

284. *Force Constants and Molecular Structure. Part III.*
Molecules containing C=O and C=C Linkages.

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The force constants of the linkages and angles in a series of molecules each built up from C-H, C-O, and C-C bonds are calculated from the known vibration frequencies. The form of the potential-energy function applicable in each case is discussed in detail. The molecules studied include ethylene, allene, formaldehyde, keten, carbon dioxide, and carbon suboxide. The results are correlated with structural properties such as the phenomenon of resonance (mesomerism) and with electronic drifts. The geometric form of the different vibrations is deduced. The relationship between force constant and bond length is discussed.

IN Part II (preceding paper) the significance of a knowledge of force constants in determining molecular structure was discussed. The general methods for the determination of the force constants of individual linkages in polyatomic molecules were outlined, and attention was drawn to various ambiguities in previous papers on this subject. In the present paper, the force constants of the linkages in a series of molecules containing bonds conventionally regarded as C-H, C=C, and C=O are calculated from the known molecular vibration frequencies. These molecules are carbon dioxide, ethylene, formaldehyde, allene, keten, and carbon suboxide. The discussion of such a series of molecules has the advantage that the particular type of molecular model must be retained essentially throughout the series. In this way any marked alteration of the force constant of a given linkage in different compounds will be most easily detectable.

The case of carbon suboxide has already been discussed in Part I (this vol., p. 1291), and that of ethylene in Part II (*loc. cit.*), and in these cases the mathematical method was explained in some detail. For this reason it is necessary here only to summarise the essential results of the calculations. It will be convenient first to discuss each molecule individually, and later to consider all the resulting data together.

1. *Ethylene.*—Suppose the masses of the hydrogen atoms are m_1 , of the carbon m_2 , and the angles \widehat{HCH} and \widehat{HCC} are θ and ϕ . By assuming a potential function of the form

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

it was possible to interpret very well all the nine planar frequencies. In this expression k_1 represents the stretching constant of the carbon-carbon bond, k_2 that of the carbon-hydrogen bond, and k_θ and k_ϕ the bending constants of the appropriate angles; k_3 could be imagined as arising from the interaction of the carbon-carbon bond with the \widehat{HCH} angle, since the frequency of the vibration largely determined by a stretching of the C-C bond is roughly equal in magnitude to that frequency which is largely determined by a change in the angle θ .

The values of the five constants in the above potential function which most adequately reproduce the molecular vibration frequencies are $k_1 = 9.8 \times 10^5$, $k_2 = 5.02 \times 10^5$, $k_3 = 0.637 \times 10^{-3}$, $k_\theta = 0.342 \times 10^{-11}$, $k_\phi = 0.594 \times 10^{-11}$.

2. *Allene*.—Suppose that the masses of the atoms are as above, and the other magnitudes as in Fig. 1. No measurements are recorded on the link lengths and angles of this molecule, which are therefore assumed to be the same as the corresponding ones of ethylene. There are 11 planar normal vibrations of this molecule, three of which are totally symmetric. Experimental determination of the frequencies has been carried out by Bourguel and Piaux (*Bull. Soc. chim.*, 1932, 51, 1041), and by Kopper and Pongratz (*Wien. Ber.*, 1932, 141, 11b, 840), both investigations dealing with the Raman spectrum. The frequencies found by the former authors were 1073 (strong), 1438 (medium), 3000 (strong), and 3072 (medium), and by the latter authors 1074 (strong), 1435 (medium), 2995 (strong), and 3060 (medium). The infra-red spectrum does not appear to have been measured. The three totally symmetrical oscillations will be most intense in the Raman spectrum and may therefore be taken as 1074, 1436, and 2997. For our present purpose we shall deal only with these frequencies; it may be profitable later to discuss the remaining types.

Kopper and Pongratz, regarding the molecules as a triatomic system $H_2C-C-CH_2$, estimated the carbon-carbon force constant. This procedure is obviously unsatisfactory.

The potential function of simple valency force field being assumed, *i.e.*,

$$2V = 4k_2\Delta_{12}^2 + 2k_1\Delta_{27}^2 + 2k_\theta\Delta\theta^2 + 4k_\phi\Delta\phi^2$$

the resulting equations for the three totally symmetric frequencies involve three independent constants k_2 , k_1 , and $(2k_\theta + k_\phi)$. If the three frequencies have the values given above, no set of values for the three constants will give an adequate agreement. The discrepancies are precisely parallel in nature to those found in the application of simple valency force field to ethylene. If we insert into the equations for allene the values for the C-H bond constant previously found for ethylene, and attempt to calculate for allene k_1 and $(2k_\theta + k_\phi)$, no real values are obtained.

This means that "cross terms" must be introduced into the potential function, and the one which at once suggested itself was that found to be so relevant with ethylene, *viz.*, $k_3\Delta_{CC}\Delta\theta$. In allene, however, it is not impossible that we ought also to introduce a second cross term of the form $k_4\Delta_{27}\Delta_{75}$, arising from an interaction between the two C-C bonds. Such a cross term has been found to be important in the case of carbon dioxide. The potential function can then be written:

