SPECTROSCOPY

1. Types of spectroscopy and molecular motions involved in spectroscopic transitions (see also Table 10.1 McQ).

Region of electromagnetic spectrum	ν (Hz)	"Name" of Spectroscopy	Type of molecular event involved in transition
1. radiowaves	10^6–10^9	NMR	nuclear spin flip [ΔE depends on $\vec{B}_{\text{external}}$]
2. microwave	10^9–10^{11}	ESR microwave	electron spin flip [ΔE depends on $\vec{B}_{\text{external}}$] rotational transitions
3. Far-IR	10^{11}–10^{13}	Far IR	rotation of small molecules
4. Infra-red	10^{13}–10^{14}	IR	Vibrations
5. Visible	$4.6\text{-}7.5 \times 10^{14}$ (400 nm-650 nm)	color	$\left\{\begin{array}{l}\text{electronic}\\\text{transitions}\end{array}\right.$
6. Ultraviolet	10^{14}–10^{16}	UV	
7. Far UV X-ray	10^{16}–10^{20}	Photoelectron spectroscopy ESCA	inner shell electronic transitions

II. Wavefunction in Born-Oppenheimer Approximation

$$\Psi(\vec{r}_e,\sigma_e,\vec{R}_N,\sigma_N) \approx \psi_e(\vec{r}_e;\sigma_e;\vec{R}_N,\sigma_N)\chi_N(\vec{R}_N,\sigma_N)$$

$$\approx \psi_e(\vec{r}_e;\vec{R}_N)\Gamma_e(\sigma_e)\chi_N(\vec{R}_N)\Gamma_N(\sigma_N)$$

III. Dipole moment operator (used for both the regular dipole moment expectation value and the transition dipole introduced).

$$\vec{\mu}_{\text{total}} = \sum_{k=\text{charged particles}} (\text{charge})_k \overrightarrow{(\text{position})}_k$$

classical expression

$$\vec{\mu}_T = \underset{\substack{\uparrow\\ \text{nuclei}}}{\sum_N} q_N \vec{R}_N - e \underset{\substack{\uparrow\\ \text{electrons}}}{\sum_i} \vec{r}_i$$

in atomic units $q_N = Z_N$ $\quad e = 1$

In the Born-Oppenheimer approximation we pick a value of the parameter $\vec{R}_N$ (nuclear positions) and calculate $\psi_e(\vec{r}_e;\vec{R}_N)$. To evaluate the dipole moment when the nuclei are at these positions, we use the standard expectation value for the electronic wavefunction:

$$\vec{\mu}(R) = \int dr_e \psi_e^*(r_e;R)\vec{\hat{\mu}}_T\psi(r_e;R)$$

where $\vec{\hat{\mu}}_T$ is the operator corresponding to the dipole moment expression ($\vec{\mu}_T$ and $\vec{\hat{\mu}}_T$ are identical since the $\vec{\mu}_T$ does not involve momenta).

$$\vec{\mu}_T^X(R) = \sum_N Z_N\vec{R}_N - \int dr_e\left(\psi_X^*\right)_e\left(\sum_i \vec{r}_i\right)(\psi_X)_e$$

In this expression we have used $\int dr_e\left(\psi_X^*(r_e;R)\right)_e(\psi_X(r_e;R))_e = 1$. The expectation value for a dipole moment of molecule in electronic state X is

$$\langle\vec{\mu}_T\rangle^X = \int \chi_N(R)\vec{\mu}_T^X(R)\chi_N(R)dR$$

IV. Probability of a transition between states a and b (from $\Psi_\alpha \to \Psi_b$)

This probability involves three factors:

(1) $v \approx \frac{E_b - E_a}{h}$ (good old chem. 1 that a match between photon energy and difference in eigenvalue is needed)

(2) The second factor comes from a treatment using time-dependent perturbation theory. The expression can be thought of as the probability that the photon interactions with the wave representing state a, Ψ_a, will change this wave into one appropriate to state b, Ψ_b, the final state.

$$\text{Prob}_{b\leftarrow a} \propto \left|\iint dR_N dr_e d\sigma_N d\sigma_e \psi_a \vec{\hat{\mu}}_T \psi_b\right|^2$$

The integral in the absolute value is called the transition dipole integral. The expression for the transition probability in terms of this integral involves several approximations (the dipole approximations):

(a) Only the interaction of the electric field (not the magnetic field) of the radiation is considered.

