IX. Molecular Spectroscopy (Chap. 12 -- read) – look at set of general slides linked here

Spectroscopic regions, vary with wavelength/frequency – different molecular motions

<table>
<thead>
<tr>
<th>Typical wavelength (cm(^{-1}))</th>
<th>Approximate energy (kcal mole(^{-1}))</th>
<th>Spectroscopic region</th>
<th>Techniques and Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^{11})</td>
<td>(3 \times 10^8)</td>
<td>(\gamma)-ray</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>(10^8)</td>
<td>(3 \times 10^5)</td>
<td>X-ray</td>
<td>X-ray diffraction, scattering</td>
</tr>
<tr>
<td>(10^5)</td>
<td>(3 \times 10^2)</td>
<td>Vacuum UV</td>
<td>Electronic Spectra</td>
</tr>
<tr>
<td>(3 \times 10^5)</td>
<td>(10^2)</td>
<td>Near UV</td>
<td>Electronic Spectra</td>
</tr>
<tr>
<td>(6 \times 10^5)</td>
<td>(5 \times 10^1)</td>
<td>Visible</td>
<td>Electronic Spectra</td>
</tr>
<tr>
<td>(10^3)</td>
<td>(3 \times 10^0)</td>
<td>IR</td>
<td>Vibrational Spectra</td>
</tr>
<tr>
<td>(10^2)</td>
<td>(3 \times 10^1)</td>
<td>Far IR</td>
<td>Vibrational Spectra</td>
</tr>
<tr>
<td>(10^1)</td>
<td>(3 \times 10^2)</td>
<td>Microwave</td>
<td>Rotational Spectra</td>
</tr>
<tr>
<td>(10^0)</td>
<td>(3 \times 10^3)</td>
<td>Microwave</td>
<td>Electron paramagnetic resonance</td>
</tr>
<tr>
<td>(10)</td>
<td>(3 \times 10^4)</td>
<td>Radio frequency</td>
<td>Nuclear magnetic resonance</td>
</tr>
</tbody>
</table>

A. Transitions between molecular states -- characterized by nuclear and electronic motion
(two main sources of state energies and distributions)

Optical Spectroscopy - Processes Monitored

UV/ Fluorescence/ IR/ Raman/ Circ. Dichroism

Analytical Methods

- UV-vis absorb. & Fluorescence
  - move e (change electronic state)
  - high freq., intense
- CD – circ. polarized absorption, UV or IR
- Raman – nuclei, inelastic scatter
  - very low intensity
- IR – move nuclei
  - low freq. & inten.
Degrees of freedom—N-nuclei, n-electrons \( \rightarrow (3N+3n) \), describe by state eqn.

Transition: \( \Delta E = hv = E_i - E_j \)
where \( i,j \) designate real (lifetime) states
Potential surfaces \( \rightarrow \) constraint on nuclear motion (PE), reflect bond stability (energy), normally excited state shallower (weaker), minimum shifted to longer bond

\[ B \begin{array}{c} \text{Br}_2 \end{array} \]

**B. Types of motion - leads to differentiation of spectroscopy types**

Translation not quantized—continuous distribution of energies

1. **Rotation** (motion of whole molecule) – sharp transitions, low energy (\( \mu \)-wave)
   --quantized angular momentum (conserved)
   \( \gamma_{JM}(\Theta, \Phi) \) where \( J=0,1,2,3, \ldots, M = 0, \pm 1, \pm 2, \ldots, \pm J \)
   \( E_J = BJ(J+1) + K^2(A-B) \)
   \( B = (h/8\pi^2c) / I \)
   linear + top moment: \( I = \Sigma mr_i^2 \)
   --bigger heavier molecules, lower \( B \) and \( \Delta E_J \)
   selection rules: IR \( \Delta J = \pm 1, 0, + top [\Delta K = \pm 1, 0] \)  Raman, \( \Delta J = \pm 2, \pm 1, 0 \)
   Thermally many levels populated: \( P_J \sim (2J+1)\exp[-BJ(J+1)/kT] \)
   pure rotation spectra -- not analytically useful —transitions weak, require long paths, etc.
   but impact all states— in vapor phase analysis see contributions
Pure Rotational *Far-IR spectrum* of CO – spacing is 2B
-- note 1st transition (23 cm\(^{-1}\)) is for \(J=5 \rightarrow J=6\) (I think)

Rotational Raman spectrum of \(\text{N}_2\) (alternating intensity due to isotope) – spacing is 4B
(left) anti-Stokes: \(\Delta J = -2\)  (right) Stokes: \(\Delta J = 2\ n\) (shifts relative to laser \(\nu_0\))

2. **Vibration** - internal motion (nuclei move to each other on a potential surface resulting from electron energy variation with nuclear position)

   – see slides on states, transitions, IR/Raman
      - Web Page has links to above notes
      - also IR developments links

   -- absorption spectra, \(\Delta E_{01} = h\nu_{\text{vib}}\) measure in infrared - light freq match vibration frequency
   -- or with Raman scattering, \(\nu_s = \nu_0 \pm \nu_{\text{vib}}\) - any region

