

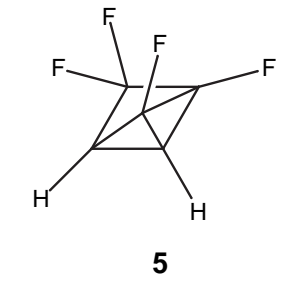
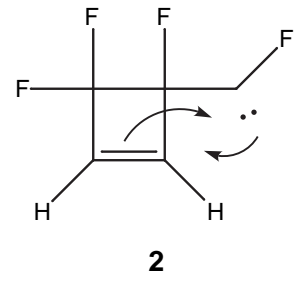
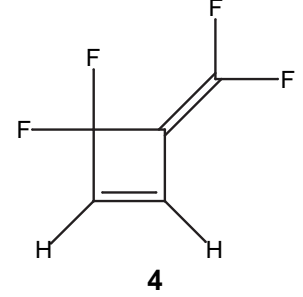
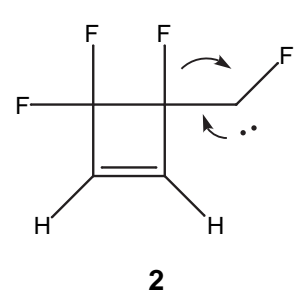
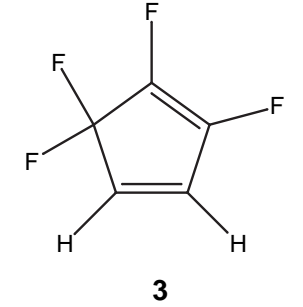
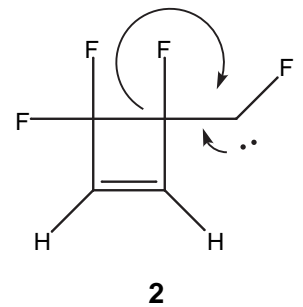
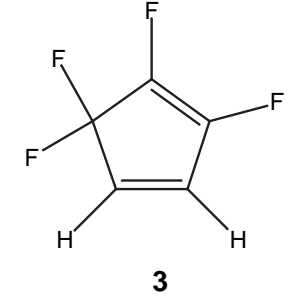
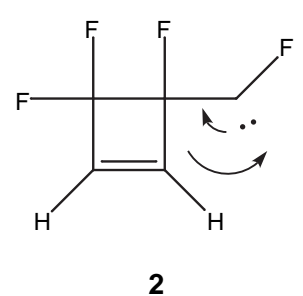
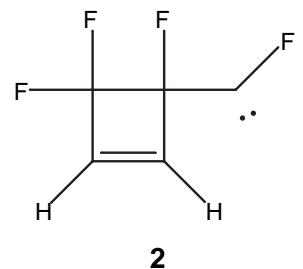
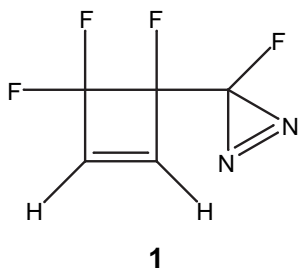
1. Congratulations! After years of trying, you have finally succeeded in making the unusual diazirine **1** shown below. You deposit **1** on a neon matrix at 10 K and irradiate it with UV light in the hopes of blowing out N<sub>2</sub> and making carbene **2**. Is the ground state of **2** expected 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!*”).

