

283. *Force Constants and Molecular Structure. Part II. Ethylene.*

By HAROLD W. THOMPSON and J. W. LINNETT.

The possibility of studying molecular structure by the determination of force constants is discussed. The principles of this method are outlined, and attention is directed to the shortcomings of some previous treatments of the subject. As a preliminary to the study of a series of related compounds containing $C=C$ and $C=O$ linkages, the relationships with ethylene are examined in detail. The assignment of the nine planar vibration frequencies is discussed and different potential functions are explored. A highly satisfactory function is discovered which has many merits and no serious defects. The force constants of this function are determined, and the precise form of the several vibrations is deduced.

The frequencies of tetradeuteroethylene are estimated.

DURING the past few years it has been established beyond doubt that in some molecules the linkages between the atoms are of a hybrid nature, showing properties intermediate between those of normal integral bonds of unperturbed structures representable by specific electronic structures. In studying theories of valency and molecular structural problems of this kind,

several properties of a link have been used as a guide to its nature. Such properties are the energy of rupture, the length, and the dipole moment. These quantities, although frequently indicating much, cannot always be used with conviction. Heats of linkage cannot always be determined accurately, and in many cases their estimation may be complicated by subsidiary processes which occur at the moment of cleavage of the molecule; in some cases, moreover, it is only the heat of formation of the entire molecule which is significant for comparative purposes. The estimation of the dipole moment of a link also sometimes involves assumptions regarding the way in which such moments are compounded within the molecule. The estimation of bond length by electron-diffraction methods, though often giving the best and most accurate value, is not always successful by virtue of the widely differing scattering powers of the different atoms.

One other property of a link—its force constant, for both stretching and bending—has the advantage over the heat of rupture in that it portrays the linkage as it actually exists, that is, uncomplicated by dissociation processes. In Part I (this vol., p. 1291), we have shown how variation of the force constants of given linkages in different molecules are closely in agreement with what would be expected on the basis of the other independent data, and it has seemed probable that a systematic examination of more cases of simple polyatomic molecules would be profitable.

Unfortunately, accurate values for the force constants of links in polyatomic molecules are not easily obtained. Early attempts to calculate them regarded the individual molecules as being composed of systems of two groups vibrating as in a diatomic system. This procedure is clearly inadequate. The method now usually employed is to obtain for the assumed molecular model relationships between the normal vibration frequencies and the masses, angles, and force constants. If the vibration frequencies are known from Raman and infra-red spectral measurements, and can be assigned to the different modes, the force constants can then as a rule be deduced. Calculations of this kind have been made by Dennison, Mecke, Lechner, Yates, Kohlrausch, Van Vleck and Cross, Howard and Wilson, Penney and Sutherland, Dennison and Sutherland, Bonner, Rosenthal, Manneback, and others (see Sutherland, *Ann. Reports*, 1936, **33**, 53—64). In Part I (*loc. cit.*) we have shown how the calculations of the force constants of the linkages in carbon suboxide justify the assumption of a hybrid structure.

In this and succeeding papers it is proposed to examine further molecules in the same manner. There are, however, several difficulties and ambiguities in the method which appear to us fundamental, though frequently ignored, and it is necessary first to discuss in some detail the general theory of the method. The difficulties can be conveniently separated into two classes: (1) those relating to the actual mathematical procedure and the assumptions involved in it, (2) those relating to the determination and assignment of the molecular frequencies.

(1) In calculating the expressions which give the frequencies in terms of the masses and force constants, it is necessary first to write down an expression for the potential energy of the vibrating model as a function of the particle displacements. This expression must be consistent with a vibration which is harmonic in character. The kinetic energy is also written down in terms of the masses and particle velocities, infinitesimally small displacements being assumed. Remembering the conditions which express no translation or rotation of the entire molecule in space, and applying Lagrange's equation, we can set up a determinantal equation, the solution of which gives the required normal vibration frequencies. This equation is in the n th power of a quantity μ such that $\nu = \sqrt{\mu}/2\pi$, n being the total number of normal vibrations. If the molecule possesses symmetry elements, and this is usually essential if the problem is to be manageable, the determinantal equation can be factorised according to the different symmetry sub-groups, and thus split into several equations each in lower powers of μ .