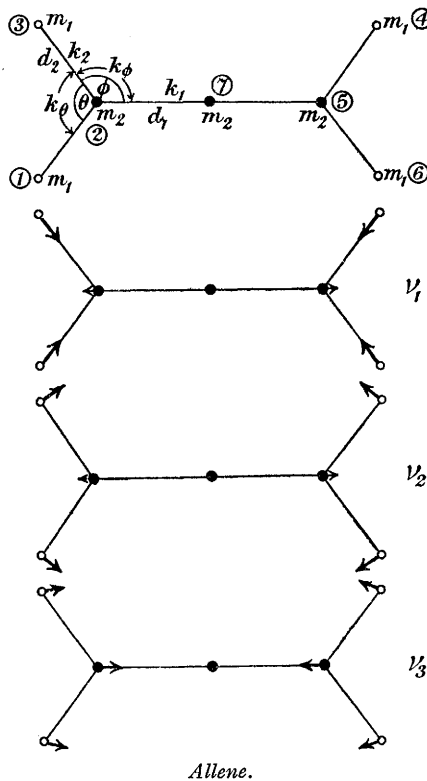
$$2V = 2k_1\Delta_{27}^2 + 4k_2\Delta_{12}^2 + 2k_\theta\Delta\theta^2 + 4k_\phi\Delta\phi^2 + 2k_3\Delta_{27}\Delta\theta + k_4\Delta_{27}\Delta_{75}$$

The equations for the frequencies are then found to be:

$$\nu_1^2 + \nu_2^2 + \nu_3^2 = (k_1 + \frac{1}{2}k_4)[A] + k_2[B] + \frac{(2k_\theta + k_\phi)}{d_2^2}[C] - \frac{k_3}{d_2^2}[D] \quad (1)$$

$$\begin{aligned} \nu_1^2\nu_2^2 + \nu_2^2\nu_3^2 + \nu_3^2\nu_1^2 = & (k_1 + \frac{1}{2}k_4)k_2 \left[\frac{A}{m_1} \right] + (k_1 + \frac{1}{2}k_4) \frac{(2k_\theta + k_\phi)}{d_2^2} \left[\frac{A}{m_1} \right] + \\ & k_2 \frac{(2k_\theta + k_\phi)}{d_2^2} [E] - k_2 \frac{k_3}{d_2^2} \left[\frac{D}{m_1} \right] - \frac{k_3^2}{d_2^2} \left[\frac{A}{2m_1} \right] \quad (2) \end{aligned}$$

FIG. 1.



Allene.

$$\nu_1^2 \nu_2^2 \nu_3^2 = k_2(k_1 + \frac{1}{2}k_4) \frac{(2k_\theta + k_\phi)}{d_2^2} \left[\frac{A}{m_1^2} \right] - \frac{k_2 k_3^2}{d_2^2} \left[\frac{A}{2m_1^2} \right] \quad (3)$$

in which $A = 1/m_2$, $B = 1/m_1 + 2 \cos^2 \frac{1}{2} \theta / m_2$, $C = 1/m_1 + 2 \sin^2 \frac{1}{2} \theta / m_2$, $D = 2 \sin \frac{1}{2} \theta / m_2$, $E = (1/m_1 + 2/m_2)/m_1$.

The above equations involve only four constants, since k_1 and k_4 always occur as a sum ($k_1 + \frac{1}{2}k_4$), and k_θ and k_ϕ as the sum ($2k_\theta + k_\phi$). These four independent constants have to reproduce the values of three frequencies, and from the values of the three frequencies given above alone it would of course be impossible to calculate the constants. There is here, however, no case of the type to which we have drawn attention in the previous paper, *i.e.*, a potential function involving more constants than the number of frequencies. Actually, in order to calculate all the 11 planar vibration frequencies, using a potential function of the present form, we should require values for seven constants k_1 , k_2 , k_θ , k_ϕ , k_3 , k_4 , and a bending constant of the C-C-C angle. We are not at present concerned with vibrations other than the three totally symmetric ones.

The value of the present procedure is as follows. We should expect to be able to use the force constants derived for ethylene in the case of allene. Taking $k_1 = 9.8 \times 10^5$, $k_2 = 5.02 \times 10^5$, $(2k_\theta + k_\phi) = 1.279 \times 10^{11}$, and $k_3 = 0.637 \times 10^{-3}$, and assuming first that $k_4 = 0$, we find values for the frequencies ν_1 , ν_2 , and ν_3 , of 3003, 1459, and 1069. The errors are +6, +23, -5. This agreement is very striking. It is possible that the discrepancies arise from anharmonic properties, but if it is desired to obtain exact agreement, this can be achieved by taking for the constant $(k_1 + \frac{1}{2}k_4) = 9.73 \times 10^5$, $k_2 = 5.0 \times 10^5$, $(2k_\theta + k_\phi) = 1.273 \times 10^{11}$, and $k_3 = 0.821 \times 10^{-3}$. The values of the frequencies then found are 2997, 1436, and 1073. Kohlrausch, regarding the molecule as a triatomic system, gives for k_1 a value 9.5×10^5 .

Two points are thus established: (i) The value of k_4 is probably zero. The calculated value of $(k_1 + \frac{1}{2}k_4)$ is so close to that of k_1 in ethylene as to suggest that there is no detectable alteration in passing from one compound to the other. If the change is assumed to be real and k_1 to be 9.8×10^5 , k_4 would have a value -0.14×10^5 . In any case it is unlikely that k_4 can be very appreciable, since the above deduced value of $(k_1 + \frac{1}{2}k_4)$ could then only result from an almost exactly compensating change in k_1 . *A priori*, such an exact balancing is unlikely. (ii) It is obvious that in passing from ethylene to allene, k_1 , k_2 , and $(2k_\theta + k_\phi)$ remain almost unchanged. The change in k_3 is very reasonable and not unexpected from the nature of the effect with which this constant deals.

The values of the constants deduced above for allene being used, the relative atomic displacements of each of the three totally symmetrical vibrations are given in Table I, and the vibrations are seen in Fig. 1.

