OUTLINE OF THE COURSE

I. *Methods of structure determination – Introduction*
    Quantum chemical foundation of techniques of structure determination
    Spectroscopy and quantum mechanics
    Properties from first-principles techniques
    The electromagnetic spectrum

II. *Spectroscopy 101*
    Classical speeds of nuclear and electronic motions
    HF in the gas phase

III. *Radiation-matter interaction*
    Interaction processes and treatments
    Classical electrostatics of molecules in weak electric fields

IV. *General characteristics of experimental techniques*
    Absorption spectroscopy
    Lasers

V.   *Rotational spectroscopy*
Classical mechanics of rigid rotation – (spinning) tops
Quantum mechanics of rigid rotation
Selection rules
Rotational spectra – Applications

VI. *Vibrational* (*infrared* (*IR*) *and Raman*) *spectroscopy*
Classical mechanics of vibrations – normal modes
Quantum mechanics of molecular vibrations
Symmetry and normal coordinates
Selection rules of infrared spectroscopy
Raman spectroscopy
Internal coordinates
The Elyashevich–Wilson GF formalism
Molecular mechanics
IR spectra – Applications

VII.   *Electron spectroscopy*

       Intensity, oscillator strength

       Vibrational structure, Franck–Condon principle

       Selection rules

       Nonradiative processes: internal conversion (IC), intersystem crossing (ISC), dissociation, and predissociation

       Radiative processes: fluorescence and phosphorescence

       Photoelectron spectroscopy

       Koopmans–principle

       Lasers revisited

VIII.   *Nuclear magnetic resonance spectroscopy* (*NMR*)

       Magnetic properties of nuclei

       Fourier-transform technique

       Chemical shift, spin-spin coupling, spin relaxation

IX.   *Gas-electron diffraction* (*GED*)

Recommended books (paperbacks):

H. W. Kroto, *Molecular Rotation Spectra*, Dover, 1992.

E. B. Wilson Jr., J. C. Decius, P. C. Cross: *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra*, Dover, 1980.

D. C. Harris, M. D. Bertolucci: *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy*, Dover, 1989.

H. Goldstein, C. P. Poole Jr., J. L. Safko: *Classical Mechanics*, 3rd ed., Pearson, 2014.

P. J. Hore, J. A. Jones, S. Wimperis: *NMR: The Toolkit* (*Oxford Chemistry Primers*), 2000.

Other useful books:

P. R. Bunker, P. Jensen, *Molecular Symmetry and Spectroscopy*, NRC Press, 1998.

I. N. Levine: *Molecular Spectroscopy*, Wiley, 1975.

I. N. Levine: *Quantum Chemistry*, 7th ed., Prentice Hall, 2013

D. A. McQuarry, J. D. Simon, *Physical Chemistry: A Molecular Approach*, USB, 1997.

I.   METHODS OF STRUCTURE DETERMINATION – INTRODUCTION

Different levels of structure determination:

- determination of the structural formula (very important in practice but we will not deal with it)
- determination of the sequence of building blocks in a macromolecule (*e.g.*, sequence analysis in proteins)
- geometry, conformations, dynamic structure ("bonding forces", molecular vibrations and rotations, etc.) $\Rightarrow$ THE PRINCIPAL TASK OF THIS COURSE

Classification of methods:

- spectroscopy (interaction of radiation and matter; absorption/emission/scattering)
- diffraction techniques (electron, neutron, X-ray)
- investigation of ionized states (mass spectrometry and related fields)

Methods evolve and improve permanently (*e.g.*, gain of Fourier techniques and lasers), time after time new techniques appear (*e.g.*, ZEKE photoelectron spectroscopy).

A lot of structural results have been collected in the past 90 years and analysed, resulting in useful empirical data:

Table 15.4 Bond Lengths in Å

Single Bonds

	H	C	N	O	S	F	Cl	Br	I
H	0.74	1.09	1.01	0.96	1.34	0.92	1.27	1.41	1.61
C		1.54	1.47	1.43	1.82	1.35	1.77	1.94	2.14
N			1.45	1.40	–	1.36	1.75	1.79	1.97
O				1.48	–	1.42	1.70	1.72	1.87
S					2.05	1.56	2.07	2.27	–
F						1.42	1.63	1.76	1.91
Cl							1.99	2.14	2.32
Br								2.28	2.47
I									2.67

Principle of spectroscopic measurements:

