

*This problem set will take slightly less time than the last one, but only slightly. Get started early.*

Some mechanical reminders: To run an AMSOL or G98 job, your input file should be named `myfile.dat`. Issue the commands `qamsol myfile.dat` or `qsubg98 myfile.dat`, respectively, and the scripts will take care of the rest. If you want to look at an output deck while a job is running, you can either `vi myfile.out` or `more myfile.out`. To examine the queue on the Origin, the command is `qstat -a`; you may find that `qstat -a | egrep chem##` (where `chem##` is your userid) to be more convenient.

Some quick notes/reminders with respect to Gaussian98:

- 1) Template files have been provided in the directory `~inst8021/G98_templates` — feel free to study them carefully to ensure you have proper file formats, memory requests (`%mem=8000000`), parallel requests (`%nproc=2`), and checkpoint naming conventions (`%chk=myfile.chk`). (Template files for AMSOL jobs are also available in `~inst8021/amsol_templates`.)
- 2) If you are entering geometric data (as opposed to reading it from the checkpoint file) you *must* end the input file with a blank line.
- 3) To find transition states *in the absence of a symmetry constraint*, use `fopt=(ts)`. If you have a symmetry constraint, you need to decide whether the reaction coordinate for the TS *breaks* the symmetry (in which case, don't use `ts` as a keyword) or *preserves* it (in which case continue to use it). If you are looking for a TS, you may often find it helpful to do `fopt=(ts, calcfrc, noeigentest)`. The other keywords request calculation of analytic force constants on the first step, that the job not die if you have other than one imaginary frequency.
- 4) You can save a *lot* of time by using useful information from previous calculations stored in the checkpoint file. *Plan* your calculations to try to save time.
  - a) Keywords `guess=read` and `geom=checkpoint` get the wave function and the geometry, respectively, from the last completed calculation. So, if you have just done an optimization, and want to follow-up with a frequency calculation, for instance, you will certainly want to use these keywords. **Note: Frequencies *must* be calculated using the same level of theory with which the geometry was optimized to correspond to true IR frequencies!** (Note that if you know ahead of time you will want frequencies after a given optimization, you can simply include the `freq` keyword in the same job as `fopt`).

b) If you just optimized a geometry at one level of theory, and want to repeat that optimization at a different level, include `readfc` in the `fopt=()` keyword, e.g., `fopt=(ts,readfc)` for a second pass at a transition-state optimization. This causes the program to start with the force constants from the previous calculation, which is efficient. **It's usually a good idea to work your way up in a geometry optimization so you don't waste a lot of computer time because of a bad initial guess.**

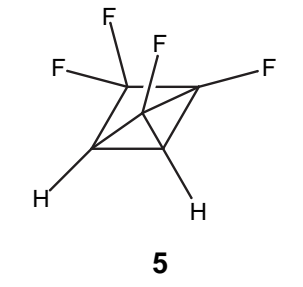
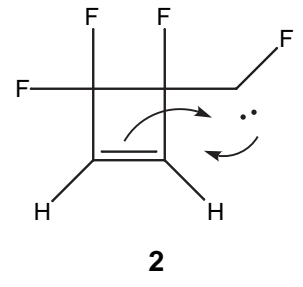
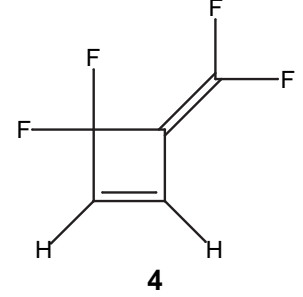
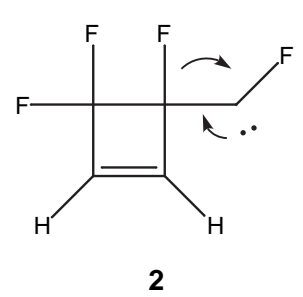
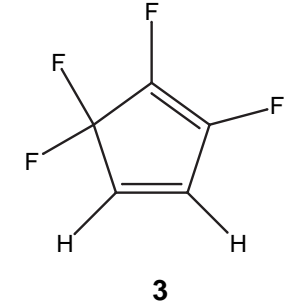
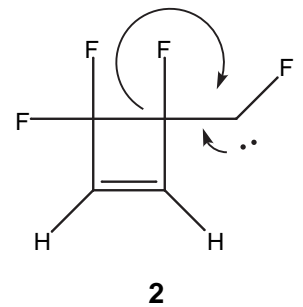
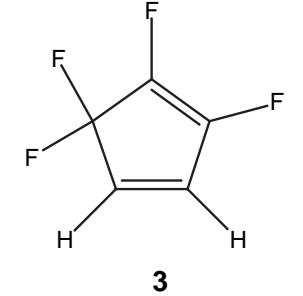
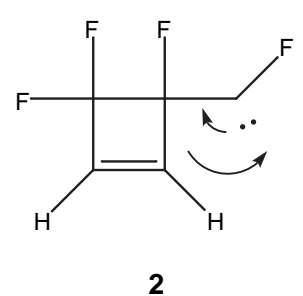
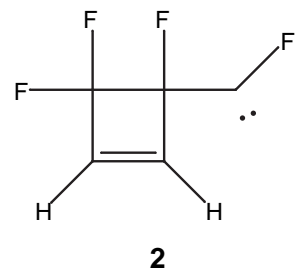
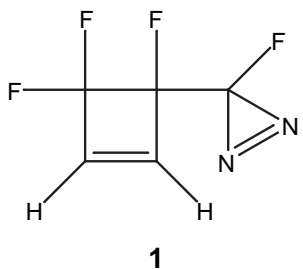
### The Problems:

