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UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
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SECOND SCHOOL ON THE USE OF SYNCHROTRON RADIATION IN SCIENCE AND TECHNOLOGY: *"JOHN FUGGLE MEMORIAL"*

25 October - 19 November 1993

Miramare - Trieste, Italy

ATOMIC AND MOLECULAR SPECTROSCOPY

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Atomic and Molecular Spectroscopy

2nd School on the use of Synchrotron Radiation in Science and Technology: "John Fuggle Memorial"

Giovanni Stefani, Dipartimento di Fisica, Terza Universita' di Roma

In Atomic and Molecular Physics the relevant potentials are:

Nuclear Potential V_n

electron-electron Potential V_{ee}

Problems will rise in including V_{ee} in the model. Not even the simple 3 charged particle problem is exactely solvable.

Many-body properties of atoms and molecules is one of the main challenges

e-e interactions can be classifed as:

Bound State (short & long range)

Continuous State (short & long range)

Photoionisation is one of the most used tools (single and double)

Near Threshold , Resonant, Direct

In each of these regimes e-e interactions have different relevance

To focalize attention on a specific form of interaction we need to:

- tune continuously the photon energy
- measure small cross sections
- measure angular distributions
- achieve high energy resolution

This implies Tunability, High Flux, Brightness

Will concentrate on :

e-e-interactions

electron spectroscopy

coincidence spectroscopy

Since the pioneering work of Madden and Codling (Phys. Rev.Lett. **10** (1963) 516) on He photoabsorption, e-e interactions have been of prime relevance. Resonances in the continuum in the 200 A region
Recently, with a resolving power of 10000 major advances have been done in the field. Domke et al. (Phys. Rev. Lett. **66** (1991) 1306) have observed more than 50 states 0.1 meV narrow in the same region.

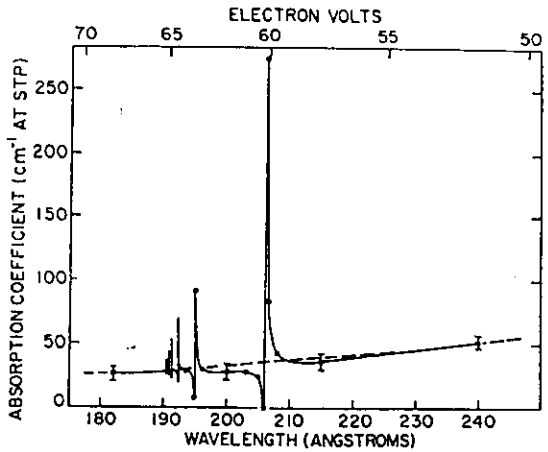


Fig. 1 Autoionization of two-electron excited states in helium converging on the double ionization potential. The data were obtained in an absorption experiment by Madden and Codling.[1]

Photoionization cross-section

$$\hbar\omega + \Psi_{i(N)} \longrightarrow \epsilon + \Psi_{f(N-1)}$$

Energy conservation

$$\hbar\omega + E_{i(N)} = \epsilon + E_{f(N-1)}$$

In single particle scheme

$$\hbar\omega + E_{i(N)} = \epsilon + E_{f(N-1,\bar{\imath})}$$

single photoionization

$$\sigma(\omega) = \frac{4\pi^2 e^2 \omega}{c} \Sigma_f |\langle \Psi_f | \hat{e} \cdot \sum_i^N \underline{r}_i | \Psi_i \rangle|^2 \delta(E_{f(N)} - E_{i(N)} - \hbar\omega)$$

$$T_{if} = \langle \Psi_f | \hat{e} \cdot \sum_i^N \underline{r}_i | \Psi_i \rangle$$

angular distribution

p = polarization

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}\left(1 + \beta\left(1 + 3p\cos 2\theta\right)\right)$$

Hartree-Fock

$$\Psi_{i(N)} = A(N)\left(\Psi_1(\underline{r}) \Psi_2(\underline{r}) \cdots \Psi_N(\underline{r})\right) \quad ; \quad \phi_i(\underline{r}) = R_{ne}(r) Y_{\ell m}(\theta,\varphi)$$

$$T_{if} = \langle \Psi_\epsilon | \hat{e}\cdot\underline{r} | \Psi_i \rangle S^{11} + \sum_{j=2}^{\prime} (-1)^{j+1} \langle \Psi_\epsilon | \hat{e}\cdot\underline{r} | \Psi_i \rangle S^{1j} + \sum_{i,j}^{N} (-1)^{j+1} \langle \Psi_\epsilon | \Psi_j \rangle P^{jl}$$

ignoring relaxation

$$S^{ij} = \delta_{ij} \quad ; \quad P^{ik} = 0 \quad ; \quad T_{if} = \langle \Psi_\epsilon | \hat{e}\cdot\underline{r} | \Psi_i \rangle$$

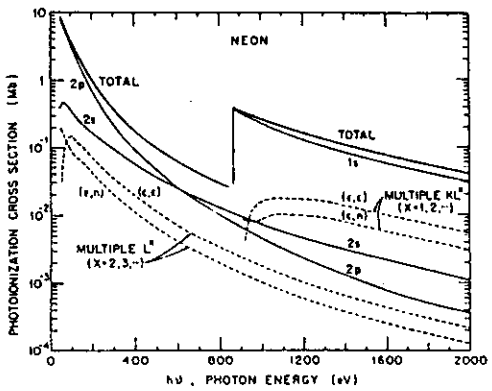
Many-electron Configuration Interaction

$$|\Psi_{i(N)}\rangle = \Sigma_m D_{im} |\Phi_{m(N)}\rangle$$

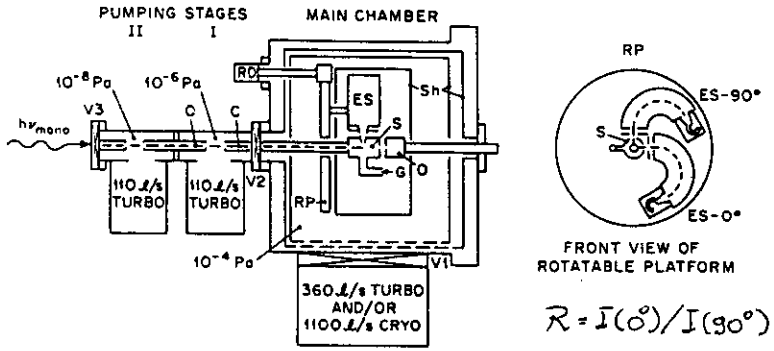
$\Phi_{m(N)}$ = Slater det. of given configuration

$$|\Psi_{f(N)}\rangle = \Sigma_n D'_{fn} |\Phi'_{n(N)}\rangle$$

Total photoabsorption cross-section



Typical experimental set up



$R = I(0°)/I(90°)$

FIG. 1. Sketch of ESSR system, showing two analyzers (ES) mounted on a rotatable platform (RP) with drive (RD) round the electron source (S), which allows the use of a gas (G) or an atomic beam from an oven (O); three magnetic hields (Sh) are used and three valves (*V*1 to *V*3) separate components; typical pressures are indicated at an estimated ressure of 10^{-2} Pa in source (S) and the high impedances provided by the capillaries (C).

$$\beta = \frac{4(R-1)}{3\rho(R+1)-(R-1)}$$

KRAUSE & CARLSON
Phys. Rev. A-24 (1981) 1374

THREE REGIMES

Threshold — Direct — Resonances

ABSORPTION

Main line — Satellites — Continuum

ABSOLUTE VALUES & PARTIAL CHANNELS

On Main line

$(nlj)\,e^-$ ejected $\leftrightarrow$ Independent particle + (correlations)

- Wrong binding energy : strong relaxation and/or polarization
- Wrong intensity : continuous or discrete satellites
- e-e interactions included by 2nd order diagrams and/or relaxed orbitals.

Strong correlation effects in 5s Xe

$- ns^2 -$

Coupling between electrons is evident in the asymmetry parameter β vs. energy

- Within LSJ coupling : $ns \longrightarrow \epsilon p$ partial wave
  hence $\beta = 2$
- Within jjJ coupling : Spin orbit coupling in continuum leads to $\epsilon p_{3/2}$ & $\epsilon p_{1/2}$ part. waves

and

$$\beta = \frac{2R^2_{\epsilon p_{3/2}} + 4R_{\epsilon p_{3/2}} R_{\epsilon p_{1/2}} \cos\Delta}{R^2_{\epsilon p_{1/2}} + 2R^2_{\epsilon p_{3/2}}}$$

R_i = radial dipole integrals Δ = relative phase

at high energy $R_{\epsilon p_{3/2}} \simeq R_{\epsilon p_{1/2}}$ $\Delta \approx 0 \longrightarrow \beta = 2$

near threshold $R_{\epsilon p_{3/2}} \neq R_{\epsilon p_{1/2}}$

Strong correlation effects in 5s Xe

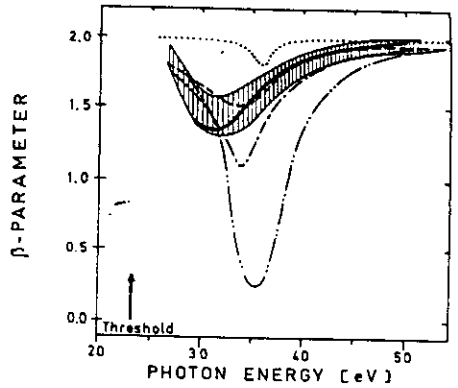


Figure 3.7. Angular distribution parameter β for 5s photoionization in xenon. Hatched region denotes mean experimental data, including error limits (from [WSK79, DSc83, FCK83a, WMS86]). The value at 40.8 eV from the first study of this problem [DDi76] has been omitted because it could not be confirmed by later experiments; for data above 55 eV see [WSK79, FCK83a, SBT83]. Theoretical values: double-dotted chain curve, RRPA (4d+5s+5p) calculation [JCh78, JCh79]; dotted curve, K-matrix (5s+5p) (velocity form results [HSt80]); broken and chain curve, RTDLDA with Gunnarsson-Lundqvist and Perdew-Zunger exchange correlation potentials, respectively [PJR84]; full curve, multi-configurational DF (5s+5p) calculation with full account of relaxation [Tul89].

