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Theory of Dielectric Absorption due to Rotational Oscillations in Crystalline Long Chain Substances

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Résumé.

L'absorption due aux oscillations rotationnelles de molécules dipolaires à l'état solide a lieu probablement dans la bande $\lambda = 1$ millimètre. On peut prévoir qu'il sera possible de mesurer cette absorption avec les méthodes expérimentales actuellement en cours de développement.

Dans le cas de cétones à longue chaîne, la symétrie cristalline laisse prévoir que si la molécule vibre d'une manière rigide, il doit y avoir deux raies d'absorption dont les fréquences sont déterminées par les forces intermoléculaires. Mais si ces forces sont du même ordre de grandeur que les forces intramoléculaires qui fixent les fréquences de torsion des molécules, il doit y avoir beaucoup plus de raies d'absorption, groupées en une ou deux bandes larges. Ainsi, la détermination du spectre d'absorption doit nous renseigner à la fois sur les forces intermoléculaires et sur celles qui fixent les fréquences de torsion des molécules en longues chaînes.

In dipolar materials, dielectric measurements are usually concerned with processes where the molecules turn by rather large angles. In many crystals, however, the turning of molecules by large angles is such a rare event that there is no measurable dielectric effect associated with it. Nevertheless, in such crystals the molecules can still execute "librations", i.e. rotational oscillations of small amplitude, around their equilibrium direction. The absorption connected with these oscillations is probably somewhere between 1 cm and 10^{-2} cm, depending on the nature of the material. So far this frequency region has been difficult from the experimental point of view and as a result no definite experimental information exists concerning librational absorption. But in view of recent developments in experimental techniques, it may be hoped that in the near future it will be possible to measure this kind of absorption. Since the libration

is governed by the forces which the molecules exert upon each other, absorption measurements would provide very valuable information concerning the inter-molecular forces in molecular crystals.

If one wants to apply such absorption measurements to the study of materials with long chain molecules, it is of course necessary to choose materials whose molecules are dipoles. From the theoretical point of view, long chain ketones with a single CO-group are particularly suitable for such a study. The dipole moment of such a ketone is in the direction of the carbon-oxygen bond, i.e. it is perpendicular to the chain axis. A picture of the crystal structure is reproduced, for instance, in a paper by H. Frohlich (*Proc. Roy. Soc. A.*, 185, 1946, p. 400, fig. 1). For an approximate discussion one may assume that the chain axes of all the molecules are parallel to each other and that the unit cell consists of two molecules the dipole moments of which lie in one plain but make an angle of about 60° with each other.

If we assume that the intra-molecular forces are much stronger than the inter-molecular forces, then we expect the molecules to vibrate rigidly. Since the molecular chains are very long, vibrations around any axis perpendicular to the chain are negligible and only rotational vibrations around the chain axis can have appreciable amplitudes. In other words, there is essentially one rotational degree of freedom per molecule. Since there are two molecules in a unit cell, the crystal will have two optically active modes of rotational vibrations. Whatever the nature and magnitude of the inter-molecular forces, it follows from simple symmetry considerations that in one of these vibrations the two molecules of a unit cell rotate in the same sense with respect to the clock (i.e. in one half of a cycle they both rotate clockwise, in the other half both rotate anti-clockwise); while in the other vibration the two molecules rotate in opposite sense, i.e. when one rotates clockwise, the other rotates anti-clockwise.

Hence, if the intra-molecular forces are strong there will be two absorption lines due to libration. On the other hand, if those intra-molecular forces which govern the twisting of the molecules around the carbon-carbon bonds are not much stronger than the inter-molecular forces, then the molecules no longer librate rigidly. In this case each molecule has many rotational degrees of freedom, approximately as many as the number of carbon-carbon bonds in the molecule. Instead of two single absorption lines there should then be two series of absorption lines, which in practice will probably result in one or two broad bands.

An experimental determination of the librational absorption spectrum of such ketones would therefore give valuable information concerning both the inter-molecular forces and also concerning those forces which govern the twisting of long chain molecules.

The present paper is a strongly abbreviated account of a theoretical investigation which has been carried out into this subject. A more detailed version will be published elsewhere.
