Chemical Physics Cumulative Exam Key

November 18, 2009

1. Franck Condon principle - Electrons make a transition from one electronic state to another so quickly that the nuclei do not move appriciably during the transition

2. Raman Spectroscopy - Vibration/Rotation involves the electronic polarizability. Must change in vibrations & must be anisotropic for rotations

3. Coupling of nuclear magnetic moments & electron spin

4. In Raman spectroscopy the incident photons may increase in energy (anti Stokes) or decrease in energy (Stokes). Stokes lines appear at frequencies lower than the incident photons while anti-Stokes are higher.

5. If a diatomic molecule is in a vibrational energy level with energy E_v and is moving in the potential $V(R)$ where R is the bond length, then the classical turning points ($R_\pm$) are those for which $V(R_\pm) = E_v$

6. $^3\Sigma_g^-$, $^1\Delta_g$ & $^1\Sigma_g^+$

7. N+1 lines with a binomial intensity distribution

8. Fluorescence - radiative decay (transitions) between two states of the same spin multiplicity.

Phosphorescence - radiative transition between two states of different spin multiplicity

Intersystem crossing - non radiative decay between two states of diffrent multiplicity

Internal Conversion - non radiative decay between states of the same multiplicity.

9. $k = \left.\frac{d^2V}{dx^2}\right|_{x=0} = 2\beta^2 D_e$ (work through details!)

10. $\hat{\mathcal{H}} = \hat{\mathcal{H}}^\circ + \hat{\mathcal{H}}'$; $\hat{\mathcal{H}}^\circ$ = Hamiltonian in absence of radiation field.

$\hat{\mathcal{H}}' = -\vec{\mu}\cdot\vec{E}$; coupling to field ; $\vec{\mu}$ = dipole moment

$\vec{E} = E^\circ \cos\omega t$

Time dependent Schrodinger equation $\hat{\mathcal{H}}\,\Psi(x,t) = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}$

use as ansatz $\Psi = a_1(t)\,\Psi_1^\circ(x,t) + a_2(t)\,\Psi_2^\circ(x,t)$

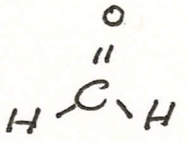
$$\hat{\mathcal{H}}^\circ \Psi_j^\circ = -\frac{\hbar}{i}\frac{\partial\Psi_j^\circ}{\partial t}$$

Insert Ψ into the Schrodinger Equation, multiply by Ψ_2° & integrate. Boundary conditions $a_1(0) = 1$, $a_2(0) = 0$. Assume $a_1(t) \sim 1$ & solve for $\frac{da_2}{dt}$

This results in $a_2(t) \cong \mu_{21} E^\circ \frac{\sin(\omega - \omega_{21})t}{\omega - \omega_{21}}$

where $\omega_{21} = \omega_2 - \omega_1 = (E_2^\circ - E_1^\circ)/\hbar$

$\mu_{21} = \langle 2 | x | 1 \rangle$ & this is not zero if 2 & 1 differ by 1 vibrational quanta.

11 

	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}_{v'}$
Γ_{red}	12	-2	2	4

4 atoms ∴ 6 vibrations

		Trans	Rot
$a_{A_1} = \frac{1}{4}(12-2+2+4) = 4$		z	–
$a_{A_2} = \frac{1}{4}(12-2-2-4) = 1$		–	R_z
$a_{B_1} = \frac{1}{4}(12+2+2-4) = 3$		x	R_y
$a_{B_2} = \frac{1}{4}(12+2-2+4) = 4$		y	R_x

∴ $\Gamma_{VIB} = 3A_1 + B_1 + 2B_2$ & all are IR & Raman active