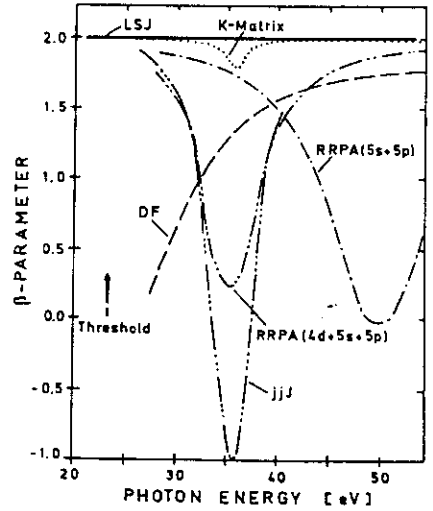
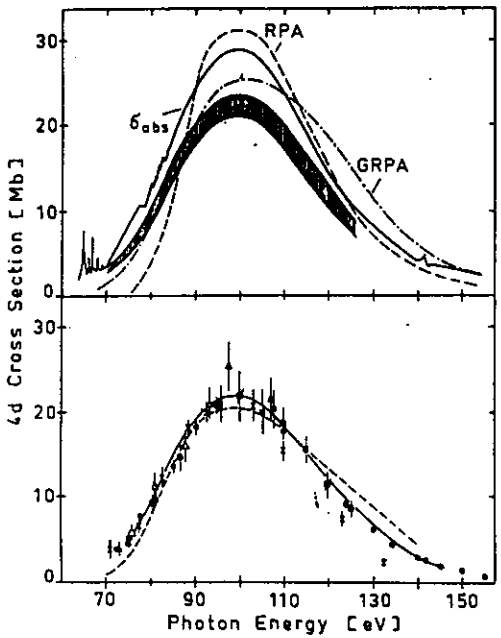


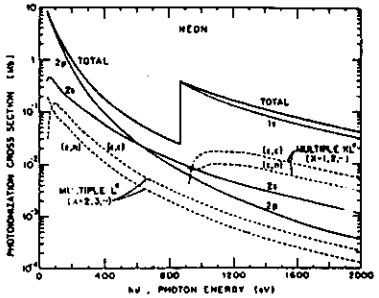
Figure 3.8. Angular distribution parameter β for 5s photoionization in xenon. Compilation of theoretical values: LSJ, Russell-Saunders coupling; *jjJ* coupling [Che78a]; DF calculation ([WWa74, OMa78, OMa79], Coulomb gauge results which correspond in the non-relativistic limit to the velocity form results); K-matrix ([HSt80], velocity form results); RRPA (5s+5p) and RRPA (4d+5s+5p) calculation [JCh78, JCh79].

From V. Schmidt Rep. Prog. Phys. 55 (1992) 1486

Redistribution of 4d strenghth in Xe



delayed "onset"



e-e interactions responsible for O.S. redistribution

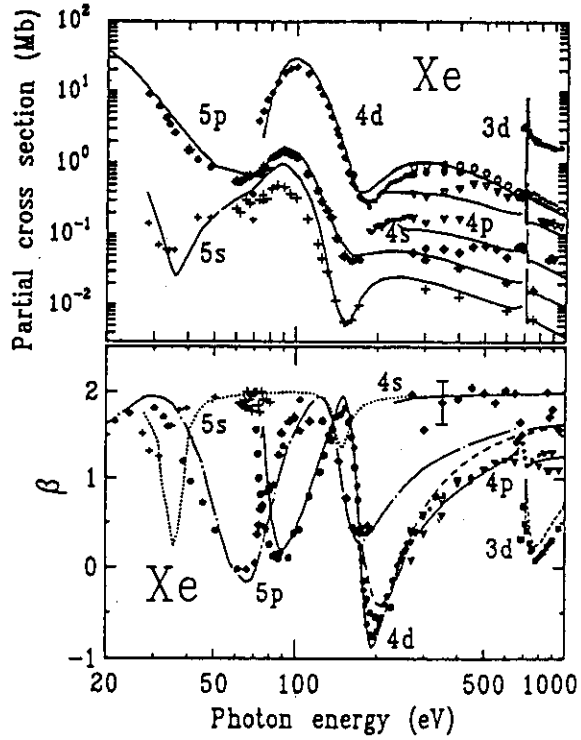
Oscillator Strength → Spectral distribution

f(excitations) & df/dε (ionisation)

* ∈ f − trapping *

- o Interchannel coupling
- o Interchannel coupling
- o Relaxation processes

Redistribution of 4d strenghth in Xe



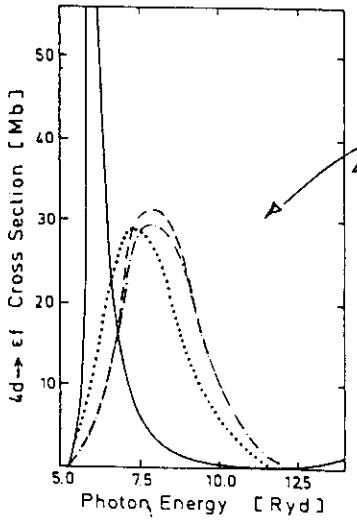
Interchannel coupling
5p-5s

Figure 1: σ and β for the subshell photoionization of Xe up to 1 keV. The different exp. data sets are from:
σ: 5p *[8] , *[9] ; 5s +[8] , +[9] ; 4d ●, o[9] , •[10] ; 4p ▼, ▽[9] , ▾[10] ; 4s ◆[9] ; 3d ■[11] ;
β: 5p *[12] , *[13]; 5s +[14], +[13] ; 4d ●[13], •[10], ...[11] ; 4p ▼, ▽[9] ; 4s ◆[9] ; 3d ■[11].

The different theoretical curves represent extended RRPA calculations

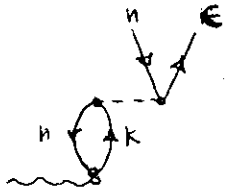
FROM: J. BECKER, AIP Conference Proceedings 205 (90) 16

Shape resonance and wavefunction collapse in 4d Xe



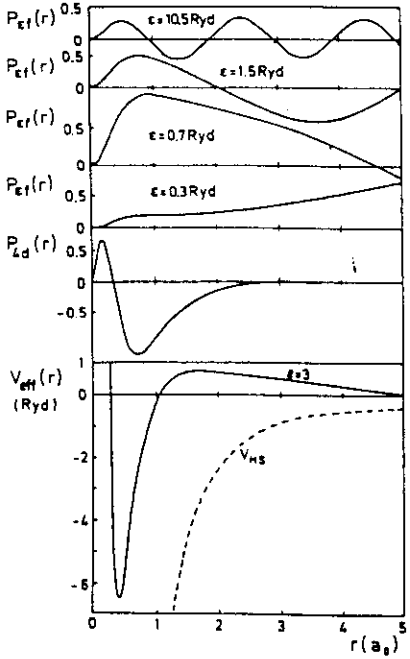
Giant Resonance

Intrachannel interaction



n = 4d

Figure 4.7. 4d → εf partial photoionization cross-section for xenon;



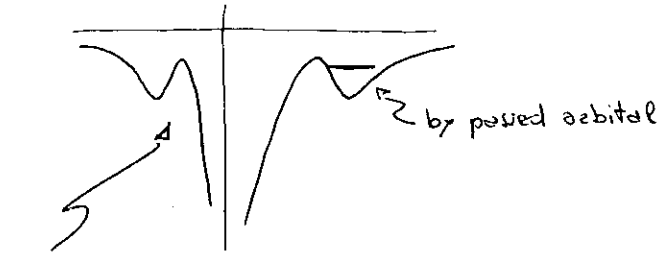
$V_{eff} = V_{(r)} + \text{Centrif. Bazziez}$

Shape resonance and wavefunction collapse in 4d Xe

Giant resonance = single particle with strong polarisation

nf orbitals located outside the atomic region
orbitals by-passed in Aufbau

4d → nf excitation absent
4d → np present



Ionisation makes barrier to collapse

Shape resonance present

Shape resonance and wavefunction collapse in 4d Xe

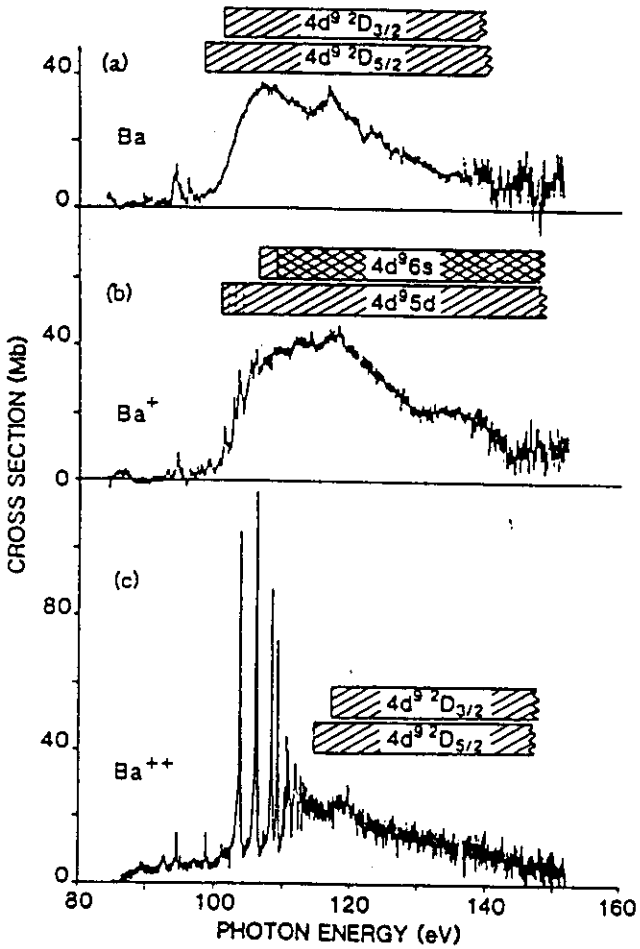
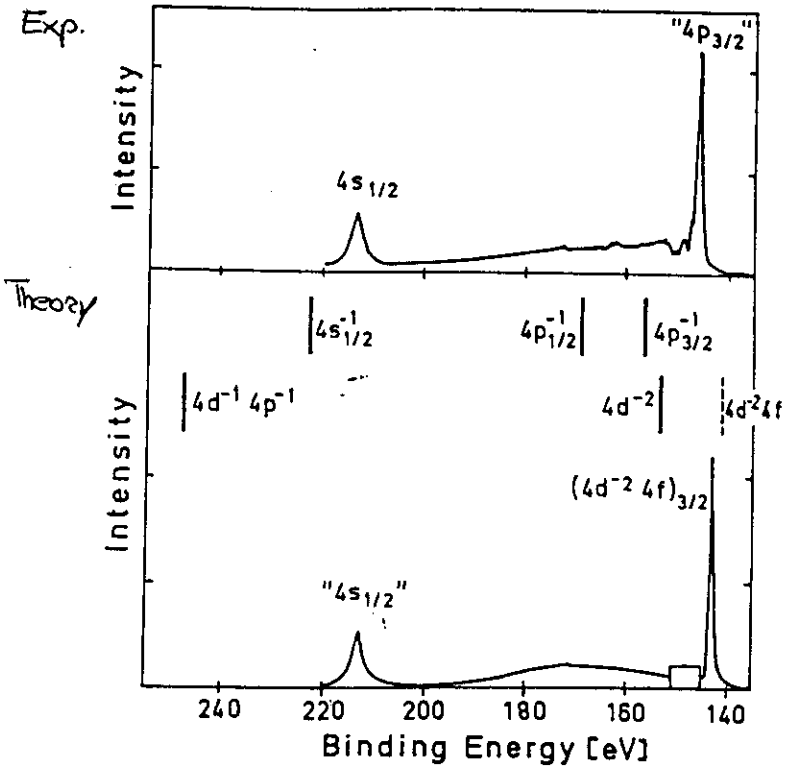


Figure 4.8. Photoabsorption cross-section of (*a*) Ba, (*b*) Ba^+ and (*c*) Ba^{2+}. Peak cross-sections of strong absorption features in Ba^{2+} are underestimated because of saturation and effects of limited resolution. The continua for the respective electron configurations are also included in the figure. From [LMS81].

