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Trends in XUV synchrotron radiation research

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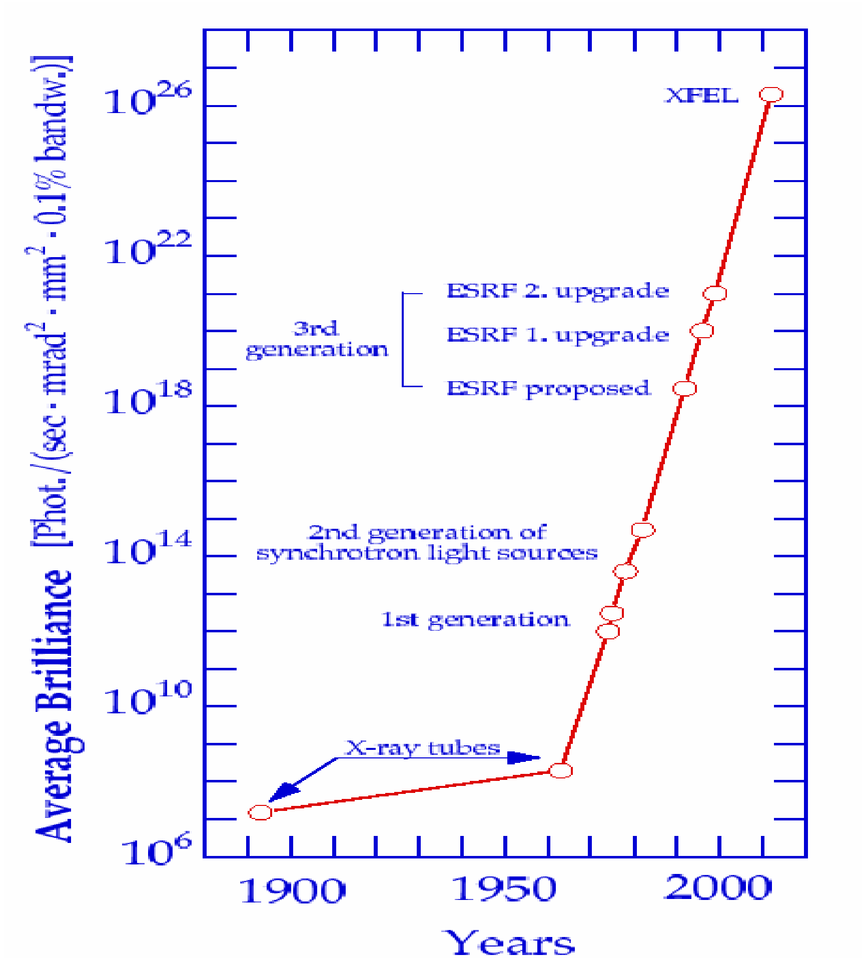
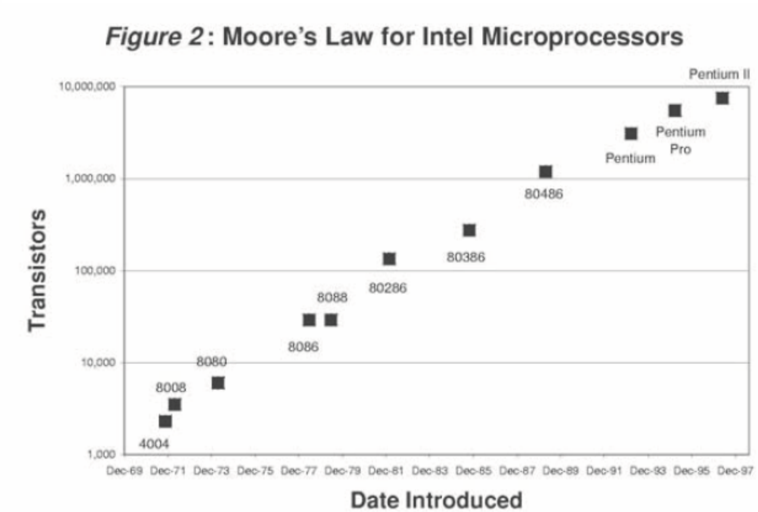
Third generation facilities

- Storage ring facilities
- Emittance <10 nmrad
- Use of insertion elements
- Use of:
  - Time structure
  - Polarization incl. Circular
  - Spatial high degree of coherence
  - Possibility of high resolution $\Rightarrow E/\Delta E \approx 10^5$

HAS HAD A TREMENDOUS IMPACT ON KEY FIELDS IN MODERN MATERIALS (WIDE SENSE) RESEARCH

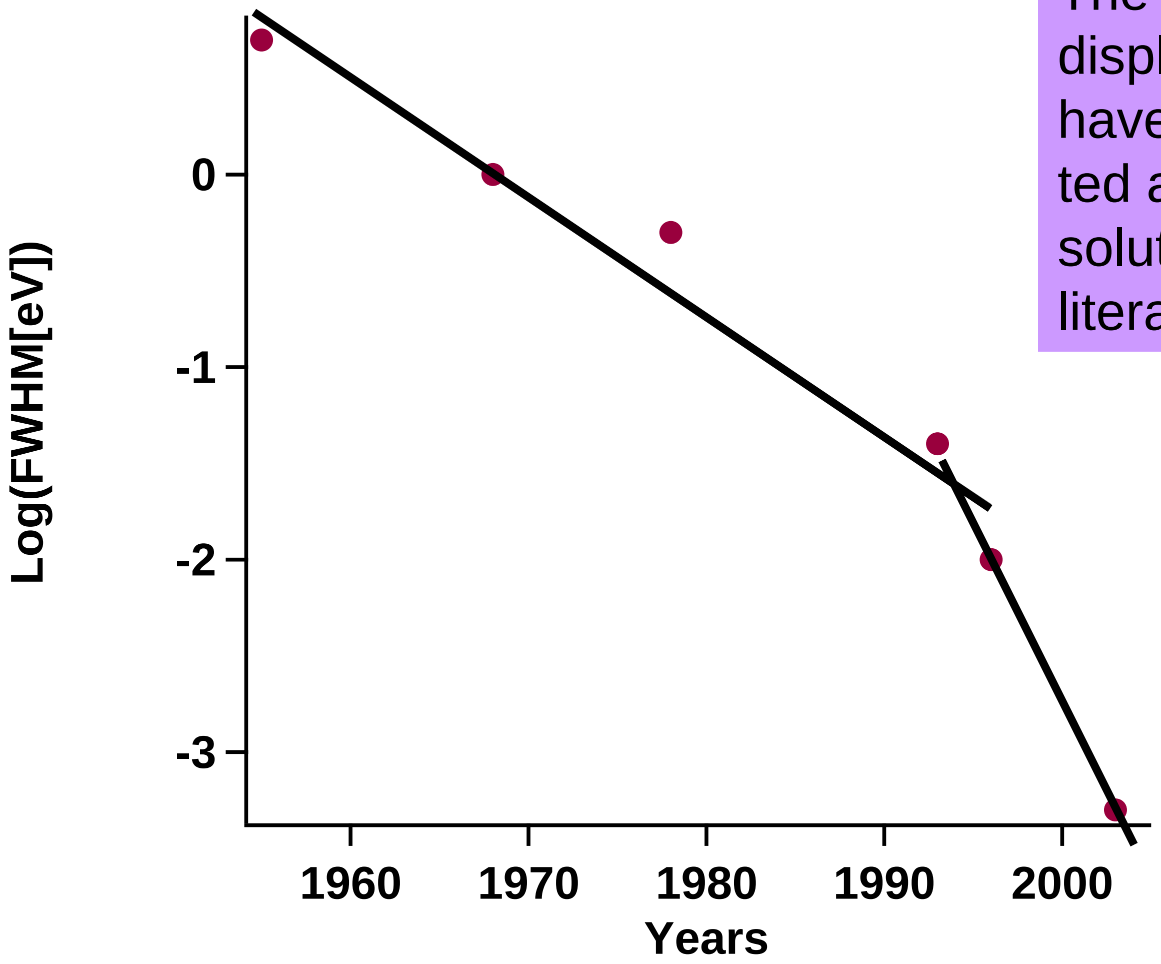
The development of the brilliance and Moore´s law





http://www.thocp.net/biographies/papers/moores_law.htm

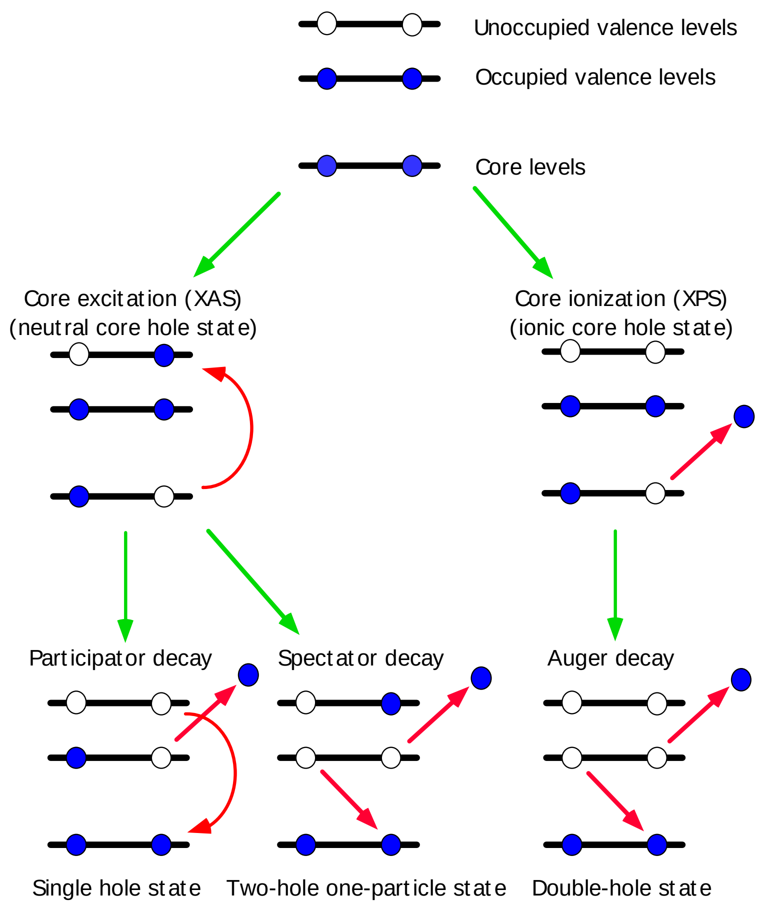
The energy resolution of electron spectrometers



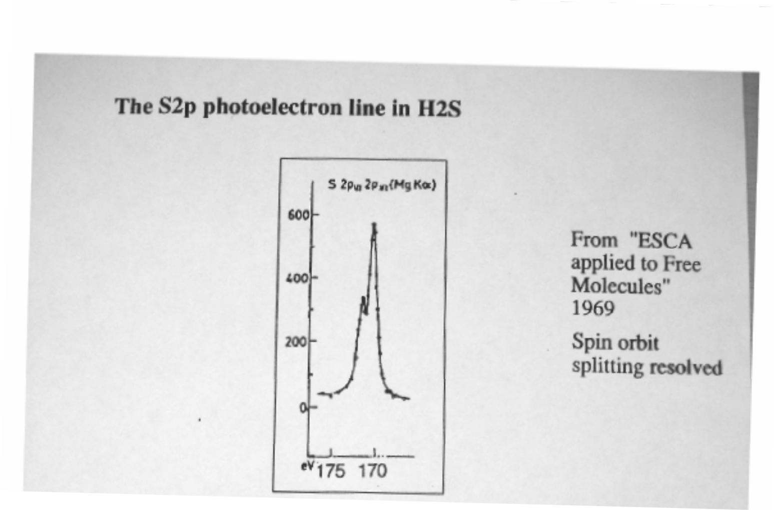
The diagram displays data that have been reported as "High Resolution" in the literature

Core electrons excitation and decay

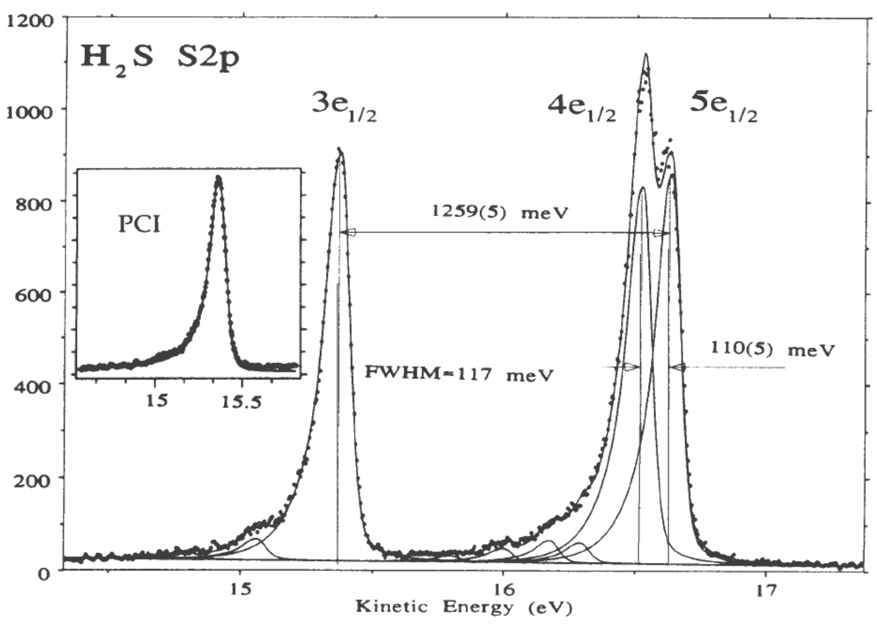
Core excitation, ionization and decay processes.



Improvement of resolution



From ESCA applied to free molecules 1969



SR excitation MAX 1993

High Resolution X-ray photoelectron spectroscopy

New effects studied at 3-G facilities

- Core levels
  - Vibrational fine structure
  - Molecular field splitting
  - Parity splitting
  - Line profiles
    - Post collision
    - Inter Atomic Coulombic Decay (ICD)

Sample handling

- Gases
- Molecular and atomic beams
- Cluster beams
- Liquid beams
- Complex surfaces
- Bulk samples

Lasers and SR sources

- Laser excitation in combination with SR and advanced spectroscopy
- Laser cooling
- Laser dissociation

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Some examples

- Inter Atomic Coulombic Decay (ICD)

Theoretical prediction:
L. S. Cederbaum, J. Zobeley, and F. Tarantelli, Phys. Rev. Lett. 79, 4778 (1997); J. Zobeley, L. S. Cederbaum, and F. Tarantelli, J. Chem. Phys. 108, 9737 (1998).

