Deviation from Lambert's Law in Measuring the Intensity of 3.5 μ Bands of Barium Stearate Films

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In studying the absolute infrared intensity in pure liquids and solids, it sometimes occurs that a sample has to be chosen considerably less thick than the wavelength. In such a case, the effect of multiple reflections upon the observed absorption coefficients comes to be appreciable, disturbing an accurate application of Lambert's law. It can be inferred from a recent study[1] that the effect of multiple reflections gives rise to a variation in apparent peak intensity depending on the sample thicknesses, in some oscillatory way, and in general converging to a maximum at zero thickness.

In order to examine this phenomenon in practice, it seems appropriate to measure the intensity of a sufficiently intense and well-isolated absorption band in samples of various thicknesses. Films of barium stearate built by the successive deposition of monomolecular layers are fairly suitable for this purpose, as the film has very intense bands at 3.51 and 3.43 μ and can be easily built up to any thickness.

The films used in the present measurements were built, following Blodgett,[2] by the repeated

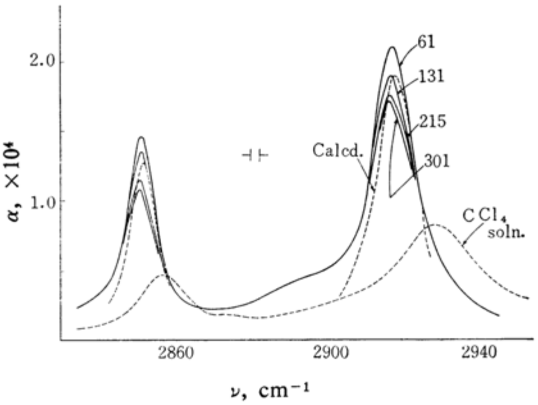

Fig. 1. 61—301: Number of monomolecular layers contained in each film.

"dip and lift" of quartz plates across the surface of water covered with a monomolecular layer. The layer was formed by dropping a 0.1% solution of stearic acid in benzene onto the clean surface of water containing minute barium chloride and potassium bicarbonate. It is known that the monomolecular layer of barium stearate formed in this way has a thickness of 24.4 Å and contains a molecule in each 20 Å^2 when deposited on a substrate.[2]

The spectra of marked bands were obtained using a Perkin-Elmer model 112 spectrometer

1) S. Maeda, G. Thyagarajan and P. N. Schatz, *J. Chem. Phys.*, **39**, 3474 (1963); S. Maeda, *Bull. Tokyo Inst. Tech.*, **59**, 17 (1964).

2) K. Blodgett, *J. Am. Chem. Soc.*, **57**, 1007 (1935); T. Tachibana, "Jikken Kagaku Kôza," Vol. 7, Maruzen, Tokyo (1950), p. 296.

equipped with a LiF prism; they are given in the figure by apparent absorption coefficients, $\alpha_{app}=(1/d)\ln(I'_0/I)$, where I'_0 is the intensity of the light transmitted by the blank substrate. "Apparent" implies the conventional use of Lambert's law without taking the multiple reflection effect into consideration. The upper and lower limits of thickness were chosen so as to give the transmittance at the peak with a reasonable accuracy. A steady increase in apparent peak intensity with diminishing thickness can be seen, indicating the characteristic features of the multiple reflection effect in extremely thin samples.

For a thin sample in which the thickness, d, is sufficiently smaller than the wavelength, λ, the following expression is valid for the reciprocal of transmittance:

$$\begin{aligned}I'_0/I=&1+(2\varepsilon_2/1+\phi)(2\pi d/\lambda)\\&+[1/(1+\phi)^2][(\varepsilon_1-1)(\varepsilon_1-\phi^2)+\varepsilon_2{}^2]\\&\times(2\pi d/\lambda)^2-[2\varepsilon_2(\varepsilon_1-\phi)/3(1+\phi)]\\&\times(2\pi d/\lambda)^3+\cdots\cdots\end{aligned}$$

where ε_1 and ε_2 denote the real and the imaginary parts of the dielectric constant of the sample, and ϕ is the refractive index of the substrate.[1] For the thinnest film, with 61 layers, the expansion parameter $(2\pi d/\lambda)$ is small enough, so that the fourth and further terms on the right-hand side may be discarded with very little error. Then, if one assumes the function of a damped oscillator model for each band, it is possible to estimate the true absorption coefficients in a good approximation, which is given by a broken-line curve in the figure.

For the sake of comparison, the absorption curve of stearic acid in a dilute carbon tetrachloride solution is given for the same region. It is strikingly different from the "built up" film, while the distinction between the acid and the barium salt is expected to be very little for the spectral features in this region. Such a marked change in an absorption intensity due to a change of state is not unusal, but it has not yet been statisfactorily explained in most cases.

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