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WINTER COLLEGE ON HIGH RESOLUTION SPECTROSCOPY

(8 January - 2 February 1990)

MULTIPHOTON DETACHMENT FROM NEGATIVE ATOMIC IONS

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Multiphoton detachment
from negative atomic ions.

motivation
Measurements
set ups
results.
Calculations
problems
the plane wave approximation
perspectives.

Multiphoton detachment from negative ions

Why negative ions?
- simpler than atoms (no low lying resonances)
- many electrons.

Why multiphoton?
- high l study
- more selective than collision studies

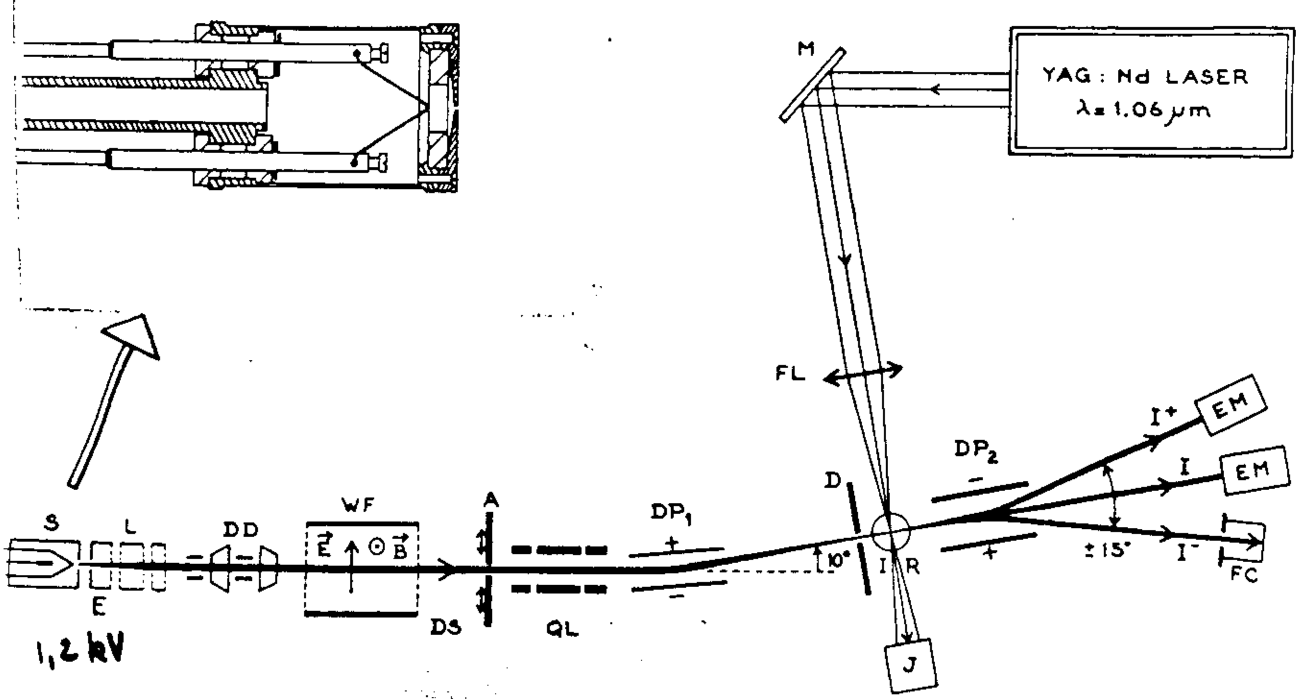
Hall - Robinson I^- ruby laser 1965
Geltman - Robinson 2-photon model potential 1967
Larson group Cl^- (87) F^- (88)
Aimé-Cotton I^- Br^- F^- Cl^- (87.88)

Calculation of cross sections
Excess photon absorption angular distribution
in negative halogen ions

NaI
NaBr
CF_4 + Ar.

Blondel, Champeau, Crubellier, Delsart
Marinescu.