| (light) source | → | monochromator | → | sample | → | detector |
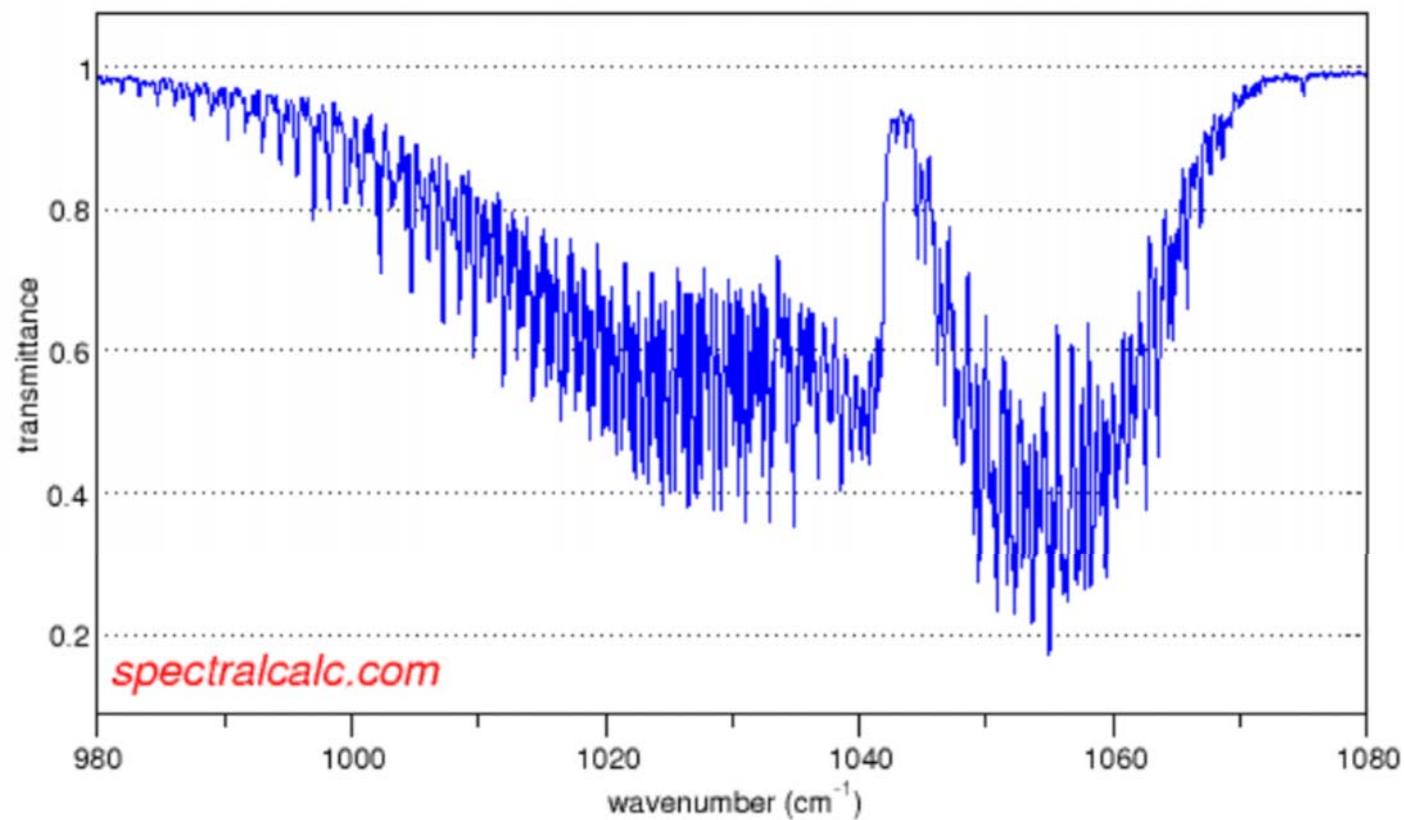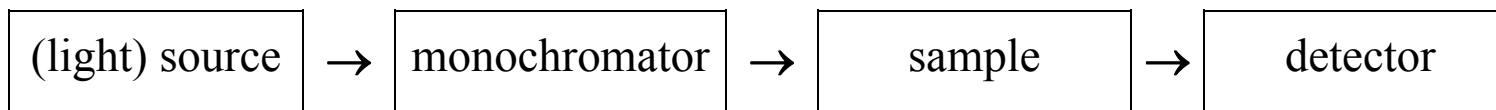
Often times the spectrum recorded as a result of a spectroscopic measurement shows intensity (I) as a function of the wavelength (λ) of the radiation ($\lambda v = c = 2.99792458 \times 10^{10}$ cm sec^{-1}, note that the value of c, the speed of light in vacuum, is set, it does not have an uncertainty).

It is even more usual to use the reciprocal of the wavelength, called wavenumber:

$$\frac{1}{\lambda}(\text{cm}^{-1}) = \frac{1}{c}v = v*,$$

For the sake of brevity, and as a possible cause of confusion, v is often written instead of $v*(\tilde{v})$.

Factors determining observed spectra

(1) Energy levels and populations (Ritz-principle: all the transitions observed occur between discrete energy levels; obtained from the solution of a quantum chemical model).

(2) Selection rules (not all transitions possible among the energy levels are allowed, see later).

Absorption spectra of molecules

a)

Energy ↑

ΔE_{12}

ΔE_{02}

ΔE_{01}

E_2

E_1

E_0

b)

Abs. Cross-section ↑

ν_{12} ν_{01} ν_{02} ν
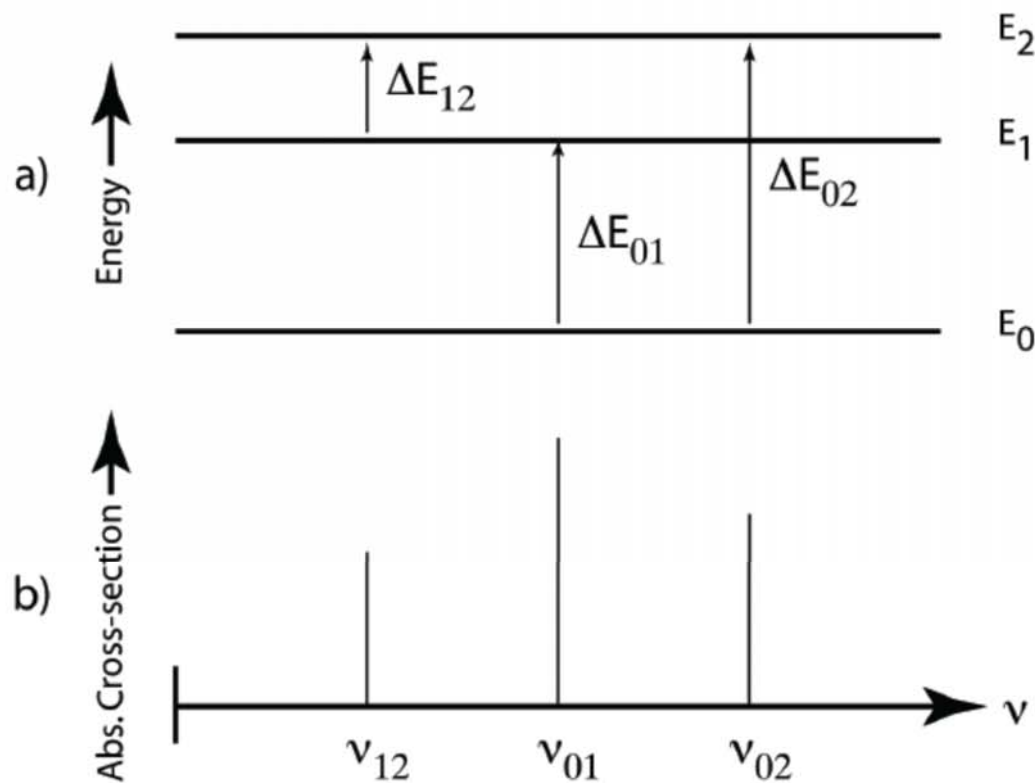
Hypothetical molecule with three allowed energy levels

Note relationship to emission!

