Rotational Spectra

Advanced Radiation and Remote Sensing

Winter Term 2016

Stefan Bühler

Meteorologisches Institut

Universität Hamburg

Acknowledgement

This section on absorption is based on a script for a radiation course, written by Björn-Martin Sinnhuber.
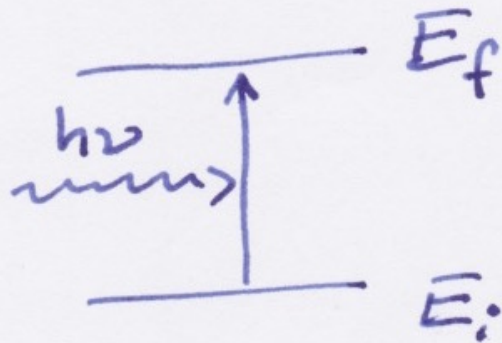
Recommended reading:
Fundamentals of molecular spectroscopy by C.N. Banwell and E.M. McCash (Mc Graw Hill)

Energy States and photons

Absorption (and emission) of a photon
can happen if a change in internal
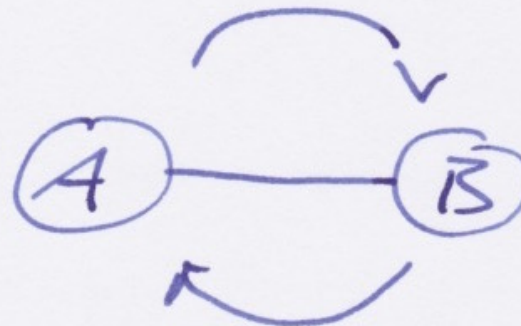energy of a molecule

$$E_f - E_i = \Delta E = h\nu ,$$

with ν the frequency of the
photon and E the state energies.

Stefan Buehler
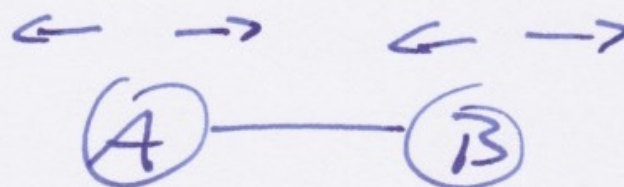
① 3

Transition types

Energy levels of a molecule are due to:
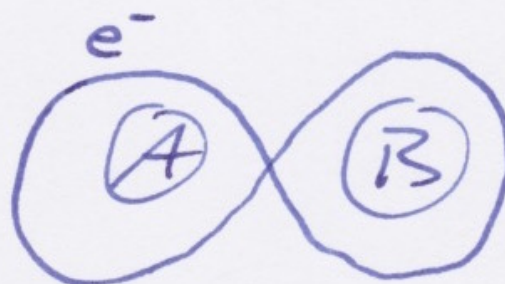
— rotation

micro-wave

— vibration

infra-red

— electronic transitions

uv / visible

Diatomic and polyatomic molecules

We will mainly discuss diatomic molecules, because they are easier to understand.
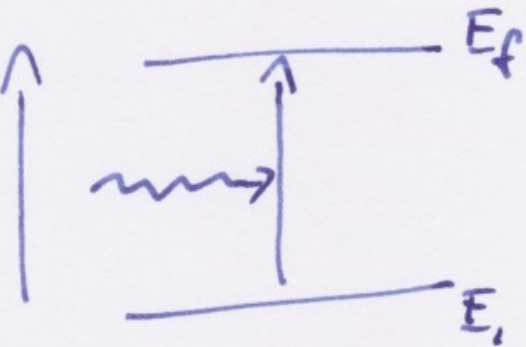
Important diatomic molecules:

O_2, N_2, NO, HCl, CO

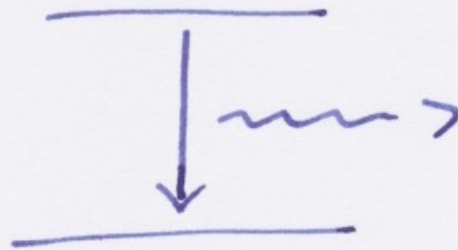Important polyatomic molecules:

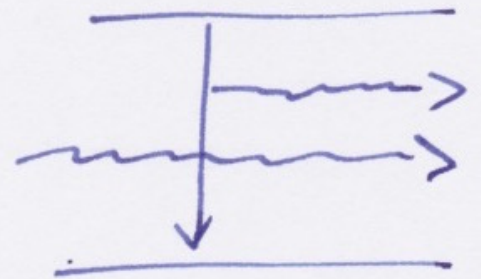O_3, H_2O, CO_2

Reminder: Three types of interaction

Absorption

Spontaneous Emission

Stimulated Emission

$$\Delta E = h\nu$$ (condition shown below)

Three conditions for absorption:

Condition 1: $\Delta E = h\nu$

Condition 2

Net absorption is proportional to the difference of occupation probabilities of states i and f: $P_i - P_f$

where P_i is given by the Boltzmann distribution (in local thermodynamic equilibrium)

$$P_i = \frac{g_i\, e^{-\frac{E_i}{kT}}}{\underbrace{\sum_{j=1}^{\infty} g_j\, e^{-\frac{E_j}{kT}}}_{Q(T)}}$$

g_i: state degeneracies (Entartung)

Names for $Q(T)$:
- Total internal partition sum
- Partition function
- Zustands-summe

(5)

Condition 3

Absorption is proportional to the electric dipole matrix element M_{if} between states i and f

$$M_{if} = \mu \iiint \Psi_f^*(x,y,z)\, \Psi_i(x,y,z)\, dx\, dy\, dz$$

↑ magnitude of dipole operator

M_{if} is a constant for each transition.

Conditions 1-3 combined lead to

$$\alpha(\nu) = n \sum_{f_i} S_{f_i}(T) \, \delta(\nu_{f_i} - \nu)$$

α: Absorption coefficient $[\frac{1}{m}]$

n: number density

S_{f_i}: line strength

$h\nu_{f_i} = \bar{E}_f - \bar{E}_i$

δ: Dirac's delta function
(actually not really true, will
be replaced later by
"line shape" function)

⑦

The line strength

$$S_{fi} = \frac{8\pi^3 \nu_{fi} |M_{fi}|^2 g_i}{3 hc \, Q(T)} \left(e^{-\frac{E_i}{kT}} - e^{-\frac{E_f}{kT}} \right)$$

Looks complicated. But note that the only true independent variable here in the temperature T. All other variables are constants of the transition, or fundamental constants.

Spectral line catalogues

...are collections of these transition parameters

There is one line in the catalogue for each spectral line. (Thousands for each molecule.

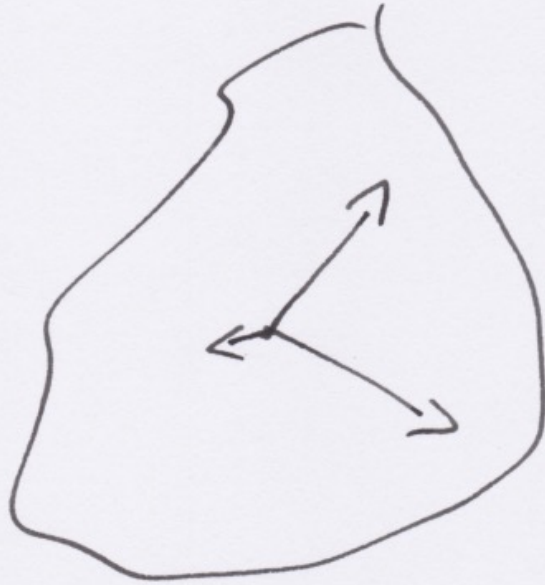Most well-known catalogue:

HITRAN

Rotational Transitions

(10)

Moments of inertia (Trägheitsmomente)

3 principal axes of rotation

3 <u>moments of inertia</u>:

$$I_A, \quad I_B, \quad I_C$$

Can be used to <u>classify</u> molecules.
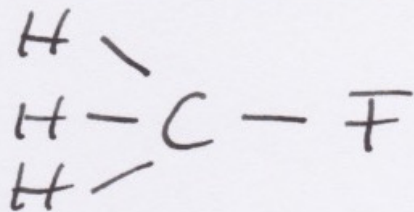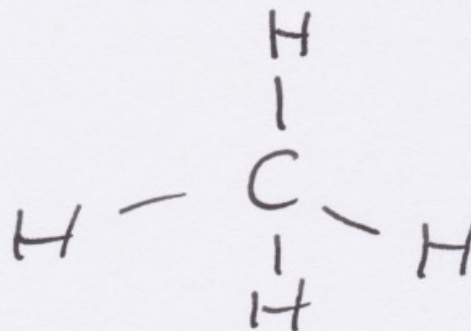
Molecule groups