The main feature of this procedure is the nature of the potential function assumed, since upon this depends the self-consistency of the calculations in any given case, and consequently the magnitudes of the different force constants involved. Two types of potential function were used initially. The first, representative of what has been called simple valency force field, assumed only forces resulting from changes in bond lengths or in the

angles between the conventional chemical bonds. The second, central force field, assumed forces between pairs of atoms in a molecule regardless of whether a conventional chemical bond joined the two atoms. The use of such potential functions has been summarised by Sutherland (*loc. cit.*). Of the two types, simple valency force field seems in general preferable, but even this is not always satisfactory. This implies the necessity of introducing into the potential function "cross terms" between the different displacement co-ordinates. In any given case the number of theoretically possible cross terms may be large; many of these, however, are negligible, and only those which are at all comparable with the main terms need be considered. The choice, *a priori*, of the proper cross terms to be used may be very difficult. If, for a given molecule, the number of independent constants in the assumed potential function exceeds the number of normal frequencies, it is not possible from the experimental data alone to determine the values of the constants. Provided a sufficiently large number of constants were assumed, a potential function could always be made to reproduce the array of observed frequencies, but this would be no test of the correctness or usefulness of the particular potential function. The only satisfactory test of a given potential function is that it shall reproduce [within the appropriate limits allowed under (2)] a greater number of frequencies than the number of independent constants which the function itself contains. *A priori* we might expect the most reasonable potential function to be that which (i) approaches most nearly to simple valency force field and reproduces all the normal frequencies, (ii) involves only constants to which a precise and visualisable meaning can be attached, and (iii) involves cross terms which by the peculiar circumstances of the particular case might be expected to be the most important.

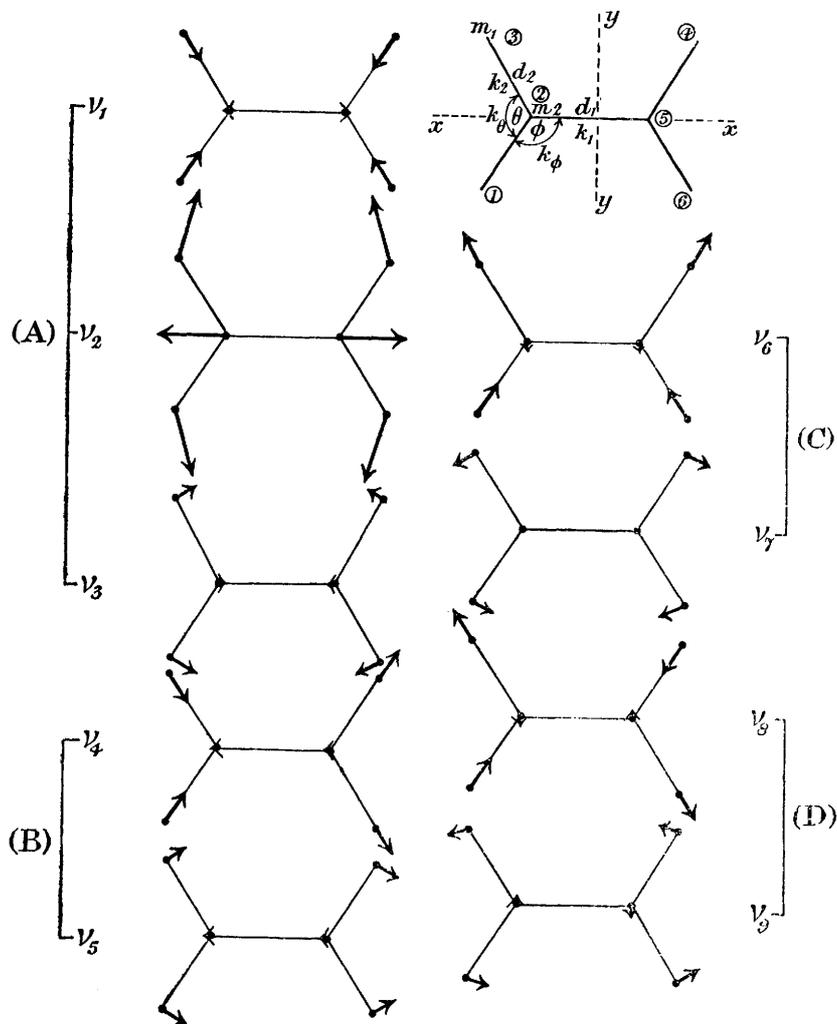
(2) In several previous papers on the present subject, attempts have been made to construct a potential function which would reproduce the observed frequencies to a degree of accuracy which seems to us meaningless. This has usually involved the introduction of a surprisingly large number of constants. Actually, the calculations refer, of course, to a harmonically vibrating model, and the frequencies determined experimentally require correction to infinitesimally small amplitude. It is not possible to predict accurately the magnitude of this correction. If a large number of combination tones can be observed in the infra-red it may occasionally be possible to estimate it. Thus for water (Bonner, *Physical Rev.*, 1934, **46**, 458) it may amount for each normal frequency to *ca.* 5%, and for hydrogen sulphide (Bailey, Thompson, and Hale, *J. Chem. Physics*, 1936, **4**, 625) to *ca.* 5%. With molecules such as carbonyl sulphide involving heavier nuclei, the error may be 1% or less (Bartunek and Barker, *Physical Rev.*, 1935, **48**, 516). Thus a potential function which reproduces the observed frequencies within these limits and has no other defects must be regarded, for the present at least, as satisfactory, and further more complicated potential functions are redundant.

