NOVEMBER, 1928 PHYSICAL REVIEW VOLUME 32

THE NEAR INFRA-RED VIBRATION SPECTRUM OF THE CARBONATES

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Abstract

An attempt has been made to solve theoretically the problem of the frequencies and intensities of the near infra-red absorption regions of the carbonate group. The assumption, that in the normal state the oxygen nuclei are located at the vertices of an equilateral triangle while the carbon nucleus lies at the center, seems justified by the x-ray investigations of the crystal structure of the group. Using a general potential energy function with three constants under the assumption that the fields of force surrounding the nuclei are central, the normal modes of infinitesimal vibration are determined, yielding four independent frequencies ν_1, ν_2, ν_3, and ν_4, of which ν_4 is optically inactive. Through the three disposable constants, ν_1, ν_2, and ν_3 may be made to coincide with the three fundamental absorption regions found experimentally by Schaefer and Schubert, and it is found that the optically inactive frequency ν_4 agrees closely with the value predicted by Schaefer, Bermuth and Matossi. From a consideration of the change of electric moment, the theoretical intensities are determined. It is found that the relative intensities obtained theoretically agree well with the values determined by Schaefer and Schubert.

IN THE near infra-red absorption spectra of the group of crystals calcite ($CaCO_3$), magnesite ($MgCO_3$), dolomite ($Mg(CO_3)_2Ca$), and others, there are observed three principal regions of absorption at 6.7μ, 11.38μ, and 14.16μ, which may be attributed to the fundamental vibrations of the carbonate radical. Of these the region at 11.38μ has been shown by Schaefer and Schubert[1] to correspond to a vibration along the optical axis of the crystal while the other two correspond to vibrations perpendicular to this axis. In addition to the three principal absorption regions there are a number of weaker absorption peaks which may be interpreted as harmonics and combinations of the fundamental frequencies. An essential point of this interpretation, however, is that besides the three observed fundamentals there must exist a fourth fundamental frequency which lies at about 9.0μ. Since this latter can not be determined directly, but only through combination bands, it is termed optically inactive.

From x-ray analysis of the structure of these carbonates, we learn that the carbonate configuration is an equilateral triangle at whose vertices are located the oxygen particles and at whose center is located the carbon particle. The distance from an oxygen atom to the carbon atom is given by Wycoff as 1.225×10^{-8} cm. The plane of the three oxygen atoms is perpendicular to the optical axis, hence it may be concluded from the work of Schaefer and Schubert that the vibrations corresponding to the regions of absorption at 6.7μ and at 14.16μ lie in the carbonate plane while that at 11.38μ is perpendicular to it.

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[1] Cl. Schaefer and M. Schubert, Ann. d. Physik, **50**, 283 (1916).

H. Kornfeld[2] has attacked the problem of the vibrations of the carbonate group with considerable success. In order to obtain the potential energy function he has assumed that each oxygen particle is the seat of a double negative charge and that the carbon particle possesses a fourfold positive charge. He has further assumed that the electron configuration that surrounds each oxygen is capable of a polarization. Using the two disposable constants α, the polarization and r, the distance of an oxygen atom from the carbon atom he has been able to correlate his theoretical values for the frequencies with the observed values with an accuracy of from 10 to 15 percent. The value of r which he found was 1.5×10^{-8}, a value somewhat larger than that given by x-ray analysis.

In the light of our present knowledge of the structure of molecules, Kornfeld's model is subject to criticism on the ground that the atoms composing a molecule are probably not completely ionized as he has assumed, but rather that there exists a large perturbation resulting in a more or less mutual sharing of electrons among the atoms. In the present note it is proposed to analyze the motion of the carbonate group by the use of a general potential energy function with three disposable constants.

Certain assumptions must, however, be made with regard to the form of the potential energy function and we shall consider that the forces surrounding each atom are central, believing that the departure from this assumption caused by the presence of polarizations will not in first approximation alter the character of the motion or the fundamental frequencies.

The assumption is made herein that the amplitudes of vibration of the nuclei are small so that the higher order terms of the potential and kinetic energy may be neglected. The system which we are considering is one of twelve degrees of freedom, but since we are chiefly interested in the vibrations we may choose only six mutual coordinates neglecting the translational and rotational motion of the group as a whole. If the displacements of the oxygen atoms with respect to each other are represented by q_1, q_2, q_3; and the displacements of the oxygens with respect to the carbon by q_4, q_5, q_6; then since the forces acting on the nuclei are considered to be central, the potential energy for an arbitrary displacement may be expressed as follows:

$$W=\sum_{i=1}^{3}f(q_i)+\sum_{k=4}^{6}F(q_k) \tag{1}$$

where f and F are unknown functions. W may be developed by Taylor's theorem, and all terms above the second order disregarded.

$$\begin{aligned}W=W_0&+(df/dq_i)_0(q_1+q_2+q_3)+(dF/dq_k)_0(q_4+q_5+q_6)\\&+(1/2)(d^2f/dq_i^2)_0(q_1^2+q_2^2+q_3^2)+(1/2)(d^2F/dq_k^2)_0(q_4^2+q_5^2+q_6^2)+\cdots\end{aligned} \tag{2}$$