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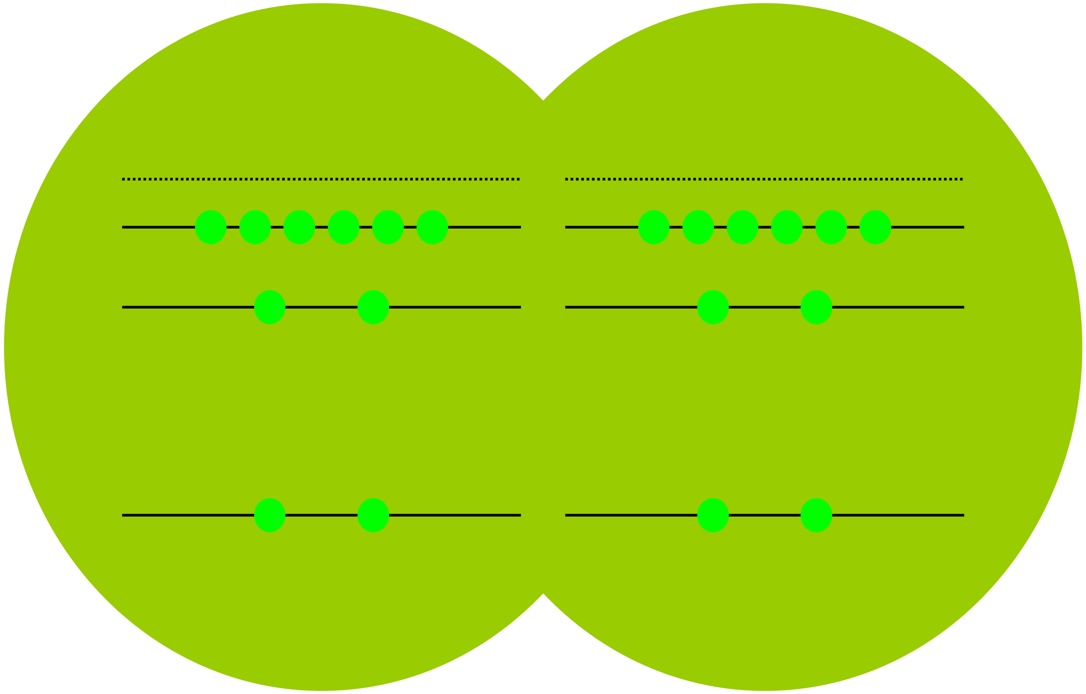
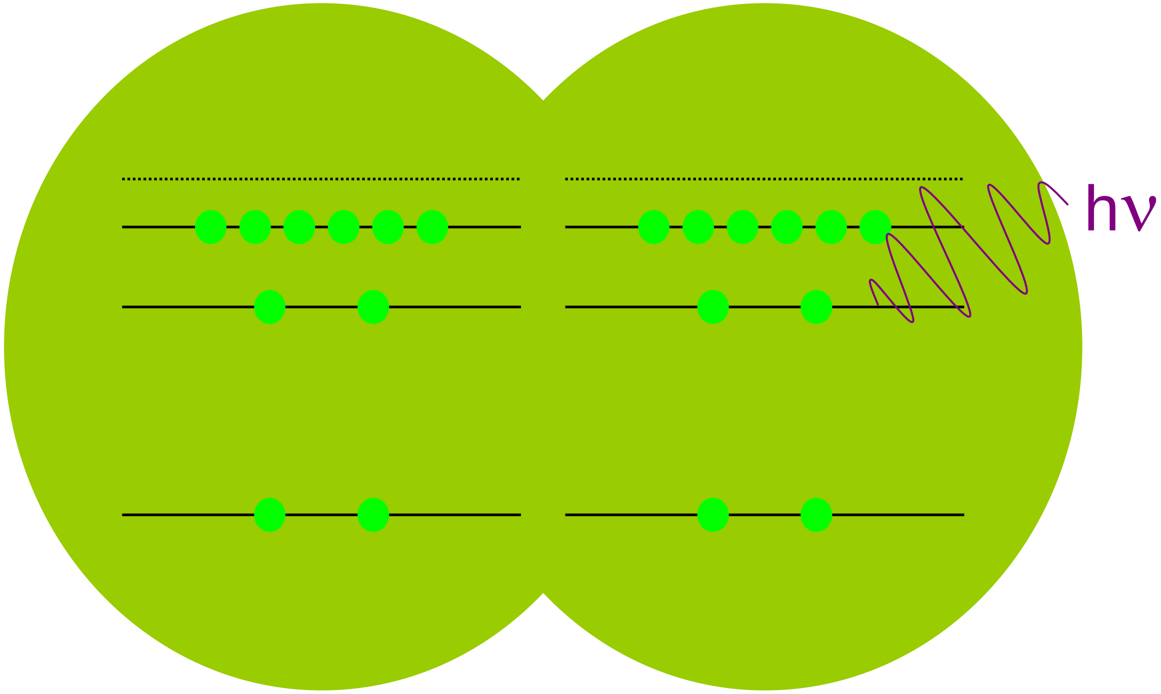
Interatomic Coulombic Decay



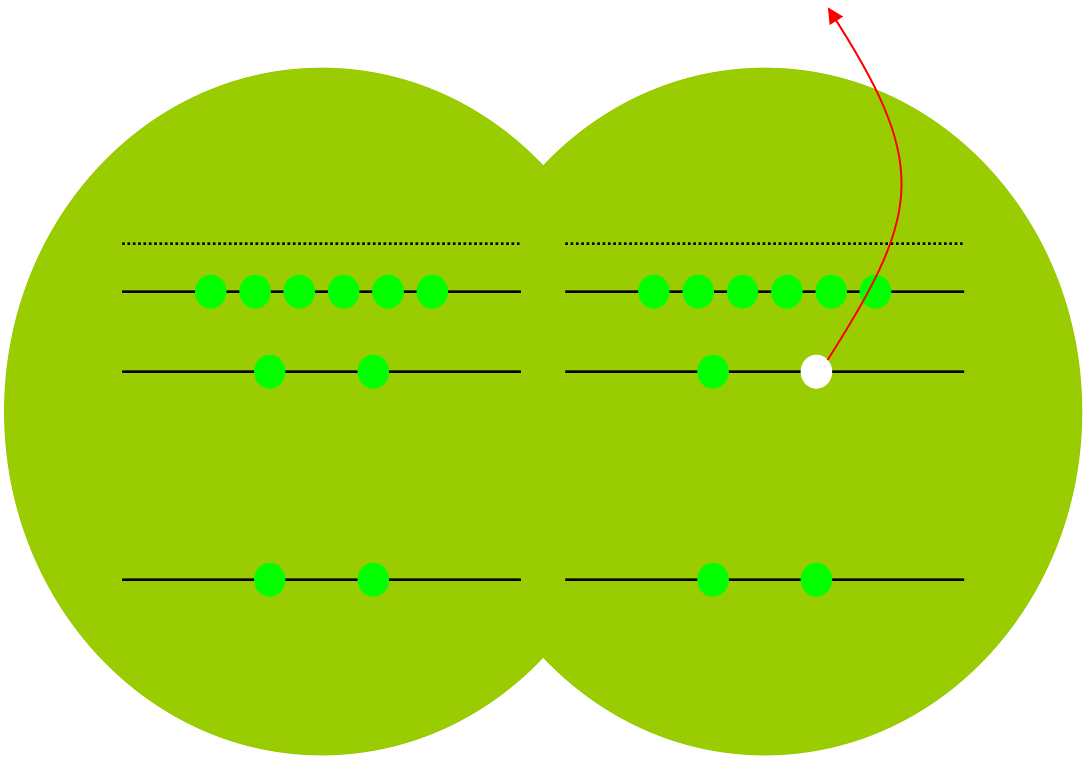
Ne dimer

Interatomic Coulombic Decay



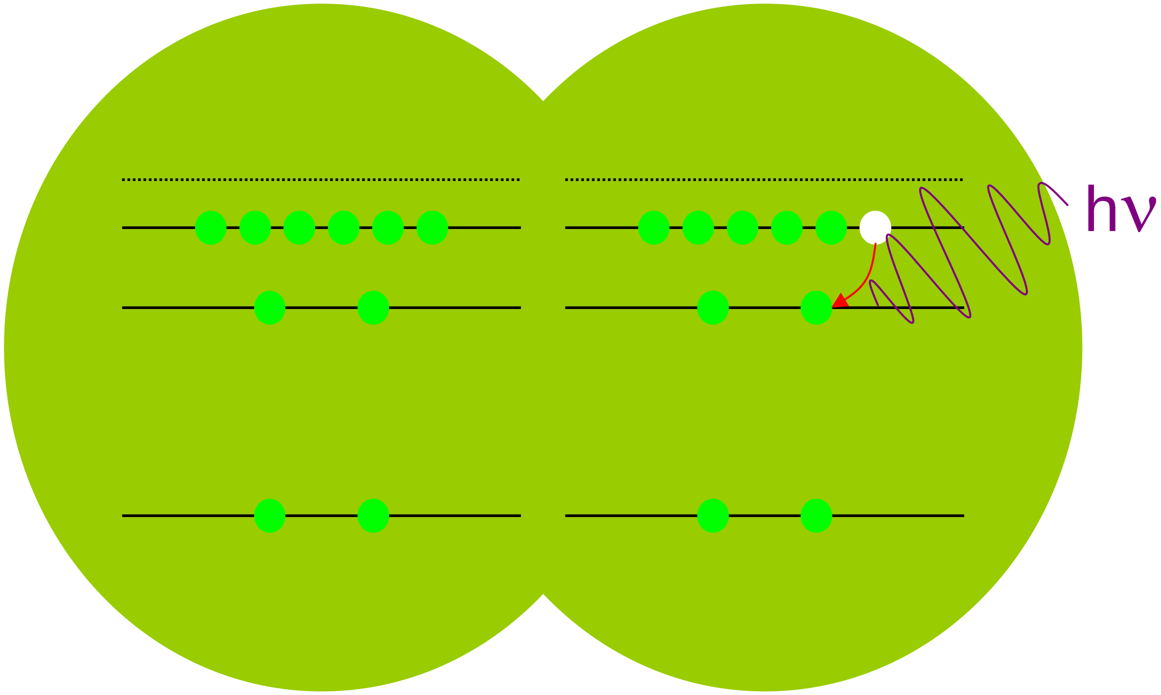
Ne dimer

Interatomic Coulombic Decay



Ne-Ne $(2s)^{-1}$

Interatomic Coulombic Decay



Radiative decay -> Ne-Ne $(2p)^{-1}$

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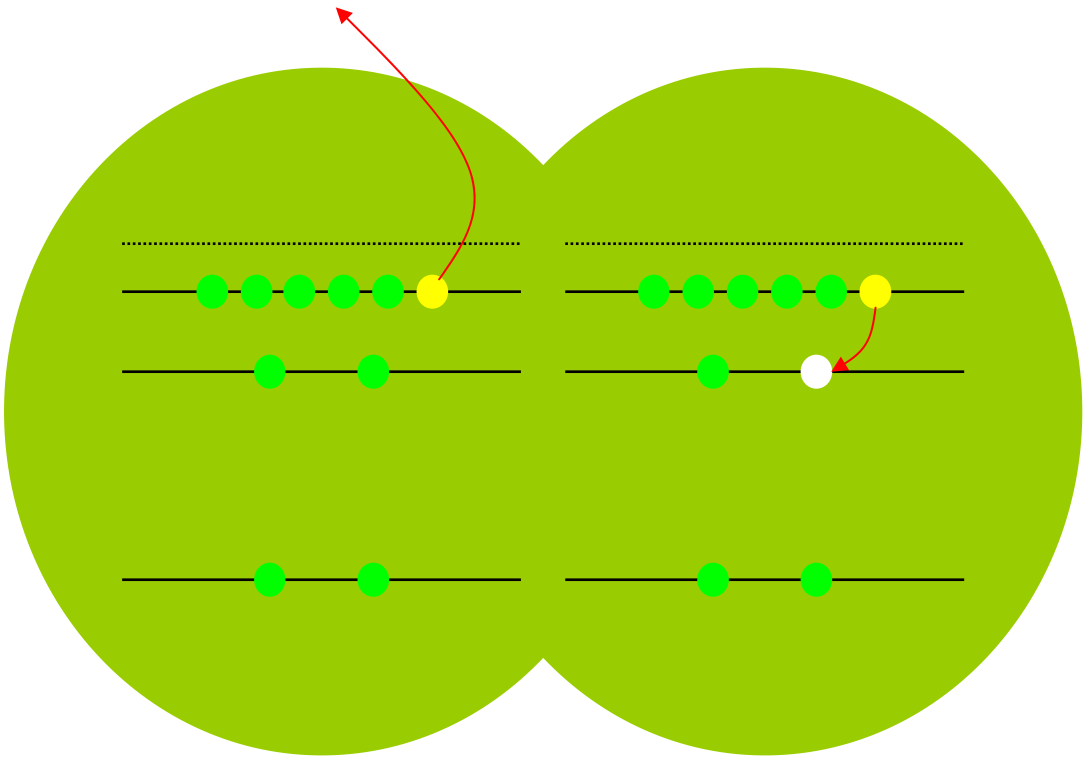
Interatomic Coulombic Decay



Interatomic Coulombic Decay, ICD

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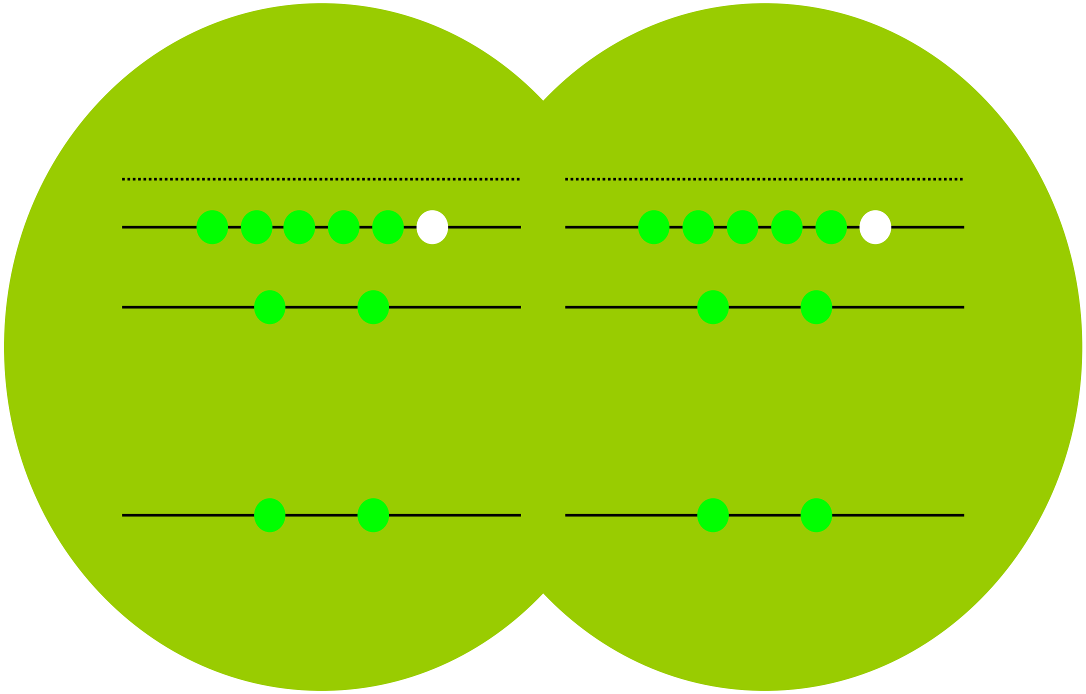
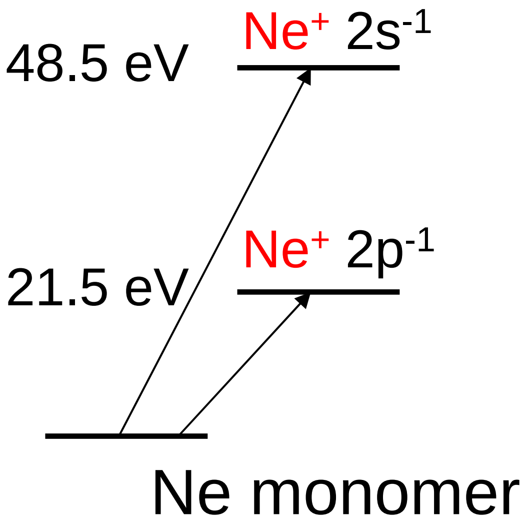
Interatomic Coulombic Decay

