Hard-X-Ray Photoemission from Atoms and Molecules

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Many phenomena in Condensed Phases are irrelevant to Atoms and Molecules.

- X-ray standing waves
- Grazing-incidence diffraction

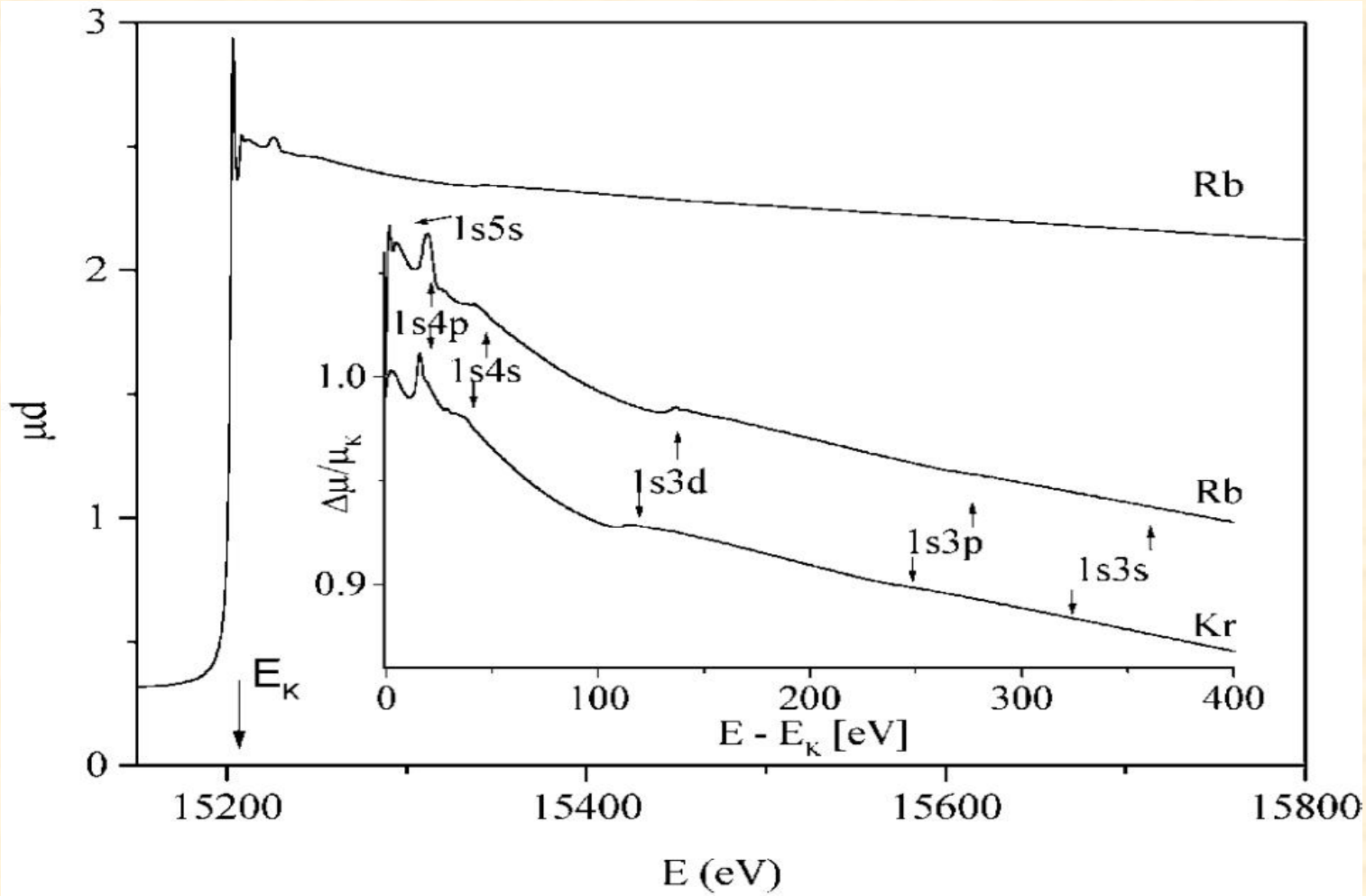
- Multilayers
- Interfaces (buried and otherwise)

- Nuclear-recoil effects

In gases, we focus mostly on fundamental interactions with x-rays.

Fundamental Interactions with Hard-X-Rays

- Higher $h\nu$ ⇨ More multi-electron effects
  - *Multiple excitation or ionization,* ***double-core*** *processes*



X-ray absorption of Rb and Kr vapor

A. Kodre *et al*., J. Phys. B **35**, 3497 (2002)

Hollow atoms?

