

1. **BOLDED basis sets** are valence-double-zeta basis sets

(a) STO-3G	(g) 6-31G	(m) 6-311G**
(b) 3-21G	(h) 6-31++G	(n) 6-311++G**
(c) 3-21+G	(i) 6-31G**	(o) cc-pVDZ
(d) 3-21+G*	(j) 6-31++G**	(p) aug-cc-pVDZ
(e) 3-21G*	(k) 6-311G	(q) cc-pVTZ
(f) 6-31G	(l) 6-311++G	(r) aug-cc-pVTZ

2 numbers after '-' → double zeta ; 3 numbers → triple zeta
in coupled cluster cases, the 'DZ' indicates double zeta

2. Doing a calculation on ozone (O₃), you switch from a minimal basis set (e.g., STO3G) to a split-valence, polarized basis set (cc-pVDZ). (i) How many contracted basis functions are involved in total for each level of theory? (ii) Based on the scaling properties of MP2 level of theory with respect the number of basis functions, how many times longer will the second calculation take than the first ? (you can provide a mathematical expression that is not reduced to a final integer). Give a citation for the source of the basis set scaling property that you use.

The minimal basis will comprise a single 1s, 2s, and three 2p functions (x, y, and z) on each oxygen. That's five basis functions total, times three oxygen atoms, is fifteen basis functions. The split valence basis set will add an extra 2s and three extra 2p functions, and one set of five 3d functions. That's a total of fourteen basis functions per oxygen atom, so forty-two basis functions in total. As MP2 theory scales as the 5th power of the number of basis functions [a], the time for the second calculation compared to the first will be formally $(42/15)^5 = 172$ times longer.

[a] C. J. Cramer *Essentials of Computational Chemistry: Theories and Models* (Wiley, Chichester, 2004).p. 221.

3. Heat of Reaction and the Gibbs Free Energy of reaction for the isomerization of cis-difluoroethylene to trans-difluoroethylene

Although simple arguments might suggest trans-difluoroethylene would be more stable (lower steric hindrance for example), there is lots of evidence to indicate the cis isomer is a little more stable than the trans. This is the so-called ‘cis effect’ (http://en.wikipedia.org/wiki/Cis%E2%80%93trans_isomerism)

Experimentally, the cis isomer is more stable than the trans isomer by 4.1(2) kJ/mol [1,2]

i.e. the $\Delta G_{\text{rxn}}^{\circ}$ for cis \rightarrow trans is +4.1(2) kJ/mol at 298 K

In condensed phases there is a big difference in dipole moment which would lead to very different intermolecular forces. But what about the isolated molecule in free space ?

Expect 4 solutions - the G2 and G3 methods, which have predefined basis sets and methods, and 2 DFT calculations with a suitable functional and a small and large basis set.

APH results: NB when computing a difference of thermodynamic properties the direction of the difference is very important !. The reaction under consideration is cis \rightarrow trans so the calculated free energy (enthalpy) difference is $G_{\text{trans}} - G_{\text{cis}}$ ($H_{\text{trans}} - H_{\text{cis}}$).

(a) Multi-level methods

	G2MP2		G3-MP2B3	
	ΔH_f	ΔG_f	ΔH_f	ΔG_f
Cis-CHF=CHF	-276.705959	-276.736454	-276.750481	-276.781119
Trans-CHF=CHF	-276.704598	-276.735006	-276.749105	-276.779636
Rxn: cis \rightarrow trans	+1.361 mH	+1.448 mH	+1.376 mH	+1.483 mH
$\Delta G_{\text{trans}} - \Delta G_{\text{cis}}$	+37.0 meV	+39.4 meV	+37.4 meV	+40.4 meV
	+3.57 kJ/mol	+3.80 kJ/mol	+3.613 kJ.mol	+3.89 kJ/mol
	+0.85 kcal/mol	+0.91 kcal/mol	+0.86 kcal/mol	+0.93 kcal/mol

Both multi-level methods predict that the **cis isomer is more stable than the trans isomer**.

