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Preparatory School to the Winter College on Optics and the Winter College on Optics: Advances in Nano-Optics and Plasmonics

6 - 17 February, 2012

Raman and fluorescent spectroscopy coupled with scanning tunnelling microscopy

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Société Tunisienne d'Optique

Winter College on Optics
Advances in Nano-Optics and Plasmonics
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Spectroscopy of atoms , molecules
Vibrational nanospectroscopy for biomolecules

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-Between which states can transition take place, producing abs. Or emis. Of e.m radiation?

-what is the probability of this transition?

-What can be learned about molecular structurefrom the intensties, line profiles, and polarisations of the molecular spectral lines?

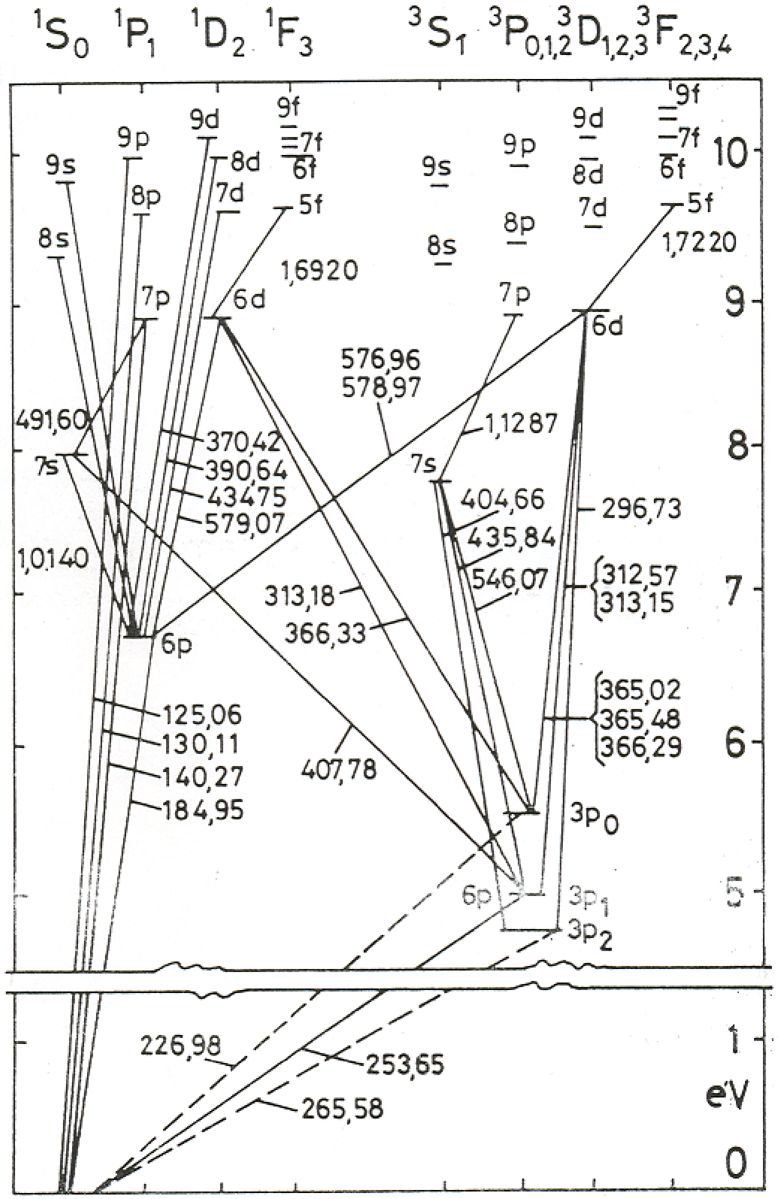
-In Polyatomic molecules, symmetry properties play a crucial role for the simplification and generalization of their representation.

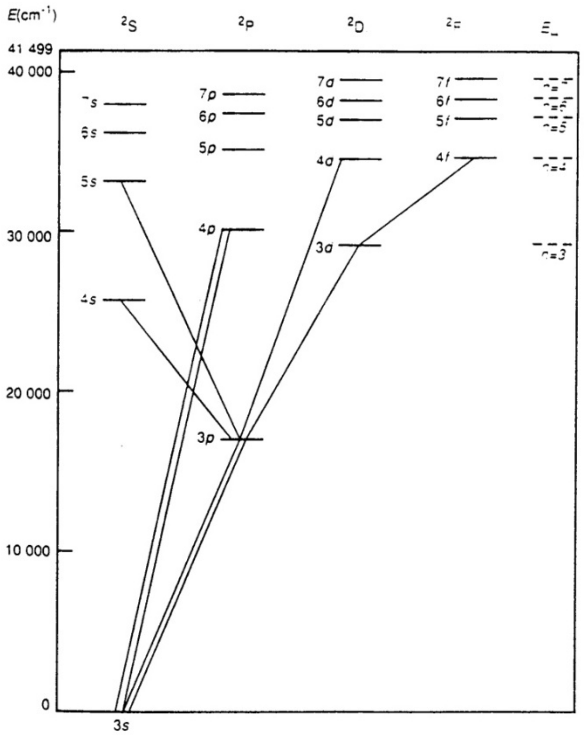
Atom-radiation Interaction

Elastic interaction

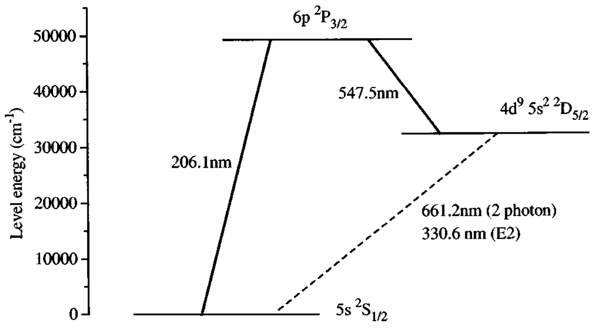
Inelastic interaction→access to different energy levels (absorption, emission– spectra of atoms or molecules)

Spectrum of mercury.





Na



Ag

- Spectra generated by dipole transitions

Spectrum is generated by transitions between different energy states according to certain selection rules- these selection rules for allowed transitions essentially reflect the requirement of conservation of angular momentum for the atom/molecule-photon system and considerations of symmetriy for the wavefunction describing the states)

For electric dipole transitions the etablishing of the selection rules concern the conditions under which the matrix element $\langle n|\mathbf{r}|i\rangle$ is non Zero

State definition and selection rules transition between energy states for an atom

Interest to the outer electrons- Law of conservation

- one atom, $\mathbf{L} = \Sigma \mathbf{l}_i$ $\mathbf{S} = \Sigma \mathbf{s}_i$
- Coupling L S—$\mathbf{J}=\mathbf{L}+\mathbf{S}$, $|L-S| \leq J \leq L+S$

