chem. Reviews 5, 533 (1928). See also Phys. Rev. 34, 1626 (1929), where a brief outline was given of the ideas presented in this present paper.
§ J. W. Ellis, Jour. Franklin Inst. 208, 517 (1929).
ognized on the basis of infrared spectra and specific heat data that the non-polar bond joining together atoms of H, C, O or N has nearly always the same elastic constant. For the stretching of the bond the value is generally about $4 \times 10^5$ dynes per cm. The latest values for the elastic constants of various bonds are tabulated by Dadieu and Kohlrausch where it may be seen how remarkably uniform these values are.

**Molecular Structure and Raman Spectra**

These five postulates permit us to draw some conclusions as to what we will expect to find in the Raman spectra. In the first place, as has already been pointed out, the frequency of the hydrogen atoms will be relatively independent of the structure of the molecule, and will appear as the fastest of all the frequencies since hydrogen is so much lighter than any of the other elements. On the other hand in compounds of heavy atoms such as chlorine or bromine we will expect to find lines corresponding to much lower frequencies. Next with regard to the frequencies depending on the molecule as a whole we may say that the more complex the molecule, the lower the range of frequency, since a complex molecule will in general permit a kind of wave motion which will be of lower frequency than that for any pairs of atoms. By this effect frequencies may be secured which are as low as one tenth the value for a single pair of atoms, since the extension of the molecule into a chain may make possible very long wave length vibrations. On the other hand the frequency cannot be increased more than perhaps twenty percent.


by increasing complexity, since the number of forces acting on any one atom is limited to the number of valence bonds which it can possess. Thus, the only way of increasing the force acting on it is by introducing some strain, such as in ring formation and this effect is very small. With this in mind we may proceed to examine the frequencies which have been experimentally observed.

**Lines associated with hydrogen.** One of the earliest regularities to be pointed out in the Raman spectra was that of the lines in the neighborhood of 3000 cm\(^{-1}\) which appear to be due to the vibration of hydrogen attached to carbon. In Fig. 1 the frequencies have been plotted for three series of chlorine derivatives of methane, ethane and ethylene, respectively. It may be seen that in all compounds where hydrogen is present we have lines in the 3000 cm\(^{-1}\) region, but that when hydrogen is no longer present as in carbon tetrachloride, hexachlorethane, and tetrachlor ethylene there are no frequencies in this region.

![Fig. 2. Frequencies observed in a number of carbon compounds.](image)

Further observation of these data, moreover, indicate that there is a region from about 1100 to 1600 cm\(^{-1}\) where this same regularity holds true. Now Dennison\(^8\) in his analysis of methane frequencies concluded that there would be two frequencies in this region, as shown by the dotted lines in Fig. 1, which correspond to motions of hydrogen of the type which we have called bending. It is a little surprising that no Raman frequencies were observed in the 1400 cm\(^{-1}\) region but this may be due to the difficulty of working with gases, or to the more rigid selection rules which we may expect to find in smaller molecules. Ellis\(^8\) also has suggested that the 6.2µ band in the infrared may be due to this type of motion. It therefore seems reasonable to say that we have in these two groups of frequencies, 3000 cm\(^{-1}\) and 1400 cm\(^{-1}\), the frequencies of the two types of motion which we would expect the hydrogen atoms to have, namely stretching and bending. Granting
this, we may proceed to an explanation of the remaining lines outside these regions which may be due to the heavier atoms.

**Carbon frequencies.** Fig. 2 shows the frequencies observed in a number of carbon compounds. As is to be expected methane shows only frequencies in the region which we have associated with hydrogen. Passing to ethane, however, as is shown in Fig. 1, we have in addition to the lines around 1400 cm\(^{-1}\) and 3000 cm\(^{-1}\) a line at 1000 cm\(^{-1}\) and as has been concluded by others,\(^1\) this appears to be the frequencies of two carbon atoms vibrating with respect to each other. The spectrum of methyl alcohol is very similar to this as we might expect since we have merely replaced a carbon by an oxygen atom.

If the frequencies in ethane at 1000 cm\(^{-1}\) are really due to the carbon-carbon vibration, we would expect it to shift when a single bond is replaced by a double bond. This is found to be true in the spectrum of ethylene in which the line at 1000 cm\(^{-1}\) disappears and the line at 1600 cm\(^{-1}\) appears.