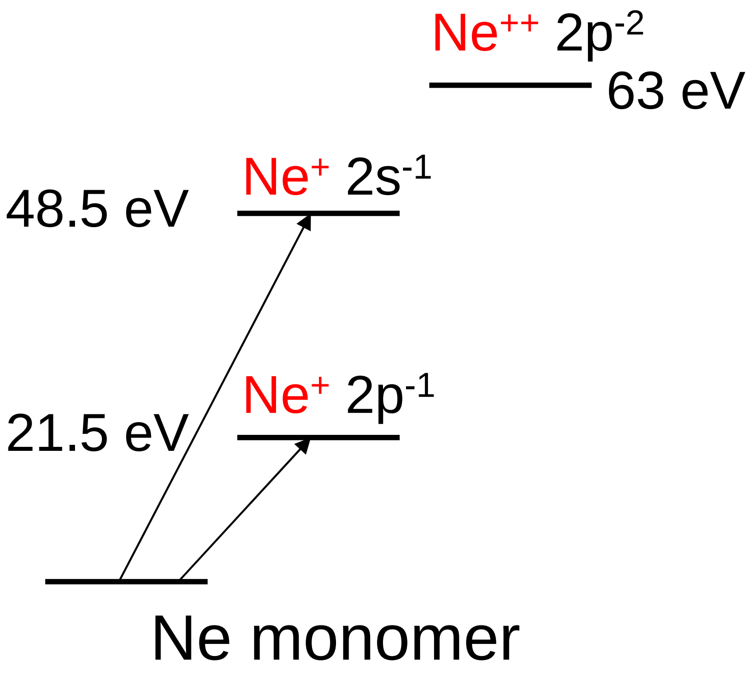


Ne $(2p)^{-1}$-Ne $(2p)^{-1}$

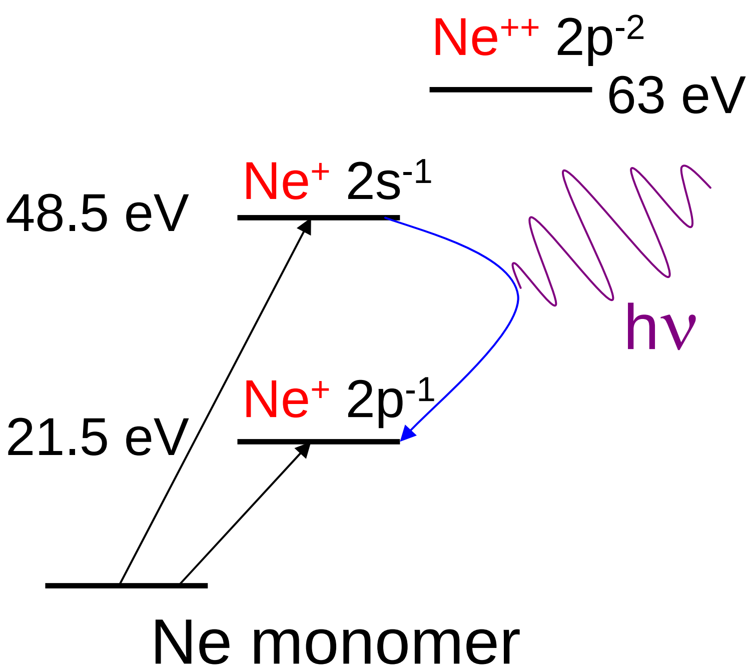
Interatomic Coulombic Decay



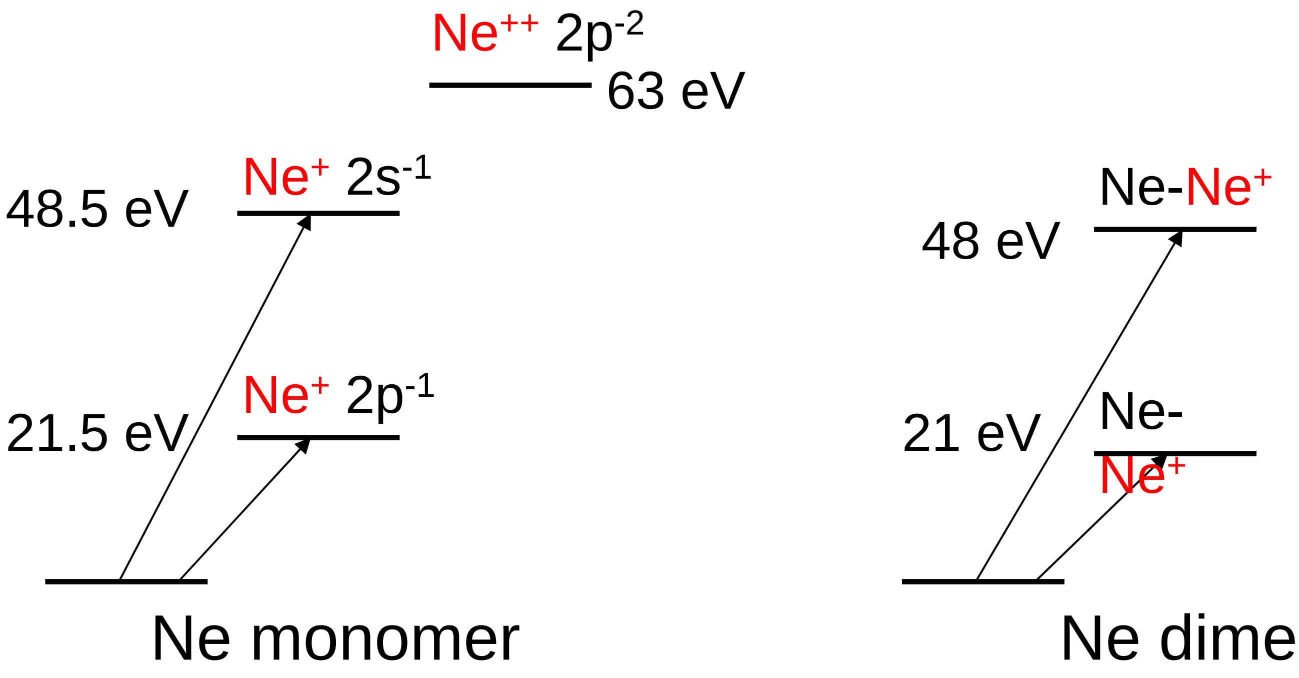
Interatomic Coulombic Decay



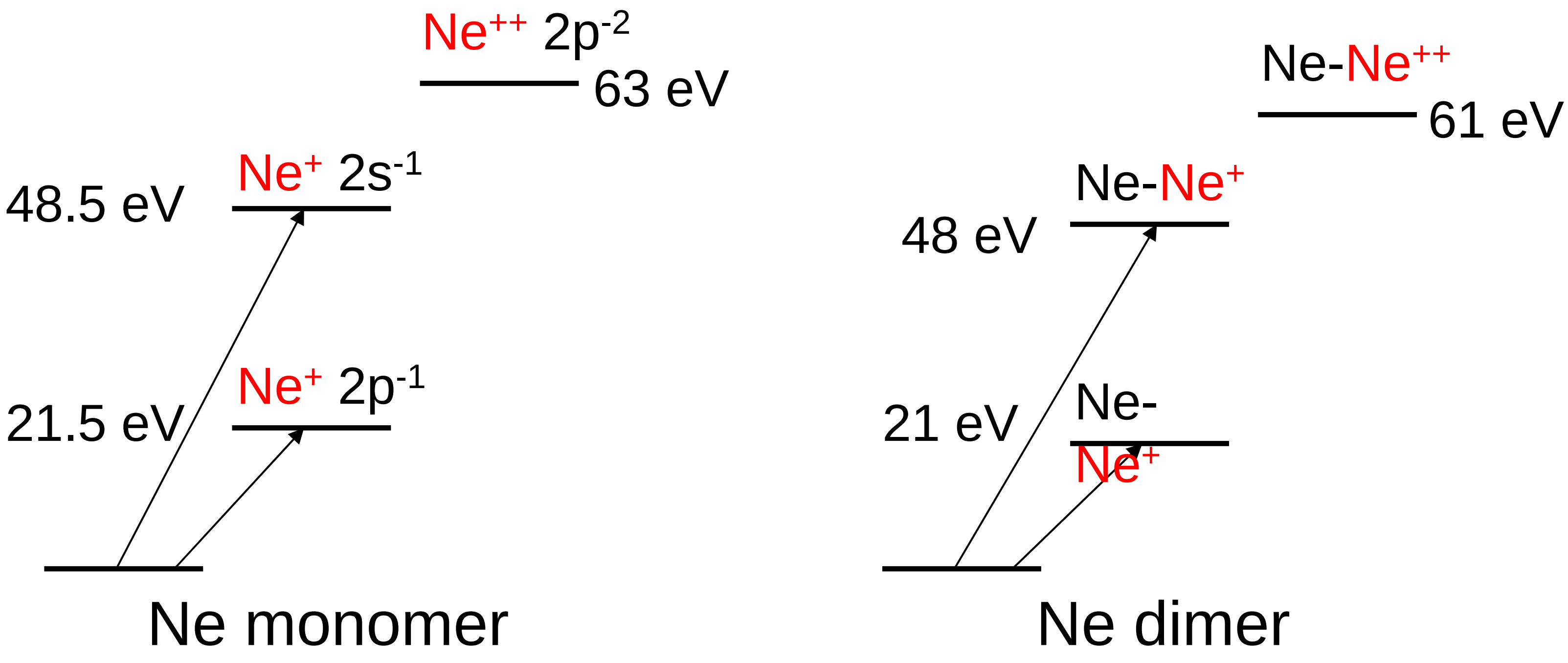
Interatomic Coulombic Decay



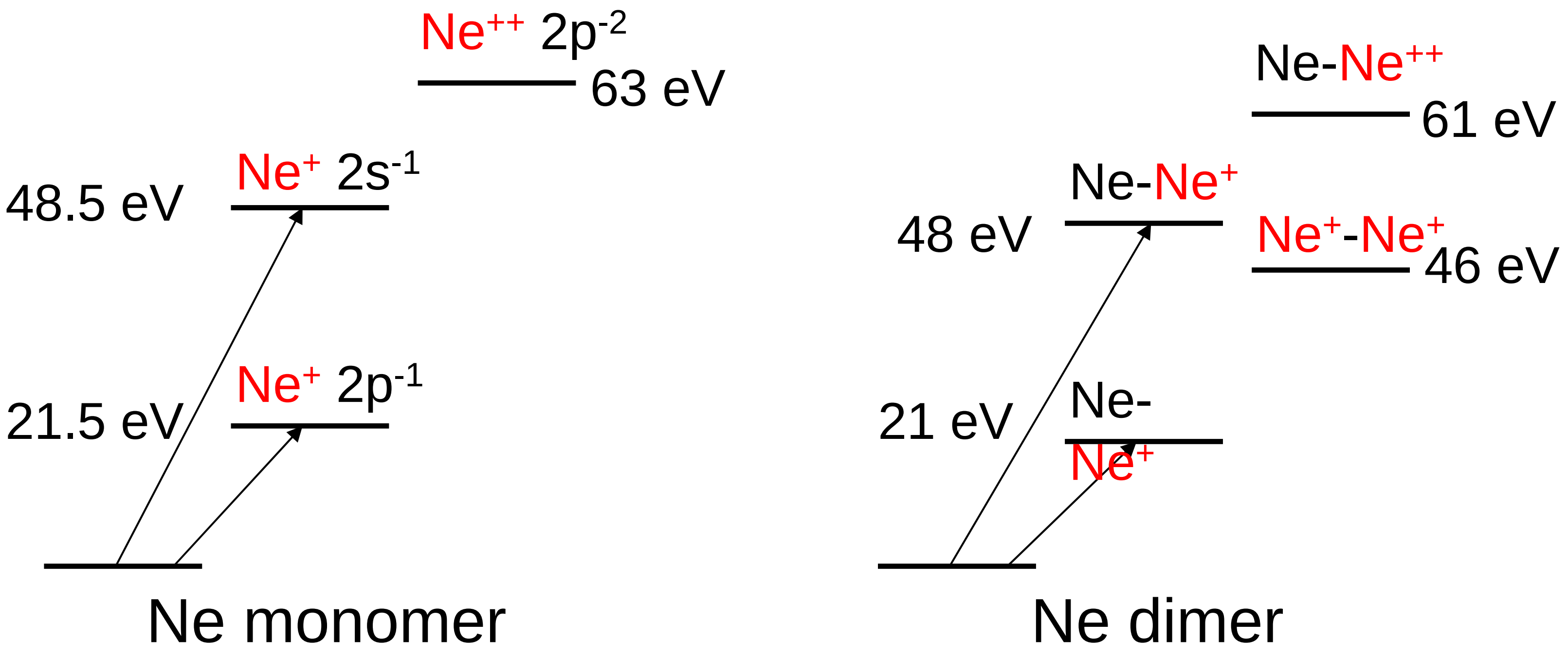
Interatomic Coulombic Decay



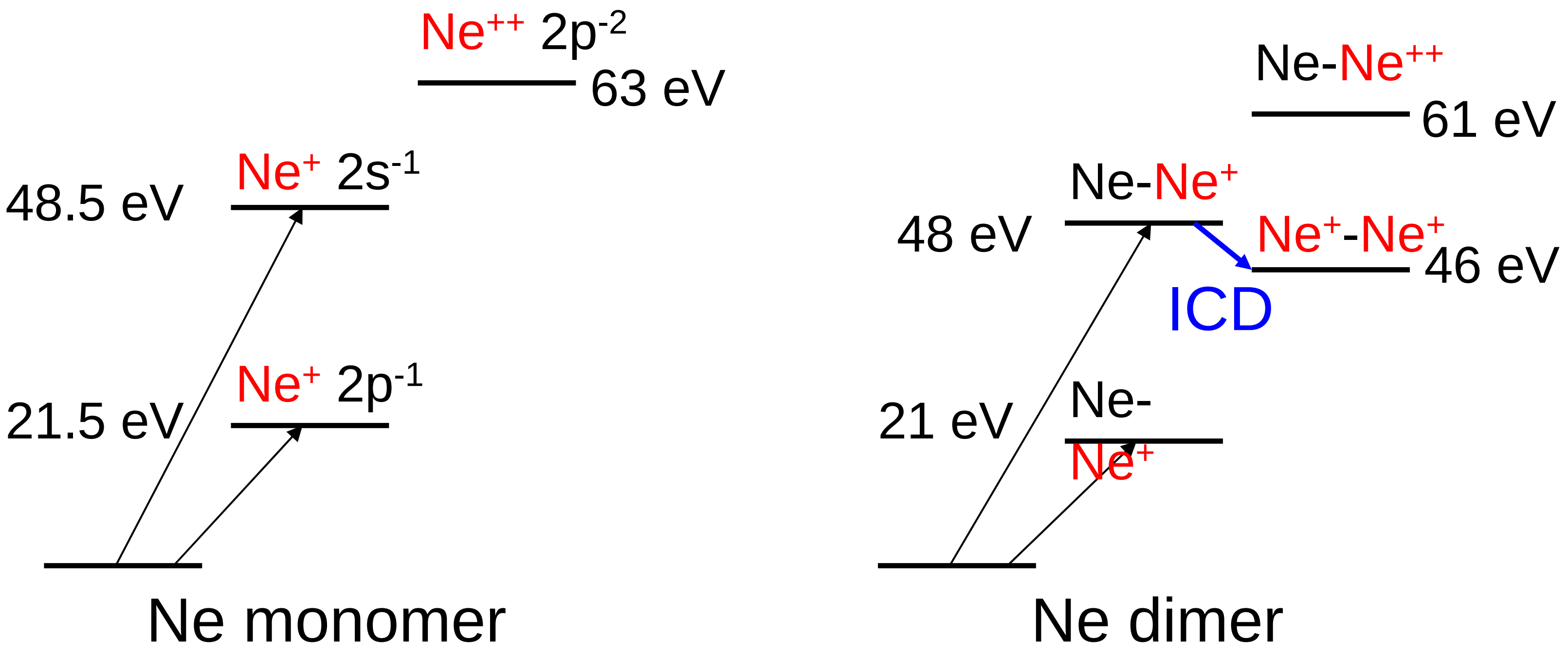
Interatomic Coulombic Decay

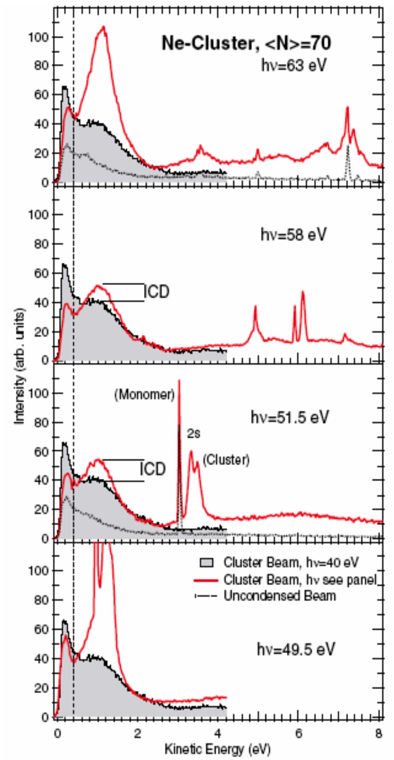


Interatomic Coulombic Decay



Interatomic Coulombic Decay





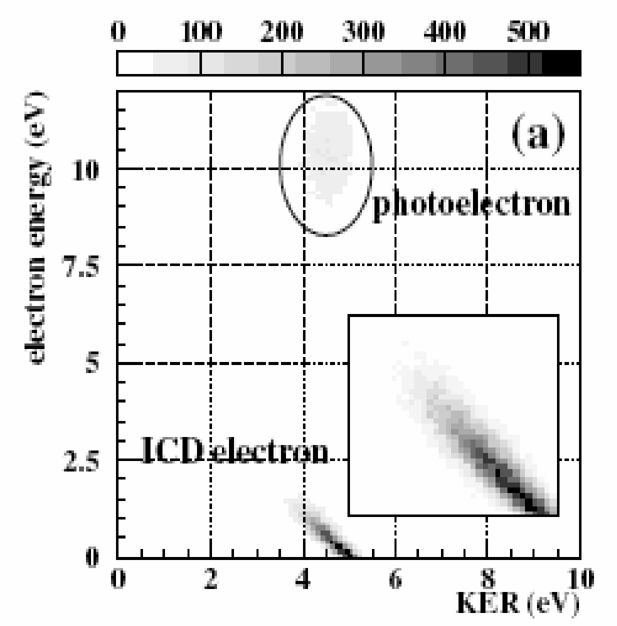
ICD-experimental evidence

First observation:
Hergenhahn and co-workers observe increase i signal of low kinetic energy electrons above Ne 2s threshold.

