Computational Chemistry I: Structure

(revised January, 2011)

Introduction

In this experiment, you will model the effect of hydrogen bonding on the spectra and other physical properties of donors and acceptors. In particular, you will calculate the structure and properties of an amino acid and its zwitterion, alone and in the presence of a single water molecule, using density functional theory (DFT) (1) calculations through Gaussian (2).

The role of the solvent in biochemical processes is a subject receiving much attention. Gas phase spectroscopists are attaching water molecules to amino acids and monitoring the change in the spectrum that results from the formation of such a complex. (3) Theoreticians are determining the number of water molecules necessary for a complex to exhibit the behavior observed in solution. (4) Aqueous glycine is almost completely zwitterionic, whereas gas phase glycine is almost exclusively neutral. (5) You will use DFT calculations to predict the structure and vibrational frequencies of each and will construct possible water-amino acid complexes, determining the above properties for these as well.

You may find this software package to be useful in your other IR and hydrogen bonding reports.

Procedure

The Chemistry Department has Gaussview and Gaussian available on the workstation in the NMR Laboratory. There are a number of other departmental computers that have Gaussian (without Gaussview) as well. The laboratory instructor will demonstrate how to build molecules with this system and then assign each student an amino acid. Build a structure that closely resembles what you believe to be the optimal structure for the amino acid. Once the molecule is built, optimize the geometry. The program will automatically vary the structure of your molecule, determining the DFT (B3LYP/6-31++g(d,p)) energy as a function of geometry until an energy minimum is found. Once you have found an energy minimum, calculate the vibrational spectrum of your molecule. If the vibrational spectrum yields one or more negative frequencies (these are actually imaginary frequencies), you have not found a true minimum. Examine the vibrational
modes in question, alter the molecule accordingly, and repeat the above procedure until all vibrational frequencies are positive (real). Rebuild the molecule as a zwitterion and optimize the structure using the above procedure.

Once you have modeled the neutral and zwitterionic forms of your amino acid, build a complex between each compound and a single water molecule. It will take some understanding of hydrogen bonding to place the water in a location that may lead to an efficient optimization. Optimize as above. You will also need to calculate the geometry and spectrum of water alone.

Calculations

Tabulate the energies and vibrational frequencies of the amino acid, zwitterion, water, and complexes. How does the presence of water influence the energy difference between the neutral and zwitterionic form? Explain shifts in the vibrational spectra between the two molecules. Does complexation influence the spectrum?

References


