C. Experiment #3, Computational Study on the Enthalpy of Formation Using Gaussian 09 and GaussView 05

Objectives:
1. Practice utilizing computational methods that were introduced during the first semester of physical chemistry.
2. Calculate the enthalpy of reaction for an isodesmic reaction.
3. Estimate the enthalpy of formation of CO_2.

Background:

What is computational chemistry? Computational chemistry (also known as molecular modeling) is the application of computer-based models to the simulation of chemical processes and the computation of chemical properties. It accounts for roughly a third of the supercomputer usage worldwide. However, improved desktop computers mean that these methods are also becoming more available to scientists who are not purely computationalists. According to a recent textbook, "Today, the situation has been reached where, in many cases, the computational chemist can substitute the computing machine for the test tube."

Computational chemistry is a valuable tool for experimental chemists to bypass tedious, time consuming, costly and sometimes dangerous experiments. In the drug industry, computer design of molecules with specified properties is now becoming more common. Furthermore, computational chemistry allows one to investigate molecules that are too unstable to be studied experimentally, analyze quantities (such as atomic charges) that are not experimentally observable, and rectify incorrect experimental assignments (for example, based on spectroscopic experimental results, Gerhard Herzberg, a Nobel Prize winning scientist, concluded that the methylene radical ($:CH_2$) with two unpaired electrons had a linear geometry. Sophisticated calculations by Bender and Schaefer, however, demonstrated that methylene was bent with a bond angle of 135.1°. Further experiments of methylene confirmed the latter assignment. The measured bond angle was 137.7°). Also, computational chemistry allows one to both calculate certain quantities, such as heats of formation, with more accuracy than can be determined experimentally (special cases only) and improve one's general understanding of chemical phenomena.

It is now generally possible to obtain molecular structures (with ~1% accuracy), reaction enthalpies (~1 kcal/mol), dipole moments and infrared intensities, vibrational frequencies (~5%), reaction free energies (~2 kcal/mol), relative acid constants (~2 pK_a units), and reaction rates (for

certain types of reactions) without doing any laboratory experiments. This may lead to a reduction in experimental cost. There is also increased safety and faster turnaround when toxic or explosive compounds are involved. There is the prospect of an improved understanding especially when we have both an experimental and theoretical perspective on a problem. There is a caveat however. Care must be taken in choice of method and interpretation of results.

The following is a brief introduction to four major methods of computational chemistry:

(1) *Ab Initio:*
Ab Initio comes from the Latin word for "from scratch". These methods are based on first principles and quantum mechanics (solving the Schrödinger equation) and use no experimental parameters in their calculations. Despite the fact that they employ some mathematical approximations, the major disadvantage of *ab initio* quantum chemistry is the heavy demands on computer power because the computational time scales as the fourth power of the basis set size. Hartree-Fock (HF) and Quantum Monte Carlo (QMC) are two common wave-function-based *ab initio* calculations. Density Functional Theory (DFT) is another type of *ab initio* calculation that is much less expensive (in terms of CPU time, memory, and disk space) than HF and QMC because it is based on total electron density rather than wave functions. It is now generally agreed that density functional theory provides the most promising approach to accurate quantum chemical calculations for large systems. *Ab initio* calculations are qualitatively good and, for very small molecules, give excellent quantitative results.

(2) Semi-empirical:
Semi-empirical methods are quantum mechanical methods that have been applied to relatively large chemical systems for over three decades. They are much faster than ab initio methods because they involve a series of approximations, restrictions, and incorporation of experimental data. One of the largest simplifications is that empirical data is used for core electrons, and only the valence electrons are considered explicitly. Different semi-empirical methods have been optimized for different purposes. The MNDO, AM1 and PM3 methods were designed to reproduce heats of formation and structures of a large number of organic molecules. Other semi-empirical methods are specifically optimized for spectroscopy. For example,

ZINDO/S is quite good at prediction of electronic transitions in the UV/VIS spectral region. One rule of thumb is that semi-empirical methods are often very good for determining structures, or for calculating relative energies for molecules that are similar to molecules in the database used. However, the results can be very erratic for other molecules, and calculations of absolute energies can be problematic.

(3) Molecular Mechanics (MM):

In molecular mechanics methods, Newtonian mechanics (classical physics) is used to predict the structures and properties of molecules. Since the theory is not based on quantum mechanics, electrons are not treated explicitly in molecular mechanics. The method treats molecules as spheres (nuclei) connected by springs (bonds). Actually, molecules are treated as though they are a collection of charged balls connected by springs. Molecular mechanics methods can be used to model very large systems such as DNA or proteins. Although these molecules are too large for semi-empirical calculations, they are manageable in MM because the approximations markedly simplify calculations. Molecular mechanics methods cannot be used to address bond making or breaking because electrons are not treated explicitly in these methods. As with semi-empirical calculations, the quality of MM calculations can be very high for systems similar to those used to parameterize the method.