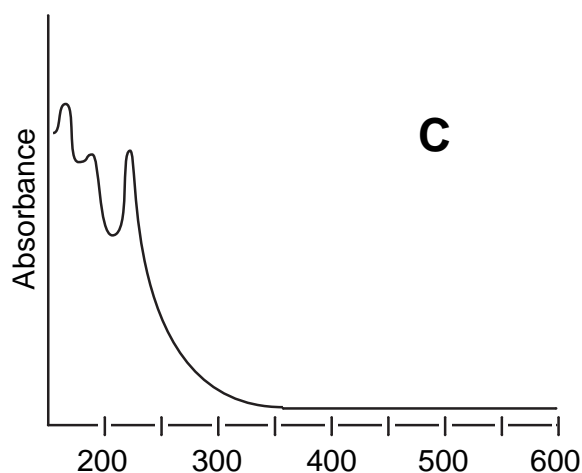
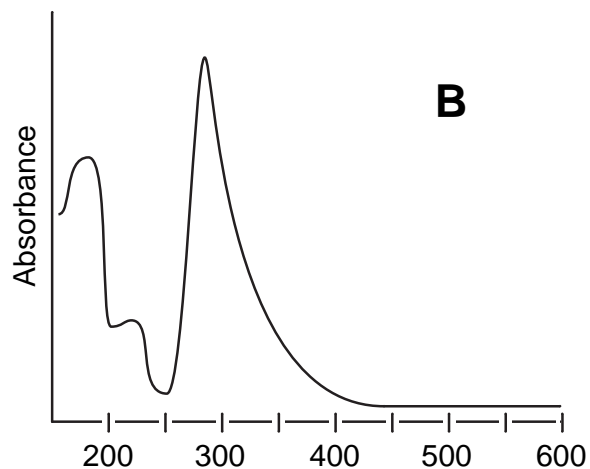
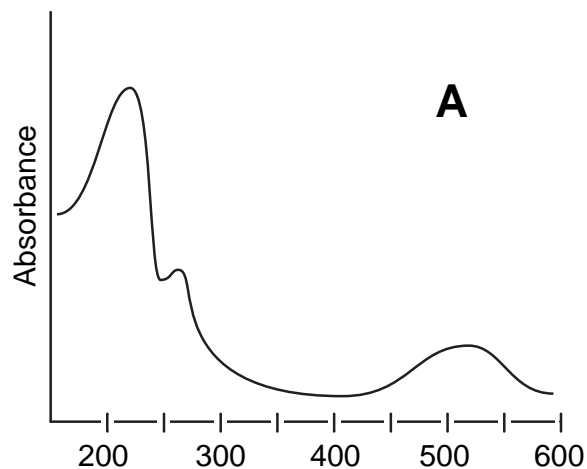
The computed *mPW1PW91/MIDI!* 298 K enthalpies for the singlet and triplet states of **2** are -587.333524 and -587.316436  $E_h$ , respectively. The singlet is thus the ground state by 10.7 kcal/mol. (Good thing, since only singlets would be expected to do the rearrangements that occupy the rest of the problem.) Analysis of  $E$ ,  $H_0$ , or  $G_{298}$  is also perfectly acceptable (all lead to the same conclusion as to the ground state).

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.





The indicated TDDFT level predicts that singlet structure **2** absorbs at 232 (s), 266 (w), and 513 (m) nm. This is consistent with spectrum A (i.e., you did indeed make the singlet carbene). Structure **3** is predicted to absorb at 178 (m), 214 (w), and 290 (s) nm, consistent with spectrum B (i.e., irradiation at 510 nm converted **2** into **3**). Structure **4** is predicted to absorb at 167 (s), 184 (w) and 227 (m) nm, consistent with spectrum C. Finally, structure **5** is predicted to have all 3 absorptions at energies higher than 160 nm, consistent with no apparent UV spectrum even though a species of mass 138 remains on the matrix.

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?

The transition state structures are shown in the below figure. Values for  $\Delta G^\ddagger$ , rate constants, and half lives are in the below table. To convert  $\Delta G^\ddagger$  to a unimolecular rate constant, we use the TST expression

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger} / RT}$$

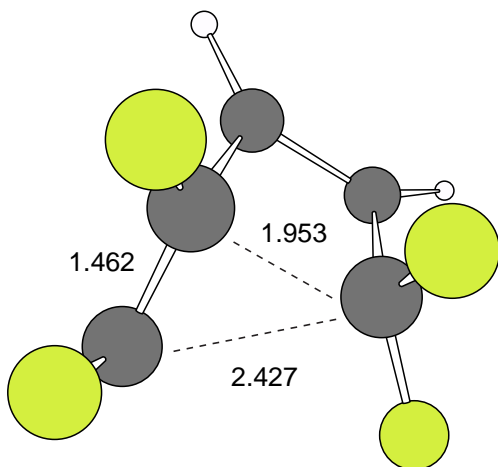
where  $k_B$  is Boltzmann's constant,  $T$  is temperature,  $h$  is Planck's constant, and  $R$  is the universal gas constant. For a unimolecular process, the half-life is