Fundamental Interactions with Hard-X-Rays

- Higher $h\nu$ ⇨ More multi-electron effects
  - *Multiple excitation or ionization,* ***double-core*** *processes*
- Higher $\boldsymbol{k}$ ⇨ Higher-order effects
  - ***Nondipole effects*** *on photoelectron angular distributions*

The Dipole Approximation

Standard transition matrix element for photoionization between initial and final states:

$$\mathcal{D}_{if} \sim \langle \psi_i \left| \mathbf{p}.\epsilon \exp(-i\mathbf{k}.r) \right| \psi_f \rangle$$

The **Dipole Approximation** – truncation of the Taylor-series expansion:

$$\exp(\pm i\mathbf{k}.r) = 1 \pm i\mathbf{k}.r - \frac{1}{2}(\mathbf{k}.r)^2 + \ldots \approx 1$$

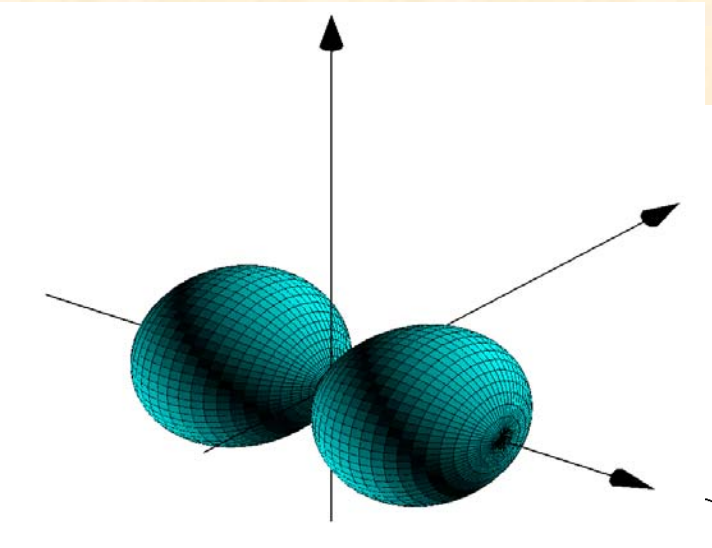
Transition matrix element for dipole photoionization:

$$\mathcal{D}_{if} \sim \langle \psi_i \left| \mathbf{p} \cdot \epsilon \right| \psi_f \rangle$$

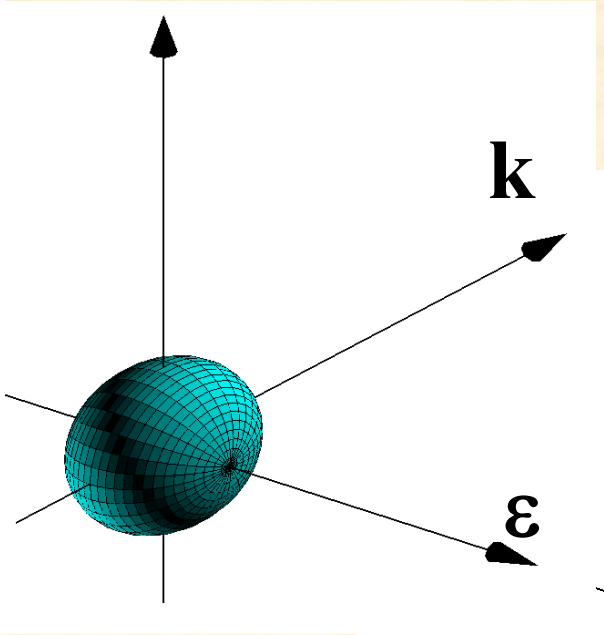
Angular distributions - dipole differential cross section for photoionization of a *randomly oriented* target by 100% linearly polarized light:

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

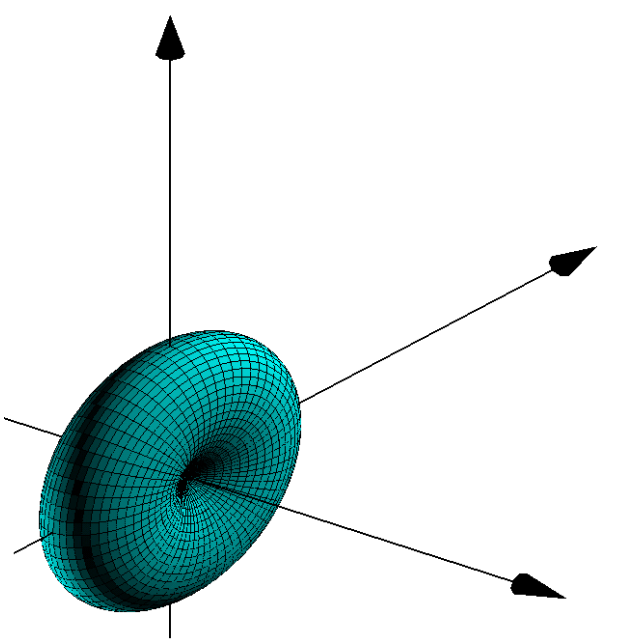
Dipolar Angular Distributions



$\beta = 2$



$\beta = 0$



$\beta = -1$

First-order correction to the Dipole Approximation

First-order-nondipole approximation - truncate the Taylor-series expansion after the second term:

$$\exp(\pm i\mathbf{k}.r) = 1 \pm i\mathbf{k}.r - \frac{1}{2}(\mathbf{k}.r)^2 + \ldots \approx 1 \pm i\mathbf{k}.r$$