FROM: LUCATORTO et al. Phys. Rev. Lett. 47 (81) 1124

The missing Xe 4p1/2 photoline



4s and 4p photoionization in xenon: upper part, experimental spectrum (average curve through the experimental points; from [Gel74, SMB76]); the lines in the middle part indicate theoretically predicted energy positions for the listed electron configurations; lower part, theoretically predicted spectrum from [WOh76].

(K.C.) $4p_j^{-1} \rightarrow 4d^{-1}5p^{-1}+k\ell$; $4p_j^{-1} \rightarrow 4d^{-1}5s^{-1}+k\ell$

$4p_j^{-1} \rightarrow 4d^{-2}+k\ell$; $4p_j^{-1} \rightarrow 4d^{-2}+4f$

Super K.C. — Giant K.C.

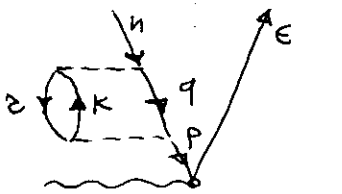
Exp. = Jolivus J. Elect. Spect. 5 (1974) 385

Theory = Wendin & Ohno Phys. Scripta 14 (1976) 78

The missing Xe $4p_{1/2}$ photoline

$4p^{-1}$ & $4d^{-2}4f$ nearly degenerate in energy

Perturb. diagram intensity $\propto \frac{\text{Coulomb Interc.}}{\Delta\epsilon}$ (large / small)

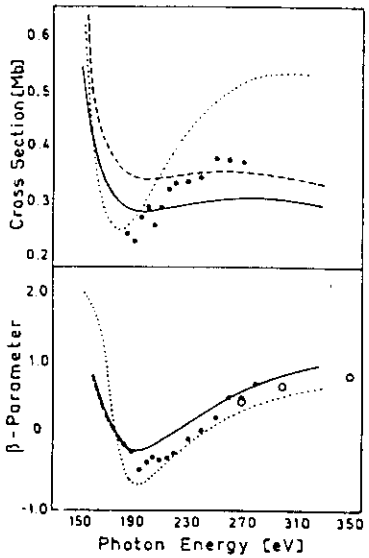


n=p=4p q=4d

n=p=4s q=4p

similar for $4s^{-1} \rightarrow 4p^{-1}4d^{-1}4f$

4p



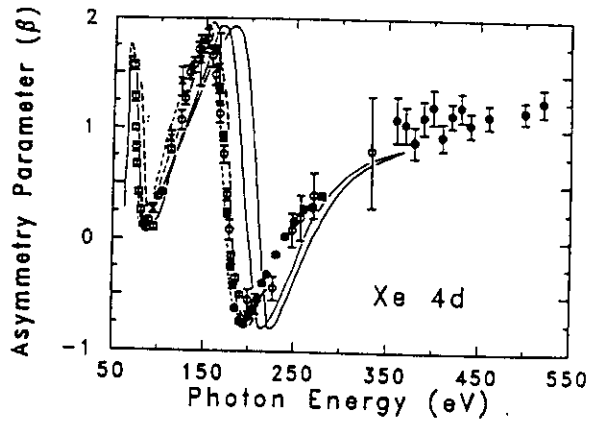
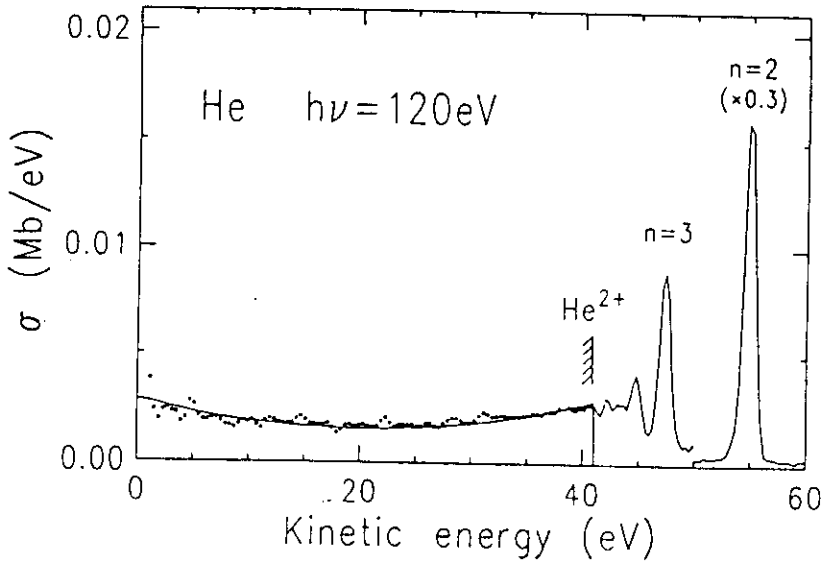


FIG. 3. Assymetry parameter of the Xe 4*d* subshell as in the bottom panel of Fig. 2, now including experimental results from Ref. 4 (×), plotted over a wider photon-energy range.

Lindle et al. Phys Rev A 37(88)3808

Figure 3.13. Partial cross-section (upper part) and angular distribution parameter β (lower part) for 4p photoionization in xenon. Note that the theoretical data refer to the whole 4p spectral distribution, but the experimental values to the $(4d^{-2}4f)\,^2P_{3/2}$ photoline only. Experimental data: solid circles, from [LFH88] (the relative cross-section values have been multiplied by a constant factor in order to place them into the vicinity of the calculated values); open circles, from [BSK89b] (there are additional data for higher energies). Theoretical data [SDe89]: full and broken curves, RRPA results including (4p+4d) shell couplings, length and velocity form results, respectively; dotted curves, theoretical values for 4d photoionization, which are in very good agreement with experimental data [LFH88].

He an example of two electron processes



Photelectron spectrum of helium satellites at 120 eV photon energy. The 1s main photoline is outside the shown energy range. Discrete satellites are characterized by the principal quantum number *n*. The double ionization threshold at 79 eV binding energy is marked as He^{2+} and the double ionization continuum for electron emission covers the range from 0 to $E_{exc} = 41$ eV kinetic energy.

Independent particle

$$\sigma^{+}(1s) = \frac{4\pi^2}{3}\alpha\omega\ell\,|\langle 1s|1s\rangle|^2 R^2_{\epsilon p,1s}$$

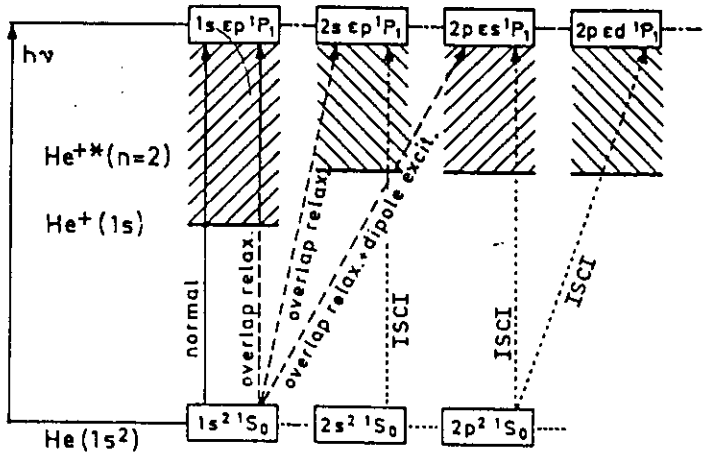
Ionisation with excitation

$$\sigma^{+*}(2s) = \frac{4\pi^2}{3}\alpha\omega\ell\,|\langle 2s|1s\rangle|^2 R^2_{\epsilon 2p,1s}$$

$$\sigma^{+*}(2p) = \frac{4\pi^2}{3}\alpha\omega 2\,|\langle \epsilon s|1s\rangle|^2 R^2_{2p,1s}$$

FROM: Wehlitz et al. Phys. Rev. Lett. 67 (91) 3764

He an example of two electron processes



Schematic representation of important electron correlations for discrete satellites in helium belonging to ionization and simultaneous excitation to $n=2$ (see

FROM: MANSON J. Electron Spec. 9 (76) 21

$He^{+*}(2s)$ shake-up ; $He^{+*}(2p)$ conjugate shake-up ; $He^{++}(\epsilon s, \epsilon' p)$ shake off

⊛ Double ionisation, difficult from single meas.

⊛ Satellite at threshold, interesting

Inner shell satellites, Ne

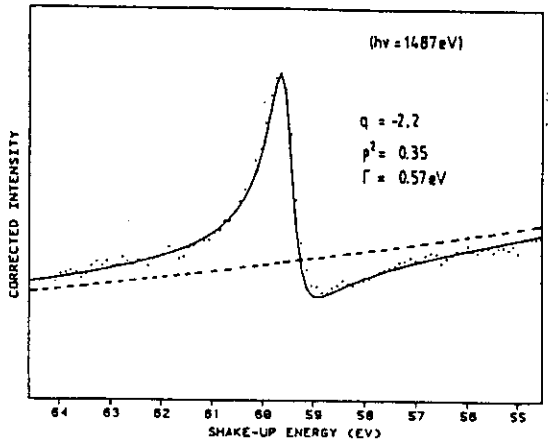


Figure 3.19. The $1s2s2p^63s$ lower shake-up satellite of neon observed with 1487 eV photons. If the shake-up energy is added to the 1s ionization energy (870 eV), one obtains the binding energy of this satellite. A small inelastic-scattering and spectrometer background has been subtracted. The dotted curve indicates the unperturbed continuum intensity, the full curve represents a fit of a Fano line profile to the experimental points with the parameters given in the figure. F

$$1s^{-1} + 1s\,2s^2\,2p^5\,k\ell \quad \text{or} \quad 1s2s2p^6\,k'\ell'$$

$$S_{Ki} = \langle \Psi_{k'}(N-1) \,|\, \Psi_i(N-1) \rangle$$

$$\frac{I_K(\epsilon')}{I_0(\epsilon)} = \frac{|\langle \epsilon' | z | i \rangle|^2}{|\langle \epsilon | z | i \rangle|^2} \frac{S_{Ki}^2}{S_{0i}^2}$$

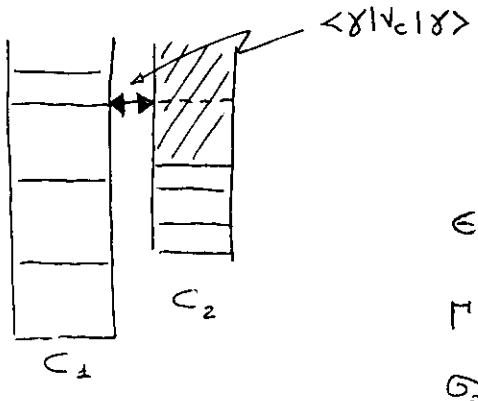
Indistinguishable states reached by two paths

