Low Frequency Raman Spectrum of Calcite

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Errata: Low Frequency Raman Spectrum of Calcite
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recognize that in this problem we are dealing with well-defined thermodynamic functions. Equation (9) derived from the laws of thermodynamics and the assumed equation of state gives β as follows:

$$\beta = (C_v + R)/C_v - (\partial\alpha/\partial v_2)_s + (\partial E/\partial v)_T nR/C_v p_2. \quad \text{(b)}$$

Since no critical points are involved, obviously the two functions α and $(\partial E/\partial v)_T$ are single valued in v, and one should thus expect β to be a single-valued function of v. However, if one needs an additional argument, the integration constant referred to by Paterson may be established as zero from the fact that Eq. (b) must reduce to $\beta = C_p/C_v = \gamma$ for the case where factors for non-ideality become vanishingly small, a condition which applies in the detonation of gaseous explosives. In fact, Paterson's argument should apply equally well to any assumed equation of state but is invalidated for one thing by the experimental verification of the hydrodynamic theory for gaseous explosives.

[1] S. Paterson, J. Chem. Phys. 16, 159 (1948).
[2] M. A. Cook, J. Chem. Phys. 15, 518 (1947).

Ignition of Explosive Gas Mixtures by Electric Sparks. Minimum Ignition Energies

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IN a recent paper[1] Lewis, von Elbe, and co-workers conclude that there exist minimum values for the energies of electric sparks which initiate flames in explosive gas mixtures, and that these values may be considered as absolute minimum values. In a second paper[2] Lewis and von Elbe develop a theory showing the existence of an absolute minimum energy in the case of flames propagated from an instantaneous point source of ignition, and they consider that the theory can be applied to capacitance sparks.

Attention must be paid to the fact that other experiments[3] have given results contradictory to the conclusions of the authors. These experiments have shown that for given mixtures effective minimum energy values exist, but that these are not absolute values and depend (1) on the voltage applied to the spark gap and (2) on the shape of the electrodes. For the best inflammable mixtures the relationship between the voltage applied to the gap and the capacity of the system is of the form CV^x = constant, with $x = 3$ when the two electrodes have sharp points, $x \simeq 6$ if one of them has a sharp point, the other being a large sphere or a plane surface, $x \simeq 9$ if the two are large spheres or plane surfaces.

No theory has been developed to explain these results. But it appears that they may agree with Lewis and von Elbe's theory provided that the following assumptions are made: (1) the maximum amount of energy distributed in the ignition zone depends directly on the energy of the fastest electrons initiating an avalanche process in the first steps of the spark discharge and (2) chain carriers in this zone are, or are generated by, charged particles, which travel through the gap with a mean velocity approximately proportional to that of particles starting from the electrodes. Since the energy of such particles is proportional to V, and because the minimum energy values are inversely proportional to V in the case of sharp electrodes, this suggests that the energy in the ignition zone depends directly on the energy per initiating particle, and that the geometry of the gap need not to be taken into account. If one of the electrodes is a plane surface, the field distribution is different, the lines of force being approximately parallel near the surface. In this case it is necessary to take into account the effect of this non-radial distribution on the density of chain carriers in active zones, such as are formed along current bursts or streamers in the spark gap during the first steps of the discharge. The factor $V^3 = (V^{\frac{3}{2}})^2$ is apparently due to this non-radial field distribution. This factor may be introduced on the assumptions (1) that the number of carriers given rise to by an electron of energy eV is proportional to V and (2) that the rate of formation of carriers depends directly on the velocity of such an electron, proportional to $V^{\frac{1}{2}}$. In the case of two spheres or plane surfaces, the proportionality to $1/V \cdot 1/V^3 \cdot 1/V^3$ appears also to be due to the geometry of the gap. The double factor $(1/V^3 \cdot 1/V^3)$ suggests that both electrodes are effective in the generation of carriers.

[1] M. V. Blanc, P. G. Guest, Guenther von Elbe, and Bernard Lewis, J. Chem. Phys. 15, 798 (1947).
[2] Bernard Lewis and Guenther von Elbe, J. Chem. Phys. 15, 803 (1947).
[3] Rodolphe Viallard, Comptes Rendus 207, 1405 (1938); J. de chim. Phys. 40, 101 (1943).

Low Frequency Raman Spectrum of Calcite

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IT has been demonstrated by Raman and Nedungadi[1] that because of their particular polarization characters two low frequency Raman lines in a $NaNO_3$ crystal are attributable to angular oscillations of NO_3 ions. Later Kastler, Rousset, and other authors[2] established that also in organic crystals (benzene, naphthalene, paradicloro-benzene, paradibromobenzene) low frequency lines, which disappear at the liquid state giving place to a continuum at the sides of the exciting line, are to be assigned to oscillations of the same type.

