FORCE CONSTANTS

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Introduction

THE vibration frequencies of a molecule having a particular shape depend
(a) on the masses of the atoms in the molecule, and (b) on the restoring
forces that come into play when the molecule is distorted from its equilibrium
configuration. Therefore, a study of the vibration frequencies supplies
information about these restoring forces.

Since it may be assumed that the atomic masses are known, the problem
of accounting for molecular vibration frequencies is one of finding out about
the restoring forces. The most marked advances have been made by
thinking of the molecule in terms of its valency bonds and supposing that
when any valency bond (or angle) is distorted a restoring force comes into
play to restore the bond (or angle) to its equilibrium value. It is found
that the restoring force may be assumed to be proportional to the distortion,
and the proportionality constant relating the force and the distortion is
called the force constant. However, this simple picture of thinking of the
molecule only in terms of the tendency of its valency bonds to return to
their original lengths and positions when distorted is not a complete one.
The result is that much work has been, and is being, done to try to discover
how this simple valency picture is best modified to account for the obser-
vations. When a suitable force field has been selected and tested for a
given molecule we obtain from the measured vibration frequencies the
numerical values of the force constants of its valency bonds and angles.
The bond force constants have been used to assess the strength of the bonds
and it has been found that the force constant of a bond between a given
pair of atoms depends on the nature of the bond—or bond order. Force
constants have been used to assess bond order. It has also been found
that other properties of the bond (such as the equilibrium length) may be
related to its force constant, and work has been done on these relationships.
There has been much less development in our understanding of bending
force constants and there is, as yet, little theory to account for their
magnitudes.

Vibration Frequency Calculations

To obtain an expression for the frequencies in terms of (a) and (b) it
is necessary to write expressions for the kinetic and potential energies of
the molecule. To do this we have to choose a co-ordinate system to
represent the positions of the atoms in the molecule. Various co-ordinate
systems may be selected but because, under ordinary conditions, a molecule
always remains close to its equilibrium form, it is easiest to represent the

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internal configuration in terms of displacement co-ordinates which measure the displacements of the atoms from their equilibrium positions. It is simplest to use Cartesian displacement co-ordinates so that, if there are N atoms in the molecule, $3N$ co-ordinates are required : $x_1, y_1, z_1, x_2, \ldots z_N$. To make our formulæ less lengthy it is convenient for us to represent these $3N$ Cartesian co-ordinates by the symbols $q_1, q_2, \ldots q_n$ (where $n = 3N$, $q_1 = x_1$, $q_2 = y_1 \ldots$ and $q_n = z_N$). The kinetic energy of the system may then be written as

$$T = \Sigma \tfrac{1}{2} m_i \dot{q}_i{}^2 \qquad\qquad (\dot{q}_i = \mathrm{d}q_i/\mathrm{d}t) \quad . \quad . \quad . \quad (1)$$

where m_i is the mass of the atom associated with the q_i co-ordinate.

We have in (1) an expression to take account of the effect of (a) on the internal movements of the molecule—the atomic masses are the coefficients in the kinetic energy (K.E.) expression. Now we must consider how (b), the restoring forces, affect the internal motions. It is easiest to represent this by writing the potential energy, rather than the restoring force, as a function of the distortions. The potential energy and restoring force are intimately related since the force along any co-ordinate, q_i, is given by $-\,\partial V/\partial q_i$. The most general form of this potential energy (P.E.) function will be

$$V = V_0 + \underset{i}{\Sigma} A_i q_i + \underset{ij}{\Sigma} \tfrac{1}{2} a_{ij} q_i q_j + \underset{ijk}{\Sigma} B_{ijk} q_i q_j q_k + \ldots \qquad . \quad (2)$$

where the summation terms cover all combinations of the co-ordinates, including squared terms. The zero of any potential-energy scale is arbitrary, so we will choose our zero so that the potential energy is zero at the equilibrium configuration (i.e., $V = 0$ when all the q_i's are zero). Therefore $V_0 = 0$. Also, the equilibrium configuration must be a minimum of potential energy, so $\partial V/\partial q_i = 0$, for all q_i's, when all the displacement co-ordinates are zero. Therefore all the A_i's are zero. Thirdly, under ordinary conditions, molecules are never distorted far from their equilibrium configurations (i.e., the q_i's are always small). This means that we may, to a first approximation, presume that the terms involving $q_i q_j q_k$ (product of three small numbers) are always small compared with terms involving $q_i q_j$ (product of two small numbers). Equation (2) may therefore be simplified to

$$V = \Sigma \tfrac{1}{2} a_{ij} q_i q_j \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This means that the variation of the potential energy along any one co-ordinate is parabolic in form for, if all the co-ordinates except q_i are zero, we have $V = \tfrac{1}{2} a_{ii} q_i^2$—i.e., the potential energy is proportional to the square of the displacement, which is the equation of a parabola having its minimum at the equilibrium configuration. Moreover, since the force along the ith co-ordinate $F_i = -\,\partial V/\partial q_i = -\,a_{ii} q_i$ when all the other q_j's are zero, the force is proportional to the displacement. The success that has attended the application of (1) and (3) to the calculation of molecular vibration frequencies implies that (3) is an adequate form for the P.E. function and that the proportionality between restoring force and displacement is, in fact, a good approximation.

The fact that restoring force and displacement are proportional to one another means that the motion will be simple harmonic. By equating the product of mass and acceleration of each atom to the restoring force acting on that atom as deduced from (3), and doing this for all the atoms in the molecule, one can obtain an expression for the vibration frequencies which is of the form [1-4]

$$\nu^{2n} - \alpha_1.\nu^{2(n-1)} + \alpha_2.\nu^{2(n-2)} - \ldots \alpha_{n-1}.\nu^2 + \alpha_n = 0 \qquad . \qquad (4)$$

where ν is the vibration frequency. The values of α_1, α_2, etc., are dependent on, and can be calculated from, the atomic masses, m_i, and the constants in the potential-energy function, a_{ij}. Equation (4) is satisfied by n values of ν^2. Some of these are zero and correspond to the small translations and rotations of the molecule which have a " vibration frequency " of zero since translations and rotations do not involve any change in the potential energy. For a non-linear molecule (4) is satisfied by $n - 6$ (i.e., $3N - 6$) positive non-zero values of ν^2. The positive values of $\sqrt{\overline{\nu^2}}$ give the vibration frequencies of the molecular system.

