

Raman Frequencies of Dioxane

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The Rotation of Some Long Molecules in the Solid State

In order to investigate the possible rotation of long molecules in crystals dielectric constant measurements have been made upon carefully purified substances with long-chain molecules in the solid and liquid states, the apparatus used being that employed in previous work.¹

The dielectric constant of ethyl undecylate drops sharply on solidification, after which it decreases slowly and uniformly with falling temperature in the manner commonly shown by polar substances in which some of the molecules may have some slight freedom of bending or rotation without the existence of any general rotational freedom.

Ethyl palmitate, which undergoes a monotropic transition from an α - to a β -form immediately upon solidification at 19.6°, shows a sharp rise in dielectric constant as solidification occurs followed within 0.5° of the freezing point by a drop twice as great. The further slow but uniform decrease of dielectric constant with falling temperature is interrupted by a slight but reproducible hump in the curve at 14.6°. The dielectric constant of the β -form, which melts at 22°, rises to that of the liquid without the sharp peak shown by the cooling curve. As no anomalous dispersion or apparently high conductance is found in the region of the $\alpha \rightarrow \beta$ transition, it is suggested that the sharp peak is due to the development of molecular freedom caused by a molecular disorder greater during the process of transition than that existing in the liquid state, where the molecules must be more or less oriented. In other words, the potential hump to be crossed by a molecule in order to rotate is lower on the average during the transition than it is in the liquid state. In the β -form, as in ethyl undecylate, it is too high to permit rotation except in rare instances, the rarity increasing with falling temperature.

The sharp drop in the dielectric constant and the molar polarization of ethyl stearate on solidification shows a reduction in the freedom of molecular rotation. However, the rise in the dielectric constant of the solid with further temperature decrease at a rate only slightly less than that in the liquid shows that a limited freedom of rotation persists down to the enantiotropic transition, which is accompanied by a small drop in dielectric constant and followed by a gradual decrease corresponding to an absence of rotational freedom like that in the solid undecylate and the β -form of the palmitate.

Cetyl alcohol resembles ethyl palmitate in that its dielectric constant rises sharply on solidification, but

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differs in that the height of the rise depends upon the frequency used in the measurement, strong anomalous dispersion occurring throughout the region between the freezing point and a transition at 32.3°, below which the dielectric constant behaves like those of the undecylate and the β -forms of the palmitate and stearate. The form existing between 47.8° and 32.3° shows the dielectric behavior of a viscous liquid. That this is not the effect of impurities giving rise to a Maxwell-Wagner effect is shown by the length of the temperature region over which the phenomenon exists, by the sharpness of the boundaries of this region and by the absence of appreciable conductance in the liquid and in the solid below the transition.

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¹ Smyth and Hitchcock, *J. Am. Chem. Soc.* **54**, 4631 (1932); *ibid.* **55**, 1296, 1830 (1933); *ibid.* **56**, 1084 (1934); Kamerling and Smyth, *ibid.* **55**, 462 (1934); Smyth and McNeight, *ibid.* **58**, 1597, 1718, 1723 (1936).

Raman Frequencies of Dioxane

As there are some discrepancies in the various published Raman frequencies of dioxane (Villars,¹ Wolkenstein and Syrkin,² Simon and Feher,³ Venkateswaran⁴) it seems desirable to submit the following values which were determined in the course of another investigation. An iron spark was used for interpolation, and an Eastman 2A filter was employed in some runs to reduce the mercury 4047A group of lines.

The values are as follows, with estimated relative intensities and mercury line sources according to the Kohlrausch designations: 433 (1-ek), 486 (2-cek), 834 (4-ceik), 852 (0-ek), 1014 (3-ek), 1107 (2-ek), 1126 (1-ek), 1216 (2-ceik), 1304 (2-cek), 1334 (0-ek), 1443 (2-cek), 1459 (1-cek), 2660 (0-ek), 2718 (1-ek), 2748 (00-ek), 2852 (4-eik), 2885 (1-e), 2966 (4-eik). With the exception of 1334 and 2748, these results check well with those of Simon and Feher. Venkateswaran's values were not at hand.

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June 19, 1937.

¹ Villars, Kohlrausch, *Raman Effect*.

² Wolkenstein and Syrkin, *J. Chem. Phys.* **3**, 594 (1935).

³ Simon and Feher, *Chem. Abs.* **30**, 2492 (1936).

⁴ Venkateswaran, *Proc. Ind. Ac. Sci.* **2A**, 279 (1935).