On the Infrared Spectra of Gases
III

The Configuration of the Carbon Dioxide Molecule and the Laws of the Intramolecular Forces

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1. According to recent investigations most of the infrared spectral bands are caused by the movements of electrically charged *atoms* or groups of atoms, whereas the lines observed in the visible and in the ultraviolet spectrum are due to oscillations of the *electrons*. Therefore, the study of the infrared spectra must be very useful for our knowledge of the atomic vibrations in the molecules. Although the investigation of infrared spectra reveals only data concerning the movements of electrically charged atoms it is, however, to be expected that the vibrations of neutral atoms are governed by the same laws. In this paper we shall mainly be concerned with the atomic vibrations in the carbon dioxide molecule. The atoms in this molecule are all electrically charged.

2. In a preceding paper[1] it was shown that the three bands at 2.7, 4.3 and 14.7 μ, which are the only bands in the infrared spectrum of carbon dioxide, correspond to three different *vibrations of the atoms*. As a triatomic molecule carbon dioxide has only three internal degrees of freedom. Therefore only three vibrations and, accordingly, three infrared bands are to be expected. From the wave-lengths of these bands the vibrational frequencies of the molecule can be calculated. The interesting question now arises: which properties must we ascribe to the carbon dioxide molecule in order to make it vibrate with just these three frequencies? In the following we will consider this problem.

3. Each of the three possible harmonic vibrations of the carbon dioxide molecule must be a complex movement of the molecule as a whole; if one atom oscillates the two others must necessarily participate in the oscillation. Each of the three harmonic vibrations of the molecule will constitute a co-ordinated synchronous vibration of all three atoms.

According to Rutherford the masses of the atoms are concentrated in the extremely small nuclei. We may therefore consider the carbon dioxide molecule as a simple system of three mass points. The masses will be $\frac{12}{N}, \frac{16}{N}, \frac{16}{N}$, where N is Avogadro's constant. Furthermore we will assume that the two oxygen atoms are fully symmetrically bound in accordance with the chemical properties of the carbon atom. The carbon dioxide molecule consequently forms an isosceles triangle, the shape of which is completely determined by the value of the vertex angle, 2θ.

The equilibrium lengths of the sides of the triangular molecule are denoted as l_1 (base) and l_2 (the two sides), and the changes in these lengths at a certain time as r_1, r_2, and r_3 (cp. fig. 1).
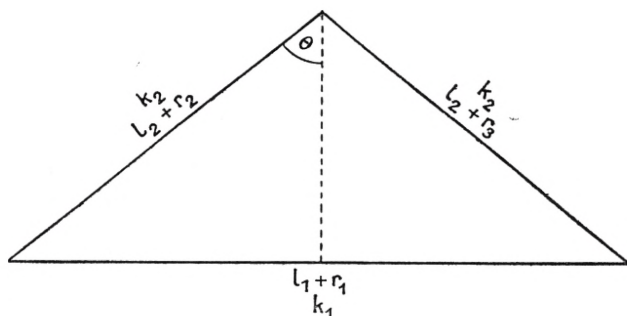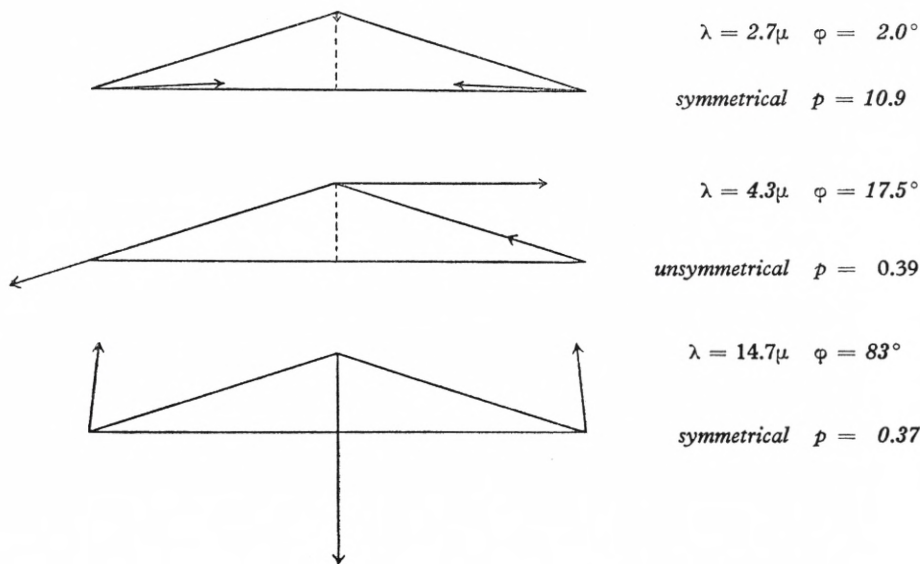

Fig. 1.

Before we can proceed any further we have to make definite assumptions about the nature of the intramolecular forces. We are going to carry through the calculations on the basis of two different hypotheses.

