MOLECULAR SPECTROSCOPY & ENERGY LEVELS NOTES

Basic Spectroscopic Facts to Know

Energy Levels for Rotation –

- Linear molecules, diatomics: $E_J = BJ(J+1) - DJ^2(J+1)^2$
- Spherical tops (SF_6, etc): $E_J = BJ(J+1)$
- Symmetric tops: $E_{JK} = BJ(J+1) + (A-B)K^2$

Energy Levels for Vibration –

- Normal modes of polyatomic molecules (SHM): $E_v = \omega_e(v+½)$
- Local modes, real diatomics, etc: $E_v = \omega_e(v+½) - \omega_e x_e(v+½)^2$

Vibrations in Electronic Spectra –

- Franck-Condon Principle: $I(v' \leftarrow v'') \propto |<\chi_{v''}|\chi_{v'}>|^2$ (Franck-Condon Factor).
- If r_e changes a lot, many vibrations excited. If r_e doesn't change then $\Delta v = 0$.
- Only totally symmetric modes can be excited with many v' in absorption.

Gross Selection Rules –

- Pure rotation in IR, Microwave: molecules with dipole moments.
- Pure rotational Raman: all molecules except spherical tops.
- Vib-Rot in IR: a dipole must change or appear in the vibrational motion.
- Vib-Rot Raman: polarisability must change in the motion.
- Electronic Spectra: all molecules.

Selection Rules for rotational level changes –

- One-photon transitions (microwave, IR, UV), no other coupled angular momentum present: $\Delta J = \pm 1$.
- One-photon, other angular moment present: $\Delta J = 0, \pm 1$.
- Two-photon (Raman): $\Delta J = 0, \pm 2$.

Selection Rules for Vibration level changes –

- IR, Raman Spectra, harmonic oscillator: $\Delta v = \pm 1$.
- Real molecules: $\Delta v = \pm 1, \pm 2$, etc (overtones much weaker than fundamental).
- Electronic Spectra: Δv = any, symmetric modes only. Intensities from Franck-Condon factors.
- Exclusion Rule: in centro-symmetric molecules IR and Raman activity are mutually exclusive.

Selection Rules for Electronic Transitions in Diatomics –

- $\Delta\Lambda = 0, \pm 1$. $\Delta S = 0$. $g \leftrightarrow u$. $+ \leftrightarrow +$, $- \leftrightarrow -$.

Branches –

- P branch $\Delta J = -1$. R branch $\Delta J = +1$. Q branch $\Delta J = 0$.
- IR Spectra in diatomics show P and R branches.
- IR Spectra in parallel bands of linear molecules: P and R.
- IR Spectra in perpendicular bands of linear molecules: P,Q,R.
- IR Spectra in parallel bands of symmetric tops: P,Q,R.
  (others are more complex).

Electronic Spectra of diatomics –

- P and R branches in $\Sigma-\Sigma$ transitions.
- P,Q and R in $\Sigma-\Pi$ or vice-versa, and most others.

Constants –

$B = h/(8\pi^2 cI)$ $I = \mu r^2$

Energy Levels and Concepts

Units and Nomenclature –

Molecular Spectroscopy uses several non-SI units. Should usually stick to the units given. Often there is a ratio of $^{hv}/_{kT}$.

Energy: cm^{-1}, Hz, eV. cm^{-1} x c (in $cm\ s^{-1}$) = Hz, i.e. cm^{-1} x $3x10^8$ x 100 = Hz.

Molecules:
cm^{-1}, eV, Hz x h, kT are all per molecule.
kJ mol^{-1}, RT imply per N molecules.
Also useful: at 298K, $kT \approx 207cm^{-1}$.

Nomenclature:
Upper state – single prime (J', B', v', etc).
Lower state – double prime (J'', B'', etc.)

What is Spectroscopy?

Change of one quantum state to another ➔ spectroscopic transition. Energy for this provided by EM radiation. Exchange of energy between radiation and matter.