(b) The electric field strength is essentially constant over the length of the molecule [i.e., the molecule is small ($\approx 10^{-10}$ m) compared to the wavelength of the radiation ($>10^{-8}$ m)].

(3) The net intensity of radiation absorbed also involves the number of atoms or molecules in the initial and final states $(\mathrm{Num})_a$ and $(\mathrm{Num})_b$. Due to stimulated emission and absorption having the same probability per molecule, one can write:

$$I_{b\leftarrow a} \propto [(\mathrm{Num}_a - \mathrm{Num}_b)]\ \mathrm{Prob}_{b\leftarrow a}$$

(an additional term due to spontaneous emission has been neglected).

V. Spin selection rules

When the wavefunction can be written as a product of a space and spin function (no spin-orbit coupling included in $\hat{H}$) as in II above, the probability of transition can be factored

$$P_{b\leftarrow a} \propto \left|\int dR_N dr_e (\psi_e^* \chi_N^*)_a \vec{\hat{\mu}}_T (\psi_e \chi_N)_b\right|^2 \left|\text{"}\int d\sigma_e \Gamma_{e_a}^* \Gamma_{e_b} \int d\sigma_N \Gamma_{N_a} \Gamma_{N_b}^* \text{"}\right|^2$$

ignoring the nuclear spin functions Γ_N for now, we see that $P_{b\leftarrow a}$ will be zero if

$$\text{"}\int d\sigma_e \Gamma_{e_a}^* (\sigma_e) \Gamma_{e_b} (\sigma_e)\text{"} = 0$$

We know how to evaluate "$\int d\sigma$" as a sum over spin, and if Γ_a and Γ_b are orthogonal (as for a singlet-to-triplet transition), then $P_{b\leftarrow a} = 0$. Thus in the dipole approximation Ψ_a and Ψ_b must represent the same spin state for an allowed transition.

VI. Evaluating the spatial part of the transition dipole integral (from II and IV) in a.u. (dropping a few tired subscripts)

$$\begin{aligned}\vec{\mu}_{b\leftarrow a} &= \int \Psi_a^* \vec{\hat{\mu}}_T \Psi_b d\tau \\ &= \int \psi_a^* \chi_a^* \left(\sum_N Z_N \vec{R}_N - \sum_i \vec{r}_i \right) \psi_b \chi_b drdR\end{aligned}$$

$$\boxed{\begin{aligned}\vec{\mu}_{b\leftarrow a} = \int \chi_a^* \left(\sum_N Z_N \vec{R}_N \right) \chi_b dR \int \psi_a^* (r;R) \psi_b (r;\ R) dr \\ - \int \chi_a^* \chi_b dR \int \psi_a^* (r;\ R) \left[\sum_i \vec{r}_i \right] \psi_b (r;R) dr\end{aligned}}$$

Note that $\psi_a(r;\ R)$ is the electronic wavefunction for state a in the Born-Oppenheimer approximations and $\chi_a(\vec{R})$ is the wavefunction for nuclear motion (relative motion), for example, in diatomic molecules

$$\chi_a(\vec{R}) = \chi_{\mathrm{vibrational}}(R) \chi_{\mathrm{rotation}}(\theta, \phi)$$

VII. Evaluating $\vec{\mu}_{b\leftarrow a}$ for transitions where $\psi_{\text{electronic}}$ does not change, i.e., pure vibrational or rotational transitions (pure nuclear transitions):

$\psi_X = \psi_a = \psi_b \qquad \chi_a \neq \chi_b$

using the “boxed” expression in VI.