Transition matrix element for first-order-nondipole photoionization:

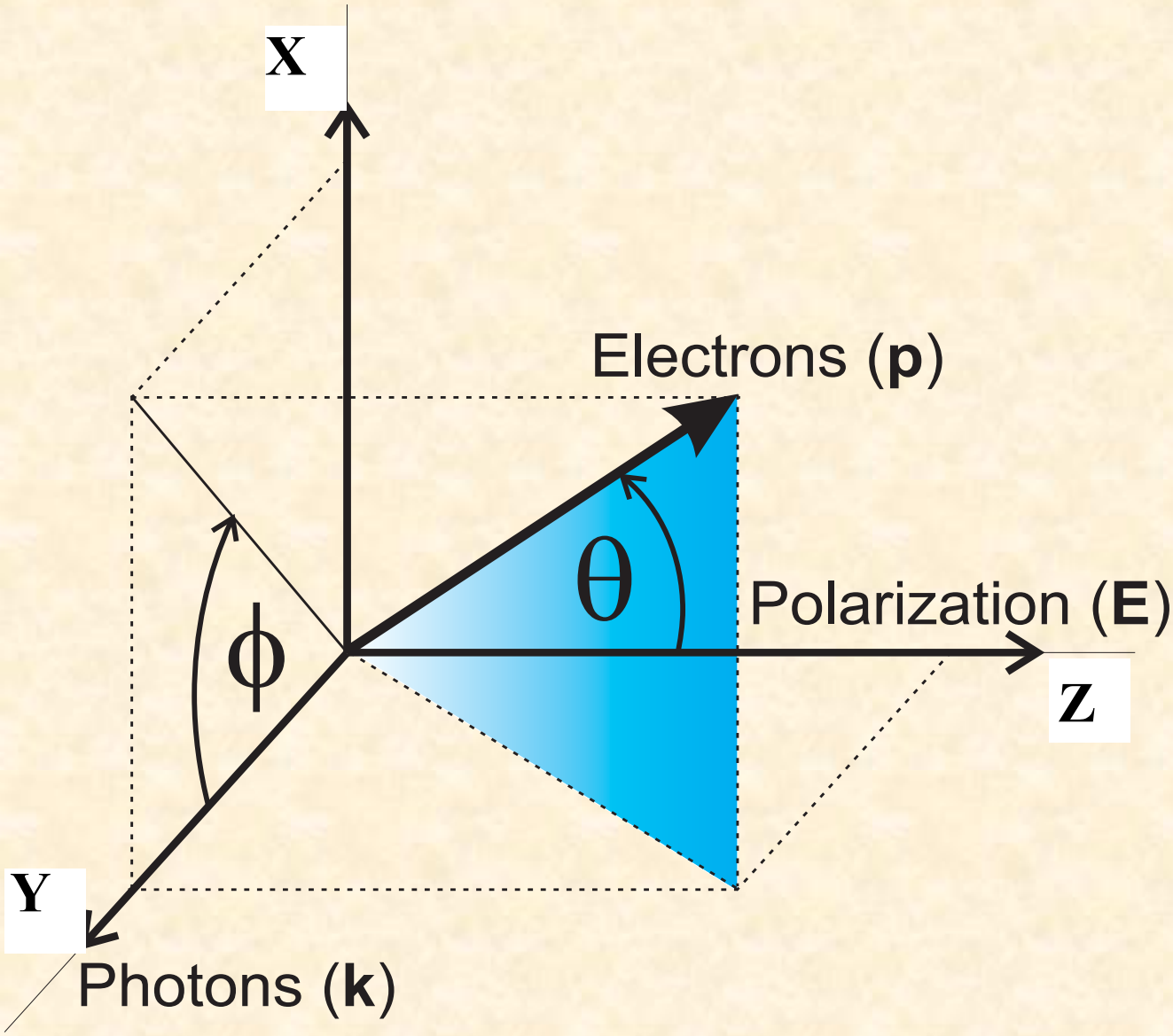
$$\mathcal{D}_{if} \sim \langle \psi_i | \mathbf{p} \cdot \epsilon(1 + i\mathbf{k} \cdot \mathbf{r}) | \psi_f \rangle$$

Angular distributions – first-order-nondipole differential cross section for photoionization of a *randomly oriented* target by 100% linearly polarized light:

$$\frac{d\sigma(h\nu)}{d\Omega} = \frac{\sigma(h\nu)}{4\pi}\left[1 + \frac{\beta}{2}(3\cos^2\theta - 1) + (\delta + \gamma\cos^2\theta)\sin\theta\cos\phi\right]$$

|E1·E1|

|E1⊗(E2,M1)|


X
Electrons (p)
θ
Polarization (E)
Z
ϕ
Y
Photons (k)