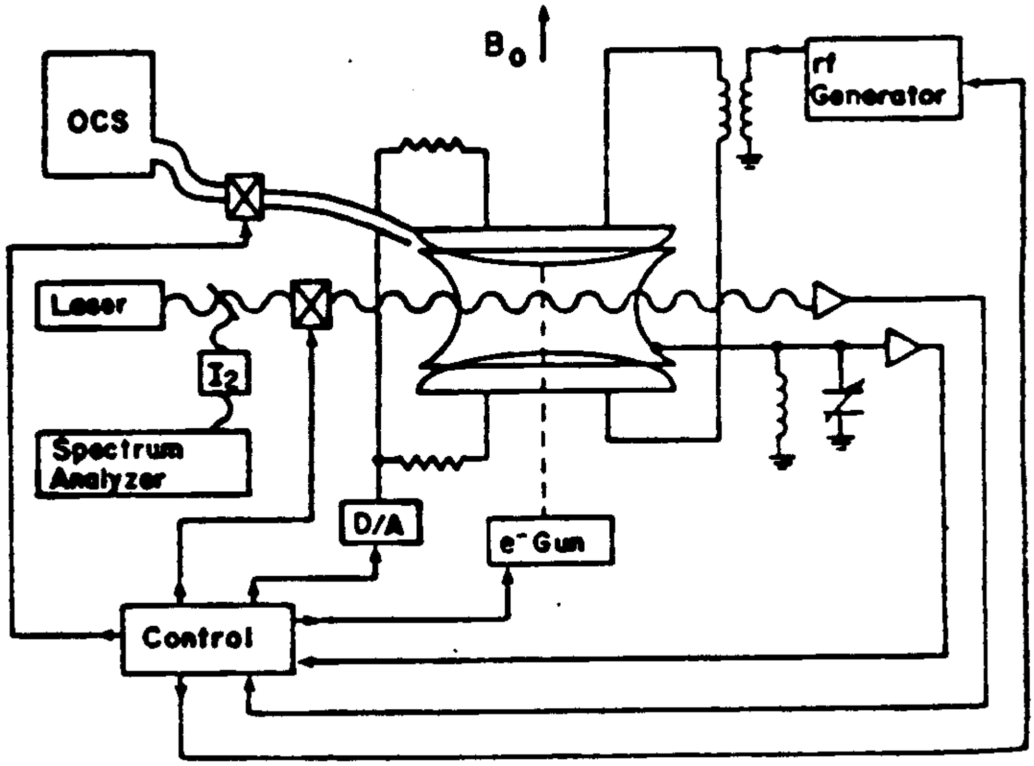
1 J 10 Hz
12 ns



1,2 kV

110 km/s → 54 km/s   21 .. 51 nm

Kwon et al Phys Rev. A 40 676 (89)



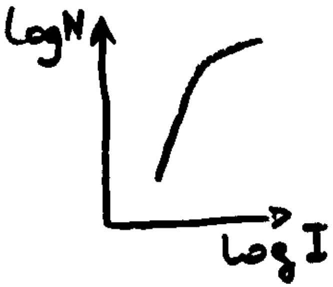
Measurement of cross section

$$N = n\int_V 1 - \exp\left[-\int dt \cdot \sigma\left(I_M f(t) g(r)\right)^3\right]$$

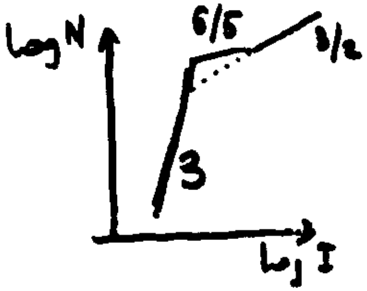
$$I(\vec{r}, t) = I_M\, g(\vec{r})\, f(t).$$

Define I_s $\quad \sigma I_s^3 \tau = 1$

$$N = n\int_V 1 - \exp - \int \frac{dt}{\tau}\left(\frac{I_M}{I_s}\right)^3 \left(f(t) g(r)\right)^3$$