S. Marburger et al.
PRL **90**, 203401 (2003)

ICD-experimental evidence

COLTRIMS



$h\nu$=58.8 eV
Below DIP

KER from dimer
Coulomb explosion

T. Jahnke *et al.*,
PRL **93**, 163401 (2004)

ICD-distance dependence

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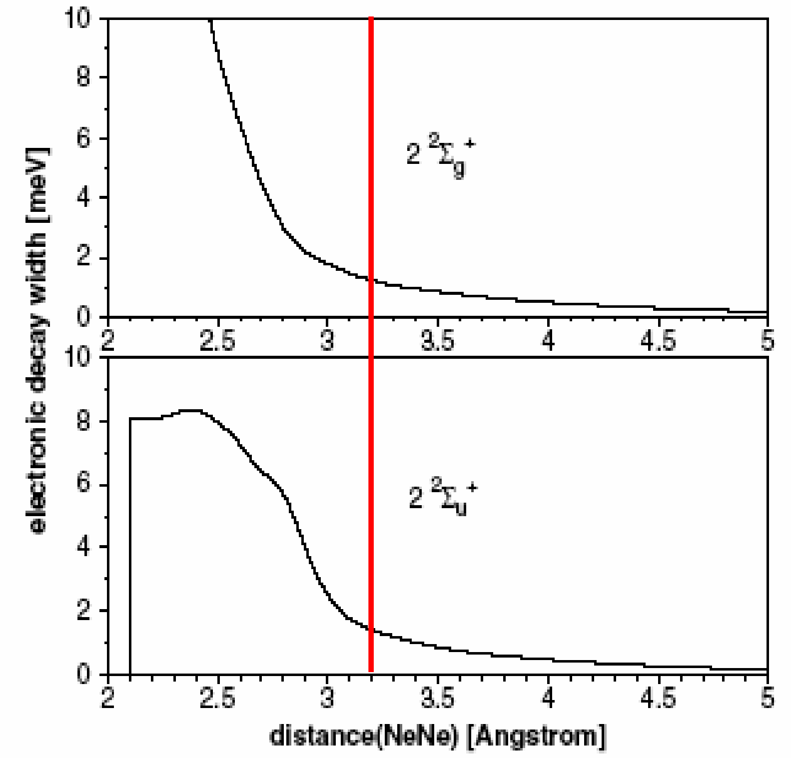
Dimer equilibrium distance

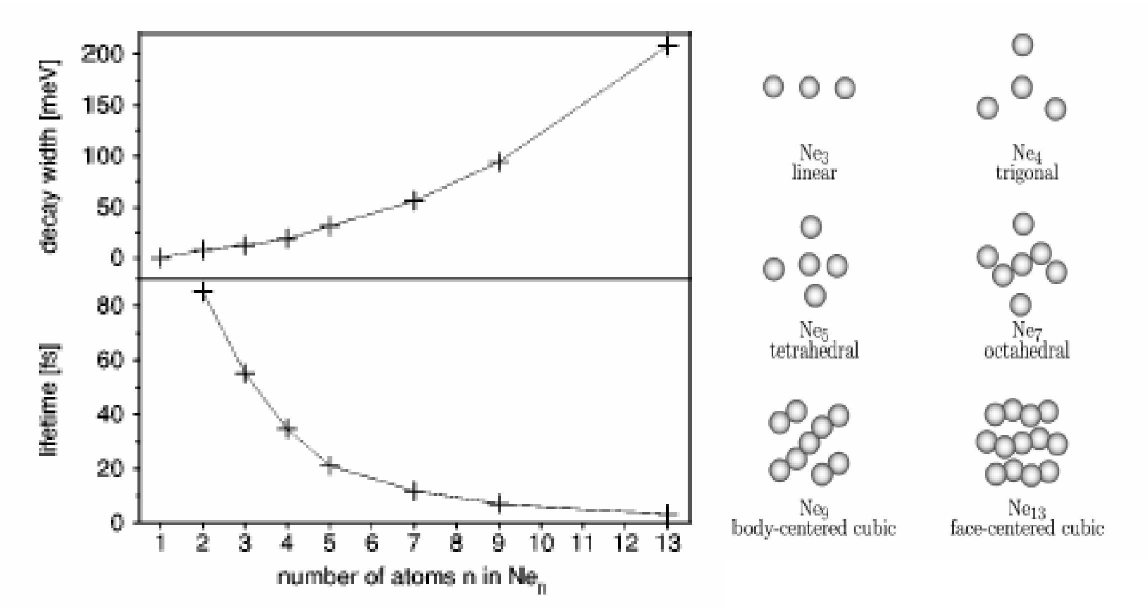


Decay width vs. internuclear distance

R. Santra *et al.*, PRL **85**, 4490 (2000)

ICD-size dependence

Size dependence of decay rate



For Ne_{13}

$\tau_{bulk} \approx 3$ fs

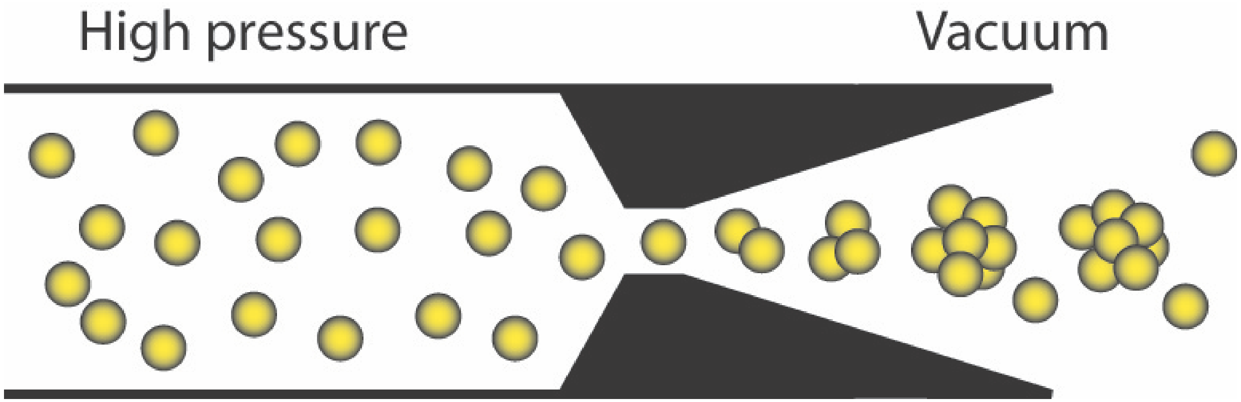
($\Gamma_{bulk} \approx 200$ meV)

$\tau_{surface} \approx 10$ fs

($\Gamma_{surface} \approx 60$ meV)

R. Santra *et al.*, PRB **64**, 245104 (2000)

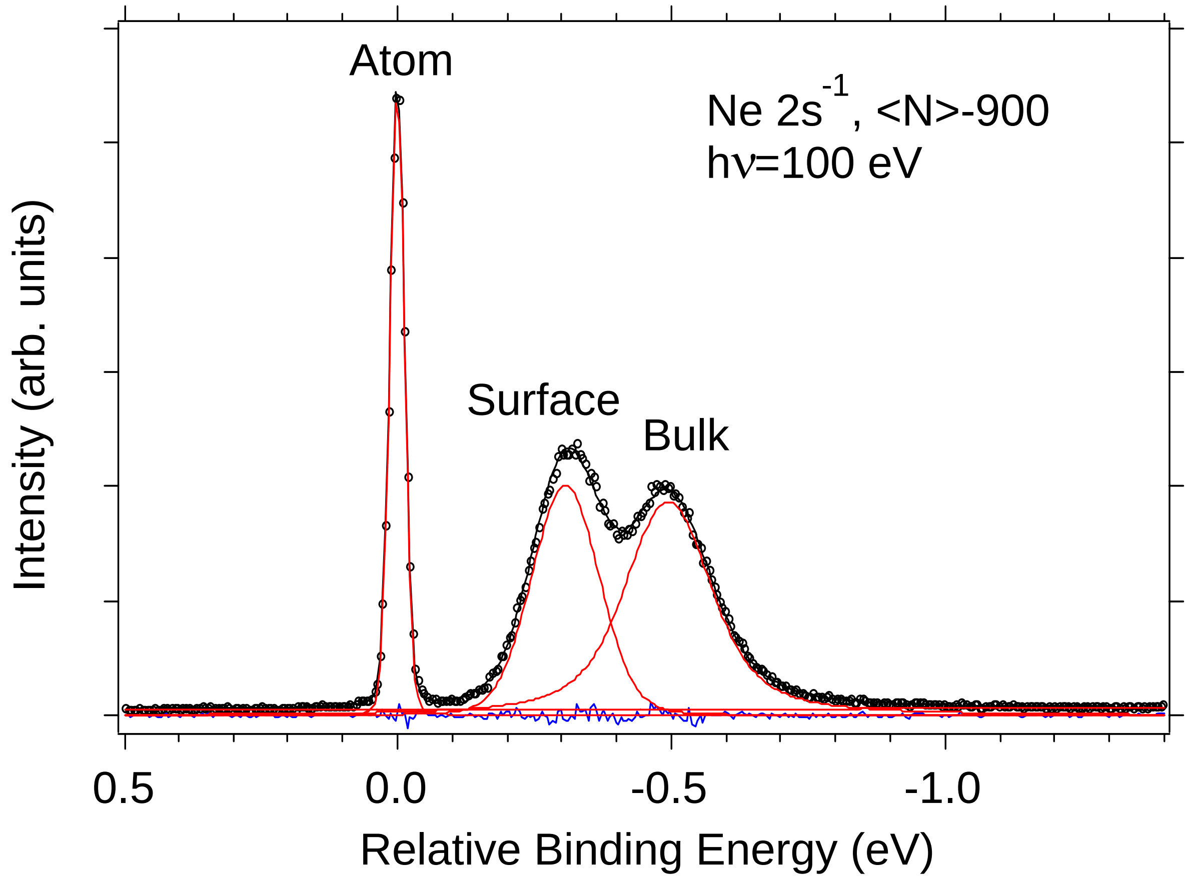
Cluster production



Distribution of sizes around <N>

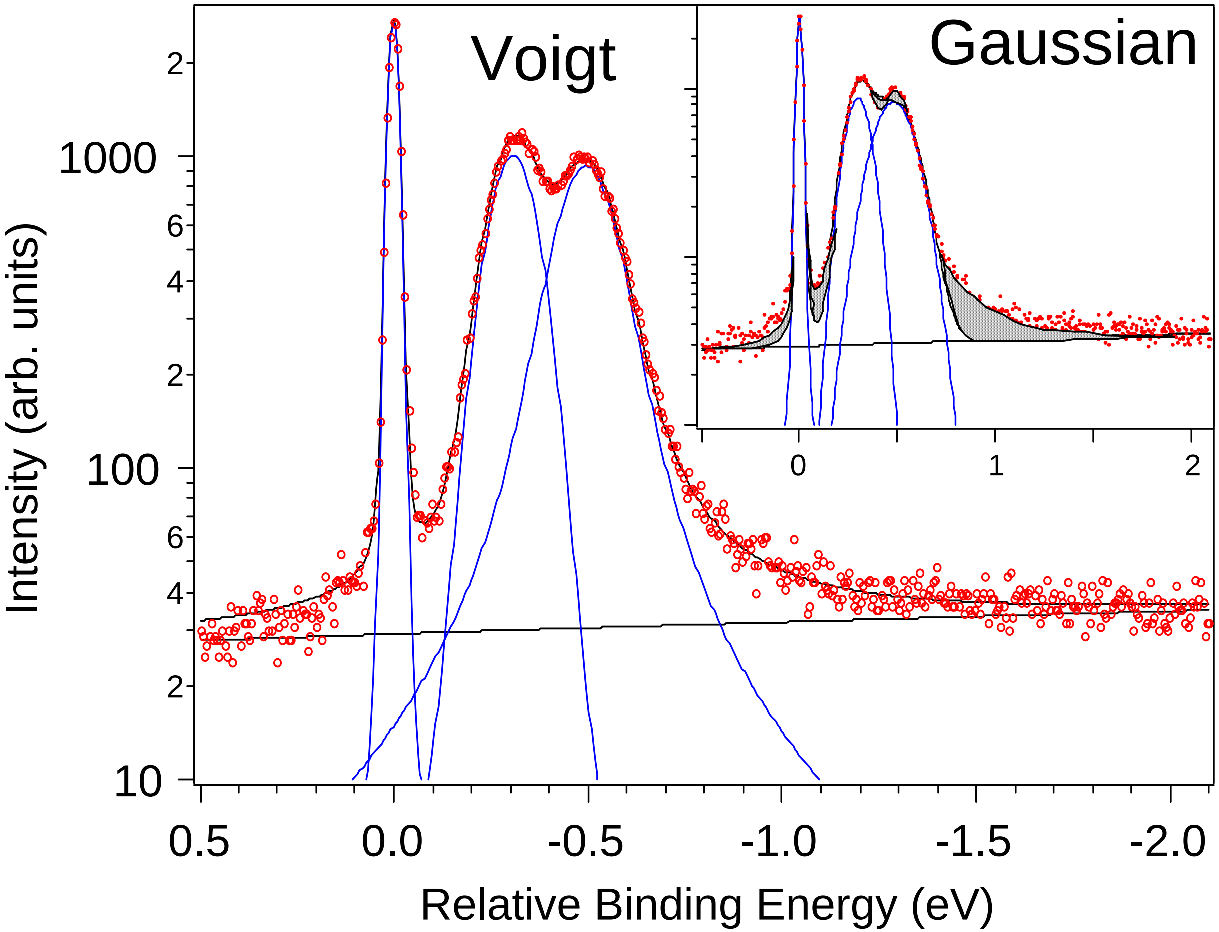
Rare gases: <N>= f(p,T,nozzle, gas)

ICD-cluster PES



G. Öhrwall *et al.*, PRL **93**, 173401 (2004)

ICD-cluster PES



Lorentzian needed to describe bulk peak! ($\Gamma \approx 100$ meV)

Surface peak close to Gaussian. ($\Gamma < 20$ meV)