First we will assume that all internal forces are central forces between the three mass points (*Central Force System*). Next we will assume central forces acting between the carbon and the oxygen atoms, but not between the two oxygen atoms. Instead of direct forces between the oxygen atoms we will introduce a deformation (bending) force, which will oppose all changes of the angle θ (*Baeyer's strain theory*). Obviously, the second system agrees with our chemical aspects of the valence forces, and we will therefore nominate it the *Valence Force System*.

4. *Central Force System.* The force caused by a small (infinitesimal) change, r, in the distance between two atoms is represented by kr in the Central Force System, where k is a constant characterizing the strength of the bond between the two atoms. If we know the values of k_1 and k_2 related to the bonds between oxygen and oxygen, resp. carbon and oxygen, and if moreover θ, i.e. the shape

Fig. 2.

$\lambda = 2.7\mu$ $\varphi =$ 2.0°

symmetrical $p = 10.9$

$\lambda = 4.3\mu$ $\varphi = 17.5°$

unsymmetrical $p =$ 0.39

$\lambda = 14.7\mu$ $\varphi = 83°$

symmetrical $p =$ 0.37

1. Solution. Central Force System.
$\theta = 72.5°$, $k_1 = 5.34 \cdot 10^6$ dyne/cm, $k_2 = 1.38 \cdot 10^6$ dyne/cm

of the molecule, is known we have sufficient data to calculate the three vibrational frequencies of the molecule.

On the other hand, it must be possible to compute k_1, k_2, and θ from the known frequencies, *which means that we are able to calculate the shape and rigidity of the carbon dioxide molecule from the measured positions of the infrared bands.* The details of this calculation will be given in the last part of the paper, but I shall state the results here. Two different solutions are obtained:
Either:

$$\theta = 72.5°, \; k_1 = 5.34 \cdot 10^6 \text{ dyne/cm}, \; k_2 = 1.38 \cdot 10^6 \text{ dyne/cm},$$
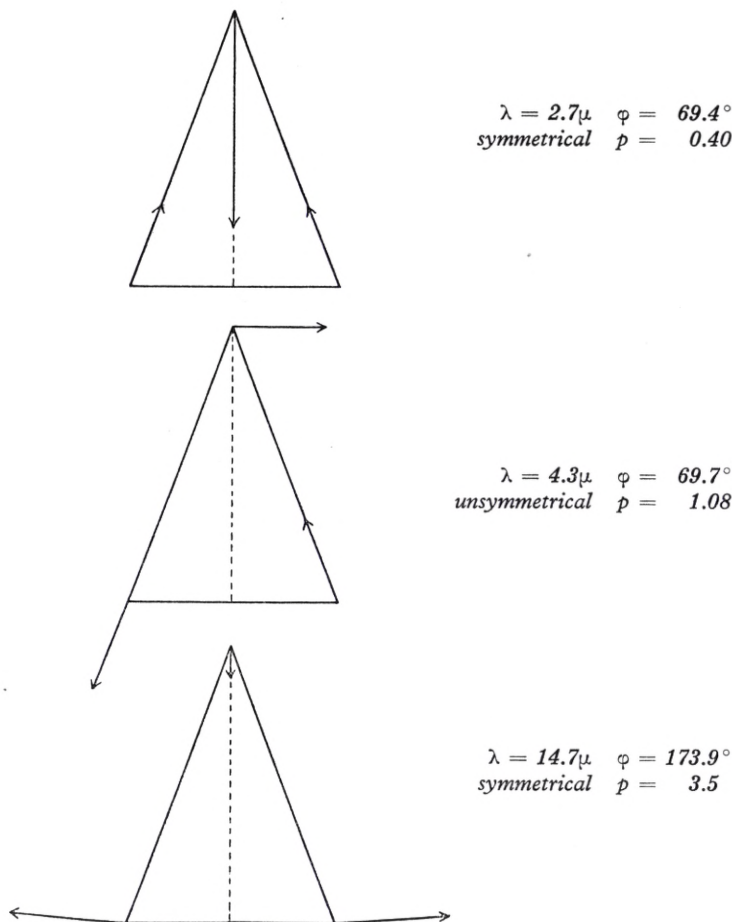
or

$$\theta = 20.3°, \; k_1 = 0.211 \cdot 10^6 \text{ dyne/cm}, \; k_2 = 3.57 \cdot 10^6 \text{ dyne/cm}.$$

Fig. 2 and 3 show a survey of the vibrations of the carbon dioxide molecule in the two cases. The arrows indicate the relative magnitudes and directions of the linear oscillations of the atoms corresponding to the different infrared bands.

φ means the angle between the base (of the triangle) and the direction of oscillation, and p the ratio between the amplitude of the oxygen atoms and the carbon atom.