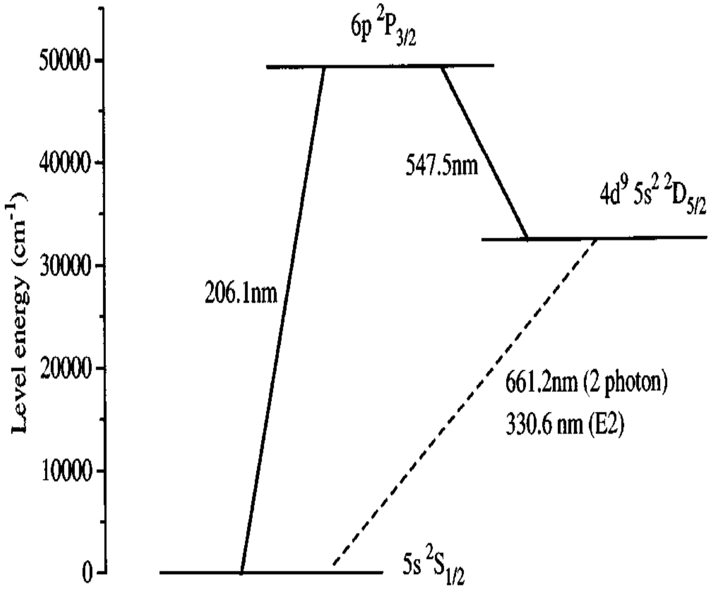
attribution to state $^{2S+1}L_J$;

Splitting: 2S+1 →multilicity

dipole transition $\langle n | r | i \rangle \neq 0$

$\Delta l = \pm 1, \Delta S = 0, \Delta J = 0, \pm 1$

- Other Coupling j j , $\mathbf{J} = \Sigma \mathbf{j}_i$



Ag states

Optical spectroscopy

Metal atoms have one outer electron as alcali atom , excitation energy of the outer electron electron ~ 3eV
For Optical radiation (λ~500nm ≈ 2,48eV) → optical spectroscopy

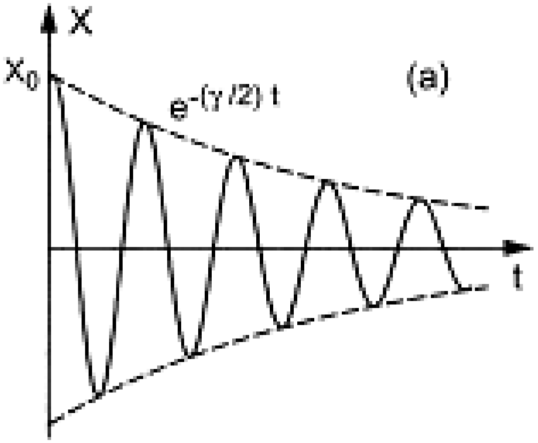
Optical spectroscopy is based on:

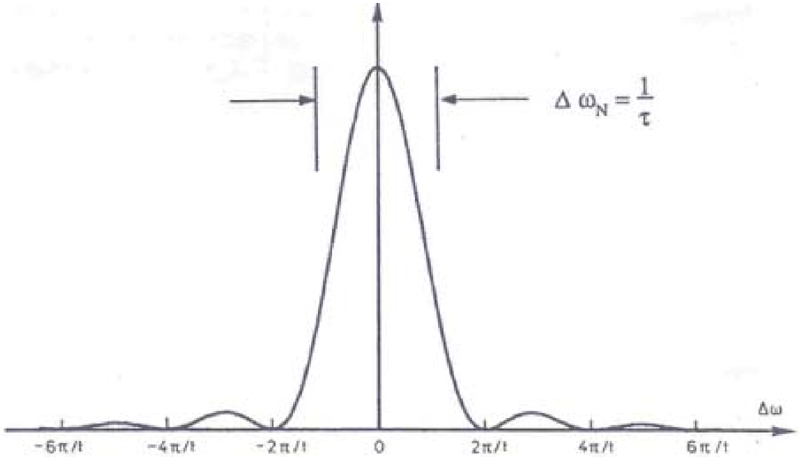
-Frequencies and Intensities of optical transitions

These can be translated to structure only in simple systems (atoms, diatomic molecules)

-Group symetry & Potential surfaces have to be known for more complex systems

Atome ~ damped harmonic oscillator





dampted classical harmonic oscillator

intensity distribution for radiating atome

τ ~how many periods oscillations before fiel decays-

$C_e(t)^2 \ \alpha\ [\sin(\Delta\omega t/2)/\ \Delta\omega t/2]^2\, t^2$

Spontaneous emission (QED traitment

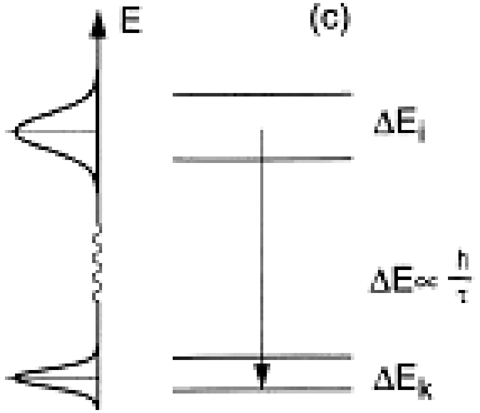
Natural radiation width,

$\Delta\nu_e = 1/2\pi\tau$ –

$\Delta\omega_e = 1/\tau$ (same result for abs.e→f

or

for emis. f→e)



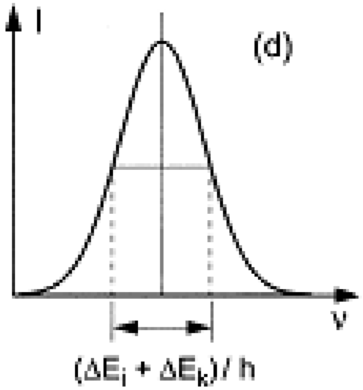
Natural linewidhts dues to
Energy uncertainties due to
limited lifetimes

(finite lifetime of the excited states)-

intensity distribution is:

$$|A(\nu)|^2 = (E_0^2\tau^2)/\pi^2\{1+[(\nu-\nu_0)/1/(4\pi\tau)]^2\}^{-1}$$

Lorentzian profile



Resulting line width Δ ν

-**Doppler width** (mvt of atoms at different speed and different directions- inhomogeneous broadening)

The intensity : $I(\omega) = I(\omega_0)\exp\{-[c(\omega - \omega_0)^2/ \omega_0 v^*)]^2\}$,

v*the most probable velocity, $v^*=[2k_B T/m]^{1/2}$

The full widht at half maximum(FWHM) ,

$$\Delta\nu_D = 2(\nu_0/c)(2RT\ln 2/M)^{1/2}; R= k_B N_A$$

We see that the Doppler widht increases linearly with the frequency ν_0 and for a given temperature is largest for small masses.

orders of magnitude:

In the VIS, λ=500nm, electronic transition

of Na_2 molecule, T=500K,

$\Delta\nu_D = 5{,}6 \times 10^7 s^{-1} \approx 56MHz$

$\Delta\nu_D \sim 0{,}001nm$ or 1000MHz in the IR is proportionally smaller, ~50MHz at 10µm