For molecules which possess some symmetry (e.g., methylene dichloride, CH_2Cl_2, which has two planes and a two-fold axis of symmetry) the algebraic equation (4) factorises. The reason for this is that, if a molecule has, for instance, a plane of symmetry, the fundamental vibrations must be either symmetric or antisymmetric to the plane and (4) factorises into two—one factor giving the frequencies of the symmetric vibrations and the other factor those of the antisymmetric vibrations. In methylene dichloride there are four symmetry types : (i) symmetric to both planes ; (ii) antisymmetric to both ; (iii) symmetric to the CH_2 plane and antisymmetric to the CCl_2 plane ; (iv) vice versa from (iii). The equation (4) in this case factorises into (i) a quartic, (ii) a linear, and (iii) and (iv) two quadratic equations in ν^2 which give the nine vibration frequencies of the methylene dichloride molecule. This factorisation simplifies the calculation problem (two quadratics may be solved more quickly than a quartic).

To calculate the fundamental vibration frequencies of a given molecule of a known configuration, we have to know the constants in (1) and (3). The constants in (1) are the atomic masses, which are always known. However, to know the a_{ij} in (3) we have to make some assumptions regarding the way in which V varies with the distortion of the molecule. That is, we have to make some assumptions regarding the force field existing within the molecule.

In practice the process is, of course, reversed. That is, knowing the atomic masses, we use the vibration frequencies to obtain information about the potential-energy function of the molecule. However, we find that the available data are inadequate for us to determine all the constants in (3) —i.e., all the a_{ij}'s. An example will show this. In methylene dichloride

[1] E. T. Whittaker, " Analytical Dynamics," Cambridge Univ. Press.

[2] G. Herzberg, " Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand Co.

[3] E. B. Wilson, J. Chem. Physics, 1939, 7, 1047.

[4] M. A. El'yashevich, Compt. rend. Acad. Sci. U.R.S.S., 1940, 28, 604.

the number of possible independent constants for the most general type of the potential-energy function (3) is seventeen. The number is reduced compared with an unsymmetric pentatomic molecule by the symmetry. But methylene dichloride has only nine fundamental vibration frequencies. One cannot determine more than nine constants from nine observed quantities. In this case a way out of the difficulty is to examine the nine fundamental frequencies of $CHDCl_2$ and the nine of CD_2Cl_2—one could also use the chlorine isotopes but the percentage change of mass is smaller and the effect on the frequencies is therefore smaller. There are now a sufficient number of observed frequencies (27) to calculate the 17 constants. Also, there is an internal check on the reliability of the treatment because there are more observed frequencies than adjustable constants. However, it is not always possible to determine all the fundamental frequencies of a molecule and it is not always possible to make use of isotopes. Then the other way out of the difficulty is used. Instead of determining more vibration frequencies, assumptions are made regarding the molecular force field (potential-energy function) which reduce the number of independent constants in (3). The two most important simplifications are the " simple valency force field " (S.V.F.F.) and the " simple central force field " (S.C.F.F.).

Special Force Fields

The assumption of the valency force field is that the only forces in the molecule are those associated with valency bonds. Though we know that in molecules non-bonded atoms do exert forces on one another, it is reasonable to suppose that these may be neglected relative to the bond forces. The S.V.F.F. assumes that, if a bond alters its length, there is a force tending to restore it to its original length which is proportional to its change in length. It likewise supposes that, if the angle between two bonds alters, there is a force, proportional to the change, which tends to restore it to its original value. This means that, on the basis of the S.V.F.F., the P.E. function (3) may be written as

$$V = \Sigma\tfrac{1}{2}k_a\Delta R_a^2 + \Sigma\tfrac{1}{2}k_m\Delta\alpha_m^2 \quad . \quad . \quad . \quad . \quad (5)$$

where ΔR_a is the change in the length of the bond " a " from the equilibrium value and $\Delta\alpha_m$ is the distortion in the angle " m ". The summations are over all bonds and angles. The constants, k, are called the force constants. Since $- dV/d\Delta R_a$ is the restoring force along the " a " bond it will be seen that, when all the distortions other than ΔR are zero, the restoring force, according to (5), is $- k_a\Delta R_a$—i.e., the restoring force is proportional to the displacement. By geometry, the ΔR and $\Delta\alpha$ may be represented in terms of the Cartesian displacement co-ordinates, q_i, and so (5) may be converted into the form of (3) (i.e., V as a function of the q's) which may be used in conjunction with (1) to obtain (4).

Let us see how this would help us with methylene dichloride, which has two C–H bonds, two C–Cl bonds, one ClĈCl angle, one HĈH angle, and four ClĈH angles. Both C–H bonds must be the same and have the

same force constant. Therefore the potential-energy function of methylene dichloride, according to the S.V.F.F., is obtained in terms of *five* force constants. If all the *nine* fundamental frequencies have been found, then the five constants may be determined. More important still, because the nine frequencies are obtained in terms of less than nine constants, a relation between the observed frequencies which is independent of the actual values of the force constants may be obtained. This may be used to check the reliability of the initial assumption (a S.V.F.F.). Let us turn to a simpler example than methylene dichloride, namely, methane. On a S.V.F.F. this has one bond-stretching constant, k_{CH}, and one angle constant, k_{HCH}. It has four fundamental frequencies which are observed in the Raman and the infra-red spectra to be 2914, 1526, 3020, and 1306 cm.$^{-1}$.[5-7] If the force field in methane were really of the S.V.F.F. type it can be shown that the following relation would hold : [2]

$$\frac{\nu_3 . \nu_4}{\nu_1 . \nu_2} = \sqrt{\frac{2}{3}\left(1 + \frac{4m_H}{m_C}\right)} \quad . \quad . \quad . \quad . \quad (6)$$

For methane the left-hand side (L.H.S.) is 0·89 and the R.H.S. 0·94, which is fairly good agreement, showing that the S.V.F.F. is quite a good approximation for methane. However, for CCl_4 the L.H.S. is 2·44 while the R.H.S. is 2·92, which is not such good agreement, the difference having risen to about 20%. Other tetrahalides, AX_4, are rather like carbon tetrachloride.

