pounds to only a very small extent. They appear to have an obstruction effect which increases the abnormal distortions of σ-electron orbits in other directions.

Other aspects of unsaturated molecules, such as bond-lengths, Pascal's constitutive correction factor λ for the multiple bonds, etc., have been discussed in terms of these concepts elsewhere[7,8].

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[1] Robertson, P. W., Dasent, W. E., Milburn, R. M., and Oliver, W. H., *J. Chem. Soc.*, 1628 (1950).
[2] Bond, G. C., and Sheridan, J., *Trans. Farad. Soc.*, **48**, 658 (1952).
[3] Kuhn, R., and Scholler, K. L., *Chem. Ber.*, **87**, 598 (1954).
[4] Williams, G., *Trans. Farad. Soc.*, **37**, 749 (1941).
[5] de la Mare, P. B. D., Ann. Rep. Progr. Chem., **47**, 126 (1950).
[6] Bayliss, N. S., *Quart. Rev. Chem. Soc.*, **6**, 319 (1952).
[7] Singh, Lakhbir, *Naturwiss.*, **43**, 466 (1956); **44**, 233 (1957).
[8] Singh, Lakhbir, *Naturwiss.*, **43**, 493 (1956).
[9] Singh, Lakhbir, *Naturwiss.*, **44**, 536 (1957).

Infra-Red Absorption of OH Bonds in Micas

IN favourable cases, infra-red absorption spectra afford a valuable adjunct to diffraction methods in crystal structure analyses. The structures of the micas have been familiar for many years, but have never included any specification for the site of the proton in the constitutional hydroxyls.

In the biotite micas (such as phlogopite, $K_2(Si_6Al_2)Mg_6O_{20}(OH)_4$), if one assumes tetrahedral environment for oxygen, three of the tetrahedral hybrid orbitals are involved with magnesium neighbours, the bond to the proton must have its axis normal to the cleavage, and steric factors preclude that the proton has a secondary association with any other oxygen. In muscovite,

$$K_2(Si_6Al_2)Al_4O_{20}(OH)_4,$$

only two orbitals are involved with aluminium neighbours, and the O—H bond axis could be normal to the cleavage as above, or could be directed toward the unoccupied cation site, thus lying no more than 15–20° inclined to the cleavage, and probably favourably disposed for secondary association with one or both near oxygen neighbours as an O—H . . . O bond.

The efficiency of absorption in the frequencies associated with the O—H bond is a function of the angle between the bond axis and the plane of the electric vector of the light. For normal incidence on a phlogopite cleavage flake, there is no resultant along the OH bond axis and no absorption in the region of the OH stretching frequency. With increasingly inclined incidence, absorption increases regularly with the increasing resultant of the plane of the electric vector on the bond axis. The observed frequency for unmodified OH stretching is 3,710 ± 20 cm.$^{-1}$. When muscovite is examined similarly, strong absorption is observed for normal incidence at 3,620 ± 20 cm.$^{-1}$, and the absorption is not markedly sensitive to moderate tilting of the flake. It is concluded that the O—H bond axis must have one or more of the orientations near the plane of the cleavage flake for the dioctahedral composition, and that the lesser frequency may be evidence of some hydrogen bonding.

A third case illustrates the precision of observations. Lepidolites present frequent instances in which analyses suggest that a trioctahedral lithium-bearing biotite and a typical muscovite are intimately parallel grown. Spectra at normal incidence and at increasingly inclined incidence to the lepidolite illustrated show absorption at the muscovite frequency with little sensitivity to orientation and absorption at the phlogopite frequency with sensitivity to orientation as in phlogopite.

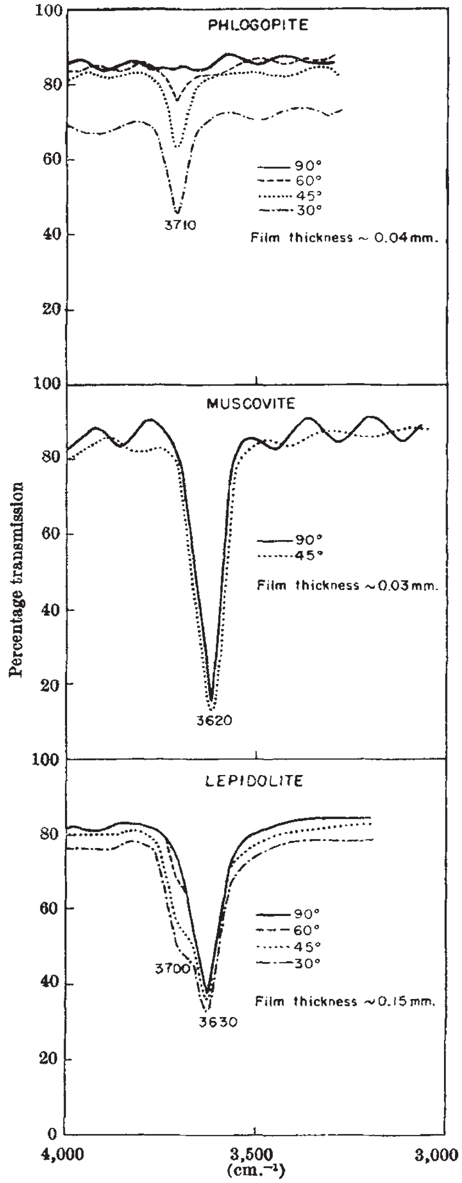

Fig. 1. Infra-red spectra of phlogopite, muscovite and lepidolite for cleavage flakes oriented at different angles to the incident beam

The spectra in Fig. 1 were recorded with a Perkin-Elmer Model 21 double-beam spectrometer with a sodium chloride prism.

We have recently learned that a more elaborate analysis, in substantial agreement with our present communication, was conducted during the War by Dr. G. B. B. M. Sutherland for the U.S. Army Signal Corps, but not published.

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