In both solutions the 4.3μ band corresponds to an unsymmetrical vibration, whereas the two other bands are ascribed to symmetrical vibrations.
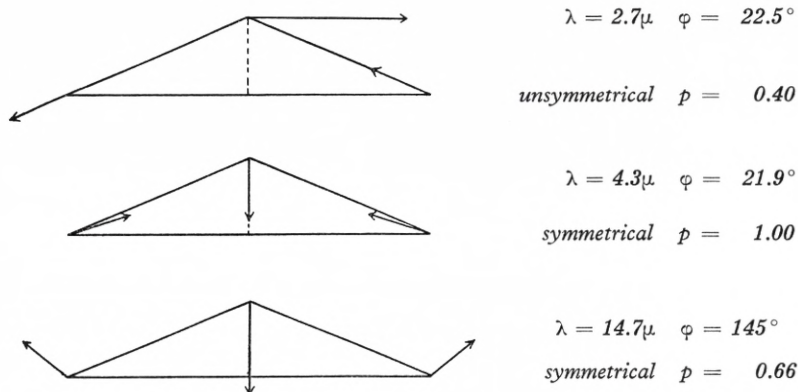
Fig. 3.

$\lambda = 2.7\mu$ $\varphi = 69.4°$
symmetrical $p = 0.40$

$\lambda = 4.3\mu$ $\varphi = 69.7°$
unsymmetrical $p = 1.08$

$\lambda = 14.7\mu$ $\varphi = 173.9°$
symmetrical $p = 3.5$

2. Solution. Central Force System.
$\theta = 20.3°$, $k_1 = 0.211 \cdot 10^6$ *dyne/cm*, $k_2 = 3.57 \cdot 10^6$ *dyne/cm*.

However, none of these solutions seems to be plausible on closer consideration. In the first, the oxygen-oxygen bond is 3.87 times stronger than the oxygen-carbon bond ($k_1/k_2 = 3.87$). From a chemical point of view this is extremely improbable. In this respect solution 2 is far better having $k_1/k_2 = 0.059$ which means a rather weak O—O bond. On the other hand, the second solution is very unsatisfactory from a stereochemical point of view because the two oxygen atoms are placed very close together.

For valence-theoretical reasons it is to be expected that no satisfactory solution

Fig. 4.

$\lambda = 2.7\mu$ $\varphi = 22.5°$

unsymmetrical $p = 0.40$

$\lambda = 4.3\mu$ $\varphi = 21.9°$

symmetrical $p = 1.00$

$\lambda = 14.7\mu$ $\varphi = 145°$

symmetrical $p = 0.66$

3. *Solution. Valence Force System.*
$\theta = 67.5°$, $k_\theta = 0.292 \cdot 10^6$ *dyne/cm*, $k_2 = 3.58 \cdot 10^6$ *dyne/cm*.

for the configuration of the carbon dioxide molecule can be obtained based on the assumption that the forces are all central forces. We are now going to investigate the configurations found on the basis of a Valence Force System.

5. *Valence Force System.* In this case, too, we can characterize the internal force system, governing the oscillations, by two constants k_θ and k_2. As before $k_2 r_2$ is the force acting between carbon and oxygen if the distance is changed with the amount r_2. k_θ is defined by the equation:
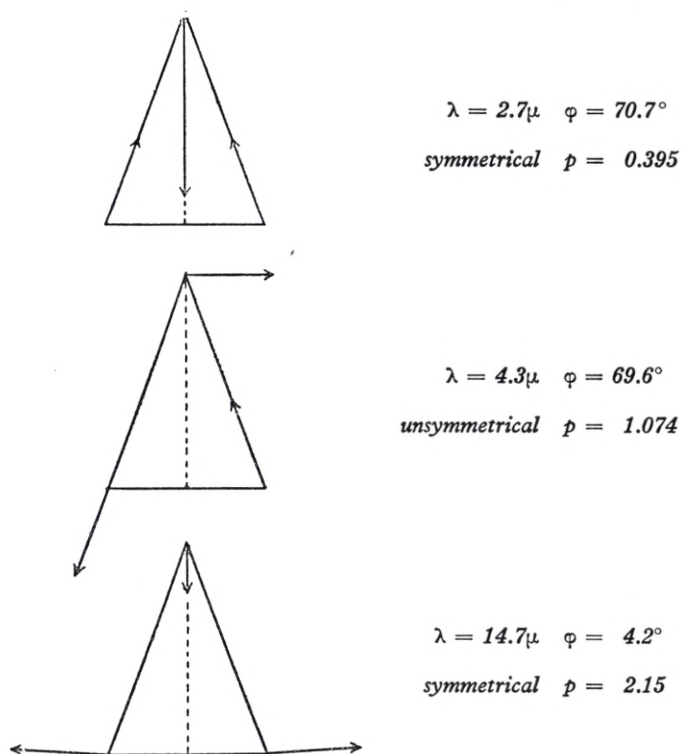
$$P_\theta = k_\theta \cdot l_2 d\theta$$

Here P_θ is the restoring force acting on the oxygen atoms if these are displaced $l_2 d\theta$ from their positions of equilibrium in a direction perpendicular to the sides of the triangle. Again, we can calculate θ, k_θ and k_2 from the (observed) wavelengths of the infrared bands, and two solutions are obtained.

