CHEM 361 L

EXPERIMENT 11

Hydrogen Bonding: Fluorescence

(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.

Fluorescence study of the Hydrogen Bond

The presence of a hydrogen bond may affect the excited-state dynamics of a molecule. Salicylic acid is known to undergo excited-state intramolecular proton transfer (ESIPT), where the hydroxyl proton is transferred to the carbonyl on the acid moiety (1).

Procedure

Prepare 50 mL of a 0.0010 M solution of salicylic acid in cyclohexane. Obtain a UV-visible spectrum of the solution in order to determine the wavelength of the absorption maximum (~300 nm). Do the same with a solution that is 0.9 M in diethyl ether and 0.0010 M in salicylic acid. Then, setting the excitation wavelength on the fluorometer to the wavelengths determined above, obtain an emission spectrum for each solution.

Calculations

Tabulate the wavelengths observed for excitation and emission maxima for each solution. Explain shifts in the maxima due to the addition of the ether.