Before discussing the merits of the S.V.F.F., we will discuss the S.C.F.F. This assumes that the only forces in molecules are those between atoms along the line joining them, whether the atoms are bonded or not. It supposes that there are no angle forces like those of the S.V.F.F. The forces are supposed proportional to the displacement, and the potential energy is therefore proportional to the squares of the displacements :

$$V = \Sigma \tfrac{1}{2} k_{AB} \Delta R_{AB}^2 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where ΔR_{AB} is the change in the distances between atoms A and B from the equilibrium value and k_{AB} is the force constant. The summation is made over all pairs of atoms. Thus in methylene dichloride there are five constants : For the two C–H bonds, for the two C–Cl bonds, for the H–H separation, for the Cl–Cl separation, and for the four Cl–H separations. If we return to the tetrahedral molecules, the S.C.F.F. gives an expression similar to (6), which may be used to test the validity of the assumptions :

$$\frac{\nu_3 . \nu_4}{\nu_2(\nu_1^2 - 4\nu_2^2)^{\frac{1}{2}}} = \sqrt{\frac{2}{3}\left(1 + \frac{4m_H}{m_C}\right)} \quad . \quad . \quad . \quad (8)$$

For methane, the L.H.S. is imaginary because $4\nu_2^2$ is greater than ν_1^2, so the S.C.F.F. gives a poor account of methane. For carbon tetrachloride, the L.H.S. is 7·96 and the R.H.S. 2·92. For $SnBr_4$, the L.H.S. is 2·14 and the R.H.S. 1·57, and this last gives the best agreement of all the tetrahedral molecules. The general conclusion, which is supported by much

[5] R. G. Dickinson, R. T. Dillon, and F. Rasetti, *Physical Rev.*, 1929, **34**, 582.

[6] G. E. MacWood and H. C. Urey, *J. Chem. Physics*, 1936, **4**, 402.

[7] J. P. Cooley, *Astrophys. J.*, 1925, **62**, 73.

other evidence, is that the S.V.F.F. is closer to the truth than the S.C.F.F. (see W. G. Penney and G. B. B. M. Sutherland [8] for triatomic molecules, and J. B. Howard and E. B. Wilson [9] for molecules of the AX_3 type). It is noteworthy that, on the whole, in the tetrahedral molecules the S.V.F.F. becomes less successful as we pass from the hydrides to the halides (*e.g.*, CH_4 to CCl_4) while the S.C.F.F. becomes more successful. This suggests that the forces between the non-bonded halogen atoms are more important than those between the non-bonded hydrogen atoms, as would be expected. A further objection to the S.C.F.F. is that it does not account for the bending vibrations of linear molecules since no interatomic distances change in such vibrations. Also it fails to account for the out-of-plane vibrations of planar molecules (*e.g.*, CH_2O). However, in this last case, the S.V.F.F. only accounts for such vibrations if some rather more complicated bending terms are included.

The general conclusion of this phase of the study of molecular force fields has been that we should base any improvements or refinements on fields of the S.V.F.F. type rather than on those of the S.C.F.F. type. Before leaving our consideration of the S.V.F.F., it is worth mentioning that some workers have made use of the unmodified S.V.F.F. in the following way. The symmetrical non-linear triatomic molecule AB_2 (H_2O type) has, on the S.V.F.F., two force constants. It has three fundamental vibration frequencies. The expression for these frequencies depends on the atomic masses, which may be taken as known, the two force constants and the BÂB angle. Because there are *three* frequencies, the *two* force constants may be eliminated and an expression obtained for the BÂB angle in terms of the three frequencies. So the angle may be calculated from the observed vibration frequencies.[10] However, the reliability of the result depends on the reliability with which the S.V.F.F. may be applied to the particular molecule. Because the S.V.F.F. is known to be only an approximate representation of the force field for most molecules, the author considers that this is a dangerous method to use to determine bond angles in molecules.

The S.V.F.F. has been extended by including in the P.E. function " cross terms " so that (5) becomes

$$V = \Sigma \tfrac{1}{2} k_a \Delta R_a^2 + \Sigma \tfrac{1}{2} k_m \Delta \alpha_m^2 + \Sigma \tfrac{1}{2} k_{ab} \Delta R_a \Delta R_b + \Sigma \tfrac{1}{2} k_{mn} \Delta \alpha_m \Delta \alpha_n + \Sigma \tfrac{1}{2} k_{am} \Delta R_a \Delta \alpha_m . \qquad . \quad (9)$$

The P.E. function is still quadratic and will lead to an equation of the form of (3) when the ΔR's and $\Delta \alpha$'s are replaced by q displacement co-ordinates. One may suppose that the cross-term $\Delta R_a \cdot \Delta \alpha_m$ is included in the P.E. function to account for the fact that, when the bond a changes its length, the equilibrium value of the bond angle α_m is affected. For example, it may be that, when the length of the C–Cl bond in CH_3Cl changes, the configuration of the methyl group which has a minimum potential energy also changes. Such effects can be allowed for by including these cross-terms, and much use has been made of them. However, by reason

[8] *Proc. Roy. Soc.*, 1936, *A*, **156**, 654.   [9] *J. Chem. Physics*, 1934, **2**, 620.
[10] D. M. Simpson, *Trans. Faraday Soc.*, 1945, **41**, 209.

of the scarcity of our data (number of frequencies available) we cannot usually introduce all the possible cross-terms. Thus, in the molecule AB_2 (H_2O type) we could have, besides the two S.V.F.F. constants, two constants associated with the two types of cross-terms : one between the two bonds, and the other between the bond and the angle. So the most general form of the valency force field requires the use of four constants. If we cannot make use of isotopes we have only three fundamental frequencies and so can determine only three constants. Therefore, in most cases, it is necessary to limit the number of cross-terms that we introduce into the V.F.F. potential energy function. The difficulty is then to know which cross-terms to include and which to omit. It must be admitted that there is no sure way of doing this. The only course to adopt is to include those cross-terms which seem to account best, most reasonably, and most easily for the departures from the S.V.F.F., but it does seem sometimes that there is little physical explanation for some cross-terms that are introduced and that the introduction of these cross-terms has resulted in the V.F.F. system becoming rather artificial. It must be stressed that it is never satisfactory to use as many unknown constants as there are observed frequencies because there is no check then whether the right set of cross-terms has been selected. That is, there is no check on the reliability of the P.E. function that has been used, and a careful check is very important as we do not yet know with any exactness the true nature or relative importance of the various interatomic forces that may occur in molecules.