$$\vec{\mu}_{b\leftarrow a} = \int \chi_a^* \left[\sum_N Z_N \vec{R}_N\right] \chi_b \, dR \overbrace{\int \psi_X^* \psi_X \, dr}^{=1}$$

$$- \int \chi_a^* \chi_b \, dR \int \psi_X^* \left[\sum_i \vec{r}_i\right] \psi_X \, dr$$

$$\vec{\mu}_{b\leftarrow a} = \int \chi_a^* \underbrace{\left[\sum Z_N \vec{R}_N - \int \psi_X^* \sum_i \vec{r}_i \psi_X \, dr\right]}_{\substack{\| \\ \vec{\mu}^X(R)}} \chi_b \, dR$$

The expression in brackets is just the dipole moment for the electronic state *X* when the nuclei are at positions signified by $\vec{R}$.

$$\vec{\mu}_{b\leftarrow a} = \int dR \;\; \chi_a^* \;\; \vec{\mu}^X(R) \;\; \chi_b$$

For these “pure nuclear transitions” we note that this integral will be zero if $\vec{\mu}^X(R)$ is constant as a function of the nuclear positions R.

$$\vec{\mu}_{b\leftarrow a} = \vec{\mu}^X(R) \underbrace{\int \chi_a^* \chi_b \, dR}_{\substack{\| \\ 0 \text{ by orthogonality}}}$$

VIII. Transitions where $\psi_a \neq \psi_b$, i.e., where electronic excitation occurs:

Using the “boxed” expression in VI

$$\vec{\mu}_{b\leftarrow a} = \int \chi_a^* \left(\sum_N Z_N \vec{R}_N\right) \chi_b \, dR_N \overbrace{\int \psi_a^* \psi_b \, dr}^{\substack{0 \text{ by orthogonality} \\ \|}}$$

$$- \int \chi_a^* \chi_b \, dR_N \int \psi_a^* \left[\sum_i \vec{r}_i\right] \psi_b \, dr$$

$$\vec{\mu}_{b\leftarrow a} = - \int \chi_a^* \chi_b \, dR_N \int \psi_a^* \left[\sum_i \vec{r}_i\right] \psi_b \, dr$$

Note: $\vec{\mu}_{b\leftarrow a}$ is not "zero" by orthogonality of the χ_a and χ_b in this case.

Since $\int \psi_a^*(r;R)\left[\sum_i \vec{r}_i\right]\psi_b(r;R)dr$ will be a function of R, $\left[\mu_{b\leftarrow a}^{\text{electronic}}(R)\right]$, and χ_a and χ_b came from differing Hamiltonians (χ_a from spring constant for electronic state a, χ_b from electronic state b), thus $\int \chi_a^*\chi_b dR \neq 0$ by orthogonality.

IX. Spectroscopy of diatomic molecules

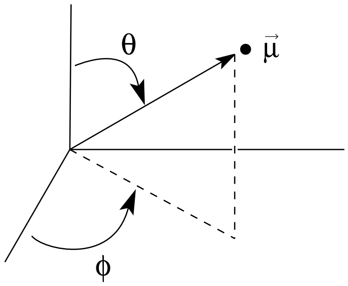
A. Pure rotation (discussion of section VIII applies):

$$\vec{\mu}_{b\leftarrow a} = \int d\vec{R}\ \chi_a^*\ \vec{\mu}^X(\vec{R})\ \chi_b$$

$$\chi = \chi_{vib}(R)\chi_{rot}(\theta,\phi)$$

$\vec{\mu}^X(\vec{R}) = \vec{\mu}^X(R,\theta,\phi)$ for electronic state *X*.

Note: For homonuclear diatomic, no dipole, $\vec{\mu}^X(\vec{R}) = 0$ and thus no allowed rotational transition in dipole approx. Heteronuclear diatomic do have dipole moments. In the "rigid rotor" approximation we only consider one fixed distance R. Will this fixed dipole moment lead to pure rotational transitions? Yes, it may. In the rigid rotator the magnitude of $\vec{\mu}^X(R)$ is fixed but its direction changes with θ, ϕ and thus pure rotational transition may be allowed.