G2 and G3 are almost indistinguishable – so use the simpler / less costly one.

(time was 35 sec for G2 and 24 sec for G3, but most of the G2 time was geometry optimization and the optimized geometry was transferred to the G3 calculation)

b) DFT with M06 and a small and large basis set

	3-21G		6-311G	
	ΔH	ΔG	ΔH	ΔG
Cis-CHF=CHF	-275.422267	-275.453487	-276.893736	-276.924915
Trans-CHF=CHF	-275.425875	-275.456225	-276.898244	-276.928767
Rxn: cis \rightarrow trans	-3.61 mH	-2.74 mH	-4.51mH	-3.85 mH
$\Delta G_{\text{trans}} - \Delta G_{\text{cis}}$	-98.2 meV	-74.5 meV	-122.6 meV	-109.5 meV
	-9.48 kJ/mol	-7.19 kJ/mol	-11.8 kJ.mol	-10.2 kJ/mol
	-1.71 kcal/mol	-1.70 kcal/mol	-1.53 kcal/mol	-1.48 kcal/mol

DFT predicts that the **trans isomer is more stable than the cis isomer**. Given that the **DFT gets the wrong answer** and it is not very dependent on basis sets so one cannot expect further optimization to change this (maybe a different functional might help but . . .). Thus, from the DFT approach I tried, the optimal approach would be to use the faster **G2-MP2 method**, especially if one wanted to survey a lot of cis-trans systems.

References

1. N.C. Craig and E.A. Entemann, J. Am. Chem. Soc 83 (1961) 3047.
($\Delta H^\circ = +3.89$ kJ/mol, $\Delta S^\circ = 5.61$ J/K/mol from 477-762) $\rightarrow \Delta G^\circ = +3.72$ kJ/mol at 298 K
2. N.C. Craig and J. Overned, J. Chem. Phys. 51 (1967) 1127. based on complete vibrational analysis, they revised $\Delta H^\circ = 4.56$ kcal/mol $\rightarrow \Delta G^\circ = +4.39$ kJ/mol at 298 K for the electronic only component of the cis \rightarrow trans isomerization reaction.

Personally, I'd trust the direct GC measurements more, but it may be that the Gaussian computed values are only electronic (I'd be surprised though; they get the S° needed to generate G° from the E° , H° from the vibrational frequencies as that is the main source of entropy difference). So it seems safe to say the average of these two values is a conservative estimate of the experimental result.

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If you want to explore this further, there is a nice exercise at
http://nbo6.chem.wisc.edu/tut_del.htm which is also on the Chem 4PB3 website

Here is the problem statement from that website

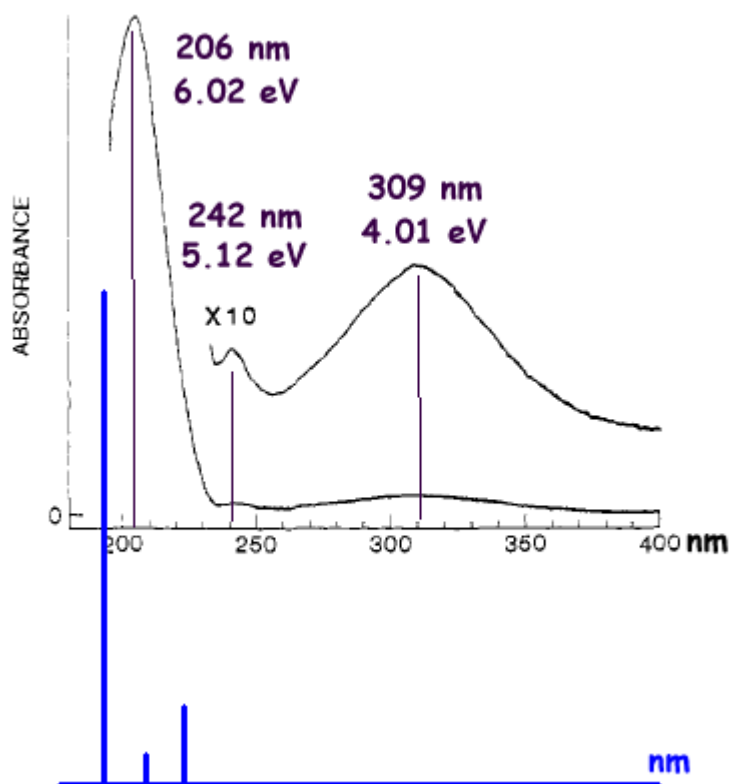
Cis vs. Trans configuration of Difluoroethene