Nondipolar Angular Distributions

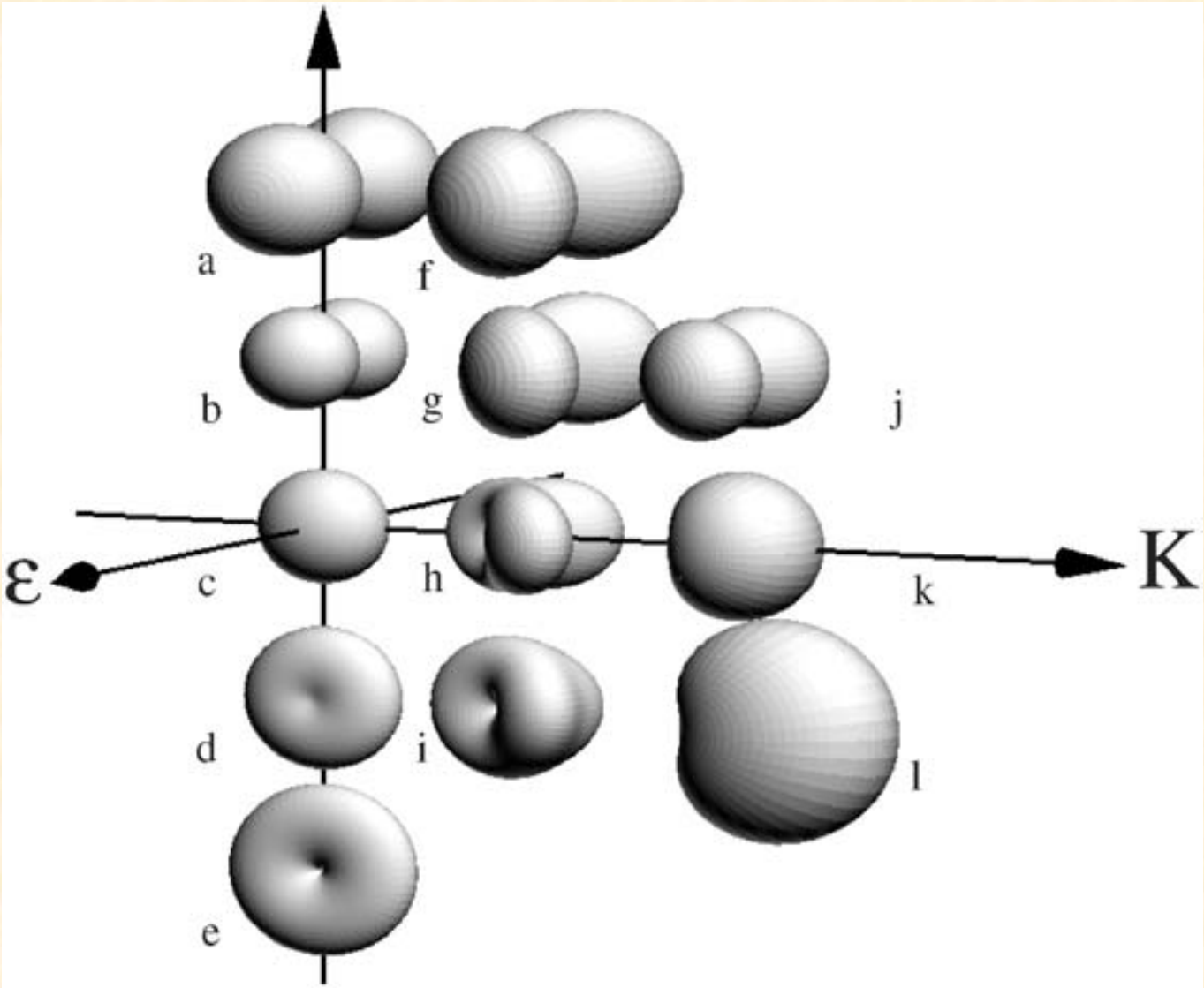
$\beta = 2$

1

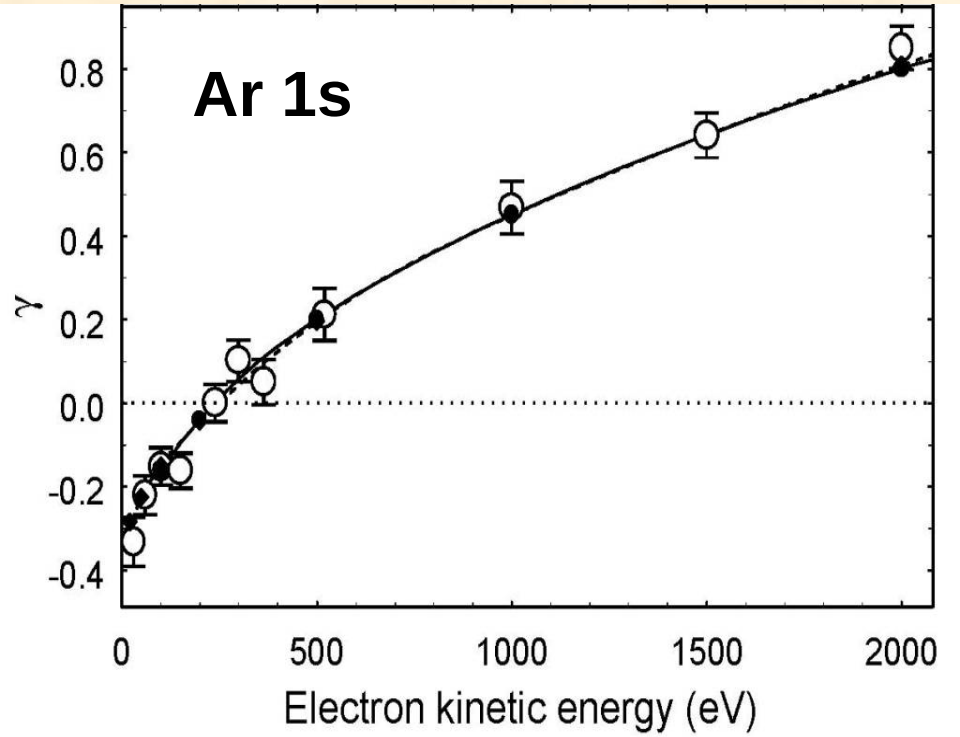
0

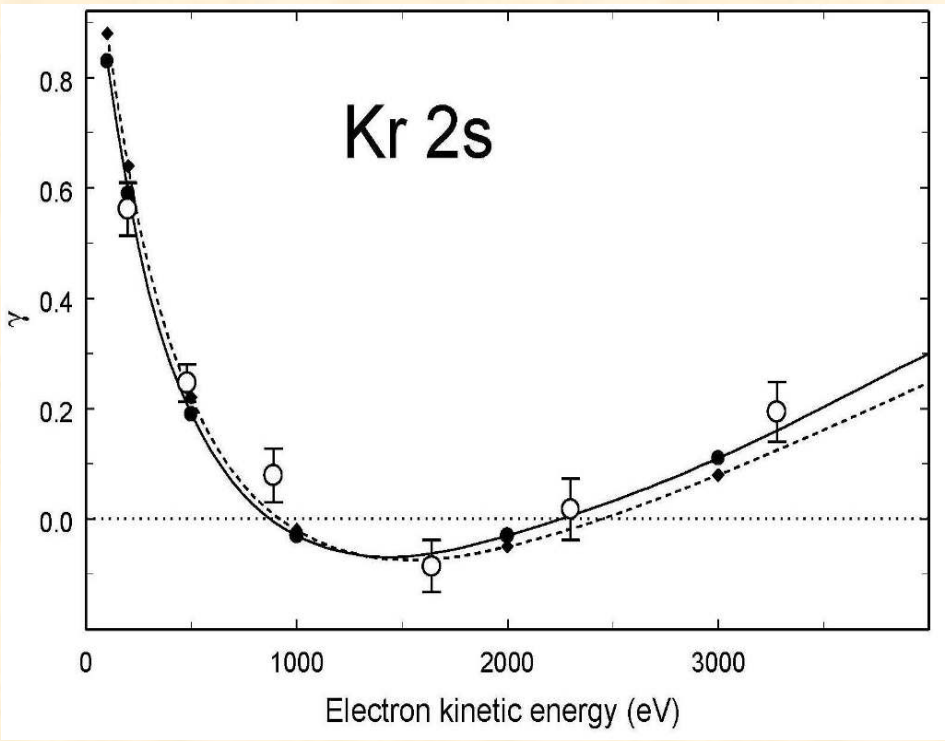
-0.5

-1



γ,δ=0 γ large δ large





Nondipole angular-distribution parameters

Ar 1*s*: BE = **3206** eV

Kr 2*s*: BE = **1921** eV

Krässig *et al*., Phys. Rev. Lett. **75**, 4736 (1995)

Jung *et al*., Phys. Rev. A **54**, 2127 (1996)

Measuring Nondipolar Angular Distributions

*Angular distributions of photoelectrons are sensitive to **amplitudes** and **phases** of transition matrix elements.*

$$\frac{d\sigma(h\nu)}{d\Omega} = \frac{\sigma(h\nu)}{4\pi}\left[1 + \frac{\beta}{2}(3\cos^2\theta - 1) + (\delta + \gamma\cos^2\theta)\sin\theta\cos\phi\right]$$