TABLE I.

Totally symmetric.	Frequency.	x_1 .	y_1 .	x_2 .
$x_1 = x_3 = -x_4 = -x_6$	$\left\{ \begin{array}{l} 2997 (\nu_1) \\ 1436 (\nu_2) \\ 1073 (\nu_3) \end{array} \right.$	+1.0	+1.614	-0.195
$y_1 = -y_3 = -y_4 = y_6$		+1.0	-0.82	-0.274
$y_2 = y_5 = 0$		+1.0	-0.12	+0.69
$x_2 = -x_5$				
$x_7 = y_7 = 0$				

If we now calculate the energy corresponding to each of the terms in the potential function, it is found that for the 2997 vibration over 98% of the energy is associated with the term representing the change in length of the C-H bond; with the 1436 vibration, however, this isolation of the energy into one term of the potential function is less marked, and although primarily associated with the deformation of the methylene group, some of the energy passes into the term representing change in the length of the carbon-carbon bond; for the 1073 vibration there is again some partitioning of the energy between the same terms as for the 1436 vibration, but the bulk of the energy is in this case in the carbon-carbon stretching term. This result seems worthy of mention, since, although it is not surprising that the methylene group deformation frequency remains as in ethylene (*ca.* 1400), we might have expected the vibration of the C-C link to have the higher of the pair of values.

3. *Keten*.—The masses of the hydrogen and carbon atoms being as before, let that of oxygen be m_3 and the other magnitudes as in Fig. 2. No experimental data are available regarding the precise form of the molecule, and we shall assume as for ethylene $\theta = 118^\circ$, $d_2 = 1.08$ A. There are good reasons for believing these values to be close to the real ones.

The molecule has two symmetry elements, one the plane of the molecule, and the other a two-fold rotation axis containing the atoms 2, 4, 5. There are nine normal vibrations, seven of which are planar, and of the planar group four ($\nu_1, \nu_2, \nu_3, \nu_4$) are symmetrical, and three (ν_5, ν_6, ν_7) antisymmetrical to this rotation axis.

The only experimental measurements of the frequencies have been made by Kopper (*Z. physikal. Chem.*, 1936, **34**, B, 396). From his data on the Raman effect it seems certain that ν_1, ν_2, ν_3 , and ν_4 have the values 2952, 2049, 1344, and 1130; ν_1, ν_3 , and ν_4 appear intense in the Raman effect, and although ν_2 is relatively feeble, it is the only frequency in the region of 2000, where it is certain that the frequency determined largely by a vibration of the C–O bond must lie. This assignment agrees with that suggested by Kopper. The assignment of the antisymmetric vibrations is not possible, and infra-red data are desirable.

As with ethylene and allene, the simple valency force field system is inadequate, and we have at once applied a potential function of the following form :

$$2V = k_1\Delta_{24}^2 + 2k_2\Delta_{12}^2 + k_3\Delta_{45}^2 + k_0\Delta\theta^2 + 2k_\phi\Delta\phi^2 + k_4\Delta_{24}\Delta\theta + k_5\Delta_{24}\Delta_{45}$$

In this function k_1, k_2, k_3 represent the force constants for the stretching of the C–C, C–H, and C–O bonds, and k_0 and k_ϕ the bending constants of the angles θ and ϕ ; k_4 represents the cross-term interaction constant found to be so serviceable in the cases of ethylene and allene. The only addition is k_5 , which introduces a cross term to represent interaction between the C–C and C–O bonds. This is to be expected on the same general grounds as the cross term involving k_4 .

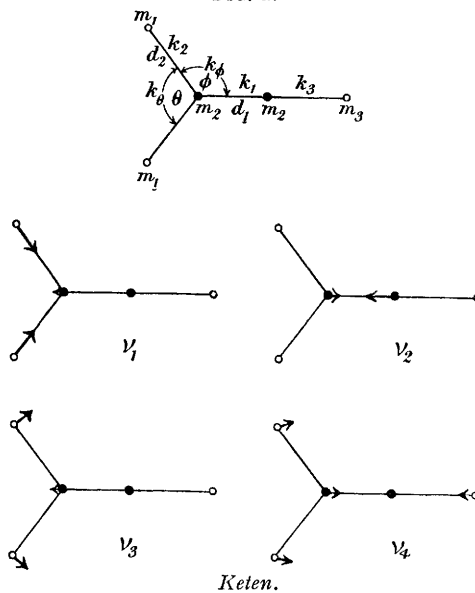
Using the above potential function, we obtain :

$$\nu_1^2 + \nu_2^2 + \nu_3^2 + \nu_4^2 = k_1[A] + k_2[B] + k_3[C] + \frac{2k_\theta + k_\phi}{d_2^2}[D] - k_5\left[\frac{A}{2}\right] - \frac{k_4}{d_2}[E] \quad (1)$$

$$\begin{aligned} \nu_1^2\nu_2^2 + \nu_2^2\nu_3^2 + \nu_3^2\nu_4^2 + \nu_1^2\nu_3^2 + \nu_1^2\nu_4^2 + \nu_2^2\nu_4^2 &= k_1k_3[F] + k_2k_3[BC] + \frac{k_3(2k_\theta + k_\phi)}{d_2^2}[DC] + \\ k_1k_2[G] + \frac{k_1(2k_\theta + k_\phi)}{d_2^2}[H] + \frac{k_2(2k_\theta + k_\phi)}{d_2^2}[J] - \frac{k_3k_4}{d_2}[CE] - \frac{k_2k_4}{d_2}\left[\frac{E}{m_1}\right] - \frac{1}{2}\cdot\frac{k_4^2}{d_2^2}[H] - \\ k_2k_5\left[\frac{B}{m_2}\right] - \frac{k_5(2k_\theta + k_\phi)}{d_2^2}\left[\frac{D}{m_2}\right] - k_5^2\left[\frac{F}{4}\right] + \frac{k_5k_4}{d^2}\left[\frac{E}{2m_2}\right] \quad (2) \end{aligned}$$

