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Author

Houjou H.

Title

Evaluation of coupling terms between intra- and intermolecular vibrations in coarse-grained normal-mode analysis: Does a stronger acid make a stiffer hydrogen bond?

Source

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Abstract

Using theory of harmonic normal-mode vibration analysis, we developed a procedure for evaluating the anisotropic stiffness of intermolecular forces. Our scheme for coarse-graining of molecular motions is modified so as to account for intramolecular vibrations in addition to relative translational/rotational displacement. We applied this new analytical scheme to four carboxylic acid dimers, for which coupling between intra- and intermolecular vibrations is crucial for determining the apparent stiffness of the intermolecular double hydrogen bond. The apparent stiffness constant was analyzed on the basis of a conjunct spring model, which defines contributions from true intermolecular stiffness and molecular internal stiffness. Consequently, the true intermolecular stiffness was in the range of 43-48 N m⁻¹ for all carboxylic acids studied, regardless of the molecules' acidity. We concluded that the difference in the apparent stiffness can be attributed to differences in the internal stiffness of the respective molecules.