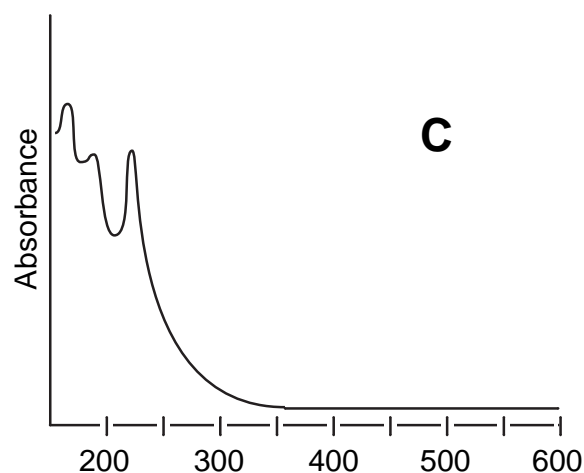
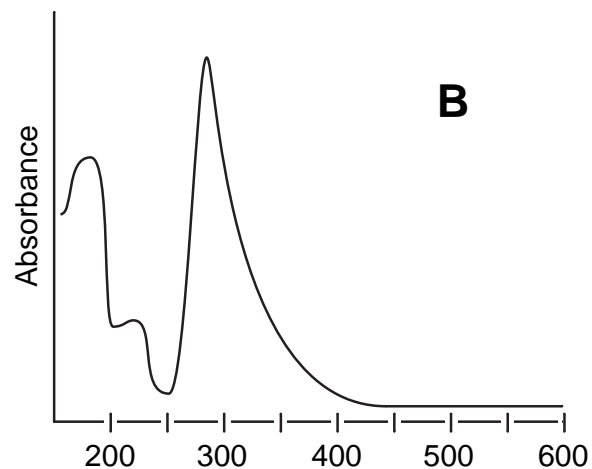
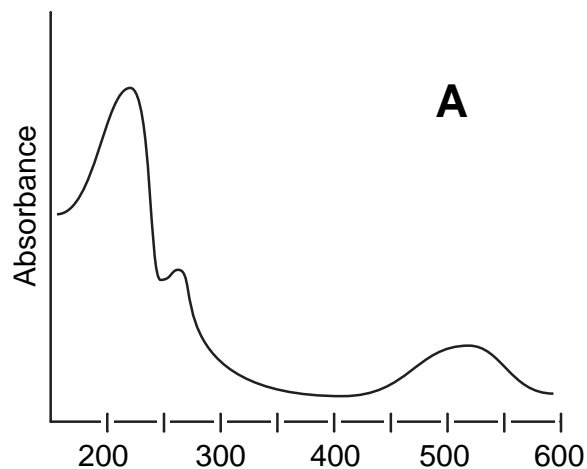
1. Congratulations! After years of trying, you have finally succeeded in making the unusual diazirine **1** shown below. You deposit **1** on a neon matrix at 10 K and irradiate it with UV light in the hopes of blowing out N<sub>2</sub> and making carbene **2**. Is the ground state of **2** expected to be a singlet or a triplet? Calculate the energies of both states (at their optimized geometries, of course) at the *mPW1PW91/MIDI!* level to answer this question (note that the MIDI! basis set is accessed using the G98 keyword “*midix*”, *not* “*midi!*”).

