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New thermochemical parameter for describing solvent effects on IR stretching vibration frequencies

Communication 1. Assessment of van der Waals interactions

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Abstract

Solvent effects on O–H stretching vibrations in several complexes with hydrogen bonding have been investigated by FTIR spectroscopy. To assess the influence of van der Waals (vdW) interactions on frequency shifts, a new parameter of solvent, $\sqrt{\delta_{\text{cav}}h^S}$, is proposed. This parameter has been derived from equations describing enthalpy of non-specific solvation. Linear correlation was established between the O–H frequency shift (with respect to the gas phase) and parameter $\sqrt{\delta_{\text{cav}}h^S}$ for a series of complexes of aliphatic alcohols with standard proton acceptors. Linear correlations with $\sqrt{\delta_{\text{cav}}h^S}$ were also observed for a series of “free” O–H and also C=O, P=O, S=O and C–Br stretching vibrations. A new method is proposed for estimating the gas-phase stretching frequency from IR spectra of solutions. In addition, frequencies of “free” X–H groups in neat bases were deduced from the experimental data.

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1. Introduction

IR spectroscopy is one of the most informative methods of investigating systems with hydrogen bonds. Such investigations are commonly performed in condensed media, typically in solutions. Effects of solvent on IR spectra always include influence of non-specific (van der Waals, vdW) interactions. For the systems with hydrogen bonding, spectral and related thermodynamic parameters involve contributions of H-bonding itself and non-specific solvation [1–6]. If X–H...B hydrogen bonding is studied via A–H stretching frequency shifts, a simple scheme of states can be applied (Fig. 1).

The most straightforward information on H-bond strength can be obtained from the gas-phase frequency shift of A–H (e.g. O–H) stretching vibration ($\Delta\nu_{\text{HB}} = \nu_2 - \nu_1$). In Fig. 1, this frequency shift is denoted as $\Delta\nu_{12}$. Owing to the dif-

ficulties in experimental determination of ν_2 , the commonly used frequency shift values are $\Delta\nu_{14}$ and $\Delta\nu_{34}$. These parameters differ from $\Delta\nu_{12}$ by the frequency shifts arising from interactions of free hydroxyl ($\Delta\nu_{13}$) and H-bond complex ($\Delta\nu_{24}$) with the solvent. If such interactions are of the van der Waals type only, the experimentally measured frequency shift ($\Delta\nu_{\text{exp}}$) can be expressed by Eq. (1).

$$\Delta\nu_{\text{exp}} = \Delta\nu_{\text{HB}} + \Delta\nu_{\text{vdW}} \quad (1)$$

If $\Delta\nu_{\text{exp}}$ is determined relative to free hydroxyl in the gas phase, then $\Delta\nu_{\text{vdW}}$ is equivalent to $\Delta\nu_{24}$. Alternatively, if the frequency of free hydroxyl is measured in a solvent S, the contribution of vdW interactions becomes more complicated: $\Delta\nu_{\text{vdW}} = \Delta\nu_{24} - \Delta\nu_{13}$, while $\Delta\nu_{\text{exp}}$ becomes closer to $\Delta\nu_{\text{HB}}$. Sometimes, the frequency of OH group in the complex is measured in the media of pure base (B). In this case, $\Delta\nu_{24}$ and $\Delta\nu_{13}$ commonly refer to different solvents because the frequency of free hydroxyl in pure base is typically inaccessible in experiment.

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