

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

## Communication 2. Assessment of cooperativity effects

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### Abstract

Solvent effects on O–H stretching vibration frequency of methanol in hydrogen bond complexes with different bases,  $\text{CH}_3\text{OH}\cdots\text{B}$ , have been investigated by FTIR spectroscopy. Using chloroform as a solvent results in strengthening of  $\text{CH}_3\text{OH}\cdots\text{B}$  hydrogen bonding due to cooperativity between  $\text{CH}_3\text{OH}\cdots\text{B}$  and  $\text{Cl}_3\text{CH}\cdots\text{CH}_3\text{OH}$  bonds. A method is proposed for quantifying the hydrogen bond cooperativity effect. The determined cooperativity factors take into account all specific interactions of the solute in proton-donor solvents. In addition, a method of estimation of cooperativity factors  $A_{\text{B}}$  and  $A_{\text{OX}}$  in system  $(\text{CH}_3\text{OH})_2\cdots\text{B}$  is proposed.

It is demonstrated that in such systems, the cooperativity factor of the  $\text{OH}\cdots\text{B}$  bond decreases and that of the  $\text{OH}\cdots\text{O}$  bond increases with increasing the acceptor strength of the base B. The obtained results are in a good agreement with the data obtained previously from matrix-isolation FTIR spectroscopy.

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### 1. Introduction

Solvent effect on frequencies of stretching vibrations obtainable from IR spectra is a well-known phenomenon [1–13]. There exist a number of approaches for analyzing infrared solvent shifts. These approaches include the reaction field model [5,12,13], several multiparameter correlations such as a Koppel–Palm [3] or Taft–Kamlet equations [3,5,6,11], relationships with empirical parameters of solvents, as  $\pi^*$ —constant (KAT) [3,9,10], acceptor number (AN) [2,5,6,11],  $G$ —factor of Allerchand–Schleyer [1,8,14] and Luck’s LMF parameter based on linear free energy relationship (LFER) [7].

In our previous communication, we developed a new approach for analyzing solvents effects on X–H frequencies in complexes with hydrogen bonding [15]. It is known that

solvent influence can be separated into effects due to specific interactions (e.g. formation of donor–acceptor complexes via hydrogen bonding between the solute and solvent molecules) and effects of nonspecific (van der Waals, vdW) interactions [7]:

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

where  $\Delta\nu_{\text{exp}}$  is the X–H stretching vibration frequency shift due to the complexation in a given environment with respect to the gas phase and  $\Delta\nu_{\text{HB}}$  and  $\Delta\nu_{\text{vdW}}$  are the frequency shifts due to hydrogen bonding and vdW interactions, respectively.

Utilizing the new solvent parameter  $\sqrt{\delta_{\text{cav}}h^S}$ , which depends upon nonspecific solvent–solvent interactions only, and using the previously proposed approach [15], we are able to calculate the contribution of vdW interactions,  $\Delta\nu_{\text{vdW}}$ . According to [16], the parameter  $\delta_{\text{cav}}h^S$  is defined as a ratio of solution enthalpy of an alkane in solvent S to McGowan characteristic volume of this alkane [17]. The  $\sqrt{\delta_{\text{cav}}h^S}$  parameter

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is somewhat similar to the Hildebrand solubility parameter  $\delta_{\text{H}}^{\text{S}} = \sqrt{\frac{\Delta H_{\text{vap}} - RT}{V_{\text{m}}^{\text{S}}}}$  [18]. However, the Hildebrand parameter is responsible for overall breaking of solvent–solvent interactions, being calculated from the vaporization enthalpy [18], whereas  $\delta_{\text{cav}}h^{\text{S}}$  is due to breaking the nonspecific solvent–solvent interactions only [16]. Thus, the parameter  $\sqrt{\delta_{\text{cav}}h^{\text{S}}}$  could be used as a measure of the nonspecific part of the interactions.

In the present study, we apply the approach [15] to evaluating H-bond cooperativity factors. Noticeable interest to this subject is due to the fact that the cooperativity phenomenon is known to affect various physico-chemical and biological processes.

The concept of cooperativity between hydrogen bonds implies that the primary H-bond formed between a proton-donor, X–H, and a proton-acceptor B, X–H...B, becomes stronger, when a third partner, A, forms another hydrogen bond with a lone pair electron of atom X (A...X) [19]. The species A may be either a cation ( $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Li}^{+}$  and  $\text{K}^{+}$ ) [20] or another proton-donor, Y–H [20,21]. In the latter case, a complex Y–H...X–H...B can be formed. The cooperativity phenomenon is being extensively studied with an accent on theoretical investigations [22–38].

According to Kleeberg et al. [20,21], the cooperativity phenomenon results not only in strengthening of the X–H...B bond, but also in strengthening of the secondary H-bond (X–H...X). Authors have proposed two cooperativity factors  $A_{\text{b}}$  and  $A_{\text{OX}}$ , defined as a slope of linear correlation between the experimental frequencies  $\nu_{\text{b}}$  and  $\nu_{\text{OX}}$  and frequency of O–H band in a  $\text{CH}_3\text{OH}\cdots\text{B}$  complexes, respectively. Detailed information on H-bond cooperativity was obtained from matrix-isolation FTIR spectroscopy by Maes and Smets [39]. In addition, experimental studies of H-bond cooperativity in solutions and matrices were performed in [40–44].

