COMPARISON OF INFRARED AND RAMAN WAVENUMBERS OF LIQUIDS: WHICH IS THE CORRECT INFRARED WAVENUMBER TO USE ?

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The peak wavenumber of a strong infrared band of a liquid sample depends on the spectrum considered, i.e., on the intensity quantity used in the spectrum [a] [b]. This has long been known [c] [d] to arise from macroscopic dielectric effects, but the size and extent of the effect is not widely recognized. It is obviously important to the comparison of wavenumbers in infrared spectra of different intensity quantities, such as the comparison of a transmission spectrum with an attenuated total reflection spectrum. It is also obviously important to the comparison of an infrared spectrum with a Raman spectrum, in particular to the determination that bands are, or are not, coincident in the two spectra, a determination that is often required when assigning spectra or determining the symmetry of a molecule. In this paper the differences that can be observed in practice will be illustrated and the correct infrared quantity to use for the comparison will be discussed with examples.

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[c] J. Fahrenfort, in M. Davies (Ed.), "Infrared Spectroscopy and Molecular Structure", Elsevier, Amsterdam (1963), p.377.

[d] J.W. Warner and M. Wolfsberg, J. Chem. Phys. 78, 1722 (1983).