Time-dependent Schrodinger Equation is important. In a weak oscillating EM field ➔ t-dependent. Perturbation Theory to describe the transition.

$$\underset{\substack{\uparrow \\ \text{interaction} \\ E}}{W_{el}} = -\underset{\substack{\uparrow \\ \text{electric} \\ \text{dipole} \\ \text{moment}}}{\mu} \cdot \underset{\nwarrow \text{radiation E-field (vectors)}}{E}$$

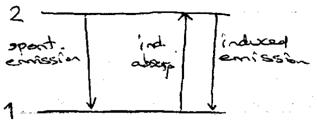
$hv = E_{upp} - E_{low}$ [variation of μ over time]

Electric dipole transitions most common in Molecular Spectroscopy, but should be aware that light waves have oscillating electric and magnetic fields, so transfer could occur magnetically:

$$W_{mag} = -\underset{\substack{\nearrow \\ \text{mag. dipole moment}}}{m} \cdot B \quad \text{] – usually very small in comparison}$$

Therefore magnetically induced transition 10^4 times less likely than electrically.
Systems with no oscillating electric dipole moment ➔ ESR and NMR.

Radiative Relaxation –



Spontaneous Emission:

Level 2 → Level 1 by relaxation, giving out a photon of energy hv_{21}.
Occurs in the absence of external radiation. Still involves transition dipole moment – quantum basis (interaction with radiation vacuum state).

If there are N_2 molecules in level 2, energy is emitted at the rate:

$$I_{21} = N_2\, hv_{12}\, A$$

Comparing this with the probability, A, of emission shows that intensity depends on v^4.
Hence, spontaneous emission irrelevant in microwave, but often dominant relaxation mechanism in UV (sets time limit for molecule in upper state).

Induced Emission / Absorption –

Coupling between oscillating transition moment and oscillating electromagnetic field.

Probability, $P_{12} = \rho(v_{12})\, B_{12}$

Where ρ is the radiation density.

Net Emission / Absorption –

Must consider populations:

↓: $I_{em} = N_2\, hv_{12}\, [A + B\rho(v_{12})]$

↑: $I_{abs} = N_1\, hv_{12} B\rho(v_{12})$

i.e. net depends on different in N_1 and N_2. Thermal Equilibrium,

$$\frac{N_2}{N_1} = e^{-(E_2-E_1)/kT}$$

Absorption Coefficients –

Linear (weak field):

$$dI = -I\alpha c dx$$

I = intensity, c = molecular concentration, α = absorption coefficient.

Integrate over path:

$I = I_o e^{-\alpha l c}$ [Beer-Lambert Law]

Orbital Approximation –

e.g. $H_2 = 1\sigma_g^{\ 2}$

$CO = 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$

Pauli: ψ_{tot} is antisymmetric wrt exchange of electrons.

i.e. $H_2\ (1\sigma_g^{\ 2}) \Rightarrow \psi = 1\sigma_g(\alpha)(1)\ 1\sigma_g(\beta)(2) - 1\sigma_g(\alpha)(2)\ 1\sigma_g(\beta)(1)$

Born-Oppenheimer Approximation –

Electrons and nuclei experience same forces of magnitude but nuclei ~ 4 times more massive, so electrons move much more rapidly.

Energy of a molecule (but not atom) depends on the relative positions of nuclei. Need to consider this. Born-Oppenheimer Approximation ➔ nuclear and electronic motion are separable and independent (reasonable as nucleus moves much slower).

Good approximation ➔ nuclei fixed.

Hence,

$$\psi_{tot} = \psi_{el}(q_{el})\ \psi_{nucl}(q_{nucl})$$

Similarly, can separate nuclear motion into vibration and rotation:

$$\psi_{tot} \approx \psi_{el}(q_{el})\ \psi_{vib}(q_{vib})\ \psi_{rot}(q_{rot})$$
$$E_{tot} = E_{el} + E_{vib} + E_{rot}$$
$$\Delta E_{el} >> \Delta E_{vib} >> \Delta E_{rot}$$

Approximation is very bad when:

Jahn-Teller Effect: direct coupling of electronic and vibrational motions.

Lambda-type Doubling: electronic and rotational coupling.

Translational –

Separated from other degrees of freedom so reference to Centre of Mass.

Also, usually only concerned with changes within molecule – only effect of translation is small (Doppler Effect).

Not usually necessary to consider since:

$$\Delta E_{trans} << kT$$

Can be separated rigorously (no approximation).

(X_o, Y_o, Z_o) = coordinates of centre of mass.

$$X_o = \frac{\sum_i m_i x_i}{\sum_i m_i}$$, and similar for Y_o, Z_o.

Particle i at (X_i, Y_i, Z_i), where $X_i = X_o + x_i$, etc.
Thus coordinates relative to centre of mass.
X_o, Y_o, Z_o variation = translational motion. Completely separately measurably from "internal" coordinations x_i, y_i, z_i.