Ethylene, formaldehyde, and similar molecules have been treated by P.E. functions of this kind by H. W. Thompson and J. W. Linnett.[11, 12] Z. I. Slawsky and D. M. Dennison,[13] and J. W. Linnett [14] have treated the methyl halides, CH_3X, in this way, and a difference between the two methods of approach brings out an important point.[15] Both treatments used the P.E. function (10) which, it is to be noted, had been arrived at quite independently :

$$V = \Sigma \tfrac{1}{2} k_{CH} \Delta R_{CH}^2 + \tfrac{1}{2} k_{CX} \Delta R_{CX}^2 + \Sigma \tfrac{1}{2} k_{HCH} \Delta \alpha_{HCH}^2$$
$$+ \Sigma \tfrac{1}{2} k_{HCX} \Delta \alpha_{HCX}^2 + \Sigma \tfrac{1}{2} k' \Delta R_{CX} \Delta \alpha_{HCX} \qquad (10)$$

There are four S.V.F.F. squared terms and one cross-term involving the constant k'. Slawsky and Dennison supposed that k_{CH} and k_{HCH} were the same in the four methyl halides as in methane. So they calculated k_{CH} and k_{HCH} from the frequencies of methane. Then, for each methyl halide, they adjusted the remaining three constants to give the six observed frequencies as well as possible. The check on the P.E. function was, in all cases, quite good. Linnett, on the other hand, concluded from a study of ethane that a P.E. function of the above type was a satisfactory one to use. He then deduced separately for each methyl halide the five constants in (10). Because four of the six frequencies are determined, almost entirely, by four of the constants, there is very little check on the P.E.

[11] J., 1937, 1376.   [12] J., 1937, 1384.
[13] J. Chem. Physics, 1939, 7, 509.   [14] Ibid., 1940, 8, 91.
[15] D. M. Dennison, Rev. Mod. Physics, 1940, 12, 175.

function for each CH_3X molecule separately. The reliability of the method depends on whether the successful test with ethane is enough. However, in this case, the two approaches do agree quite well. Linnett finds that k_{HCH} is virtually constant throughout the series, as assumed by Slawsky and Dennison. However, he finds that the constant k_{CH} increases from 4·71 to 5·00 × 10^5 dynes/cm. on passing from methyl fluoride to the iodide. The study of the methyl halides therefore raises the question : To what extent is it justifiable to use a force constant determined in one molecule for an apparently identical bond in another molecule ? One would have said that the C–H bonds in the methyl halides were all very nearly the same, but the above treatment suggests that their force constants do, in fact, change not inconsiderably from one halide to another (6%). The conclusion would therefore seem to be that we must be very careful in transferring a constant determined in one molecule to another even if the two bonds appear similar, though the results for the k_{HCH} constant show that in certain cases such a transfer is satisfactory.

F. Stitt [16] treated ethane with a V.F.F. of the type represented by (9). By using the determined frequencies of both C_2H_6 and C_2D_6 Stitt was able to introduce a large number of cross-terms (6) into his P.E. function and dealt with this molecule most completely and very satisfactorily. B. L. Crawford and S. R. Brinkley [17] studied together acetylene, ethane, methyl-acetylene, dimethylacetylene, hydrogen cyanide, methyl cyanide, and the methyl halides. As far as possible they transferred both squared and cross-term constants from molecule to molecule. For example, they used the force constants they found necessary for the methyl group in ethane for that group in all the other molecules studied—and similarly for the acetylenic and cyanide groupings. That is, they went a stage further than Slawsky and Dennison in transferring cross-term as well as squared-term constants from molecule to molecule. The agreement they obtained between calculated and observed frequencies was most satisfactory. They calculated, for all the molecules, 84 frequencies with 31 constants, which implies that the procedure adopted, namely, transfer of constants, was reliable. Linnett [18] treated methyl- and dimethyl-acetylene and methyl cyanide with a much simpler force field based on the one he had successfully used for ethane. He used an entirely new set of constants for methyl- and dimethyl-acetylene and calculated the 25 frequencies of these two molecules satisfactorily, using 11 adjustable constants. Linnett obtained a value for the C–C bond force constant in these acetylene derivatives which was different from that obtained by Crawford and Brinkley and showed that his value was more in agreement with the observed bond length, the correctness of Douglas Clark's empirical relationship (see later) being assumed. He therefore questioned whether Crawford and Brinkley were justified in transferring constants so liberally from one molecule to another. The transfer of constants in the series of chlorinated derivatives of methane was studied by H. H. Voge and J. E. Rosenthal,[19] but the number of frequencies

[16] J. Chem. Physics, 1939, 7, 1115.   [17] Ibid., 1941, 9, 69.
[18] Trans. Faraday Soc., 1941, 37, 469.   [19] J. Chem. Physics, 1936, 4, 137.

only exceeded the number of adjustable constants by one, so that the test cannot be regarded as very convincing.

A quite different, but very realistic, potential-energy function has been used by H. C. Urey and C. A. Bradley [20] for a number of molecules of the CCl_4 type (tetrahedral). They superimposed on the S.V.F.F. (one bond and one bending constant in this case) a repulsion potential of the form $V' = a/R^n$ between the non-bonded atoms. Using the four frequencies of the tetrahedral molecules, they are able to calculate the two S.V.F.F. constants and a and n. In fact, they assumed n to be 7 throughout, and found that they could account for the four frequencies each of CCl_4, $SiCl_4$, $TiCl_4$, $SnCl_4$, CBr_4, and $SnBr_4$ with the three adjustable constants (a and the two S.V.F.F. constants for each molecule). They found that the repulsions which had to be assumed between the non-bonded atoms were of the same order as those required for similar repulsions in other circumstances. Urey and Bradley also considered the ions SO_4^- and ClO_4^- and found that, by adding an additional Coulombic repulsion force between the oxygen atoms, the observed frequencies could be accounted for. Rosenthal has treated the tetrahalides with a more general potential-energy function and has considered her results in the light of Urey and Bradley's assumptions.

This section has shown repeatedly that the problem in obtaining force constants is : How is one to choose a sufficiently general force field and yet not have too many unknown constants for a particular molecule ? The ideal method of approach is to obtain as many frequencies of a given structure as possible by using isotopic molecules. For instance, F. Miller and B. L. Crawford [21] have been able to deduce and check the most general form of the P.E. function for the non-planar distortions of the benzene molecule by using the vibration frequencies of benzene and a number of its deuterated derivatives. However, this method of approach is not always possible and we are often forced to use simplified forms. For such purposes the modified valency force systems are the most satisfactory. Moreover, the chemist always finds such systems more useful than any other, even the more general ones, because it gives him results in terms of valency bonds with which he is accustomed and equipped to deal. It is the determination of the force constants of individual bonds in the molecule which the chemist particularly requires, for with these he may assess similarities and differences between bonds in different molecules. However, these bond-force constants must be obtained by using a P.E. function (a force field) whose reliability for the molecule or molecules in question has been satisfactorily tested.

