Computational Chemistry III: Substituent Effects

(last revision: January, 2019)

Introduction

The frequency of the stretching vibration of the carbonyl group is studied using the infrared spectrum. The force constant of the bond is affected by the electron distribution in the bond and on adjacent atoms. Substituents that withdraw electrons from the carbonyl group will increase the force constant, thereby increasing the observed stretching frequency.

There are two effects that are responsible for the shift in the C=O frequency: inductive (polarization of σ-bonds) and mesomeric (overlap of lone pairs with the carbonyl πorbitals). Reduced mass changes due to substituents should be small, and hydrogen bonding will be minimized by using a nonpolar solvent.

Procedure

The instructor provided you with a selection of reagents, all of which have the same general formula : CH₃-C(O)Y , where Y is the substituent. You have acquired the IR spectrum for each of the reagents. Using Gaussview, build each of these molecules and optimize the geometry using the b3lyp DFT method and the 6-31++g(d,p) basis set. Once you have optimized the geometry for a particular molecule, perform a frequency calculation for the optimized structure. If one or more of the frequencies are negative, consult the lab instructor regarding potential subsequent steps.

Calculations

Determine the shift (relative to acetaldehyde: Y= H) in the carbonyl stretching frequency for each substituent. Plot the shift vs. σ and σ*: determine the degree of correlation for each. It may be worthwhile to see if the calculated shift is influenced by the partial atomic charges predicted in the Gaussian calculation. The report for the accompanying experiment (Measurement of Substituent Effects by Infrared Spectroscopy) should be included in the report for this experiment.
Reference