$\nu_{ij} = \Delta E_{ij}/h$

Beer's law

Light intensity I transmitted by a homogeneous sample is related to the incident intensity I_0 by the following relation:

$$I = I_0 \exp(-\varepsilon c \ell) \, ,$$

where ℓ is the path length, c is the molar concentration, and ε is the molar absorption coefficient (in $\text{L mol}^{-1} \text{cm}^{-1}$). Light intensity decays exponentially: probability that absorption occurs along the path of light is proportional to the intensity of the remaining radiation. *Note*:

- Beer's law can only be applied if the incoming intensity I_0 is low enough that the molecular state populations are essentially unperturbed by it, the redistribution of molecules into excited states by the light beam would otherwise materially change ε for different photons within the beam;

- Beer's law is strictly valid only in very thin optical samples;

- absorbance: $A = \varepsilon c \ell = \log(I_0 / I)$, transmittance: $T = I / I_0$.

About the foundation of chemistry

Adolphe Quetelet (1796-1874), *Instructions Populaires sue le Calcul des Probabilities, tarlier, Brussels, 1828, p.230.*

The more progress physical sciences make, the more they tend to enter the domain of mathematics, which is a kind of centre to which they all converge. We may even judge the degree of perfection to which a science has arrived by the facility with which it may be submitted to calculation.

A. Compte (1798-1857), *Philosophie Positive, 1830.*

Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational and contrary to the spirit of chemistry. If mathematical analysis should ever hold a prominent place in chemistry –an aberration which is happily impossible– it would occasion a rapid and widespread degeneration of that science.

Paul A. M. Dirac (1902-1984), *Proc. Roy. Soc. (London)* **1929**, *123*, 714:

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

Even today a lot of (mostly experimental) chemists view the use of (quantum) theory in chemistry with utter skepticism. Some completely disapprove the use of digital computers in chemistry as "measurement devices". Some feel that the theoretical techniques are too complex and complicated to learn and employ in everyday research. Some are very skeptical about the usefulness of computational results, they do not believe that theory can provide accurate results for chemical phenomena.

Many of these scientists are grossly underinformed or simply biased due to their lack of proper education.

Frederick Soddy (second half of the 20th century):

Chemistry has been termed by the physicists as the messy part of physics, but that is no reason why the physicists should be permitted to make a mess of chemistry when they invade it.

Quantum chemical foundation of spectroscopy

Understanding the characterization of spectroscopic techniques:

$$\hat{H} \cong \hat{H}_{el} + \hat{H}_{vibr} + \hat{H}_{rot} + \hat{H}_{transl} + \hat{H}'$$

$$\Psi_{spatial} \cong \Psi_{el} \cdot \Psi_{vibr} \cdot \Psi_{rot} \cdot \Psi_{transl}$$

$$E_{spatial} \cong E_{el} + E_{vibr} + E_{rot}$$

If we also consider spin coordinates:

$$\Psi = \Psi_{spatial} \cdot \Psi_{el.\,spin} \cdot \Psi_{nucl.\,spin}$$

$$E \cong E_{spatial} + E_{el.\,spin} + E_{nucl.\,spin}$$

Coordinates corresponding to electron and nuclear spin become important when external fields (electric and/or magnetic) are present but they can be omitted during most of the course and for most methods of structure determination.

Symbiosis of quantum mechanics and spectroscopy

Quantum mechanics (representing the only general theory for chemistry)

fundamental physical constants

$\Downarrow$ *electronic Schrödinger equation*

first-principles molecular constants

$\Downarrow$ *nuclear Schrödinger equation*

first-principles energy levels, transitions, and properties

- Pure and direct approach, based on an involved mathematical foundation

- A huge task from a computational point of view, approximations must be introduced (see Dirac's quote) $\Rightarrow$ computed energy levels and properties are always approximate

- Occasionally all required properties can be computed (the results are approximate but complete)

Spectroscopy (representing chemical experiments)

experimentally observed transitions $E' - E'' = h\nu$

$\Downarrow$ *interpretation; spectrum assignment; model*

molecular parameters and properties

- Empirical, inverse approach, often requiring expensive instruments
- Exact energy level differences in the limit (accuracy vs. precision)
- Interpretation and assignment of a complex, high-resolution spectrum may be quite difficult and time-consuming if not impossible
- Though most models employed are based on quantum mechanics, they often contain a considerable number of assumptions
- Not all required molecular parameters or properties can be determined by the measured transitions (often accurate but incomplete, unlike complete but inaccurate theory)

The link between the microscopic (quantum chemistry, spectroscopy) and the macroscopic (thermodynamics) worlds is provided by statistical mechanics.

Properties obtainable by first-principles techniques

- molecular structures (equilibrium and effective, rotational spectra)

- rotational-vibrational energy levels, transition intensities, and lineshapes (IR and Raman spectra)

- electronic states and energy levels (UV and visible spectra)

- thermochemistry (bond energies; temperature-dependent $\Delta_r H(T)$, $\Delta_f H(T)$, $\Delta S(T)$, $\Delta G(T)$, $C_v(T)$, $C_p(T)$, accurate in the gas phase, less accurate in condensed phases)

- reaction kinetics and reaction dynamics (barrier heights, transition states, rate parameters, reaction mechanisms, potential energy (hyper)surfaces, cross sections)

- ionization potentials (photoelectron spectra, UPS, XPS)

- Franck−Condon factors (transition probabilities)

- dipole moments, polarizabilities, and higher multipoles

- electron density maps and population analyses

- etc.

The electromagnetic (EM) spectrum

Region	Wavelength	Wavenumber/cm^{-1}	Frequency/Hz	Molecular process
Radio wave	> 25 cm	< 0.04	< 1.2 GHz	nucl. spin orientation (NMR)
Microwave (MW)	0.04–25 cm	0.04–25	1.2–750 GHz	molecular rotations
Far infrared (FIR)	25–400 μm	25–400	7.5×10^{11}–1.2×10^{13}	floppy vibrations
Infrared (IR)	2.5–25 μm	400–4000	1.2×10^{13}–1.2×10^{14}	fundamental vibrations
Near infrared (NIR)	0.8–2.5 μm	4000–12500	1.2×10^{14}–3.7×10^{14}	overtone vibrations
Visible (V)	400–800 nm	12500–25000	3.7×10^{14}–7.5×10^{14}	valence electronic transitions
Near ultraviolet (UV)	200–400 nm	25000–50000	7.5×10^{14}–1.5×10^{15}	valence electronic transitions
Vacuum UV (VUV)	10–200 nm	50000–1×10^{6}	1.5×10^{15}–3×10^{16}	Rydberg trans.; ionization
Soft X-rays	10–100 Å	1×10^{6}–10×10^{6}	3×10^{16}–3×10^{17}	ionization from inner shell
X-rays	1–10 Å	10×10^{6}–100×10^{6}	3×10^{17}–3×10^{18}	ionization from inner shell
Gamma rays	< 1 Å	> 100×10^{6}	> 3×10^{18}	nuclear decay