G. Glockler and J. Y. Tung [22] have suggested that it is convenient in the case of, for example, triatomic molecules of the water type which, on the general V.F.F., have four force constants (see p. 79), to plot three of the force constants against the fourth. One can then see quickly and easily what are the possible sets of values of the four constants, though which four is the correct set cannot be decided with any certainty. Glockler

[20] *Physical Rev.*, 1931, **38**, 1969.   [21] *J. Chem. Physics*, 1946, **14**, 282.
[22] *Ibid.*, 1945, **13**, 388.

and Tung, in addition, suggest an arbitrary method of deciding which set of force constants is the correct one. However, there does not seem to be any sound basis for the method suggested, and the author agrees with D. M. Simpson [23] that " the information obtained by using it should not be considered entirely reliable."

Nature of Experimental Data

The vibration frequencies that are used in force-constant calculations are obtained mostly from infra-red [24] and Raman spectra,[25—28] though ultra-violet, fluorescence, and resonance spectra may be used to a limited extent. In what has been said in previous sections it has been presumed that all the vibration frequencies of the molecule under consideration had or could be determined. Except for the simpler molecules, this by no means represents the position. It is often difficult to decide, for instance, which infra-red bands are fundamentals and which combinations or over-tones. In addition, when a molecule has some symmetry it is important to assign each observed fundamental frequency to its proper symmetry class. This is necessary so that we may know which frequencies are to be accounted for by a given factor of the algebraic equation (4). The assignment of frequencies to their proper symmetry classes is made possible by the application of selection rules which tell us which vibrations are forbidden to appear in the infra-red spectrum and which in the Raman spectrum.[2] The polarisation of the scattered radiation in the Raman effect may also be used to help us make the correct assignment. The contours or fine structure of the infra-red bands may be used similarly. But even with all these aids it is often impossible to decide what the correct assignment is. The present position is conveyed by a few examples. For water,[29] acetylene,[30] ethylene,[31] carbon dioxide,[32] the methyl halides,[2] and many other molecules of a similar complexity all the frequencies are known and correctly assigned. For ethylene oxide, *cyclo*propane,[33] the vinyl halides,[34] propylene,[35] propane,[36] and even ozone [10, 37] no complete and certain assignment has been made.

[23] *J. Chem. Physics*, 1946, **14**, 294.

[24] R. B. Barnes, R. C. Gore, U. Liddel, and V. Z. Williams, " Infra-red Spectro-scopy," Reinhold Publishing Corp.

[25] J. H. Hibben, " The Raman Effect and its Chemical Applications," Reinhold Publishing Corp.

[26] G. B. B. M. Sutherland, " Infra-red and Raman Spectra," Methuen.

[27] G. Glockler, *Rev. Mod. Physics*, 1943, **15**, 111.

[28] D. M. Dennison, *ibid.*, 1931, **3**, 280.

[29] B. T. Darling and D. M. Dennison, *Physical Rev.*, 1940, **57**, 128.

[30] G. Herzberg and J. W. T. Spinks, *Z. Physik*, 1934, **92**, 87.

[31] G. K. T. Conn and G. B. B. M. Sutherland, *Proc. Roy. Soc.*, 1939, *A*, **172**, 172.

[32] A. Adel and D. M. Dennison, *Physical Rev.*, 1933, **43**, 716.

[33] J. W. Linnett, *J. Chem. Physics*, 1938, **6**, 692.

[34] H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, 1945, **41**, 236.

[35] E. B. Wilson and A. J. Wells, *J. Chem. Physics*, 1941, **9**, 319.

[36] K. S. Pitzer, *ibid.*, 1944, **12**, 310.

[37] A. Adel and D. M. Dennison, *ibid.*, 1946, **14**, 379.

The accuracy of the determination of the observed frequencies is variable. Those obtained from the Raman spectra are accurate to 1 cm.$^{-1}$ if a reasonably good spectrometer has been used. In the infra-red, if the fine structure can be accounted for, the centre of the .band may be placed even more accurately. However, some bands have very complex contours and it is often difficult to place the centre of such bands accurately. The same is even more true if bands overlap. Other difficulties, such as resonance between vibrational energy levels, may also make it difficult to determine the classical fundamental frequencies.

The theory of molecular vibrations considers the isolated molecule. However, the Raman spectrum is very often obtained by using the liquid, and it is uncertain how much the internal vibration frequencies are affected in this state by the intermolecular forces. In some cases the effect seems to be slight. Thus the totally symmetric vibration of the benzene ring gives a Raman shift of 993 cm.$^{-1}$ if the gas, and 994 cm.$^{-1}$ if the liquid, is used. On the other hand, the observed value of the C–Cl valency vibration in CH_3Cl changes from 732 to 709 cm.$^{-1}$ on passing from the gas to the liquid.[2] So far it has not been found possible to assess what the change is likely to be for a given vibration, but in most cases it is probable that the percentage error from this source is small.

The assumption in (3) that the potential energy is a quadratic function of the displacement co-ordinates is an approximation. This means that the motion is not strictly simple harmonic and the observed frequencies are different from the values they would have if the displacements were infinitesimal. The assessment of this anharmonicity correction necessitates the observation of a large number of overtone and combination frequencies and is hardly ever possible. So we are forced to use the uncorrected frequencies which are observed as if they were the fundamental frequencies for S.H.M. In doing this we introduce an error into the derived force constants which may be considerable. For instance, for the water molecule the anharmonicity correction averages 4%.[29] This means that the force constants derived by using the positions of the infra-red bands will be 8% different from the true force constants derived for vibrations involving infinitesimal displacements. For nitrous oxide the error in the force constants would be less—about 3%.[2] It must always be realised that the force constants derived from observed frequencies are subject to this error. When comparing force constants of similar bonds in different molecules it is presumed that the anharmonicity correction is likely to be very much the same in all cases. Thus for the C–H valency vibration in HCN the anharmonicity correction to the frequency is 4% (3312 to 3452) whereas for the O–H vibration in water it is $4\frac{1}{2}$% (3652 to 3825). For all bonds between the same pair of atoms (e.g., all C–H bonds) it is even more likely to be the same.

