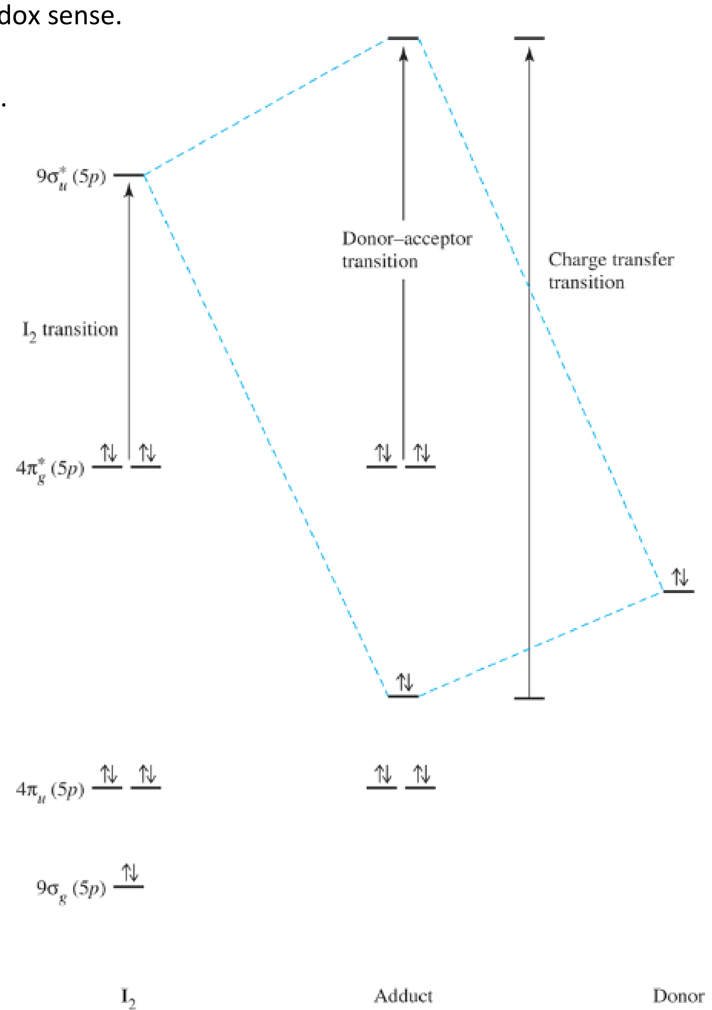
Chemistry 242: Donor-Acceptor Complexes of Iodine **SUNY College at Oneonta, Bill Vining**

Iodine, I_2, is a highly colored, fairly volatile solid. It's color arises from an Electronic transition from a pi-antibonding orbital to a vacant sigma antibonding orbital (see figure below left).

Although iodine, like all the halogens, is an oxidizing agent it is less strong than Br_2, Cl_2, or F_2 due to the relatively high energy of its valence orbitals. In many cases it will therefore act as an electron acceptor in a Lewis acid-base sense as opposed to a redox sense. This experiment explores the ability and tendency of Lewis bases To form Lewis acid-base complexes with I_2.

MO Diagram of I_2



MO Diagram of I_2-Base Complex

In this experiment we analyze the acid-base interaction by comparing the energies of the I2 transition to that of the donor-acceptor transition. The higher the energy the absorption, the stronger the acid-base interaction.

Experimental:
Prepare dilute solutions of I_2 in the solvents provided: hexane, methanol, toluene, and acetonitrile. Measure the UV-VIS spectrum from 350 nm – 700 nm. Note that since we are interested only in the energy of the electronic transition, you do not need a specific concentration. However, for an accurate absorption peak you should have the absorption at the peak less than around 1.5 absorption units.

Be careful: some of the solvents will dissolve the plastic UV-VIS cuvettes so use the glass ones provided (which are very expensive and should be handled with great care).

In addition, you should determine the I_2 transition by measuring the spectrum of gas-phase I_2. Think about how to obtain this.

Finally, I_2 is well known to form the I_3^- ion, which is soluble in water. Prepare this by dissolving I_2 in a solution of potassium iodide and record its spectrum. Perform an exploration of whether I_2 can form similar complexes with other halide anions using the salts provided. Record their spectra as well.

Hazards: Avoid handling the organic solvents used or getting them on your skin.

Analysis:
For each Lewis base, compare the energy of the measured electronic transition and determine (that is, calculate) the "bond strength" of the I_2-base interaction, in kJ/mol. Compare these values to common covalent bond strengths (for example, a C-C bond, or a Cl-Cl bond) and to the strengths of intermolecular forces (measured as enthalpy of vaporization values).

Is there any relationship between the acid-base interaction strength and the dipole moment of the base used?

Look for any other trends you can see from the experimental data.