m/micro: 10^{-6} q/atto: 10^{-18} M/mega: 10^{6} E/exa: 10^{18} 800 nm = 800×10^{-9} m = 8000×10^{-10} m = 8000 Å

n/nano: 10^{-9} z/zepto: 10^{-21} G/giga: 10^{9} Z/zetta: 10^{21} 100 nm = 100×10^{-9} m = 1000×10^{-10} m = 1000 Å

p/pico: 10^{-12} y/yocto: 10^{-24} T/tera: 10^{12} Y/yotta: 10^{24}

f/femto: 10^{-15} P/peta: 10^{15}
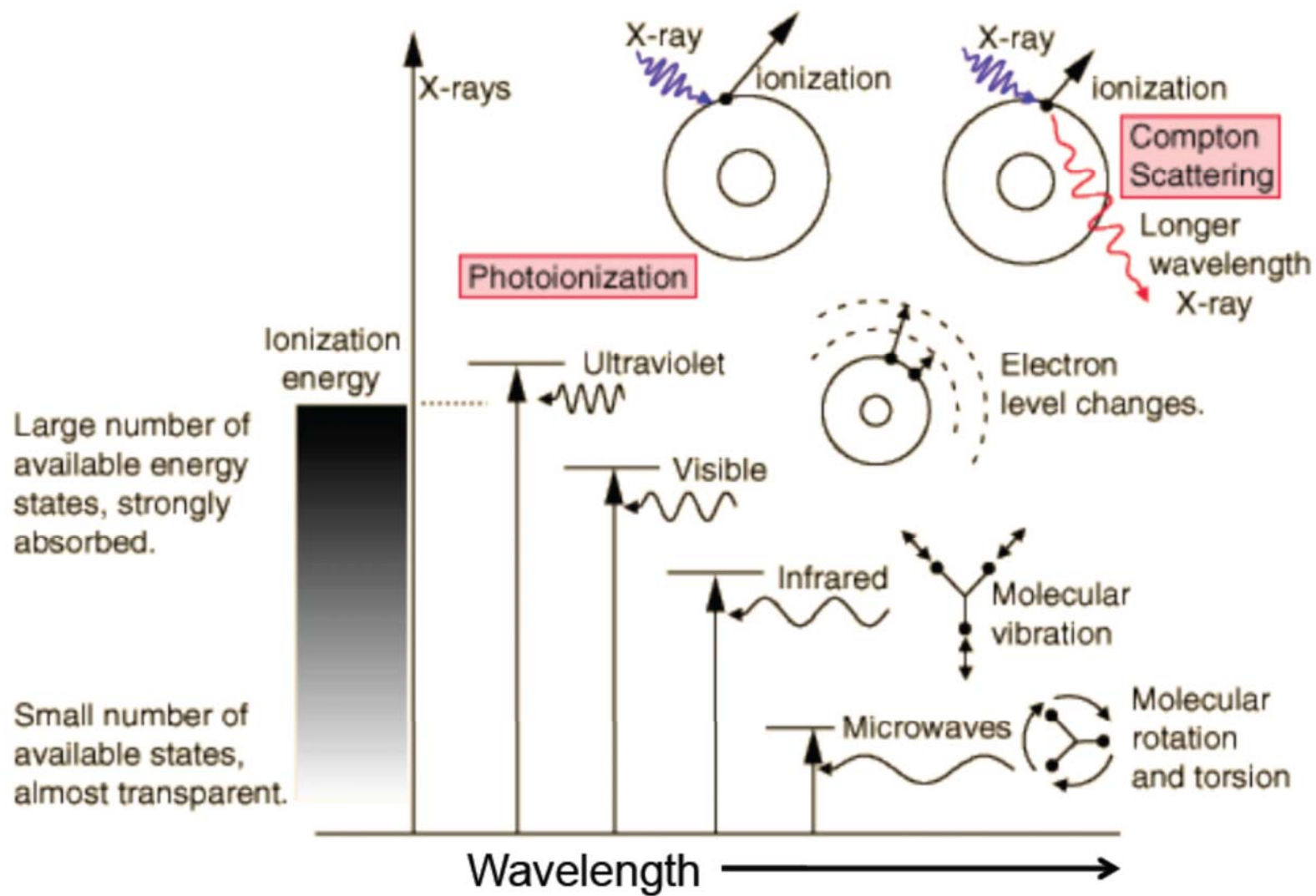
II. SPECTROSCOPY 101

A)   The (classical) speed of the electron in a H atom

The virial theorem of classical mechanics states that if the interaction potential can be written in the form $V(r) = cr^n$, than $\langle T \rangle = \frac{n}{2}\langle V \rangle$. For the motion of the electrons $V(r) := r^{-1}$; thus, $\langle V_{el} \rangle = -2\langle T_{el} \rangle$ and $E_{total} = -\langle T_{el} \rangle$. For the first Bohr orbit

$$-\frac{e^2}{(4\pi\varepsilon_0)a_0} = \langle V_{el} \rangle = -2\langle T_{el} \rangle = -2\left(\frac{m_e}{2}\langle v_e^2 \rangle\right)$$

from which, based on the definition of the atomic unit $a_0 = \frac{(4\pi\varepsilon_0)h^2}{(2\pi)^2 m_e e^2}$ (Bohr radius),

$$v_{e,rms} = \frac{2\pi e^2}{(4\pi\varepsilon_0)h} = 2.188\times10^6 \text{ m s}^{-1}.$$

Thus, the electron, in the ground state of the H atom, moves about two orders of magnitude (1/137) slower than the speed of light in vacuum (c is about 3×10^8 m s^{-1}). The periodic time, based on $v_{e,rms}\tau_e = 2\pi a_0$, is $\tau_e = 1.52\times10^{-16}$ s, $i.e.$, 0.152 fs.

B)   Data for HF in the gas phase:

(K. Huber, G. Herzberg: *Constants of diatomic molecules*, Van Nostrand, 1979)

Observed absorption band: 3962 cm^{-1}
Rotational constant: $B_e = 20.9557$ cm^{-1}
Dissociation energy: $D_0 = 5.869$ eV (process: HF $\rightarrow$ H + F)
Ionization energy: IE$_1$ = 16.039 eV (process: HF $\rightarrow$ HF$^+$ + e$^-$)

Question #1: What is the wavelength and the frequency of the absorption observed? Which region is this in the EM spectrum?