$\chi_{rot} = Y_{J,M_J}(\theta,\phi)$ for spherical harmonics

$$E_J = \frac{\hbar^2}{2\mu R_e^2} J(J+1)$$

$$I = \mu R_e^2$$

$$\Delta E_{J+1\leftarrow J} = \frac{\hbar^2}{2I}[(J+1)(J+2) - J(J+1)] = \frac{\hbar^2}{2I}2(J+1)$$

$$\frac{\Delta E}{h} = v_{J+1\leftarrow J} = \frac{h}{8\pi^2 I}2(J+1) = 2B_e(J+1)$$

$$B_e = \frac{h}{8\pi^2 I} \text{ in Hz} \qquad B_e = \frac{h}{8\pi^2 Ic} \text{ in cm}^{-1}$$

$$B_e = \frac{h}{8\pi^2\mu}\left\langle\frac{1}{R^2}\right\rangle$$

Spacing between lines in rotational spectrum **(see Fig. 6.6 McQ)** is $2B_e$.

$$\left(\frac{\Delta E}{h}\right)_{1\leftarrow 0} = 2B_e,\ \left(\frac{\Delta E}{h}\right)_{2\leftarrow 1} = 4B_e,\ \left(\frac{\Delta E}{h}\right)_{3\leftarrow 2} = 6B_e, \text{ etc.}$$

Selection rules: When will integral for $\vec{\mu}_{b\leftarrow a}$ be non-zero—only when $J_a - J_b = \Delta J = \pm 1$.

$\Delta E_{rotation} \approx 2 \times 10^{-23}$ J = 1.00 cm^{-1} = 3×10^{10} Hz

kT at 300° ≈ 4×10^{-21} J.

B. Pure vibrational transitions (discussion of Section VII applies)

Here the only change in quantum state involves χ_{vib} (R). For a transition from a state a with vibrational quantum number v_a to one with v_b.

$$\vec{\mu}_{b\leftarrow a} = \int dR \chi^*_{v_a}(R)\vec{\mu}^X(R)\chi_{v_b}(R)$$

For this to be non-zero $\vec{\mu}^X$(R), the dipole moment for electronic state *X*, must vary with R since χ_{v_a} and χ_{v_b} are orthogonal.

(a) Wavefunctions approximated by harmonic oscillator solutions

$$\chi_v(R) \approx N_v e^{-\alpha R^2/2} H_v(a^{1/2}R)$$

$$E_v = (v + 1/2)h\nu_X$$

$$\Delta E = E_{v+1} - E_v = h\nu_X = \frac{h}{2\pi}\left(\frac{k_X}{\mu}\right)^{1/2}$$

where the subscript X indicates that the frequency of vibration and force constant are those relevant to electronic state X.

(b) Selection rules: Using the relationship for $\mu_{b\leftarrow a}$ above and harmonic oscillator χ's one finds that $\mu_{b\leftarrow a} = 0$ unless $\Delta v = \pm 1$. These transitions where $\Delta v = \pm 1$ are called fundamental transitions. Transitions where $\Delta v = 2$ (overtones) are also observed (weaker) due to the fact that the actual vibrational wavefunctions are not exactly those of the harmonic oscillator.

(c) The energy difference between vibrational levels (for $\nu = 10^{14}$ Hz)

$$\Delta E \approx 3000\ \mathrm{cm}^{-1}$$

compared to $kT = 200\ \mathrm{cm}^{-1}$ at 300°. Thus most molecules will be in ground state at room temperature and spectrum will reflect transitions from $v_a = 0$ state. However some molecules will be in first excited state, $v_a = 1$, and transitions originating in $v_a = 1$ are called hot bands.

(d) The vibrations in polyatomic molecules are treated by a Normal Coordinate Analysis.

C. Vibration-rotation spectra

(a) Note that rotational energy levels are much more closely spaced than vibrational levels.