1 step $\longrightarrow 1s2s^22p^5(^1P/^3P)\epsilon'_p(^2S^e)\epsilon_p\ ^1P_1$

2 step $\longrightarrow 1s2s2p^63s\ ^3P^e\epsilon_p \longrightarrow 1s2s^22p^5(^1P/_{2p})\epsilon'_p\epsilon_p\ ^1P_1$

FROM: SVENSSON et al. Phys. Rev. Lett. 58 (87) 2639

Parametrization of resonances



absorption x-sec

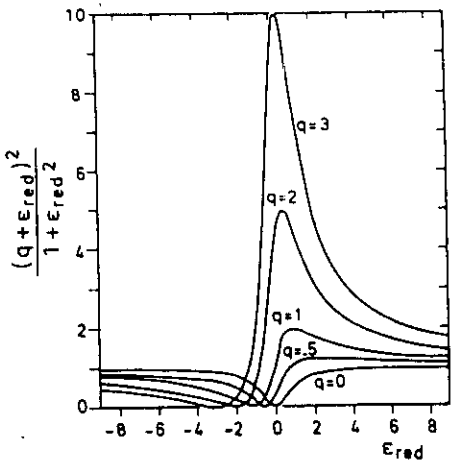
$$\sigma = \sigma_a \frac{(q+\epsilon_2)^2}{1+\epsilon_2}$$

$$\epsilon_2 = \frac{(E-E_2)}{\Gamma/2}$$

$$\Gamma = 2\pi |\langle\gamma_0|\Sigma \frac{1}{2_{ij}}|\gamma_c\rangle|^2$$

$$\sigma_a = \frac{4\pi^2}{3}\alpha\omega |D_0|^2$$

$$q = \frac{1}{\Gamma/2} \frac{\langle\gamma_0|\Sigma\frac{1}{2_{ij}}|\gamma_c\rangle\langle\gamma_c|z|\psi_i\rangle}{\langle\gamma_0|z|\psi_i\rangle}$$



. Line profiles of a Fano resonance for different values of the q-parameter. From

FROM : FANO Rep. Prog. Phys. 46 (83) 97

Two electron excited states He

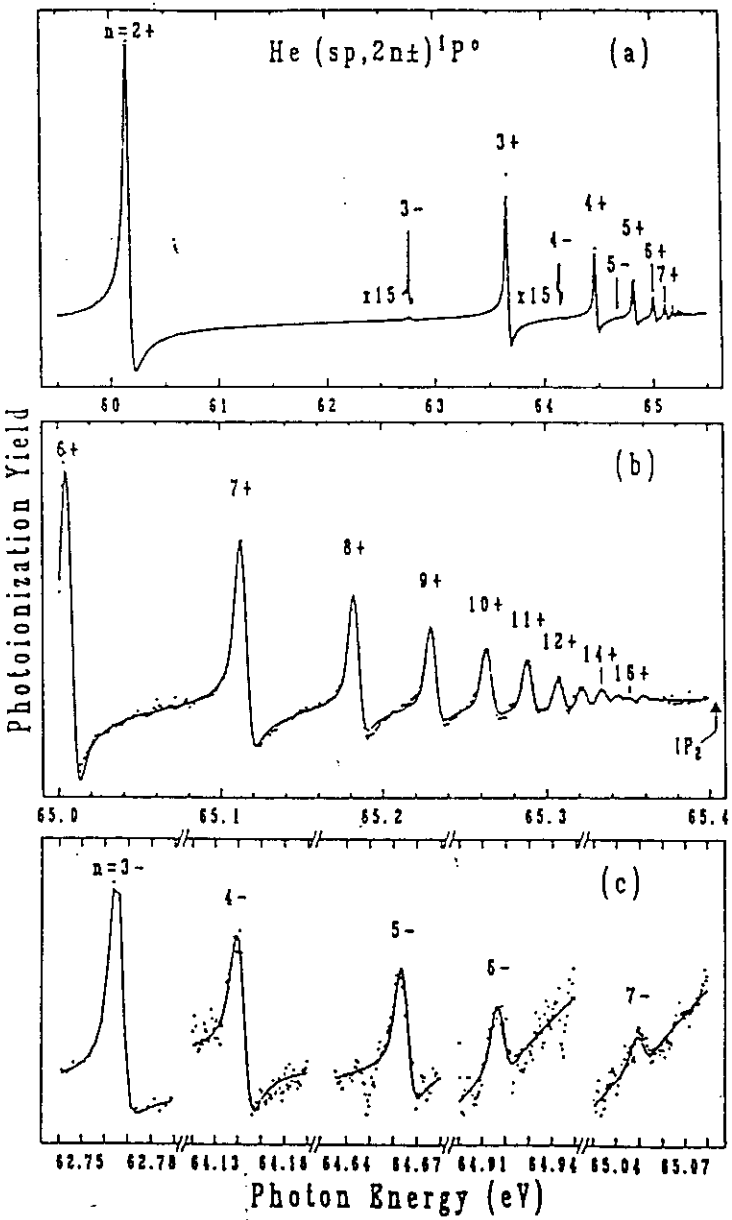
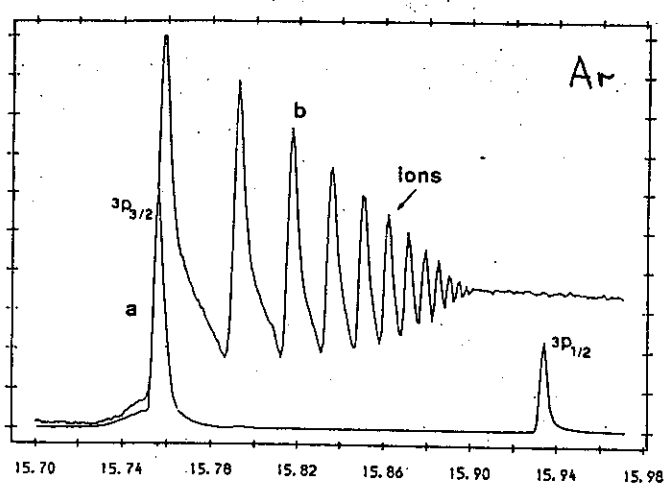


Figure 4.9. Doubly excited states of helium below the threshold for $He^{+*}(n=2)$: overview; (*b*) magnification of the $n>6$ region; (*c*) $sp2n-$ states. From

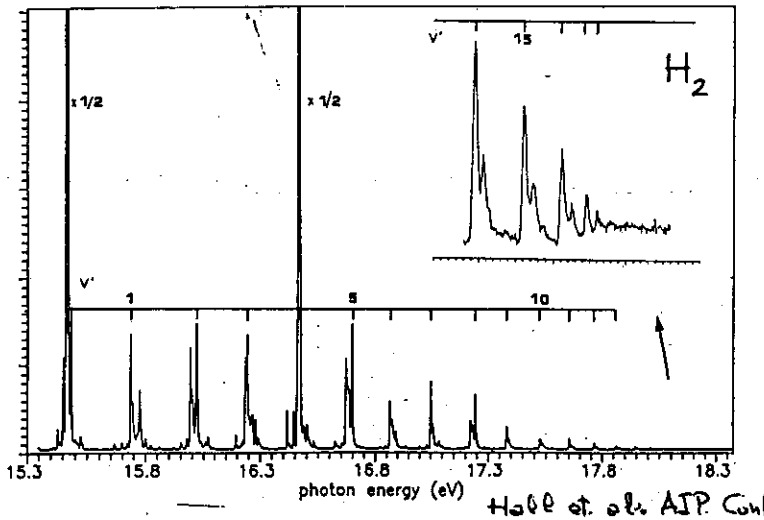
Threshold spectroscopy
ion detection and high energy resolution



$3p_{3/2} \rightarrow ns$

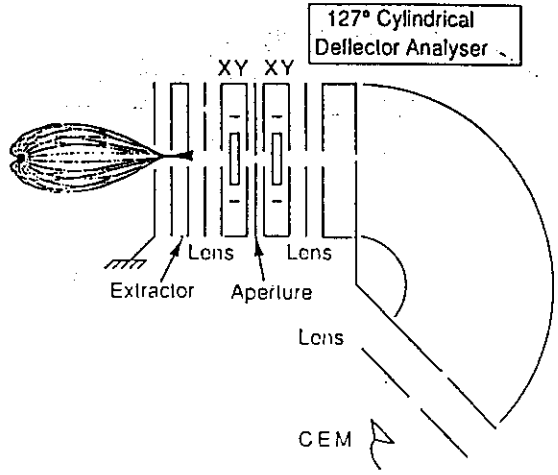
$\hbar\omega$ [eV]

Ar threshold photoemission spectrum (a) and ion Ar^+ spectrum (b) From: Hall et al. Meas. Sci. Technol. 3 (92) 316