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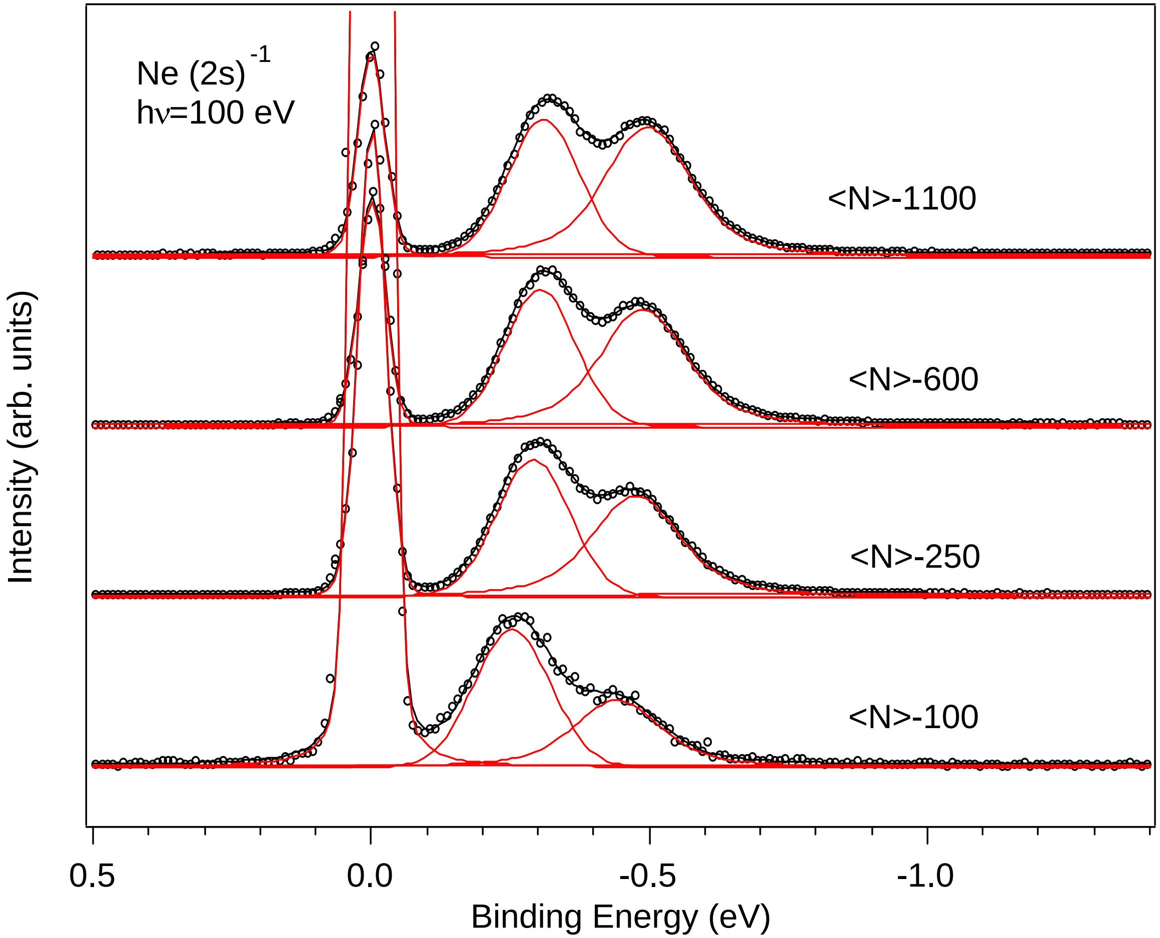
ICD-size dependence



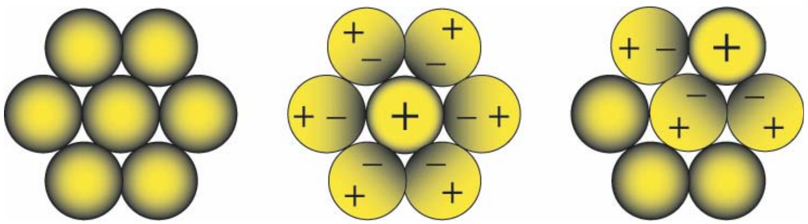
Width independent of size for range 100-1000 atoms:

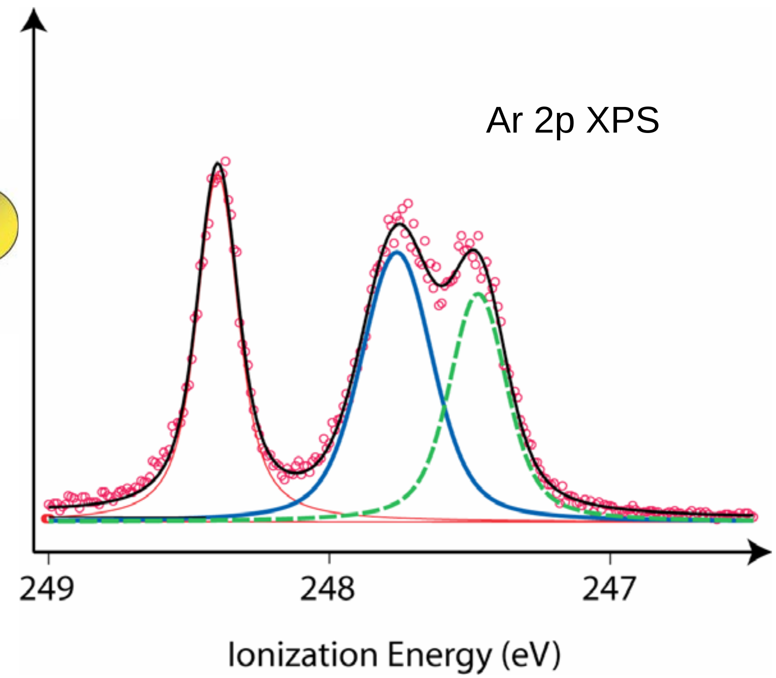
$\Gamma_{bulk} \approx 100$ meV

$\Gamma_{surface} < 20$ meV

Rare-gas clusters Core levels

1. Polarization screening



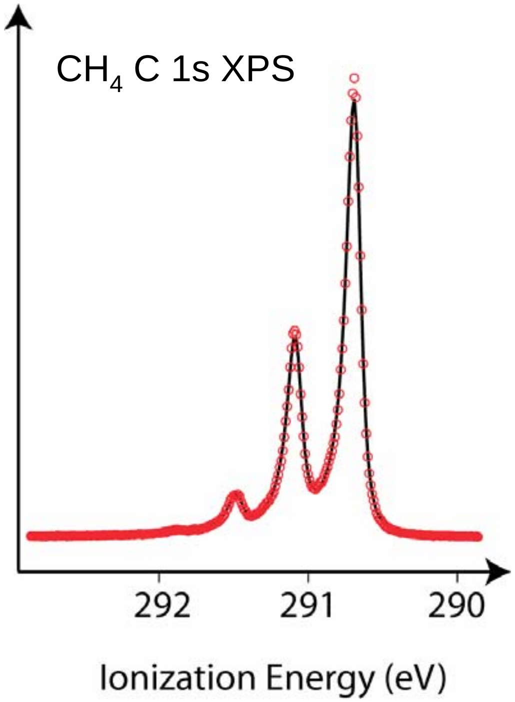


2. Vibrations

Gaussian limit of Linear coupling approximation

3. Size distribution

Vibrations in molecules



Well described in terms of the Franck-Condon principle

Harmonic approximation: independent contributions from each normal mode

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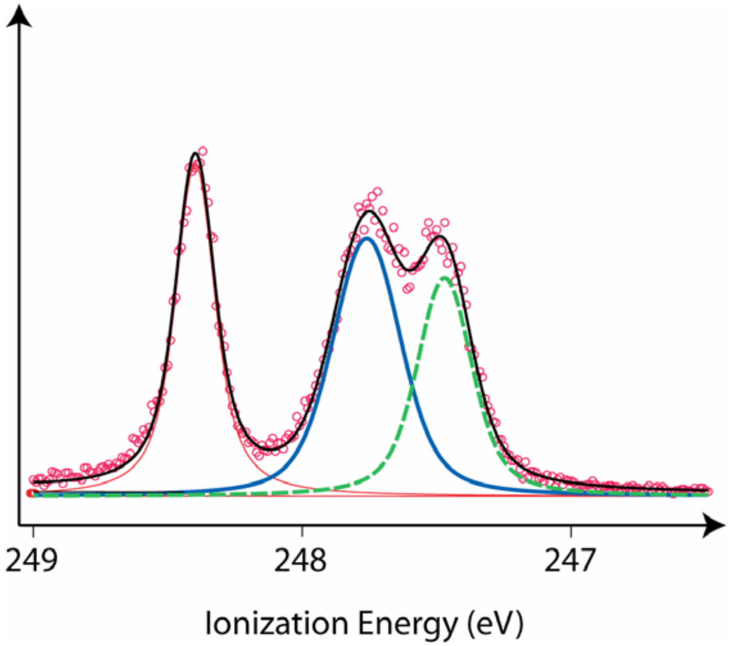
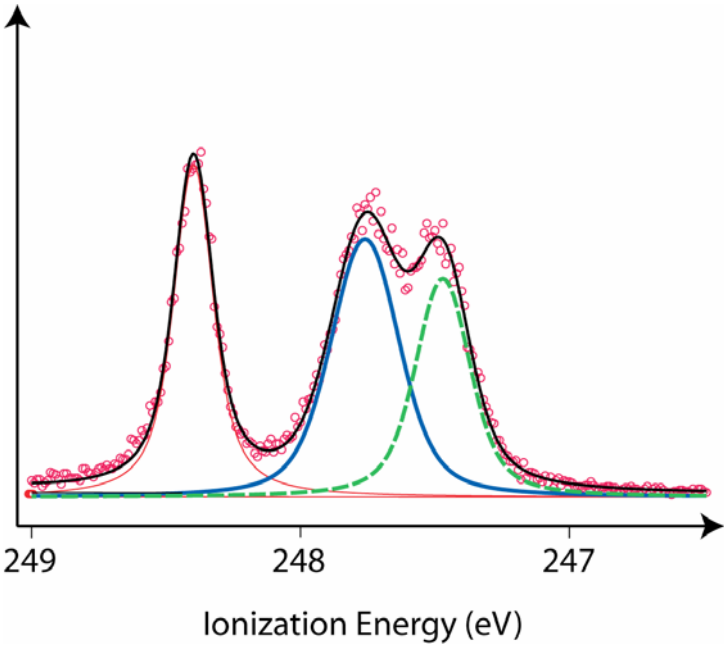
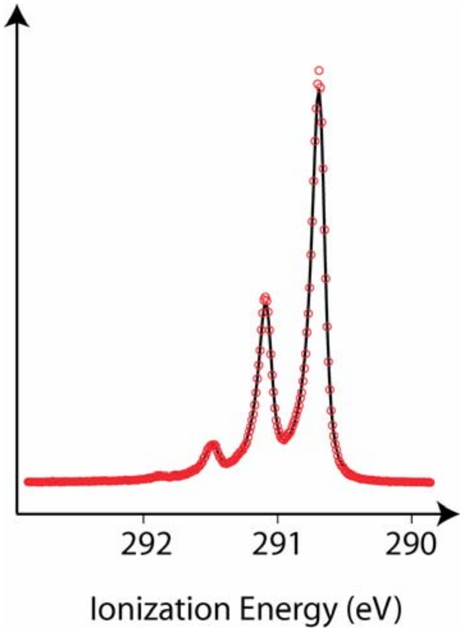
Vibrations in clusters



Vibrations in clusters



+



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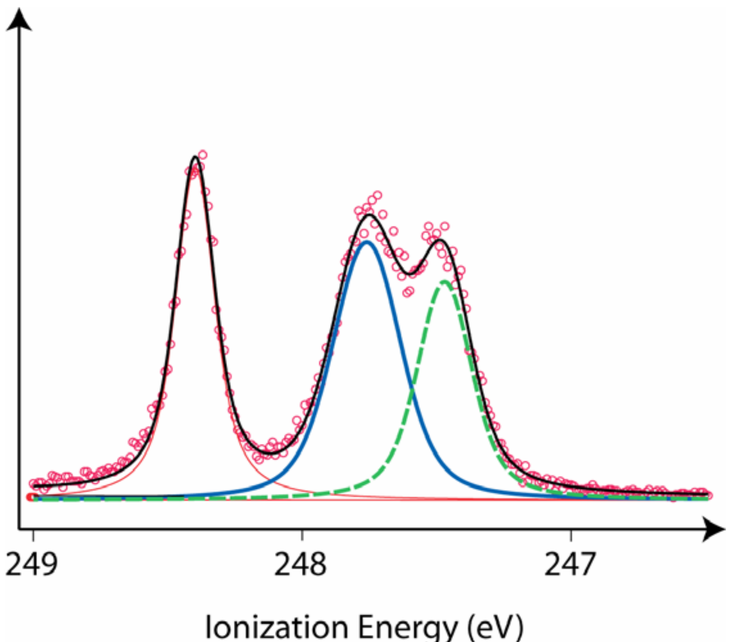
Vibrations in clusters



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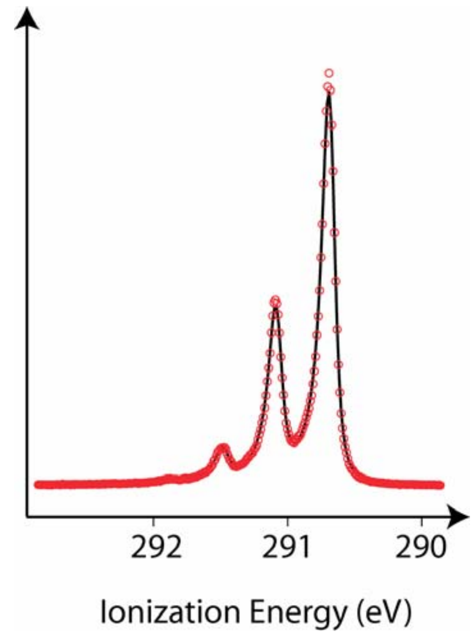

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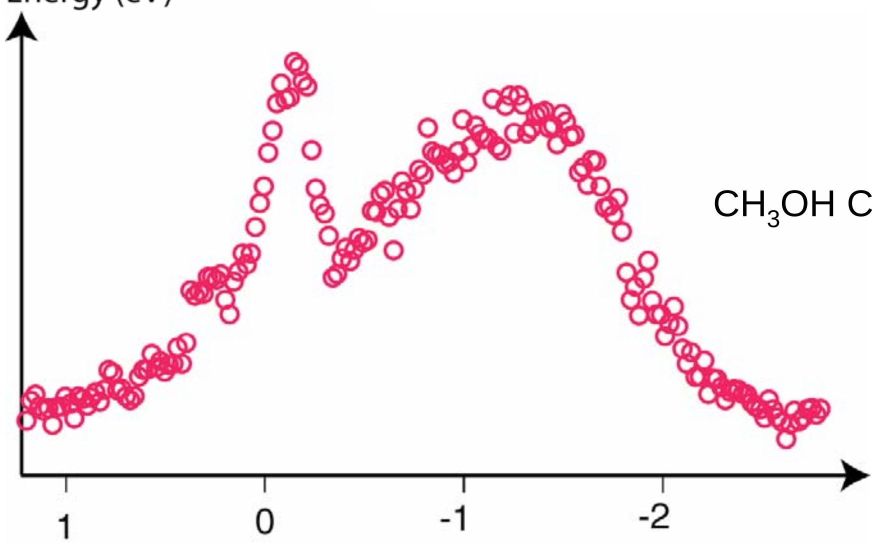
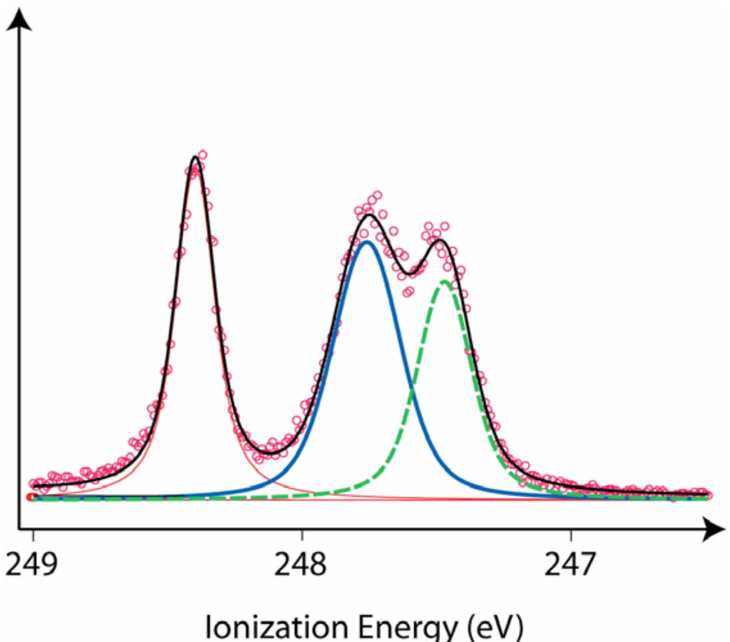
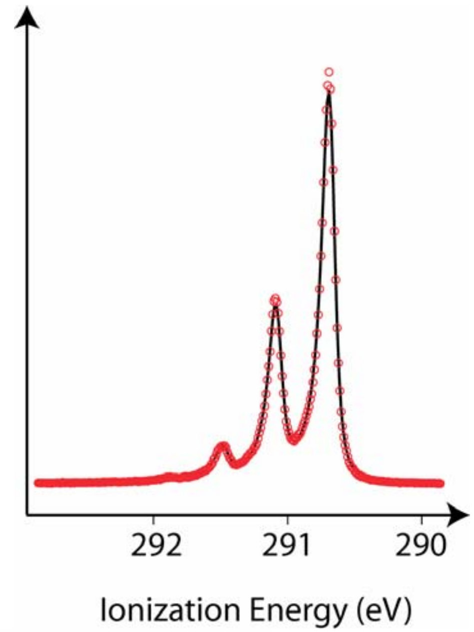


