262. *The Spectrum and Molecular Structure of Carbon Suboxide, and Evidence for Hybrid Links.*

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In a recent paper, measurements on the ultra-violet absorption spectrum of carbon suboxide were described (Thompson and Healey, *Proc. Roy. Soc.*, 1936, *A*, **157**, 331). As then explained, the analysis of the complex system of diffuse bands observed in the region of 3200 A. was made the more difficult since no data were at that time available about the Raman or infra-red vibration frequencies of this molecule. On the basis of the observed intensity distribution, and by a consideration of the rules of Herzberg and Teller (*Z. physikal. Chem.*, 1935, *B*, **21**, 410), an analysis was, however, attempted, and approximate vibration frequencies in the excited electronic state consistent with these rules were determined. The modes of vibration of the molecule are shown in Fig. 1. The values suggested by the spectral work were $\nu_1(s) = 840$, $\nu_2(s) = 2160$, $\nu_4(a) = 1227$, with three smaller deformation oscillations 150, 240, and 540, designated respectively as $\delta_2(a)$, $\delta_3(s)$, and

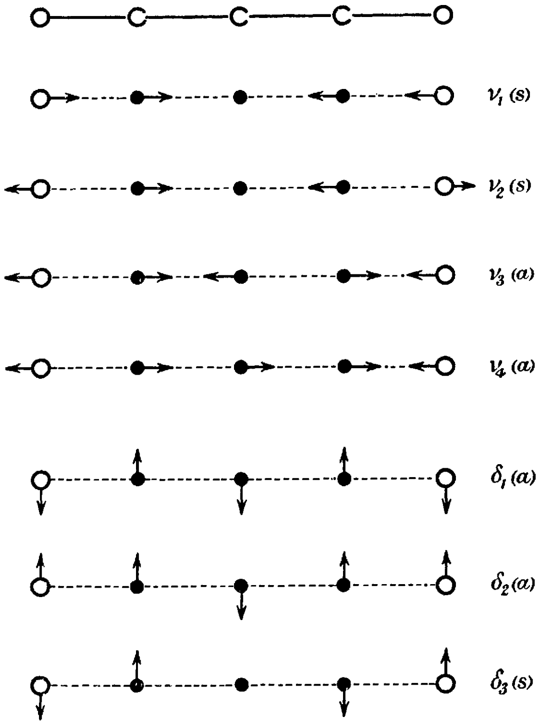
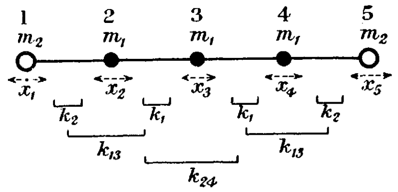


Fig. 1.

Fig. 2.



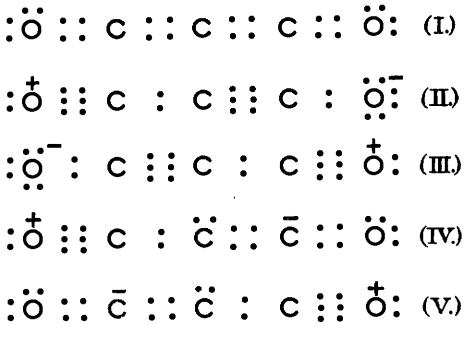


Fig. 3.

$\delta_1(a)$. The assignment of the three deformation frequencies to specific modes of vibration was, however, less definite than in the case of the valency vibrations.

It was hoped to make measurements in the photographic infra-red which might provide further evidence. Simultaneously with the publication of the above work, however, Engler and Kohlrausch published measurements, in which the experimental difficulties associated with the determination of the Raman spectrum were overcome (*Z. physikal. Chem.*, 1936, *B*, **34**, 214). The vibration frequencies obtained in the Raman spectrum are remarkably in agreement with those derived from the analysis of the spectrum, in regard to both magnitude and assignment. This provides a striking example of the justification of the use of the rules of Herzberg and Teller in analysing complex spectra, and seems worthy of record. Moreover, there is now sufficiently certain knowledge of the vibration frequencies to make it possible to calculate the linkage force-constants and to draw inferences concerning the molecular structure.

