Spectral plasma diagnostics by molecular spectra and continuum

Petr Vašina and Jan Janča

Department of Physical Electronics, Masaryk University, Brno, Czech Republic

# I. Molecular spectra
OH radical - influence of resolution

molecular spectrum measured with sufficiently high resolution composes from many lines

moderate or low resolution – spectral bands are observed – one band results from superposition of many individual lines – see N_2 spectrum, next page

measured spectrum

decreasing resolution

decreasing resolution
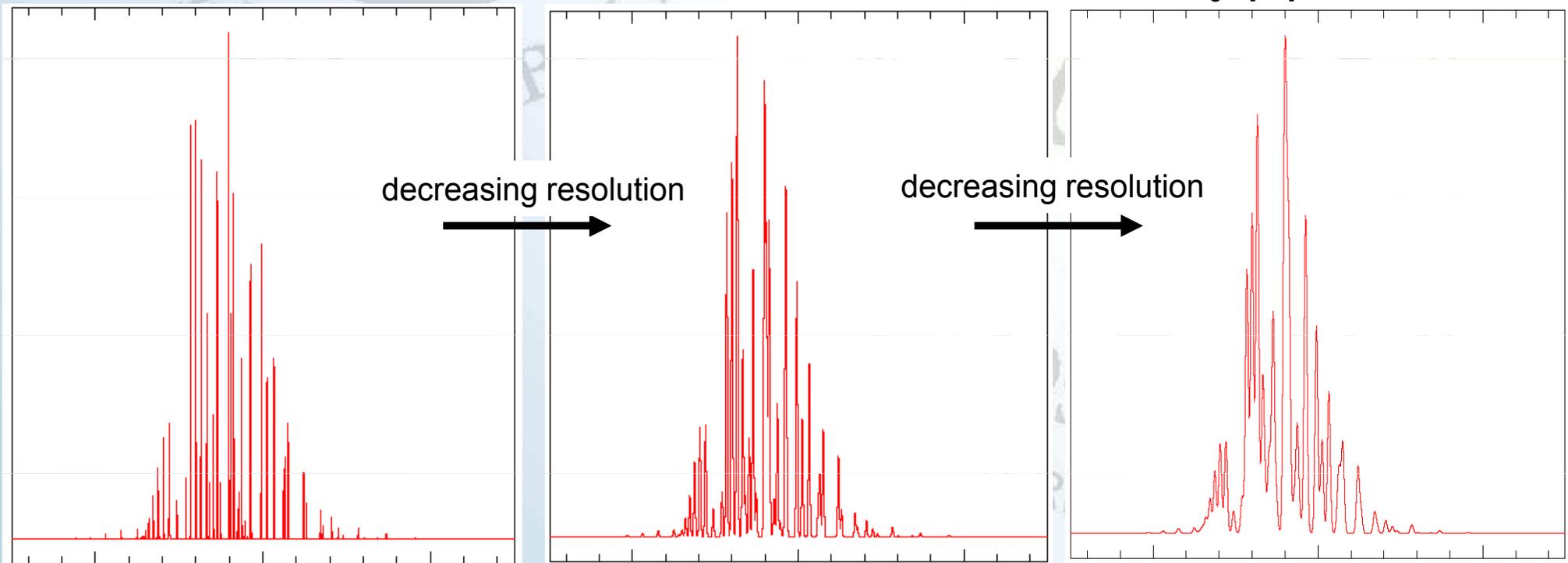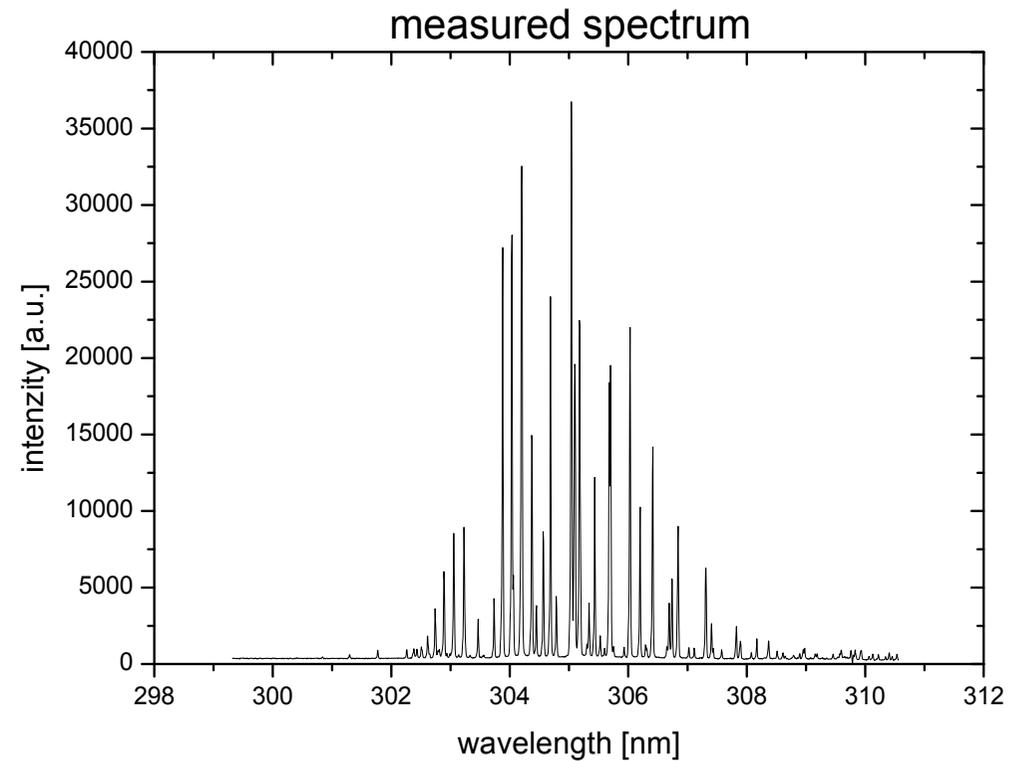
simulated spectrum using LIFBASE 2.0.55 program