Answer #1: Since $\tilde{\nu} = 1/\lambda = 3962$ cm^{-1}, $\lambda = 2.52$ μm, $\nu = c\tilde{\nu} = 1.19 \times 10^{14}$ s^{-1}, infrared region.

Question #2: What molecular process is involved and how rapid is this process?

Answer #2: Fundamental vibration of HF, 1.19×10^{14} vibrations/s, the period is 8.40 fs (fast process, about 10 fs).

Question #3: Compare the speed of the vibration to an average, classical rate of the electronic motion (take the H atom). What are the implications for the BO approximation?

Answer #3: The orbital period of an electron in the first Bohr orbit of the H atom is 1.52×10^{-16} s. Thus, the valence electrons in HF undergo roughly

$$\frac{8.40 \cdot 10^{-15} \text{s/vibration}}{1.52 \cdot 10^{-16} \text{ s/orbit}} = 55 \frac{\text{orbits}}{\text{vibration}}$$

This result supports the Born–Oppenheimer approximation, which assumes that nuclei move slowly enough to allow electrons to adjust instantaneously to nuclear motions (rotations are lot slower than vibrations).

Question #4: How many IR photons ($\tilde{\nu}$ = 3962 cm^{-1}) would it take to reach the threshold for bond dissociation?

Answer #4: $D_0 = 5.869 \text{ eV} \left(\frac{8065.5 \text{ cm}^{-1}}{1 \text{ eV}} \right) = 47336 \text{ cm}^{-1} = 135 \text{ kcal mol}^{-1}$

#IR photons $= 47336 \text{ cm}^{-1} / 3962 \text{ cm}^{-1} = 12$

- Electronic transitions
  - UV and visible wavelengths

- Molecular vibrations
  - Thermal infrared wavelengths

- Molecular rotations
  - Microwave and far-IR wavelengths

- Each of these processes is quantized

$\sim 10^{-18}$ J

Increasing energy

$\sim 10^{-23}$ J

III. RADIATION-MATTER INTERACTIONS

In the most general sense, spectroscopy deals with the interaction of electromagnetic radiation (*e.g.*, light) with matter (*e.g.*, molecules).

The most important molecular properties which determine the extent of the interaction:

- electric multipole moments (q, μ, $\mathbf{Q}$, etc.)
- tensor of electric polarizability (α, $\mu_{ind} = \alpha\mathbf{E}$)

Useful definitions (N electric charge e_n (nuclei and electrons), defined with respect to an arbitrary space-fixed origin via $\mathbf{r}_n$ position vectors; the V integration volume includes all the charges or the complete charge distribution):

	point charges	electric charge distributions
molecular charge	$q = \displaystyle\sum_{n=1}^{N} e_n$	$q = \displaystyle\int_V \rho(\mathbf{r})d\mathbf{r}$
electric dipole moment	$\mu = \displaystyle\sum_{n=1}^{N} e_n\mathbf{r}_n$	$\mu = \displaystyle\int_V \mathbf{r}\rho(\mathbf{r})d\mathbf{r}$

An example: Place two charges at $\mathbf{r}_1$ and $\mathbf{r}_2$ with respect to an *O* origin, whereby $+Q = e_1$ and $-Q = e_2$. By convention, the vector connecting the two charges, $\mathbf{R}$, ($\mathbf{R} = \mathbf{r}_1$ - $\mathbf{r}_2$), points toward the positive charge and thus the dipole moment vector is:

$$\boldsymbol{\mu} = +Q \cdot \mathbf{r}_1 + (-Q) \cdot \mathbf{r}_2 = Q(\mathbf{r}_1 - \mathbf{r}_2) = Q\mathbf{R}.$$

Let's state first what we will not speak about in the following:

♦ time-dependent perturbation theory (though we state why it would be necessary: within a semiclassical model it describes induced absorption, induced emission, and the equations determining transition dipole moments

♦ computation of Einstein-coefficients (they determine the rate of a transition between two energy levels)

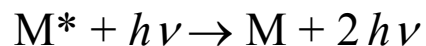# Processes of interaction:

A) *Induced (stimulated) absorption*

$$M + h\nu \rightarrow M^*$$
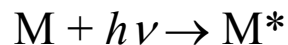
Rate of stimulated absorption:

$$W(\text{absorp.}) = B\rho$$

where B is the Einstein coefficient of stimulated absorption and ρ is the energy density at the transition frequency.
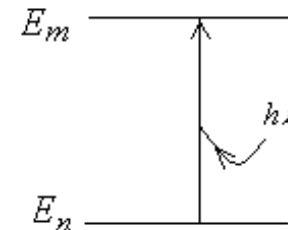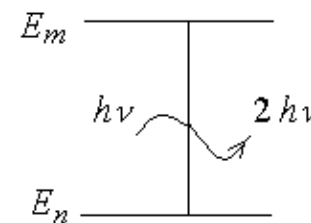
B) *Induced (stimulated) emission*

$$M^* + h\nu \rightarrow M + 2\,h\nu$$

Rate of stimulated emission:

$$W(\text{stim. em.}) = B'\rho$$

where $B'(B_{m \rightarrow n})$ is the Einstein coefficient of stimulated emission.

C*) Spontaneous emission*

$$M^* \rightarrow M + h\nu$$

Rate of spontaneous emission:

$$W(\text{spont. em.}) = A, \quad A = \frac{8\pi h \nu^3}{c^3} B$$
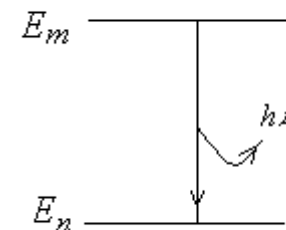
where A is the Einstein coefficient of spontaneous emission (the so-called Einstein A coefficient). Spontaneous emission happens with some probability even without the presence of external EM fields.