   -- states describe motion in nuclear degrees of freedom: (3N-6) unless linear (3N-5)
      Multidimensional for polyatomics, many states, most spectra lowest transition: 0\(\rightarrow\)1

   a. **Characteristic frequencies** -- property of atoms/bonds – ex. diatomic: \(\nu = (2\pi)^{-1}(k/\mu)^{1/2}\)

      \(k \rightarrow\) curvature of potential surface - \(\partial^2 E/\partial Q^2\) - typically stronger bond, bigger \(k\)
      -- \(k\) increase, frequency increase (eg. C=C \(~1600 \text{ cm}^{-1}\), and C\(=\)C \(~2200 \text{ cm}^{-1}\))
      -- mass increase, frequency decrease (eg. HCl \(~2800 \text{ cm}^{-1}\), DCl \(~2100 \text{ cm}^{-1}\))
Polyatomics, frequencies characteristic of structural elements, i.e. mass and bond strength

Called *group frequencies:* Book list Typical frequencies for given functional groups

e.g.– formaldehyde, below, qualitative analysis and orgo books often list them in tables (below)

<table>
<thead>
<tr>
<th>Group</th>
<th>Approximate Frequency (cm⁻¹)</th>
<th>Group</th>
<th>Approximate Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH</td>
<td>3600</td>
<td>C=O</td>
<td>1750–1600</td>
</tr>
<tr>
<td>-NH₂</td>
<td>3400</td>
<td>C=O</td>
<td>1750–1600</td>
</tr>
<tr>
<td>≡CH</td>
<td>3300</td>
<td>C≡N</td>
<td>1600</td>
</tr>
<tr>
<td>≡C≡C</td>
<td></td>
<td>C≡C</td>
<td>1650</td>
</tr>
<tr>
<td>≡C≡C</td>
<td></td>
<td>C≡N</td>
<td>1600</td>
</tr>
<tr>
<td>≡C≡C</td>
<td></td>
<td>C≡O</td>
<td>1200–1000</td>
</tr>
<tr>
<td>≡CH₂</td>
<td>3030</td>
<td>C=S</td>
<td>1100</td>
</tr>
<tr>
<td>-CH₃</td>
<td>2970 (asym. stretch)</td>
<td>C=F</td>
<td>1105</td>
</tr>
<tr>
<td></td>
<td>2970 (sym. stretch)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1460 (asym. deform.)</td>
<td>C=Cl</td>
<td>725</td>
</tr>
<tr>
<td></td>
<td>1375 (sym. deform.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>≡CH₂</td>
<td>2930 (asym. stretch)</td>
<td>C=Br</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td>2860 (sym. stretch)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1470 (deformation)</td>
<td>C=I</td>
<td>550</td>
</tr>
<tr>
<td>-SH</td>
<td>2580</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-C≡N</td>
<td>2250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡C</td>
<td>2220</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b. Selection rules (result of harmonic oscillator properties, violated when anharmonic)

\[ E_{\text{vib}} = \sum (\nu_i + \frac{1}{2}) h \nu_i \]

\[ \Delta \nu_i = \pm 1, \Delta \nu_j = 0 \quad \text{for} \quad i \neq j \quad \text{so} \quad \Delta E_i = h \nu_i \]

fundamental transitions in 100-4000 cm⁻¹ range, lightest = highest (H₂)
**harmonic potential**: parabola \( (1/2 kQ^2) \)  
**anharmonic potential** reflect dissociation \( (E = 0, \text{ at } Q = \infty \text{ atoms}) \) & nuclear repulsion \( (E = \infty \text{ at } Q = 0) \)

3. **Vapor** -- rotation-vibration transitions combine \( (\Delta J = 0, \pm 1) \), can get complex \( (\text{NH}_3) \)

IR Diatomic (linear) no pure vib transition seen, many lines above, two dominant branches:

- R - adding \( (\Delta J = +1) \) or below
- P - subtracting \( (\Delta J = -1) \) rotational energy, result from many rotational states: \( |JM\rangle \), populated thermally \( n_J = n_0(2J+1)\exp[-BJ(J+1)/kT] \)
Thus frequencies characteristic of structural elements
Called **group frequencies**: Typical frequencies for given functional groups

- formaldehyde, below, and table next page and orgo books

**Condense phase** -- broaden vibrational bands (couple to matrix—libration→rotation, phonons→translation, both hindered in condensed phase, have band of energies)

Discriminate structures: various $\text{C}_3\text{H}_7\text{O}_2\text{N}$ molecules

Various ethers – “fingerprint”

Larger molecules, polymers - bands overlap, broaden apparent spectra.
Repeating functional groups can characterize polymer (subunits) and the variation in frequencies, intensities can be used to determine structure. Very useful for sensing change especially in biopolymers, e.g. see peptide shifts with secondary structure
4. Analytical -- Vibrational spectra useful for qualitative discrimination (examples, nitrobenzene, ethers, Raman-IR complementary.)