for atoms moving at thermal velocity



for fast ions

$$(\tau > \frac{R}{v})$$

$f(t)$, $g(r)$ measured

N-shape is calculated

and fitted with experimental points

$\longrightarrow I_s \longrightarrow \sigma$

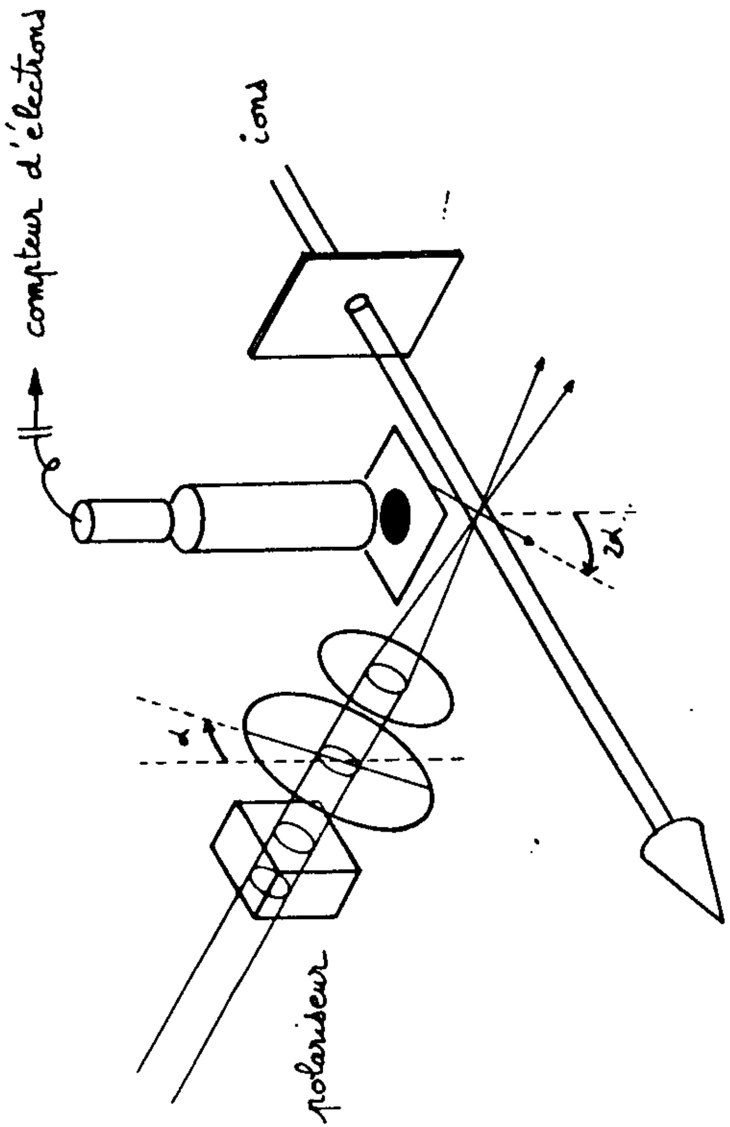
Experimental data

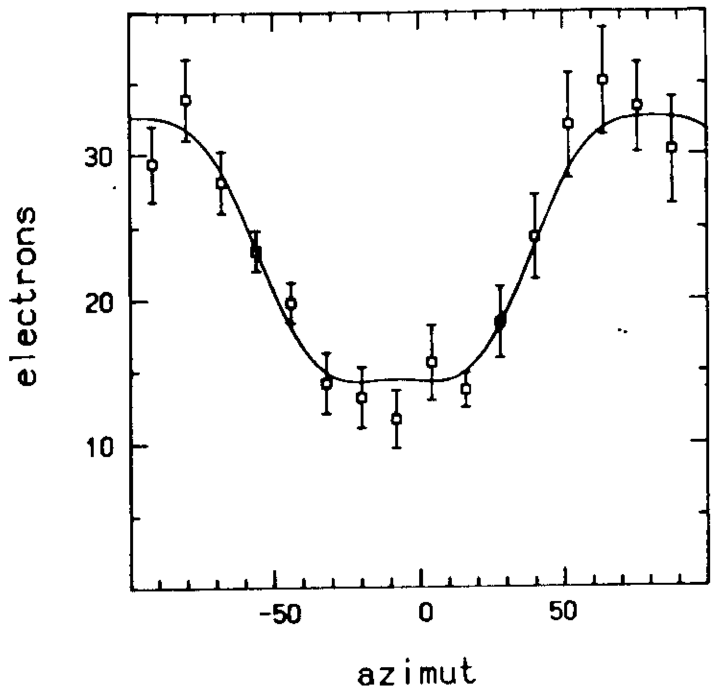
Summary of experimental data. The wavelength is in micron, n is the number of absorbed photons, the detachment cross section is in unit of $cm^{2n}s^{n-1}$.

species	wavelength	n	cross section	reference
I^-	0.69	2	$2.0 \pm 1.2 \quad 10^{-49}$	1
I^-	1.06	3	$3.5 \pm 1.4 \quad 10^{-82}$	2
Br^-	1.06	3	$1.7 \pm 0.7 \quad 10^{-82}$	2
F^-	1.06	3	$6.5 \pm 2.2 \quad 10^{-83}$	2
Cl^-	1.06	4	$9.2 \pm 4.6 \quad 10^{-114}$	3
F^-	1.06	3	$9.4 \pm 5.1 \quad 10^{-83}$	4
F^-	0.53	2	$2.0 \pm 0.7 \quad 10^{-50}$	4
Cl^-	0.66	2	$1.3 \pm 0.9 \quad 10^{-50}$	5

(1) Hall et al 1965
(2) Blondel et al 1989
(3) Blondel – 1990.
(4) Kwon et al 1989
(5) Trainham et al 1987

