CHEM 361 L

EXPERIMENT 9

Hydrogen Bonding: IR

(last revised: January, 2014)

Introduction

The hydrogen bond occurs when a hydrogen attached to an electronegative atom (usually fluorine or oxygen, but occasionally nitrogen) is attracted to a neighboring electronegative atom in its vicinity. The neighboring atom may be on a different molecule (intermolecular hydrogen bond) or on the same molecule (intramolecular hydrogen bond). The enthalpy of a hydrogen bond is typically in the 4- 40 kJ mol^{-1} range, compared to the much higher values expected for covalent bonds (100-600 kJ mol^{-1}). Experiments 9-11 utilize spectroscopic methods (IR, UV- visible, fluorescence) to explore the nature of the hydrogen bond.

IR study of the Hydrogen Bond

The presence of a hydrogen bond stretches and weakens the covalent bond (X-H) attached to the hydrogen participating in the hydrogen bond. This, in turn, lowers the observed vibrational frequency of the X-H stretching vibration. This vibration is also broadened by proton exchanges and combination bands involving the hydrogen bond stretching motions. The absolute intensity of the X-H stretching mode is also substantially enhanced by hydrogen bonding. In this experiment, you will determine the effects of concentration, solvent, and substituents on the infrared spectrum of hydrogen bonding species.

Procedure

(a). Prepare solutions of benzyl alcohol in carbon tetrachloride having concentrations of 0.5, 0.25, 0.125, 0.0625, 0.031, and 0.016 M. Acquire infrared spectra (3000-5000 cm^{-1}) of these in a fixed-path cell, using the solvent as a reference. Identify the free and hydrogen bonded O-H vibrations.

(b). Prepare 0.016 M solutions of benzyl alcohol in each of the following solvents: benzene, acetonitrile, and pyridine and acquire the infrared spectrum of each in the same manner as above.

(c). Prepare 0.125 M solutions of p-chlorophenol, p-cresol, p-hydroxyanisole, o-nitrophenol, and phenol, and acquire the infrared spectrum of each in the same manner as above.

Calculations

Plot the frequency of the hydrogen bonded O-H stretch (part (a).) versus concentration. For part (b)., determine the shift in the vibrational frequency of this stretch relative to that in carbon tetrachloride, then tabulate the shifts as a function of solvent. Does any solvent property correlate with the observed shifts? If so, plot the relationship. For part (c)., integrate the free and hydrogen-bound O-H peaks. Do the relative areas correlate with the properties (for example, σ values) of the substituents in the *para* position of the phenol?