Electron-diffraction measurements have made it almost certain that carbon suboxide has a linear symmetrical structure (Brockway and Pauling, *Proc. Nat. Acad. Sci.*, 1933, **19**, 860; Boersch, *Wien. Ber.*, 1935, **144**, IIb, 1). The symmetry group is then $D_{\infty h}$, and there will be three strong Raman frequencies $\nu_1(s)$, $\nu_2(s)$, and $\delta_3(s)$ (Placzek, *Leipziger Vorträge*, 1931, 71). The Raman measurements confirm this completely. The values found and assigned by Engler and Kohlrausch are $\nu_1(s) = 843$, $\nu_2(s) = 2200$, $\delta_3(s) = 586$. It seems possible that another frequency, 1176, observed very feebly in the Raman effect may be regarded as $2\delta_3(s)$. Alternatively, the two very feeble Raman frequencies found at 1114 and 1176 may arise from impurities which are very difficult to remove from this substance.

It will be seen that the values given by Engler and Kohlrausch for $\nu_1(s)$ and $\nu_2(s)$ agree closely with those determined from the spectrum. It must be remembered that the latter values refer to the excited state, but, as previously explained, Duncan's collected data (*J. Chem. Physics*, 1935, **3**, 384) suggest that no considerable change is, in general, to be expected on electronic excitation. The frequency 586 assigned by Engler and Kohlrausch to $\delta_3(s)$ is paralleled by the magnitude 540 assigned by Thompson and Healey to $\delta_1(a)$. If we adopt the assignment of Engler and Kohlrausch, there is an additional confirmation of the spectral analysis, for the more intense of the weaker bands found will then correspond to the excitation of the symmetric deformation oscillation.

We can therefore now assume that with fair accuracy $\nu_1(s) = 843$ and $\nu_2(s) = 2200$, and it seems, further, unlikely that resonance splitting can lead to perturbed values. The force constants of the linkages of the molecule can now be calculated. The equations connecting the frequencies of the parallel vibrations with the force constants and masses, on the assumption of simple valency force field, *i.e.*, forces only between adjacent atoms connected by a conventional chemical bond, have already been given (Thompson and Healey, *loc. cit.*). By substituting the known frequency magnitudes, imaginary roots are obtained for the force constants. This implies the necessity of introducing "cross-terms" in the potential function expressing the potential energy as a function of the atomic displacements. Engler and Kohlrausch have attempted to make this correction by using a potential function essentially equivalent to that of a central force field. This type of field has, however, in general not proved any more successful than the simple valency force field and frequently less so, and we prefer to use a modified form of the potential function employed by Van Vleck and Cross (*J. Chem. Physics*, 1933, **1**, 357) and by Howard and Wilson (*ibid.*, 1934, **2**, 630), which has been shown to be so satisfactory for many other simple molecules.

For instance, for the water molecule Van Vleck and Cross use the expression

$$V = \tfrac{1}{2}[k_1(\Delta r_1)^2 + k_2(\Delta r_2)^2 + 2k_3 r_1^{\circ 2}(\Delta\gamma)^2 + k_{12}\Delta r_1\Delta r_2 + \sqrt{2}k_{13}r_1^{\circ}(\Delta r_1\Delta\gamma + \Delta r_2\Delta\gamma)]$$

in which r_1, r_2 are the O–H separations, and γ is the angle $\widehat{\mathrm{HOH}}$. It transpires that k_{12} is much less than k_1 or k_2 ($k_{12} \cong 0{\cdot}1k_1$), and that k_{13} is very much smaller than k_{12}. We shall for our present purpose neglect the "cross-terms" involving k_{13}. Howard and Wilson (*loc. cit.*) have similarly found such "angular" cross-terms to be very small in comparison with the "atom-separation" cross-terms.