From its singlet state, carbene **2** may rearrange in 3 possible ways (two different 1,2-alkyl shifts leading to the same product **3** and a 1,2-fluorine atom shift leading to product **4**) and it may add across the cyclobutene double bond to make the wildly strained polycyclic **5**.

After your initial radiation, you take the UV spectrum **A** shown below. You tune your laser to 510 nm (the long wavelength absorption band in **A**) and blast away again. Afterwards, you observe the new UV spectrum **B**. You tune your laser down to the new “long” wavelength band at 290 nm, and once again flash the matrix. Afterwards, you record the UV spectrum **C**. You then crank your laser down to its lowest setting, 220 nm, and take your last shot at your poor molecule. When you are done, the spectrum is completely bleached (no peaks observed down to 160 nm, the limit of your window). However, when you warm the matrix up and allow the effluent to pass into a mass spectrometer, you record a dominant mass peak at 138 amu.

Using time-dependent density functional theory, predict the 3 longest wavelength UV absorptions for the ground state of **2** and possible products **3-5**. The keywords line to use, after having optimized each geometry, is `# td mpw1pw91/midix guess=read geom=checkpoint`, where you will simply change the checkpoint file each time to reflect which molecule you are computing. Based on these calculations, explain what structures you cycled through in your experiment.





Now, still at the *mPW1PW91/MIDI!* level of theory, find any *one* of the transition state structures connecting the ground state of **2** to its possible products **3** to **5**. Provide a picture of the structure with key heavy-atom bond lengths labeled. What is the imaginary frequency associated with your TS structure? What is the free energy difference (i.e.,  $\Delta G$ ) between **2** and your TS structure? Based on that difference, what is the rate constant for your unimolecular rearrangement that would be predicted from transition-state theory at 10 K? At 298 K? If this reaction were to be the *only* reaction by which **2** reacted, what would be the half-life for disappearance of **2** at 10 K? At 298 K?

2. Here continues a problem that will carry over to the final exam. We add to the data at:

[pollux.chem.umn.edu/~kinsinge/8021/8021.2003/ProbSets-Exams/2003/C3H7NO/](http://pollux.chem.umn.edu/~kinsinge/8021/8021.2003/ProbSets-Exams/2003/C3H7NO/)

Your present task is to update your structure on the potential energy surface (PES) with a calculation at the B3LYP/6-31G\* level (since there is no double slash, this implies re-optimizing the geometry). The most efficient way to do this will be to read in the force constants and geometry from your RHF frequency calculation (i.e., `fopt=(readfc) geom=checkpoint, guess=read`) as keywords. *Nota bene*: if you were using `fopt=ts` you will need to continue to use `ts`, of course. Once you have a reoptimized structure, do a new frequency calculation at the B3LYP/6-31G\* level and update your entry with that data.

Finally, compute the aqueous solvation free energy for your DFT structure using the SM5.42R/B3LYP/MIDI! model in MN-GSM (MN-GSM is a solvation module for G98—MIDI! is a highly efficient basis set optimized for use in solvation calculations). A complete `.dat` file for accomplishing this can be gotten by issuing the command:

```
cp ~inst8021/PS3_data/mysolv.dat .
```

Edit `mysolv.dat` to change the checkpoint file name to whatever your checkpoint file *is* named (and be sure you are in the same directory as your checkpoint file) and you should be able to submit the job immediately. When the calculation completes, add the solvation free energy to the website data. Report only one position after the decimal place.

The solvation free energy will appear in the following form in the output file:

```
(9) DeltaG-S(liq) free energy of solvation
(9) = (6) - (0) -10.304 kcal/mol
```

(where the above example is taken from the instructor's `mysolv.out` file)