

**10.637: IN CLASS WORKSHEET, LAB 4**

This worksheet should be filled in to the best of your ability during in-class time and returned to the TA at the end of the class period on **10/12/23** or uploaded to Canvas by **11:59PM EDT** (Thurs). Please answer questions to the best of your ability. You may work with a partner and ask questions, but you must hand in your own work.

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**A. Ethylene: Geometry optimization**

1. What is the final energy (in Hartrees) of the optimized ethylene molecule from this HF/cc-pVTZ calculation? -78.06

2. Experimental results for the geometric properties of ethylene are provided in the table below. Fill in the table for the optimized ethylene molecule geometry of MMFF94 and HF/cc-pVTZ.

|        | C=C bond length (Å) | C-H bond length (Å) | H-C-H angle (°) |
|--------|---------------------|---------------------|-----------------|
| HF     | 1.314               | 1.074               | 122             |
| MMFF94 | 1.336               | 1.085               | 121             |
| Expt.  | 1.330               | 1.074               | 116             |

3. Which method (MMFF94 or HF/cc-pVTZ) is in better agreement compared to experiments for the C=C bond length? For the C-H bond length? Why might this be?

MMFF94 is better for C=C bond, and HF is better for C-H bond

maybe because C=C bond has two electrons, there are more correlations

**B. Ethylene: Hessians and ionization potential calculation**

1. What is the wavenumber (in  $\text{cm}^{-1}$ ) of the bending normal mode (with nonzero/greatest intensity)? The symmetric stretch? The asymmetric stretch?

|       | bending ( $\text{cm}^{-1}$ ) | symmetric stretch ( $\text{cm}^{-1}$ ) | asymmetric stretch ( $\text{cm}^{-1}$ ) |
|-------|------------------------------|--|---|
| HF    | 1085                         | 3267                                   | 3368                                    |
| Expt. | ~900                         | ~3000                                  | ~3100                                   |

2. How do your results compare to the experimental (expt.) values? bigger than experiment

3. What is the vertical IP of ethylene from HF/cc-pVTZ total energy differences?

Report your answer in eV: 9.0

4. What is the vertical IP of ethylene, according to Koopmans' theorem?

Report your answer in eV: 10.4

5. How do the calculated IP values (from total energy differences and Koopmans' theorem) compare to the experimental value of 10.5 eV? very similar

6. Given what you have observed about HF frequencies and IP values, what missing ingredient from HF do you believe could improve agreement with experiment? Explain your reasoning in the context of both frequencies and ionization potentials:

For IP values, HF/cc-pVTZ total energy considers more electron correlation than Koopman's theorem method, but it is more different from experiment. It means that HF/cc-pVTZ consider electron correlation in a wrong way

**Extra Credit (3.5pts):**

1. (1.5pts) Insert/attach an overlaid and labeled image of the ethylene spectra below.  
Scaling factor: 0.920 Gaussian width: 66.0

**see attachment**

2. (0.5pts) Calculated value of IP for benzene via total energy differences? 7.9 eV  
Calculated value of IP for benzene via Koopmans' theorem? 9.2 eV  
Note that the experimental value for the IP of benzene is 9.24 eV. Does HF/cc-pVTZ give greater error for the IP of benzene or the IP of ethylene? Why might this be?

**The error is almost the same, it might because benzene and ethylene properties are similar**

3. (1pts) Insert/attach an overlaid and labeled image of the benzene spectra below.  
Scaling factor: 0.9200 Gaussian width: 58.0

**see attachment**

4. (0.5pts) Comment on the fit of a scaling factor of 0.9 for the spectra in benzene and in ethylene. Is there a difference? Why might this be?

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