HYDROGEN BONDING IN BINARY MIXTURES OF TETRAHYDROFURAN AND WATER: A CONCENTRATION DEPENDENT RAMAN STUDY AND AB-INITIO CALCULATIONS

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Keywords: hydrogen bonding, binary mixture, tetrahydrofuran, water, ab-initio calculations

Abstract: This contribution reports on the wavenumber shifts and linewidth changes observed for the Raman bands of the C-O and C-C stretching vibrations of tetrahydrofuran (THF) in a series of binary mixtures with water. Experimental results are compared with ab-initio calculations on THF and hydrogen-bonded THF-water complexes.

The Raman spectroscopic analysis of vibrational relaxation processes such as vibrational dephasing is a powerful approach of investigating dynamical processes in liquids. It is possible to identify two principal mechanisms for interpreting the relaxation process. The first process involves a change in the quantum state of the relevant normal mode, while the second process is related to the phase decay of the vibrational wavefunction [1-2]. Both processes can contribute to the spectral band shape and thereby to the vibrational correlation function obtained from them. In most cases, however, vibrational band profiles are determined predominantly by vibrational dephasing.

Raman spectra of neat tetrahydrofuran (THF) and its binary mixtures with water were investigated in the wavenumber intervals 1000 – 800 cm⁻¹ and 1100 – 975 cm⁻¹; mixtures with mole fractions of 0.1, 0.3, 0.5, 0.7 and 0.9 of the reference system THF were analyzed. Figure 1 shows the Raman spectra of neat THF and two binary mixtures with THF mole fractions of 0.5 and 0.1 in the wavenumber region 1000 – 800 cm⁻¹. For neat THF, the observed asymmetric band shape is due to the presence of two peaks at ~ 914 cm⁻¹ and ~ 909 cm⁻¹, which are assigned to the symmetric C-O and C-C stretching vibration, respectively. The peak position of the band at ~ 914 cm⁻¹ shows a downshift (red shift) of ~ 7 cm⁻¹ upon dilution, which can be explained with the help of optimized geometries obtained for THF and hydrogen-bonded THF-water complexes using ab-initio calculations at the MP2 level. In the binary mixture (THF + H₂O), the oxygen atom of the cyclic ether linkage in THF is the hydrogen bond acceptor. The C-O bond length increases upon formation of the hydrogen bonded complex. The reduced C-O bond order explains the observed shift to lower wavenumbers upon dilution. The linewidth for this mode increases linearly upon dilution by ~ 10 cm⁻¹, which is basically due to diffusion of the solvent molecule. On the other hand, the other peak at ~909 cm⁻¹, which is assigned to the C-C stretching mode, shows an upshift (blue shift) of ~ 2 cm⁻¹ upon dilution. In addition, a new band at ~ 896 cm⁻¹ is observed, which is assigned to the hydrogen bonded complexes of THF and water; it also shows a downshift of ~ 9 cm⁻¹ at extreme dilution. This assignment is confirmed by the observation that the Raman intensity ratio of the bands associated with hydrogen-bonded THF and “free” THF shows a sudden rise after C = 0.5. The maximum in the linewidth vs. concentration plot at C = 0.5 and the linear variation in the wavenumber position is explained by Bondarev and Mardaeva’s concentration fluctuation model [3].
Fig. 1. Isotropic part of the Raman spectra in the wavenumber interval 1000–800 cm$^{-1}$ for neat THF and (THF + H$_2$O) mixtures with THF mole fractions of C = 0.5 and 0.1. The concentration dependence of wavenumber shifts and linewidths is obtained from the corresponding band profile analysis.

The spectra in the region 1100 – 975 cm$^{-1}$ show a similar double peak nature. One of the peaks is sharp and appears at ~ 1029 cm$^{-1}$ and the other one is broad and appears at ~ 1070 cm$^{-1}$. The peak at ~ 1029 cm$^{-1}$ shows an upshift (blue shift) of ~ 4 cm$^{-1}$, while the peak at ~ 1070 cm$^{-1}$ shows a very significant downshift of ~ 16 cm$^{-1}$ upon dilution. In addition to the optimized geometries, vibrational wavenumbers of THF and its hydrogen-bonded complexes were calculated using ab-initio theory at the MP2 level. The theoretical results are used to understand and explain the concentration dependent changes in the spectral features in terms of hydrogen bonding.

Acknowledgements:
The authors are thankful for support through DST-DAAD Exchange Program and one of us (BPA) is thankful to the AvH-Stiftung for a support through ‘Wiederaufnahme’.

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