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Title

Low-frequency modes of the benzoic acid dimer in chloroform observed by the optical Kerr effect

Source

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Abstract

The low frequency Raman spectral density associated with the intermolecular hydrogen-bonding interaction of benzoic acid in chloroform was investigated through the ultrafast optically-heterodyne-detected optical Kerr effect. The low-frequency solute Raman spectrum was obtained by Fourier transform analysis and subtraction of the solvent spectrum from the solution spectrum. The resulting difference spectrum has a broad band below 150 cm(-1) with a peak at around 80 cm(-1). Previous studies of aromatic liquids suggest that the origin of such a low-frequency band is librational motion, although intermolecular hydrogen-bonding modes in benzoic acid may also contribute. To clarify these contributions to the low-frequency band, methyl benzoate was used to estimate the librational component; its structure is similar to benzoic acid, but it forms no intermolecular hydrogen bonds. Both librational and intermolecular modes were found to contribute to the low-frequency Raman spectrum of the dimer and thus can be separated. These experimental results were compared with the results of density functional theory calculations. In addition, the effect of deuteration on the Raman spectrum was also investigated. 