Example of spectra – N_2 second positive vibration bands
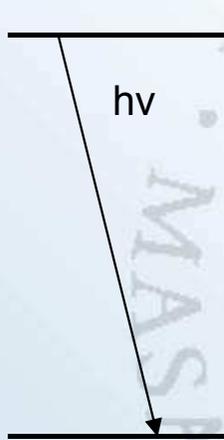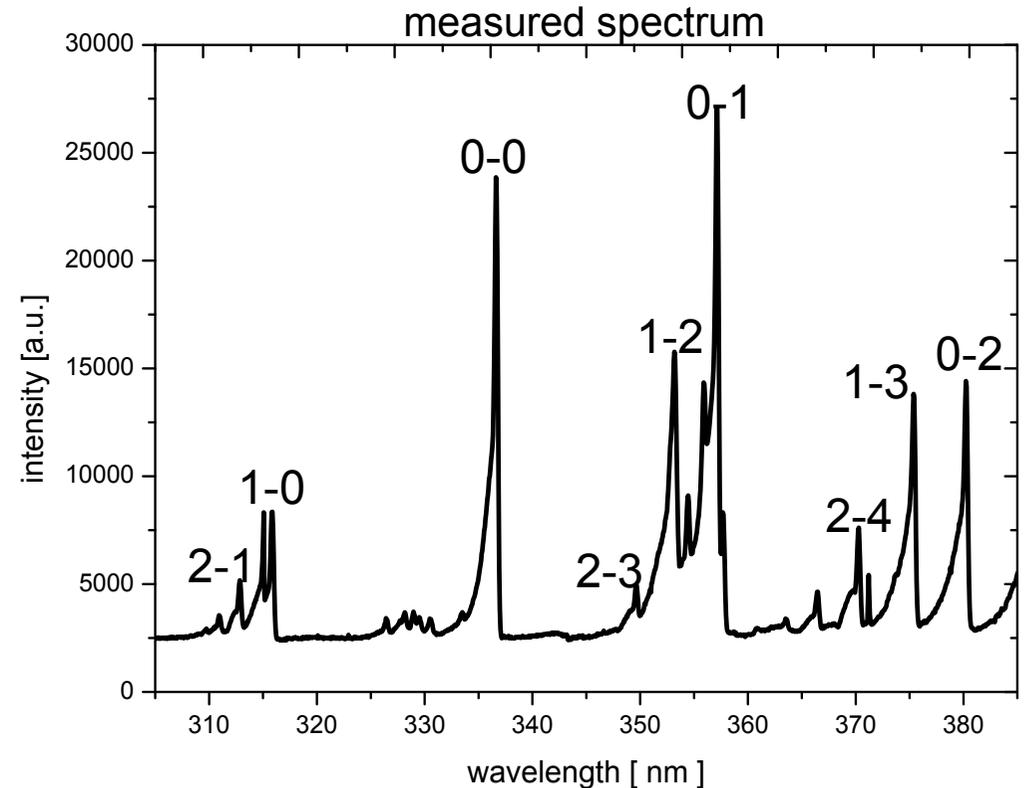
Atomic spectroscopy

hv

- Energy levels are defined by the configuration of all electrons in the electron cloud of the atom
- Change of the electrons configuration may give rise to the emission of a photon – "jump from higher energy level to the lower one"

Molecular spectroscopy

- Energy levels are defined by the configuration of all electrons in the electron cloud of the molecule
- Change of the electrons configuration may give rise to the emission of a photon – "jump from higher energy level to the lower one"
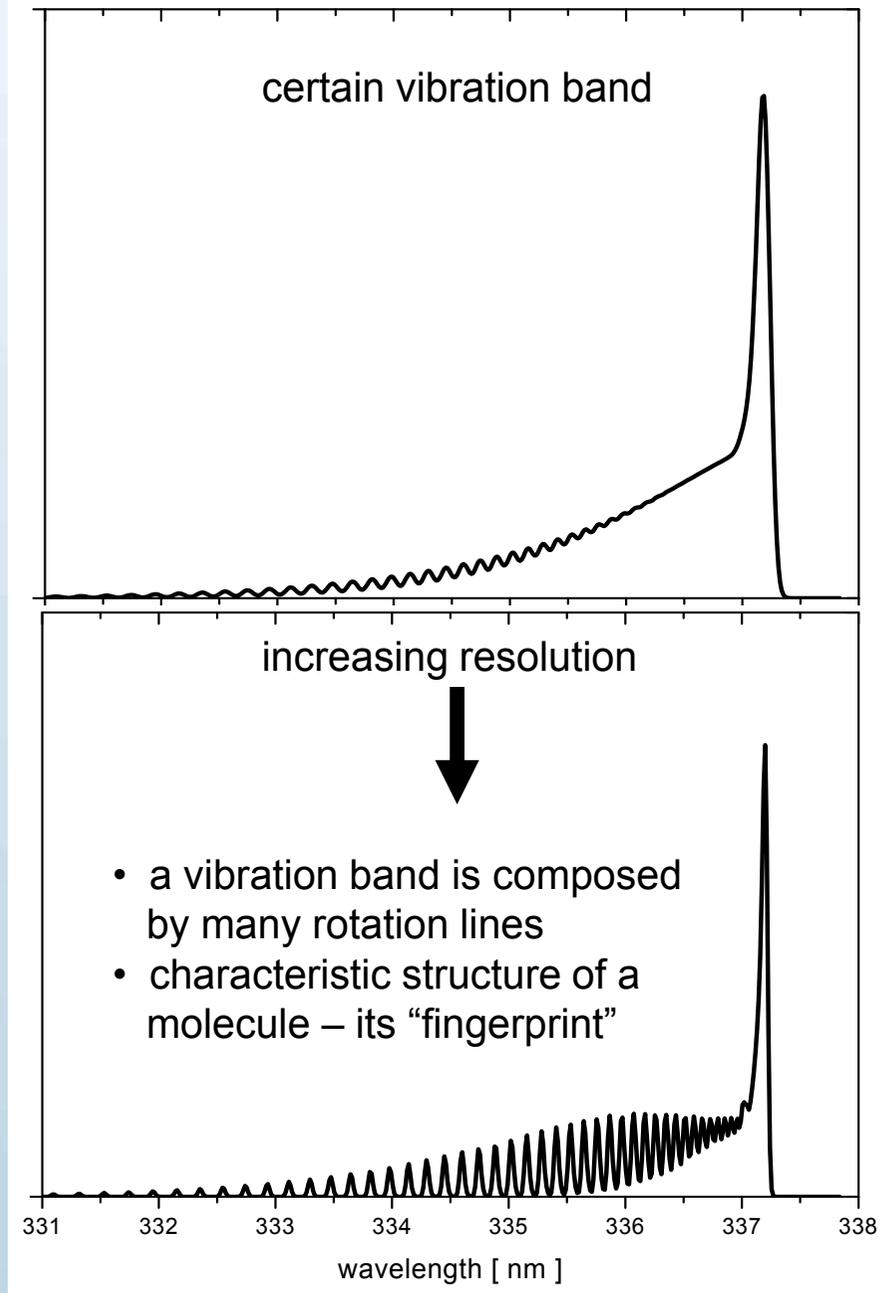
HOWEVER – simultaneously with the jump from the higher energy lever to the lower one, the molecule can **change its state of vibration and rotation**

molecular spectra will be a little more complicated

measured spectrum

0-1

0-0

1-2

1-3   0-2

1-0

2-4

2-1   2-3

intensity [a.u.]

30000

25000

20000

15000

10000

5000

0

310   320   330   340   350   360   370   380

wavelength [nm]

- same electronic transition
- different vibrations at higher and upper electronic state
- vibration bands

Example of spectra – N_2 second positive vibration bands, rotation lines

certain vibration band

increasing resolution

- a vibration band is composed by many rotation lines
- characteristic structure of a molecule – its "fingerprint"

331 332 333 334 335 336 337 338

wavelength [nm]

emitting a photon
    molecule may change simultaneously
- configuration of electron cloud (notation, selection rules)
- vibration (energy, selection rules, population of states)
- rotation (energy, selection rules, population of states)

molecular plasma spectroscopy in UV-VIS region
    all three events take places simultaneously
    object of our study

We will treat electronic states,
                    rotations and
                            vibration separately.