-Collision broadening

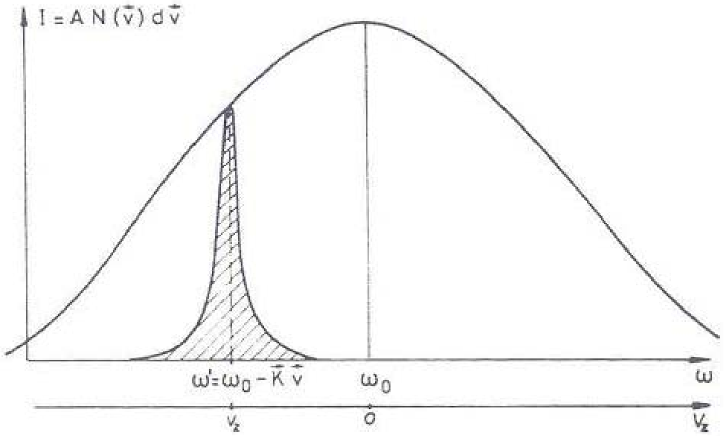
with increasing pressure , the atoms undergo frequent collisions → collision broadening, Lorentz profile (between different kind of atoms) or Holtsmark broadening (collision between same kind of atoms), the 2 mechanisms are treated as pressure broadening

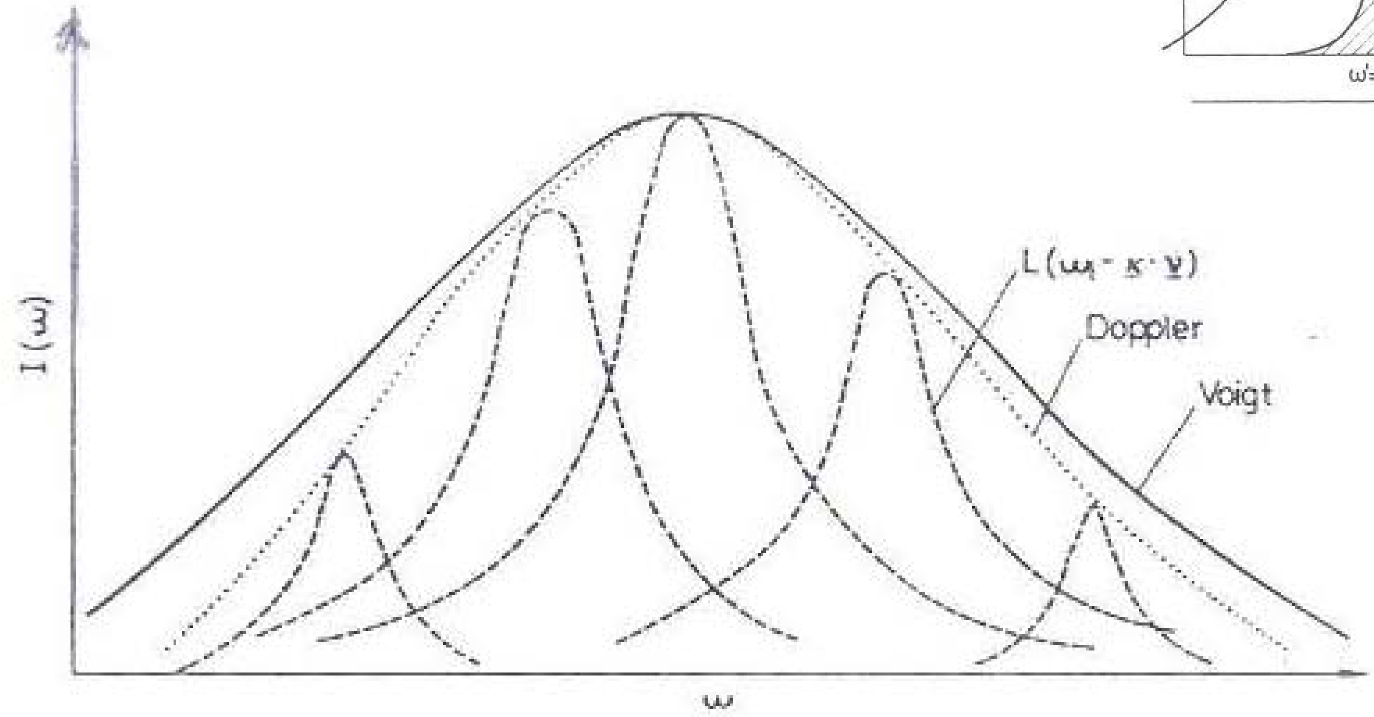
$$\Delta\nu_{coll}\,(P,T)= \Delta\nu_{coll}\,(P_0,T_0)P/P_0\,(T/T_0)^{1/2}$$

orders of magnitude:

For Lorentzian , broad. at atmos.pres. &room T is 0,5-5 GHz

Profile of a spectral line affected by Pressure + temperature effect





Molecules

- A molecule is formed by the binding of 2 or more atoms in such a way that the total energy is lower than the sum of the energies of the constituants. The bonds are normally of ionic or covalent nature. Particularly weak bonds occur in van der Waals molecules

Classically light is emitted by a system only if its electric dipole moment is changed-This rule is valid by QM and is also valid for molecule

- The dynamic of a molecule is more complicated

and is connected to movement of electrons and nucleus with E_e, E_v,E_r , with $E_e >> E_v >> E_r$

Electronic states of diatomic molecules

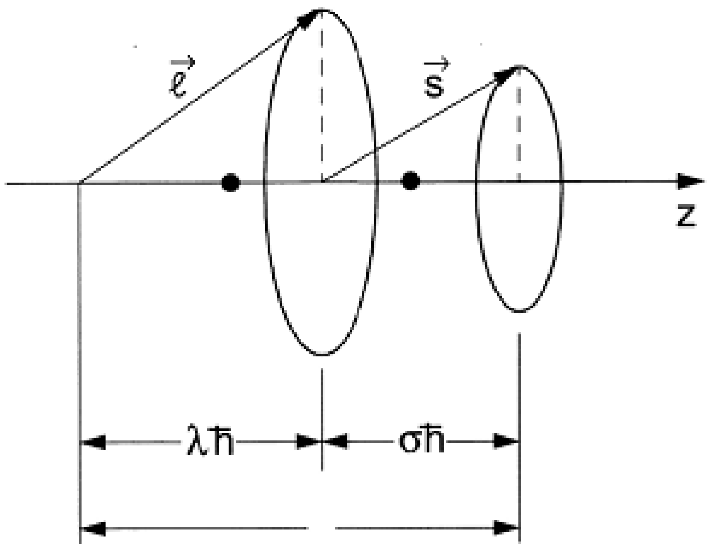
- Electronic angular momentum

Each electron(**l,s**), precesses around the internuclear axix(**z** axix) → electric current around **z** → **B** along the z axis

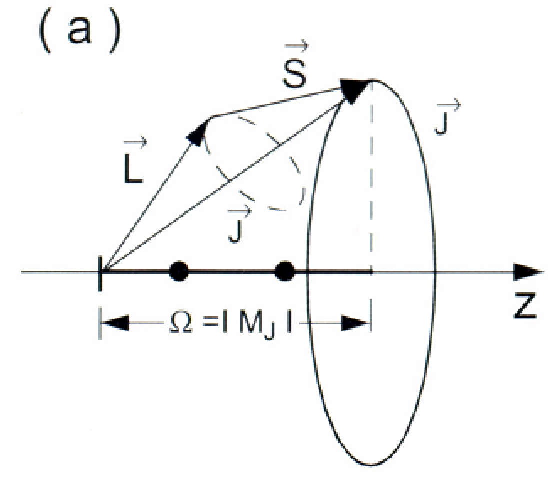
The electrons experiences this magnetic fiel and and aligns its spin magnetic moment either // or ant// to it