The magnitudes of the observed frequencies for a given molecule may be misleading for a second reason, *viz.*, the possibility of a resonance between two close normal frequencies or a normal frequency and a close overtone level, since the resonance will lead to displacements.

In some of the cases previously studied and referred to above, it has been found impossible to obtain a completely satisfactory mathematical solution to some of the problems. The point which we wish to make from the above considerations is that from a chemical standpoint it may be better to renounce completely "idealistic" and in any case often unrealisable solutions in favour of others which, though not perfect, are nevertheless perfect within the limits of the available knowledge. This seems to us to be the only way of making satisfactory comparisons of force constants in series of related compounds, and it is just this problem which is of chemical interest. A similar view has been expressed by Barnes, Bonner, and Condon (*J. Chem. Physics*, 1936, **4**, 772).

In the present paper we discuss calculations of the molecular structure and force constants of ethylene. These will be explained in detail, since they form the basis of similar considerations on the series of molecules ethylene, allene, carbon dioxide, formaldehyde, keten, and carbon suboxide (see Part III). All these molecules are built up from what are usually regarded as C=C and C=O linkages. The case of carbon suboxide has been treated separately in Part I.

1. *The Normal Vibrations of Ethylene.*—There are nine planar normal vibrations of the ethylene molecule. The molecule can be regarded as having two planes of symmetry other than the plane of the molecule; both are perpendicular to the latter, and one contains the C-C bond (plane x/x) and the other (plane y/y) is perpendicular to this bond. The group of nine vibrations splits into four sub-groups: Class A contains three totally symmetrical oscillations (ν_1, ν_2, ν_3), *i.e.*, symmetric to both x/x and y/y . Class B contains two oscillations (ν_4, ν_5) each symmetric to the x/x plane but antisymmetric to the y/y plane. Class C



contains two oscillations (ν_6, ν_7) each symmetric to the y/y plane but antisymmetric to the x/x plane. Class D contains two oscillations (ν_8, ν_9) each antisymmetric to both the x/x and the y/y plane. The magnitudes and assignments of the frequencies have been discussed by Mecke (*Z. physikal. Chem.*, 1932, **17**, B, 1), by Sutherland and Dennison (*Proc. Roy. Soc.*, 1935, *A*, **148**, 250), by Teller and Topley (*J.*, 1935, 885), and by Bonner (*J. Amer. Chem. Soc.*, 1936, **58**, 34). The data are summarised in Table I, the last column of which gives the values which we have taken below and which seem most probable.