Linear

$$H - CL$$

$$I_A = 0 \quad I_B = I_C$$

Symmetric top

$$H - C - F$$ with two additional H atoms bonded to C

$$I_A \neq 0 \quad I_B = I_C \neq I_A$$

Spherical top

$$H - C$$ with H above, H below, and H to the right (methane)

$$I_A = I_B = I_C$$

Asymmetric top

$$H - O - H$$
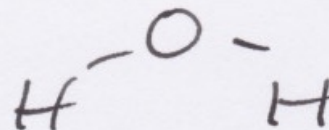
$$I_A \neq I_B \neq I_C$$

(10B)

Classical ~~klei~~ mechanics
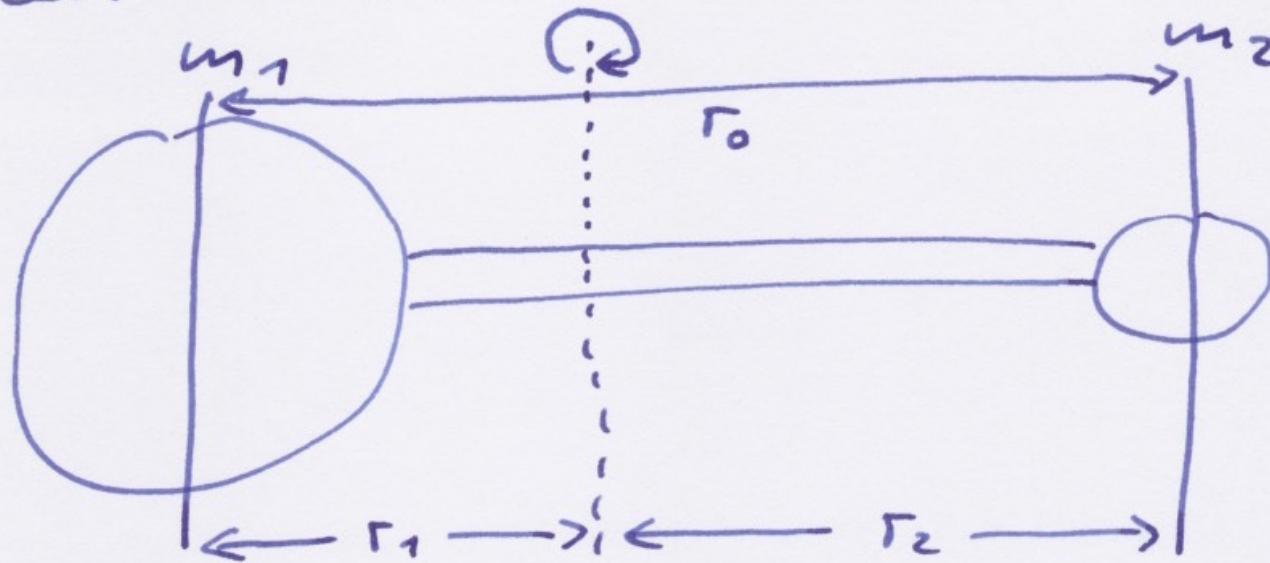
Rotational energy:

$$E_r = \frac{1}{2} I \omega^2 = \frac{J^2}{2I}$$

with ω: angular frequency (Kreisfrequenz)

I: moment of inertia (~~Dreh~~moment) Trägheits

J: angular momentum $J = I \cdot \omega$

(Dreh~~moment~~)
impuls)

⑪

Reduced mass for diatomic molecule

$$r_0 = r_1 + r_2$$

Defines centers of gravity:

$$\boxed{m_1 r_1 = m_2 r_2}$$

$$I = \sum_i m_i r_i^2$$

$$\boxed{I = \mu r_0^2}$$

Theory says, that relative motion is that of a single particle with reduced mass μ:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{or} \quad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

12

Reduced mass extreme cases

$$m_1 = m_2 \implies \mu = \frac{m_1^2}{2m_1} = \frac{1}{2}m_1 = \frac{1}{2}m_2$$

$$m_1 \gg m_2 \implies \mu \rightarrow \frac{m_2}{\boxed{\frac{m_1 + m_2}{m_1}} \approx 1}$$

$$\mu \rightarrow m_2$$

Quantum mechanical energie levels

$$H = \frac{J^2}{2I}$$

$\longleftarrow$ -- angular momentum

$\longleftarrow$ -- moment of ~~intia~~ inertia

$\uparrow$ Hamiltonian (total energy)

leads to ~~beas~~ allowed energy solutions:

$$\bar{E}_J = \frac{\hbar^2}{2I} J(J+1) \quad \text{with} \quad J = 0, 1, 2, \ldots$$

$$\hbar = \frac{h}{2\pi}$$

Planck constant

J: rotational quantum number

(14)