For nuclei with small nuclear charges the coulping **l,s** is usually weaker than the coupling of l with internuclear axis (molecular axis), in this case **l** & **s** precess independently around the internuclear axis and their projections are ħλ or ħσ

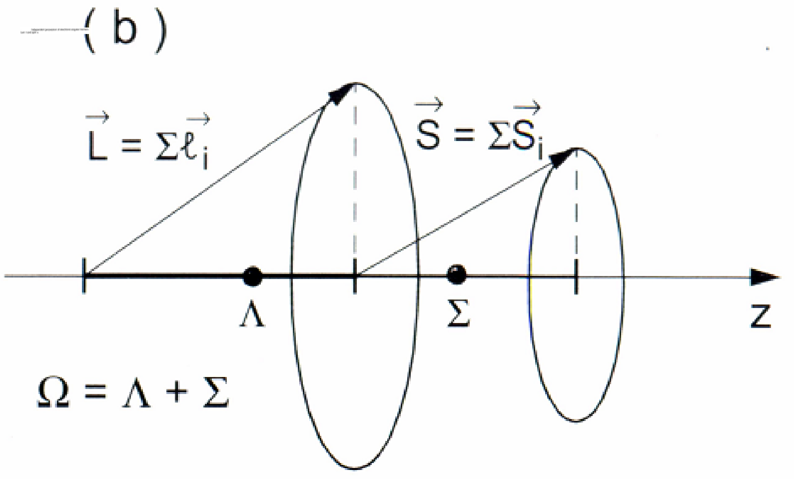
Independant precession of electronic angular momentum **l** and spin **s**



Angular momentum coupling



L-**S** coupling



Independant coupling of **L** and **S** to the molecular axis **z**

As the magnetic field **B** is propotionnel to **l**, than to λ And the expectation magnetic spin momentum $\boldsymbol{\mu}_s$ is proportionnel to the electron spin projection **σ** → the interaction energy between **l** & **s** is

$$W = A \lambda \sigma$$

A fine molecular structure depends on the molecular state This interaction energy depending on the angular momentum projections create a fine structure splitting of molecular terms:

-For molecule with single electron, $\sigma = \pm \frac{1}{2} \rightarrow$ each energy level in electronic state with $\lambda = A\, \lambda$

-For molecule with more than one electron,, angular momentum are added depending on the relative Coupling strenght

Ex:

Consider molecule AB (Z_A electrons, Z_B electrons)

a) A-B as one nucleus ($Z_A + Z_B$)electrons, → the electrons move in a spherical symetric potential of this nucleus and their total angular momentum **J** must be constant- For light atoms we may assume **L-S** coupling($L=\Sigma l_i$; $S= \Sigma s_i$); the total angular momentum is **J**= **L**+ **S** and its absolute value is:

$J = [J(J+1)]^{1/2}$

B) we increase the internuclear distance A-B until it reaches the equilibrium distance Re→ the electrons move in a cylindrically symetricfield of the 2 nucleus A & B

The total angular momentum **J** of the electrons is no more constant because the field creates a torque **D**= d**J**/dt which leads to a precession of **J** around the internuclear axis, We can therefore observe only the time average of **J,** i.e. the projection of $M_j\hbar$

On the internuclear axis, that means J is not a good quantum number

The quantum number of this projection Ω ;

$$\Omega = |Mj| ; Mj= J, J-1, J-2, \ldots 1/2 \text{ or } 0$$

If the spin-orbit coupling energy ALS in the united atom is smaller than the couling of L to the internuclear axis (which is true for light atms) then L & S will be decoupled by the axial electric field and precess independently around the internuclear axithe projection of L and S on the internuclear axis are well defined andthey are on s , in this case their projection are expressed in terms of the quantum numbers Λ & Σ

$$\Lambda = |M_L| ; \Lambda = 0,1,2,\ldots,L$$

$$\Sigma = M_s = s, \ldots,-s$$

And the projection of the total angular momentum is :

$$\Omega = |\Lambda + \Sigma|$$

Names: for Λ = 0 , 1,2,3, States are called Σ , Π, Δ, Φ

Note:

Each state Λ is twofold degenerate in nonrotating molecules the two projections $\pm M_l\hbar$ the nergy lead to the same energy in the axial electric field of the nuclei. In other words for non rotating molecules the energy does not depend on the sense of rotation of electrons

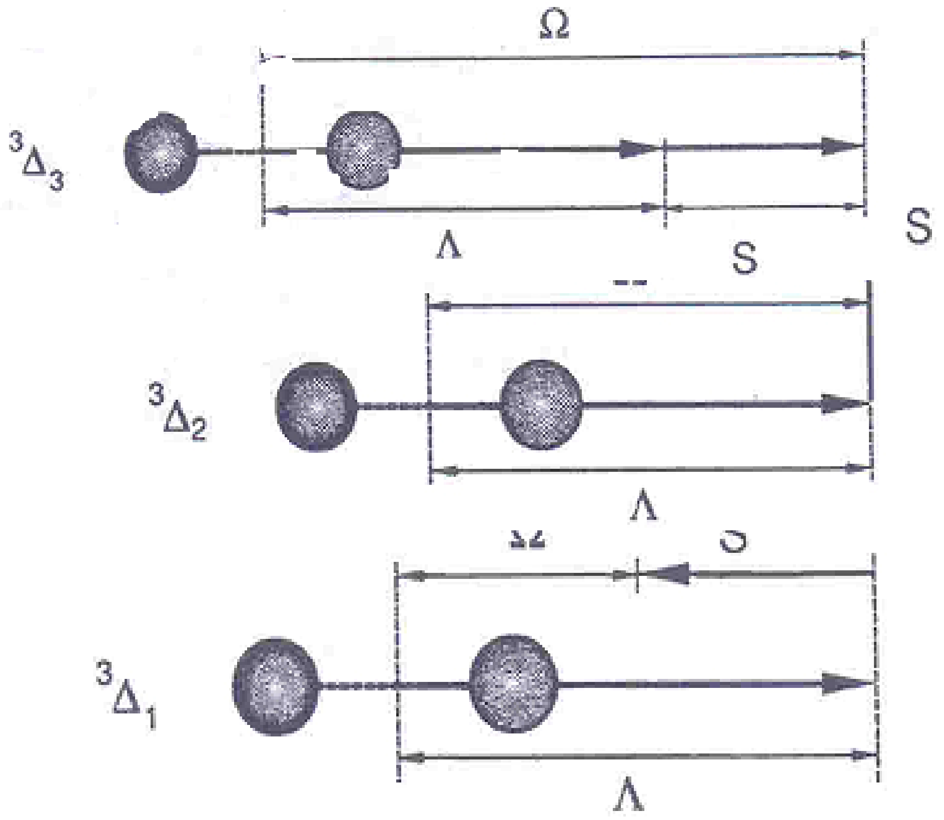
The energy of a molecular state depends on the