$$t_{1/2} = \frac{\ln 2}{k}$$

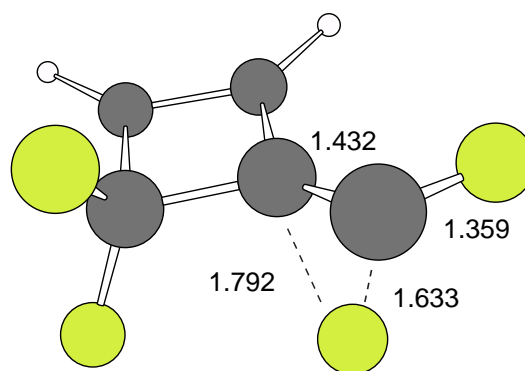
where  $k$  is the rate constant.

One subtle point that should be mentioned is that the table below assumes the  $\Delta G^\ddagger$  value computed at 298 K (the default for G98) to be a constant. We could, in fact, compute it for 10 K using specific keywords to cause G98 to use that temperature, and we would expect it to be different (unless there is a coincidental cancellation between the temperature dependencies of the enthalpies and entropies of activation), but we will not do so, in the interests of simplicity.

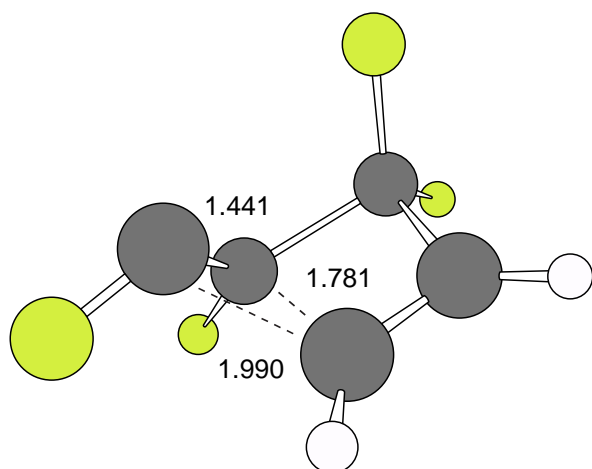
TS structure	$\Delta G^\ddagger$ , kcal/mol	$k$ , s <sup>-1</sup> (298 K)	$k$ , s <sup>-1</sup> (10 K)	$t_{1/2}$ , s (298 K)	$t_{1/2}$ , s (10 K)
<b>2</b> to <b>3</b> path 1	4.6	$2.8 \times 10^9$	$3.7 \times 10^{-89}$	$2.5 \times 10^{-10}$	$1.9 \times 10^{88}$
<b>2</b> to <b>3</b> path 2	9.9	$3.6 \times 10^5$	$3.6 \times 10^{-205}$	$1.9 \times 10^{-6}$	$1.9 \times 10^{204}$
<b>2</b> to <b>4</b> path 1	32.8	$5.6 \times 10^{-12}$	0	$1.2 \times 10^{11}$	$\infty$
<b>2</b> to <b>5</b> path 1	18.5	$1.6 \times 10^{-1}$	0	4.2	$\infty$



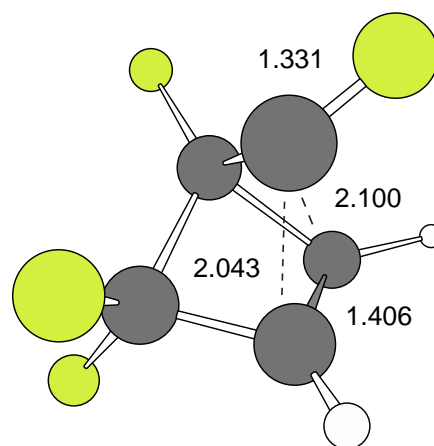
**2 to 3 path 1**



**2 to 4 path 1**



**2 to 3 path 2**



**2 to 5 path 1**

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 foxt=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)

Sensible values constitute satisfactory completion of this problem.