The three totally symmetric vibrations ν_1, ν_2, ν_3 , are intense in the Raman effect; ν_4 and ν_5 should be found as fundamentals in the infra-red; and ν_6 and ν_7 should also appear as fundamentals in the infra-red. In the case of ν_4 and ν_5 , the vibration involves a change in

the electric moment parallel to the axis of least inertia, and a marked Q -branch would be expected, whereas the vibrations ν_6 and ν_7 should give a doublet structure (\perp band). On this basis it is possible to assign the several frequencies. The remaining pair (ν_8 and ν_9) should appear in the Raman effect, though probably feebly. There seems to be general

TABLE I.

Frequency.	Mecke.	Sutherland & Dennison.	Teller & Topley.	Bonner.	
ν_1	3019	3019	3019	3019	3019
ν_2	1623	1623	1623	1623	1623
ν_3	1342	1342	1342	1342	1342
ν_4	2988	2988	2990	2988	2988
ν_5	1444	1444	1444	1444	1444
ν_6	3107		3110	3107	3107
ν_7	~1100		950?	950	950
ν_8	3240		3240	3069	(3069)
ν_9	~970		1100 or 1160?	950	?

agreement regarding the assignment of all the frequencies except ν_8 and ν_9 , although the discussion by Teller and Topley of ν_4 and ν_6 , is somewhat confused.* In the earlier Raman measurements of Dickinson, Dillon, and Rasetti (*Physical Rev.*, 1929, **34**, 582), a feeble line at 3240 cm^{-1} was assigned to ν_8 . Bonner, on the other hand, found a feeble line at 3069 and assigned this to ν_8 . It seems on the whole probable that 3069 is the more likely value. At the same time, Bonner's measurements were made with liquid ethylene, and selection rules may break down under such conditions. In Bonner's Raman measurements a line observed at 950 is attributed by him to ν_9 , but for similar reasons this might really be the frequency ν_7 . The frequency ν_9 was taken by Teller and Topley (on the basis of specific-heat data) to be 1100, 1160, or 730. Mecke gave for ν_7 and ν_9 the values 1100 and 970, with uncertain assignment. Taking $\nu_7 = 950$, we should then have $\nu_9 = 1100$. To summarise, therefore, although the assignment of the first seven frequencies seems definite, yet that of the last two is uncertain.

In attempting to calculate the force constants of the linkages, Sutherland and Dennison considered only the "parallel" frequencies $\nu_1, \nu_2, \nu_3, \nu_4, \nu_5$. By means of a special type of potential function they were able to reproduce these frequencies fairly well, but they did not deal with the remaining vibrations. They deduced the relationship and adjusted the

$$\nu_4^2 + \nu_5^2 + \frac{m_2 + 2m_1}{m_2} \cdot \frac{\nu_1^2 \nu_2^2 \nu_3^2}{\nu_4^2 \nu_5^2} = \nu_1^2 + \nu_2^2 + \nu_3^2 \quad \dots \quad (I)$$

observed frequencies slightly so as to fit this equation, on the assumption that the relationship provided a satisfactory proof of the applicability of the particular potential function. This is, however, not satisfactory, since a simple valency force field system (or any field which regards the CH_2 groups as non-interacting units) will provide the above relationship.

Bonner employed a more complicated potential function involving six constants (for planar vibrations) and attempted to determine the values of the constants for each class of vibrations. There are several serious weaknesses in his treatment. First, the cubic equation which he obtained for the frequencies ν_1, ν_2, ν_3 gives imaginary roots for the constants. Bonner attributes this to approximations in the potential function and adopted values for the constants which most nearly fitted the equation. Further, there are other small inconsistencies in the values of the constants obtained for the remaining pairs of frequencies. Finally, Bonner used for ethylene the structure previously suggested by

Badger, *viz.*, $\theta = 126^\circ$ ($\widehat{\text{HCH}}$) $d_{\text{CH}} = 1.04 \times 10^{-8}$, and $d_{\text{CC}} = 1.37 \times 10^{-8}$ cm. It now appears that more accurate values are $\theta = 118^\circ$, $d_{\text{CH}} = 1.08 \times 10^{-8}$, and $d_{\text{CC}} = 1.33 \times 10^{-8}$ (see Penney, *Proc. Roy. Soc.*, 1937, *A*, **158**, 306).