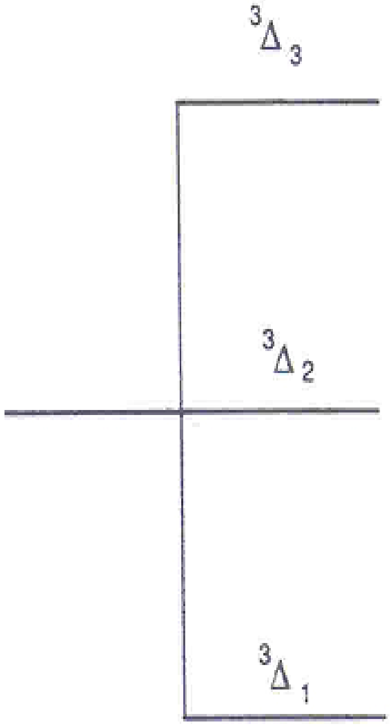
- principal quantum number n
- the quantum number Λ and the spin Σ and on
- the quantum number $\Omega = | \Lambda + \Sigma |$

As Σ can assume 2S+ 1 values from Σ = -S to +S, an electron configuration with givenvalues of S and Λ results in 2S+1 different molecular states which are called fine structure terms,

Diatomic molecular state ${}^{2S+1}\Lambda_{\Omega}$ with appropriate letter X,A,B, C,…

An electronic state energy will be : $T_e^{\Lambda,\Sigma} = T_0 + A\,\Lambda\Sigma$


Ω
$^3\Delta_3$
Λ
S
S
$^3\Delta_2$
Λ
$^3\Delta_1$
Λ


$^3\Delta_3$
$^3\Delta_2$
$^3\Delta_1$

Example of diatomic interaction potentiel - spectroscopy and analysis

Alkaline earth oxides are known as thermal conductors and electrical insulators. The beryllium particularly and its derivatives present important interest for in medical , plasma physics and in nuclear physics, where they are used as protection layers (coating material for Tokamak)

The nature of the bonding in these compounds was subject to several controversies. A pronounced ionic character was established for most of them, such as in BeO. Many spectroscopic (caracteristiques) features of the gas phase neutral isolated molecules have been deduced (exp.analysing the chemiluminescence Fourier Transform spectra [2–6] and theor.from *ab initio theoretical studies.)*

while Very few are known on the ionized species-

To understant the structure of the system , it is necessary to study the spectroscopy and the metastability of beryllium oxide cation, BeO+.

Investigations have been done theoretically:

-Highly correlated wavefunctions are used to deduce the transition moments and the spin–orbit coupling matrix elements between these electronic states.

-A set of accurate spectroscopic data is then deduced for the bound electronic states of BeO+.

-For the upper electronic states, rapid spin–orbit-induced predissociation processes are identified.

-the BeO^+ potential curves together with those of BeO ($X\,^1\Sigma^+$) *are used to predict the* single ionization spectrum of beryllium monoxide

Example of diatomic interaction potentiel - spectroscopy and analysis

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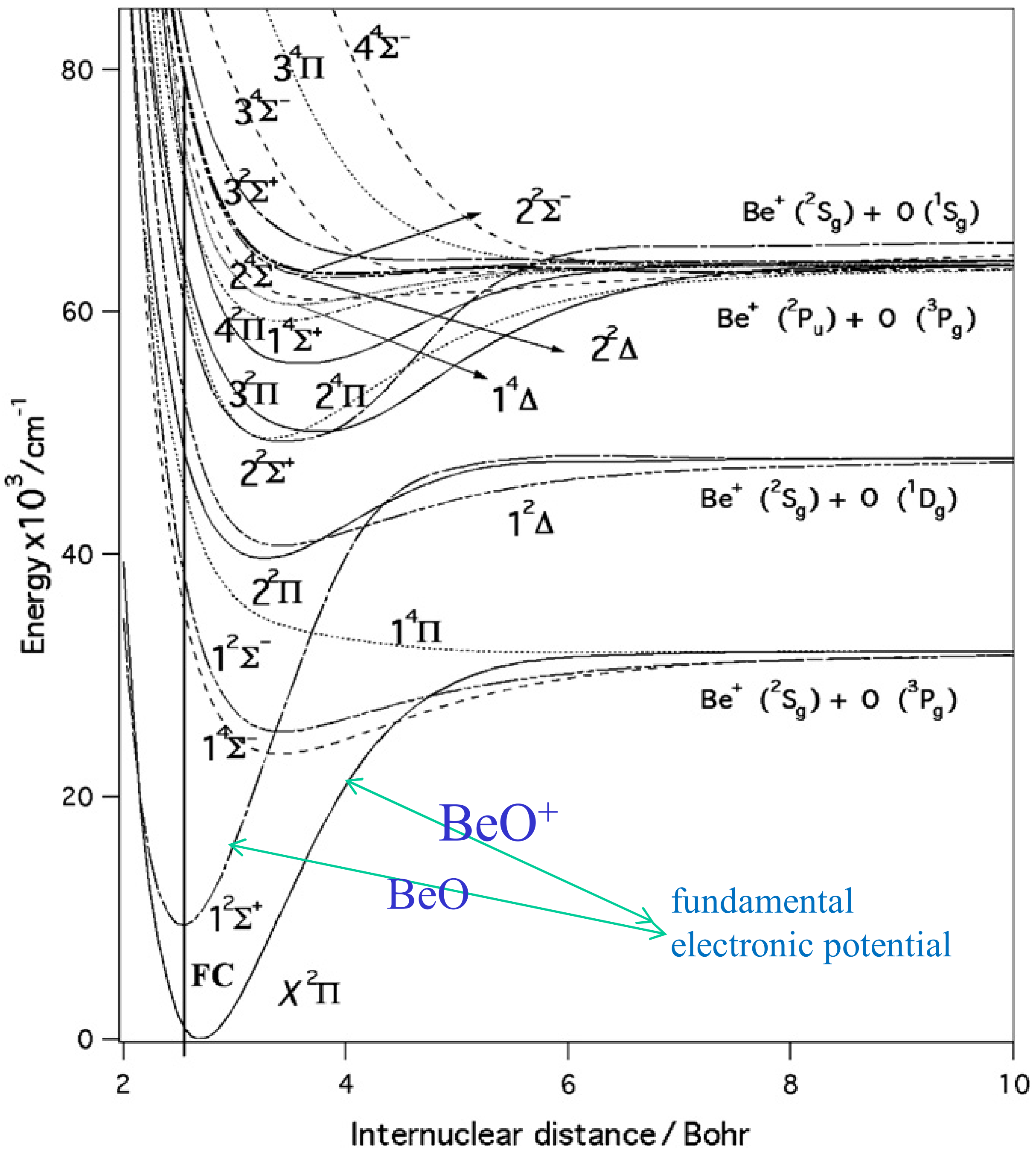
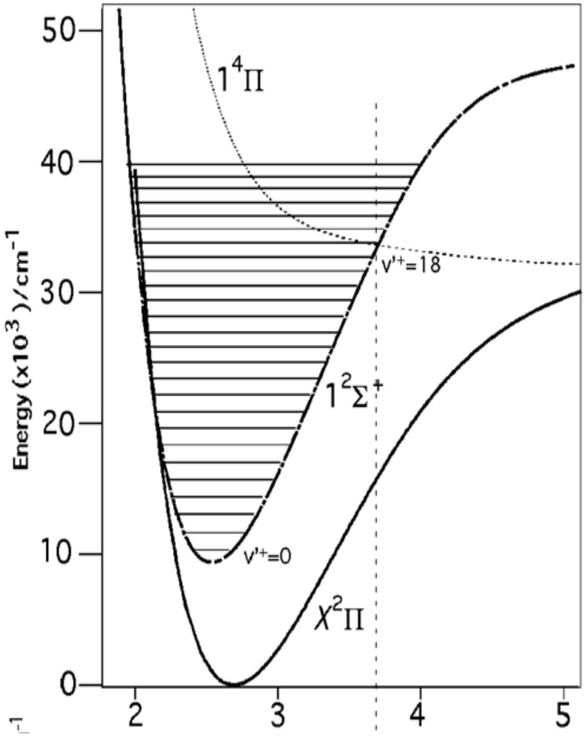
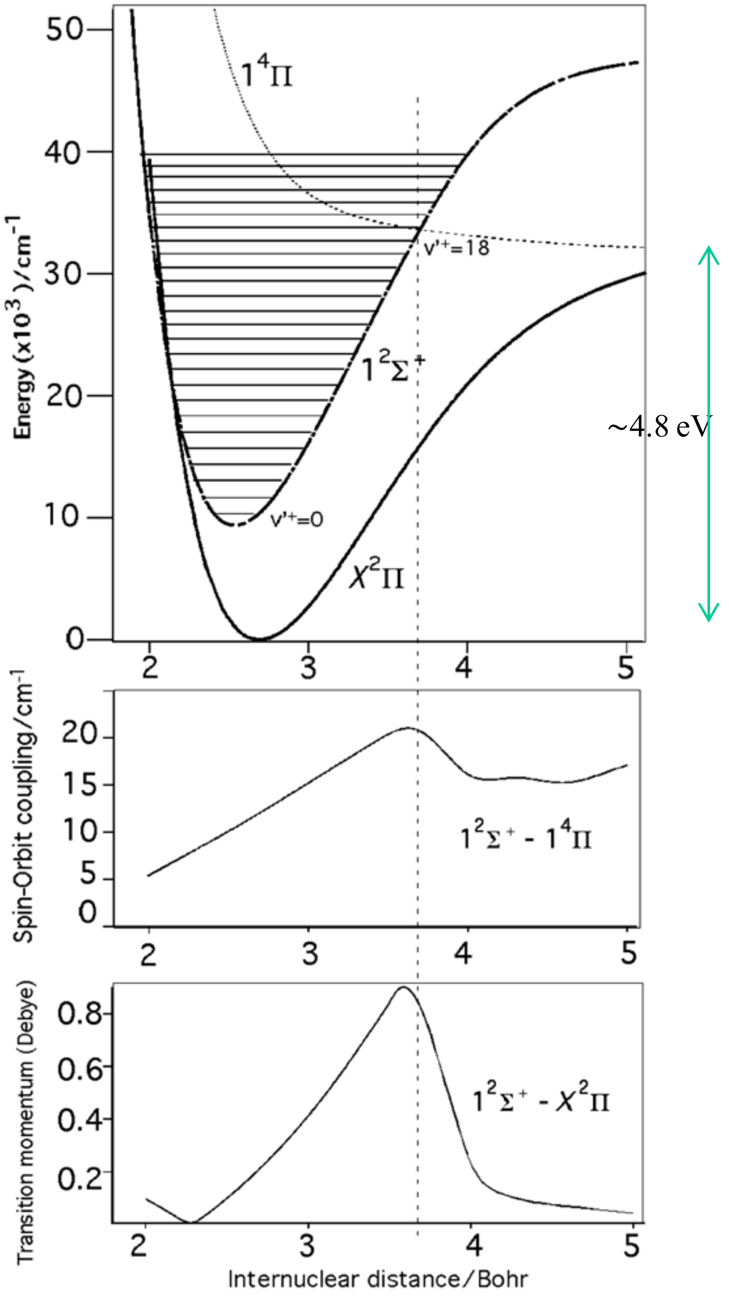
while Very few are known on the ionized species-

