CHEM 361 L

EXPERIMENT 10

Hydrogen Bonding: UV-Visible

(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 9-12 utilize spectroscopic methods (NMR, IR, UV- visible, fluorescence) to explore the nature of the hydrogen bond.

UV-Visible study of the Hydrogen Bond

The presence of a hydrogen bond will affect the electronic excitation energy of a molecule. Transitions involving nonbonding electrons on oxygen or nitrogen (n,π^* transitions) move to shorter wavelengths as solvent polarity is increased, while π,π^* transitions are red shifted with increasing solvent polarity. This is presumably due to the fact that the hydrogen bond involves the nonbonding electrons, and the bond must be broken in the course of the transition. The weaker red shift effect involves the greater stabilization of the excited state species by a more polar solvent. This *solvatochromic effect* will be observed in nitromethane and acetone, leading to spectroscopic estimates of the energy of the hydrogen bonds.

Procedure

Obtain a spectrum of pure hexane, ensuring that it is transparent to at least 200 nm. Then, using pure hexane as a reference, add small amount of spectrograde nitromethane to the sample cuvette. The best way to achieve this addition is to barely wet the tip of a Pasteur pipette with the nitromethane, then dip the tip into the cuvette while lightly stirring. Acquire the spectrum, recording the location of the high intensity peak (~210 nm). Add a small drop of nitromethane to the cuvette and acquire a new spectrum, recording the location of the weaker peak (~270 nm). Repeat this procedure using ethanol and water as solvents, then using acetone as solute (hexane, ethanol, and water as solvents). You may only be able to observe one transition for acetone (~270 nm).

Calculations

Tabulate the wavelengths of the observed transitions as a function of solvent for each solute. Since hexane will not hydrogen bond, determine shifts relative to the hexane solution peaks. For the blue-shifted transitions, determine the energies of the solute-solvent hydrogen bond.