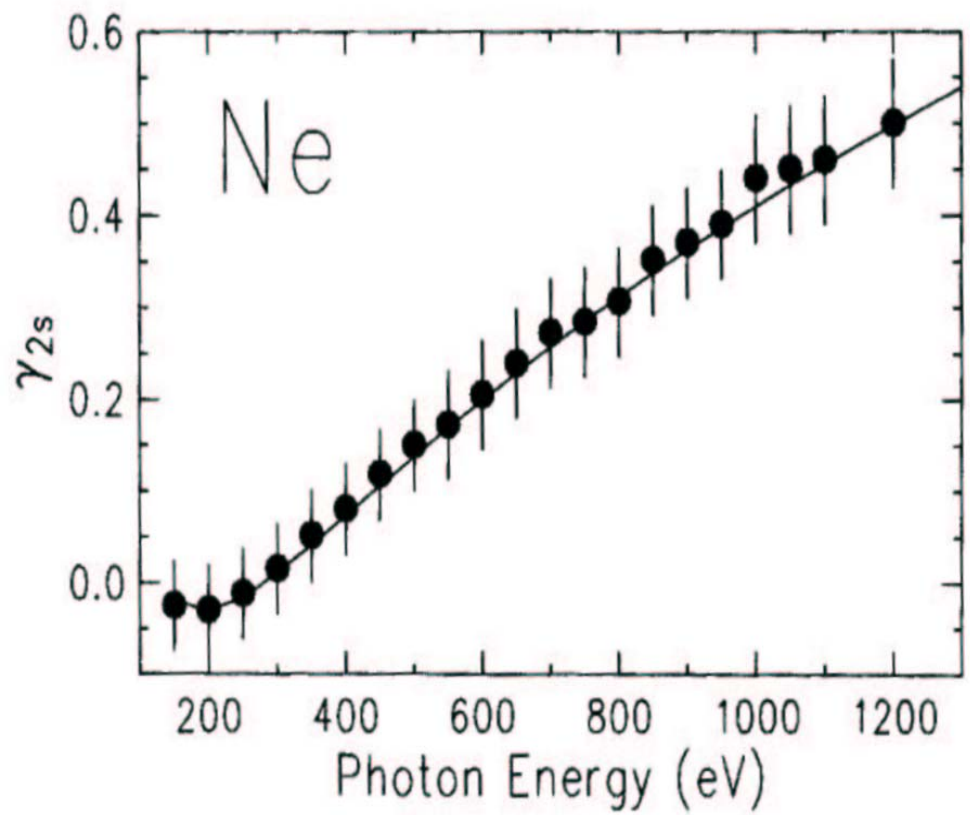
A. $\theta = 54.7°, \Phi = 0°$: $I \sim \sigma(h\nu)\,[1 + (3\delta + \gamma)(2/27)^{1/2}]$ "nondipole"

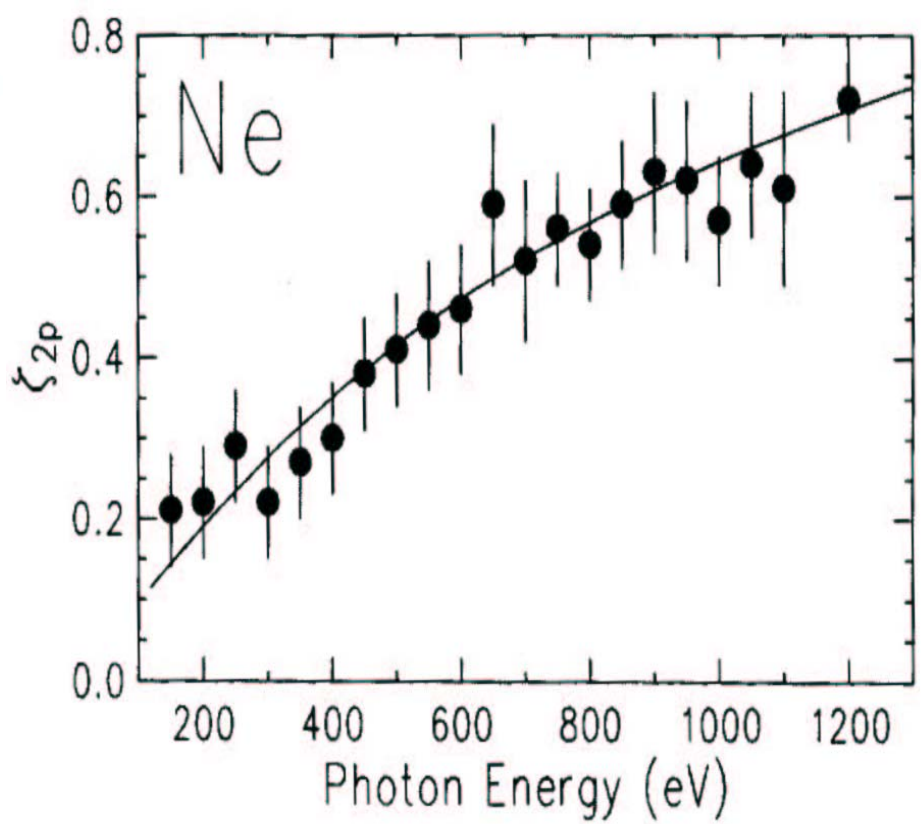
B. $\theta = 54.7°, \Phi = 90°$: $I \sim \sigma(h\nu)$ "dipole"

Define $\zeta = 3\delta + \gamma$ as a nondipole parameter

($\delta = 0$ for s subshells)

Neon valence (2*s*, 2*p*) nondipole photoionization





Experiment: *Hemmers et al. JESRP* ***123****, 257 (2002)*
Theory: *Bechler and Pratt [PRA* ***39****, 1774 (1989);* ***42****, 6400 (1990)]*
Cooper [PRA ***42****, 6942 (1990);* ***47****, 1841 (1993)]*

Fundamental Interactions with Hard-X-Rays

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  - ***Nondipole effects*** *on photoelectron angular distributions*
  - ***Drag currents***

Drag Currents

First-order nondipole effects yield **forward-backward asymmetries** in photoelectron emission, producing a **net flux of electrons** along the axis of the photon beam.