Br^- à trois photons $\lambda = 1064$ nm

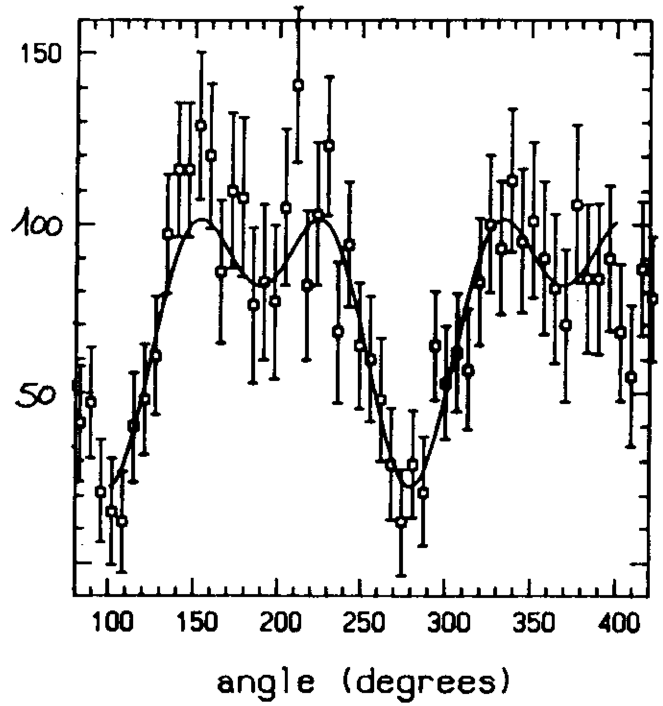




D : da025.dat
T : da025.plt

Br^- à deux photons

$\lambda = 532$ nm



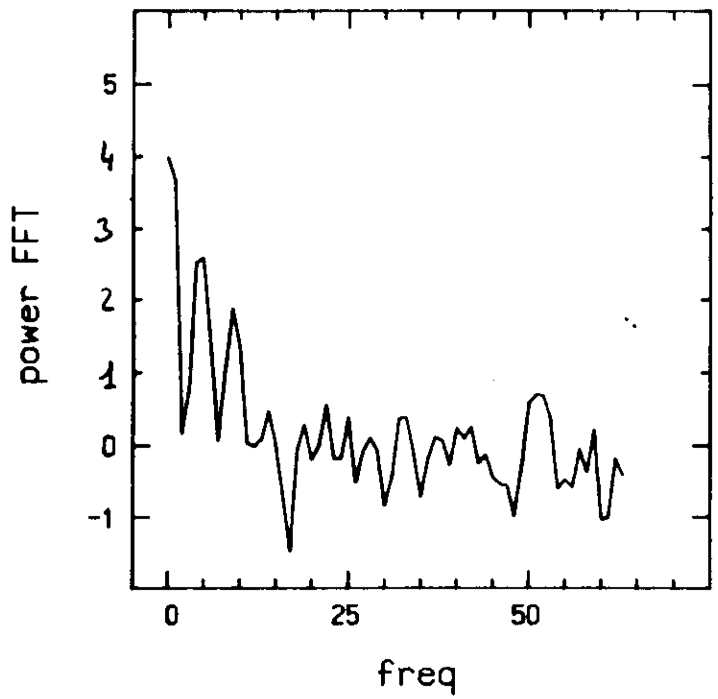
$$\frac{d\sigma}{d\Omega}(\theta) = A\left(1 + \beta_1 P_2(\cos\theta) + \beta_2 P_4(\cos\theta)\right)$$

D : gbr11.dat

T : gbr11a.plt

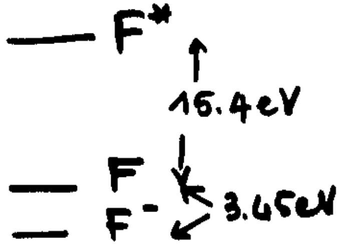
Br^- à deux photons

$\lambda = 532$ nm



T : gbri10.mcs

Calculation of cross sections



Hartree Fock $2p^6$

MCHF $2p^6 + 2p^4 p'^2 + \ldots\ldots$

$2p^4 p'^2 \xrightarrow{\hbar\omega} 2p^4 p' \varepsilon l' \xrightarrow{\hbar\omega} 2p^5 \varepsilon l$

→ high lying intermediate states neglected.

Frozen Core

overlap $\left[\langle \ldots 2p^5 | \ldots 2p^5 \rangle\right]^2 = 0.916$
(in F^* … in F)

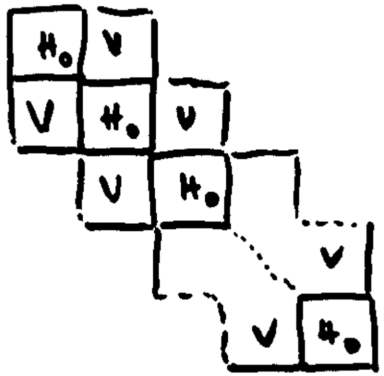
Analytic representation (Clementi)

Complex dilatation method with finite basis of Slater type functions

F.C. H.F. vs F.C. plane wave

Calculation of cross sections

$H = H_0 + V$



dressed ion $|i\rangle|N\rangle$

$|i\rangle = |p^5 n l\, SLJ\rangle$

$|nl\rangle = \psi(r)\, Y_{lm}(\theta,\varphi)$

$\psi(r)$ developped on Slater type functions

For excited states, the outer electron evolves in the field created by the neutral core.

⇒ asymptotically: plane wave.