1,2-difluoroethene exists in *cis* and *trans* isomers: Of the two, **the *trans* isomer is expected to be significantly more stable**, on the basis of steric and electrostatic factors, because the two bulky F atoms and the repelling negative charges of the two CF bond dipoles are maximally separated in this configuration. **However, the *cis* isomer is actually found to be very similar in energy.**

4. Using **MP2/6-31G(d)** calculate (1) the **ground state** and (2) **first 5 excited states of methylene cyclopropene**. (keywords: # RCIS(NStates=5)/6-31+G(D) Density=All Test)

- (a) Compare your results to experiment [1,2] and other theory [3].
 (b). How does the **electronic excitation calculation** interpret the **experimental spectrum** ?

#	Sym.	f	eV		nm	
			calc	Exp [1]	calc	exp
1	¹ B ₂	0.05	5.48	4.01	226	309
2	¹ B ₁	0.02	5.91	5.12	210	242
3	¹ A ₂	0.0	6.30	-	197	-
4	¹ B ₁	0.03	6.38	-	194	-
5	¹ A ₁	0.37	6.41	6.02	193	206



Using the keywords indicated in the statement of the problem the 5 excited states are at higher energy than the experimental, but do show the observed pattern of (from low_E to high_E), small, smaller and large transitions.

The calculation did not include a solvent effect, but the experiment was matrix isolation in frozen pentane (-78 C - that might actually be a mis-print and actually be pentane at liq. N₂ (78 K).

Gaussian can include the effect of a solvent as an averaged dielectric.

(c) How well do your ground state orbital energies compare to the photoelectron spectroscopy results ?

orbital	Exp't (Vert) [2]	calculated	Ratio(C/E)	character
2b ₂ (HOMO)	8.41	7.88	0.94	$\pi(\text{C}=\text{C}) - \pi(\text{ring})$
4b ₁	10.96	11.81	1.08	$\sigma(\text{C-H})+$
1b ₂	13.1	13.64	1.04	$\pi(\text{C}=\text{C}) + \pi(\text{ring})$
6a ₁	13.1	14.14	1.08	$\sigma^*(\text{C-C})$
3b ₁	14.3	15.61	1.09	$\sigma(\text{C-H})$ on CH ₂
5a ₁	15.9	17.64	1.11	$\sigma(\text{C}=\text{C}) - \text{C-H}(\text{ring})$
4a ₁	18.1	20.49	1.13	