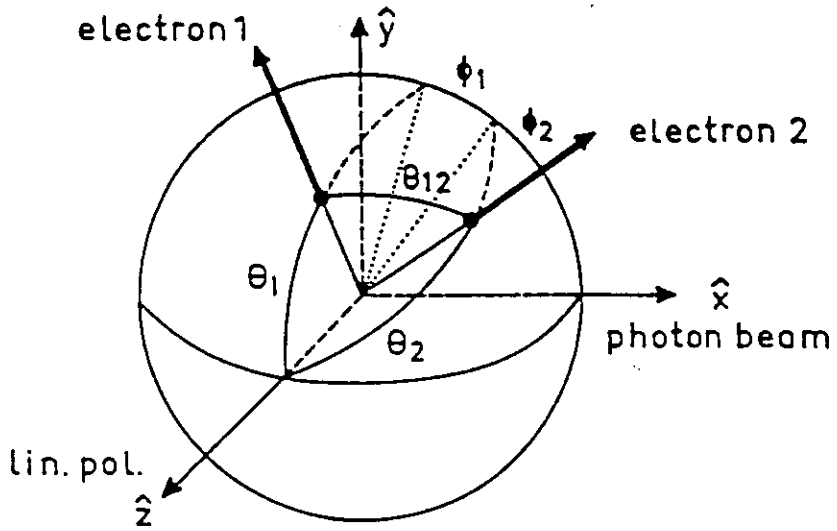
Hall et. al. AIP Conf. 258 (92) 135

The threshold spectrometer

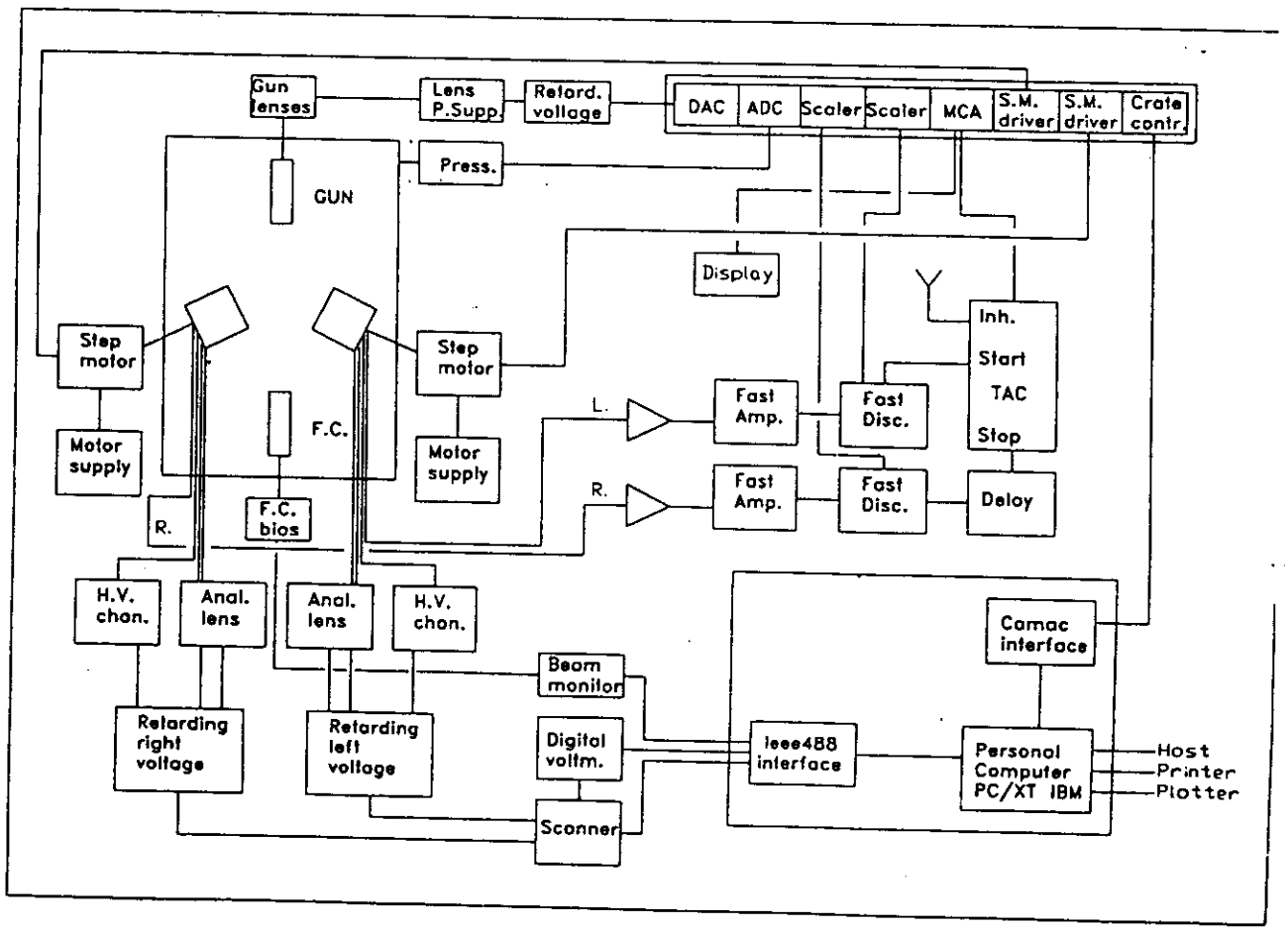


Direct double photoinization DPI

Schematic of DPI experiment

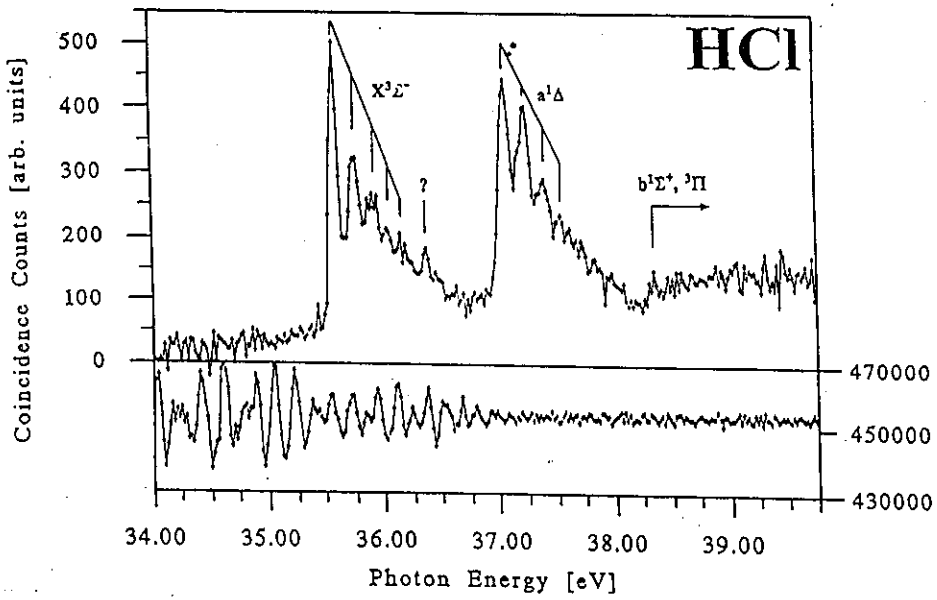


Coincidence set up



DPI

Coincidence experiments started in 1972 with e-ion coincidence
(Danby and Eland, J. Mass Spectrom. Ion Phys 8 , 153)
e-e coincidence experiments started in 1987
(Lablanquie et al. Phys. Rev. Lett. 58, 992)



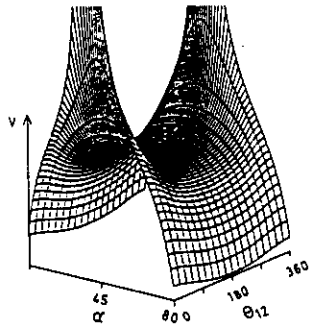
A.G. McConkey et al. (1993)

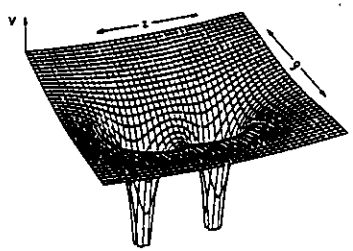
DPI at threshold, Wannier region

Close to threshold He DPI ideal case for correlated motion of 2 e^- in the continuum.

3 charged particles boundary conditions

Wannier theory is expected to hold (symmetry in the angular distribution).





$$\frac{d^4\sigma}{dE_1\,dE_2\,d\Omega_1\,d\Omega_2} = |\mathcal{B}|^2(\cos\theta_1+\cos\theta_2)^2\exp\{\gamma\}\cdot \delta(E_1+E_2-E_{exc})$$

$$\gamma = -4\ln 2\,(\theta_{12}-180^\circ)^2/\theta^2_{fwhm}$$

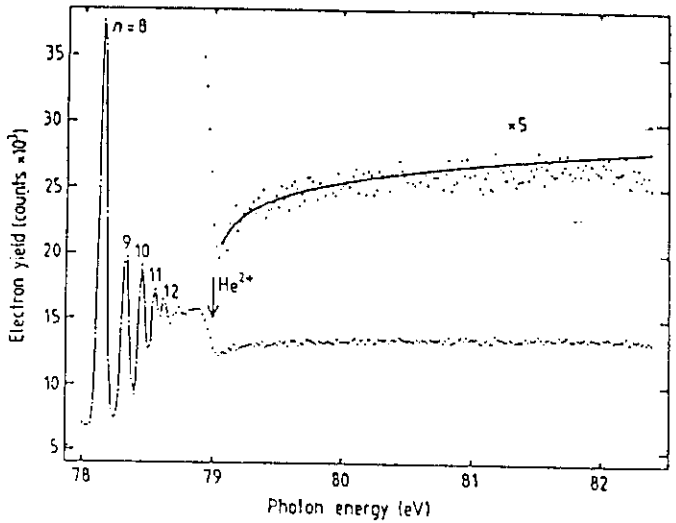
$$E_{exc} = E_1 - E_2 = \hbar\omega - E_{th}$$

$$\frac{d^3\sigma}{dE_1\,d\Omega_1\,d\Omega_2} = |\mathcal{B}|^2(\cos\theta_1+\cos\theta_2)^2\exp\{\gamma\}$$

$$\theta_{fwhm} = \theta_0 E_{exc}^{1/4}$$

$$\frac{d\sigma}{dE} = \text{cost} = \frac{\sigma}{E_{exc}}$$

DPI at threshold, Wannier region



. Threshold photoelectron spectrum of helium over an energy range in the region of the double-ionization threshold; photon bandpass 60 meV. The smooth full curve in the expanded inset is a fit to the data of the Wannier threshold law with the exponent $n = 1.056$, equation (4.19). From

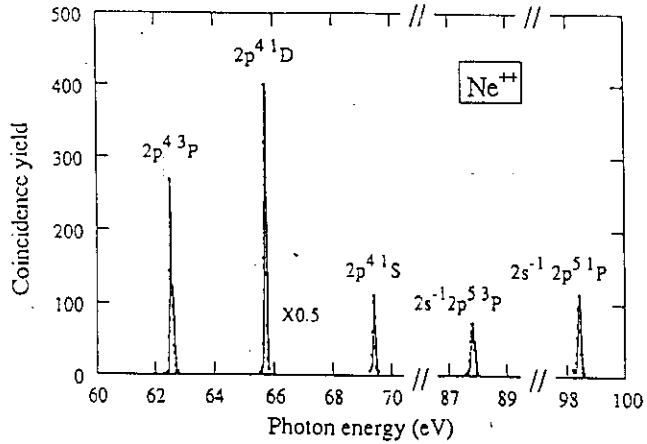


Figure 2a: TPEsCO spectrum of Ne over the photon energy range 62 to 100 eV

FROM : Wan... + al. TDP B 22 (1980) 1460

DPI at intermediate energies

$$\hbar\omega + \Psi_i(N) \longrightarrow \Psi_f(N-2) + \epsilon + \epsilon'$$

a first order approach

Energy conservanion

$$\hbar\omega + E_i(N) = \epsilon + \epsilon' + E_f(N-2)$$

In single particle scheme

$$\hbar\omega + E_i(N) = \epsilon + \epsilon' + E_f(N-2, \bar{\imath}, \bar{\jmath})$$

DPI cross section

$$\sigma^{(2)}(\omega) = \frac{4\pi^2 e^2 \omega}{c} \sum_f |T_{if}|^2 \delta(\epsilon + \epsilon' + E_f(N-2) - E_i(N))$$

$$T_{if} = \langle \Psi_f | \hat{e} \cdot \sum_1^N \underline{r}_i | \Psi_i \rangle$$

Differential cross section

$$\frac{d^6\sigma}{d\underline{K}\, d\underline{K}'} = \frac{4\pi^2 e^2 \omega}{c} |T_{if}|^2 \delta(\epsilon + \epsilon' + E_f(N-2) - E_i(N))$$

Selection rules

- $d^6\sigma \neq 0$ if $K_z \neq 0$, $K_z' \neq 0$ $\quad \hat{z} \parallel \hat{e}$
- $d^6\sigma$ invariant if $\epsilon, \epsilon', K_z, K_z'$ identical
- $d^6\sigma = 0$ if $\epsilon = \epsilon'$ and $K_z = K_z'$