Details concerning these solutions are indicated in fig. 4 and 5.

Of these two "valence-force" solutions the first appears to be the more plausible for several reasons. The two oxygen atoms are not found to be too close together, as $\theta = 67.5°$. Moreover, the constants representing the rigidity of the molecule seem to have plausible values. k_θ is considerably smaller than k_2 which means that it is far more easy to 'bend' the molecule than to diminish the distance between oxygen and carbon, a result that seems most probable. On the other hand, certain features point in favour of the last solution. I only want to point out that investigations of the far infrared spectrum seem to show that the carbon dioxide molecule rotates rather slowly, as there is no absorption between 20μ and 300μ. If the molecule had the extended shape indicated by solution 1 and

Fig. 5.

$$\lambda = 2.7\mu \quad \varphi = 70.7°$$
$$\text{symmetrical} \quad p = 0.395$$

$$\lambda = 4.3\mu \quad \varphi = 69.6°$$
$$\text{unsymmetrical} \quad p = 1.074$$

$$\lambda = 14.7\mu \quad \varphi = 4.2°$$
$$\text{symmetrical} \quad p = 2.15$$

4. Solution. Valence Force System.
$\theta = 20.4°, k_\theta = 0.742 \cdot 10^6 \ dyne/cm, k_2 = 3.56 \cdot 10^6 \ dyne/cm$

3, one would expect a fast rotation about the long axis because of the small moment of inertia about this axis.

It would, of course, not be possible to observe the rotation in the far infrared if the molecule did not possess an electrical polarity perpendicular to this axis. It is, however, very probables that the molecule corresponding to solution 3 is polar in this direction.

If one assumes the carbon-oxygen bond to be of the same strength in carbon monoxide as in carbon dioxide one calculates a wave-length 5.2 μ according to solution 1 for the absorption band in carbon monoxide, whereas the other three solutions all give 3.2 μ. As the band in carbon monoxide is situated at 4.7 μ, it follows that our hypothesis leads to a value of the right order of magnitude for the absorption wave-lenght, but nothing more. After all we have no reason

for assuming the same bond-strength in carbon monoxide as in carbon dioxide. At the calculation the following relation is used:

$$\lambda = 2\,\pi\,c \sqrt{\frac{C \cdot O}{CO} \cdot \frac{1}{k_2\,N}}$$

$$c = 3 \cdot 10^{14};\ N = 65 \cdot 10^{22}.$$

6. *On the deviation of the carbon dioxide molecule from the linear form.* Although the solutions based upon the "Valence Force" system are more plausible in several respects than those based on the "Central Force" system one can, however, raise one rather serious objection to these. It might be expected that the angle strain force would tend to keep the oxygen atoms in diametrically opposed positions. According to organic chemistry the carbon valencies are all equal and tetrahedrally distributed. Hence, the molecule must be linear. In our solutions, however, we have found it to be non-linear. This result is supported by the specific heat of carbon dioxide as the rotational energy is found to be $\frac{3}{2}RT$, whereas it should be RT for a linear molecule. The valence force system, to which we were led through our calculations, does not quite correspond to the valence force system expected from the organic chemistry.

In order to explain the deviation from the linear form one might assume that there were attractions between the oxygen atoms besides the assumed valence forces. The deviation would then be the result of a competition between this attraction and a Baeyer valence angle strain. Unfortunately, it is not possible in this case to calculate the shape of the molecule and the coefficients of the internal forces without making new arbitrary assumptions with respect to the dependence of the attractive forces on the distance between the oxygen atoms and with respect to the dependence of the valence angle strain on the bending of the molecule. Depending upon whether the attractive force or the valence angle strain changes with the higher power of the variable, the molecule will approach a valence force, respectively central force, molecule.

The bent form of the carbon dioxide molecule might also be explained as a centrifugal effect of the rotation. If the rigidity of the molecule initially is very low, but becomes very high after a certain bending, a resulting bending could be explained. The carbon dioxide molecule was then to be compared with a system of two small sticks connected with a universal joint only allowing a certain limited bending. In this case it would, on the other hand, be difficult to understand why the frequencies of the atomic oscillations are independent of the rotation.

7. *The influence of the rotation on the infrared bands of the carbon dioxide mole-*

cule. As previously shown[2] it is generally to be expected that an infrared band caused by atomic vibrations will appear as a *triplet* comprising two broad components and a sharp central line. For diatomic molecules, however, the band will be simpler. In this case the sharp central line will be missing* because the rotational axis will be perpendicular to the direction of vibration.