2. *Calculation of the Force Constants.*—It is profitable first to consider the application to the case of ethylene of simple valency force field. If we take the masses of the hydrogen

* These authors argue from the contour of the infra-red band that $\nu_4 = 3110$ and $\nu_8 = 2990$, but in their subsequent calculations they employ the converse assignment.

atoms to be m_1 , of carbon atoms m_2 , and the angles $\widehat{\text{HCH}}$ and $\widehat{\text{HCC}}$ to be θ and ϕ , and the other magnitudes as in the figure, the potential function is

$$2V = 4k_2\Delta_{12}^2 + k_1\Delta_{25}^2 + 4k_\phi\Delta\phi^2 + 2k_\theta\Delta\theta^2$$

k_1 and k_2 are the stretching constants of the C-C and C-H bonds, and k_θ and k_ϕ of the respective angles. Using the general method and remembering that for class A $\Delta\theta = -2\Delta\phi$, for class B $\Delta_{25} = 0$ and $\Delta\theta = -2\Delta\phi$, for classes C and D $\Delta_{25} = 0$ and $\Delta\theta = 0$, we then find,

$$\text{A.} \quad \nu_1^2 + \nu_2^2 + \nu_3^2 = k_2P + k_1R + \frac{(2k_\theta + k_\phi)}{d_2^2}Q \quad \dots \quad (\text{i})$$

$$\nu_1^2\nu_2^2 + \nu_2^2\nu_3^2 + \nu_3^2\nu_1^2 = k_1k_2 \cdot \frac{R}{m_1} + \frac{k_1(2k_\theta + k_\phi)}{d_2^2} \cdot \frac{R}{m_1} + \frac{k_2(2k_\theta + k_\phi)}{d_2^2}S \quad \dots \quad (\text{ii})$$

$$\nu_1^2\nu_2^2\nu_3^2 = \frac{k_1k_2(2k_\theta + k_\phi)}{d_2^2} \frac{R}{m_1^2} \quad \dots \quad (\text{iii})$$

$$\text{B.} \quad \nu_4^2 + \nu_5^2 = k_2P + \frac{(2k_\theta + k_\phi)}{d_2^2}Q \quad \dots \quad (\text{i})$$

$$\nu_4^2\nu_5^2 = \frac{k_2(2k_\theta + k_\phi)}{d_2^2}S \quad \dots \quad (\text{ii})$$

$$\text{C.} \quad \nu_6^2 + \nu_7^2 = k_2Q + (k_\phi/d_2^2)P \quad \dots \quad (\text{i})$$

$$\nu_6^2\nu_7^2 = (k_2k_\phi/d_2^2)S \quad \dots \quad (\text{ii})$$

$$\text{D.} \quad \nu_8^2 + \nu_9^2 = k_2Q + (k_\phi/d_1^2)4R + (k_\phi/d_2^2)P + (k_\phi/d_1d_2)T \quad \dots \quad (\text{i})$$

$$\nu_8^2\nu_9^2 = \frac{k_2k_\phi}{d_1^2} \cdot \frac{4R}{m_1} + \frac{k_2k_\phi}{d_2^2}S + \frac{k_2k_\phi}{d_1d_2} \cdot \frac{T}{m_1} \quad \dots \quad (\text{ii})$$

in which $P = \{1/m_1 + 2 \cos^2 \frac{1}{2}\theta/m_2\}$, $Q = \{1/m_1 + 2 \sin^2 \frac{1}{2}\theta/m_2\}$, $R = 2/m_2$,
 $S = \{(1/m_1)(1/m_1 + 2/m_2)\}$, $T = 8 \cos \frac{1}{2}\theta/m_2$.