  $T_{if} \propto A(\epsilon, \epsilon') [Y_{10}(\hat{K}) + Y_{10}(\hat{K}')]$
- $d^6\sigma = \text{Max}$ if $\vec{K} = \vec{K}' \parallel \hat{e}$

DPI DCS the angular distributions

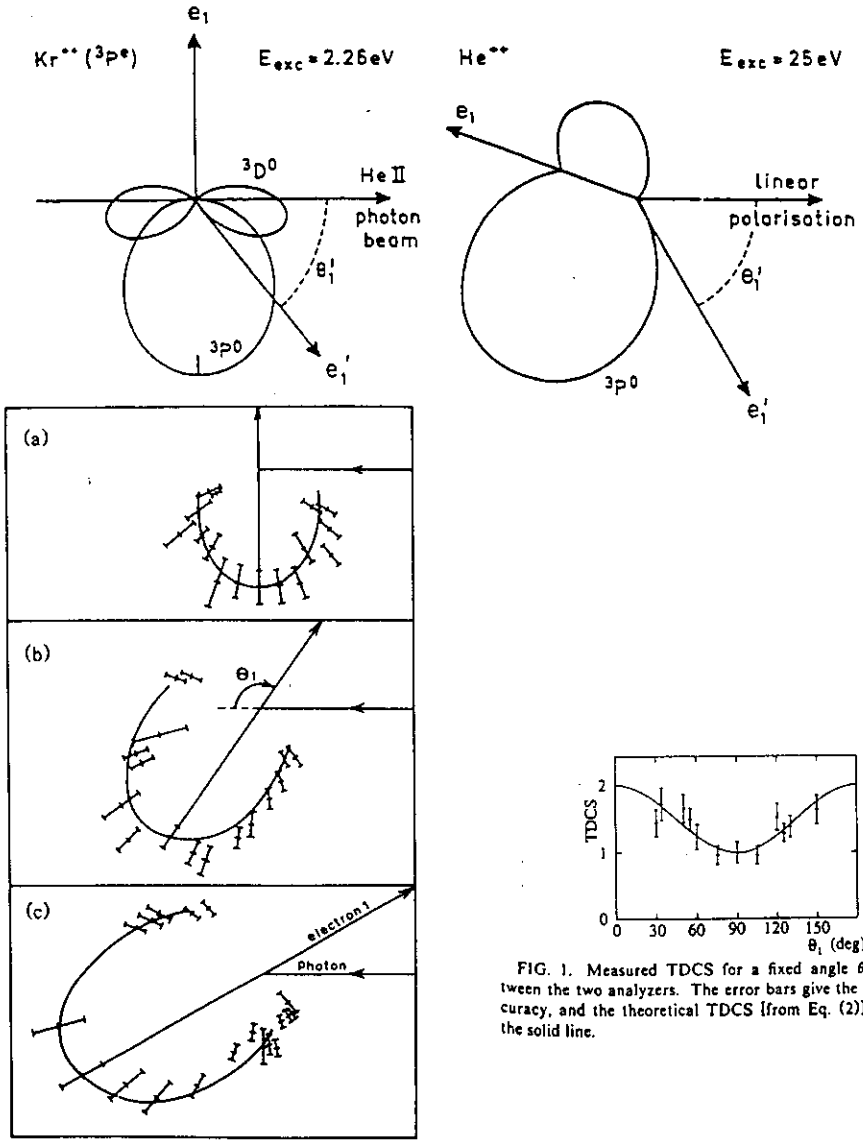


FIG. 2. Measured TDCS for fixed positions of the first electron: (a) $\theta_1 = 90°$, (b) $\theta_1 = 125°$, (c) $\theta_1 = 150°$. The incoming photon beam and first electron are indicated by arrows, and the polar representation with a normalization which is common to (a)–(c) is used.

FIG. 1. Measured TDCS for a fixed angle $\theta_{12} = 180°$ between the two analyzers. The error bars give the statistical accuracy, and the theoretical TDCS [from Eq. (2)] is shown by the solid line.

FROM: MAZEAU et al.
Phys. Rev. Lett. 67 (91) 820

DPI DCS the angular distributions

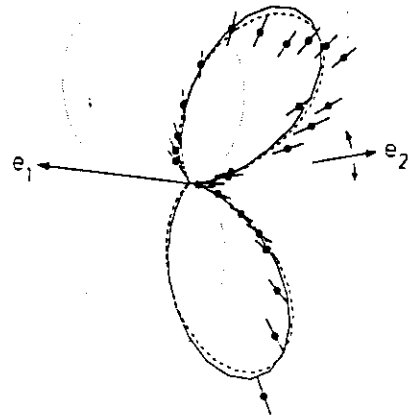


FIG. 2. Relative values of experimental and theoretical TDCS for the double photoionization of helium at $h\nu = 99$ eV in the plane perpendicular to the photon beam: direction of electron e_1 fixed; electron e_2 at different angles. For further details see text.

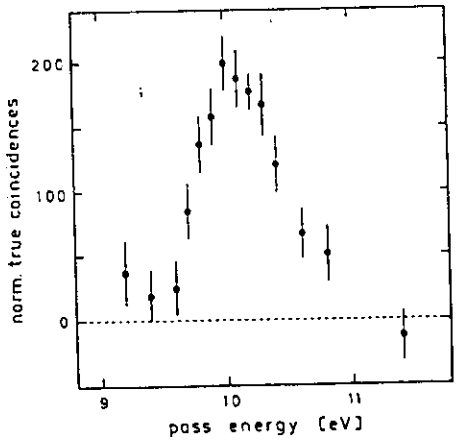


FIG. 1. Coincidence counts as a function of the pass energy E_2 of spectrometer 2 with the pass energy of spectrometer 1 set to $E_1 = E_{exc}/2 = 10$ eV.

FROM: Schwarzkopf et al.
Phys. Rev. Lett. 20 (93) 3008

DPI in molecules

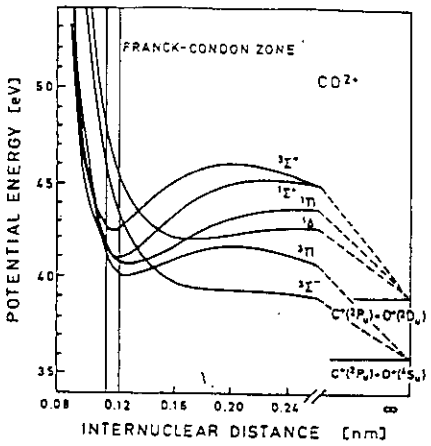
The full fragmentation pattern has been studied for H_2

V. Schmidt an coworkers
Phys. Rev. Lett. 63 (1989) 2040

For larger molecules will be difficult unless results from several experiments are combined or: coincidence of the two electrons with the fragment ions is performed

Various kind of e-ion, ion-ion coincidence experiments have been performed (*)

The CO_2 molecule



PIPICO has shown C^+ O^+ pairs from autoionization of CO^{+*}

(*) NENNER I. & BESWICH J.A. "Handbook of S.R." 1982

DPI in molecules

TPEsCO Threshold Photoelectron Coincidence Spectra

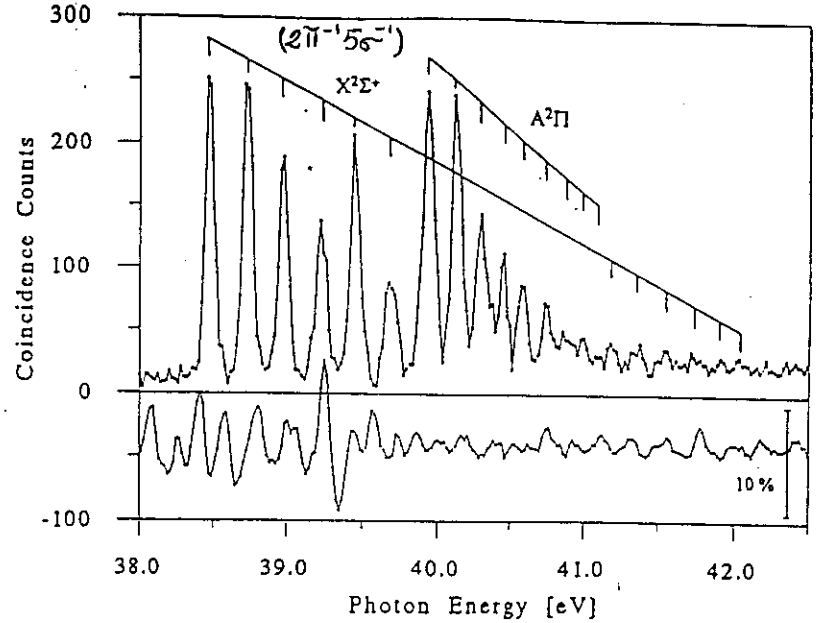


Figure 4a: TPEsCO spectrum of NO^{2+} over the photon energy range 38 to 42.5 eV. The lower spectrum in the figure is the sum of the threshold spectra collected in both analyzers.

$$E(v) = T_0 + \omega_e (v+1/2) - \omega_e x_e (v+1/2)^2$$

Table 2: Molecular constants

		exp.	ref. 33	ref. 34
$X^2\Sigma^+$	T_0(eV)	38.39±0.05	39.42	38.56
	ω_e(meV)	255±19	277	261
	$\omega_e x_e$(meV)	3±1	4	3
$A^2\Pi$	T_0(eV)	39.85±0.007	39.96	40.02
	ω_e(meV)	186±4	170	184.
	$\omega_e x_e$(meV)	4.5±0.4	3	4.6
$B^2\Sigma^+$	T_0(eV)	43.16±0.015		
	ω_e(meV)	272±18		
	$\omega_e x_e$(meV)	20±4		

DPI at High energy: Correlation spectroscopy

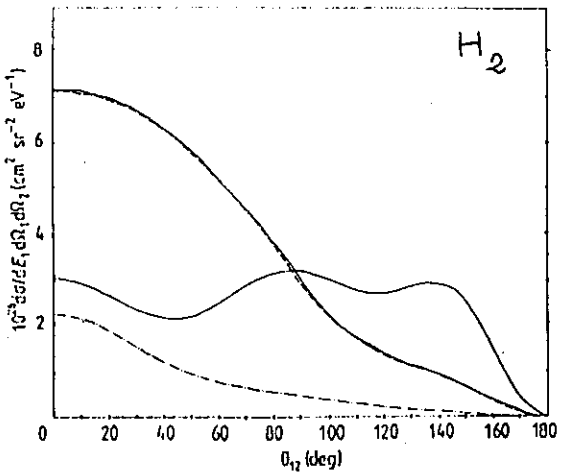
In 1977 Neudatchin et al.( ) proposed the high energy (hv,2e) coincidence experiments to investigate the double ionization of atoms and molecules. These experiments should represent the natural generalization of impulsive (e,2e) experiments. The goal of the proposal ( ) was to develop a spectroscopy of doubly charged ions that would enable the direct determination of the partial two-electron Fourier amplitude

$$\psi_{if}(k_1,k_2)=\frac{1}{2\pi}\int dr_1 dr_2 \psi_{if}(r_1,r_2)e^{i(k_1\cdot r_1+k_2\cdot r_2)}$$

of the many-electron wavefunction $\psi_i(r_1,r_2,.....r_N)$ projected on an arbitrarily selected state $\psi_f(r_3,r_4,.....r_N)$ of the doubly charged ion

$$\psi_{if}(r_1,r_2)=\int dr_3..dr_N \psi_f^*(r_3,...r_N)\psi_i(r_1,...r_N)$$

The importance of studying these quantities becomes clear when a two electron system is considered. In this case $\psi_{if}(k_1,k_2)$ is merely the wave function of the two electron system in the momentum space representation. It contains all the details of the structure of the system and in particular the momentum distribution of the relative motion of the electrons in the degree of freedom $r_{12}=r_1-r_2$. This motion is dominated by electron-electron correlations. In many-electron systems if the transition i→f involves the knock-out of two electrons from the same orbital then $\psi_{if}(k_1,k_2)$ characterizes the electron-electron correlations in that orbital, viceversa if the transition involves electrons from different orbitals then $\psi_{if}(k_1,k_2)$ enables the study of electron-electron correlations in different orbitals . The sensitivity of the technique can be inferred from a theoretical study of the double photoionization of H_2 molecule



e-e angular distributions
$\hbar\omega = 296$ eV
$K_1 = K_2 = 5\,a_0^{-1}$

—— CI 5 conf.
--- LCAO HO
=== Corr. W.F.