Interaction potential [f(R)] & Electronic states of BeO$^+$ correlating to the four lowest dissociation limits





Predissociation of BeO^+

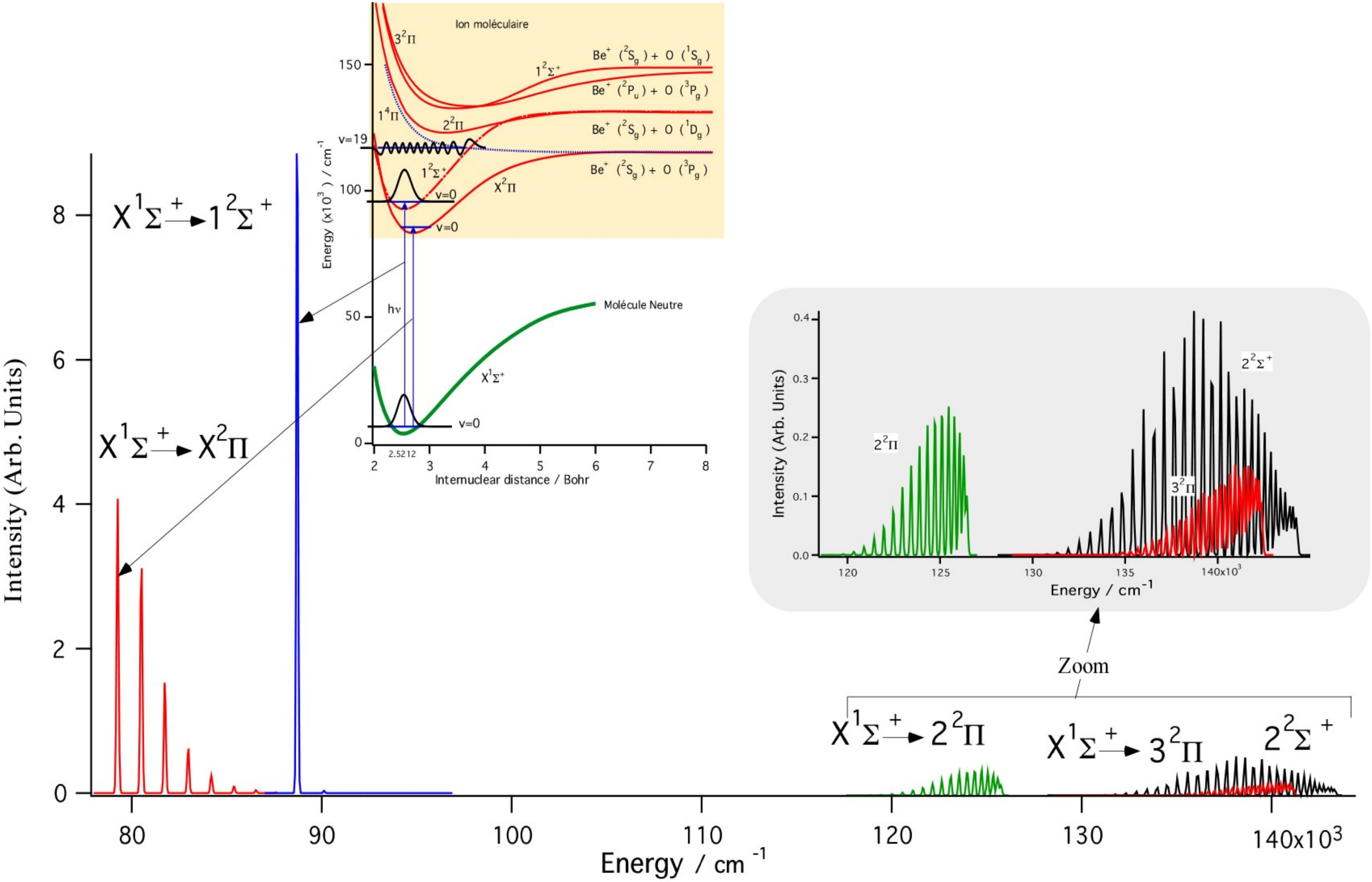


(a) Interaction Potentials of the $X^2\Pi$, $1^2\Sigma^+$ *and* $1^4\Pi$ *states*