There has always been considerable dispute among chemists as to whether a double bond is stronger or weaker than a single bond. This question has been ably discussed by Fajans\(^{12}\) and the Raman frequencies substantiate his conclusions. If we make use of Eq. 1 and calculate the elastic constant for these two frequencies, we find that the shift is that which would correspond approximately to the doubling of the elastic constant. This is an additional confirmation that we have identified the line correctly. Moreover if we examine compounds in which there are double bonds such as the C=O bond in acetaldehyde and acetone we find frequencies in this region. Over twenty compounds have been examined by Dadieu and Kohlrausch\(^1\) in which these frequencies due to the double bond appear. If we increase the strength of the binding still further by passing to the triple bond we find higher frequencies just as should be expected. Fig. 3 shows the frequencies observed for a number of compounds containing triple bonds.

This group of frequencies shows very well the way in which a frequency depending principally on the strength of one particular bond, in this case the triple bond, may also be influenced by the structure of the molecule.

If we regard these groups as of the type \( X-C=Y \) it may be seen that the frequency will depend on the linkage \( X-C \) and on the mass of \( X \) as well as on \( C=Y \). Thus in acetylene, since the hydrogen, \( X \), is light, the only effective force for this vibration is \( C=Y \), giving a frequency of about 1950 cm\(^{-1}\). In compounds of the cyanide type, however, where \( X \) is a heavy atom the force \( X-C \) also contributes to the vibration and we find the frequencies in the neighborhood of 2200 cm\(^{-1}\). It is particularly interesting to note that in KC≡N the frequency is again lower. It seems quite possible that this is due to the fact that the K—C bond is presumably polar and much weaker than the C—C bond.

Another interesting compound in this connection is allyl iso-thiocyanate where we have a carbon atom between two double bonds. Two double bonds so placed are as effective as a triple bond and we find a corresponding frequency.

**Effect of increasing molecular complexities.** Having identified the above lines which correspond to vibrations of pairs of atoms we may proceed to examine the frequencies which appear to be due to vibrations of the molecule as a whole. The simplest illustration of the effect of increasing the complexity may be seen by comparing methyl and ethyl alcohol. We may regard these as diatomic and triatomic molecules respectively since the hydrogens are so light that they do not affect appreciably the vibration of the heavy atoms. In methyl alcohol we have a single line at 1000 cm\(^{-1}\) due to the C-O vibration, as would be expected for a diatomic molecule. In a triatomic molecule, however, we would expect three fundamental frequencies since the total number of degrees of freedom is nine and of these three will be translational, and three rotational for the molecule as a whole, leaving three for vibration. Now according to our postulates the effective forces joining the atoms will be the forces of the two chemical bonds, namely C-C and C-O. For each of these bonds we will expect one restoring force if the bond is stretched and another restoring force if the angle between the two bonds is altered corresponding to a bending of the molecule. It is a little difficult to say off-hand what the relative values of these two forces will be but from the analogy of the stretching and bending frequencies for hydrogen attached to carbon, we may expect the bending force to be only about one-quarter as strong as the stretching force.

This particular case has been carefully investigated by Yates.\(^{13}\) He has assumed forces of this type and finds that there should result one comparatively low frequency corresponding to the bending of the molecule and two frequencies not far from that for the diatomic molecule. If we ascribe the three frequencies between 1200 and 1400 cm\(^{-1}\) in the ethyl alcohol spectrum to hydrogen, the three remaining lines are in good accord with Yates' calculation. The spectrum of acetaldehyde which may similarly be regarded as a triatomic molecule shows a close resemblance to that of ethyl alcohol as

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\(^{13}\) Yates, The character of the elastic forces in the homopolar chemical bond. See succeeding article.
might be expected. If it is true that the line at 450 cm\(^{-1}\) corresponds to a bending of the molecule then the fact that this frequency becomes only slightly higher in passing from ethyl alcohol, C-C-O, to acetaldehyde, C-C=O indicates that doubling the bond decreases the ease of bending only slightly. On the other hand the appearance of the line at 1600 cm\(^{-1}\) shows that the force involved in stretching has been greatly increased.