The parallel vibration frequencies are then derived as follows. Let the masses of carbon and oxygen be respectively m_1 and m_2, and the force constants of the carbon–carbon and carbon–oxygen links be k_1 and k_2, and suppose the displacements of the atoms along the molecular axis are x_1, x_2, x_3, x_4, x_5.

Case I. For the symmetrical frequencies, $x_1 = - x_5, x_2 = - x_4, x_3 = 0$. Also, regarding contractions of a link as positive, we have

$$\Delta_{12} = x_1 - x_2 \qquad \Delta_{34} = x_3 - x_4$$
$$\Delta_{23} = x_2 - x_3 \qquad \Delta_{45} = x_4 - x_5$$

The kinetic energy is given by

$$T = m_2\dot{x}_1^{\,2} + m_1\dot{x}_2^{\,2} + \tfrac{1}{2}m_1\dot{x}_3^{\,2}$$

The potential function is taken as

$$V = k_1\Delta_{23}^2 + k_2\Delta_{12}^2 + \tfrac{1}{2}k_{13}\Delta_{12}\Delta_{23} + \tfrac{1}{2}k_{35}\Delta_{34}\Delta_{45} + \tfrac{1}{2}k_{24}\Delta_{23}\Delta_{34}$$

in which $k_{13} = k_{35}$. Substituting for $\Delta_{12}, \Delta_{23}, \ldots$, etc., applying Lagrange's equation, and solving the resulting determinantal equation, we have

$$\mu^2 - \mu\left[(k_1 + \tfrac{1}{2}k_{24})\left\{\frac{1}{m_1}\right\} + k_2\left\{\frac{1}{m_1} + \frac{1}{m_2}\right\} - k_{13}\left\{\frac{1}{m_1}\right\}\right]$$
$$+ \left[(k_1 + \tfrac{1}{2}k_{24})k_2\left\{\frac{1}{m_1m_2}\right\} - \frac{k_{13}^2}{4}\left\{\frac{1}{m_1m_2}\right\}\right] = 0 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the frequencies ν are given by $\nu = \sqrt{\mu}/2\pi$. If the masses are expressed in atomic weights, and we write $\mu = \nu^2 \times 5{\cdot}863 \times 10^{-2}$, the force constants are given in dynes per cm.

Case II. Similarly for the antisymmetric frequencies, $x_1 = x_5, x_2 = x_4$, introduction of a condition for no translation gives

$$m_1\,(x_2 + x_3 + x_4) + m_2\,(x_1 + x_5) = 0$$

The expressions for the kinetic and potential energies being used as before, the solution is

$$\mu^2 - \mu\left[(k_1 - \tfrac{1}{2}\,k_{24})\left\{\frac{3}{m_1}\right\} + k_2\left\{\frac{1}{m_1} + \frac{1}{m_2}\right\} - k_{13}\left\{\frac{1}{m_1}\right\}\right]$$
$$+ \left[k_2(k_1 - \tfrac{1}{2}\,k_{24})\left\{\frac{3}{m_1m_2} + \frac{2}{m_1^2}\right\} - \frac{k_{13}^2}{4}\left\{\frac{3}{m_1m_2} + \frac{2}{m_1^2}\right\}\right] = 0 \quad . \quad . \quad . \quad (2)$$

Considering first the symmetrical vibrations given by equation (1), we have two known frequencies but four unknown constants. If the pair of antisymmetric frequencies were known, we should be able to solve equations (1) and (2) for the four constants. In the circumstances, however, the only alternative is to attempt to determine the values of the constants k_{13} and k_{24} from other data. A molecule which is apparently highly suitable for this purpose is carbon dioxide. For this molecule $m_1m_2m_3$ in which $m_1 = m_3$, using the potential function $V = 2\{\tfrac{1}{2}k_1\Delta_{12}^2\} + \tfrac{1}{2}k_{13}\Delta_{12}\Delta_{23}$, we obtain expressions for the parallel vibrations :

$$\text{Symmetric : } \mu = (k_1 + \tfrac{1}{2}k_{13})\left\{\frac{1}{m_1}\right\}$$

$$\text{Antisymmetric : } \mu = (k_1 - \tfrac{1}{2}k_{13})\left\{\frac{1}{m_1} + \frac{2}{m_2}\right\}$$