For all practical cases it is very good approximation. The basic of such factorization is the Born-Oppenheimer approximation.

$$\psi = \psi_e(r, R)\psi_v(R)\psi_r(\phi, \theta)$$

$$E = E_e + E_v + E_r$$
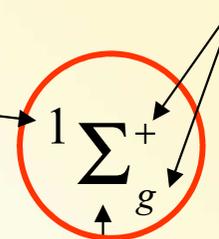
Classification of electronic states

components of the spin angular momentum along internuclear axis are $\Sigma\hbar$

$$\Sigma = S, S-1,\ldots,-S$$

$\underbrace{\qquad\qquad}$ multiplicity – 2S+1

symmetry properties of electronic wave function

$$S = 0$$

$$^{1}\Sigma_{g}^{+}$$

two potential curves of I$_2$ molecule

$$\Lambda = 0$$
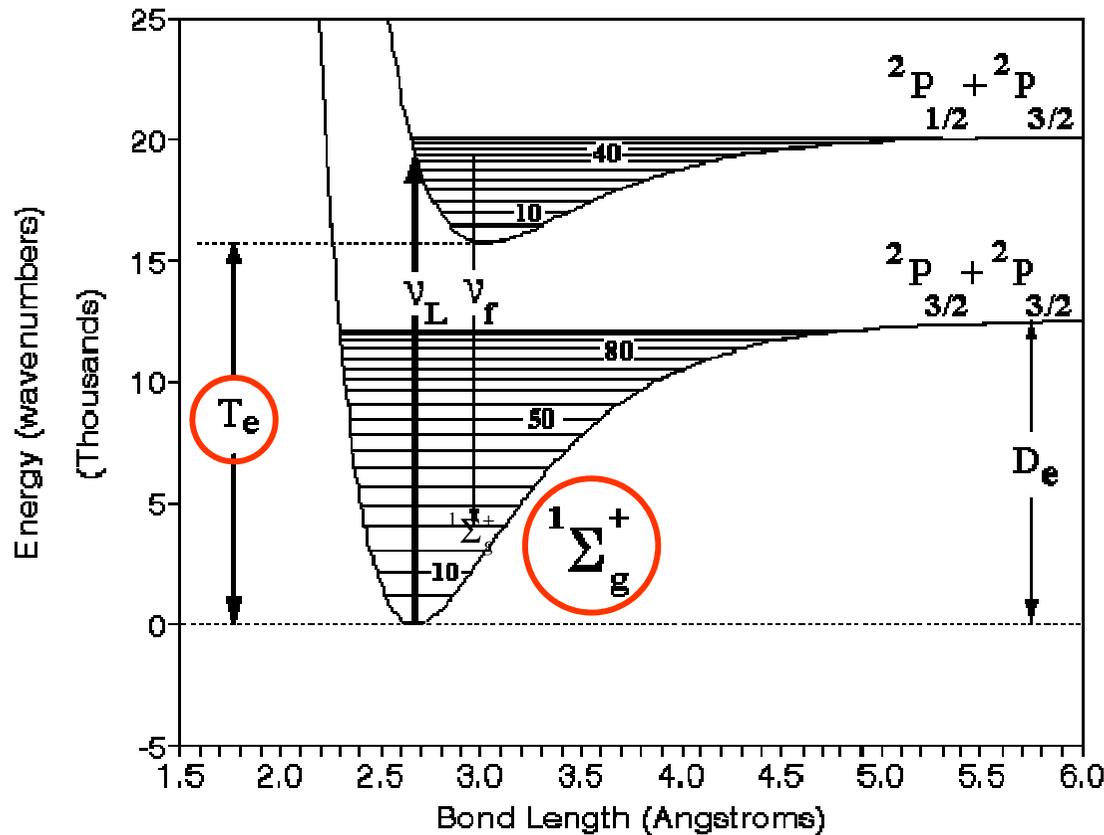
component $\Lambda\hbar$ of the orbital angular momentum along the internuclear axis

$$\Lambda = 0,1,2,3,4$$

designation $\Sigma, \Pi, \Delta, \theta, \Gamma$

T_e energy of the electronic state
energy of vibrations and rotations must be added

picture taken 18.6.2007 from : **http://itl.chem.ufl.edu/4411L_f00/i2_lif/i2_lif_il.html**

Vibration of molecule, dissociation

harmonic oscillator

$$\frac{d^2\psi_v}{dx^2} + \left(\frac{2\mu E_v}{\hbar^2} - \frac{\mu k x^2}{\hbar^2}\right)\psi_v = 0$$

anharmonic oscillator

$$E_v = h\nu\left(v + \frac{1}{2}\right)$$
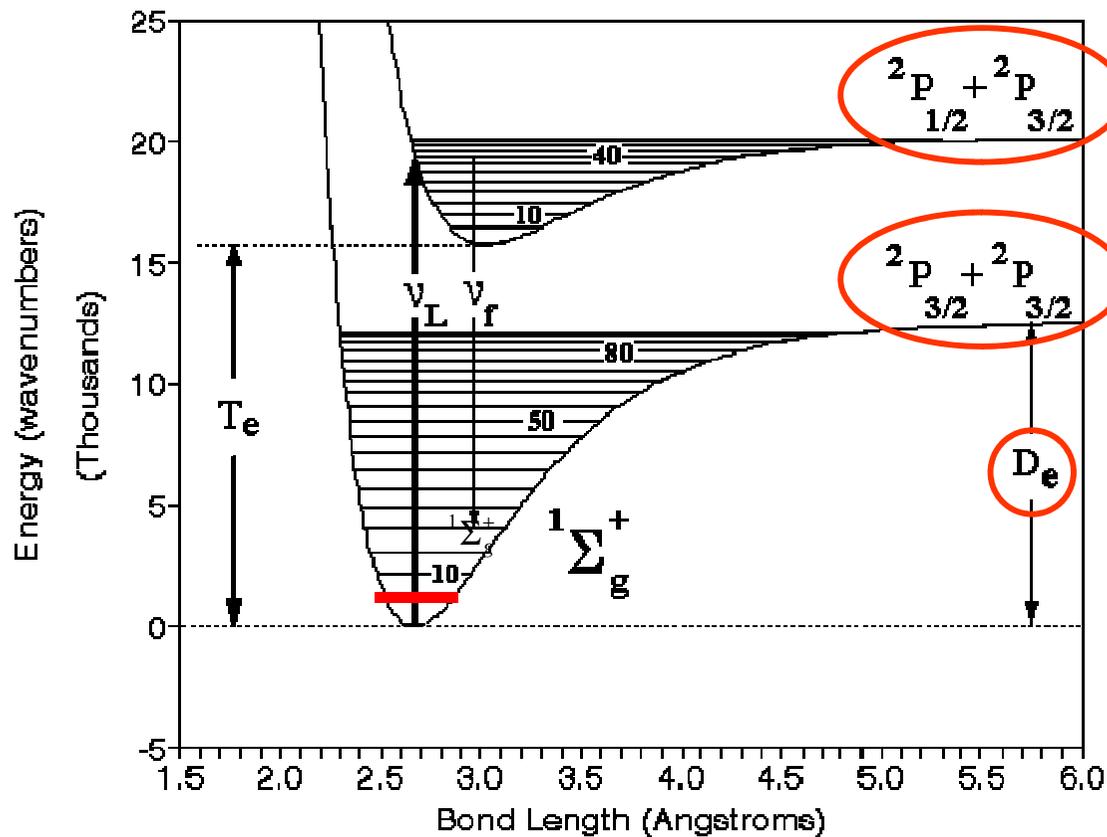
parabolic shape curve, no dissociation

$$E_v = h\nu\left(v + \frac{1}{2}\right) - \alpha h\nu\left(v + \frac{1}{2}\right)^2 + \ldots$$

non-parabolic shape curve
non-equidistant differences between levels
dissociation