Wavenumbers

Energy (differences) can be conveniently expressed in <u>wavenumbers</u> (Kaisers)

$$\tilde{\nu} = \frac{\Delta E}{hc} \quad \left[\frac{1}{cm}\right]$$

or in frequency (Hz)

$$\nu = \frac{\Delta E}{h} \quad [Hz] ,$$

so they translate directly to the observed spectrum.
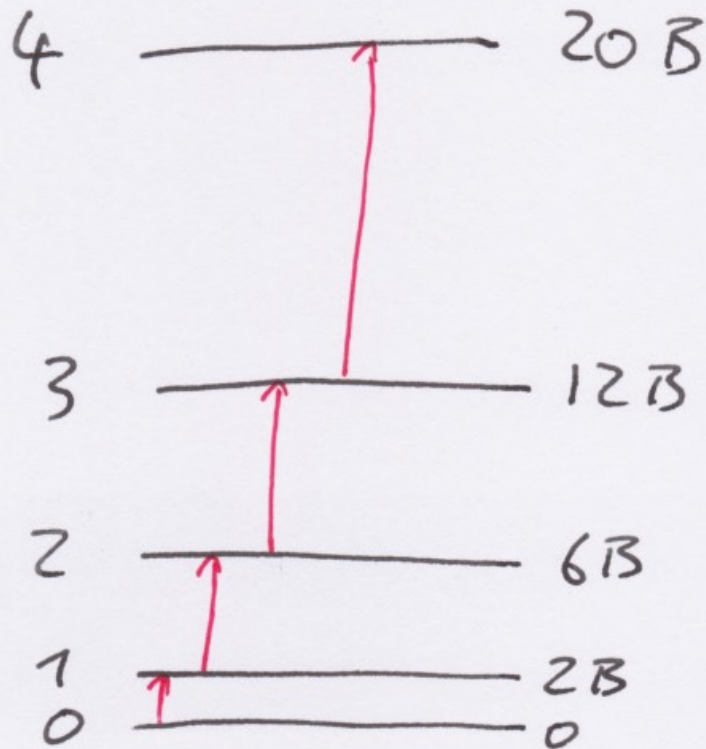
(15)

Rotational constant

Energy levels in wavenumbers:

$$\varepsilon_J = \frac{E_J}{hc} = \left(\frac{h}{8\pi^2 I c} \right) J(J+1)$$

$$= B$$

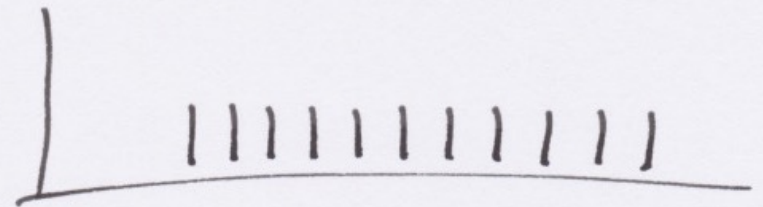B is called rotational constant. It is inversely proportional to the moment of inertia I.

Stefan Buehler

What energy levels do we get?

J $\qquad$ ε_J

Energy difference
of adjacent
levels $(\Delta J = 1)$:

~~4B~~ $2B, 4B, 6B, 8B, \ldots$

4 —————— $20B$

3 —————— $12B$

2 —————— $6B$

1 —————— $2B$
0 —————— 0

$\lfloor$ | | | | | | | | | | |

$\Rightarrow$ equidistant
spectral lines!

(17)

Selection rules

From Q.M., it turns out that the only transitions that are allowed are in fact the $\Delta J = \pm 1$ ones. All other transitions are forbidden. This is an example of a selection rule. So the full spectrum of a diatomic molecule is

$$\tilde{\nu}_{J \to J+1} = 2B(J+1) \qquad J = 0, 1, 2, \ldots$$

⑱

Exercise

In the exercise, we look at the rotational spectra of some simple molecules.

$\textcircled{19}$