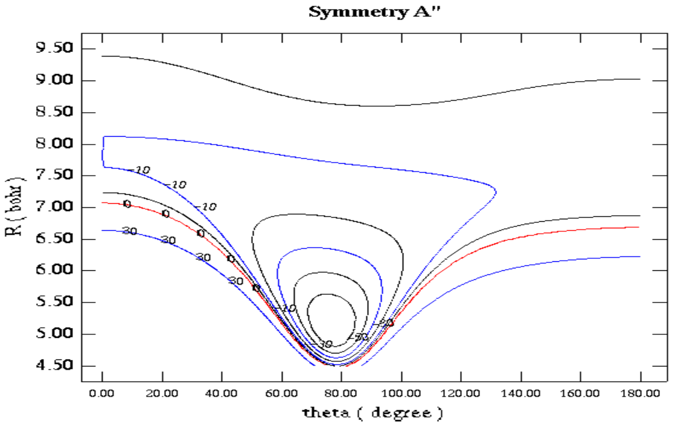
(b) the spin–orbit coupling between the $1^2\Sigma^+$ and $1^4\Pi$

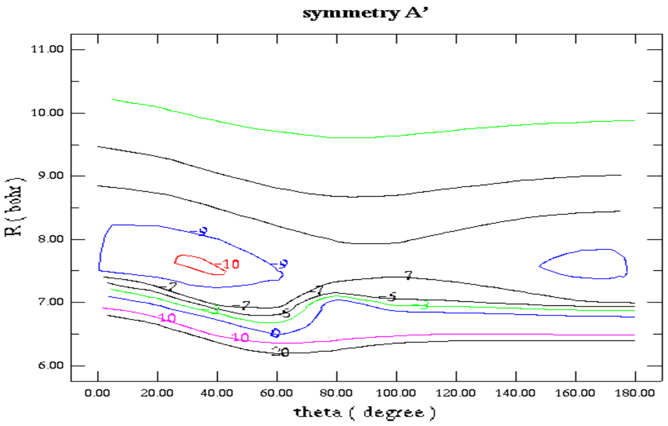
(c) the transition moment between the $1^2\Sigma^+$ *and* the $X^2\Pi$ *states versus the internuclear distance.*

In (a), the horizontal lines correspond to the vibrational levels of the $1^2\Sigma^+$ as deduced variationally.



Ref/ H.Ghalila et al J. Phys. B: At. Mol. Opt. Phys. **41 (2008) 205101**

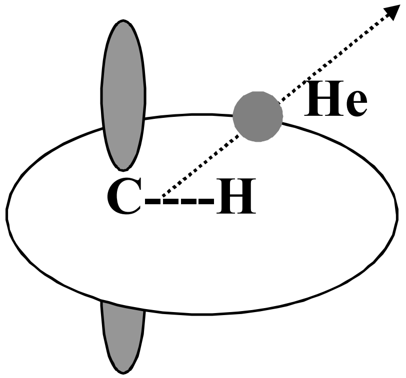




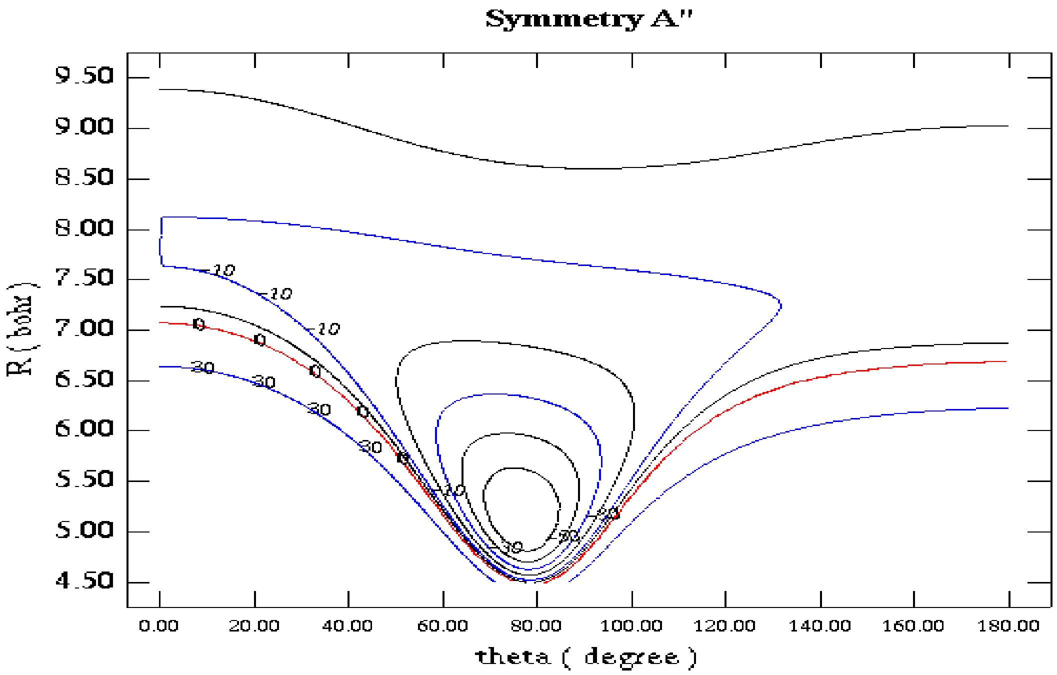
Les courbes des niveaux (CEPA/AVQZ) de CH-He dans l’état électronique de symétrie A”

Les courbes des niveaux (CEPA/AVQZ) de CH-He dans l’état électronique de symétrie A’, ..

