

Chemical Physics Cumulative Examination November 18, 2009
Molecular Spectroscopy

1. (5 points) What is the Franck-Condon principle?
2. (5 points) What is the general selection rule for Raman spectroscopy?
3. (5 points) What is the origin of hyperfine splitting in ESR spectroscopy?
4. (5 points) What does one mean by Stokes and anti Stokes lines?
5. (5 points) What does one mean by “the classical turning point “in a diatomic molecule?
6. (10 points) What are the symmetries of the molecular states of O_2 that correlate to the ground state asymptote.
7. (10 points) In ESR spectroscopy if a doublet radical contains N equivalent protons how many lines would you expect to see? What are their relative intensities?
8. (10 points) Define each of the following:

Fluorescence

Phosphorescence

Intersystem crossing

Internal conversion

9. (15 points) The Morse potential for a diatomic molecule has the form

$$V(x) = D_e (1 - \exp(-\beta x))^2$$

where $x = R - R_e$, β is a parameter specific for each diatomic and D_e is the dissociation energy. Derive an expression for the force constant in terms of β and D_e

10. (15 points) Outline the theoretical procedure for deriving the selection rule for a vibration transition in a diatomic molecule. You may use a two state model and assume the electromagnetic field of the radiation has the form $\vec{E} = \vec{E}_0 \cos(\omega t)$
11. (15 points) Determine the symmetries of the normal modes of formaldehyde. Which normal modes are Raman active? Which are IR active?

Potentially useful information

The character table of the C_{2v} point group

C_{2v}	\hat{E}	\hat{C}_2	σ_v	σ'_v		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

$$a_i = \frac{1}{h} \sum_{\hat{R}} \chi(\hat{R}) \chi_i(\hat{R}) = \frac{1}{h} \sum_{\text{classes}} n(\hat{R}) \chi(\hat{R}) \chi_i(\hat{R})$$