CH_3OH C 1s XPS

Vibrations in clusters



+



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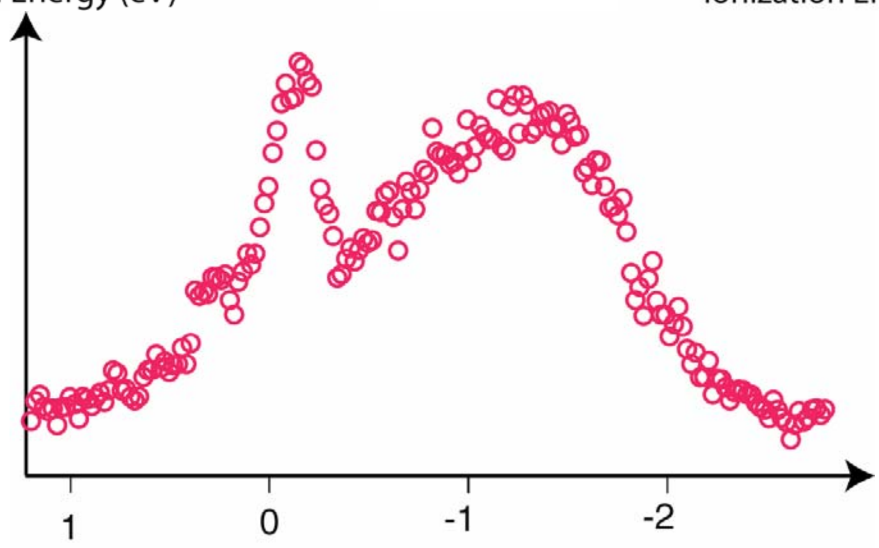

?

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Vibrations in clusters

Complication: many modes

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Vibrations in clusters

Complication: many modes

BUT

Force constants:
Intra-molecular: strong
Inter-molecular: weak

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Vibrations in clusters

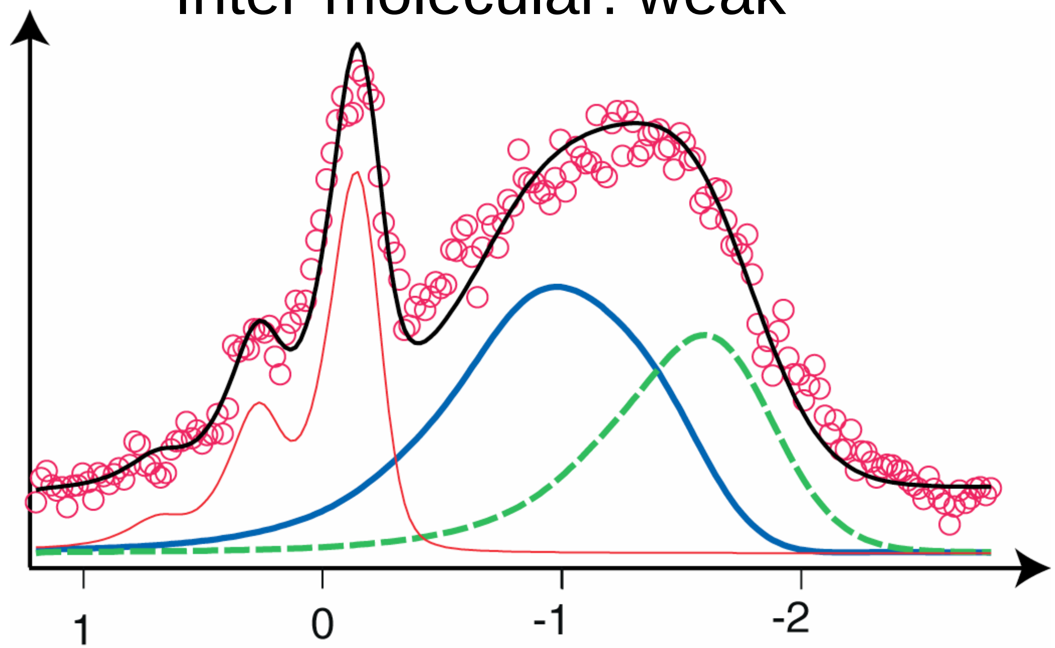
Complication: many modes

BUT

Force constants: Intra-molecular: strong
Inter-molecular: weak

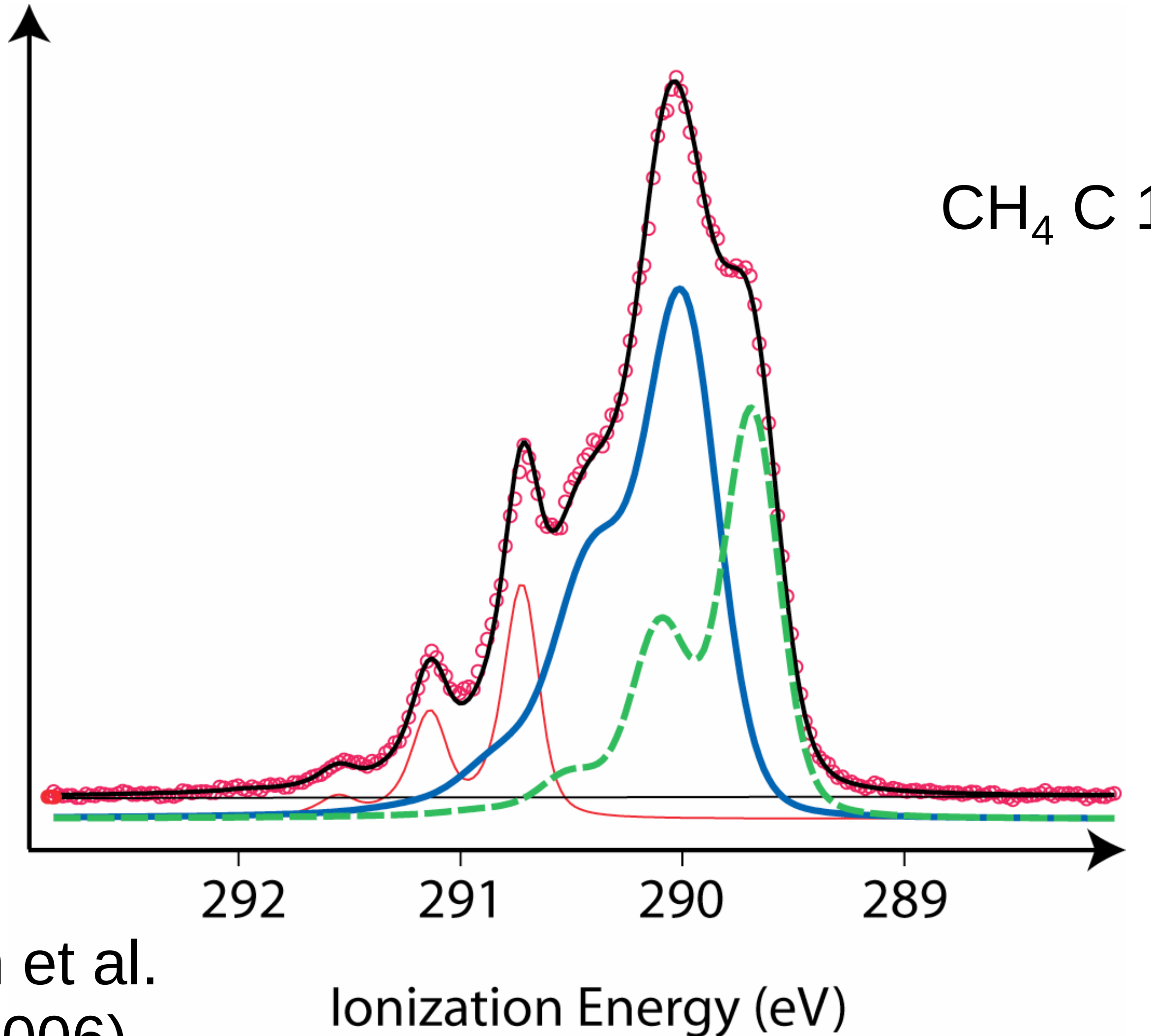
⇓

Separation of contributions



Hydrogen bonding can be studied!

Vibrations resolved in core electron spectrum of cluster



CH_4 C 1s XPS

H. Bergersen et al.
CPL (subm 2006)

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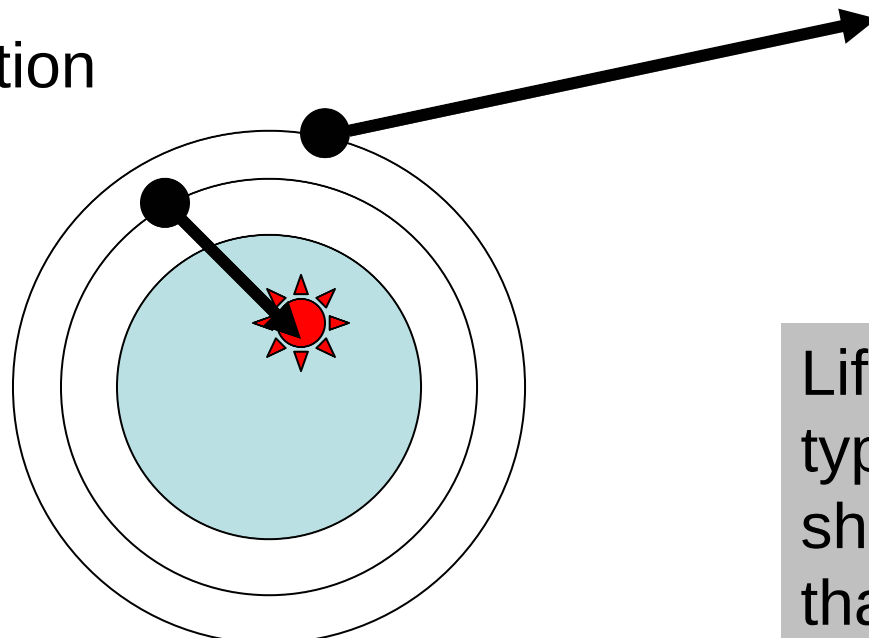
Core hole states have short lifetimes

Core holes look like a positive charge for the outer electrons

The Auger transition fills the core hole on very short timescale



Life-times typically shorter than 3 fs (100 meV)

Example Ne1s

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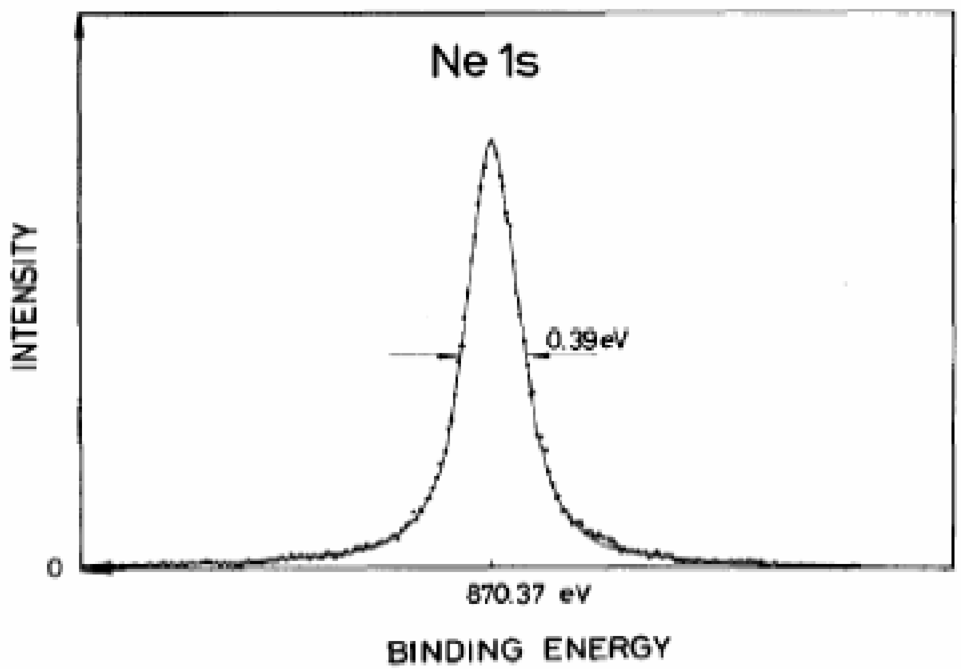

Figure 15. A high resolution recording of the Ne 1s line. The measured full width at half maximum, FWHM, is 0.39 ± 0.02 eV.

Early example
Ne 1s lifetime
width of 0.28 eV
(Δt=1,2 fs)

Analysis of
Voigt Profile
(Lorenztian tails)

U. GELIUS, E. BASILIER, S. SVENSSON, T. BERGMARK and K. SIEGBAHN

Journal of Electron Spectroscopy and Related Phenomena, 2 (1974) 405–434

Why short lived core hole states ?

- The Auger transitions
- Coulomb matrix element

$$\int \varphi_v^*(\mathbf{r}_1)\varphi_v^*(\mathbf{r}_2)\frac{1}{r_{12}}\varphi_c(\mathbf{r}_1)\varphi_\varepsilon(\mathbf{r}_2)\,\mathbf{dr}_1\mathbf{dr}_2$$

Valence orbitals

Core orbital

Continuum orbital

Local character

One center

Integrals dominate for molecules

•Continuum orbital can have any symmetry.
•No selection rules (except parity).
•This integral is large whenever Auger process is energetically possible.

Core Hole states are short lived

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From Chen& Crasemann 1974 (Ar)

TABLE VII. Radiationless transition probabilities (in multiples of 10^{-3} a.u.) and fluorescence yields (in multiples of 10^{-4}) for an Ar $2p$ vacancy in the presence of a partially filled $3p$ shell, for given initial multiplet states.

