

1. (12) a) Sketch the proton magnetic resonance spectra of $\text{CH}_2\text{FCH}_2\text{COOH}$.
(Ignore possible spin-spin interactions with fluorine.)
- b) Sketch the ESR spectrum of CH_3CH_2 assuming that $a(\text{CH}_2) > a(\text{CH}_3)$.
- c) Sketch the ESR spectrum of CH_3CH_2 assuming that $a(\text{CH}_3) > a(\text{CH}_2)$.
2. (10) Consider the pure rotational Raman spectrum of N_2 . The observed transitions are:
- | | |
|-------------------------|-------------------------|
| 19.908 cm^{-1} | 43.762 cm^{-1} |
| 27.857 cm^{-1} | 51.721 cm^{-1} |
| 35.812 cm^{-1} | 59.662 cm^{-1} |

What is the rotational constant B_0 (in cm^{-1})?

Estimate the centrifugal distortion constant D_0 (in cm^{-1})

3. (12) a) Sketch the normal modes of H_2CO .

b) Indicate above which modes are IR active.

c) Indicate above which modes are Raman active.

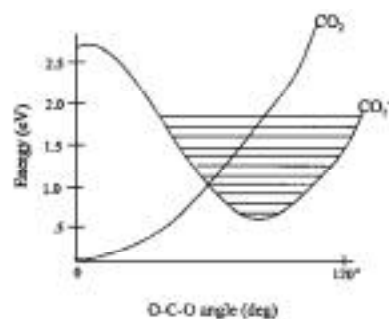
4. (12) The bonding potential energy curves of CO_2 and CO_2^- are sketched in the adjacent picture

The horizontal lines represent the vibrational levels with $v=0$ being indicated for CO_2 and $v=0-9$ for CO_2^- .

a) estimate the adiabatic electron affinity (EA).

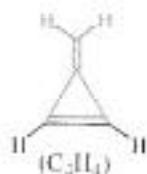
b) estimate the vertical EA.

c) Sketch the vibrational structure that one would see in the electron transmission spectrum ($\text{CO}_2 + e^- \rightarrow \text{CO}_2^-$) for CO_2 .



d) Suppose that you were able to form CO_2^- in its $v=0$ level. Estimate the photon energy required to vertically detach an electron from CO_2^- .

5. (12) Consider the following hydrocarbon.



a) Sketch the π orbitals of this molecule (with π_1 being most stable, π_2 next most stable, etc.).

b) Label each of the above orbitals according to symmetry (i.e., according to the representations of the appropriate character table).

c) Write the Hückel Hamiltonian for this species.

d) Is the HOMO - LUMO transition dipole allowed? Show your work.

6. (10) Consider the 1-dimensional particle-in-the-box problem. $V=0$ for $0 \leq x \leq a$, and $V=\infty$ otherwise.

Choose a trial wavefunction $c_1 f_1 + c_2 f_2$, where $f_1 = (1-x^2)$, and $f_2 = (1-x^4)$.

a) Evaluate the energy with the above trial wavefunction and compare to the exact energy of the ground state.

b) What are the best values of c_1 and c_2 ?

7. (12) Consider an atom in the following electronic configuration. $1s^2 2s^2 2p^3 3d$. List the term symbols for all possible electronic states (don't worry about J values).

8. (8) Based on what you have learned about molecular orbitals give an explanation of why CS_2 is linear but CS_2^- is highly bent.


9. (12) Suppose that you have prepared hexatriene in its all trans conformation



a) Is the HOMO-LUMO $\pi \rightarrow \pi^*$ transition dipole allowed?

b) Is the HOMO-LUMO+1 transition dipole allowed?

Now suppose that the molecule is in the cis conformation.

c) Is the HOMO-LUMO transition dipole allowed in the cis conformer  ?

d) Is the HOMO-LUMO+1 transition allowed in the cis conformer?

Answers should be supported by symmetry-based arguments.

HOMO = highest occupied molecular orbital
LUMO = lowest unoccupied molecular orbital
LUMO+1 = 2nd lowest unoccupied molecular orbital