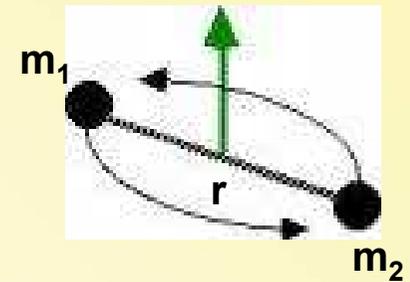**two potential curves of I_2 molecule**

molecule dissociate to two atoms
one in $^2P_{3/2}$ state one in $^2P_{1/2}$

molecule dissociate to two atoms
both in $^2P_{3/2}$ ground state

dissociation energy

Note that for simplicity
potential curves do not show rotational levels

Rotation of molecule

rigid rotor
$$E_J = \frac{L^2}{2I} = \frac{h^2}{8\pi^2 I} J(J+1) = hcBJ(J+1)$$

$$L^2 = \hbar J(J+1) \qquad I = \frac{m_1 m_2}{m_1 + m_2} r^2$$

angular momentum   moment of inertia

B depends on both - **configuration of electron cloud**

Example:
equilibrium position for lower state
  r_l = 2.7 A r_l^2 = **7.3** A^2
equilibrium position for upper state
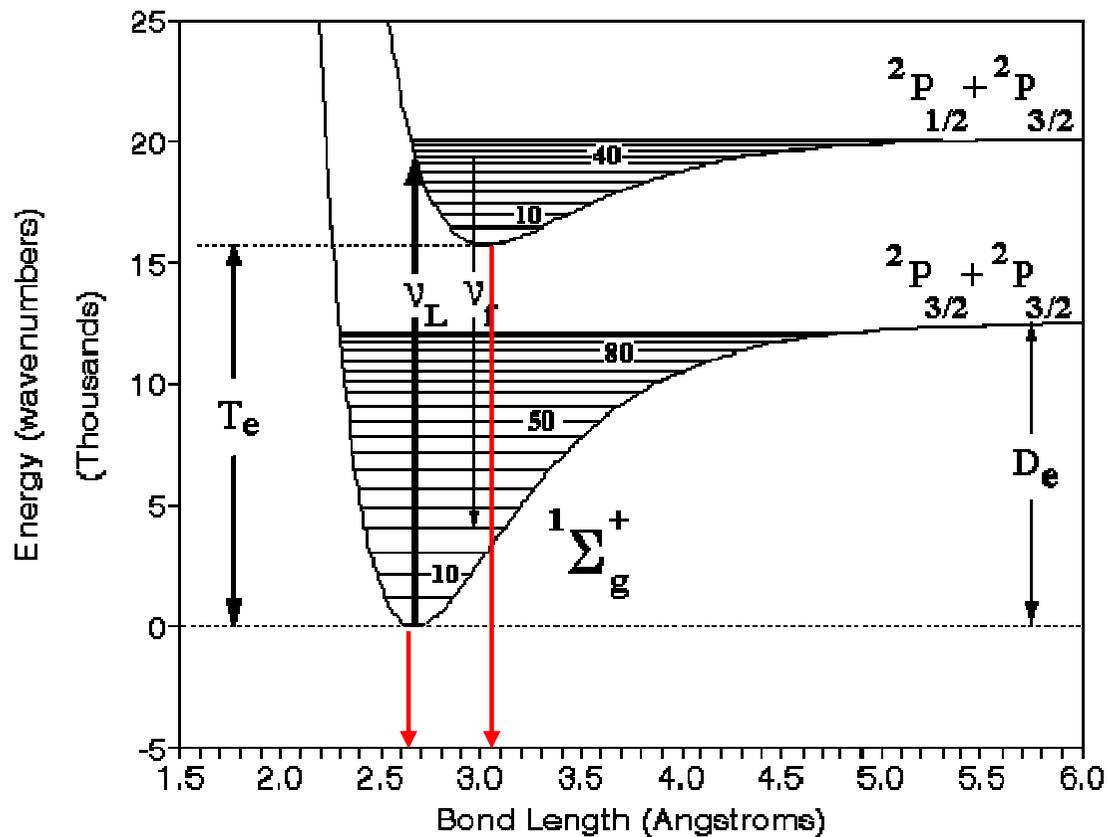 r_u = 3.1 A r_u^2 = **9.6** A^2

- **vibration state of the molecule**

more vibrating molecule has higher r^2 than less vibrating one

$$B = B_e - \alpha_e \left(v + \frac{1}{2}\right)$$

two potential curves of I$_2$ molecule

picture taken 18.6.2007 from : **http://itl.chem.ufl.edu/4411L_f00/i2_lif/i2_lif_il.html**

Selection rules

$${}^{1}\Sigma_{g}^{+}$$

	selection rule	examples of transitions	
		allowed	forbidden
1	$\Delta\Lambda = 0, \pm 1$	$\Sigma - \Sigma, \Pi - \Sigma, \Delta - \Pi$	$\Delta - \Sigma, \Phi - \Pi, \Phi - \Sigma$
2	$\Delta S = 0$	${}^{3}\Sigma - {}^{3}\Sigma, {}^{3}\Pi - {}^{3}\Sigma$	${}^{3}\Sigma - {}^{1}\Sigma, {}^{3}\Pi - {}^{1}\Sigma$
3	$+ \nleftrightarrow -, + \leftrightarrow +, - \leftrightarrow -$	$\Sigma^{+} - \Sigma^{+}, \Sigma^{-} - \Sigma^{-}$	$\Sigma^{+} - \Sigma^{-}, \Sigma^{-} - \Sigma^{+}$
4	$g \leftrightarrow u, u \nleftrightarrow u, g \nleftrightarrow g$	$\Sigma_{u}^{+} - \Sigma_{g}^{+}, \Pi_{g} - \Sigma_{u}^{+}$	$\Sigma_{g}^{+} - \Sigma_{g}^{+}, \Pi_{u} - \Sigma_{u}^{-}$

	selection rule	example of transition	
		allowed	forbidden
5	Δv not limited	$\Pi(v = 3) - \Pi(v = 1)$	-
6	$\Delta J = 0, \pm 1$	$\Sigma(J = 9) - \Sigma(J = 10)$	$\Pi(J = 5) - \Sigma(J = 2)$