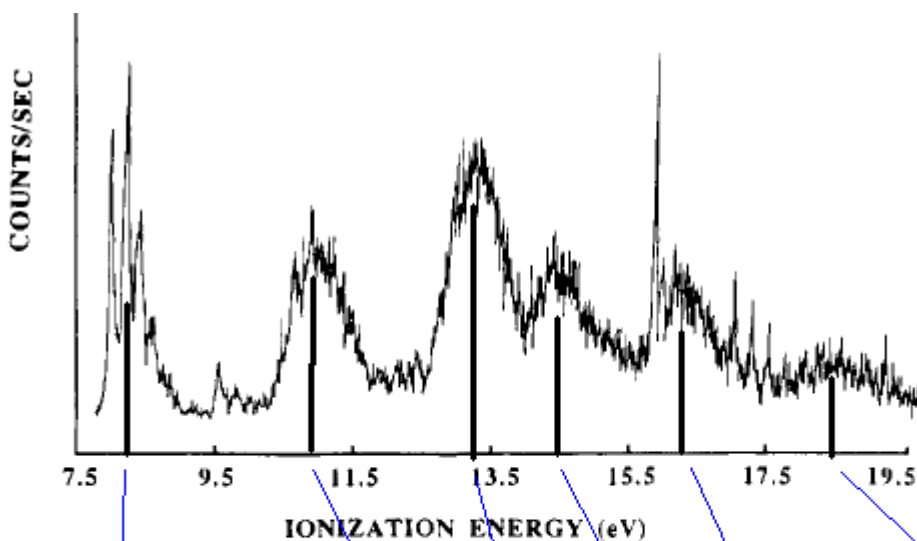
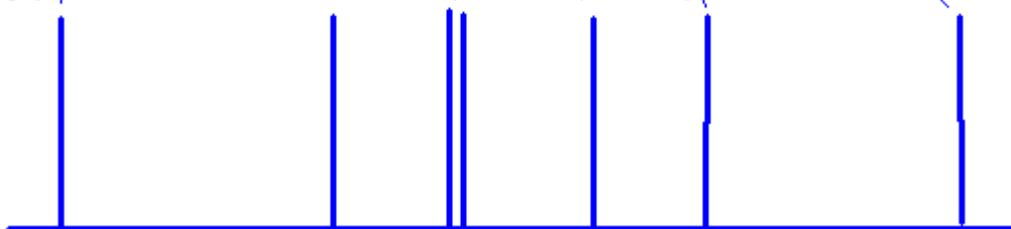
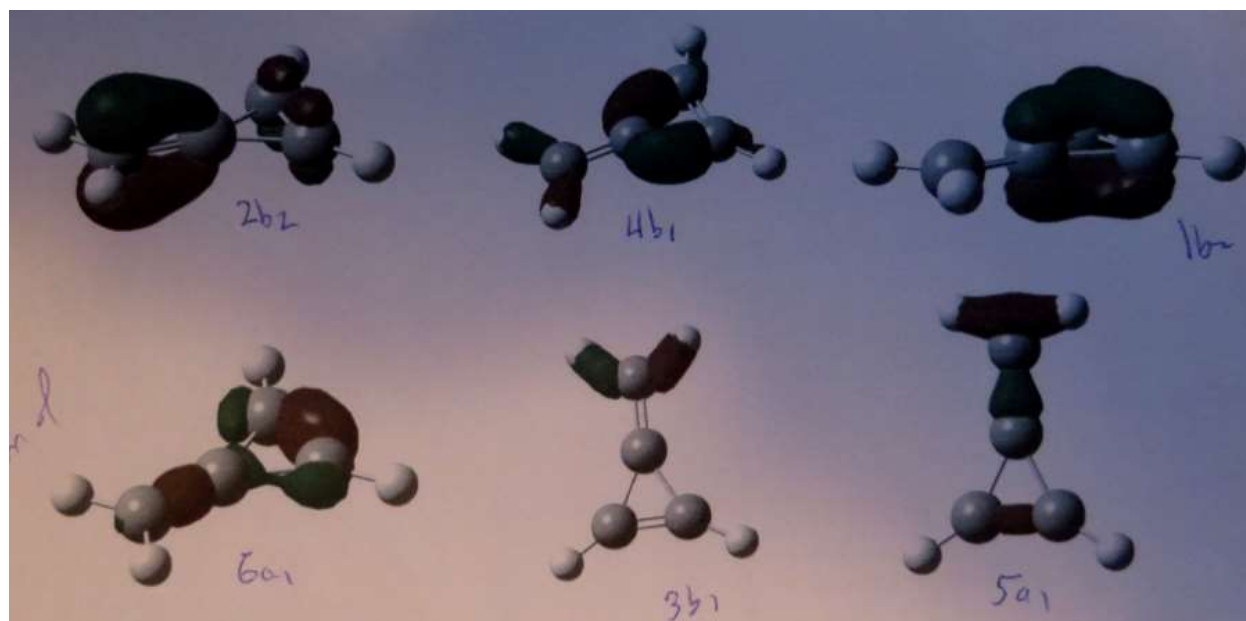
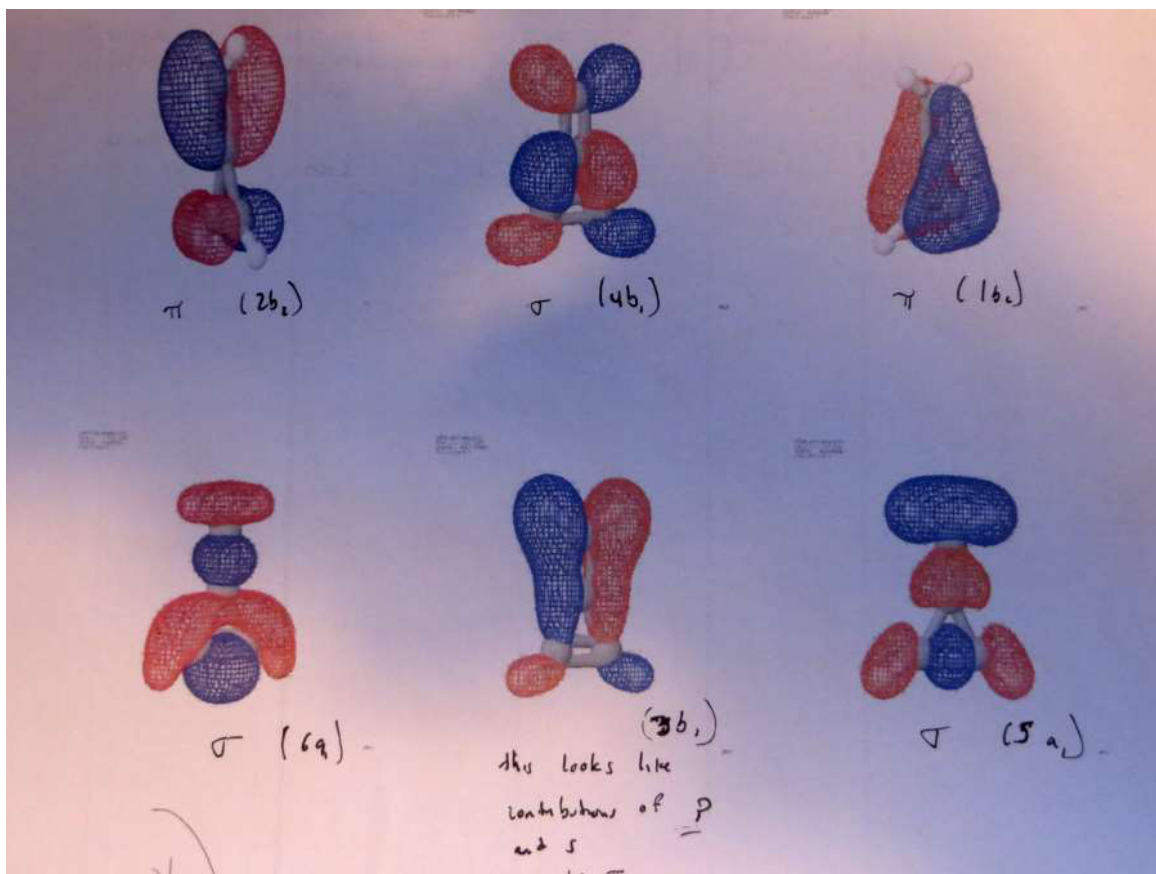