$$\begin{aligned} \nu_1^2\nu_2^2\nu_3^2 + \nu_1^2\nu_2^2\nu_4^2 + \nu_2^2\nu_3^2\nu_4^2 + \nu_1^2\nu_3^2\nu_4^2 &= k_1k_2k_3\left[\frac{C}{m_1m_2} + \frac{B}{m_2m_3}\right] + \\ \frac{k_1k_3(2k_\theta + k_\phi)}{d_2^2}\left[\frac{C}{m_1m_2} + \frac{D}{m_2m_3}\right] + \frac{k_2k_3(2k_\theta + k_\phi)}{d_2^2}[JC] + \frac{k_1k_2(2k_\theta + k_\phi)}{d_2^2}[K] - \frac{k_2k_3k_4}{d_2}\left[\frac{EC}{m_1}\right] - \\ \frac{k_3k_4^2}{2d_2^2}\left[\frac{C}{m_1m_2} + \frac{D}{m_2m_3}\right] - \frac{k_2k_4^2}{d_2^2}\left[\frac{K}{2}\right] - \frac{k_2k_5(2k_\theta + k_\phi)}{d_2^2}\left[\frac{J}{m_2}\right] - \frac{1}{4}k_2k_5^2\left[\frac{C}{m_1m_2} + \frac{B}{m_2m_3}\right] - \\ \frac{k_5^2(2k_\theta + k_\phi)}{4d_2^2}\left[\frac{C}{m_1m_2} + \frac{D}{m_2m_3}\right] + \frac{k_2k_5k_4}{d_2}\left[\frac{E}{2m_1m_2}\right] \quad (3) \end{aligned}$$

FIG. 2.



Keten.

$$\nu_1^2 \nu_2^2 \nu_3^2 \nu_4^2 = \left\{ \frac{k_1 k_2 k_3 (2k_\theta + k_\phi)}{d_2^2} - \frac{1}{4} \cdot \frac{k_2 k_5^2 (2k_\theta + k_\phi)}{d_2^2} - \frac{1}{2} \frac{k_2 k_3 k_4^2}{d_2^2} \right\} \{L\} \quad (4)$$

in which: $A = 2/m_2$, $B = 1/m_1 + 2 \cos^2 \frac{1}{2} \theta / m_2$, $C = 1/m_2 + 1/m_3$, $D = 1/m_1 + 2 \sin^2 \frac{1}{2} \theta / m_2$, $E = 2 \sin^2 \frac{1}{2} \theta / m_2$, $F = 1/m_3^2 + 2/m_2 m_3$, $G = 2/m_1 m_2 + 2 \cos^2 \frac{1}{2} \theta / m_2^2$, $H = 2/m_1 m_2 + 2 \sin^2 \frac{1}{2} \theta / m_2^2$, $J = 1/m_1^2 + 2/m_1 m_3$, $K = 2/m_1 m_2^2 + 2/m_1^2 m_2$, $L = (2m_1 + 2m_2 + m_3)/m_1^2 m_2^2 m_3$.

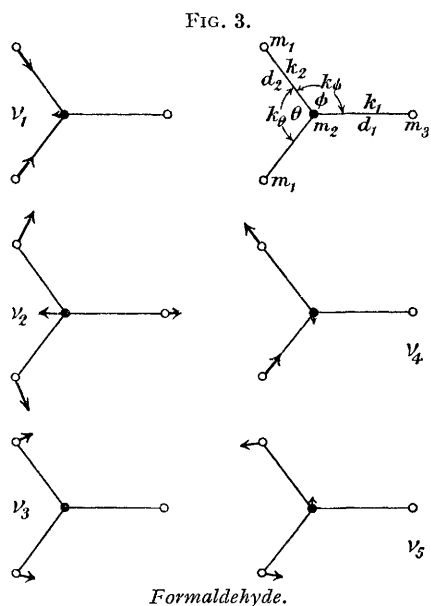
We thus have four frequencies and six independent constants. Were it not for the guidance provided by the considerations with ethylene and allene, the problem would be insoluble. We can, however, see that the value of k_2 determines ν_1 , and hardly affects the values of the remaining frequencies. The value of k_2 which is most suitable is 4.85×10^5 . The results with ethylene and allene suggest that suitable values for k_1 and k_4 are 9.8×10^5 and 0.8×10^{-3} . Taking these values, we then find $k_3 = 12.3 \times 10^5$, $(2k_\theta + k_\phi) = 1.12 \times 10^{-11}$, $k_5 = 1.0 \times 10^5$. Small errors in the values assumed for k_1 and k_4 do not at all seriously affect the deduced values for the other three constants, and the success of the method lies, as will be seen, in the remarkable self-consistency of all the results subsequently obtained. With the values $k_2 = 4.85 \times 10^5$, $k_1 = 9.8 \times 10^5$, $k_3 = 12.3 \times 10^5$, $(2k_\theta + k_\phi) = 1.12 \times 10^{-11}$, $k_4 = 0.8 \times 10^{-3}$ and $k_5 = 1.0 \times 10^5$, the calculated frequencies are $\nu_1 = 2954$, $\nu_2 = 2048$, $\nu_3 = 1349$, $\nu_4 = 1123$, the errors being +2, -1, +5, and -7.

