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On the use of unpolarized infrared spectroscopy for quantitative analysis of absorbing species in birefringent crystals

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Abstract

There is an understandable desire to use simple unpolarized infrared analysis of unoriented anisotropic samples to extract quantitative information, rather than using more demanding polarized techniques. Owing to the fact that unpolarized infrared absorbance in birefringent media deviates from the Beer-Lambert law, previous studies have either warned against using unpolarized spectroscopy for quantitative purposes, or have used flawed error analysis to justify using simple averages of integrated absorbance of multiple absorbance bands as a proxy for total integrated polarized absorbance in the principal spectra. It is shown here that unpolarized infrared absorbance is correctly calculated by averaging in the transmission domain. The errors in estimates of principal absorbance by averaging of unpolarized absorbance spectra are evaluated using correct theory of unpolarized infrared transmission. Correction schemes for integrated absorbance based on linear-absorbance error calculations are shown to be inappropriate. A theory is developed that allows the sum of the polarized principal absorbance spectra to be estimated from multiple unpolarized measurements of randomly oriented samples. The systematic errors that arise when averaging in the absorbance domain are avoided by use of exact theory rather than an approximation. Numerical simulation shows that applying the new procedure to 10 unpolarized measurements of OH stretching bands in olivine results in convergence of the estimated total integrated principal polarized absorbance to within 10% of the true value for a sample size of 10 measurements, but the technique is limited to spectral regions that do not contain absorption bands that are simultaneously intensely absorbing and strongly anisotropic.

Keywords: Infrared spectroscopy, unpolarized, quantitative, hydroxyl, olivine