LEVIN et al.
J. Phys. B 17 (1984) 1525

DPI at High energy: Correlation spectroscopy

In this approximation the DPI x-section factorizes as:

$$\frac{d^5\sigma}{d\Omega_1\, d\Omega_2\, dE} \propto \frac{K_1 K_2}{\omega}\left|\psi_{if}(K_1,K_2)\right|^2$$

Experiment Kinematics

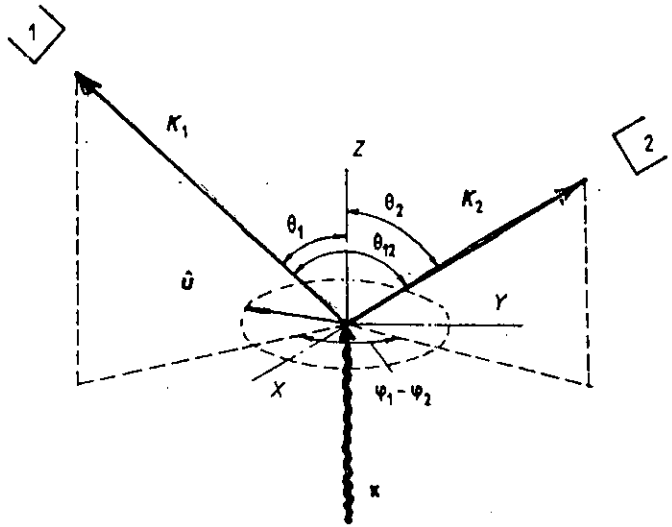
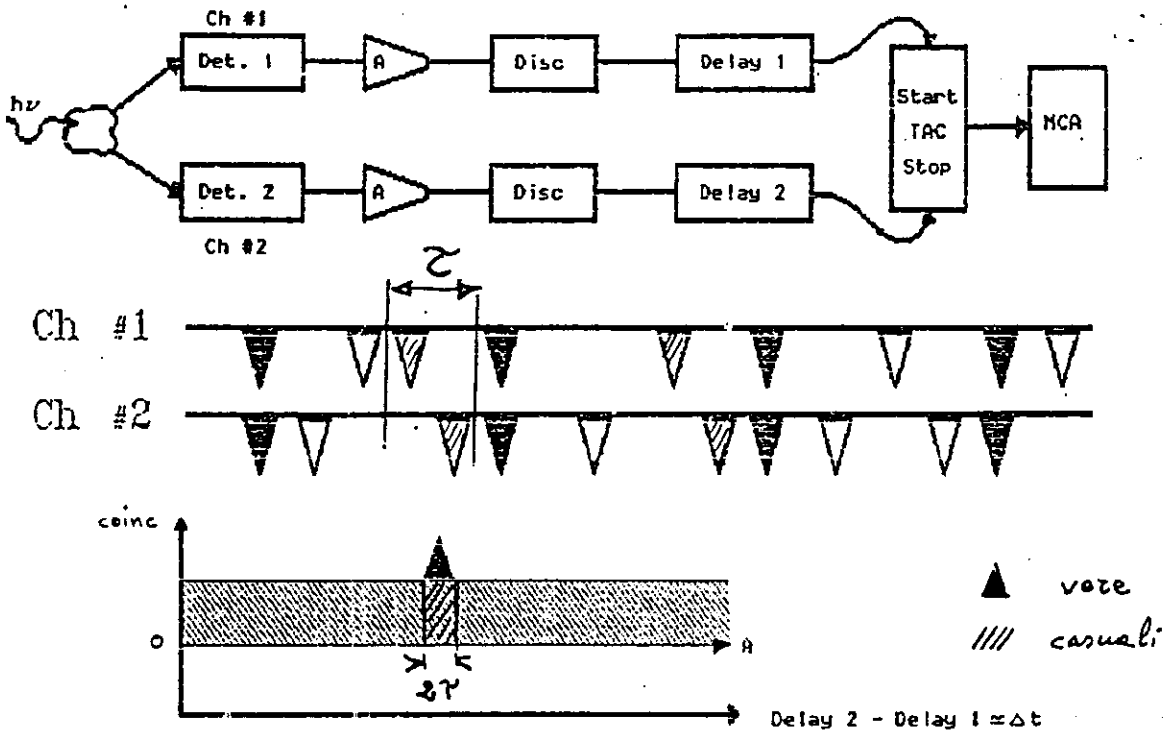


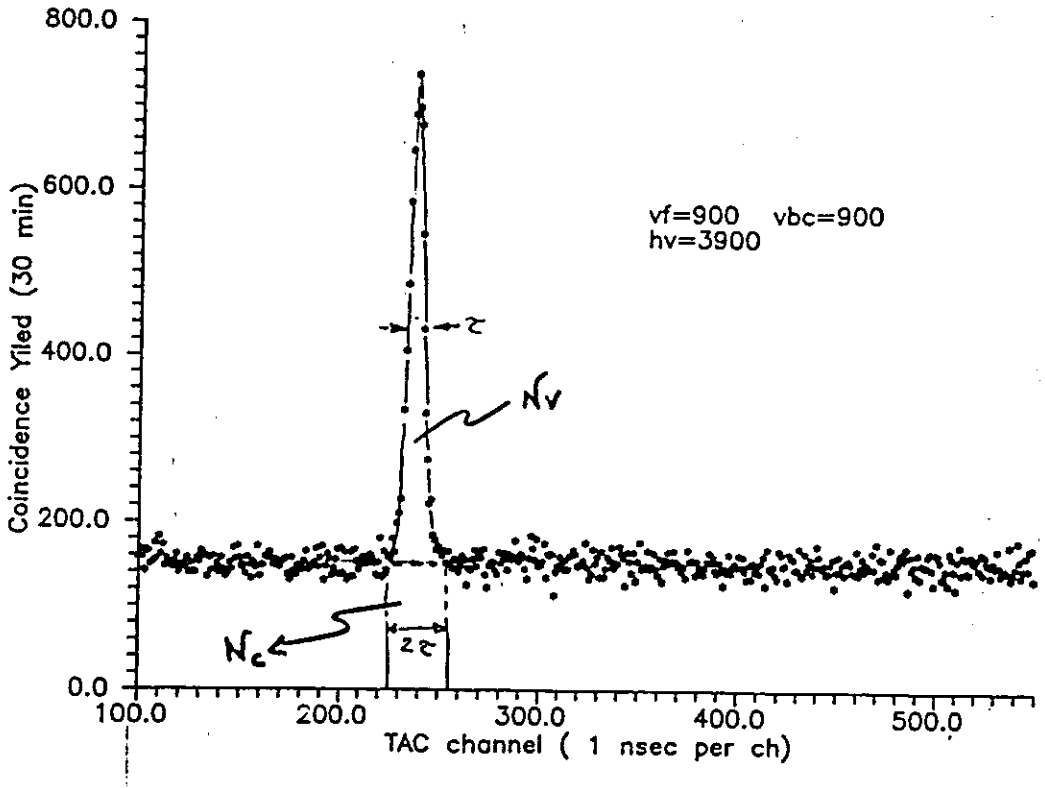
Figure 1. Geometry of a possible experimental set-up for the (γ, 2e) process

On the experimental problems in coincidence spectroscopy



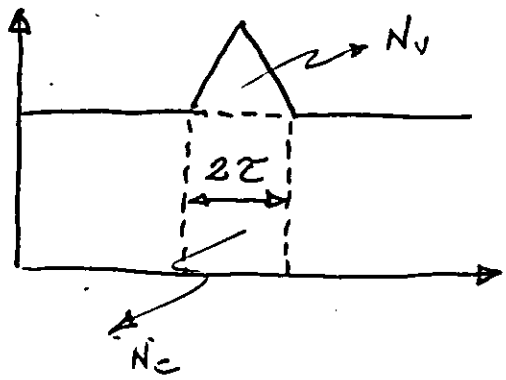
Sorgente "continua" se $\tau > \tau_p$

τ: tempo risolutivo coincid.
τ_p: durata impulso luce



On the experimental problems in coincidence spectroscopy

COINCIDENCE OPTIMIZATION



To minimize error

$$\varepsilon = \frac{N_V}{N_C}$$

as small as possible

Single Rate $\quad R_i = \sigma_i I_{ph}(\delta\ell)\,\Delta E_i\,\Delta\Omega_i\,\rho_i$

Chance C. Rate $\quad R_C = R_1 R_2 \ell\tau$

True C. Rate $\quad R_V = \sigma_V I_{ph}(\delta\ell)\Delta E_c \Delta\Omega_1 \Delta\Omega_2 \rho_1 \rho_2$

$$\varepsilon \propto \left(\frac{\sigma_V}{\sigma_1 \sigma_2}\right) \frac{(2\tau)^{-1}}{I_{ph}(\delta\ell)} \frac{\Delta E_c}{\Delta E_1 \Delta E_2}$$

ε_{MAX} for $I_{ph} \to 0$!

for $\delta\ell \to 0$!