Initial hole configuration	Initial multiplet term	Auger rate	Fluorescence yield
$(2p)^{-1}(3p)^{-1}$	^1S	9.210	0.954
	^1P	0.479	18.34
	^1D	10.235	0.859
	^3S	0.133	66.15
	^3P	10.906	0.806
	^3D	0.347	25.31
$(2p)^{-1}(3p)^{-2}$	$^2P^{(1)}$	9.556	1.000
	$^2P^{(2)}$	3.38	2.828
	$^2P^{(3)}$	1.686	5.669
	$(^3P)^2S$	0.544	17.566
	$^2D^{(1)}$	14.690	0.651
	$^2D^{(2)}$	0.481	19.832
	$(^3P)^4S$	15.859	0.603
	$(^3P)^4P$	0.150	63.635
	$(^3P)^4D$	0.285	33.56
	$(^1D)^2F$	0.2676	35.717

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Extensive calculations Chen et al 1990

- Hunt for an x-ray laser ?
- Extensive calculations
- A few core excited states with longer lifetimes
- No explanation of narrow lines only output from code

M. H. Chen, F. P. Larkins, and B. Crasemann, At. Data Nucl. Data Tables 43, 1 (1990).

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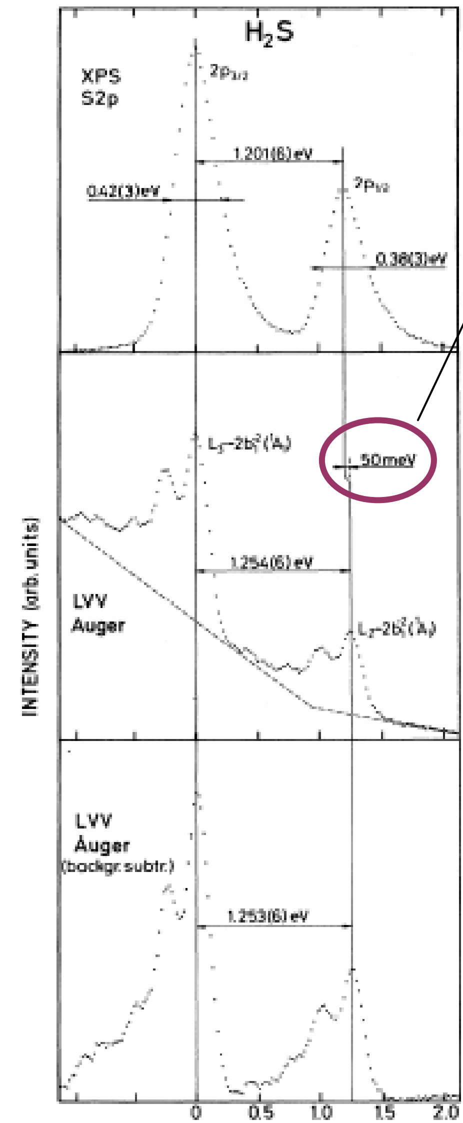
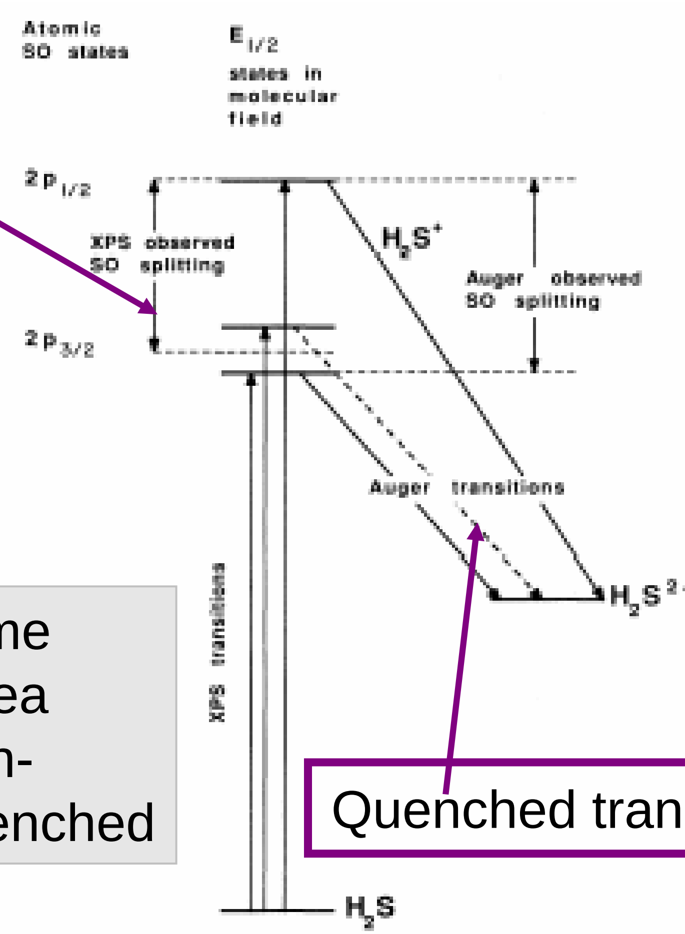
First clue: Quenched Auger transition?



50 meV shift



However, at this time nobody had any idea WHY an Auger transition would be quenched

Quenched transition?

S. Svensson, A. Naves de Brito, M. P. Keane, N. Correia,* and L. Karlsson

PRA 43, 6441 (1991)

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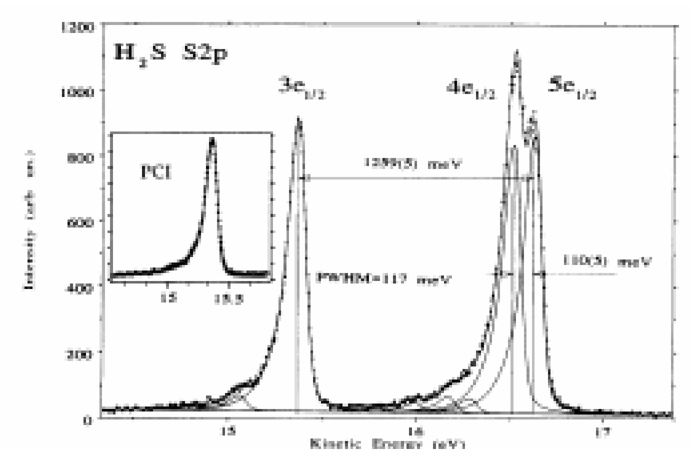
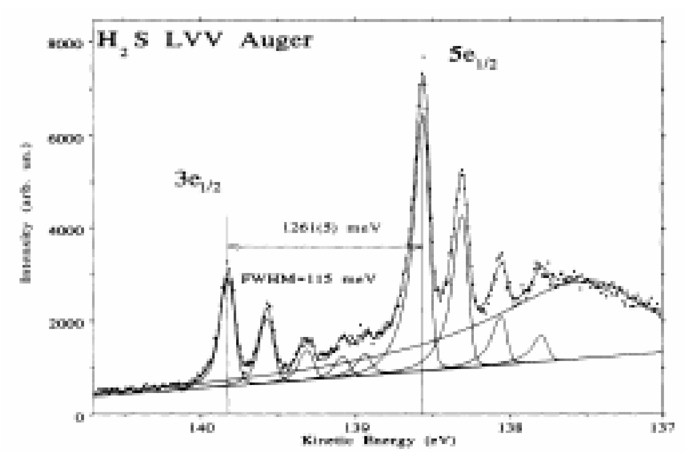
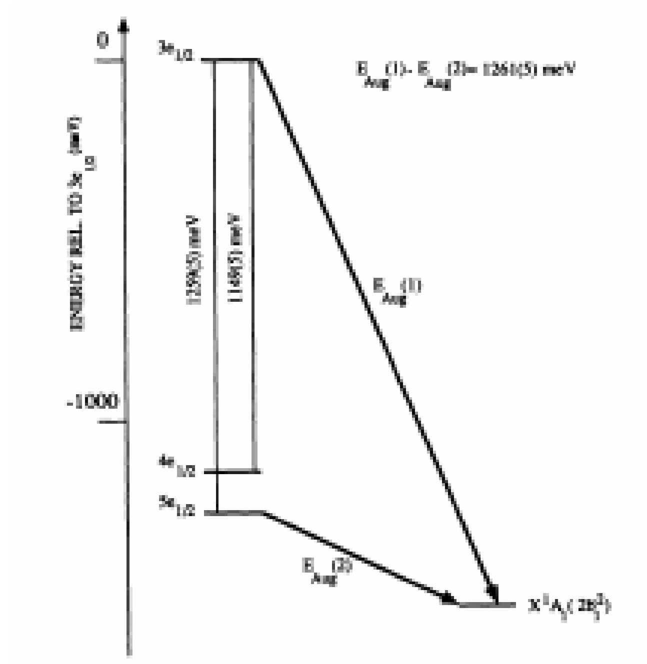
The molecular field splitting of S2p in H_2S resolved 1994 using SR







CLEARLY OBSERVED QUENCHED TRANSITION

Svensson et al PRL 72, 3021

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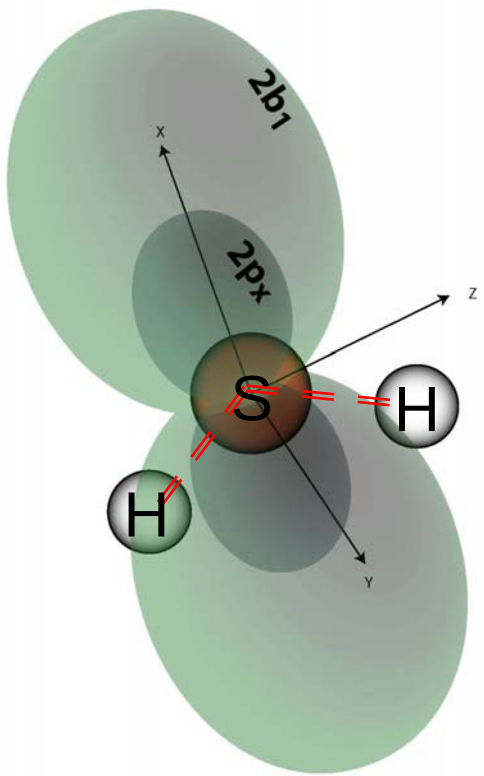
Propensity rule is the clue!



The Auger decay
Is strong only to the 2px
Orbital oriented along the x-
Axis as the 2b1 orbital

Molecular field splitting:

Oriented core orbitals!

PROPENSITY RULE

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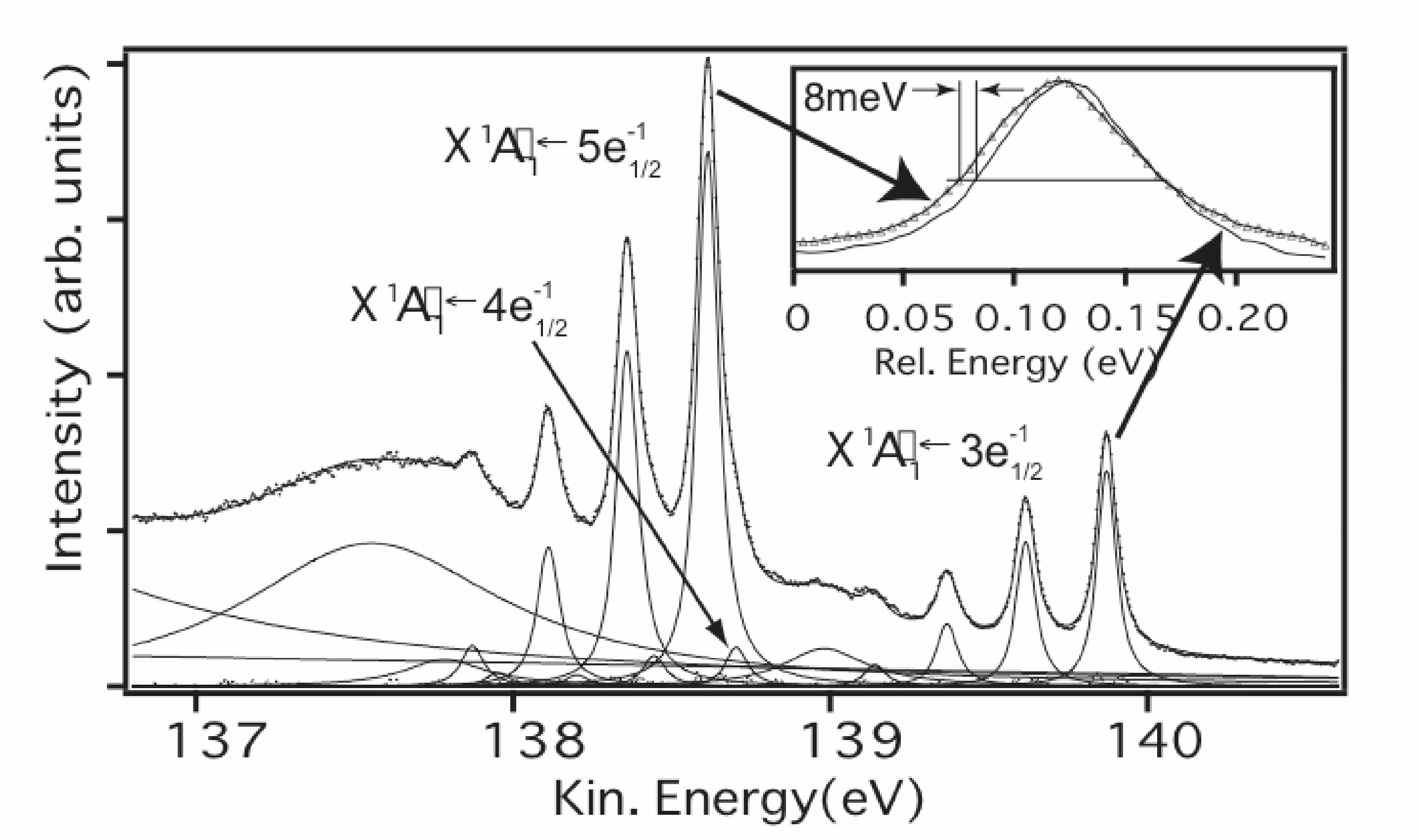
The Auger lines have different widths



The 3e1/2 lines are narrower than the 5e1/2 lines

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Calculations

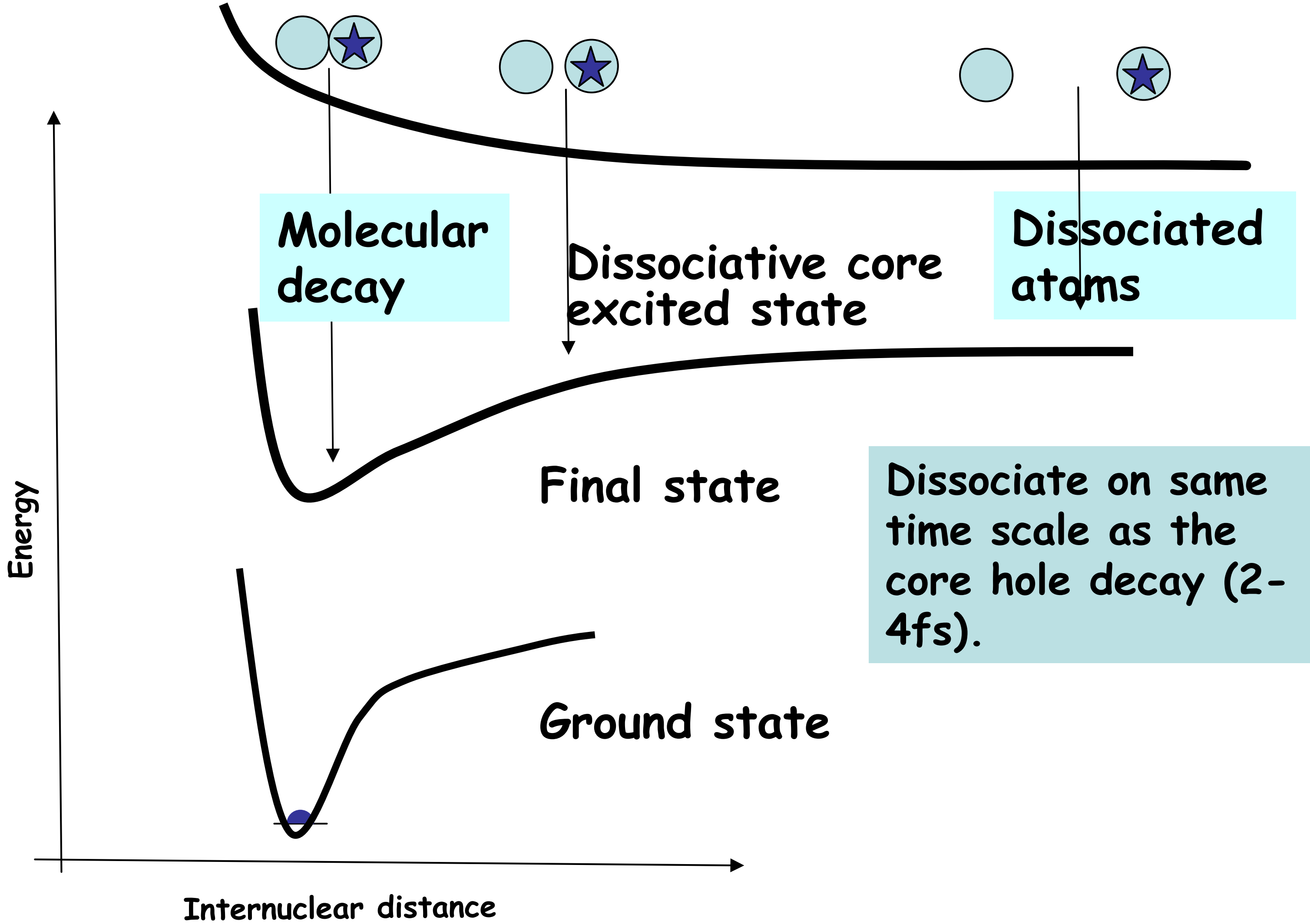
TABLE IV. Experimental and theoretical lifetime widths of the $3e_{1/2}$ and $5e_{1/2}$ core-hole states of H_2S^+.