→ FC . FE approximation

6558 M Crance

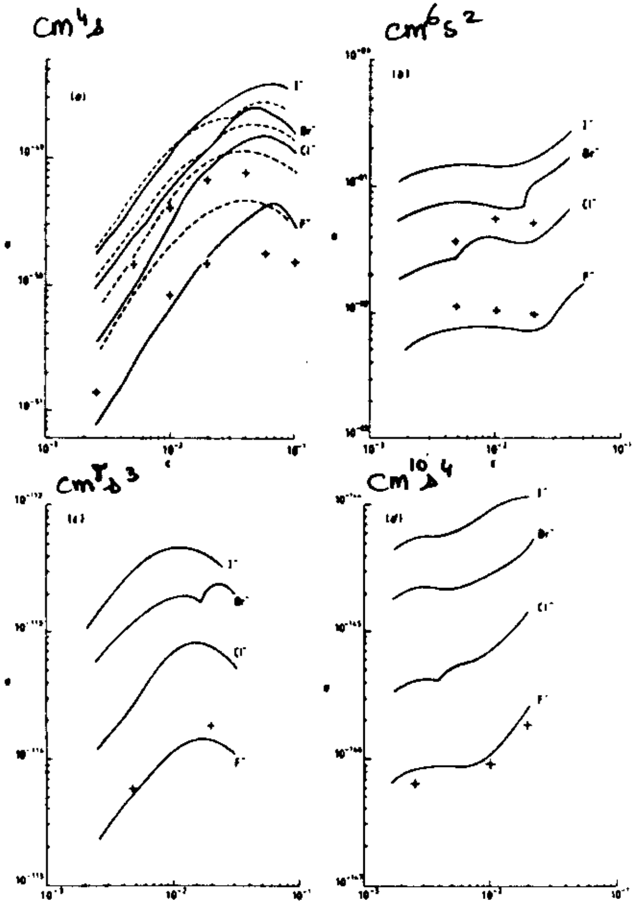


Figure 1. Cross section (in units of $cm^{2q} s^{q-1}$) for q-photon detachment from negative ions of fluorine, chlorine, bromine and iodine (q = 5) as a function of electron energy (in atomic units). (a) q = 2; (b) q = 3; (c) q = 4; (d) q = 5. Full curves: frozen-core free-electron approximation, crosses: frozen-core Hartree-Fock approximation, broken curves: calculation of Robinson and Geltman (1967).

The plane wave approximation

$$\sigma = \sum_{\varepsilon} \left\{ \langle g | V G V G \cdots V | \varepsilon \rangle \right\}^2$$

(G: green functions; V: dipole interaction)

$G V G \cdots V | \varepsilon \rangle$

- independent of element
- calculated analytically.

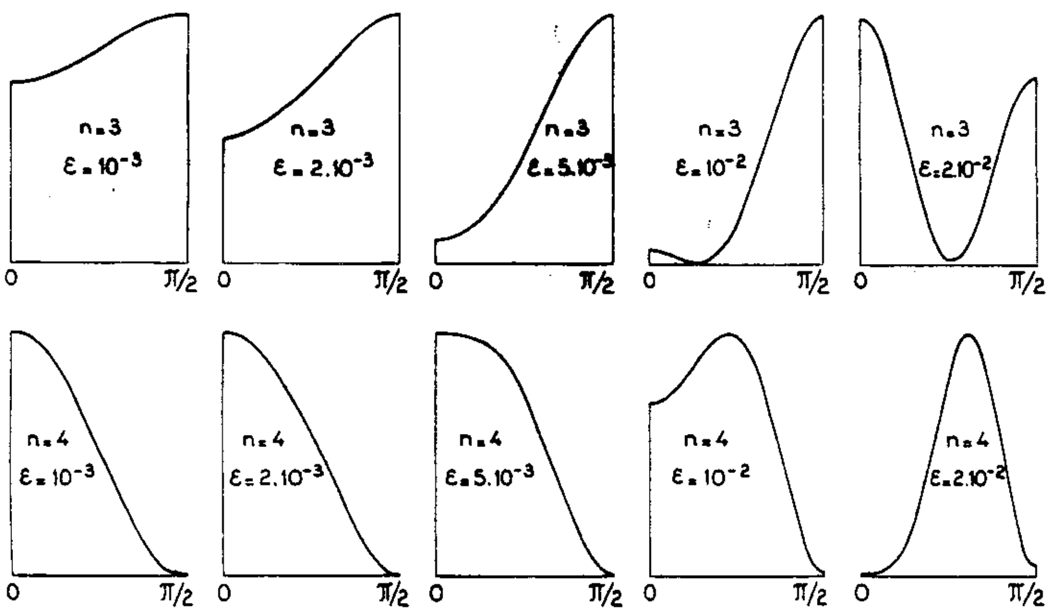
→ angular distributions

→ excess photon absorption

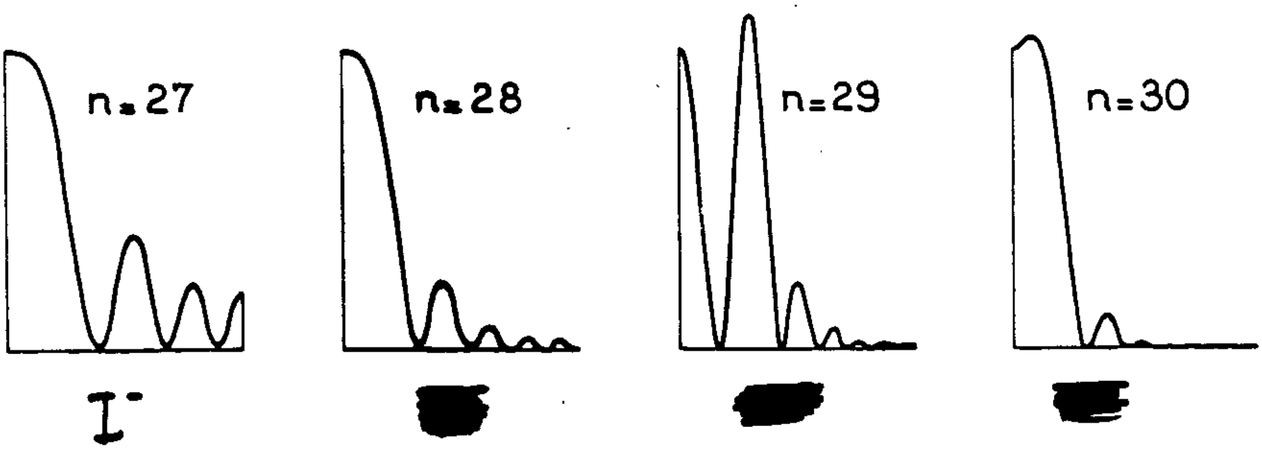
- Results
- length vs velocity form.

n. photon detachment → electron energy ε (a.u.)