This macroscopic flux is known as a **drag current**.

The theoretical expression for a macroscopic drag current is

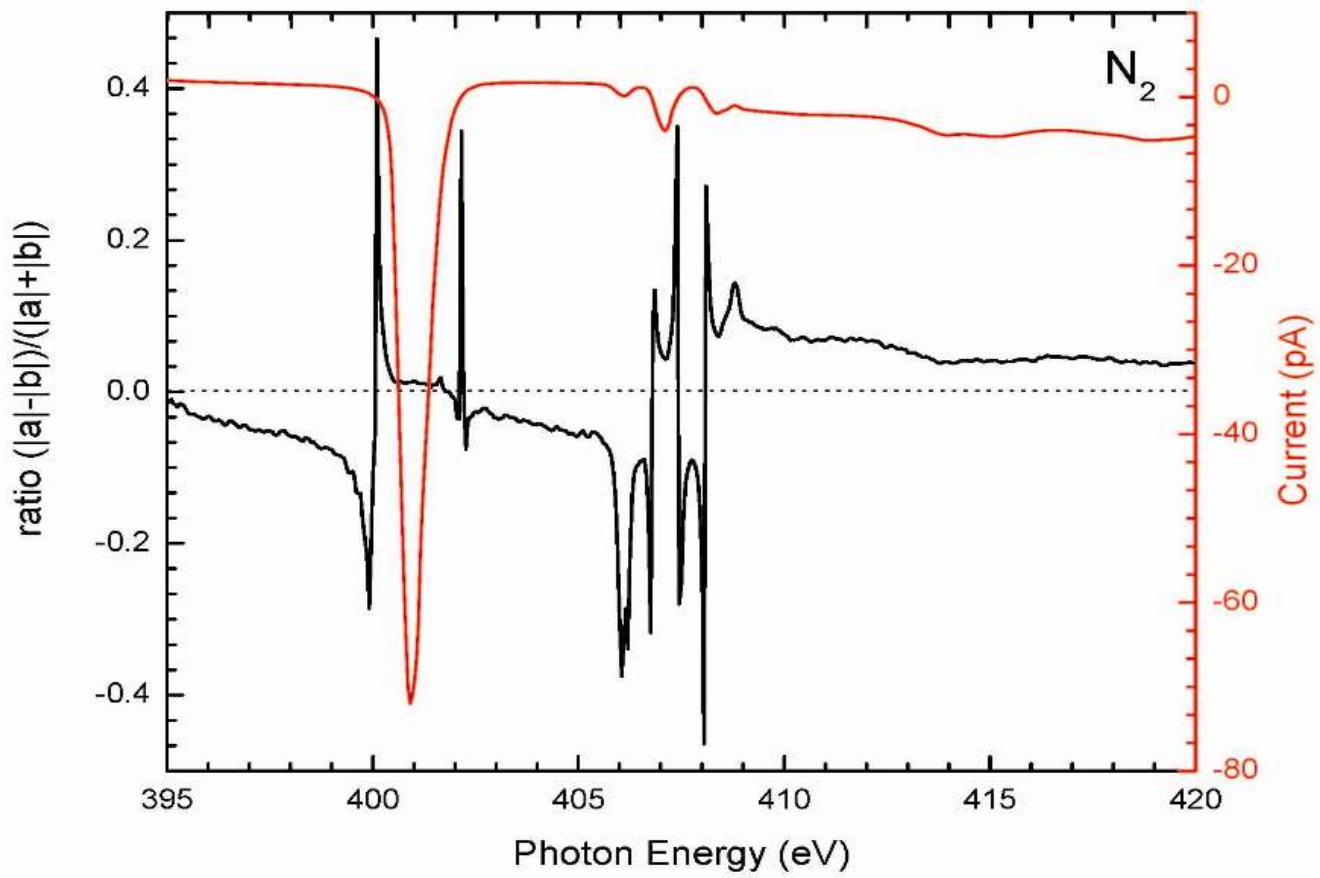
[M.Ya. Amusia *et al.*, Phys. Rev. A **63**, 052512 (2001)]

$$J \sim \gamma/5 \cdot \sigma_{Ph}(\omega)/\sigma_{AE}(\varepsilon)$$

$$(\zeta = \gamma + 3\delta)$$

$\sigma_{Ph}(\omega)$ = photoionization cross section
$\sigma_{AE}(\varepsilon)$ = electron elastic scattering cross section

Drag currents, a form of light pressure, influence processes in stellar and planetary atmospheres and are likely to be involved in large-scale astrophysical phenomena.



