

Name: _____

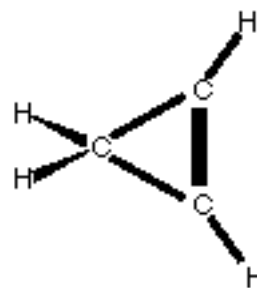
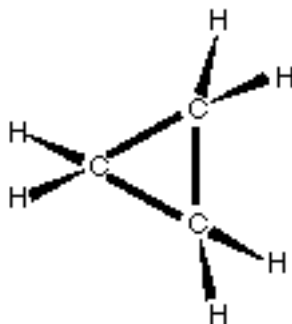
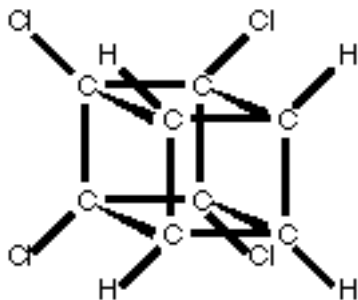
Fundamental Constants

Speed of light, $c = 2.997925 \times 10^8 \text{ m s}^{-1}$ $\pi = 3.14159$ Planck's constant, $h = 6.62618 \times 10^{-34} \text{ J s}$ Boltzmann's constant, $k = 1.38066 \times 10^{-23} \text{ J K}^{-1}$ Atomic mass unit, $amu = 1.66056 \times 10^{-27} \text{ kg}$ $e^x = 1 + x + x^2/2 + (x \ll 1)$

1. Given the black body radiation formula below and the knowledge that the peak in the sun's energy spectrum occurs at 480 nm, estimate the exterior temperature of the sun. For full credit demonstrate how the black body radiation formula leads to Wein's law (the final step of this proof requires that $e^{hc/\lambda kT} - 1$ be approximated by $e^{hc/\lambda kT}$). (25 points)

$$U = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$

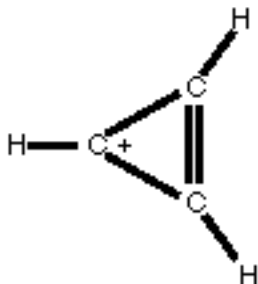
2. The ground-state wavefunction the hydrogen atom has the form $\psi(r) = Ne^{-ar}$. Normalize this spherically symmetrical function. The volume element is $d\tau = \sin\theta d\theta d\phi r^2 dr$, with $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$, $0 \leq r < \infty$. The final integral will require you to integrate by parts, $u dv = uv - \int v du$. (25 points)
3. Write out all of the allowed (using a table of microstates) term symbols for the electronic configuration p^3 . (25 points)
4. Compute the relative populations of the lowest five rotational energy levels for the molecule $^{12}\text{C}^{16}\text{O}$ where the mass of ^{12}C is 12.000000 amu, ^{16}O is 15.994915 amu and the ground state bond length is 113.07 pm. (25 points)
5. Describe the point group for each of the following molecules. (25 points)



C_6H_{12}
cyclohexane
boat conformation

6. Describe the Born-Oppenheimer approximation and its significance in quantum mechanics and spectroscopy. (25 points)

7. Describe what a Franck-Condon principle is and its importance to spectroscopy. (25 points)
8. For the molecule cyclopropene carbocation given below, calculate the irreducible representation for all of the 18 degrees of freedom in this molecule. Determine which of these irreducible representations describe translation, rotation and vibration. Finally, determine which of the vibrational modes are IR and Raman active. (25 points)



D_{3h}	E	σ_h	$2C_3$	$2S_6$	$3C_2$	$3\sigma_v$	$h = 12$
A_1'	1	1	1	1	1	1	z^2, x^2+y^2
A_2'	1	1	1	1	-1	-1	R_x
A_1''	1	-1	1	-1	1	-1	
A_2''	1	-1	1	-1	-1	1	z
E'	1	2	-1	-1	0	0	$(x, y), (xy, x^2-y^2)$
E''	1	-2	-1	1	0	0	$(xz, yz) (R_x, R_y)$

9. For the cyclopropene carbocation, set up the molecular orbit calculation for the orbitals of this molecule. Use the Hückel approximations to simplify the equations which describe the molecular orbitals and solve the secular equation to determine the energy levels. Comment on the stability of the carbocation relative to the carboanion. The equation below will help in solving this problem. (25 points)

$$(\alpha - E)^3 + 2\beta^3 - 3(\alpha - E)\beta^2 = (\alpha - E + 2\beta)(\alpha - E - \beta)^2$$

10. Show mathematically or pictorially what would happen to an equilibrium magnetization in the rotating frame when the pulse sequence $90_x - - 180_x - - \text{acq.}$ is applied to a single on-resonance spin. What fundamental NMR parameter can be measured in this manner by varying the delay τ . Notice that this sequence is very similar to the inversion recovery sequence, $180_x - - 90_x - \text{acq.}$ (25 points)