(4) Molecular Dynamics (MD):

MD calculations are used to simulate the time-dependent behavior (also known as motion, dynamics, vibrations, or trajectory) of molecules. Any one of the three techniques listed above can be used to calculate molecular trajectories, however MM is most common. MD makes it possible to study the dynamic behavior of a collection of thousands of separate molecules, for example diffusion of a solute molecule through a liquid. MD can even be used for calculations involving large bio-molecules in solution.

Procedure:

1. Consider the following reaction:

$$CH_3CHO + CH_3CH_3 \rightarrow (CH_3)_2CO + CH_4$$
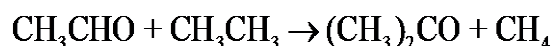
In this reaction, there are twelve single bonds and one (C=O) double bond in both the reactants and products. This is called an *isodesmic* reaction. Because of this conservation of the total number and types of

bonds, very good results can be obtained relatively inexpensively due to the cancellation of errors on the two sides of the reaction. In this task we will compute the enthalpy of reaction, ΔH_{rxn} using the following procedure.

    a. Optimize the structures using HF/6-31G(d)

    b. Determine the zero point energy correction by computing the frequencies of the optimized geometry using the same method/basis set as above. This is done by selecting the frequency option in the setup and extracting the zero-point energy correction from the Gaussian output file. After the job is done running you want to keep the window open and scroll up until you see the following list of numbers:
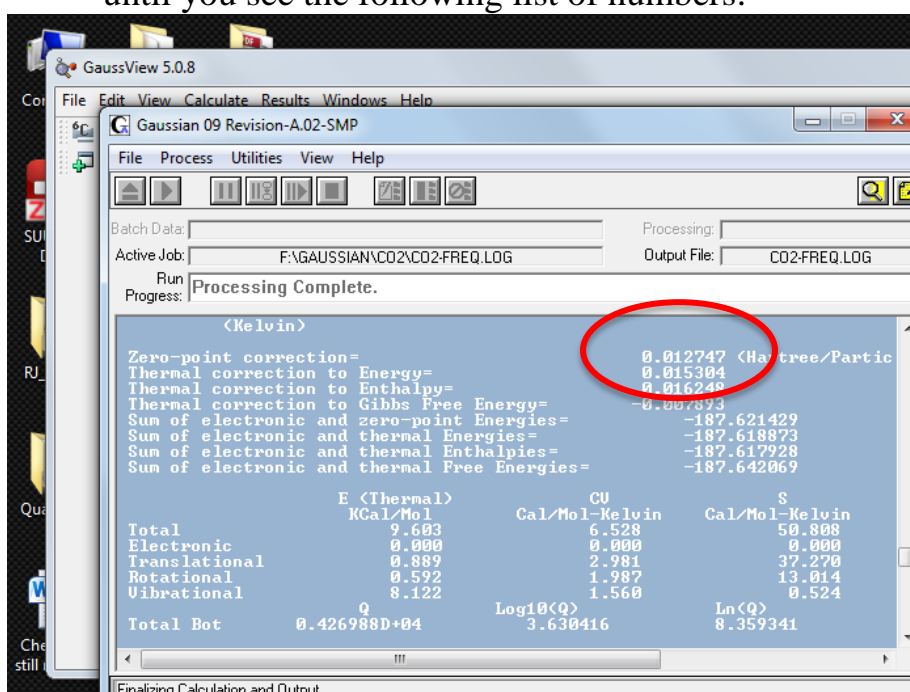
    c. Calculate the energy at the B3LYP/6-311+G(3df,2p) level.

    d. Gather all of the calculation data in a table similar to the following:

System	E(step c)	ZPE(step b)	E^0 (difference between c and b)
Ethane			
Acetaldehyde			
Methane			
Acetone			

e. Using the values for E^0, calculate the enthalpy of reaction. Compare your results to the experimental value of -9.9±0.3kcal/mol.

2. In this task we will be predicting the heat of formation of CO_2 via another isodermic reaction.

$$CO_2 + CH_4 \rightarrow 2H_2CO$$
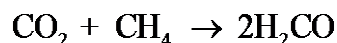
   a. Using the same method as task #1 calculate the enthalpy of reaction, ΔH_{rxn}.
   b. Calculate the heat of formation, $\Delta H_f(CO_2)$ using the following equation:

$$\Delta H_f(CO_2) = -[\Delta H_{rxn} - \Delta H_f(CH_4) + 2\Delta H_f(H_2CO)]$$

   Use the experimental values of heats of formations for methane and formaldehyde, which are -16.0 and -25.0 kcal/mol respectively.
   c. Compare the calculated heat of formation for CO_2 to the predicted value of -94.64 kcal/mol.