The difficulty here arises from uncertain values of the two vibration frequencies. This is the result of resonance splitting caused by the fact that $\nu_1(s) \simeq 2\delta(s)$. Adel and Dennison (*Physical Rev.*, 1933, **46**, 716) attempted to determine the unperturbed values of the frequencies, and gave $\nu_1(s) = 1320$, and $\nu_2(a) = 2350$. Insertion of these values into the above expressions gives $k_1 = 15{\cdot}24 \times 10^5$ and $k_{13} = 2{\cdot}22 \times 10^5$. Assuming the same values for the carbon dioxide frequencies and taking k_{13} as zero, Penney and Sutherland

(*Proc. Roy. Soc.*, 1936, *A*, **156**, 654) found $k_1 = 16{\cdot}4 \times 10^5$ and $14{\cdot}1 \times 10^5$, mean $15{\cdot}2 \times 10^5$, in agreement with our present value.

For carbon suboxide, the values of both k_{13} and k_{24} will be close to that of k_{13} in carbon dioxide. We may expect some minor alteration, however, and examination of other related cases such as that of carbon disulphide suggests that we may reasonably take for carbon suboxide the values $k_{13} = 2{\cdot}3 \times 10^5$, and $k_{24} = 2{\cdot}4 \times 10^5$. Using these values, we can now employ the two symmetrical frequencies and equation (1) and find $k_2 = 14{\cdot}87 \times 10^5$ or $8{\cdot}76 \times 10^5$, with corresponding values of k_1 of $14{\cdot}15 \times 10^5$ or $24{\cdot}86 \times 10^5$. The second pair of values is clearly impossible, and the first must therefore be taken.

It is now of interest to compare these values with the "normal" values of the force constants for the various carbon–carbon and carbon–oxygen linkages. These "normal" values must be determined from molecules in which the linkages are definitely undisturbed by such phenomena as resonance (mesomerism). For the carbon–carbon linkages such molecules would appear to be ethane, ethylene, and acetylene. In ethane, using the potential function of Dennison and Sutherland (*Proc. Roy. Soc.*, 1935, *A*, **148**, 250), we find that $k_{CC} = 4{\cdot}96 \times 10^5$. If a potential function of the Van Vleck and Cross type is used, the value is *ca.* $4{\cdot}9 \times 10^5$. For ethylene, Dennison and Sutherland give $k_{CC} = 9{\cdot}79 \times 10^5$. In a succeeding paper it will be shown that, if other potential functions are used, the value of k_{CC} is approximately $9{\cdot}0 \times 10^5$. It is clear that the true value is close to this. The force constant of the carbon–carbon link in acetylene is given in a later paper as $15{\cdot}73 \times 10^5$, and in deuteroacetylene it is $15{\cdot}93 \times 10^5$. The abnormally high value of the carbon–hydrogen constant in these molecules suggests that there may be some unexpected peculiarity about their structure, leading to a value for the carbon–carbon constant which is not quite "normal"; but there is no doubt that the carbon–carbon triple bond has a force constant close to $15{\cdot}8 \times 10^5$.