Uses of Force Constants

Before considering the uses of force constants, we will see what is the order of magnitude of these quantities. The bond-force constants are

usually measured in dynes/cm. and measure the restoring force that would come into play if the bond were stretched 1 cm. if the law of force assumed persisted to such large separations. The force constant of the C–C bond in ethane is 4.5×10^5 dynes/cm., and constants as low as 2×10^5 and as high as about 20×10^5 are known. If the C–C bond in ethane, whose equilibrium length is 1.55 A., is stretched by 0.1 A. the restoring force exerted $(-k\Delta R)$ is 4.5×10^{-4} dyne and the potential energy $(\frac{1}{2}k\Delta R^2)$ is 2.25×10^{-13} erg per molecule greater than the equilibrium energy. This energy per molecule corresponds to 3260 cals. per g.-mol. and, if the force of N molecules in the same configuration could be added together, the force would correspond to 2.73×10^{11} tons weight per g.-mol.—nearly a million million tons weight. Angle-bending constants are measured in dyne-cm./radian (*i.e.*, ergs/radian). The bending constant of the HĈH angle is about 0.5×10^{-11} dyne-cm./radian. So, if the angle is distorted by 0.1 radian (5.73°) the potential energy increases by 0.25×10^{-13} erg. This is equivalent to 362 cals. per g.-mol. The force on the hydrogen atom which is at the end of the C–H bond whose length is 1.09 A. is $k.\Delta\alpha/R$ and this is 0.46×10^{-4} dyne. We see that the forces necessary to distort a molecule by bending the bonds is of the order of a tenth of the force necessary to alter the length of the bonds by a similar amount. Because of this, the vibrations which involve changes in a bond length have a higher frequency than those which involve mainly a bending of that bond.

Much more interest has naturally been focused on the bond-stretching constants than on the bending constants, and we will consider the former now. The following table records a number of these force constants. To show the variation that may obtain in the results for the force constants of a particular bond one may quote the figures for the C–Cl bond in methyl chloride : these are 3.44,[38] 3.61,[19] 4.42,[13] 3.35,[14] 3.64,[17] and 3.37×10^5 dynes per cm.[39] The last is probably the best.

It has been pointed out that force constants are related to the positions of the atoms in the Periodic Table. Thus the force constants of the bonds B–H, C–H, N–H, O–H, and F–H are 3.6, 5.0, 6.5, 7.6, and *ca.* 9.0×10^5 (all uncorrected for anharmonicity). Reference to the table will show other series. This relation to the Groups the atoms occupy in the Periodic Table appears in the empirical formulæ of Douglas Clark, Linnett, and Gordy.

Reference to the table shows that force constants vary with bond order. For those bonds which involve carbon as one member, the force constants of single bonds are about 5×10^5 or rather less, those of double bonds about 10×10^5, and those of triple bonds about 15×10^5 dynes per cm. or rather more. The variation of force constant with bond order for bonds between a given pair of atoms means that the force constant may be used to assess bond character in the way that bond lengths have been so widely employed. An example of this is provided by carbon dioxide. In carbon monoxide the CO force constant is 18.5×10^5 dynes per cm., and in form-aldehyde it is about 12.3×10^5. In carbon dioxide it is 15.5×10^5. This

[38] G. B. B. M. Sutherland and D. M. Dennison, *Proc. Roy. Soc.*, 1935, *A*, **148**, 250.
[39] H. D. Noether, *J. Chem. Physics*, 1942, **10**, 664.

TABLE

This table lists the bond-stretching force constants in dynes per cm. $\times 10^{-5}$; *i.e.*, a force constant of $5\cdot0 \times 10^5$ is recorded as $5\cdot0$. The constants for diatomic molecules are corrected for anharmonicity but those for polyatomic molecules are not. The probable correction is that 8% should be added to the uncorrected constants of those bonds of which one member is hydrogen, and 2 or 3% should be added in other cases (see text).

Bond.	Molecule.	$k \times 10^{-5}$, dynes/cm.	Bond.	Molecule.	$k \times 10^{-5}$, dynes/cm.
H–H	H_2	5·76	N–H	$CH_3\cdot NH_2$	6·3
Li–Li	Li_2	0·25	N–H	NH_4^+	5·4
Na–Na	Na_2	0·17	N–H	$NH_2\cdot CO\cdot NH_2$	6·4
K–K	K_2	0·10	O–H	H_2O	7·6
Rb–Rb	Rb_2	0·08	O–H	$CH_3\cdot OH$	7·6
Cs–Cs	Cs_2	0·07	S–H	H_2S	4·0
Li–H	LiH	1·03	Se–H	H_2Se	3·1
Na–H	NaH	0·78	P–H	PH_3	3·1
K–H	KH	0·56	Si–H	SiH_4	2·7
Rb–H	RbH	0·51	C–C	C_2H_6	4·5
Cs–H	CsH	0·47	C–C	C_2H_4	9·8
F–H	HF	9·7	C–C	C_2H_2	15·6
Cl–H	HCl	5·2	C–C	C_6H_6	7·6
Br–H	HBr	4·1	C–C	$CH_3\cdot C\vdots CH$	5·5
I–H	HI	3·1	C–C	$CH_3\cdot C\vdots C\cdot CH_3$	5·5
N–N	N_2	22·8	C–C	$CH_3\cdot C\vdots CH$	15·3
N–N	N_2^+	20·0	C–C	$CH_3\cdot C\vdots C\cdot CH_3$	15·3
O–O	O	11·8	C–C	$CH_3\cdot CN$	5·3
O–O	O_2^+	16·5	C–C	$CH_2\vdots CO$	9·8
C–O	CO	18·9	C–C	$CH_2\vdots C\vdots CH_2$	9·7
C–O	CO^+	19·7	C–C	C_3O_2	14·9
N–O	NO	15·9	C–C	C_2N_2	6·7
C–S	CS	8·4	C–N	HCN	18·1
P–N	PN	10·1	C–N	$CH_3\cdot CN$	17·5
P–P	P_2	5·5	N–C	$CH_3\cdot N\vdots C$	16·3
S–S	S_2	5·0	C–N	$CH_3\cdot NC$	5·45
Cl–Cl	Cl_2	3·3	C–N	C_2N_2	17·5
Br–Br	Br_2	2·5	C–N	ClCN	16·7
I–I	I_2	1·7	C–N	BrCN	16·8
I–Cl	ICl	2·4	C–N	ICN	16·8
I–Br	IBr	2·1	C–O	CH_2O	12·3
B–H	B_2H_6	3·6	C–O	$CH_2\vdots CO$	12·3
C–H	CH_4	5·0	C–O	CO_2	15·5
C–H	CH_3F	4·7	C–O	C_3O_2	14·2
C–H	CH_3Cl	4·9	C–S	CS_2	7·5
C–H	CH_3Br	4·95	C–F	CH_3F	5·6
C–H	CH_3I	5·0	C–Cl	CH_3Cl	3·4
C–H	C_2H_4	5·1	C–Br	CH_3Br	2·9
C–H	C_2H_6	5·1	C–I	CH_3I	2·3
C–H	C_2H_2	5·9	C–Cl	ClCN	5·3
C–H	HCN	5·9	C–Br	BrCN	4·2
C–H	CH_2O	4·4	C–I	ICN	2·9
N–H	NH_3	6·5			

