Determination of Optical Constants of Single Crystal by ATR*1

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(Received June 13, 1968)

Very few measurements of absolute absorption intensities have been made on the infrared spectra of single crystals, because the thin layers of single crystals required are quite difficult to prepare, and it is also difficult to measure the thickness. It is, however, desirable to measure the intensities for single crystals, as they provide important knowledge related to the intermolecular forces when compared with those for the polycrystalline films.[1] Recently the infrared spectra of a single crystal, an anisotropic medium, have been successfully obtained by applying the ATR technique.[2] The determination of the infrared intensities of single crystals will also be possible if the optical constants can be obtained by the same method.[3] No attempt to do so has, however, yet been made, because there is an inevitable difficulty in making a good contact between the crystal sample and the high-index material.

We are developing a method of measuring optical constants of single molecular crystals by the ATR technique. The method is based on the determination of the true reflectivity for the perpendicular polarization, R_s. The reflecting surface of the sample is polished, and it is fixed firmly to the KRS-5 hemicylinder. After the R_s curve is recorded, we correct the R_s for the incompleteness of the contact as follows: A) The reflectivity for parallel polarization, R_p, goes down to zero at the principal angle, θ_p, in non-absorbing regions. If the optical contact is not complete, then the appreciable energy at θ_p, which is due to the lack of optical contact, is detected as R_p. Measuring the minimum R_p at θ_p, we obtain $R_s(\text{true}) = R_s(\text{observed}) - R_p$ (at $\theta = \theta_p, k=0$). B) In non-absorbing regions the R_s is observed at a small angle of incidence, one where the total reflection does not occur. Then it is compared with the R_s calculated theoretically at the same incident angle. The difference between observed and calculated R_s values may be attributed to the energy resulting from the incompleteness of the contact. After the true R_s curves are thus obtained with two different incident angles, the n and k values are calculated on the basis of Frenel's formulae.

To illustrate the results obtainable with this method, we have measured the ATR spectra of an iodoform single crystal for the ν_4(E) CH bending band. Using a hexagonal bipyramidal iodoform, and taking the reflecting surface as the (0001) plane, the R_s (true) curves have been obtained. Then the n, k and α have been calculated by following Fahrenfort's method,[4] with some modifications suggested by Hansen,[5] using a FACOM 270—20 computer.

The calculated n and α values are shown in Fig. 1. The intensity $A_{\text{crystal}(0001)}$ is

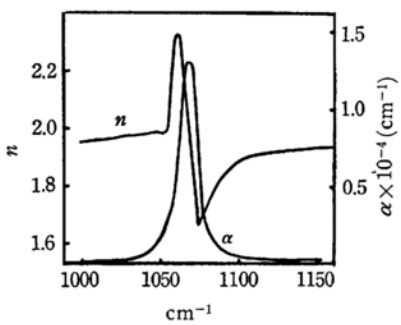

Fig. 1. Refractive index, n, and absorption coefficient, α, of CHI_3 single crystal in (0001) plane.

19.4 ± 4 cm/μmol, which is compared with the value 9.9 ± 0.5 cm/μmol for $A_{CS_2\,\text{soln.}}$. Iodoform belongs to the C_6^6 space group and the molecular axes of CHI_3 lie perpendicular to the (0001) plane, so that the ν_4 has all the intensity in this plane if the oriented gas model is assumed. $A_{\text{crystal}(0001)} = (3/2) A_{\text{soln.}} \times$ (field parameter). The details and a discussion will be published in the near future.

*1 Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

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