In the present study, solvent effects on OH stretching vibration frequency shifts of methanol have been investigated by FTIR spectroscopy. Based on our previous approach [15], we determine the cooperativity factors and analyze the influence of the acceptor strength on the hydrogen bond cooperativity in solutions and pure base media.

## 2. Experimental

All chemicals were commercial products and were purified as described in the literature [45]. The amount of water in solvents was controlled spectroscopically. FTIR spectra were recorded with a Vector-22 Bruker spectrometer. For each spectrum, 64 scans were accumulated with a set resolution of  $1\text{ cm}^{-1}$ .  $\text{CaF}_2$  cells of 1.0 and 0.1 mm path lengths were utilized. All measurements were carried out at 298 K.

Solution enthalpies were measured at 298 K using a differential quasi-adiabatic calorimeter [46]. The volume

of calorimetric cell was  $100\text{ cm}^3$ . The ultimate solute concentrations did not exceed  $0.03\text{ mol l}^{-1}$ . The absence of a concentration dependence of the heat effect was controlled by successive dissolution of several weighed samples. The results were obtained as an average of four to six measurements. We have determined enthalpies of solution of several alkanes in 3-methylpyridine:  $\Delta H_{\text{soln}}^{n\text{-hexane}/3\text{-MetPy}} = 4.8(2)\text{ kJ/mol}$ ,  $\Delta H_{\text{soln}}^{n\text{-decane}/3\text{-MetPy}} = 7.5(2)\text{ kJ/mol}$  and  $\Delta H_{\text{soln}}^{n\text{-dodecane}/3\text{-MetPy}} = 8.8(2)\text{ kJ/mol}$ . Using molecular volumes of the alkanes  $V_{\text{X}}$  [17], the magnitude of  $\delta_{\text{cav}}h^{\text{S}}$  for 3-methylpyridine was calculated:  $5.0 \times 10^2\text{ kJ cm}^{-3}$ .

## 3. Results and discussion

The frequency of an X–H band in a X–H...B complex is sensitive to vdW interactions with the solvent [1,7]. It has been found that the contribution of vdW interactions to X–H frequency shift could be as high as 90% of the frequency shift of the X–H...B complex formed in the gas phase [7]. H-bonded complexes represent suitable objects for studying how vdW interactions affect the frequencies shifts, because solvent molecules cannot interact specifically with X–H bond of the complex. It has been shown previously that frequency shifts  $\Delta\nu_{\text{exp}}$  of O–H stretching band of methanol in complexes with proton-acceptors,  $\text{CH}_3\text{OH}\cdots\text{B}$ , can be well described by the solvent parameter  $\sqrt{\delta_{\text{cav}}h^{\text{S}}}$ , responsible for nonspecific solute–solvent interactions [15]. In the case, when the solvent is a proton-donor (Y–H) capable to cooperative specific interaction (e.g. Y–H...X–H...B or Y–H...X–H...B...H–Y), this results in an additional shifting of the X–H band. For an (X–H...B)<sub>Y–H</sub> complex, the contribution due to cooperative specific interactions,  $\Delta\nu_{\text{coop}}$ , should be additive to other contributions, so that:

$$\Delta\nu_{\text{exp}} = \Delta\nu_{\text{HB}} + \Delta\nu_{\text{vdW}} + \Delta\nu_{\text{coop}} \quad (2)$$

We suggest the following approach to evaluating the  $\Delta\nu_{\text{coop}}$ . First of all, parameters  $\sqrt{\delta_{\text{cav}}h^{\text{S}}}$  of different aprotic and proton-donor solvents have to be determined. Next, using aprotic solvents only, parameters of the dependence between  $\Delta\nu_{\text{exp}}$  and  $\sqrt{\delta_{\text{cav}}h^{\text{S}}}$  for the complex X–H...B must be calculated [15]. While  $\Delta\nu_{\text{HB}}$  is a constant in this series, the value of  $\Delta\nu_{\text{vdW}}$  is a function of  $\sqrt{\delta_{\text{cav}}h^{\text{S}}}$ . From the linear dependencies of  $\Delta\nu_{\text{exp}}$  upon  $\sqrt{\delta_{\text{cav}}h^{\text{S}}}$ , using the  $\sqrt{\delta_{\text{cav}}h^{\text{S}}}$  magnitude for a proton-donor solvent, we can compute the value ( $\Delta\nu^* = \Delta\nu_{\text{HB}} + \Delta\nu_{\text{vdW}}$ ) [15]. Consequently, the contribution  $\Delta\nu_{\text{coop}}$  could be determined as a difference ( $\Delta\nu_{\text{exp}} - \Delta\nu^*$ ). Then, the cooperativity factor  $A_{\text{b}}$  is obtained using the ratio:

$$A_{\text{b}} = \frac{\Delta\nu_{\text{exp}}}{\Delta\nu^*} \quad (3)$$

It should be noted that the calculated value  $A_{\text{b}}$  depends upon the way of how the “free” X–H stretching vibration frequency [ $\nu_{\text{free}}^{\text{X–H}}$ ] is determined. We can utilize the monomer frequency measure in the gas phase, [ $\nu_{\text{free}}^{\text{X–H}}\text{gas}$ ], inert solvent

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