The relative amplitudes of the masses in the several vibrations can now be evaluated as in the previous cases. The values are given in Table II. In Fig. 2 the vibrations

TABLE II.

Symmetric.	Frequency.	x_1 .	y_1 .	x_2 .	x_4 .	x_5 .
$x_1 = x_3, y_1 = -y_3$ $y_2 = y_4 = y_5 = 0$	2954	+1.0	+1.64	-0.2	+0.04	-0.01
	2048	+1.0	+1.71	+2.88	-7.42	+3.28
	1349	+1.0	-0.81	-0.28	-0.03	+0.10
	1123	+1.0	-0.26	+0.49	-0.04	-0.46

are drawn to scale. If the energies corresponding to the various terms of the potential function are now evaluated for each vibration, the following results emerge. In the



2954 vibration, more than 96% of the energy is located in the C-H bonds; in the 2048 vibration, *ca.* 55% of the energy is in the C-O linkage, and *ca.* 40% in the C-C linkage, *i.e.*, nearly all the quantum is collected into these two bonds; in the 1349 vibration *ca.* 75% of the energy is in the deformation of the $\widehat{\text{HCH}}$ angle, the remainder being distributed largely between the C-O and C-C linkages; in the 1123 vibration 40% of the energy is in the C-C bond and *ca.* 25% in each of the terms representing a stretching of the C-O bond and the deformation of the $\widehat{\text{HCO}}$ angle. In each of the last three vibrations there is less than 1% of the energy in the C-H bonds, in agreement with the fact that the value of the C-H bond force constant has little influence upon these frequencies. While the 1349 vibration can be regarded as largely confined to a deformation of the methylene group, the vibrations 2049 and 1123 are much less completely associated with the vibration of a particular bond or the deformation of a particular angle.

4. Formaldehyde.—With atomic masses as before, let the angles $\widehat{\text{HCH}}$ and $\widehat{\text{HCO}}$ be θ and ϕ , as in Fig. 3. There are six normal vibration frequencies of this molecule, five of which are planar. Of the planar frequencies

three are symmetrical and two antisymmetrical to the symmetry axis. Two matters call for immediate attention: first, the experimental data relating to the molecular shape, and secondly, the experimental determination and assignment of the several normal frequencies. The shape of the molecule has been discussed by Dieke and Kistiakowsky (*Physical Rev.*, 1934, 45, 4), who, from an analysis of the ultra-violet absorption bands, determined the moments of inertia in the ground state. The values of these moments of inertia were 24.33×10^{-40} , 21.39×10^{-40} , and 2.941×10^{-40} g.-cm.². Three independent quantities are necessary to define the shape of the molecule completely, viz., d_1 , d_2 , and θ . Dieke and Kistiakowsky assumed $\theta = 110^\circ$, whence $d_2 = 1.15$ and $d_1 = 1.19$ A. In the light of more recent knowledge with related molecules, these values may need revision. Whatever the value of d_1 , we might expect d_2 to be lower and θ rather higher than the values used by Dieke and Kistiakowsky. With the values for the moments of inertia given above, different values of θ give the values of d_2 and d_1 shown in Table III.

TABLE III.

Temp.	110°	112°	114°	116°	118°	120°
d_2	1.15	1.136	1.122	1.109	1.097	1.086
d_1	1.185	1.191	1.197	1.203	1.208	1.213

After considering all the evidence, it seems best to assume $\theta = 114^\circ$. This gives $d_2 = 1.122$ and $d_1 = 1.197$ A. This value of d_1 agrees within the limits of error with the electron-diffraction data (Brockway, *Rev. Mod. Phys.*, 1936, 8, 261), which suggest 1.15 ± 0.05 A. Further justification for the correctness of the magnitudes chosen will become apparent later.

The experimental determinations of the vibration frequencies of formaldehyde are not very satisfactory. The earlier data are summarised by Sponer ("Molekülspektren," Vol. I, p. 86) and by Mecke ("Hand- und Jahrbuch der Chem. Physik," Vol. 9, ii, 377), but these were largely based on Raman spectral measurements with formaldehyde solution. Undoubtedly more accurate values are to be taken from the measurements of Nielsen (*Physical Rev.*, 1934, 46, 117) in the infra-red. The molecule is an asymmetric top with $A \neq B \neq C$ and $A \cong B/10$, according to Dennison's nomenclature (*Rev. Mod. Physics*, 1931, 3, 280). According to Nielsen, "parallel" bands with a Q -branch structure are found at 2974, 2781, 1744, 1503, and 1166 cm.⁻¹, and "perpendicular" bands with more or less definite doublet structure at 2795, 1338, and 1040. The band at 1040 appears to need more careful examination. Other, feebler bands occur at longer wave-lengths. It is clear that not all the frequencies just given can be fundamentals, and it is not easy with such a well-spaced array of values to distinguish the fundamentals from the combination tones. A greater difficulty arises, however, with the group of frequencies at about 2800, since there is a distinct possibility of resonance splitting of one or more of these with a harmonic of a lower frequency such as 1503. It seems certain that ν_2 and ν_3 , two of the symmetrical planar vibrations, are 1744 and 1503, and ν_5 , one of the two antisymmetric planar frequencies, is 1338. The non-planar frequency ν_6 may be 1166. We can then assume $\nu_1 = 2781$, and $\nu_4 = 2795$, though it is perhaps better to take each as 2800. The remaining bands appear to be explicable by $2794 \cong 2\nu_3$, $1040 \cong (\nu_1 - \nu_2)$ or $(\nu_4 - \nu_2)$ according to its contour, when adequately known.