Quantitative: S/N and concentration can be limiting factors (less sensitive than uv-vis)
Raman issue -- internal standard needed, no absolute intensity

C. Electronic Transitions
1. To bound state -- include, rot. and vib./ transitions to unbound states poorly defined

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**Figure 9-13** (a) Infrared and (b) Raman spectra of nitrobenzene. Raman--polarizability/IR--dipole

**Figure 9-15** (a) Infrared and (b) Raman spectra of 1-meth hexane. Complementary bands for an

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6-2 Energy level diagram showing some of the electronic states in H₂ at a state of N₂ obtained by ionizing H₂. Only the singlet state manifold is sh
**vertical transition most intense** (no nuclear geom. change) [Franck-Condon]—shape diagnostic

Molecular electronic transitions also involve excitation of vibrations → band profile/info

**Optical Spectroscopy – Electronic, Example Absorption and Fluorescence**

Essentially a probe technique sensing changes in the local environment of fluorophores

What do you see?

[protein example]

Intrinsic fluorophores
cg. Trp, Tyr

Change with tertiary structure, compactness

Amide absorption broad, Intense, featureless, far UV ~200 nm and below

Frequency shifts complex, since due to overall vibronic profile on electronic state, overlap

Fluorescence and absorbance often mirror each other from F-C transition intensity profile

Analytically use the peak, maximum intensity, pure electronic transition between them
2. Intensity depend on types (allowed or forbidden)
   organic -- closed shell--in VUV (radical lower Energy)
   -- \( \pi \)-system in UV, dominant utility--arenes,
   heteroaromatics, Azines -- non-bonded electron pairs, heavy hetero-atoms (lower energy)
Transition metal complexes -- open shell
d-d -- vibronic allowed (parity forbidden, Δl = 0)), weak but visible/characteristic

Cs$_3$CoCl$_5$

MgO: Ni$^{2+}$

Charge Transfer & d-p -- intense/higher energy
f-f & spin change (ΔS ≠ 0) -- very weak

KMnO$_4$ in KClO$_4$

U$^{4+}$ in Cs$_2$ZrCl$_4$

D. Measurement: (Appendix E)

1. Beer-Lambert Law  A = εbc  experimental observable
   Dipole strength computed: D = |<g|μei|ex>|$^2 = 0.92 \times 10^{-38}$ $\int_\varepsilon/\nu$ dv (esu-cm)$^2$

2. Einstein coefficient: absorption = emission (stimulated) ~ emission (spontaneous)
   $B_{ij} = 8\pi^3 D/3h^2 g_I$  $B_{ii} = g_i/g_j B_{ij}$  oscillator strength: $f_{ij} = 2.5 \times 10^{-34} B_{ij}/\lambda m$
3. Jablonski diagram -- follow the energy

Vibrational Relaxation (VR)—energy transfer from one vibrational level to another or to “heat”, i.e. general K.E. of surroundings (via collision)

Non-radiative decay (NR) — energy lost outside of molecule, usually from a non-emitting state

Internal conversion - IC—move energy to another electronic state with minimal loss ($\Delta S=0$),

Intersystem crossing - ISC—move energy to triplet manifold from singlets (or vice versa) with little loss – violates $\Delta S = 0$, so weak or slow process

Fluorescence —radiative relaxation of excited state ($\Delta S=0$)

Phosphorescence—radiative relaxation of state with spin change (typical $T_1 \rightarrow S_0$)

Quantum Yield—ratio of photons out to photons in or rates of processes: $\phi = k_F/k_F+k_{nr}$

Lifetimes and Quenching— $k_F = 1/\tau$ if fluorescence is only process, but if add quencher, lower quantum yield, shorten lifetime, $\tau$, because of competition with quenching

Homework

Discussion: Chap 12: #6, 11, 13

To hand in: Chap 12: # 1, 4, 9,
Links

Spectroscopy magazine, workbench columns
http://www.spectroscopymag.com/spectroscopy/article/articleList.jsp?categoryId=2942

Spectroscopy now has current happenings in various areas
http://www.spectroscopynow.com/coi/cda/list.cda?catId=2524&type=Link&sort=az&chId=7

Kaiser Optical Raman tutorial
http://www.kosi.com/raman/resources/tutorial/

Akron Organic Molecular spectroscopy unit:
http://ull.chemistry.uakron.edu/analytical/Mol_spec/

UIC’s organic course IR tutorial (Paul Robert Young), UC Boulder lab course and a UK course:
http://chipo.chem.uic.edu/web1/ocol/spec/IR1.htm
http://orgchem.colorado.edu/hndbksupport/irtutor/main.html
http://www.shu.ac.uk/schools/sci/chem/tutorials/molspec/irspec1.htm

General spectroscopy comments from Korean site:

Companies

Thermo molec spec—FTIR mostly
http://www.thermo.com/com/cda/category/category_lp/1,2152,312,00.html

Analytik Jena
http://www.analytik-jena.de/e/bu/as/molec/molec.html