For the carbon–oxygen single bond we can regard methyl alcohol as a diatomic system (H_3C)–(OH), which gives a value $4{\cdot}99 \times 10^5$ (Sidgwick, "The Covalent Link," p. 123), or we can take the value given by Dennison and Sutherland, *viz.*, $4{\cdot}96 \times 10^5$. The most satisfactory unperturbed carbon–oxygen double link would appear to be that in formaldehyde. The accurate assignment of the several frequencies is difficult in this case, owing to the possibility of resonance splitting. Dennison and Sutherland (*loc. cit.*) give $k_{CO} = 13{\cdot}45 \times 10^5$. In a succeeding paper a somewhat lower value is obtained, but it is clear that the value is close to 13×10^5. In carbon monoxide we have what must approach to a triple bond between carbon and oxygen, and the frequency 2169 gives $k_{CO} = 18{\cdot}6 \times 10^5$ (Sidgwick, *op. cit.*, p. 123). We thus have:

Force constant ($\times 10^5$) of:	Carbon–carbon link.	Carbon–oxygen link.
Normal single	4·9	4·98
Normal double	9·5	13·0
Normal triple	15·8	18·6
In carbon suboxide	14·9	14·15

From these figures it is at once clear that in carbon suboxide the carbon–carbon and the carbon–oxygen linkages are not simple double bonds. This is particularly noticeable of the former, which behave almost, but not entirely, like triple bonds. This is moreover true, even if we assume the potential function used by Kohlrausch, which gives $k_{CO} = 13{\cdot}9 \times 10^5$ and $k_{CC} = 11{\cdot}1 \times 10^5$. (Actually, if we take Kohlrausch's values it might be more accurate to compare them with the values calculated for the "normal" constants by using a similar type of potential function.) The structure of the molecule might then be represented by a formula of the type $O\underset{---}{=}C\underset{---}{=}C\underset{---}{=}C\underset{---}{=}O$. The possibility of such a structure arising from resonance (mesomerism) between structures (I), (II), and (III) of the five possible forms shown in Fig. 3 has been suggested by Pauling and Brockway on the basis of electron-diffraction measurements and this result appears to provide a good example of the way in which mesomerism can be detected in simple molecules by a study of link force constants. According to Brockway and Pauling, the C–C distances are 1·29 ± 0·03 A., and the C–O 1·20 ± 0·02 A.; and according to Boersch, they are 1·27 A. and 1·18 A. Double bonds being assumed throughout, addition of the covalent radii gives 1·34 A.

and 1·27 A. Now, according to Badger's empirical rule (*J. Chem. Physics*, 1934, **2**, 128)

$$(r_e - d_{ij}) = \sqrt[3]{1{\cdot}86 \times 10^5/k_{ij}}$$

where d_{ij} in the present case is 0·68 for each link. Taking the values found above for the force constants, we find $r_{\mathrm{CC}} = 1{\cdot}20$ A., and $r_{\mathrm{CO}} = 1{\cdot}18$ A. Agreement with the electron-diffraction data is therefore not exact as is indeed not surprising, but it is certain that the linkage lengths are far below those required for normal double bonds.

All the above considerations suggest that it may be profitable to consider in a similar manner the force constants of links in related series of molecules, and use the results as a guide to the nature of the bonds involved. This subject is carried further in papers shortly to follow.

Finally, by assuming the force constants determined above for the linkages in carbon suboxide, it is also possible at once to calculate the magnitude of the two antisymmetrical vibration frequencies which have so far not been determined experimentally. The required formula was given above (2). The calculated values are $\nu_3(a) = 2505$, $\nu_4(a) = 1618$. According to Kohlrausch, they would be $\nu_3(a) = 2458$, $\nu_4(a) = 1627$.

SUMMARY.

Recent values of the vibration frequencies of the carbon suboxide molecule, determined by Engler and Kohlrausch's Raman spectral measurements, confirm values previously derived from a study of the ultra-violet absorption spectrum, and strikingly justify the use of the rules of Herzberg and Teller in analysing complex spectra.

By a consideration of the vibration frequencies of the molecule and by a choice of a suitable potential-energy function for the vibrations, the force constants of the linkages in the molecule have been calculated. The values obtained clearly show the existence of a resonance hybrid structure agreeing with previous independent results of Brockway and Pauling.

The antisymmetric vibration frequencies of the molecule have been calculated.

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