Fig 1



Excess photon absorption



CO_2 laser

Fig. 3

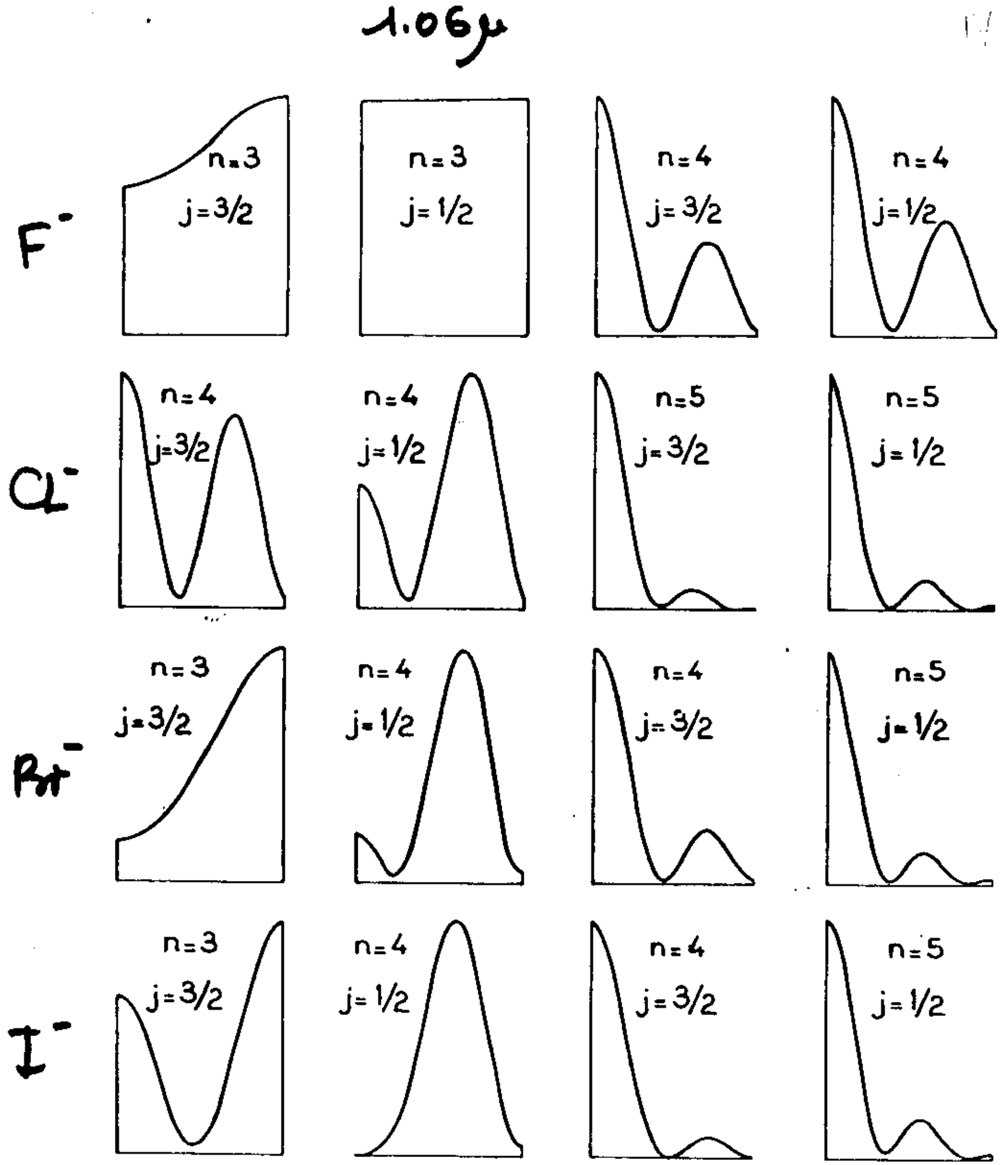
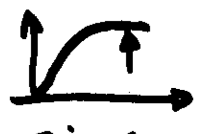


fig 2

Multiphoton detachment general trends.

Comparison with multiphoton ionisation.



$\sigma^{(n)}$ versus n

Define saturation intensity $\sigma^{(n)} I_s^n T =$ $\quad T = \frac{\hbar}{E.A.}$

Example F^-, $\mathcal{E} = .04$ a.u.

$n = 4 - 30$

$I_s = 10^{14.72} / n^{2.19}\ \mathrm{W cm^{-2}}$

$E_s = 10^{10.8} / n^{1.095}\ \mathrm{V m^{-1}}$

$\rightarrow$ quiver motion $v_s = \frac{q E_s}{m \omega} = \frac{q E_s}{m} \frac{n}{E.A.}$

Saturation when quiver velocity $\simeq$ mean orbital velocity.

For atoms: Saturation when

Intensity x geometrical section x T = ionisation potential.