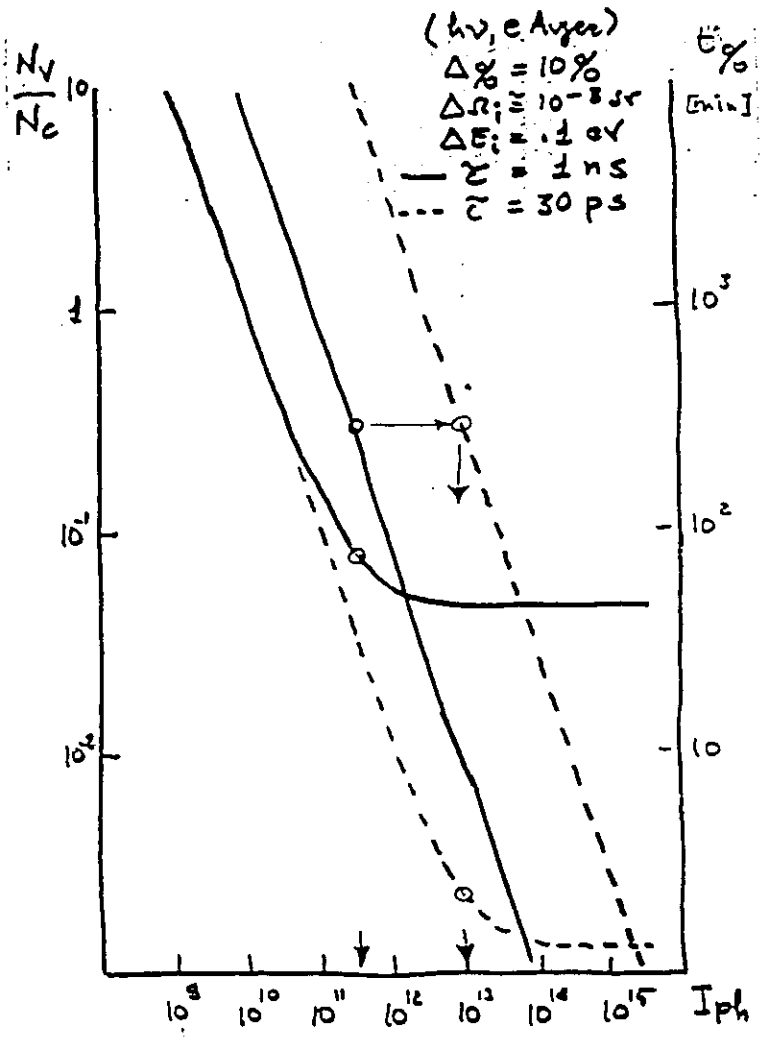
$$\Delta_\% = \frac{\Delta N_V}{N_V} \longleftarrow \text{Acc. time} = t_\%$$

$$t_\% = \frac{\sqrt{2}}{\rho_1 \rho_2 \Delta\Omega_1 \Delta\Omega_2} \frac{1}{\Delta_\%^2} \frac{1}{\sigma_c} \times$$

$$\times \left[\frac{1}{I_{ph}\,\delta\ell\,\Delta E_c} + \frac{\sigma_1 \sigma_2}{\sigma_c} 2\tau\right]$$

$\Rightarrow$ $t_\%$ min $\Rightarrow \Delta\Omega_i$ large ; τ short $\Leftarrow$

On the experimental problems in coincidence spectroscopy



How to minimize τ ?

i) Detectors (MCP $\simeq$ 10 ÷ 100 ps)

ii) Electronics (TAC+MCA / TDC $\simeq$ 10 ÷ 100 ps)

iii) Trajectories (> 200 ps (e^-); ~ 100 ns (I^+))
After compensation

(iii) Most severe. To reduce:

a) Hardware or Software Compensation

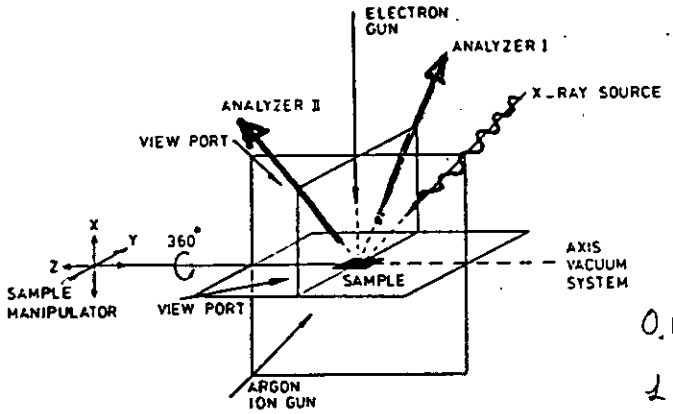
b) Reduce $\Delta\Omega_i$!

On the experimental problems in coincidence spectroscopy

$h\nu + A \longrightarrow A^+(\kappa^{-1}) + e_{ph}$

$\longrightarrow A^{++} + e_A$

H.W. HAAK et al. Rev. Sci. Instr. 55 (1984) 696
Phys. Rev. Lett. 41 (1978) 1825



16 ns

0.03 – 01 /s

1 . 0.3 V/F

8°

Fig. 3.1. Geometric arrangement of various components on the vacuum system.

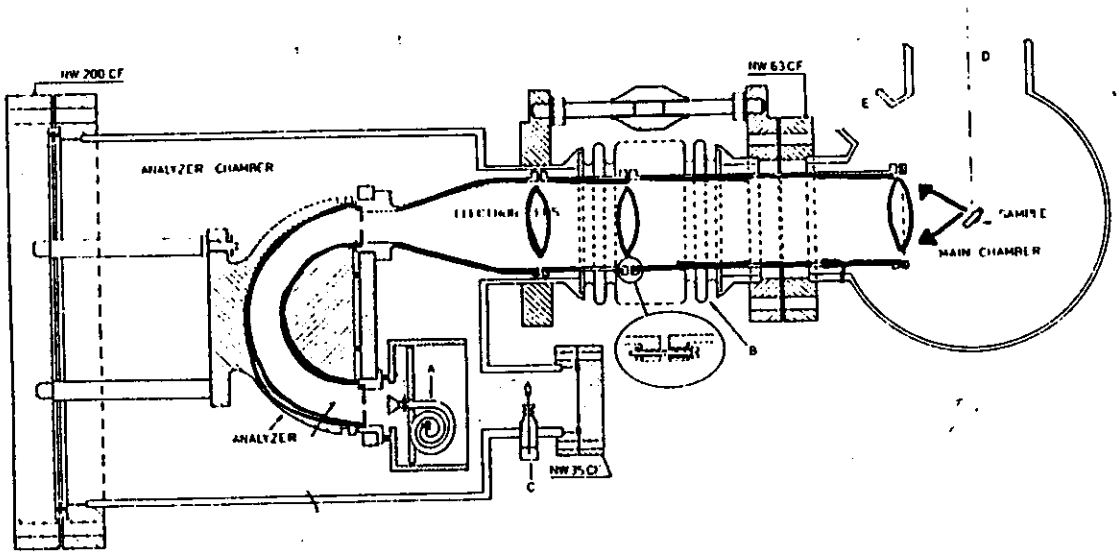


Fig. 3.12. The mechanical construction of the analyzer and electron lens in the vacuum chamber, the magnetic shielding is omitted. The inset shows the electrical insulation between the various lens parts by means of a ceramic ring.

FOR A REVIEW!
GRANNEMAN & VANDERWIEL
Handbook of Synchrotron R
1982

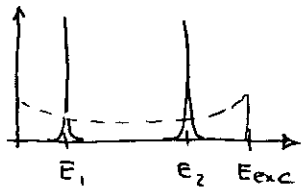
Inner shell photoionization and coincidence experiments

A two step process

Energy sharing not even

$E_1 = h\nu - E_B^+$

$E_2 = h\nu - E_B^{++}$



To establish complete fragmentation pattern only directional dependence is needed.

If 2step hold coincidence is not needed.

$\therefore$ $C(e_1, e_2)$ are important if:

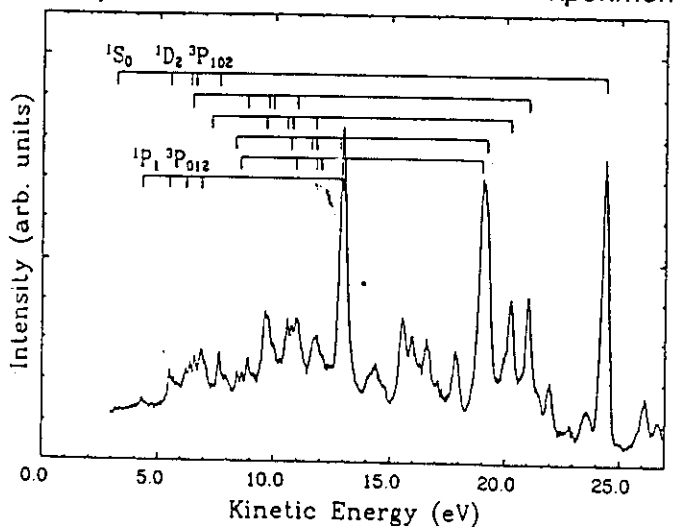
i) LSJ not valid → several Auger amplitudes might contribute.

ii) Complex systems, e.g. $Xe\,4d_{5/2} \rightarrow 6p$ → $Xe^+ + e_1$, → $Xe^{++} + e_2$; → $Xe^{++} + e_1 + e_2$

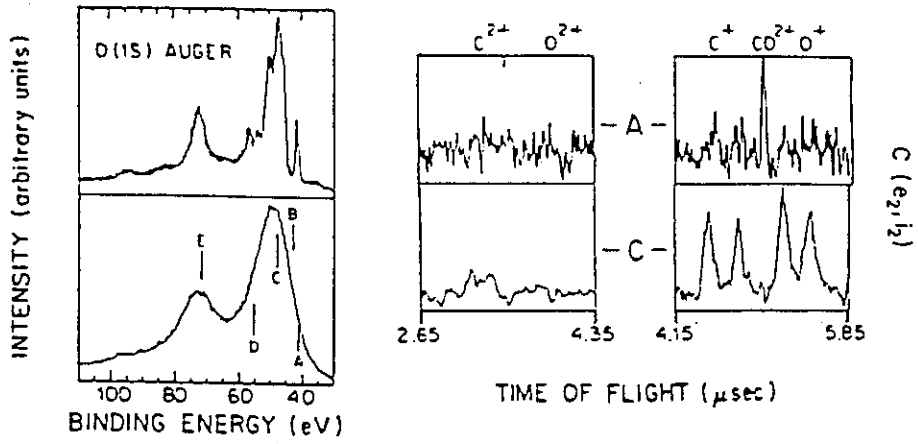
iii) Post collision interactions are present

iv) In molecules to identify fragmentation patterns associated with given valence-hole configurations.

Inner shell photoionization and coincidence experiments



. Low-energy part of the resonant Auger spectrum of xenon taken at the $4d_{5/2}$ -> 6p resonance (65.1 eV). The first-step decay leads to the following spectator lines: $5s^05p^6(^1S_0)6p$ at 12.96eV; $5s^25p^35d6p$ at 18.98eV, 19.20eV and 20.24eV; $5s^15p^5(^1P)7p$ at 21.05eV and $5s^15p^5(^1P)6p$ at 24.38eV. The marks indicate corresponding first and second step Auger lines.



$C(e_2,I_2)$ coincidences in inner-shell photoionization of CO. Left part: O(1s) Auger spectra taken with (bottom) and without (top) the ion extraction field applied across the ionization region; right part: two examples of $C(e_2,I_2)$ coincidence spectra obtained with Auger electrons from the energy regions A and C, respectively.

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