Substituting in B (i) and B (ii) the values $\nu_4 = 2988$ and $\nu_5 = 1444$, we find $k_2 = 5.0 \times 10^5$ or 1.18×10^5 dynes/cm. The latter value is clearly impossible and, taking the former, we find $(2k_\theta + k_\phi) = 1.28 \times 10^{-11}$ dyne cm. per radian. Substituting these values in A (i), we find $k_1 = 8.95 \times 10^5$, and in A (ii), $k_1 = 9.53 \times 10^5$. Thus there is some inconsistency in the equations of groups A and B and this also extends to classes C and D. Taking mean values of the constants, however, *viz.*, $k_1 = 9.0 \times 10^5$, $k_2 = 5.0 \times 10^5$, $(2k_\theta + k_\phi) = 1.28 \times 10^{-11}$, $k_\phi = 0.60 \times 10^{-11}$, $k_\theta = 0.34 \times 10^{-11}$, and $\theta = 118^\circ$, $d_1 = 1.33$, $d_2 = 1.08 \times 10^{-8}$, we calculate the frequencies given in Table II.

TABLE II.

Frequency.	Obs.	Calc.	Diff.	Frequency.	Obs.	Calc.	Diff.
ν_1	3019	3014	- 5	ν_6	3107	3095	-12
ν_2	1623	1723	+100	ν_7	950	955	+ 5
ν_3	1342	1230	-112	ν_8	(3069)	3108	+39
ν_4	2988	2986	- 2	ν_9	950 or 1160?	1206	?
ν_5	1444	1445	+ 1				

In view of the uncertainty in the values for ν_8 and ν_9 , and the simplicity of the potential function assumed, the other frequencies are strikingly well reproduced with the exception of ν_2 and ν_3 . This result indicates that the force field involved is not far removed from that of simple valency force system. This result might have been shown equally well by inserting into the relationship (I) above, the values of the observed frequencies. As already explained, this relationship can be deduced from the potential function of simple valency force field.

It is natural to examine the possible causes of the discrepancy in the values of ν_2 and ν_3 .

Presumably it implies the necessity of introducing into the potential function one or more cross terms, and we are led to enquire which of the many possible of such terms are most likely to be concerned. We may proceed in one of two ways. (a) We may set up generalised potential functions of different kinds, using a large number of constants, not all of which have a precise and direct significance, and find that function, and the values of its constants, which most satisfactorily reproduces the entire set of frequencies. The disadvantages of this method have been referred to in the introduction. (b) We may add to the potential function of simple valency force field only such cross terms as appear to be important from the peculiar nature of the specific problem. This seems to us preferable.

The frequencies ν_2 and ν_3 are found experimentally to be roughly equal in magnitude. Now it is known from a series of examples that the deformation of a methylene radical results in a frequency of *ca.* 1400, and the extension of a C=C bond in one of *ca.* 1600. It would not therefore be surprising if, in the case of ethylene which contains both these structural units, excitation of one oscillation were inevitably to a great extent accompanied by excitation of the other. This means that a change in d_1 is likely to occur simultaneously with a change in θ . We have therefore examined the effect of introducing into the simple function a cross term representing this effect. We write

$$2V = k_1\Delta_{25}^2 + 4k_2\Delta_{12}^2 + 2k_\theta\Delta\theta^2 + 4k_\phi\Delta\phi^2 + 2k_3\Delta_{25}\Delta\theta$$