Dipole approximation
length vs velocity

$$H^v = H_P^v + H_F - \frac{q_\alpha}{m_\alpha} \vec{p}_\alpha \vec{A}_\perp(0) + \frac{q_\alpha^2}{2m_\alpha} \vec{A}_\perp^2(0)$$

Göppert-Mayer transformation:

$$T = \exp\left[-\frac{i}{\hbar} q_\alpha \vec{r}_\alpha \vec{A}_\perp(0)\right]$$

$$H^L = T H^v T^+ = H_P^v + H_F - q_\alpha \vec{r}_\alpha \vec{E}_\perp(0)$$

H^v and H^L correspond to different gauge
→ different Lagrangian.

H_P^v and H_P^L: same expression but different physical meaning:
the eigenstates of H_P^L have a definite energy
— H_P^v don't.

Choice large r.....

Dipole approximation
length vs velocity.

$$\langle \varphi_a | V | \varphi_b \rangle$$

$$\langle \varphi_a | V G V \dots | \varphi_e \rangle$$

Equivalent when the wave functions for initial and final state are eigenfunctions of a same Hamiltonian.

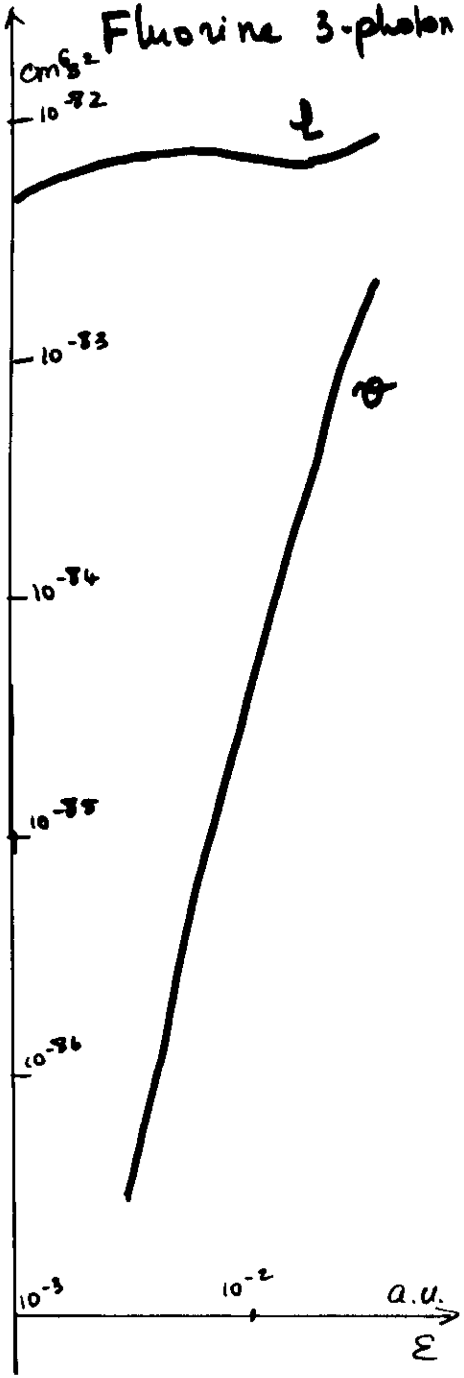
In the plane wave approximation.

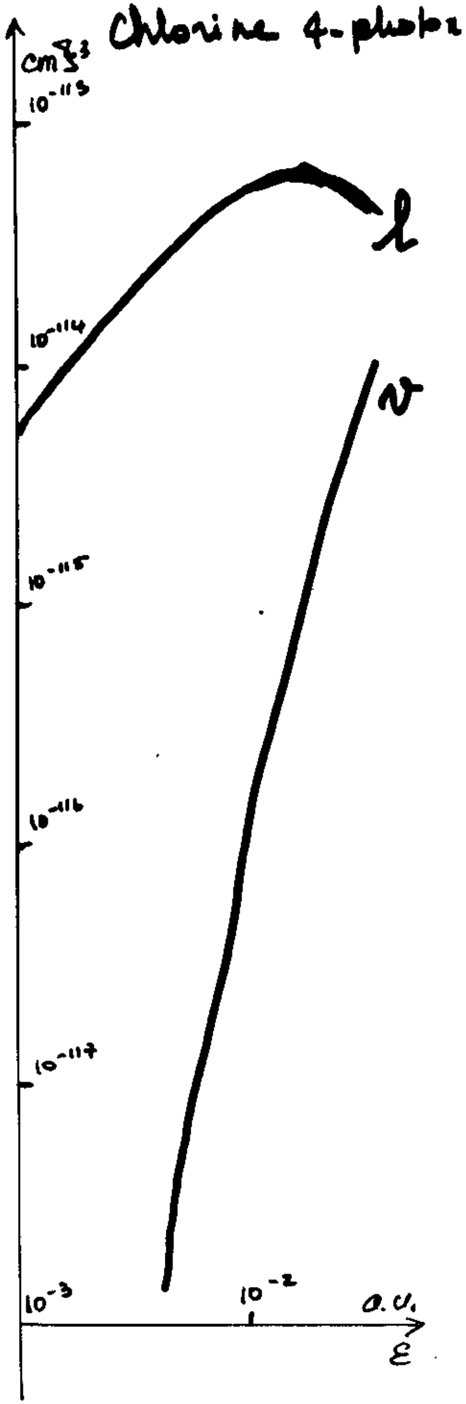
$$H_0 = K + W \qquad H_0 \varphi_g = E_g \varphi_g$$

final and intermediate states.

$$\begin{cases} K\varphi_i = E_i \varphi_i \\ K\varphi_f = E_f \varphi_f \end{cases}$$

NO EQUIVALENCE





Plane wave approximation for <oions

$$\langle g | V G_{PW} V G_{PW} V \ldots\ldots | e_{PW} \rangle .$$

g has a finite size

It is equivalent to consider P.W. in a "box".