shows, at once, that the C–O bond in carbon dioxide is intermediate between that in formaldehyde and that in carbon monoxide.[12] It may therefore be said to be more than a double but less than a triple bond. A similar

example is provided by cyanogen chloride,[40] ClCN, in which the C–Cl bond has a force constant of 5.3×10^5 as against 3.4×10^5 for the C–Cl bond in methyl chloride. This shows that the C–Cl bond in cyanogen chloride is stronger than a single bond, an observation which can be accounted for by supposing that the real electronic structure is intermediate between

$$-\overset{|}{\underset{|}{C}}l-C\equiv N- \qquad \text{and} \qquad \diagdown Cl=C=N\diagup$$
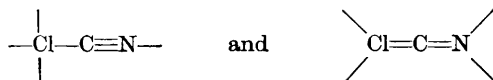
Several other similar examples of the use of force constants in this way may be quoted (C_3O_2,[41] C_2N_2,[40] C_6H_6,[42] methyl- and dimethyl-acetylenes [18]), but, in fact, the method has not been used as much as it might have been because of the difficulty of finding a satisfactory, tested, P.E. function for all but the simplest molecules. It is to be hoped that as our knowledge of molecular-force fields increases, this method of assessing bonds will be used more and more.

One special case may be mentioned. The force constant of the C–H bond can be determined with fair accuracy in a large number of molecules. This is possible because the C–H bond vibration frequency is so much greater than all the other vibration frequencies of many organic molecules that it can be treated separately.[3] Linnett [43] calculated the force constants of a number of C–H bonds and found that they varied from 4.4×10^5 in aldehydes to 5.9×10^5 dynes per cm. in acetylene. It is interesting and surprising that the force constant of this bond which is, in all cases, written as C–H varies over a range of *ca.* 30%. It appears that three factors affect the force constant : (*a*) The nature of the bond orbital, whether sp, sp^2, or sp^3 hybridised ; (*b*) the electrostatic state of the bond, this being affected by neighbouring groups [44] (cf. Gordy) ; (*c*) resonance with various ionic structures. Other M–H bonds were studied with similar results but the treatment of the N–H and O–H bonds has been improved by R. E. Richards.[45]

Another important feature of force constants is the relation they bear to bond lengths. R. M. Badger [46] first pointed out, from a study of diatomic molecules, that as the bond between a given pair of atoms becomes stronger (*i.e.*, the force constant bigger) its equilibrium length becomes shorter, and he proposed the empirical relationship

$$k = A/(R_e - B)^3 \qquad . \qquad . \qquad . \qquad . \qquad (11)$$

where R_e is the equilibrium bond length and A and B are constants. He found that their values depended on the positions in the Periodic Table of the atoms forming the diatomic molecule, and gave a table of suitable values for A and B.[47] A second relation was proposed by C. H. Douglas Clark,[48] who suggested that

$$kR_e^6 = C \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (12)$$

[40] H. W. Thompson and J. W. Linnett, *J.*, 1937, 1399.   [41] *Idem, ibid.*, p. 1291.
[42] R. C. Lord and D. H. Andrews, *J. Physical Chem.*, 1938, **41**, 149.
[43] J. W. Linnett, *Trans. Faraday Soc.*, 1945, **41**, 223.
[44] H. C. Longuet-Higgins, *ibid.*, p. 233.   [45] *Trans. Faraday Soc.*, in the press.
[46] *J. Chem. Physics*, 1934, **2**, 128.   [47] *Ibid.*, 1935, **3**, 710.
[48] *Phil. Mag.*, 1934, **18**, 459 ; 1936, **22**, 1137.

The value of the constant, C, depends also on the position in the Periodic Table of the atoms forming the molecule, and Douglas Clark and K. R. Webb [49] have given formulæ from which C may be determined. Other relations have been suggested by H. S. Allen and A. K. Longair,[50] and by M. L. Huggins.[51] Linnett [52] suggested a potential-energy function for diatomic molecules which, with various empirical assumptions, led to a relation between k and R_e.[53] The author considers that the most useful of these relationships is that of Douglas Clark because it combines sufficient accuracy with great simplicity. For instance, it gives better results than Badger's equation, and it has the great advantage that there is only one constant (C) instead of two $(A$ and $B)$. G. B. B. M. Sutherland [54] has given an explanation of the Douglas Clark relationship and this has been discussed by Linnett.[52]

These relationships were developed for diatomic molecules but have been tested for individual links in polyatomic molecules. Badger found that his relation was quite successful with C–H, C–O, C–S, and S–O links in triatomic molecules, and H. W. Thompson and J. W. Linnett [55] found that both it and Douglas Clark's relation gave good results for C–H, C–O, and C–C links in a variety of molecules. J. J. Fox and A. E. Martin [56] pointed out that, for C–C links in polyatomic molecules, kR_e^5 was more nearly constant than kR_c^6. It seems to the author that a modified Douglas Clark relation $kR_e^n = C$ may be useful, n and C being fixed by reference to perhaps three molecules for which k and R_e are both known. Then, in other molecules, k may be used to calculate R_e for bonds between the same pair of atoms. There is no doubt that this possibility of deducing R_e from k is very valuable as it can be used to check results obtained by more direct methods (spectroscopic and electron diffraction), and there are cases (e.g., some C–H bonds) where the direct methods cannot be employed.

Badger considered also the application of his equation to molecules of the AX_4 and the BX_6 type in which repulsion between the non-bonded atom is considerable.[47] He found that he could account for his results if he supposed that the repulsions between the X atoms caused a considerable stretching of the AX (or BX) bond. Thus for CCl_4 he concluded from the force constants obtained by J. E. Rosenthal [57] that the C–Cl bond was stretched by 0·19 A. from the value it would have had if there had been no repulsion between the X atoms. This is a surprising result because it implies that the C–Cl bond in methyl chloride, in which such stretching must be very small, and that in CCl_4 have about the same length only because of a balancing of various quite large factors.