Only three of the four constants that appear in this expression for the potential energy are independent since the equilibrium condition imposes the relation:

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[2] H. Kornfeld, Zeits. f. Physik **26**, 205 (1924).

$$(df/dq_i)_0=(1/3^{1/2})(dF/dq_k)_0. \qquad (3)$$

It is found convenient for calculation to express the potential energy in slightly different coordinates. The coordinates used are the q_1, q_2, q_3 defined above, and three others, x, y, z, components of a vector R which represents the distance of the carbon particle from the center of gravity of the oxygen nuclei. The kinetic and potential energies for infinitesimal displacements may quite readily be determined under the conditions that the linear and angular momenta of the molecules shall be zero, by letting each coordinate vary independently and then studying the total resultant displacement of each nucleus. Treating the energy expressions in the usual manner to determine the normal modes of vibration, the characteristic determinant,[3] the roots of which determine the frequencies may be written in this case:

$$\left(\frac{3}{\mu}\lambda-\frac{3\cdot 3^{1/2}}{2}\beta\right)\left(\frac{\lambda}{3}-\frac{1}{3}-\alpha\right)\left(\frac{2}{\mu}\lambda^2-\lambda\left[1+\frac{1}{\mu}+\frac{3^{1/2}}{2}\beta\left(1+\frac{1}{\mu}\right)+\frac{3}{\mu}\alpha\right]\right.$$
$$\left.+3^{1/2}\beta+\frac{3\cdot 3^{1/2}}{4}\alpha\beta+\frac{3}{2}\alpha\right)^2=0,$$

where:

$$\alpha=K_1/K_2\ ;\quad \beta=c/K_2\ ;\quad \mu=(M+3m)/M\ ; \qquad (4)$$

$$\frac{1}{a}\left(\frac{dF}{dq_k}\right)_0=\frac{c}{2}\ ;\quad \left(\frac{d^2f}{dq_i^2}\right)_0=K_1\ ;\quad \left(\frac{d^2F}{dq_k^2}\right)_0=K_2.$$

and where a is the normal side of the equilateral triangle configuration. The roots of the determinant shall be denoted by λ_1, λ_2, λ_3, and λ_4, where λ_2 and λ_3 are the double roots and where $\lambda_2>\lambda_3$. These give rise to four independent frequencies, ν_1, ν_2, ν_3 and ν_4, where

$$\nu_i=(1/2\pi)(K_2\lambda_i/m)^{1/2}$$

These frequencies are respectively:

$$\nu_1=\frac{1}{2\pi}\left(\frac{K_2}{m}\right)^{1/2}\left[\frac{3^{1/2}\beta\mu}{2}\right]^{1/2};\quad \nu_4=\frac{1}{2\pi}\left(\frac{K_2}{m}\right)^{1/2}(1+3\alpha)^{1/2}$$

$$\nu_2=\frac{1}{2\pi}\left(\frac{K_2}{m}\right)^{1/2}\left\{\frac{2+3^{1/2}\beta(\mu+1)+6\alpha}{8}+\left[\frac{\mu-1}{2}\left(\frac{1}{2}+\frac{3^{1/2}\beta}{4}\right)+\frac{3\alpha}{4}\right]\right\}^{1/2} \qquad (5)$$

$$\nu_3=\frac{1}{2\pi}\left(\frac{K_2}{m}\right)^{1/2}\left\{\frac{2+3^{1/2}\beta(\mu+1)+6\alpha}{8}-\left[\frac{\mu-1}{2}\left(\frac{1}{2}+\frac{3^{1/2}\beta}{4}\right)+\frac{3\alpha}{4}\right]\right\}^{1/2}$$

The system is degenerate since while it has six degrees of vibrational freedom, only four independent frequencies enter into its motion.

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[3] E. T. Whittaker, A Treatise on the Analytical Dynamics, 3rd edition, p. 178.

A study of the motion reveals that ν_1 corresponds to a vibration of the carbon nucleus along the axis of symmetry of the model, the distance between the oxygen nuclei remaining unchanged. Since λ_2 and λ_3 are each double roots two arbitrary constants occur in the motion corresponding to ν_2 and ν_3. This corresponds to a motion of the carbon particle in the plane perpendicular to the axis of symmetry, the path being an ellipse subject to the restriction that the sum of the squares of the major and minor axes is a constant. The eccentricity as well as the orientation of the path will depend on the arbitrary constants involved. The frequency ν_4 corresponds to a motion of the oxygen nuclei symmetrical with respect to the axis of symmetry, the carbon remaining fixed at the center of gravity. It should be noted that this latter is the inactive frequency, for unlike the other three vibrations there is here no changing electric moment.