This theory for the influence of the rotation has recently been confirmed by the investigations of Burmeister and Eva v. Bahr. In one respect only a certain discrepancy between theory and experiment consists. According to the existing observations the sharp central line seems to be missing also in triatomic molecules like carbon dioxide and water vapour. These molecules seem to obey the theory for diatomic molecules. One must, however, remember that it is only possible to observe a sharp line in the absorption spectrum if a narrow slit is used. New investigations of the emission spectra of these gases would be very desirable for clarifying this point. In the emission spectrum the central line should be observable even if it is ever so sharp.

Quite apart from details the investigations of Burmeister and Eva v. Bahr have proved that the influence of the rotation on the infrared bands is unmistakable. It is furthermore possible to draw important conclusions from its general features.

Generally, it is not to be expected that the influence of the rotation on the three carbon dioxide bands should arise from the same rotation. To get a general survey of the conditions one has to remember that the radiating molecular vibrator has a definite axis of vibration, viz. the direction of a corresponding linear oscillator radiating in the same way. For the two symmetrical vibrations of carbon dioxide this axis of vibration coincides with the symmetry axis of the molecule, and for the unsymmetrical vibration it is an axis perpendicular to it in the plane of the molecule. As the two symmetrical vibrations possess the same axis they must be influenced in the same way by the rotation, whereas one must expect a separate behaviour of the unsymmetrical vibration. Therefore, if we had precise measurements of the structure of the bands it would be possible to decide which

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* W. C. Mandersloot (Diss. p. 51, Amsterdam 1914) who as the first has tried to explain the disappearance of the sharp line, seems to be of the opinion that according to his explanation the central component might disappear for all molecules (cp. p. 58 ff.). The way Mandersloot has treated the problem seems hardly permissible. He separates the actual rotation in rotations about the axis of vibration and perpendicular to it, and only the last rotation is being considered. One must, however, as I previously have done, treat the problem reversely. One must separate the oscillation in two components, one parallel to the rotational axis and one perpendicular to it. The first component will radiate unperturbed of the rotation, whereas the second component will radiate the frequencies $v_s \pm v_r$. As to Mandersloot's note pag. 51 (resp. Thesis IV) the following may be said. I have not assumed the *axis of oscillation* to have an arbitrary direction within the molecule, but that *the rotational axis* may have any possible orientation within the molecule. Only for linear, i.e. especially diatomic, molecules this assumption is not correct.

band corresponds to the unsymmetrical vibration and to find out if the molecules are rotating faster about the symmetry axis or about a line perpendicular to this axis in the plane of the molecule.

At first glance one might be inclined to think that the decision could be made from the present measurements. Whereas the distance between the components of the double bands at 4.3 μ and 14.7 μ approximately give the same rotational frequency[3] ($2.7 \cdot 10^{11}$, resp. $2.4 \cdot 10^{11}$), the structure of the band at 2.7 μ seems to give a considerably greater frequency of rotation[4] (about $17 \cdot 10^{11}$). This band should therefore correspond to the unsymmetrical vibration and the molecule should have the highest rotational frequency as well as the lowest moment of inertia about an axis perpendicular to the symmetry axis. If we compare these demands with the above four solutions we find that none of them are satisfactory. Only in the third solution does the band at 2.7 μ correspond to the unsymmetrical vibration, but unfortunately the moment of inertia about the symmetry axis here is much smaller than that about an axis at right angles to it.

Eva v. Bahr[4] is, too, of the opinion that the double band at 2.7 μ is not to be explained as due to rotation, but that it is of another, yet unknown, origin. The band is of quite another type than the usual rotational bands. Each of the two bands at 2.7 μ is in all probability a rotational double band. If these were associated with a low rotational frequency this would be in agreement with solution 3.

8. *Absolute size of the amplitudes of the vibrations and the dimension of the molecule.* The above treatment of the problem is permissible only if the amplitudes of the vibrations are really small compared with the dimensions of the molecule.

First, I have verified this for the hydrogen chloride molecule. From the value of the most probable rotational frequency the following moment of inertia is calculated:[5]

$$\mathfrak{J} = 0.54 \cdot 10^{-39}$$

From this the distance, l, between the atomic centres is computed by means of the equation:

$$\mathfrak{J} = \frac{l^2}{N} \cdot \frac{Cl \cdot H}{HCl}$$

For $N = 65 \cdot 10^{22}$ one gets:

$$l = 1.89 \cdot 10^{-8}$$

This value is of the same order of magnitude as the molecular dimensions of similar molecules calculated on the basis of the kinetic theory of gases.

In order to calculate the amplitudes of the vibrations we compute first the rigidity of the bonds between the atoms. The force, P, acting between the atoms when the distance changes with the amount, r, is equal to

$$P = kr \, .$$

The coefficient, k, is determined by the equation:

$$k = (2 \pi \nu)^2 \cdot \frac{Cl \cdot H}{HCl} \cdot \frac{1}{N} \tag{1}$$

If a denotes the amplitude of the vibration, we have for the vibrational energy (E_v):

$$E_v = \tfrac{1}{2} k a^2 \tag{2}$$

Hence, from equations 1 and 2:

$$a = \frac{1}{2 \pi \nu} \cdot \sqrt{\frac{HCl}{H \cdot Cl} \cdot 2E_v \cdot N} \tag{3}$$

If we put the vibration energy equal to one quantum we have

$$E_v = h\nu .$$

Further, if we insert the values

$$h = 6.4 \cdot 10^{-27} \text{ and } N = 65 \cdot 10^{22}$$

we get

$$a = 0.158 \cdot 10^{-8} .$$

This means that the amplitude of the vibration is 8.3 per cent of the length of the molecule.