Résultats de Calcul des surfaces de potentiel d’interaction de CH-He

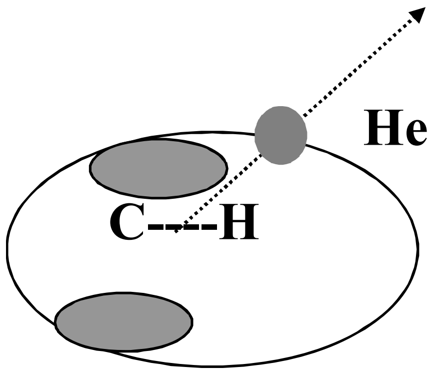


$^2A''$

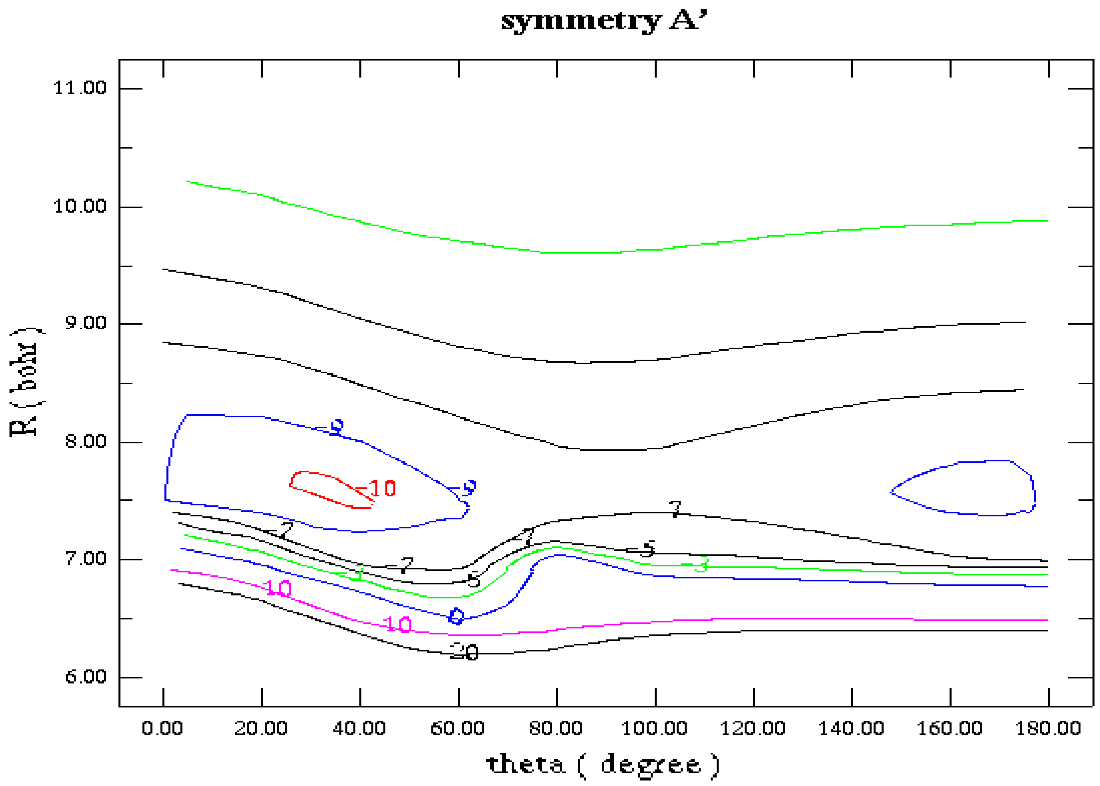


Un seul minimum: $D_e = 60\ cm^{-1}$ ($\theta = 80°$, $R = 5.2$ u.a)

Au voisinage du minimum: $\Delta\theta = \pm 10° \longrightarrow \Delta V = 30\ cm^{-1}$



$^2A'$

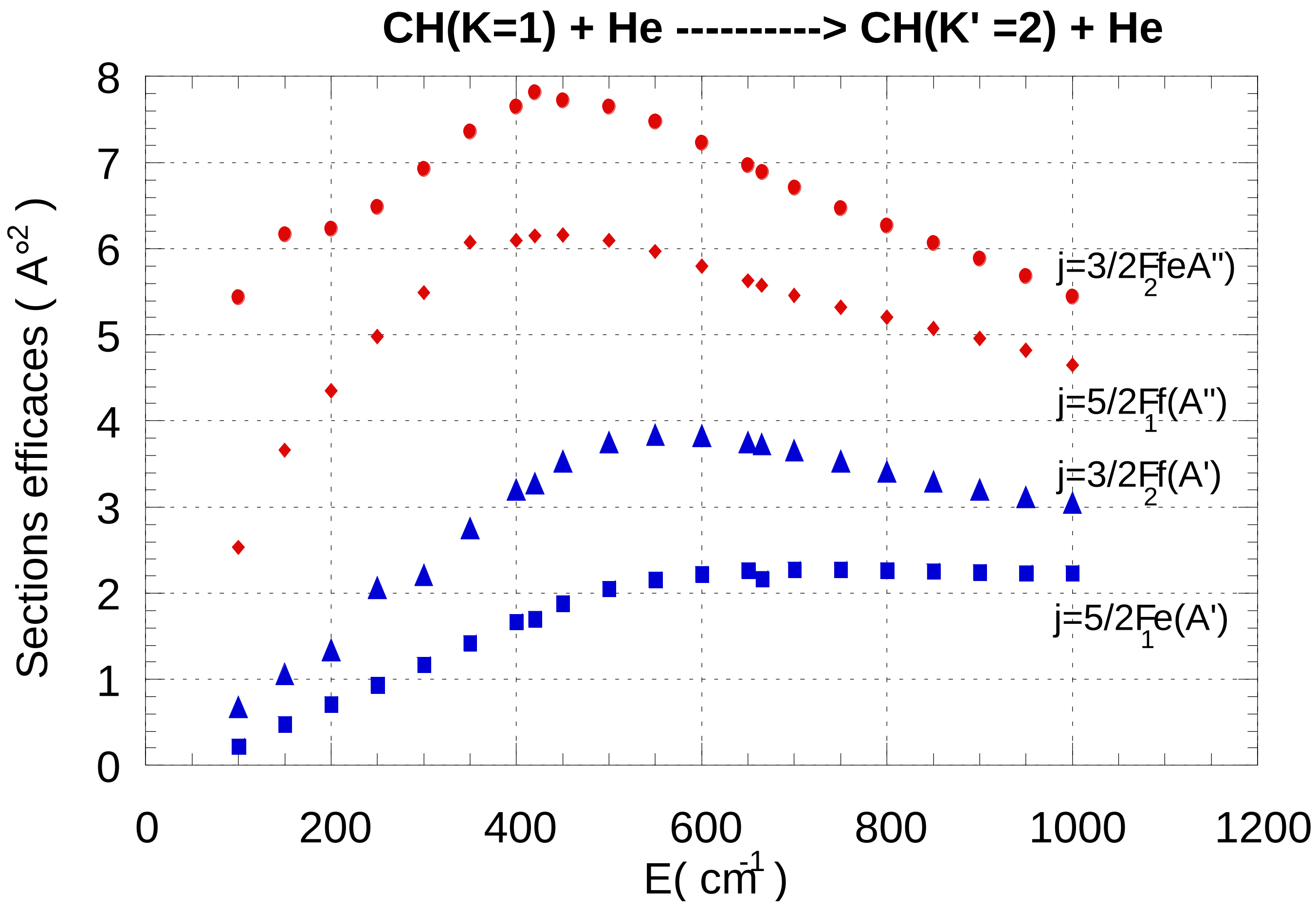


Deux minimums: $D_e = 10$ cm^{-1}

$$\begin{cases} \theta = 180°\ ,\ R = 7.5 \text{ u.a} \\ \theta = 0 - 40°\ ,\ R = 7.5\text{-}8.0 \text{ u.a} \end{cases}$$

Au voisinage du minimum: $\Delta\theta = \pm 10°$ → $\Delta V = 1$ cm^{-1}

2. Résultats du calcul des sections efficaces effectives d’excitation rotationnelle



Thank you