However, for $NaNO_3$ the question has not yet been cleared entirely; in fact, we are not aware that the presence of two low frequency Raman lines, both attributable to angular oscillations, has been explained. Also the calcite, which has a structure analogous to the $NaNO_3$, presents two low frequency Raman lines. We have examined the polarization state of these lines illuminating a calcite crystal parallel to the optic axis, and collecting the diffuse light perpendicular to it.

In Fig. 1 (a) and (b) the microphotometer curves of two spectra relative to the electric vector, and respectively parallel and perpendicular to the optic axis, are repro-
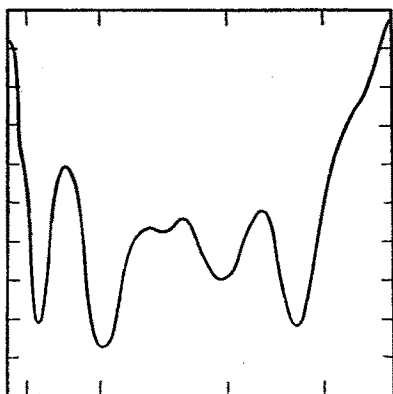
FIG. 1. Microphotometer curves of Raman spectra of calcite relative to the electric vector (a) parallel and (b) perpendicular to the optic axis.

First plane

Second plane

Third plane

FIG. 2. Situation of a CO_3 ion relating to the nearest Ca ion appertaining to the two adjacent planes.

duced. Examination of these shows that, as for $NaNO_3$, while the internal lines (1088 and 1437 cm^{-1}) are polarized with the electric vector perpendicular to the optic axis, both the external lines (155 and 282 cm^{-1}) are polarized with the electric vector parallel to the optic axis. This result shows that in calcite crystal the CO_3 ions can execute angular oscillations around axes perpendicular to the optic axis with two different frequencies. The angular oscillations of the ions appertaining to a certain domain of the crystal shall give a non-zero resultant only if they are incoherent or coherent and in phase. However, since external lattice oscillations are in question, the last seems to be the only possibility.

An explanation of the possibility of two angular oscillating frequencies in phase for all the ions appertaining to a certain domain of the crystal can be derived from the examination of the calcite lattice structure. The calcite lattice is constituted by lattice planes of Ca alternated with planes of CO_3, perpendicular to the optic axis. Figure 2 shows the situation of a CO_3 ion relating to the nearest Ca ions appertaining to the two adjacent planes: each atom O is at equal distance from two atoms Ca. Now if we displace the CO_3 ion in its plane, for instance in the direction indicated in Fig. 2, the atom O aligned with C in this direction maintains itself at equal distance from the two Ca; for the other two atoms O, on the contrary, the equi-
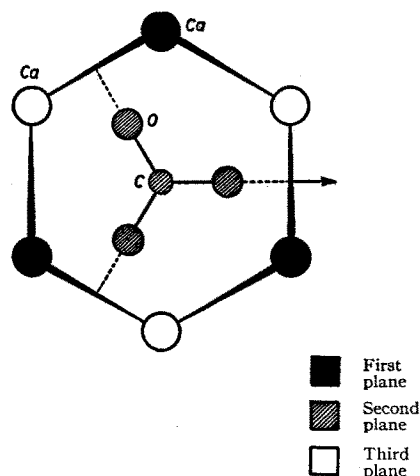
distance conditions are altered: while for the one the distance from the inferior Ca increases and the distance from the superior Ca decreases, for the other the opposite occurs. Therefore, there will arise a moment which tends to turn the ion around the translation direction.

The situation of CO_3 relating to Ca is always such that a translation of the Ca lattice relating the CO_3 lattice perpendicularly to the optic axis causes, in the CO_3 ions, a moment which tends to turn every one in the same sense. So the angular oscillations of CO_3 ions cannot be independent of the oscillations of the two lattices of Ca and CO_3, the one against the other, but only oscillations are possible which consist in translatory motions perpendicular to the optic axis, accompanied by a periodical variation in the orientation of the CO_3 ions. Then the conditions are similar to the ones of two coupled oscillators, which form a system capable of oscillating with two frequencies. These two external frequencies of calcite should be active in the infra-red. They could correspond to two reflection maxima found by the residual-ray method, considering that by this method the oscillation frequencies of a crystal can be established only approximately.[3]

[1] C. V. Raman and T. M. K. Nedungadi, Nature 143, 679 (1939).
[2] For the bibliography on this argument see A. Kastler and A. Rousset, Phys. Rev. 71, 455 (1947).
[3] C. Schaefer and M. Schubert, Ann. d. Physik 50, 283 (1916).