Passing to more complicated molecules, we now find low frequencies appearing presumably corresponding to the presence of wave motion involving more than three atoms. Moreover, the number of lines increases, and as we get to heptane we find a fairly even distribution of the lines from the hydrogen region down to the low frequencies. The experimental observation of these more complex compounds is somewhat difficult because of the tendency for fluorescence which gives a continuous background, masking many of the lines. A number of the lines are also of very low intensity so that the agreement between different observers for compounds of the complexity of heptane is rather poor. For that reason, it is dangerous to draw too definite conclusions. However, one or two points seem worth mentioning. Lewis\(^{14}\) in a study of the possible frequencies in compounds of this type points out that the frequencies should be fairly evenly distributed from the lowest, corresponding to the longest wave-length possible in the chain, up to the highest, corresponding to the vibration of a pair of atoms. Pentane and heptane have spectra in accord with this view. It also seems worth noticing that the number of lines below the hydrogen region, which we may take as ending at about 1100 cm\(^{-1}\) corresponds roughly to the number of degrees of freedom for internal vibration of the heavy atoms which would be calculated from the number of atoms present in the molecule. Thus for heptane we should have \((3\times 7) - 6 = 15\). In the region below 1100 cm\(^{-1}\) where these frequencies should appear we find fifteen lines for heptane and twelve for pentane, but for octane there are only ten, so that the argument is hardly conclusive.

Conclusions

The way in which the above postulates accounts for the great majority of Raman lines may be seen from the following calculation. We take 5\(\times 10^6\) and 0.6\(\times 10^6\) dynes per cm for the stretching and bending constants respectively of the single non-polar bond. These are the best average values from the latest data and the actual values for the various bonds do not appear to deviate from these by more than ten per cent. We can then calculate the ranges in which frequencies should appear in the different compounds, from the atomic weights and number of bonds involved. The variation in frequencies between different compounds is thus considered to be due only to the variation in the masses of the atoms and in the number and position of the bonds. The stretching constant for a double bond is taken as twice that for a single bond, and for a triple bond, thrice.

\(^{14}\) A. B. Lewis, Coupled vibrations with applications to the specific heat and infrared spectra of crystals. P. 568, this issue.
The values of the frequency which would be expected for the vibration of pairs of atoms can be calculated quite simply with the help of Eq. (1). The results of these calculations have been summarized in Table I. The values for C-H, C-O, and C-N are in good agreement with the observed lines which have been attributed to these bonds.

The case of \( \text{C}_2\text{H}_5\text{Cl} \) is not so clear. It has been difficult to say just which Raman line is due to the vibration of the Cl. However, a series has been observed in the infra-red by Ellis\(^{15} \) which appears to be due to this type of motion and its fundamental frequency agrees very well with that calculated here.

The \( \text{C} = \text{C} \) bond in ethylene has a frequency which is well accounted for if we take the elastic constant as twice that for the single bond. With the \( \text{C} = \text{O} \) bond, however, we find the frequency to be quite a bit higher. Here the carbon is also joined to two other carbon atoms and since these bonds probably make an angle of about 109° with the double bond we may say as

\[
\text{T. col. s; E. E3o n(l Co nl po l n(l}
\]

A first approximation that the effective force acting on that side of the carbon atom will be about equal to a single bond. An approximate calculation then gives the frequency as 1790 cm\(^{-1} \) which accounts at least qualitatively for the increase in frequency over the value for ethylene.

In the same way we find that \( \text{C} \equiv \text{C} \) in acetylene has a frequency accounted for by thrice the value for the single bond while the \( \text{C}_2\text{H}_2 - \text{C} \equiv \text{N} \) frequency lies higher by about the amount we should expect from the addition of the extra bond to the carbon atom.

The calculation of the bending frequencies may be made most simply in the case of molecules like methane or carbontetrachloride. One of the types of motion with the slow frequency will be that where the central atom stands still and the outer atoms vibrate toward and away from each other in pairs without stretching the bonds. In other words, we have a pure type