We shall only be concerned with the planar frequencies, and therefore take $\nu_1 = 2800$, $\nu_2 = 1744$, $\nu_3 = 1503$, $\nu_4 = 2800$, $\nu_5 = 1338$.

In the calculation of the force constants, we may first consider a simple valency force field, with a potential function involving four constants, k_1 (C=O), k_2 (C-H), with k_θ and k_ϕ as before. This fails to reproduce the values of the frequencies, the failure being parallel to that found with ethylene and allene, and relating mainly to the pair ν_2 and ν_3 . It is natural, therefore, to explore the utility of a potential function of the form found to be so successful with ethylene and allene. This involves five constants and is as follows:

$$2V = k_1\Delta_{24}^2 + 2k_2\Delta_{12}^2 + k_\theta\Delta\theta^2 + 2k_\phi\Delta\phi^2 + k_3\Delta_{24}\Delta\theta$$

The equations for the symmetrical frequencies ν_1 , ν_2 , and ν_3 are then

$$\nu_1^2 + \nu_2^2 + \nu_3^2 = k_1[A] + k_2[B] + \frac{2k_\theta + k_\phi}{d_2^2}[C] - \frac{k_3}{d_2}[D] \quad (1)$$

$$\nu_1^2\nu_2^2 + \nu_1^2\nu_3^2 + \nu_2^2\nu_3^2 = k_1k_2[E] + \frac{k_1(2k_\theta + k_\phi)}{d_2^2}[F] + \frac{k_2(2k_\theta + k_\phi)}{d_2^2}[G] - \frac{k_2k_3}{d_2}\left[\frac{D}{m_1}\right] - \frac{k_3^2}{2d_2^2}[H] \quad (2)$$

$$\nu_1^2\nu_2^2\nu_3^2 = \frac{k_1k_2(2k_\theta + k_\phi)}{d_2^2}[H] - \frac{1}{2}\frac{k_2k_3^2}{d_2^2}[H] \quad (3)$$

and for the antisymmetric frequencies ν_4 and ν_5 :

$$\nu_4^2 + \nu_5^2 = k_2[C] + \frac{k_\phi}{d_2^2}[B] + \frac{k_\phi}{d_1^2}[2A] + \frac{k_\phi}{d_1d_2}[J] \quad (4)$$

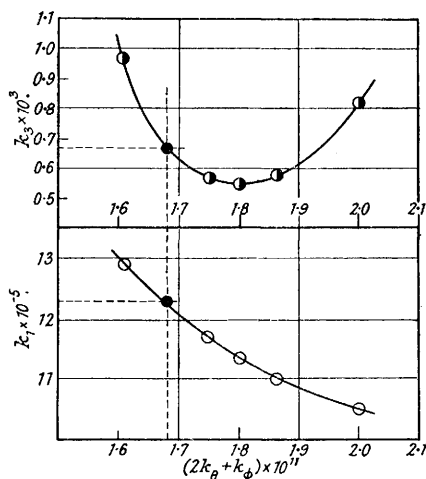
$$\nu_4^2\nu_5^2 = k_2k_\phi[G] + \frac{k_2k_\phi}{d_1^2}[2F] + \frac{k_2k_\phi}{d_1d_2}\left[\frac{J}{m_1}\right] \quad (5)$$

in which $A = 1/m_2 + 1/m_3$, $B = 1/m_1 + 2 \cos^2\frac{1}{2}\theta/m_2$, $C = 1/m_1 + 2 \sin^2\frac{1}{2}\theta/m_2$, $D = 2 \sin\frac{1}{2}\theta/m_2$, $E = 1/m_1(1/m_2 + 1/m_3) + 2 \cos^2\frac{1}{2}\theta/m_2m_3$, $F = 1/m_1(1/m_2 + 1/m_3) + 2 \sin^2\frac{1}{2}\theta/m_2m_3$, $G = 1/m_1 + 2/m_1m_2$.

From equations (4) and (5) we can at once solve for k_2 and k_ϕ . We find $k_2 = 4.1 \times 10^5$, and $k_\phi = 0.93 \times 10^{-11}$. The value of k_2 is seen to be lower than that found for ethylene and allene. This difference may in part arise from the somewhat approximate value taken for ν_4 , but there is no doubt that the value must be markedly less than the corresponding value for ethylene. The value for k_ϕ found for ethylene was 0.594×10^{-11} . It is not surprising that in formaldehyde this constant is somewhat different, since, apart from other reasons discussed below, the angle involved in one case is \widehat{HCC} and in the other \widehat{HCO} .

Turning to the three symmetric frequencies, we find that in order to reproduce the frequency $\nu_1 = 2800$ we must, regardless of plausible variations in the other constants,

FIG. 4.