The three totally symmetric frequencies are then given by :

$$A. \quad \nu_1^2 + \nu_2^2 + \nu_3^2 = k_2P + k_1R + \frac{(2k_\theta + k_\phi)}{d_2^2}Q - \frac{k_3}{d_2}W \quad \dots \quad (iv)$$

$$\nu_1^2\nu_2^2 + \nu_2^2\nu_3^2 + \nu_1^2\nu_3^2 = k_1k_2\frac{R}{m_1} + \frac{k_1(2k_\theta + k_\phi)}{d_2^2} \cdot \frac{R}{m_1} + \frac{k_2(2k_\theta + k_\phi)}{d_2^2}S - \frac{k_2k_3}{d_2} \cdot \frac{W}{m_1} - \frac{k_3^2}{d_2^2} \cdot \frac{R}{m_1} \quad \dots \quad (v)$$

$$\nu_1^2\nu_2^2\nu_3^2 = \frac{k_1k_2(2k_\theta + k_\phi)}{d_2^2} \cdot \frac{R}{m_1^2} - \frac{k_2k_3^2}{d_2^2} \cdot \frac{R}{m_1^2} \quad \dots \quad (vi)$$

in which P , Q , R , and S are as before, and $W = 4 \sin \frac{1}{2}\theta/m_2$. The equations for the remaining frequencies of all types are as already given, since in all cases $\Delta_{25} = 0$. Examination of the data shows that the values of the constants which are most overall consistent are $k_1 = 9.8 \times 10^5$, $k_2 = 5.02 \times 10^5$, $k_\theta = 0.342 \times 10^{-11}$, $k_\phi = 0.594 \times 10^{-11}$, and $k_3 = 0.637 \times 10^{-3}$. The values of the frequencies then calculated are shown in Table III.

TABLE III.

Frequency.	Obs.	Calc.	Diff.	Frequency.	Obs.	Calc.	Diff.
ν_1	3019	3018	-1	ν_6	3107	3101	-6
ν_2	1623	1623	0	ν_7	950	950	0
ν_3	1342	1343	+1	ν_8	(3069)	3114	?
ν_4	2988	2993	+5	ν_9	950 or 1160?	1203	?
ν_5	1444	1444	0				

4. *Discussion of the Above Results.*—The agreement found on using the new potential function is remarkable, and since the values calculated are being compared with the observed values (uncorrected for anharmonicity) it is perhaps even accidental. There is, however, no doubt that the treatment given is essentially sound, and some of its merits over those previously attained can be summarised as follows :

(i) The potential function using five independent constants reproduces very closely all seven well-established frequencies, *i.e.*, it is valid for more frequencies than the number of constants it contains.

(ii) All the constants used in the potential function have an exact and obvious physical meaning, and reasons for the relative importance of the only cross term employed can be understood. Further, the magnitude of the cross-term force constant is small compared with those of the principal constants.

(iii) In contrast with the method of Sutherland and Dennison, the present treatment deals not only with the "parallel" vibrations, but also with the perpendicular vibrations.

(iv) The cubic giving ν_1 , ν_2 , and ν_3 has real roots for the force constants and is thus preferable to that of Bonner.

(v) The type of potential function used can be at once carried over to the case of allene, for which, the same values being taken for the constants, the frequencies of the molecule are reproduced. This is perhaps the greatest success of the entire method, and is explained in Part III.

The only obvious defect of the method and results concerns ν_8 and ν_9 . If $\nu_8 = 3069$, the calculated value (3114), though not close, is not seriously in error. The calculated value of ν_9 is 1203. This at once suggests that the observed frequency estimated by Teller and Topley as *ca.* 1160, should be assigned to ν_9 . After examining all the evidence, we regard this as probable. A small error in the calculated values of ν_8 and ν_9 might be removed by the insertion of a second small cross term, perhaps of the type $k_4\Delta_{12}\Delta_{23}$.

5. *The Form of the Ethylene Vibrations.*—By using the above method and results, the relative amplitudes of the atomic nuclei in each of the vibrations have been calculated. The results are given in Table IV, and in the figure the vibrations are drawn in accordance with them.

TABLE IV.