\[
\text{Table I.}
\]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Compound</th>
<th>( \mu )</th>
<th>( k )</th>
<th>Frequency</th>
<th>Obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C} - \text{H} )</td>
<td>( \text{H}_2\text{C} - \text{CH}_3 )</td>
<td>1.0</td>
<td>5 \times 10^5 \text{ dynes/cm}</td>
<td>2920 cm(^{-1} )</td>
<td>2950 (^{14} )</td>
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<tr>
<td>( \text{C} - \text{C} )</td>
<td>( \text{H}_2\text{C} - \text{CH}_3 )</td>
<td>7.5</td>
<td>5</td>
<td>1070</td>
<td>990 (^{14} )</td>
</tr>
<tr>
<td>( \text{C} - \text{O} )</td>
<td>( \text{H}_2\text{C} - \text{OH} )</td>
<td>8.0</td>
<td>5</td>
<td>1030</td>
<td>1031 (^{15} )</td>
</tr>
<tr>
<td>( \text{C} - \text{Cl} )</td>
<td>( \text{C}_2\text{H}_2 - \text{Cl} )</td>
<td>23.6</td>
<td>5</td>
<td>600</td>
<td>596 (^{14} )</td>
</tr>
<tr>
<td>( \text{C} = \text{C} )</td>
<td>( \text{H}_2\text{C} = \text{CH}_2 )</td>
<td>7.0</td>
<td>10</td>
<td>1560</td>
<td>1600 (^{12} )</td>
</tr>
<tr>
<td>( \text{C} = \text{O} )</td>
<td>( \text{HC} = \text{C} )</td>
<td>8.0</td>
<td>15</td>
<td>1790</td>
<td>1704 (^{10} )</td>
</tr>
<tr>
<td>( \text{C} = \text{C} )</td>
<td>( \text{C}_2\text{H}_2 - \text{C} = \text{N} )</td>
<td>7.0</td>
<td>20</td>
<td>1990</td>
<td>1950 (^{14} )</td>
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</table>

<table>
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<th>Bond</th>
<th>Compound</th>
<th>( \mu )</th>
<th>( k )</th>
<th>Frequency</th>
<th>Obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H} - \text{C} - \text{H} )</td>
<td>( \text{CH}_4 )</td>
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<td>0.6</td>
<td>1430</td>
<td>1520 (^{11} )</td>
</tr>
<tr>
<td>( \text{C} - \text{C} - \text{O} )</td>
<td>( \text{CH}_3 - \text{CH}_2 - \text{OH} )</td>
<td>0.5</td>
<td>0.6</td>
<td>480</td>
<td>450 (^{11} )</td>
</tr>
<tr>
<td>( \text{Cl} - \text{C} - \text{Cl} )</td>
<td>( \text{C}_2\text{Cl}_4 )</td>
<td>17.5</td>
<td>0.6</td>
<td>249</td>
<td>216 (^{11} )</td>
</tr>
</tbody>
</table>

\(^{13} \) R. G. Dickinson, R. T. Dillon, and F. Rasetti, Phys. Rev. 34, 582 (1929).

\(^{14} \) M. Daure, Compt. Rend. 188, 1492 (1929).

\(^{15} \) Ellis, Phys. Rev. 28, 25 (1926).
of bending motion. As a first approximation we can treat this by means of Eq. (1) since the motion of a pair of atoms will be the same as if they were directly joined by an elastic force. Giving the value of 0.6 dynes per cm to this effective force which we believe is brought about by the bending of the bonds, we find values as shown in the second part of Table I. The first agrees fairly well with the value ascribed by Dennison9 to this type of motion in methane. The second agrees with the slowest observed Raman frequency, and there is evidence that this frequency is the one associated with this type of motion in a study of molecular models to which reference will be made later.

The case of ethyl alcohol which is more complex has been treated by Yates.13 With these values in his equation we find 480 cm\(^{-1}\) for the frequency due to bending, in good agreement with the slowest observed Raman line.

The calculated frequencies are indicated in Fig. 1 by the vertical lines in the crosses at the top of the figure. The horizontal lines indicate roughly what we should expect from the modification of the frequency by additional bonds or chain formation. Thus, as we have seen in the case of C=O the frequency is raised about five per cent by the addition of the two bonds on the left of the carbon. On the other hand by lengthening out the carbon chain as in pentane the original C-C frequency can in a sense be modified to perhaps a third of its value or less.

It may be seen that for the compounds, for which the Raman shift frequencies have been plotted in the figures, we find frequencies just in those ranges which we would expect according to the structure. This seems to be the best evidence we have that the postulates regarding the nature of the mechanical system in the molecule are reasonable and that the Raman frequency shifts do correspond to fundamental mechanical frequencies.

Considerable light has also been thrown on this problem by a study of mechanical models of molecules16 which was based on the ideas developed by C. F. Kettering on the nature of elasticity in molecules. The problem has also been discussed from several other points of view by Yates13 and Lewis14 to whose papers reference has already been made. The conclusions drawn from these different lines of approach to the problem seem to be in substantial agreement.

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