N$_2$ second positive system

$${}^{3}\Pi_{u} - {}^{3}\Pi_{g}$$
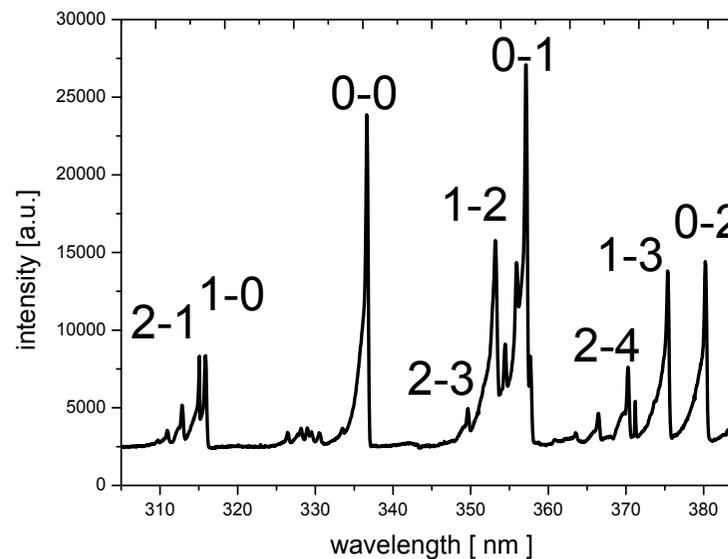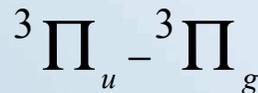
Origin of R,P,Q branches

	selection rule	example of transition	
		allowed	forbidden
5	Δv not limited	$\Pi(v=3)$ - $\Pi(v=1)$	-
6	$\Delta J = 0, \pm 1$	$\Sigma(J=9)$ - $\Sigma(J=10)$	$\Pi(J=5)$ - $\Sigma(J=2)$

$$h\nu = E^{'} - E^{''} =$$

$$T_e^{'} + E_v^{'} + hcB_J^{'}J^{'}(J^{'}+1) - T_e^{''} - E_v^{''} - hcB_J^{''}J^{''}(J^{''}+1)$$

since measured spectral band corresponds to the transition, where the upper and lower electronic and vibration states of molecule are the same

$$h\nu = E^{'} - E^{''} =$$

$$E^{'-''} + hcB_J^{'}J^{'}(J^{'}+1) - hcB_J^{''}J^{''}(J^{''}+1)$$
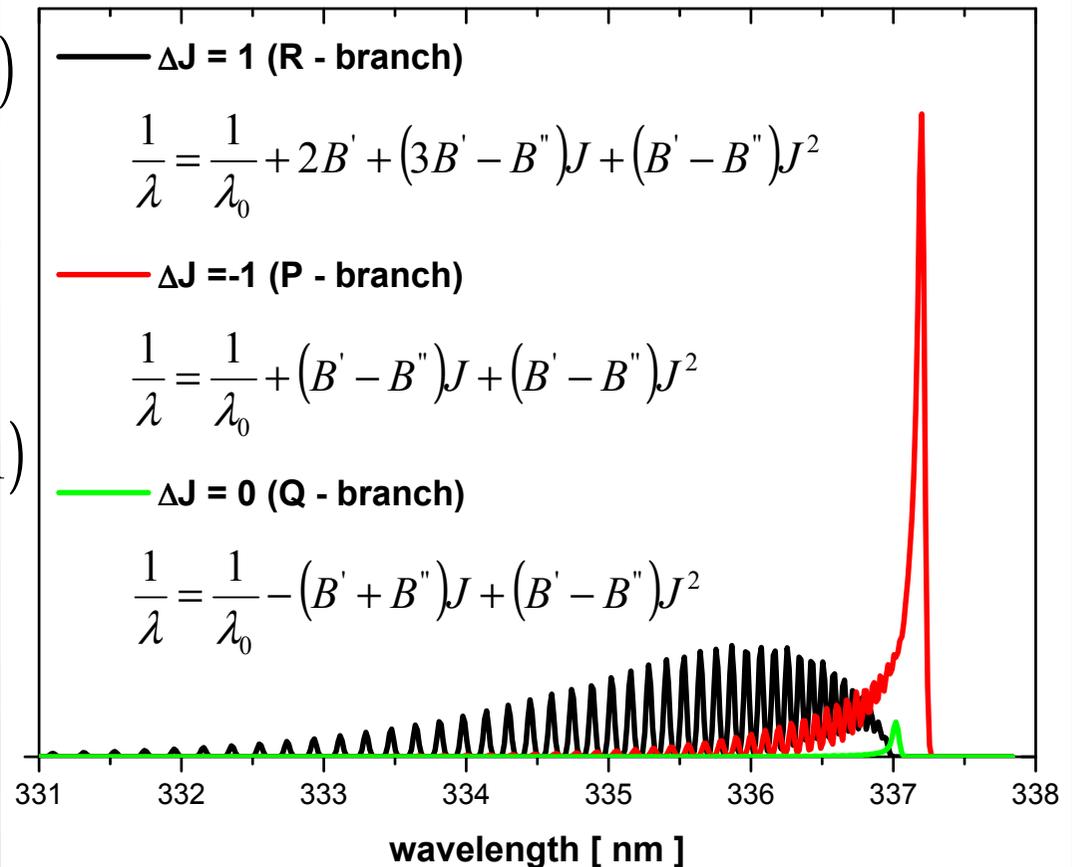
according to selection rules

$$J^{'} = J^{''} + 1 \text{ or } J^{'} = J^{''} \text{ or } J^{'} = J^{''} - 1$$

in the example case, since B'>B"
    P branch form the head of band
    R branch form the tail

——— $\Delta J = 1$ (R - branch)

$$\frac{1}{\lambda} = \frac{1}{\lambda_0} + 2B^{'} + (3B^{'} - B^{''})J + (B^{'} - B^{''})J^2$$

——— $\Delta J = -1$ (P - branch)

$$\frac{1}{\lambda} = \frac{1}{\lambda_0} + (B^{'} - B^{''})J + (B^{'} - B^{''})J^2$$

——— $\Delta J = 0$ (Q - branch)

$$\frac{1}{\lambda} = \frac{1}{\lambda_0} - (B^{'} + B^{''})J + (B^{'} - B^{''})J^2$$

wavelength [nm]

Intensity of rotation line

Einstein coefficient   constant characterizing intensity of a certain band (same E'-E", v'-v")

intensity of a line in general

$$A_{n"v"J"}^{n'v'J'} = F_{n"v"}^{n'v'} H_{J'J"}(\text{branch}, J')$$

$$I_{n"v"J"}^{n'v'J'} = N_{n'v'J'} h \nu A_{n"v"J"}^{n'v'J'}$$

Hőnl-London factor factor representing importance of R,P,Q branches at a given band
• depends on branch type (R,P,Q)
• depends on J'

number of particles at the given upper electronic level, at the given state of vibration and rotation

$$\psi = \psi_e(r, R)\psi_v(R)\psi_r(\phi, \theta)$$

at equilibrium characterized by temperature T one may write

$$H_{J'J"} = \left| \iint \psi_r^{'*} \psi_r^{"} \sin\theta \, d\theta \, d\phi \right|^2$$

$$N_{n'v'J'} = N_{n'v'} \frac{hcB_v'(2J'+1)}{kT} \exp\left(\frac{-hcB_v' J'(J'+1)}{kT}\right)$$

the recommended normalization for $H_{J'J"}$

$$\sum_{J'} H_{J'J"} = g(2J"+1)$$

g = 2S+1 for Σ - Σ transitions
g = 2(2S+1) for all other transitions

Finally, intensity of a rotation line at a given band is proportional to

$$I_{n"v"J"}^{n'v'J'} \approx C\nu^4 H_{J'J"}(J')(2J'+1)\exp\left(\frac{-hcB_v' J'(J'+1)}{kT}\right)$$