If we put

$$E_v = \frac{RT}{N}$$

i.e. we equalize the vibrational energy with the mean value required by the classical theory, we find for 18° C

$$a = 0.041 \cdot 10^{-8}$$

an amplitude corresponding to only about 2 per cent of the length of the molecule.

It is easy in a similar way to calculate the amplitudes of the vibrations for the carbon dioxide molecule if the force constants (k) are known.

I have carried out these calculations for the third solution only; it should, however, suffice to demonstrate the smallness of the amplitudes in a simple case.

The results of the calculation are given in the following table.

Vibrational Amplitudes for CO_2. Third Solution. Valence Force System. $\theta = 67.5°$.
a) The vibrational energy equals one quantum.

As the dimensions of the carbon dioxide molecule certainly exceeds 10^{-8}, it follows from the table that to a good approximation we are entitled to consider the vibrations of the carbon dioxide molecule as infinitesimal.

This is, however, not absolutely correct. It is therefore natural that the vibrational frequencies are not completely independent of the vibrational energy, i.e.

Band at	Ampl. of C-atom	Ampl. of O-atom
14.7μ	$2.8 \cdot 10^{-10}$	$1.84 \cdot 10^{-10}$
4.3μ	$5.8 \cdot 10^{-10}$	$2.6 \ \cdot 10^{-10}$
2.7μ	$3.4 \cdot 10^{-10}$	$1.36 \cdot 10^{-10}$

b) The vibrational energy equals the classical value for 18° C

Band at	Ampl. of C atom	Ampl. of O atom
14.7μ	$1.49 \cdot 10^{-10}$	$0.98 \cdot 10^{-10}$
4.3μ	$1.66 \cdot 10^{-10}$	$0.75 \cdot 10^{-10}$
2.7μ	$0.77 \cdot 10^{-10}$	$0.31 \cdot 10^{-10}$

that the infrared bands are shifted a little with the temperature. Such a shift is in fact observed for the 6 μ band of water vapour and for the 4.3 μ carbon dioxide band[6] (cf. ref.[7]).

9. The considerations presented above are rather incomplete and have not resulted in unambiguous conclusions. Nevertheless, I believe them to be of a certain interest, because they indicate a way in which we may investigate the limitations of our usual mechanical concepts. If the results of new and more complete investigations of infrared spectra should turn out to be incompatible with considerations like those used above, this might probably indicate that we have to resort to similar revolutionary intuitions for explaining the radiation connected with the vibrations and rotations of the molecules as has been done recently by N. Bohr[8] in the case of electronic radiation.

ON THE METHOD USED FOR THE CALCULATIONS

10. *Calculation of the infinitesimal vibrations of a carbon dioxide molecule assuming central forces (cf. 3 and 4).* The vibrations have been calculated by means of Lagrange's equations of motion:

$$\frac{\partial (T-U)}{\partial r_i} = \frac{d}{dt} \frac{\partial T}{\partial r_i'}, \quad i = 1, 2, 3. \tag{1}$$

where T is the kinetic energy and U the potential energy. First, expressions for U and T are formed:

$$U = \tfrac{1}{2}k_1 r_1^2 + \tfrac{1}{2}k_2 \ r_2^2 + \tfrac{1}{2}k_2 r_3^2 \tag{2}$$

4*

and

$$T = \frac{1}{2N}[A\,r_1'^2 + B r_2'^2 + B r_3'^2 + 2D r_2' r_3' + 2E r_1' r_3' + 2E r_1' r_2'] \tag{3}$$

In equation 3 N is Avogadro's constant and the coefficients A, B, D, E, have the following values:

$$\left.\begin{aligned} A &= \frac{m_2}{2} + \frac{m_1 m_2}{2M} \cdot \mathrm{tg}^2\,\theta, \qquad B = \frac{m_1 m_2}{2M\cos^2\theta} \cdot \frac{M + m_1 \cos^2\theta}{M - 2m_2 \cos^2\theta} \\[2mm] D &= \frac{m_1 m_2}{2M\cos^2\theta} \cdot \frac{M\sin^2\theta - 2m_2\cos^2\theta}{M - 2m_2\cos^2\theta}, \qquad E = -\frac{m_1 m_2}{2M} \cdot \frac{\sin\theta}{\cos^2\theta} \\[2mm] m_1 &= 12, \qquad m_2 = 16, \qquad M = m_1 + 2m_2 = 44 \end{aligned}\right\} \tag{4}$$