Proof of Einstein's results from above. At equilibrium, the net change between matter and the EM field is zero. Thus, for a two-state system n and m, with populations N_n and N_m, and $E_n < E_m$,

$$N_m \left(\frac{N_n}{N_m} \rho(\nu_{mn}, T) B_{n \to m} - \rho(\nu_{mn}, T) B_{m \to n} - A_{m \to n} \right) = 0$$

and thus

$$\rho(\nu_{mn}, T) = \frac{A_{m \to n}}{B_{n \to m} \left(\frac{N_n}{N_m} \right) - B_{m \to n}}$$

From the Boltzmann distribution of statistical mechanics we also know that

$$\frac{N_n}{N_m} = \left(\frac{g_n}{g_m}\right) \exp\left(\frac{\Delta E_{nm}}{kT}\right) = \left(\frac{g_n}{g_m}\right) \exp\left(\frac{h\nu_{nm}}{kT}\right)$$

and assuming no degeneracies ($g_n = g_m = 1$) we can write that

$$\rho(\nu_{mn}, T) = \frac{A_{m\to n}}{B_{n\to m}\left[\exp\left(\frac{h\nu_{nm}}{kT}\right) - \frac{B_{m\to n}}{B_{n\to m}}\right]}$$

When in 1900 Planck studied black-body radiation, he derived the following formula:

$$\rho(\nu_{mn}, T) = \frac{8\pi h\nu_{mn}^3}{c^3} \frac{1}{\exp\left(\frac{h\nu_{nm}}{kT}\right) - 1}$$

Therefore, comparing the two expressions results in

$$B_{n\to m} = B_{m\to n} \text{ and } A_{m\to n} = B_{n\to m}\frac{8\pi h\nu_{nm}^3}{c^3}$$

Q.E.D.

## Routes to discuss radiation-matter interactions

A)   Quantum field theory (*quantum electrodynamics, QED*)

- The energy levels of the molecule are quantized.
- The electromagnetic radiation is quantized (real and virtual photons).
- The time-independent interaction causes mixing of the near-degenerate states of the molecule and the radiation.
- Explains spontaneous emission.

B)   Semiclassical theory (simpler, we will remain within the realm of this theory)
- The energy levels of the molecule are quantized.
- The electromagnetic radiation is described classically.
- A time-dependent interaction, $H'(t) = -\mu \cdot \varepsilon \cdot \cos(2\pi\nu t)$, is responsible for energy exchange between the field and the molecule and it causes a transition.
- Not the photons, as they are not mentioned here, but the radiation energy is transferred during absorption or emission.
- Spontaneous emission cannot be explained within this model.

Electromagnetic waves
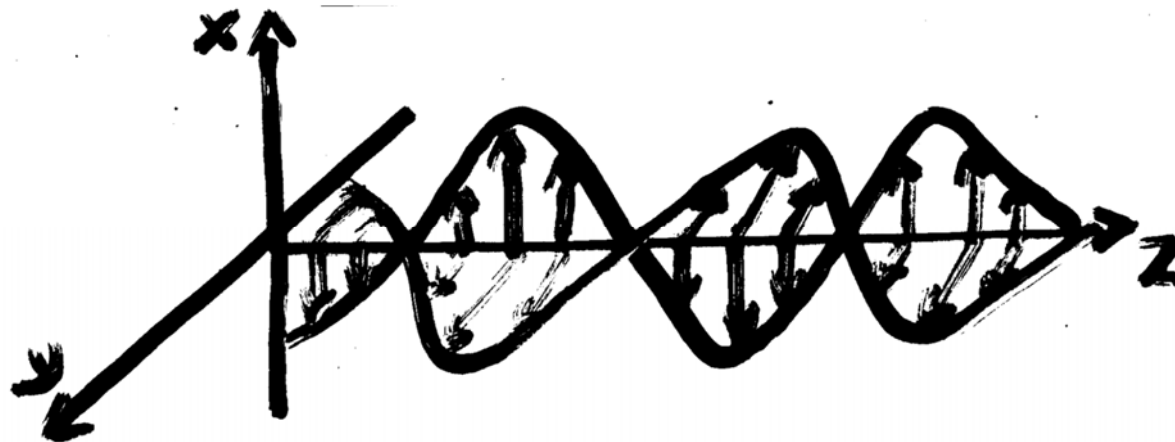
This is a plane-polarized (*xz*) light wave traveling in the *z* direction. The **E** electric field and the **B** magnetic field vectors are indicated at various points on the *z* axis, the space and time variations are:

$$\mathbf{E}(\mathbf{r},t) = \mathbf{i}\varepsilon_x = \mathbf{i}\varepsilon_x^0 \cos(2\pi v t - 2\pi z/\lambda)$$

$$\mathbf{B}(\mathbf{r},t) = \mathbf{j}B_y = \mathbf{j}B_y^0 \cos(2\pi v t - 2\pi z/\lambda),$$

where ε_x^0 and B_y^0 are the maximum magnitudes of **E** and **B**, respectively, λ is the wavelength (distance between successive crests of **E**), and ν is the frequency (the number of crests of **E** that pass a fixed point in space each second; the notation $2\pi\nu = \omega$ is often employed). Obviously, $\lambda\nu = c = 2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}}$ and according to Maxwell's laws $\varepsilon_x^0 = B_y^0$.

    Both the electric and the magnetic components of electromagnetic radiations interact with the electrons of the atoms and the molecules. The relative strength of the two interactions can be estimated the following way. Let's consider a particle with charge q and speed **v**. When it moves across an EM field characterized by vectors **E** and **B**, the so-called Lorentz-force acting on the particle, in CGS units, is

$$\mathbf{F} = q\left(\mathbf{E} + \frac{\mathbf{v}}{c} \times \mathbf{B}\right)$$

As $\varepsilon_x^0 = B_y^0$, the relation of the magnetic and electric forces is v/c. We saw for the H atom that $v_{\mathrm{H,rms}}/c = 1/137$. We'd accept that for other valence electrons this relation holds (core electrons may move considerably faster). As a result, it is a good approximation if we neglect the interaction of the molecule with the magnetic field, and concentrate only on **E**.

Classical electrostatics of molecules in weak electric fields

Electrostatics utilizes Coulomb's law: the force between two charges is proportional to the inverse second power of their distance (note the relation between potential and force).