Since the rotation quanta are relatively small (~ 10^{-4} eV), translation and rotation thermalize almost immediately. Thus, temperature determined from rotational spectra ("rotation temperature") is usually very close to the temperature of the neutral gas.

higher temperature = molecule rotates more = shape of spectra changes
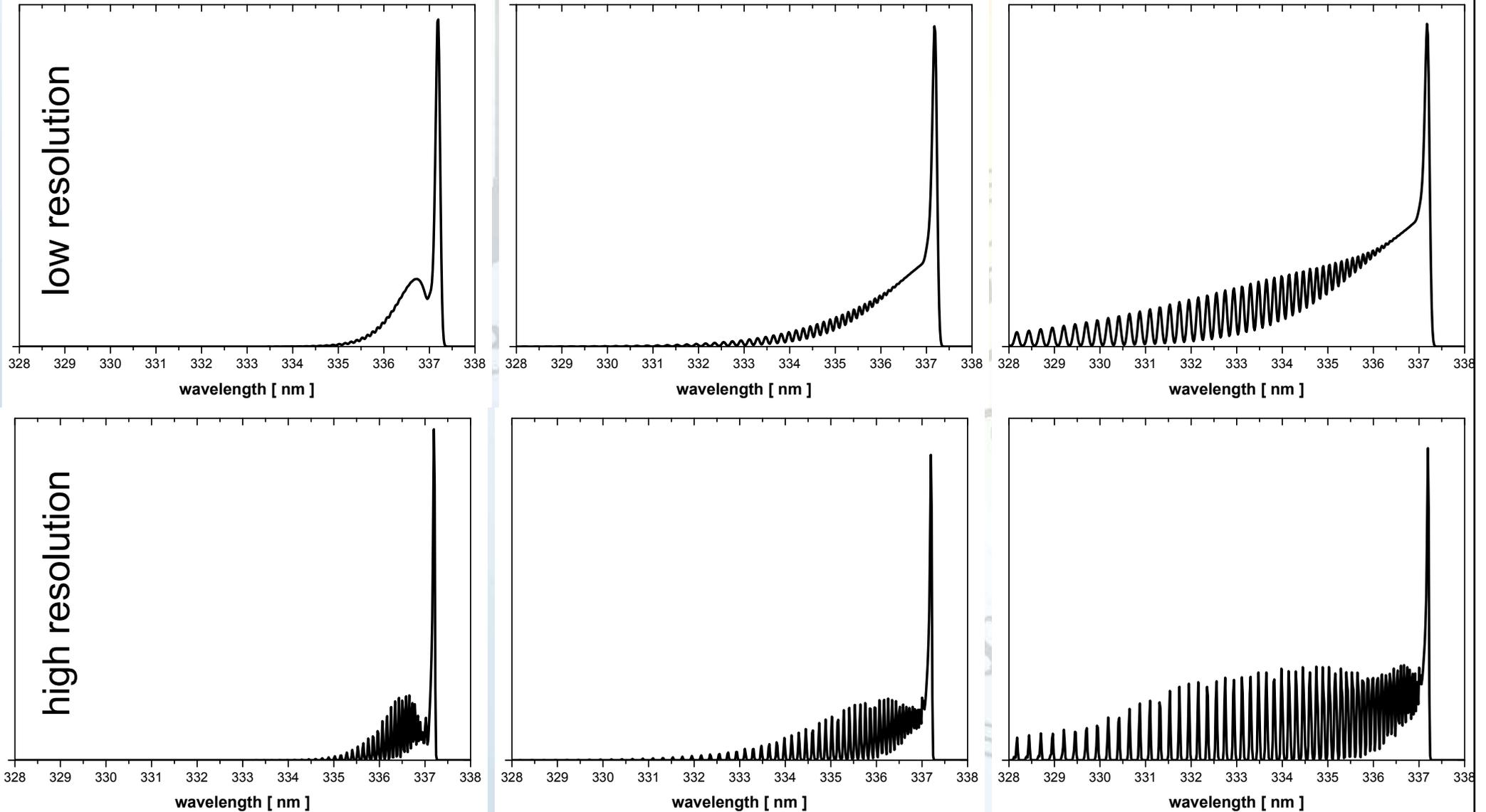
Change of the band shape with temperature

in order to estimate the rotation temperature – measured spectra are simulated

- resolution, instrumental function, line broadening
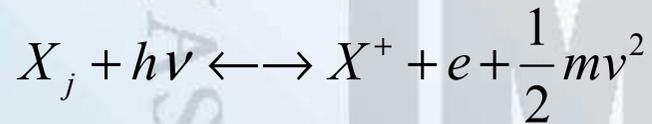- temperature (distribution of rotation states)

II. Continuum spectra

up to now one has been entirely concerned with line radiation involving transitions between two bonded states
(note that even molecular bands were composed by many lines)

plasma with appreciable degree of ionization

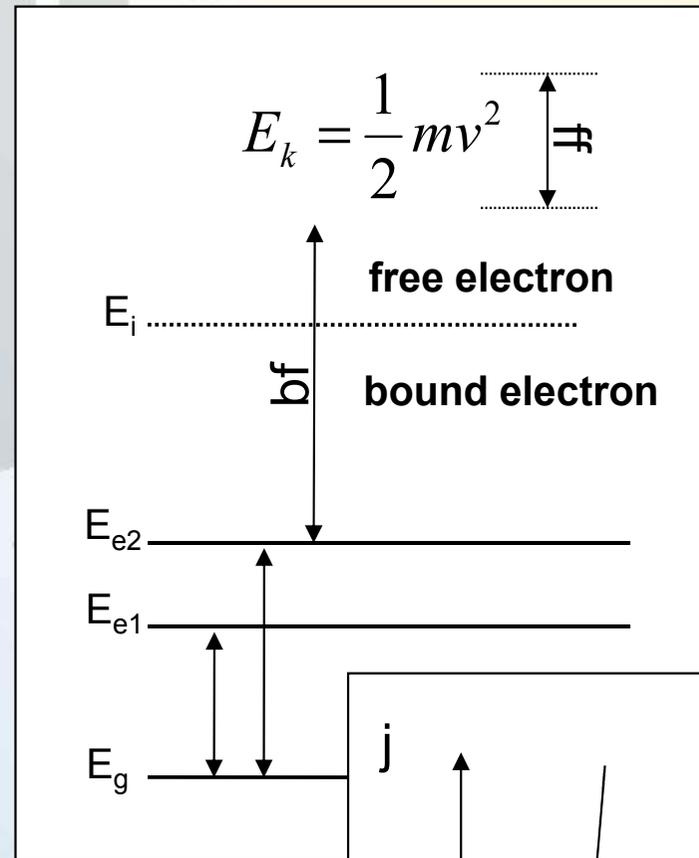• radiative transition between bound and free states