Core-hole state	Experiment (meV)	Theory (meV)
$3e_{1/2}$	64 ± 2	68
$5e_{1/2}$	74 ± 2	83

Bueno et al PHYSICAL REVIEW A 67, 022714 (2003)

How can we produce long lived states????

ULTRAFAST DISSOCIATION



Dissociate on same time scale as the core hole decay (2-4fs).

OCS S 2p→σ* excitation

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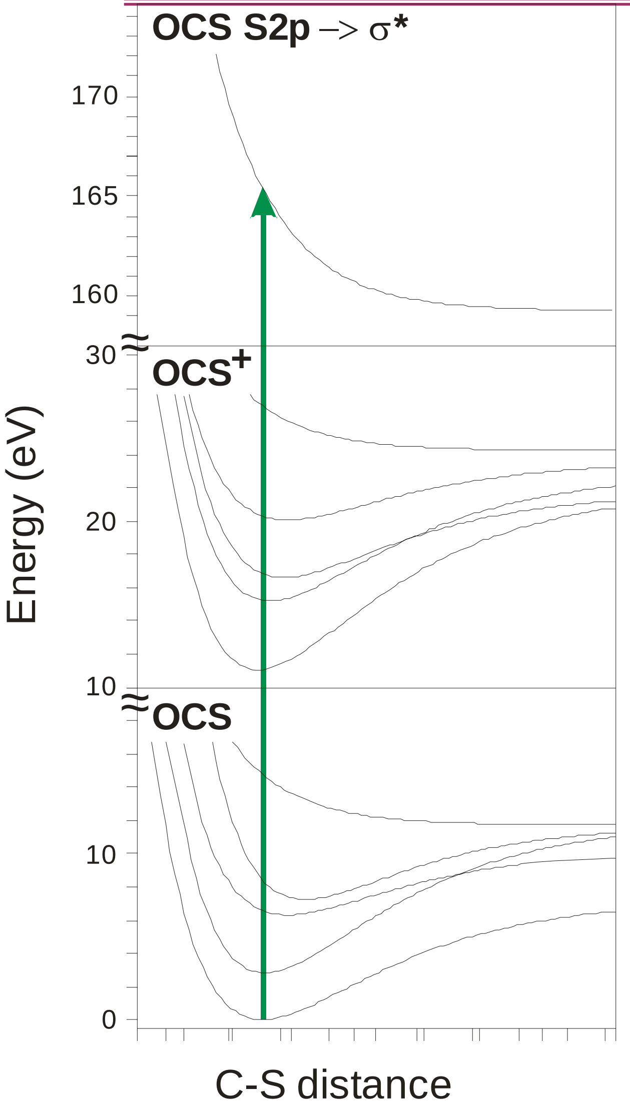
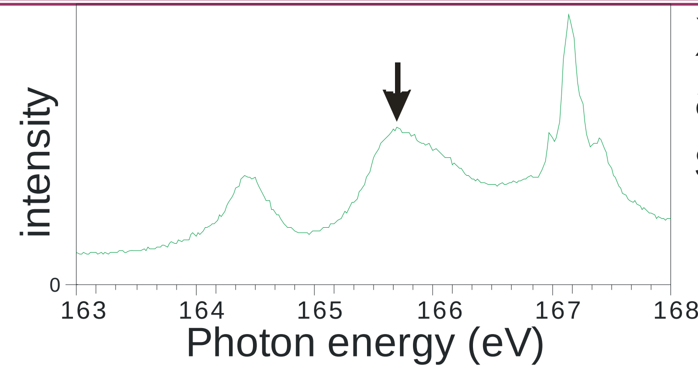
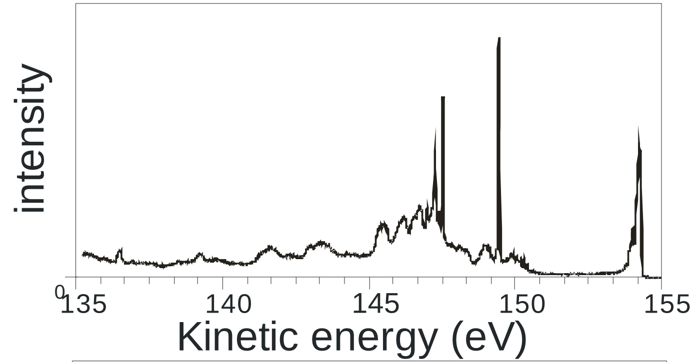
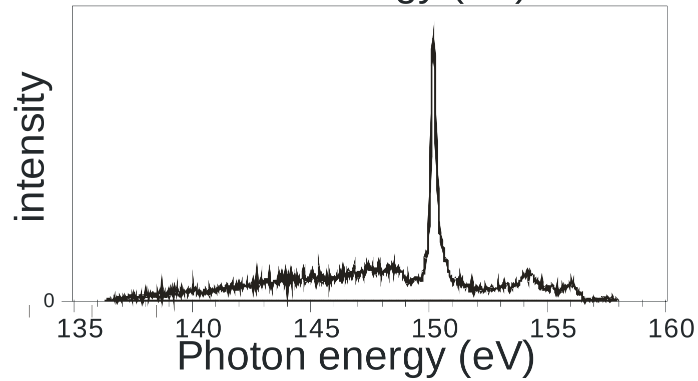




X-ray absorption spectrum

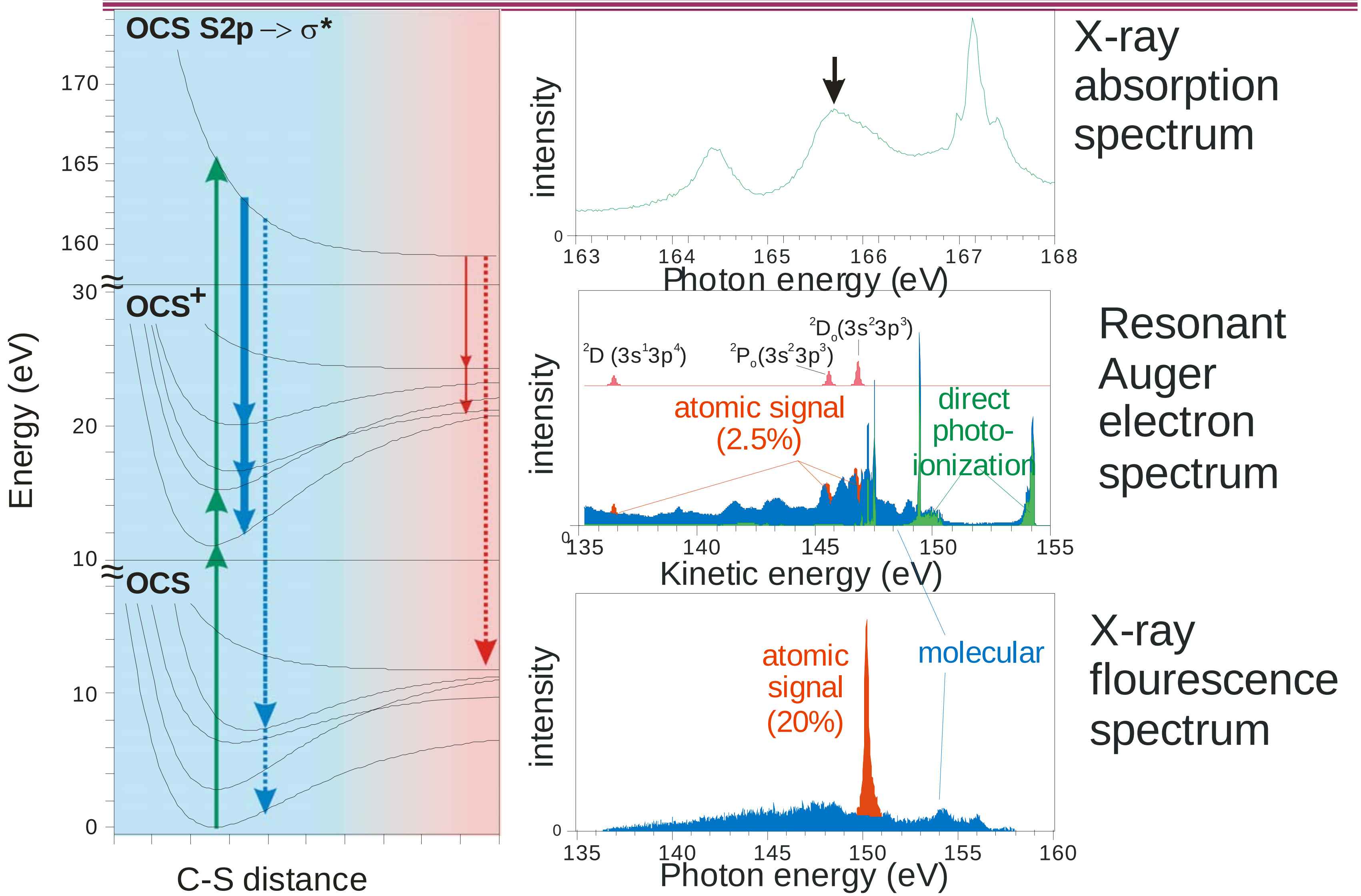


Resonant Auger electron spectrum

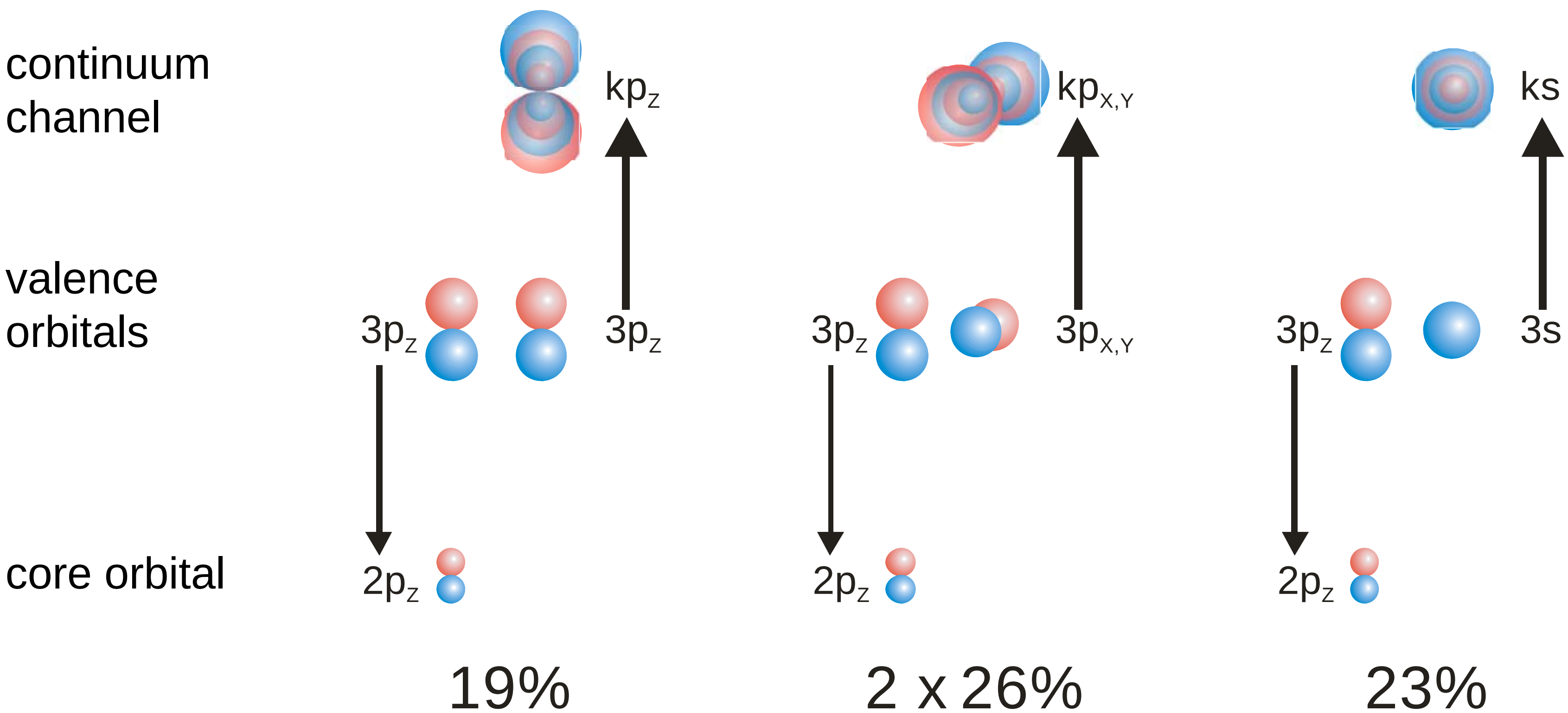


X-ray flourescence spectrum

EXTREMELY WEAK atomic signals in RAES
But strong signal in X-ray fluorescence



Preferred orientation in $L_{2,3}MM$ Auger decay
And SPIN FLIP IS FORBIDDEN!



95%

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Calculation of S2p53p5 states

term	weight (%)	E (eV)	Γ_A (meV)	Γ_X (μeV)
$^1S_0$	94	164.28	201.1	22
$^1D_2$	92	162.95	214.6	20
$^3P_1$	90	161.86	213.6	21
$^3P_0$	94	161.71	234.1	21
$^3P_2$	92	161.21	229.5	21
$^3D_1$	79	160.40	7.6	21
$^3S_1$	77	159.81	25.4	20
$^3D_2$	94	159.66	20.7	20
$^3D_3$	100	159.16	7.4	20
$^1P_1$	82	158.94	11.2	21
OCS (S $2p^{-1}\sigma^*$)	–	–	82.8	28

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General phenomenon

- The ULTRA FAST dissociation produces core excited S* molecules in lowest energy states
- These states have long lifetimes
- Fluorescense decay of minor importance for lifetime
- The Atomic XES signal seen only because the Auger decay is weak
- The core excited atoms fly 10-30 A
- ”Atomic grenade”

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General phenomenon

•The lowest terms of $2p^5 3p^n$ configurations.

•Long-lived atomic 2p core-hole states are generally the energetically lowest ones with their configuration.

•These states will be preferentially populated in a dissociation process of a core-excited molecular state where transitions via a multitude of avoided crossing typically lead to the energetically lowest states.

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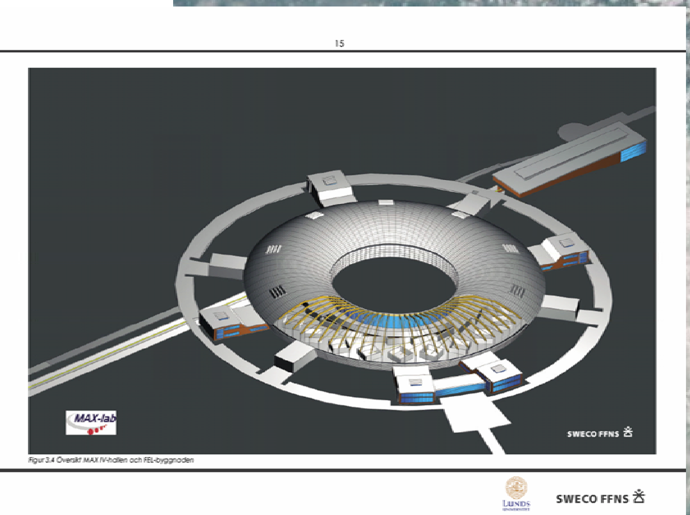
Final comment

I have been active in SR based electron spectroscopy for over 30 years. I have been surfing on a wave of Brilliance. 11 orders of magnitude high! We are now facing another very big (7 orders of magnitude) and coherent wave of brilliance.

30 MORE YEARS THANKS!



MAX IV planned project