For a point charge e located at position $\mathbf{r}$ under an external (scalar) electrostatic potential $\phi(\mathbf{r})$, the energy of interaction with the potential is

$$W = e\phi(\mathbf{r}).$$

$\phi(\mathbf{r})$ can be expanded in a Taylor-series about $\mathbf{r} = \mathbf{0}$ (whose location is arbitrary) as

$$\phi(\mathbf{r}) = \phi(\mathbf{0}) + x\frac{\partial\phi}{\partial x}(\mathbf{0}) + y\frac{\partial\phi}{\partial y}(\mathbf{0}) + z\frac{\partial\phi}{\partial z}(\mathbf{0}) +$$

$$\frac{1}{2}\left[\begin{array}{l} x^2\dfrac{\partial^2\phi}{\partial x^2}(\mathbf{0}) + y^2\dfrac{\partial^2\phi}{\partial y^2}(\mathbf{0}) + z^2\dfrac{\partial^2\phi}{\partial z^2}(\mathbf{0}) + \\[2mm] 2xy\dfrac{\partial^2\phi}{\partial x\partial y}(\mathbf{0}) + 2xz\dfrac{\partial^2\phi}{\partial x\partial z}(\mathbf{0}) + 2yz\dfrac{\partial^2\phi}{\partial y\partial z}(\mathbf{0}) \end{array}\right] + ...$$

which can be written in a much simpler form as

$$\phi(\mathbf{r}) = \phi(\mathbf{0}) + \mathbf{r} \cdot \nabla \phi(\mathbf{0}) + \frac{1}{2}\sum_{ij} x_i x_j \frac{\partial^2 \phi(\mathbf{0})}{\partial x_i \partial x_j} + \dots ,$$

where the components of $\mathbf{r}$ are expressed either as (x, y, z) or as (x_1, x_2, x_3).

Since the electric field $\mathbf{E}(\mathbf{0})$ at the origin is related to $\phi(\mathbf{0})$ by $\mathbf{E}(0) = -\nabla \phi(\mathbf{0})$, this implies that

$$\phi(\mathbf{r}) = \phi(\mathbf{0}) - \mathbf{r} \cdot \mathbf{E}(\mathbf{0}) + \frac{1}{2}\sum_{ij} x_i x_j \frac{\partial}{\partial x_i} \frac{\partial \phi}{\partial x_j}(\mathbf{0}) + \dots =$$

$$= \phi(\mathbf{0}) - \mathbf{r} \cdot \mathbf{E}(\mathbf{0}) - \frac{1}{2}\sum_{ij} x_i x_j \frac{\partial E_j}{\partial x_i}(\mathbf{0})$$

For a molecule consisting of N point charges e_n at locations $\mathbf{r}_n$, the W interaction energy becomes

$$W = \left(\sum_n^N e_n\right)\phi(\mathbf{0}) - \left(\sum_n^N e_n \mathbf{r}_n\right) \cdot \mathbf{E}(\mathbf{0}) - \frac{1}{2}\sum_n^N e_n \sum_{ij}(\mathbf{r}_n)_i (\mathbf{r}_n)_j \frac{\partial E_i(\mathbf{0})}{\partial(\mathbf{r}_n)_j} + \dots .$$

Thus, our final expression takes the following form (to be remembered):

$$W = q\phi(\mathbf{0}) - \boldsymbol{\mu} \cdot \mathbf{E}(0) - \frac{1}{6}\sum_n \sum_{ij} Q_{ij}^{(n)} \frac{\partial E_i(\mathbf{0})}{\partial(\mathbf{r}_n)_j} + \dots$$

This expansion illuminates how the various electric multipoles interact with an external field:

1st term: interaction of the molecular charge with the scalar potential ϕ

2nd term: interaction of the molecular dipole moment with the electric field $\mathbf{E}$

3rd term: interactions between the various electric field gradients $\partial E_i / \partial(\mathbf{r}_n)_j$ and the

corresponding components of the electric quadrupole moment tensor $Q_{ij}^{(n)}$
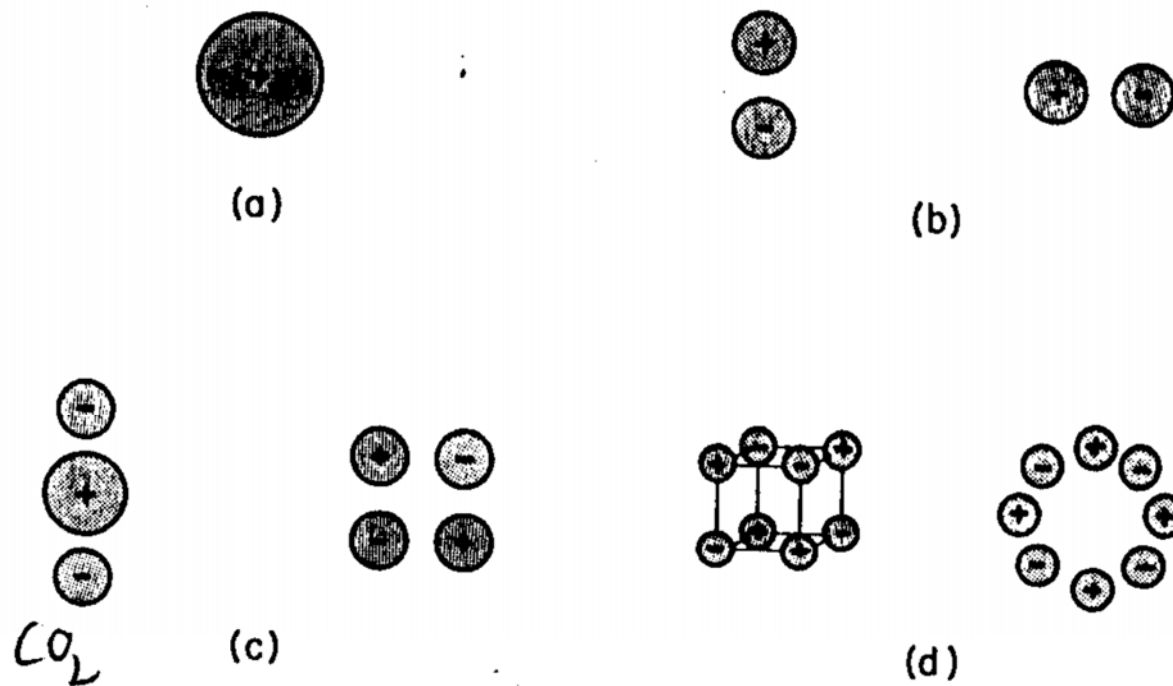
Examples for different electric multipoles:

Figure 1.2 Examples of charge distributions with (a) nonzero charge, (b) nonzero dipole moment, (c) nonzero quadrupole moment, and (d) nonzero octupole moment.