$$X_j + h\nu \longleftrightarrow X^+ + e + \frac{1}{2}mv^2$$

• photoionization – absorption of photon
• radiative recombination – emission of photon

$$h\nu = E_i - E_{e2} + \frac{1}{2}mv^2$$

fb continuum will

• be the most pronounced at lower wavelengths
• have fingerprints of energy levels of concerned species

$$E_k = \frac{1}{2}mv^2$$

free electron

E_i

bf

bound electron

E_{e2}

E_{e1}

E_g

j

ν

• radiation emitted or absorbed by the free electrons in the neighborhood of ion

• called braking radiation, deceleration radiation or bremsstrahlung
bremsem – to brake
strahlung – radiation

ff continuum will
• be pronounced at higher wavelengths
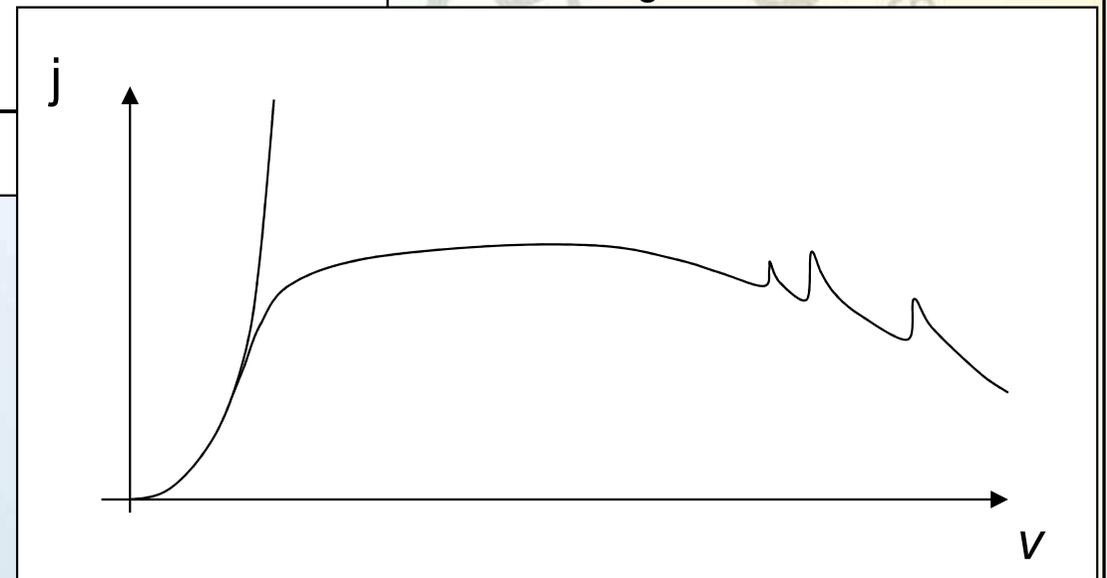
Continuum spectra –fb continuum

- emissivity (power emitted by solid angle per Hz by unit volume) of bf continuum follows for H-like ions and all highly excited species
- assumtion Maxwellian velocity distribution for the electrons

$$j^{bf} = \frac{128\pi^4}{3\sqrt{3}}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^5 \frac{mz^4}{c^3 h^3 (2\pi mkT)^{3/2}} n_i n_e e^{-h\nu/kT} \underbrace{\sum_{n\geq n_c}\frac{1}{n^3} e^{\frac{z^2\chi_H}{n^2 kT}} G_n^{bf}}_{}$$

edge structure
"taping on lower and lower states"

$$E_k = \frac{1}{2}mv^2$$

free electron

E_i

bf | **bound electron**

E_{e2}

E_{e1}

E_g

- in the regions between the edges a plot of $\ln\left(j^{bf}(\nu)\right)$ versus ν give a straight line, where T pertains to the Maxwellian velocity distribution of the electrons and not to any ratio of populations of excited states

- there exist a region of frequencies (the transitions which involve the region of energy levels very close to ionization threshold), where the edge structure can be neglected.

- for $\nu > \nu_g$ plotting $\ln\left(j^{bf}(\nu)\right)$ versus ν gives a straight line with slope h/kT

element	V_g [10^{15}Hz]
C	0.843
N	0.950
O	1.007
Ar	0.690
Xe	0.49-0.80

j

ν
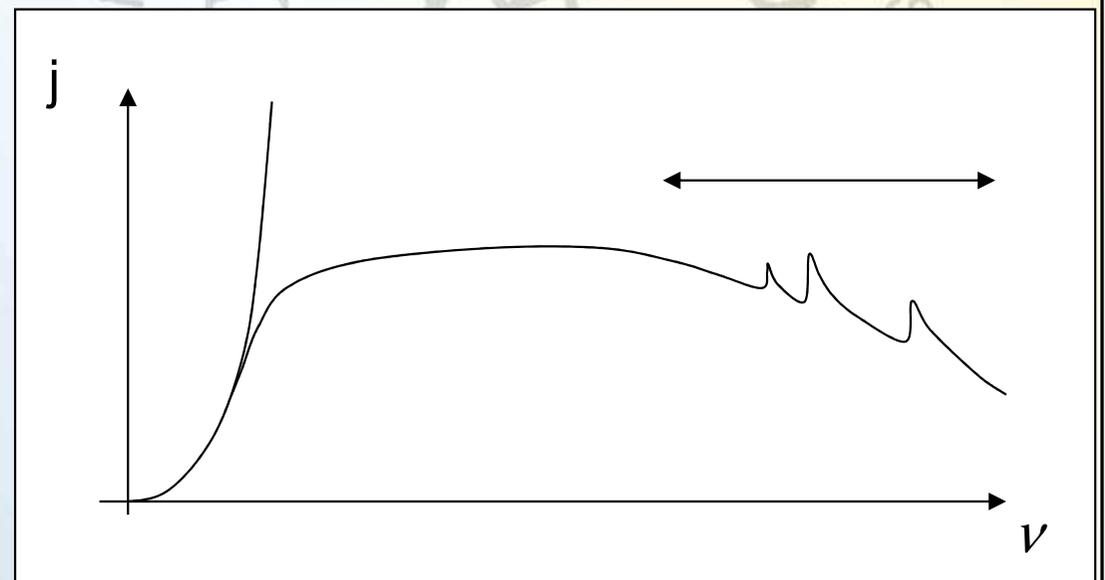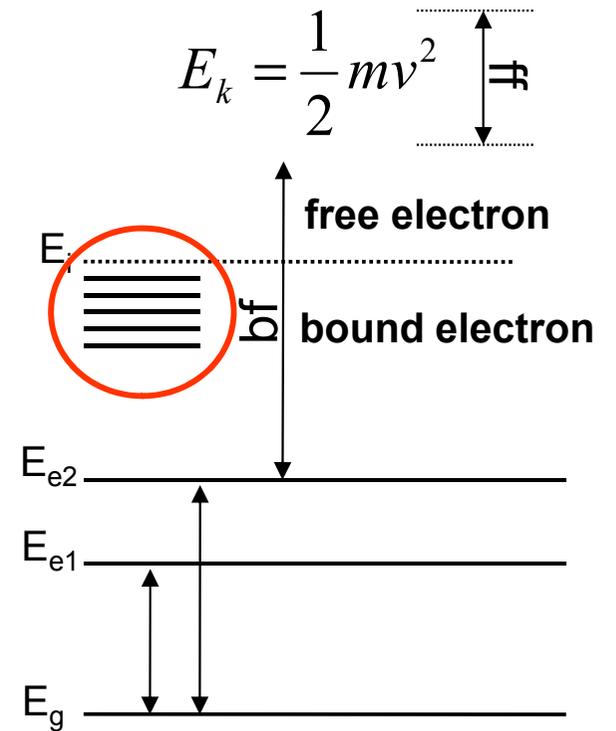
Continuum spectra – fb + ff continuum

