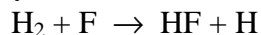


You may use any computational resources you like, Web based, commercial packages, Excel, or calculator. You may use any text reference. But, you may not use the active involvement of any person, either by voice, video, messaging, e-mail, smoke-signal, etc. Of course, you can ask me questions, especially about issues involving problems with the software. Save all your molecule structures. If you use a Mac or PC, give your Mac or the PC number. If you use WebMO give the name of the host (sona or iris12). Give the names of all the files that you generated. This problem is due before the final. The report form is attached. This problem is worth 25 points.

Question

Part 1. The reactions between H₂ and F₂ can be used as the basis for very powerful chemical lasers. This is because the reactions are very exothermic and produce products in highly excited vibrational states. One of the possible reactions is:



Calculate the Gibbs Free Energy change for this reaction using statistical mechanics techniques. The data for the reactants and products can be found in the data table from our class notes. This table, "Diatomic Spectroscopic Constants," is available on the PChem Web site if you have lost your copy.

Part 2. The D₀ for HF is listed as 5.869 eV. This is the spectroscopic dissociation energy, which is the dissociation energy from the lowest energy vibrational state to give ground state atoms. Use molecular orbital theory to calculate the theoretical dissociation energy (make sure to do the zero point energy correction—you may use the spectroscopically derived fundamental vibration frequency values from the data table). Since HF, H, and F are so small you can use the best available method and basis set to get the best possible energy estimate. Once you have your new D₀ for HF, repeat Part 1 with your new theoretical D₀. Calculate the % difference in the Gibbs Free Energy of the reaction.

Computational Hints:

In using advanced methods, it is common to do a geometry optimization at a lower level and the final energy calculation at a higher level using a single point calculation. Single point calculations are sometimes listed as "Energy" calculations in Set-up menus. In fact, some advanced calculations in some software packages can't do geometry optimizations at the more advanced levels. In listing the computation level for such two-step calculations, it is conventional to list them in the order: (single point property calculation method)/(geometry optimization method). For example, HF/6-311+G**//HF/3-21G* uses HF/3-21G* to do the geometry optimization and HF/6-311+G** to calculate the final energy or other properties.

In Spartan on the PC: To get just a single atom: in the Expert mode click on the divalent bond icon (-●-), click on the atom in the period table, and then click on the screen. Then delete the unfilled valences. If you get an error in Spartan (usually for the

calculation for the F atom) that the SCF calculation runs out of cycles, use the following keywords:

SCFCYCLES=500 ENERGY=2e-6

in the options dialog box. The ENERGY keyword decreases the tolerance for convergence of the energy in the SCF procedure. The default value is 1×10^{-6} , so the change isn't that different. Don't forget the energy conversion applet to make things easier.

Report: $\text{H}_2 + \text{F} \rightarrow \text{HF} + \text{H}$ Name _____

Using all spectroscopic data:

$\Delta_r G^\circ$ (298.15K) = _____ kJ/mol (or attach a printout if possible)

I used _____ to calculate this value. (e.g which program or spreadsheet)

The Spartan based energies for the necessary species for the D_0 calculation are:

_____ : _____ units: _____

_____ : _____ units: _____

_____ : _____ units: _____

I used the following method and basis set _____

or a two-step calculation at _____ // _____

The final D_0 = _____ eV with $\tilde{\nu}_0$ = _____ cm^{-1} and

zero point energy = _____ eV

My computer was _____ My files are: _____

Using all spectroscopic data except the molecular orbital based D_0 :

$\Delta_r G^\circ$ (298.15K) = _____ kJ/mol (or attach a printout)

% difference _____