IV. GENERAL FEATURES OF EXPERIMENTAL TECHNIQUES

Emission spectroscopy is largely confined to the visible (V) and ultraviolet (UV) regions of the EM spectrum. Absorption spectroscopy is, generally speaking, a more frequently used technique in all regions of the spectrum.

Absorption spectroscopy

| (light) source | $\rightarrow$ | monochromator | $\rightarrow$ | sample | $\rightarrow$ | detector |
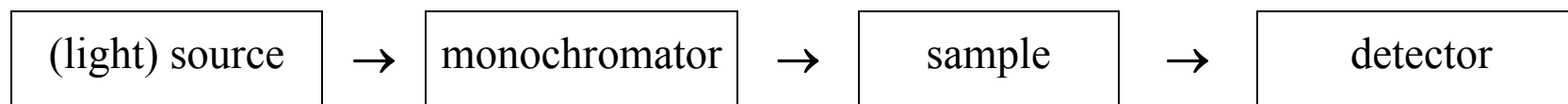
I. Sources of radiation

They usually work in a wide range of wavelength (frequency), except some, like the lasers.

A) Black body emulators

Globar: SiC rod, 6-8 mm in diameter and 50 mm in length. Resistively heated to 1300–1500 K. $\lambda \in$ (1 µm, 40 µm) → good infrared source. Emulates a black body.

Blackbody radiation (Planck):

$$\rho(v,T)dv = \frac{8\pi h v^3}{c^3}\frac{dv}{\exp\left(\dfrac{hv}{kT}\right)-1}$$

B) High pressure arc lamps (*e.g.*, Xe arc lamp)

continuous radiation ($Xe + e^- \rightarrow Xe^* + e^-$, $Xe^* \rightarrow Xe + hv$)
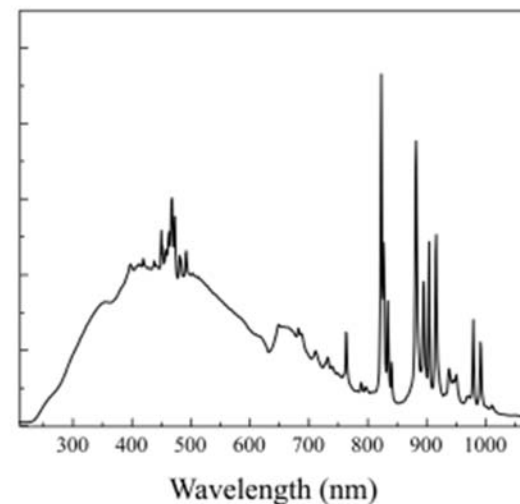Xe gas at 20-100 atm
tungsten poles 1-10 mm apart
collisions broaden atomic lines
good source of visible radiation almost down to 200 nm
used, for example, in IMAX projectors

300 400 500 600 700 800 900 1000

Wavelength (nm)

C)   Other discharge lamps

For example, the high voltage spark discharge in He produces far ultraviolet (VUV) radiation in the 100 to 60 nm range. He Iα radiation ($1s^2 \leftarrow 1s2p$) at 21.22 eV is responsible for this.

D)   Synchrotron radiation

An important source of VUV and X-ray radiation, but due to the apparatus' large size, its use is still not routine (there are several large-scale synchrotron facilities in the EU).

E)   Lasers (will be discussed later at length)

Lasers

LASER is an acronym for <u>L</u>ight <u>A</u>mplification by <u>S</u>timulated <u>E</u>mission of <u>R</u>adiation.

Einstein's B coefficients have the property that $B_{n \to m} = B_{m \to n}$. Thus, the competition between (induced, stimulated) absorption and stimulated emission depends only on the difference in the populations of the nth and mth energy levels ($E_n < E_m$), N_n and N_m, respectively:

$$h\nu_{mn} = E_m - E_n$$

$$\frac{dN_m}{dt} = N_n \rho(\nu_{mn}, T) B_{n \to m} \quad \text{(absorption)}$$

$$\frac{dN_m}{dt} = -N_m \rho(\nu_{mn}, T) B_{m \to n} \quad \text{(stimulated emission)}$$

Net rate: $(N_n - N_m)\rho(\nu_{mn}, T)B_{n \to m}$

Case I: $N_n > N_m$

This occurs in systems near or at thermal equilibrium (Boltzmann distribution). Hence absorption exceeds stimulated emission, resulting in a net energy loss for an incident beam of radiation of frequency ν_{mn}.

Case II: $N_n < N_m$

This represents a population inversion far from equilibrium, achieved by some means of pumping. The system in which the population inversion has been created is the active medium. Here stimulated emission exceeds absorption, resulting in an amplification of an incident beam with frequency ν_{mn}.

"Components" of lasers:

A system with a unique set of energy levels
Some means of achieving population inversion
A resonant optical cavity

II. Monochromators

Apart from experiments employing lasers it is often necessary to tune the radiation so that its change as a function of wavelength can be observed.

A)   Prisms (glass or quartz)

Wavelength is tuned by rotating the prism. Glass prisms can be employed to 360 nm (resolving power is greatest in the blue and violet), quartz prisms to 185 nm (resolving power is greatest in the 200–300 nm range).

B)   Diffraction grating

Parallel grooves ruled on a reflective glassy or metallic material with spacings of about 1 µm (1000 nm), comparable of the wavelength of visible light. The quality of the grating is closely connected to the degree of precision with which the straightness, the parallelism, and the equidistance of the grooves are controlled.

C)   Interferometers

III. Absorption samples and cells

The windows must transmit the particular radiation, and the length of the cell must be sufficient for high absorbance (effective lengths of several km can be achieved).

Gases at low pressure (to avoid pressure broadening of the lines) are used for high-resolution work. MW spectroscopy requires gaseous samples so that the rotational structure can be observed.

In the solid state rotations are quenched; vibrational and electronic structure are broadened. Samples may be pure crystals, mixed crystals, or solid solutions (rare gas matrices at low temperatures).

Matrix isolation techniques are useful to study unstable species.

IV. Detectors

A) Photoemissive and photomultiplier tubes

Photomultiplier tubes are employed in the visible and UV regions. Each incoming photon kicks out an electron from the surface of a photosensitized material, the electrons are accelerated, they kick out further electrons (cascade effect), at last resulting in a measurable electric current.

B) Photodiodes

C) Thermocouples

D) Golay pneumatic detector

E) Acoustic detectors

F) CCD (charge-coupled device)