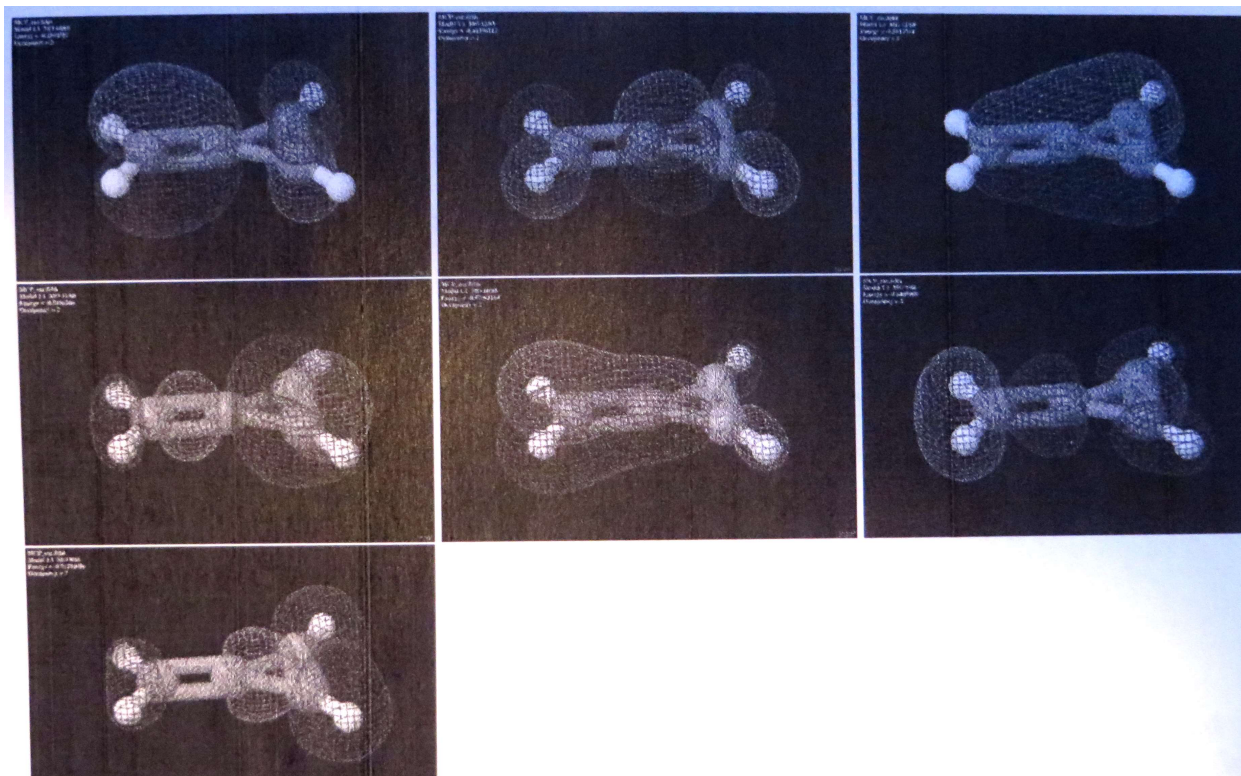
Figure 1. He I photoelectron spectrum of methylenecyclopropene. The sharp peaks between 15.5 and 17.5 eV result from nitrogen.



