

Coordination and molar refractivity

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• Ultrarot-Absorptionsspektren
primäre Koordination, die Atom-
ladung den Absorptions-Wellen-
länge die Verwendung der Mol-
Änderungen der (primären und

absorption spectra of some silica
coordination, atomic number,
wave lengths for the major bands.
in predicting or determining
try) is illustrated.

infra-red absorption spectra
information on coordination of
infra-red absorption spectra
similar crystallographically, is
that the differences in such
bond length and configuration.
of similar structures it is difficult to
of similar frequencies to certain

distinction of sillimanite from
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To proceed from the space group symmetry to the permitted vibration modes is straightforward enough; but so far it has been impossible even to detect all expected bands in the spectrum of most solids, due largely, no doubt, to the very broad bands encountered. However in cases, such as quartz itself, which have been studied in detail it is possible to group the absorption bands in the 2-25 μ region into cation-anion stretching, cation-cation stretching and various cation-anion bending and distorting vibrations. Of these the cation-anion stretching occurs at the highest frequencies and constitutes the strongest absorption. In a crystal chemical study of this type this cation-anion bond is the one which can and does reflect the more significant structural changes such as coordination changes resulting in bond-length changes. Hence an examination of the strong absorptions at highest frequency should be of primary interest.

Moreover, in simple structures of high symmetry there is reason to hope that certain associations will be evident when absorption spectra of known-structure materials are compared. The most satisfactory groups of phases for such a study would be groups of isomorphs and groups of polymorphs.

These same phases, especially the polymorphs of GeO_2 , are of value in studying changes in molar refractivity. Not many substances are available which exist in two reconstructively related polymorphic forms, each of which can persist to room temperature. One such substance is GeO_2 which exists in a six-coordinated rutile form and a four-coordinated quartz form.

Infra-red absorption spectra

In our early work² on coesite and GeO_2 data were reported to show clearly the ability to distinguish major coordination changes by absorption spectroscopy. The results in Figs. 1, 2, and 3 summarize the information and deductions to date. The empirical and qualitative nature of these results is emphasized although this may not detract from their usefulness.

The most significant spectra should be those of the GeO_2 polymorphs. Spectra for the polymorphic series SiO_2 quartz, SiO_2 tridymite, SiO_2 cristobalite, SiO_2 glass and SiO_2 coesite are also shown (Fig. 2). The isomorphous series BPO_4 , AlPO_4 , GaPO_4 , FePO_4 , BaAsO_4 , AlAsO_4 and

² RUSTUM ROY, Isomorphism and polymorphism of silica. Mellon Institute Symposium on "Defect structure of quartz and glassy silica", May 22, 1957.