(See Figure 10-2, McQ)

(b) Vibrational-rotational transitions occur between $(v', J') \leftarrow (v, J)$.

In Fig. 10-3 McQ—all transitions are from $v = 0$ to $v' = 1$ with differing J' and J.

(See Figure 10-3, McQ)

Basic transition energy $\nu = 2550\ \mathrm{cm}^{-1} = 7.6 \times 10^{13}$ Hz = IR.

D. Electronic and electronic-vibrational spectra

1. Here we use the relationships in section VIII for the transition dipole.

$$\vec{\mu}_{b\leftarrow a} = -\int \chi_a^* \chi_b dR \int \psi_a^* \left[\sum_i \vec{r}_i\right] \psi_b dr$$

The second integral, the electronic transition dipole, gives the effectiveness of a photon’s electric field in changing electronic wavefunction ψ_a of the initial state to wavefunction ψ_b of the final state (or vice versa).

The transition can also involve changes in vibrational level $(v' \leftarrow v)$.

(See Figures 10.9, 10.10, 10.17, 10.19 in McQ)

Note that the wavefunctions χ_a come from a hamiltonian having the potential energy of electronic state a, while χ_b come from a different hamiltonian, that for electronic state b. Thus χ_a and χ_b are not orthogonal. The integral

$$\int \chi_a^*(R)\chi_b(R)dR$$

is the overlap of the vibrational wavefunctions for states a, b and is called the ***Franck Condon Factor***.

Since an electronic transition occurs rapidly with respect to vibration, the Franck-Condon Factors give the probability that the molecule in the initial vibrational level is at R and that the final vibrational level has a high probability at the same R. Thus if the two vibrational states have high probabilities at similar R's, the Franck Condon Factors are large and the transition can be intense. If they do not, the resulting small Franck Condon Factor gives a weak transition.

(See Figures 10.17 and 10.19 in McQ)

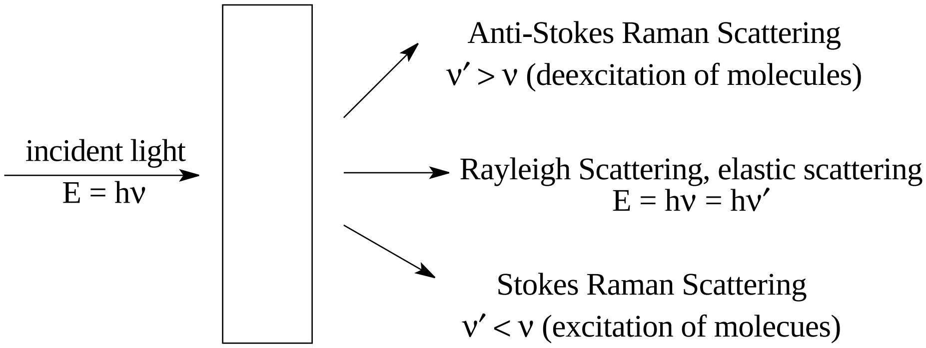
Example: I_2 **Fig. 13.9 McQ & Simon (on ERes).**

In this figure, all peaks correspond to $\pi^* \leftarrow \pi$ transition in I_2, but with differing ground and excited vibrational levels. The relative intensities are determined by

$$\int \chi_{v}^{A}\chi_{v'}^{B}\, dR \qquad \text{-}\textit{Franck Condon Factors.}$$

E. Raman scattering

Raman scattering is not the usual absorption process but refers to inelastic scattering of light, i.e., the energy of the photons scattered differs from the incident energy. There are many applications of Raman scattering. One common one is to use incident light in the visible or UV range and to measure scattered light whose energy has been altered by vibrational energy absorption-emission. The quantum mechanics of Raman scattering is more complicated than simple absorption.



Stokes scattering leaves the scatterer (molecule) in a higher energy state, and anti-Stokes scattering leaves the molecule in a lower energy (deexcited) state.

(See Raman Figures in ERes)