[49] Trans. Faraday Soc., 1941, 37, 293.
[50] Phil. Mag., 1935, 19, 1032.
[51] J. Chem. Physics, 1935, 3, 473 ; 1936, 4, 308.
[52] Trans. Faraday Soc., 1940, 36, 1123.
[53] J. W. Linnett, ibid., 1942, 38, 1.
[54] Proc. Ind. Acad. Sci., 1938, 8, 341.
[55] J., 1937, 1396.
[56] J., 1939, 884.
[57] Physical Rev., 1934, 46, 1934.

W. Gordy [58] has recently introduced a relation between the force constant, bond order (N), bond length (R_e) and the electronegativities (x_A and x_B) of the bonded atoms. The relation is of the form

$$k = aN(x_A . x_B/R_e^2)^{\frac{3}{4}} + b \qquad . \qquad . \qquad . \qquad . \quad (13)$$

where a and b are constants (for most pairs of atoms 1·67 and 0·30, respectively). Gordy shows that (13) may be applied widely to bonds in diatomic and polyatomic molecules when the bond is not distorted by forces between non-bonded atoms. He gives a table of electronegativities and uses measured values of R_e to predict k when N is known. In other cases he predicts R_e from k when N is known, and in a few cases he determines the bond order when k and R_e are both known (e.g., BrCN). He also considers the effect of a charge being located on the atoms and shows that a positive charge, by affecting the electronegativity terms, will cause an increase in the force constant, if N remains the same.

There has been no detailed work on the relation between the heat of dissociation of a bond and its force constant. Fox and Martin [56] for C–C bonds, and G. Glockler and G. Matlack [59] for O–O bonds have shown that the graphs of both k and D against R_e are smooth curves. This implies a smooth relation between k and D. For C–C bonds Fox and Martin pointed out that kR_e^2/D was a constant quantity. Linnett [53] used the P.E. function he had suggested to calculate the heats of dissociation of some diatomic molecules from the observed force constants, but the data available were not accurate enough to provide a satisfactory test. It may also be noted that the C–H bond in methane has both a higher force constant and a higher dissociation energy than the C–H bond in ethane.

Force constants have been used to calculate unobserved frequencies. It may happen that, for a given molecule, one or two vibration frequencies cannot be determined. In such circumstances it may be possible to test a P.E. function with the frequencies that have been observed, use them to calculate the force constants, and with these to calculate the unobserved frequency or frequencies. Before Stitt's [16] complete treatment of ethane this approach was employed for that molecule, but the frequency predicted by this method was later found to be quite wrong. This use of force constants will become increasingly valuable when we know more about molecular force fields, for very often it is impossible to determine all the vibration frequencies experimentally. Yet, for certain purposes such as the calculation of thermodynamic quantities, it is necessary to know *all* the molecular frequencies. The possibility of calculating the frequencies of one molecule by using force constants obtained from another similar one is very liable to error because of the uncertainty of transferring force constants (see p. 80). Eventually, it may be hoped that we shall be able to predict the values of force constants in molecules that have not been examined experimentally, and so calculate their vibration frequencies.

It was pointed out on p. 79 that cross-terms probably account for

[58] *J. Chem. Physics*, 1946, **14**, 305.   [59] *Ibid.*, p. 503.

the effect of a change of one part of the molecule on the configuration of another part. It has been suggested that the large cross-term constant for the interaction between the two bonds in CO_2 is to be explained by the resonance in this molecule. When one C–O bond lengthens it favours one of the single–triple bond structures (O—C≡O) with the result that a shortening of the other C–O bond more readily accompanies a lengthening of the first C–O bond.

Bending Force Constants

Up to the present less consideration has been given to bending-force constants than to valency-stretching force constants. The reason for this is that it has been impossible to account for the changes that occur in these constants. For instance, although it is found that the HĈH angle has a bending constant which is constant throughout the methyl halides (0.5×10^{-11} dyne-cm./radian),[14] yet the HĈH angle in ethylene has a much smaller bending constant (0.36×10^{-11}).[11] Admittedly, the electron distribution in the two cases is different because the bond hybridisation is different but the change is nevertheless surprisingly big. Again, the C—C⟨^{H} bending constant is 0.66×10^{-11},[14] the C=C⟨^{H} 0.6×10^{-11},[11] but the C≡C—H is 0.24×10^{-11}.[17] It is surprising that the change from the double to the triple bond is so much greater than the change from the single to the double. Also, it might have been expected that the change would have been in the other direction and that the angle involving the triple bond would have been the most rigid. This change in the rigidity of the above angles may possibly be explained by the fact that in ethane there are four atoms round the carbon, in ethylene three, and in acetylene only two. Regularities can, nevertheless, be observed in bending constants. Thus the X—C⟨^{H} constants in methyl fluoride, chloride, bromide, and iodide are 0.9, 0.7, 0.62, and 0.55×10^{-11}. Where both bonds are multiple, as in carbon dioxide, the bending constant is 0.75×10^{-11}. It is interesting that this is smaller than that of F—C⟨^{H} which involves only single bonds. On comparing similar bond arrangements round the same atom it is found that the bending constant of C≡C—H is 0.25 and of C≡C—C 0.35×10^{-11} dyne-cm./radian.[17]

Some of the above irregularities in bending constants certainly arise because some are obtained by using unsatisfactory force fields. The results obtained for bending constants are, because they are small relative to the stretching constants, much more dependent on the type of cross-terms that are introduced and, because of this, it is probable that many of the values obtained are unreliable. When a given type of force field is used throughout a series of molecules (e.g., the methyl halides) it is found that similar angles (e.g., HĈH angles) have a single value for their bending constants throughout the series, and also that a graded series of angles (e.g., X—C⟨^{H}) have a steadily varying value of the bending constant. This suggests that we

may hope for advances in the interpretation of the bending constants. This may be easier when more is known of the forces between non-bonded atoms.

Summary

In this report as much space has been spent on an examination of the force fields that have been employed as has been spent on the uses of the force constants obtained. Unfortunately, this represents the position. More time has been spent since 1930 in examining the merits of various force fields than in using the constants obtained for the elucidation of chemical problems. Moreover, the position today is still that, for many polyatomic molecules, we are by no means sure what sort of force field is best. It is in this direction that development must come first, and only after this can we hope to extend the chemical applications of force constants. This development will be aided by the investigation of the spectra of isotopic molecules (^{13}C, ^{15}N, etc., being used as well as deuterium) since these will provide, for any given molecular system, more measured vibration frequencies. The extension of our knowledge of force fields in molecules may then increase our understanding, not only of the valency bond, but also of the other forces that are exerted between the component atoms of a molecule.