take $k_2 = 4.3 \times 10^5$. This value is only slightly different from that obtained for k_2 from the antisymmetric vibrations. If the slight difference is real, it may be attributed to the necessity of a further interaction term in the potential function of the type $k_{23}\Delta_{12}\Delta$, in which case we should for the antisymmetric vibrations replace k_2 by $(k_2 - \frac{1}{2}k) = k_2'$ and for the symmetric by $(k_2 + \frac{1}{2}k) = k_2''$. This would give $k_2 = 4.2 \times 10^5$ and $k = 0.2 \times 10^5$. Assuming that $k_2'' = 4.3 \times 10^5$ and $k_\phi = 0.93 \times 10^{-11}$, we now have three unknown constants k_1 , k_θ , and k_3 , and only two frequencies so far unconsidered. Thus it is necessary to fix the value of one constant in order to calculate the other two. If we select a value for $(2k_\theta + k_\phi)$ it is possible from the equations (1), (2), and (3), by using the frequencies 2800, 1744, 1503, to calculate the associated values of k_1 and k_3 . The results for different values of $(2k_\theta + k_\phi)$ are shown in Fig. 4. It is possible from the curves of this figure to read off the range of plausible values

for the three constants. On the other hand, it is probably fair to estimate the force constant of the C-O link (k_1) from the value found with keten. If we take $k_1 = 12.3 \times 10^5$, $(2k_\theta + k_\phi) = 1.68 \times 10^{-11}$ and $k_3 = 0.67 \times 10^{-3}$. Since k_ϕ was found above to be 0.93×10^{-11} , this means that $k_\theta = 0.375 \times 10^{-11}$.

Thus, taking the values $k_2 = 4.2 \times 10^5$ ($k_2'' = 4.3$, $k_2' = 4.1$), $k_1 = 12.3 \times 10^5$, $k_\theta = 0.375 \times 10^{-11}$, $k_\phi = 0.93 \times 10^{-11}$, and $k_3 = 0.67 \times 10^{-3}$, we find $\nu_1 = 2802$, $\nu_2 = 1744$, $\nu_3 = 1506$, $\nu_4 = 2806$, and $\nu_5 = 1340$. The errors are + 2, 0, + 3, + 6, + 2.

The relative amplitudes of the atomic nuclei in the different vibrations can now be evaluated as in the previous cases. The results are summarised in Table IV.

TABLE IV.

Type.	Frequency.	x_1 .	y_1 .	x_2 .	y_2 .	x_4 .	y_4 .
Symmetrical. $x_1 = x_3; y_1 = -y_3$	2802	+1.0	+1.46	-0.21	0	+0.03	0
	1744	+1.0	-2.47	-1.53	0	+1.02	0
	1506	+1.0	-0.58	+0.07	0	-0.18	0
Antisymmetric. $x_1 = -x_3; y_1 = y_3$	2806	+1.0	+1.68	0	-0.29	0	+0.01
	1340	+1.0	-0.15	0	+0.33	0	-0.23

These are used in Fig. 3. On calculating the energies as in the earlier examples, it is found that in the cases of the two vibrations *ca.* 2800, nearly all the energy is located in the C-H bonds. With the 1744 vibration, about 75% of the energy is in the C-O bond, and the greater part of the remainder is associated with angular deformation. With the 1506 vibration, this state of affairs is reversed, about 75% of the energy being in the deformation of the angle, and the bulk of the remainder in the vibration of the C-O bond. Examination shows a parallelism between these vibrations and those of ethylene, and the calculations of the energies show that care must be observed in attributing vibrations to particular parts of the molecule from the amplitude diagram alone.

5. *Carbon Dioxide*.—The linear vibrations of this molecule have been discussed in Part I. The observed frequencies require resonance splitting and the potential function of simple valency force field needs modification. Using one cross term, so that

$$2V = k_1\Delta_{12}^2 + k_1\Delta_{23}^2 + k_2\Delta_{12}\Delta_{23}$$

it was found that $k_1 = 15.24 \times 10^5$ and $k_2 = 2.22 \times 10^5$. The significance of these results in connexion with the present calculations is discussed below.

6. *Carbon Suboxide*.—The four linear vibrations of this molecule have been treated in Part I, in which, by analogy with carbon dioxide, a potential function was used which incorporated cross terms representing the interaction between the C-O and C-C (k_3) bonds on the one hand, and between the C-C and C-C (k_4) bonds on the other. All the experimental data could be well interpreted by values $k_{CO} = 14.87 \times 10^5$, $k_{CO} = 14.15 \times 10^5$, $k_3 = 2.3 \times 10^5$, and $k_4 = 2.4 \times 10^5$. With $k_4 = 0$, values of k_3 less than 0.85×10^5 give imaginary roots for the main constants k_{CO} and k_{CO} . With $k_4 = 0$ and $k_3 = 1.0 \times 10^5$, the values obtained for k_{CO} and k_{CO} are obviously impossible. The significance of the chosen values of the constants k_3 and k_4 and of the resulting values of k_{CO} and k_{CO} are again discussed below.

7. *Carbon Monoxide and Acetylene*.—In Part II the force constant of the C-O bond in the ground state of carbon monoxide was shown to be 18.6×10^5 , and for acetylene $k_{CO} = 15.8 \times 10^5$ and $k_{CH} = 5.8 \times 10^5$.

Discussion.

The above results are collected together for comparison in Table V.

TABLE V.

Molecule.	k_{OH} $\times 10^{-5}$.	k_{CC} $\times 10^{-5}$.	k_{CO} $\times 10^{-5}$.	\widehat{HCH} k_{θ} $\times 10^{11}$.	\widehat{HCC} k_{ϕ}' $\times 10^{11}$.	\widehat{HCO} k_{ϕ}'' $\times 10^{11}$.	$(2k_{\theta} + k_{\phi})$ $\times 10^{11}$.	$(2k_{\theta} + k_{\phi}')$ $\times 10^{11}$.	$k_{\mu} \times 10^3$.*	\widehat{CCC} k_s' $\times 10^{-5}$.	\widehat{CCO} k_s'' $\times 10^{-5}$.
C ₂ H ₄	5.02	9.8	—	0.342	0.594	—	1.279	—	0.637	—	—
CH ₂ :C:CH ₂ ...	5.00	9.73	—	—	—	—	1.273	—	0.821	0.0	—
CH ₂ :CO	4.85	9.8	12.3	—	—	—	1.12	—	0.8	—	1.0
CH ₂ O	4.3	—	12.3	0.375	—	0.93	—	1.68	0.67	—	—
CO ₂	—	—	15.24	—	—	—	—	—	—	—	2.2
C ₃ O ₂	—	14.87	14.15	—	—	—	—	—	—	2.3	2.4
CO	—	—	18.6	—	—	—	—	—	—	—	—
C ₂ H ₂	5.8	15.8	—	—	—	—	—	—	—	—	—

* k_{μ} is the constant expressing the cross term between the angle \widehat{HCH} and the bond leading away from it, *e.g.*, in ethylene, the C=C bond.