Consider $\quad -Z < z < Z$.

Basis: set of orthogonal functions which tends to be complete when $Z \to \infty$

$e^{ik_n z} \qquad k_n Z = n\pi \quad (\mathrm{mod}\,\pi)$

$$\langle k' | \frac{d}{dz} | k \rangle = i k\, \delta(k' - k)$$

$$\begin{cases} \langle k' | z | k \rangle = \dfrac{(-1)^{n-n'}}{i(k-k')} \\ \langle k | z | k \rangle = 0 \end{cases}$$

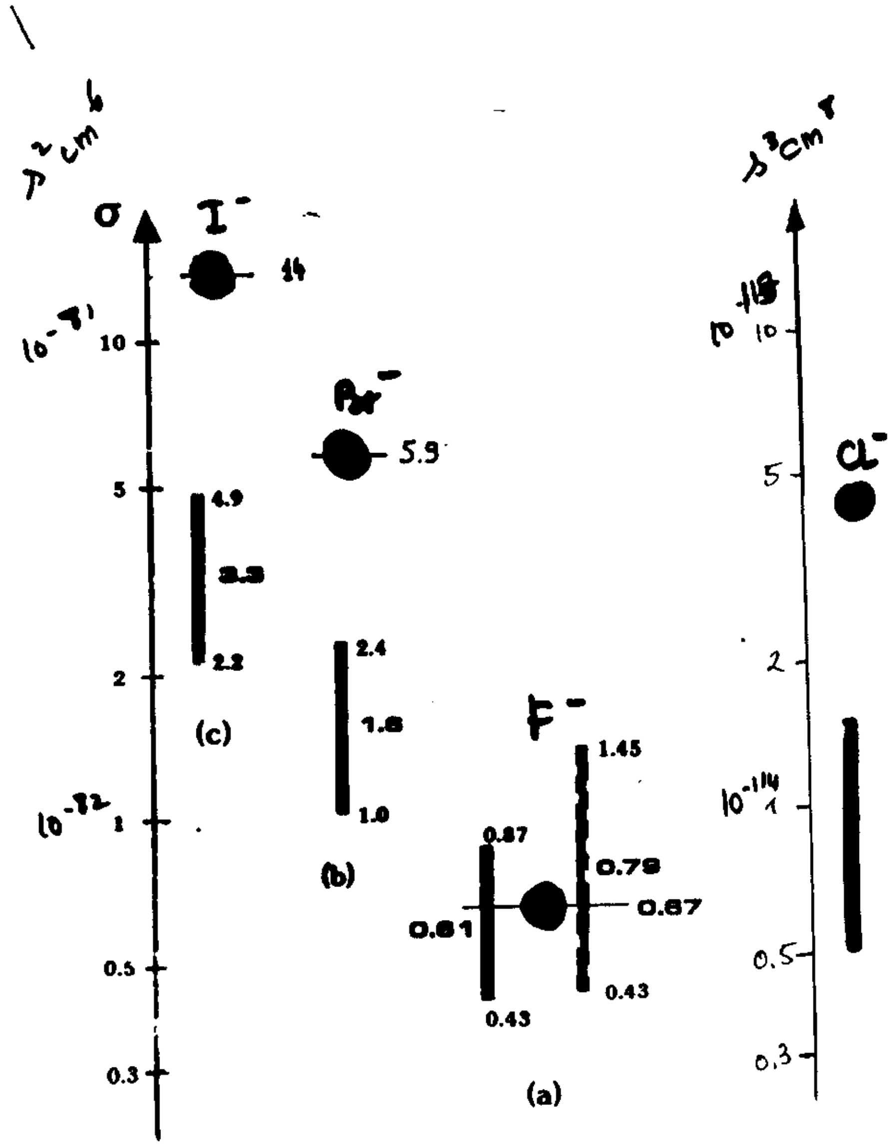
$\frac{d}{dz} \to$ strictly no transition by absorption

z simulates transitions between continuum states.

Plane wave approximation
length vs velocity

Plane waves are meant to simulate continuum states of <o ions.
In this respect
$\langle \varepsilon_{PW} | V_L | \varepsilon'_{PW} \rangle$ reproduces the properties of $\langle \varepsilon_I | V | \varepsilon'_I \rangle$ better than $\langle \varepsilon_{PW} | V_V | \varepsilon'_{PW} \rangle$

Threshold laws
n-photon transition towards $\varepsilon \ell$
length $\to \varepsilon^{\ell+\frac{1}{2}}$ Right
velocity $\to \varepsilon^{n+3/2}$ Wrong
Examples



* Orsay
* Charlottesville

FIGURE 3

46 pour 13.8 à 4.7

Calculation of cross sections.

Improvements needed.
- better initial state (MCHF)
- better continuum states.
- taking into account double excitation

→ realized, up to now, only for 2-photon detachment.