The theoretical frequencies which the model predicts contain three constants α, β, and K_2 which may be determined by using the observed values of the three bands. The experimental work of Schaefer and Schubert shows that the absorption regions at $6.7\mu(447\times10^{11})$ and $14.16\mu(212\times10^{11})$ are due to vibrations of the carbon in the plane of the model. Since $\lambda_2>\lambda_3$ and $\lambda_i\propto\nu_i^2$ we can immediately identify ν_2 and ν_3 with the frequencies 447×10^{11} and 212×10^{11} respectively. The region at $11.38\mu(263.5\times10^{11})$ is evidently due to a vibration of the carbon nucleus perpendicular to the plane of the model since it disappears when the spectrum is observed with the crystal cut perpendicular to the optical axis. Hence we identify ν_1 with the frequency 263.5×10^{11}. The values obtained for these constants are:

$$\alpha=0.263;\qquad \beta=0.248;\qquad K_2=3.064\times10^4.$$

Knowing these values it is now possible to compute theoretically the position of the band corresponding to the inactive frequency ν_4, and we obtain the value 8.98μ which is in good agreement with that predicted by Schaefer and his collaborators.[4]

We now proceed to the computation of the values of the theoretical intensities. It may be shown that the integral of the coefficient of absorption α over an absorption region is associated with the amplitude of the change of the electric moment by the relation:

$$(g_0/g_i)\int\alpha_\nu d\nu=KA^2{}_i\nu_i \tag{6}$$

where A_i denotes the amplitude of the change of the electric moment and where g_0 and g_i are the *a priori* probabilities of the normal and the ith states respectively and where K is a constant independent of ν_i. α_ν is the absorption coefficient which is to be determined experimentally. Following the notation of Dennison[5] we shall let ρ_i^2 equal the left member of (6) and be defined as the experimental intensity, while the right member shall be defined as the theoretical intensity.

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[4] Cl. Schaefer, C. Bermuth, and F. Matossi, Zeits. f. Physik **39**, 648 (1926).

[5] D. M. Dennison, Phil. Mag. **1**, 195 (1926).

In accordance with the assumptions made earlier that the forces acting upon the nuclei are central, it is now assumed that each nucleus may be thought of as the seat of an effective charge and hence that the change of electric moment is directly proportional to the displacements of the carbon nucleus with respect to the center of gravity of the oxygen atoms. It is to be expected that this assumption will hold best in comparisons between the intensities of bands corresponding to motions involving the same direction of displacement of the carbon atom, that is between the bands at 6.7μ and 14.16μ, and to hold less well for the 11.38μ band where the carbon vibrates perpendicular to the plane of the oxygens. According to the assumption just stated A_i, the amplitude corresponding to the fundamental band ν_i will be given by the product of the amplitude of the normal coordinate and K_i, a proportionality constant between the displacement of the carbon and the normal coordinate.

$$A_i^2 = hK_i^2/2\pi m\nu_i$$

The theoretical intensities of the active frequencies appear in the fourth column of Table I, where the constant is so chosen that the theoretical and experimental intensities of the band at 6.7μ are in agreement.

TABLE I.

	Frequency (Theo.)	Frequency (Obs.)	Direction of vibration of electric moment relative to line of symmetry	(Theo.) ρ_i^2	(Obs.) ρ_i^2
ν_1	263.4×10^{11}	263.5×10^{11}	$\parallel$	34	17
ν_2	447.0	447.	$\perp$	30	30
ν_3	211.9	212.	$\perp$	4	4
ν_4	334.0	330. (predicted value)	...	0	0

The fifth column of the table contains the experimental intensities as estimated from the reflection curves of Schaefer and Schubert. Due to the extreme intensity of absorption of the fundamental bands in the carbonates, the values for α have never been measured. It may readily be proved, however, that to every maximum of absorption there exists a corresponding maximum of reflection, i.e., where r, the reflection coefficient becomes a maximum. The two maxima do not exactly coincide, the reflection maximum being displaced slightly toward the longer wave-lengths. It may further be shown that for the range of reflections in which we are interested the reflection coefficient r is approximately proportional to the absorption coefficient and hence the observed reflection curves already mentioned may be used for determining the experimental intensities. The *a priori* probabilities g_0 and g_i are all to be taken equal to unity since the measurements of Schaefer and Schubert were made with a crystal cut parallel to the optical axis. No claim is made that the experimental intensities here given are of any great precision, but it is believed that they are of the right order of magnitude.

In conclusion we may say that by using a simplified potential energy function with three disposable constants, it has been possible to correlate three of the four independent frequencies ν_1, ν_2, ν_3, to the three fundamental absorption regions measured experimentally by Schaefer and Schubert, while it has been shown that the fourth, optically inactive frequency ν_4 coincides very closely with the value predicted by Schaefer, Bermuth and Matossi from combination bands. A comparison of the theoretical and experimental intensities has been made resulting in an agreement which we believe to be real and to furnish at least a partial vindication of the simplicity of the method which we have employed.

I wish to utilize this opportunity to express my gratitude to Professor D. M. Dennison at whose suggestion I undertook this problem and who through his many helpful suggestions has aided me in the preparation of this paper.

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July 30, 1928.