The important conclusions to be inferred from these results are: (i) A comparatively simple potential-energy function has been found to interpret satisfactorily the vibration frequencies of each of the molecules of a closely related series. The constants and cross

terms involved in the potential function have a precise physical meaning, and can, subject to certain limitations, be carried over from one molecule to the next.

(ii) The numerical values of the corresponding constants required in the different cases are as a rule very close to each other, and differences can be understood and explained in terms of well-known phenomena. Moreover, this method of considering together related molecules of a series has the advantage that any ambiguities in the mathematical treatments are frequently removed.

(iii) The values of the force constants which have been derived appear to substantiate ideas arrived at previously by different methods, that two effects may be important in determining the electronic structures of the molecules considered. These effects are (a) the existence of resonance hybrids, and (b) the occurrence of electron drifts in a molecule as the result of the presence of some group which tends to attract or repel electrons. These several conclusions can be illustrated by a consideration of the data themselves.

First, the close parallelism between the relationships with ethylene and allene is very noticeable. The constants k_{CH} , k_{CO} , and $(2k_{\theta} + k_{\phi})$ are within narrow limits identical, and the values of k_{μ} are close. Identical values of k_{μ} would not be expected. The parallelism between the results with keten and formaldehyde is less marked but still very noticeable.

In passing, however, from ethylene, allene, formaldehyde, and keten to carbon dioxide and suboxide, we notice an abrupt and marked alteration in the force constants of both C-C and C-O linkages. In the last two molecules the values are intermediate between the values associated with double and triple bonds. This result is interpreted as implying the presence of hybrid links, arising from the existence of a mesomeric structure. Such structures for these molecules are already well known. Attention should here be directed to one other point. In the case of allene, the cross-term constant $k_{\text{C-O-O}}$ was found to be zero; with keten the corresponding constant $k_{\text{O-C-O}}$ has a value which must be close to 1.0×10^5 . In the case of carbon dioxide there is no doubt that the same cross term is not 1.0×10^5 but about 2.2×10^5 . In the same way with carbon suboxide $k_{\text{C-O-O}}$ and $k_{\text{O-C-O}}$ appear to have greater significance than might have been inferred from the consideration of allene and keten alone. We have assumed as very likely values in this case 2.4×10^5 and 2.3×10^5 , although it must be admitted that these are approximations. It is certain, however, that the values are not far from the correct ones, since lower values for the two constants lead to values for the main constants which are either imaginary or obviously impossible. We may perhaps understand the relatively enhanced importance of such cross terms as $k_{\text{O-C-O}}$ in carbon dioxide as follows. The molecule is supposed to exist as a hybrid of the forms (i) $\text{O}=\text{C}=\text{O}$, (ii) $\text{O}-\text{C}=\text{O}$, and (iii) $\text{O}=\text{C}-\text{O}$. If the C-O link 1, 2 contracts in a vibration, the molecule may be imagined as passing more towards the form (ii) or (iii), and consequently the C-O linkage 2, 3 will tend to lengthen. This means that the potential energy in the system will be greater than would be expected from the mere vibration of the one link, and would necessitate including an additional term in the potential function.

The variations in the C-H bond-constant in ethylene, allene, keten, and formaldehyde, and the associated variation in the bending constants are easily explained if it is supposed that the carbonyl group tends to draw electrons away from the remainder of the molecule. None of these molecules appears to be capable of existence in hybrid form. In formaldehyde the electronic drift will lead to greater weakening of the C-H bond than in keten. This is suggested by the figures calculated. In the same way in formaldehyde there is a small increase in k_{θ} which may suggest a greater localisation of electrons around the carbon atom. In keten the value of $(2k_{\theta} + k_{\phi}')$ is slightly lower than in ethylene and allene. We should expect the pull exerted by the carbonyl group to diminish on passing to the other end of the molecule. It would then be reasonable to expect only a small decrease in k_{OH} , as is found, but electrons in the C-C bond might to some extent leave the vicinity of the carbon atom of the methylene group, leading to the low value of $(2k_{\theta} + k_{\phi}')$.

The correlation of the calculated force constants with the interatomic distances, and the examination of the applicability of the relationships of Badger (*J. Chem. Physics*, 1934, **2**, 128; 1935, **3**, 710) and of Clark (*Phil. Mag.*, 1934, **18**, 459; 1936, **22**, 1137), are dealt with fully in a succeeding paper. It may, however, be observed that the value

assumed for the angle of the methylene group in formaldehyde leads to values for d_1 and d_2 (when calculated from the measured moments of inertia) both of which are in good agreement with the formulæ of Badger and Clark.

The above results and the conclusions inferred from them suggest that it may be profitable to consider related series of molecules in a similar manner to that described. It seems possible by such a systematic treatment to calculate force constants of linkages in simple molecules much more accurately than hitherto, and moreover, to do so without the necessity of employing potential-energy functions of undue complexity.

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