(d) Plot all the orbitals for which there is a photoelectron band below 20 eV binding energy, and discuss their bonding character.

NB the MO plot results will depend on (charge contour level) & method of plotting.





(e) How might you go **beyond Koopman's Theorem** ? (describe the method, do not do the calculation)

Koopman's Theorem states that the ground state orbital energies (in a HF calculation) are the -ve of the ionization potential (IP) of the corresponding orbital. This neglects (1) relaxation of the whole system to an (n-1) electron system and (2) change in correlation energy. The only reason KT works at all is that these two effects are of opposite sign and tend to roughly cancel.

The correct way to compute ANY transition energy is to compute the energy of each state separately (at the geometry of the initial state of the transition), and then take the difference in the energy (including any vibrational state energy, in principle). This is called a **Δ SCF calculation**. However if you do NOT use a post-HF method, the Δ SCF method will only correct for relaxation but not correlation. Thus a method like HF MP2 with a reasonably large basis would be a way to get better IPs - but 8 separate calculations would be needed (g.s. plus 7 ion states).

References

1. excited states: SW Staley & TD Norden, J Am Chem Soc 106 (1984) 3699
2. PES: SW Staley and TD Norden, J Am Chem Soc 111 (1989) 445
3. theory: M. Mehrhoff, R. Gonzalez-Luque & B.O. Roos, Theor Chim Acta 94 (1996) 143