After insertion of the expressions for T and U the Lagrangian equations take the following form:

$$\left.\begin{aligned} A\frac{d^2 r_1}{dt^2} + E\frac{d^2 r_2}{dt^2} + E\frac{d^2 r_3}{dt^2} + N k_1 r_1 &= 0 \\[2mm] E\frac{d^2 r_1}{dt^2} + B\frac{d^2 r_2}{dt^2} + D\frac{d^2 r_3}{dt^2} + N k_2 r_2 &= 0 \\[2mm] E\frac{d^2 r_1}{dt^2} + D\frac{d^2 r_2}{dt^2} + B\frac{d^2 r_3}{dt^2} + N k_2 r_3 &= 0 \end{aligned}\right\} \tag{5}$$

The solutions of these equations have the following form:

$$\left.\begin{aligned} r_1 &= a_1 \sin\left(t \cdot \frac{2\pi}{T} + \alpha\right) \\[2mm] r_2 &= a_2 \sin\left(t \cdot \frac{2\pi}{T} + \alpha\right) \\[2mm] r_3 &= a_3 \sin\left(t \cdot \frac{2\pi}{T} + \alpha\right) \end{aligned}\right\} \tag{6}$$

The period of vibration, T, and the amplitudes, a_1, a_2, a_3 must satisfy the following three equations:

$$\left.\begin{aligned} \left(A - \frac{N k_1}{4\pi^2} T^2\right) a_1 + E a_2 + E a_3 &= 0 \\[2mm] E a_1 + \left(B - \frac{N k_2}{4\pi^2} \cdot T^2\right) a_2 + D a_3 &= 0 \\[2mm] E a_1 + D a_2 + \left(B - \frac{N k_2}{4\pi^2} \cdot T^2\right) a_3 &= 0 \end{aligned}\right\} \tag{7}$$

If we introduce

$$\frac{N}{4\pi^2} \cdot T^2 = x \qquad (8)$$

and then eliminate a_1, a_2, and a_3, we get:

$$\begin{vmatrix} A - k_1 x & E & E \\ E & B - k_2 x & D \\ E & D & B - k_2 x \end{vmatrix} = 0 \qquad (9)$$

This determinant 9 can be transformed as follows:

$$[k_2 x - (B - D)] \cdot [x^2 k_1 k_2 - x(k_1(B+D) + k_2 A) + (B+D)A - 2E^2] = 0 \quad (9a)$$

If λ_1, λ_2, and λ_3 are the wave-lengths of the carbon dioxide bands the following values of x must satisfy equation 9a:

$$\lambda_1^2 \cdot \frac{N}{4\pi^2 c^2}, \quad \lambda_2^2 \cdot \frac{N}{4\pi^2 c^2}, \quad \lambda_3^2 \cdot \frac{N}{4\pi^2 c^2} \qquad (10)$$

In these expressions c is the velocity of light. We shall denote the numerical values of these three expressions as α_1, α_2, and α_3.

Because α_1, α_2, and α_3 are roots of equation 9a the following three relations are valid:

$$\left. \begin{aligned} k_2 \alpha_1 &= B - D \\ k_1 k_2 \alpha_2 \alpha_3 &= (B+D)A - 2E^2 \\ k_1 k_2 (\alpha_2 + \alpha_3) &= k_1(B+D) + k_2 A \end{aligned} \right\} \qquad (11)$$

One must remember, however, that it is sufficient if a similar set of relations with permuted α-indices are satisfied.

By insertion of the values for A, B, D, E in equations 11 one obtains:

$$\left. \begin{aligned} k_2 \alpha_1 &= \frac{m_1 m_2}{M - 2 m_2 \cos^2 \theta}; \quad k_1 k_2 \alpha_2 \alpha_3 = \frac{m_1 m_2^2}{2 M \cos^2 \theta} \\ k_1 k_2 (\alpha_2 + \alpha_3) &= k_2 \frac{m_2}{2 M} \cdot \frac{m_1 + 2 m_2 \cos^2 \theta}{\cos^2 \theta} + k_1 \frac{m_1 m_2}{M \cos^2 \theta} \end{aligned} \right\} \qquad (12)$$

From equations 12 one finds k_1, k_2, and $\cos^2 \theta$. After elimination of k_1 and k_2 one gets a second order equation in $\cos^2 \theta$. Afterwards α_1 is changed for α_2, resp. α_3, and these equations are solved. In total one would expect six values for $\cos^2 \theta$. Four of these are, however, imaginary in θ and only two real solutions are obtained.

After the calculation of k_1, k_2, and θ, the amplitudes are found from the equations 7.

For the root (α_1), which was put equal to $\dfrac{B - D}{k_2}$ (equation 11) one gets:

$$a_1 = 0, \qquad a_2 = - a_3. \qquad (13)$$

And for the two other roots (α_2 and α_3) one gets:

$$\frac{a_2}{a_1} = \frac{a_3}{a_1} = -\frac{E}{B+D-k_2\alpha} = -\frac{A-k_1\alpha}{2E} \tag{14}$$

Finally, one can calculate the vibrations of each individual atom from the changes of the atomic distances (a_1, a_2, a_3) by means of the following relations.

