

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

## Communication 2. Assessment of cooperativity effects

Boris N. Solomonov\*, Mikhail A. Varfolomeev,  
Vladimir B. Novikov, Alexander E. Klimovitskii

*Chemical Institute, Kazan State University, Kremlevskaya 18, Kazan 420008, Russia*

Received 7 May 2005; received in revised form 8 July 2005; accepted 13 July 2005

### 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  $A_b$  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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**Keywords:** Hydrogen bonding; Cooperativity; Methanol; IR-spectroscopy

### 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

\* Corresponding author. Tel.: +7 8432 315343; fax: +7 8432 315346.  
E-mail address: Boris.Solomonov@ksu.ru (B.N. Solomonov).