- emissivity of fb continuum in the wavelength where edge structure can be neglected

$$j^{bf} = \frac{16\pi}{3\sqrt{3}}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^3 \frac{z^2}{mc^3(2\pi mkT)^{1/2}} n_i n_e \left(1 - e^{-h\nu/kT}\right)$$

- emissivity of ff continuum

$$j^{ff} = \frac{16\pi}{3\sqrt{3}}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^3 \frac{z^2}{mc^3(2\pi mkT)^{1/2}} n_i n_e\, e^{h\nu/kT}$$

- combining these two types of emission, there is a region of frequencies where

$$j^{bf} + j^{ff} = \frac{16\pi}{3\sqrt{3}}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^3 \frac{z^2}{mc^3(2\pi mkT)^{1/2}} n_i n_e$$

- equation does not depend on
- LTE was not assumed, only Maxwellian distribution for electrons
- knowing **absolute value of emissivity** (calibrated measurement) and **T_e** (from relative evolution of bf continuum) one can derive the **product $n_i n_e$ absolutely**

$$E_k = \frac{1}{2}mv^2$$

free electron

E_i ....

bf | **bound electron**

E_{e2}

E_{e1}

E_g

at low frequencies

- ff continuum dominates
- since absorption coefficient increases as $1/\nu^3$ plasma is getting optically thick whatever the particle density
- al low frequency emission hit the blackbody curve and $j \sim \nu^2$ (Reyleigh-Jean aproximation)
- moreover, at plasma frequency, the emission fall absurdly to zero

j

j

blackbody curve

ν
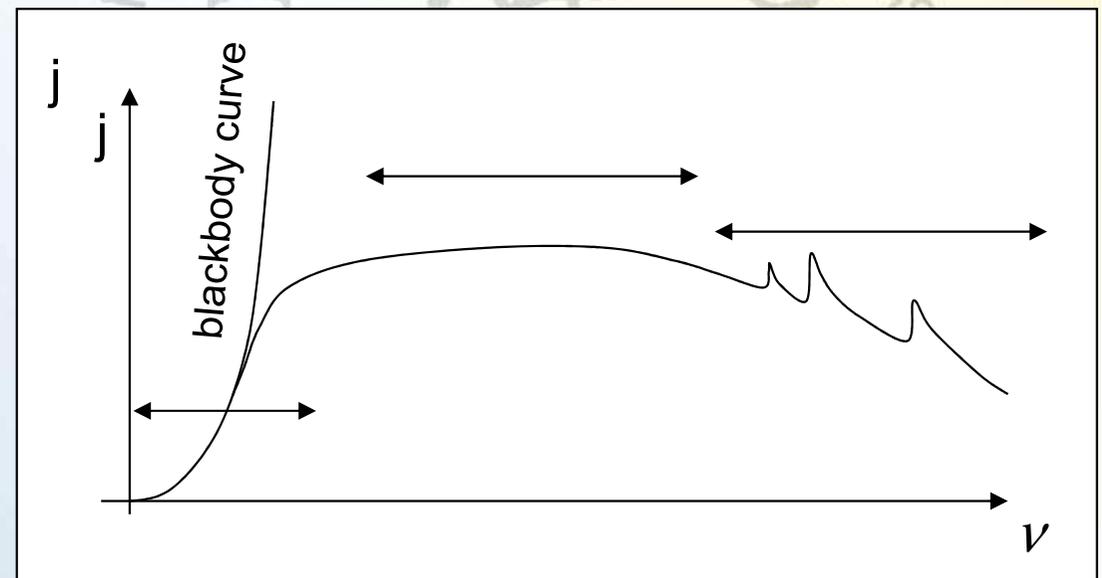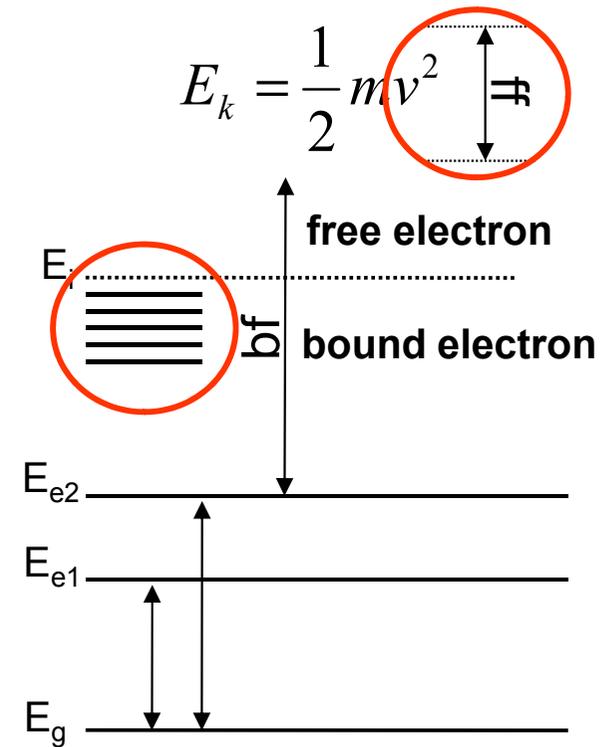
Conclusion

- spectral plasma diagnostics
  - in situ
  - non-invasive
  - easy to perform
  - little hard to analyse

- molecular spectra and continuum
  - plasma monitoring
    - identification of species (impurities)
    - plasma stability
  - quantitative analyses
    - plasma parameters (n_e, T_e)
    - particle densities
    - plasma chemistry

- efforts in interpretation are rewarded by manifold results

- there exist many good books about this subject where one can learn more

  - A. Thorne, U. Liezén, S. Johansson : Spectrophysics, Principles and Applications, Springer, 1999
  - J. M. Hollan : Modern Spectroscopy, John Wiley & Sons, 1996
  - I. Kovacz : Rotation Structure in the Spectra of Diatomic Molecules, Adam Hilger Ltd., 1969
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