	Symmetry class.	Frequency.	x_1 .	y_1 .	x_2 .	y_2 .
A.	$\left\{ \begin{array}{l} x_1 = x_3 = -x_4 = -x_6 \\ y_1 = -y_3 = -y_4 = y_6 \\ x_2 = -x_5 \\ y_2 = y_5 = 0 \end{array} \right\}$	ν_1	+1.0	+1.63	-0.24	0
		ν_2	+1.0	-3.62	-3.48	0
		ν_3	+1.0	-0.51	+0.12	0
B.	$\left\{ \begin{array}{l} x_1 = x_3 = x_4 = x_6 \\ y_1 = -y_3 = y_4 = -y_6 \\ x_2 = x_5 \\ y_2 = y_5 = 0 \end{array} \right\}$	ν_4	+1.0	+1.59	-0.17	0
		ν_5	+1.0	-0.73	-0.17	0
C.	$\left\{ \begin{array}{l} x_1 = -x_3 = x_4 = -x_6 \\ y_1 = y_3 = y_4 = y_6 \\ x_2 = x_5 = 0 \\ y_2 = y_5 \end{array} \right\}$	ν_6	+1.0	+1.69	0	-0.28
		ν_7	+1.0	-0.51	0	+0.085
D.	$\left\{ \begin{array}{l} y_1 = y_3 = -y_4 = -y_6 \\ x_1 = -x_3 = -x_4 = x_6 \\ x_2 = x_5 = 0 \\ y_2 = -y_5 \end{array} \right\}$	ν_8	+1.0	+1.79	0	-0.32
		ν_9	+1.0	-0.23	0	+0.305

Using these values of the relative amplitudes, we can now calculate the percentage of the energy of each particular vibrational quantum which is associated with each term of the potential function. An interesting result is found with the three totally symmetric vibrations ν_1 , ν_2 , ν_3 . Whereas with the vibration $\nu_1 = 3018$ over 95% of the energy is located in the $k_2\Delta_{12}^2$ term, *i.e.*, in the C-H bond, in the case of $\nu_2 = 1623$ and $\nu_3 = 1343$, the localisation of the energy into one particular term, though noticeable, is less pronounced. For the 1623 vibration, there is still a preponderance of energy (*ca.* 80%) in the term corresponding to the stretching of the C=C bond, and similarly for the 1343 vibration in the term corresponding to the deformation of the CH₂ group. It is nevertheless seen that with ν_2 and ν_3 the individuality of the vibration is less definite. This is significant in the light of the previous discussion of the cross term.

6. *The Frequencies of Tetradeuteroethylene.*—The success of the above treatment appears to justify a calculation of the nine planar frequencies of tetradeuteroethylene. In this case, however, the heavier deuterium atoms lead to a decrease in the deformation frequency of the CH₂ group, whereas that of the C=C bond is unaffected. Thus, it may be that the interaction previously referred to is less prominent, *i.e.*, k_3 is smaller than in the case of ethylene. In Table V are given (i) the frequencies calculated on simple valency force field with $k_3 = 0$, $k_1 = 9.8 \times 10^5$, $k_2 = 5.02 \times 10^5$, $k_\theta = 0.342 \times 10^{-11}$, $k_\phi = 0.594 \times 10^{-11}$; (ii) the frequencies calculated with $k_3 = 0.637 \times 10^{-3}$, and (iii) the values suggested recently by Manneback and Verleysen (*Nature*, 1936, **138**, 367).

The values to be expected should then lie between the limits given by (i) and (ii). It is

TABLE V.

Frequency.	(i).	(ii).	(iii).	Frequency.	(i).	(ii).	(iii).
ν_1	2166	2160	2283.9	ν_6	2291	2291	2308.0
ν_2	1780	1686	1428.8	ν_7	742	742	758.3
ν_3	866	902	1008.9	ν_8	2323	2323	2325.0
ν_4	2101	2101	2152.5	ν_9	1016	1016	678.1
ν_5	1187	1187	1072.8				

seen that these values differ noticeably from those given by Manneback and Verleysen. It would be valuable to have experimental data on this point. In any case, however, we cannot attach any importance to the accuracy attempted by Manneback and Verleysen.

THE OLD CHEMISTRY DEPARTMENT,
UNIVERSITY MUSEUM, OXFORD.

[Received, June 1st, 1937.]