LCAO Approximation –
From Orbital Approximation, electronically:

$\psi = \phi_1\phi_2 \ldots \phi_n$ [each ϕ represents 1 electron]

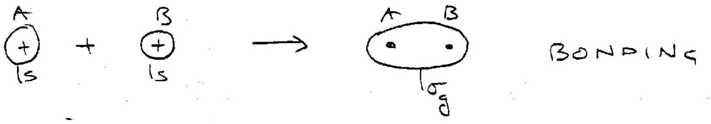
LCAO ➔ Linear Combination of Atomic Orbitals,
$\phi = \sum_m c_m \chi_m$ where, c_m = mixing coefficient, χ_m = atomic orbital.

Variation Principle – adjust c_m so that energy is as low as possible (more accurate).
LCAO Approach works for small molecules, but computationally very difficult.

Bonding & Antibonding Molecular Orbitals –
Consider H_2. $H^\bullet$ ➔ $\chi = N e^{-r}$ (1 electron). Label each H $1s_A$ and $1s_B$.
Consider symmetry,
Molecule is symmetrical, so match e-density, $\propto |\psi|^2$ ➔ ψ identical round each nucleus or same except for change of sign.
Hence,

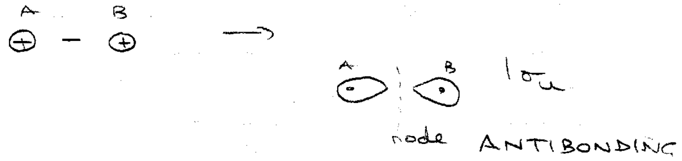
$$\phi = c_A 1s_A + c_B 1s_B$$

$c_A = c_B$,
$\phi = 1s_A + 1s_B$ [Normalisation not included]

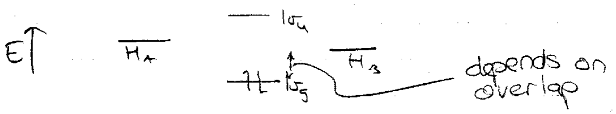


σ ➔ cylindrically symmetric about A-B.
g ➔ gerade, symmetric wrt centre of symmetry.

However, can also have:
$c_A = -c_B$ [e-density still the same]
$\phi = 1s_A - 1s_B$



This gives



Selection Rules –

$$\text{Intensity} \propto (N'' - N') < \psi' | \mu_z | \psi'' >^2$$

μ_z is the key factor.

$$\mu_z = \sum_{\alpha=x,y,z} \lambda_{z_\alpha} \mu_\alpha$$

Pure rotational spectrum,

$$\psi_{el}' = \psi_{el}'' \ \& \ \psi_{vib}' = \psi_{vib}''$$

Symmetry tells us that observation of rotational transition requires the molecule to have a non-zero electric dipole moment.

First integral (λ_α)gives rotational selection rules:

$$\Delta J = 0, \pm 1$$

$$\Delta\Lambda \text{ (or } \Delta K) = 0, \pm 1$$

Second integral (μ) cannot be factorised into only vibrational / electronic parts.

Expand μ_α as power series in vibrational coordinate Q.

Vibrational transition ➔ first term vanishes.

2nd term ➔ use orthogonality and factorises.

Hence, for allowed vibrational transition, dipole moment must change as vibration occurs.

Also, $\Delta v = \pm 1$ for simple harmonic oscillator.

Allowed electronic transition, must contain totally symmetric molecular point group (Σ^+ for diatomics).

Symmetric vibration (e.g. for diatomics) = and Δv_α .

Non-symmetric vibration - $\Delta v_\alpha = 0,2,4\ldots$ (odd changes the symmetry).

Inversion and Parity Rule –

$$E^* f(X,Y,Z) = f(-X,-Y,-Z) \text{ where } E^* = \text{parity.}$$

$$E^*\psi = \pm\psi \qquad + \Rightarrow \text{even parity, } - \Rightarrow \text{odd parity.}$$

$\langle \psi' \mid \mu_z \mid \psi'' \rangle \neq 0$ for allowed, ➔ integrand symmetric wrt E*. μ_z is antisymmetric, therefore $\psi'\psi''$ must be antisymmetric.

Hence,

$$+ \leftrightarrow - \text{ is allowed, } + \leftrightarrow + \text{ and } - \leftrightarrow - \text{ are forbidden.}$$

Parity Rule different for magnetic dipole (even). Gives opposite result.

Centrosymmetrically,

Electric g ↔ u allowed.

Magnetic g ↔ g / u ↔ u are allowed.