When $a_1 = 0$ and $a_2 = -a_3$, the carbon atom is vibrating perpendicular to the symmetry axis and the oxygen atoms vibrate along the isosceles of the triangle. To characterize a vibration it is sufficient to know a quantity, p, defined in the following way:

$$p = \frac{\text{amplitude of the O-atoms}}{\text{amplitude of the C-atom}}$$

One can calculate p from the equation:

$$p = \frac{12}{32} \cdot \frac{1}{\sin \theta} \tag{15}$$

For the two other vibrations, where $a_2 = a_3$, the angle between the base of the triangle and the direction of vibration of the oxygen atoms is determined by:

$$\operatorname{tg} \varphi = \frac{12}{44} \cdot \frac{2 \cdot \dfrac{a_2}{a_1} - \sin \theta}{\cos \theta} \tag{16}$$

And p is expressed by:

$$p = \frac{12}{32} \cdot \frac{1}{\sin \varphi} \tag{17}$$

11. *Calculation of the infinitesimal vibrations of a carbon dioxide molecule assuming valence forces* (cf. 5). In this case the expression for T, the kinetic energy, is identical with equation 3. The potential energy, U, is given by:

$$U = \tfrac{1}{2}k_2r_2^2 + \tfrac{1}{2}k_2r_3^2 + \tfrac{1}{2}k_\theta l^2 d\theta^2. \tag{18}$$

By transformation, insertion of ν_3 for $d\theta$, we get:

$$U = \tfrac{1}{2}k_1r_1^2 + \tfrac{1}{2}(k_2 + k_1\sin^2\theta)r_2^2 + \tfrac{1}{2}(k_2 + k_1\sin^2\theta)r_3^2$$
$$+ k_1\sin^2\theta\, r_2r_3 - k_1\sin\theta\, r_1r_3 - k_1\sin\theta\, r_1r_2. \tag{20}$$

Here, too, $k_1 = \dfrac{k_\theta}{4\cos^2\theta}$ is introduced.

If we integrate the Lagrangian equations as done above we get the following equation, instead of 9a, for the determination of x:

$$[k_2 x - (B - D)] \cdot [k_1 k_2 x^2 - (k_1(B + D) + A(k_2 + 2k_1 \sin^2\theta) \\ + 4Ek_1 \sin\theta)x + A(B + D) - 2E^2] = 0 \tag{21}$$

Again if α_1, α_2, α_3 are defined by the relations 10 we get for the evaluation of k_1, k_2, and θ the three equations:

$$k_2\alpha_1 = B - D, \quad k_1 k_2 \alpha_2 \alpha_3 = A(B + D) - 2E^2 \\ k_1 k_2(\alpha_2 + \alpha_3) = (B + D + 2A\sin^2\theta + 4E\sin\theta)k_1 + Ak_2 \tag{22}$$

resp. the corresponding equations with permuted α's.

After insertion of the numerical values for A, B, D, E one gets:

$$k_2\alpha_1 = \frac{48}{11 - 8\cos^2\theta}, \quad k_1 k_2 \alpha_2 \alpha_3 = \frac{384}{11} \cdot \frac{1}{\cos^2\theta} \\ k_1 k_2(\alpha_2 + \alpha_3) = k_2 \cdot \frac{8}{11} \cdot \frac{3 + 8\cos^2\theta}{\cos^2\theta} + k_1 \cdot \frac{16}{11}(11 - 8\cos^2\theta) \tag{23}$$

After elimination of k_1 and k_2 one finally obtains:

$$\frac{\alpha_2 \alpha_3}{\alpha_1} \cdot \frac{3 + 8\cos^2\theta}{11 - 8\cos^2\theta} + \alpha_1 \frac{(11 - 8\cos^2\theta)^2}{33} = \alpha_2 + \alpha_3 \tag{24}$$

from which $\cos^2\theta$ is found.

From equations 23 k_1 and k_2, and from 20 k_θ are easily found.

The calculation of the proportions between a_1, a_2, and a_3 is carried through in the following way. For the root (α_1), which is put equal to $\dfrac{B - D}{k_2}$, one has as before:

$$a_1 = 0, \quad a_2 = -a_3. \tag{25}$$

And for the two others $(\alpha_2$ and $\alpha_3)$:

$$\frac{a_2}{a_1} = \frac{a_3}{a_1} = -\frac{A - k_1\alpha}{2(E + k_1\alpha \sin\theta)} = -\frac{E + k_1 \sin\theta}{B + D - 2\alpha k_1 \sin^2\theta - \alpha k_2} \cdot \tag{26}$$

The calculation of the vibrations of each individual atom from a_1, a_2, and a_3 proceeds in exactly the same way as for central forces.

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