Drag current near the N 1*s* edge in molecular nitrogen

(First measurements from ALS BL 8.0)

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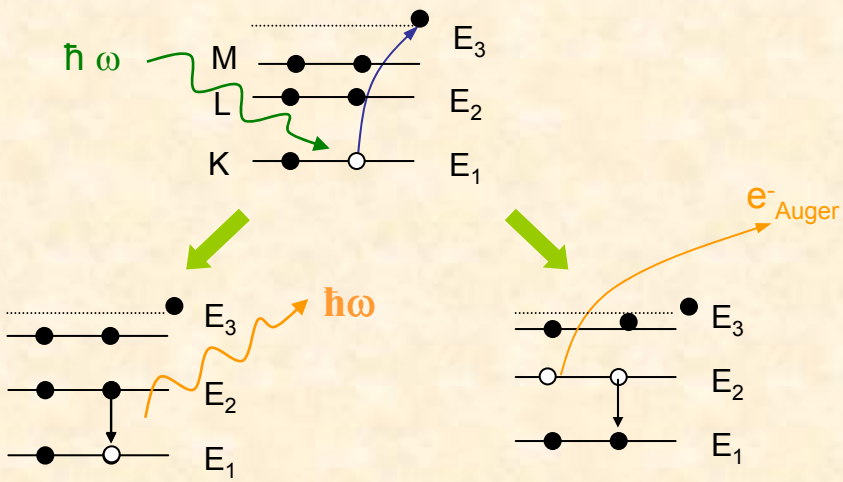
  - ***Nondipole effects*** *on photoelectron angular distributions*
  - ***Drag currents***
- Higher $h\nu$ ⇨ Deeper levels ⇨ Shorter lifetimes
  - *Intrinsic femtosecond 'clock'*
  - *Ultrafast dissociation*
  - ***Resonant Inelastic X-ray Scattering (RIXS)***

Resonant Inelastic X-Ray Scattering

Resonant Photoexcitation

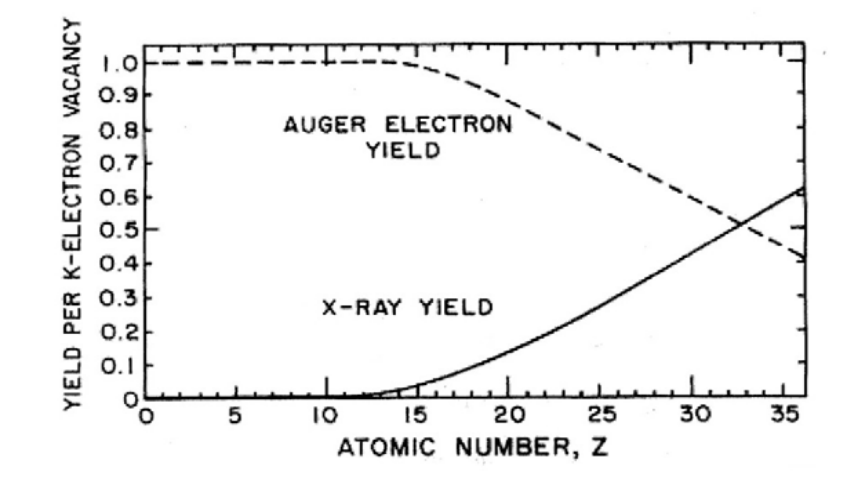


Resonant x-ray emission

KV or KL

Resonant Auger

KLL



natural width $\tau \sim$ ***Z (BE)*:** femtosecond nuclear dynamics?

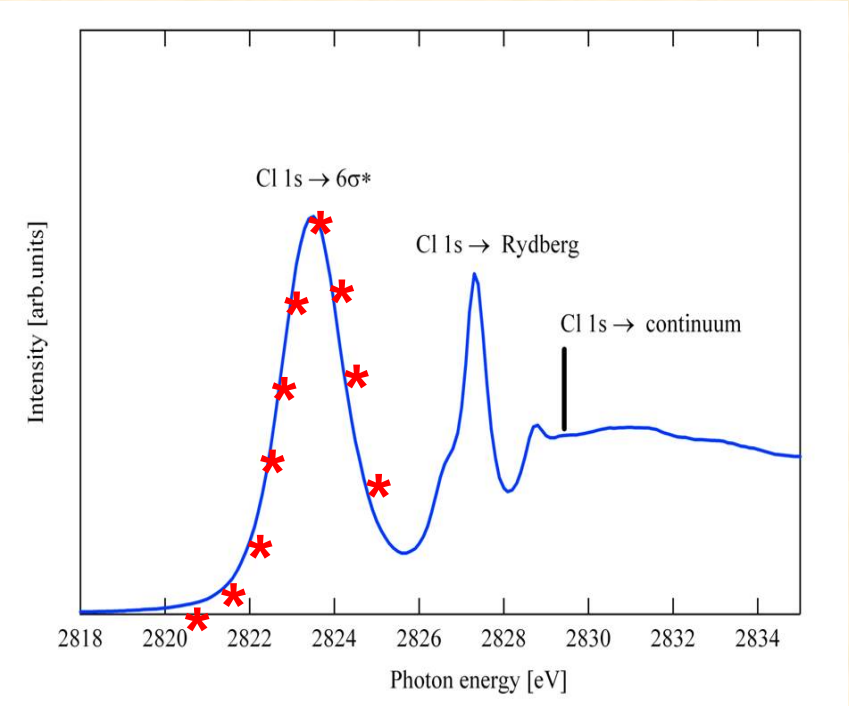
Kramers-Heisenberg

(effective duration time)

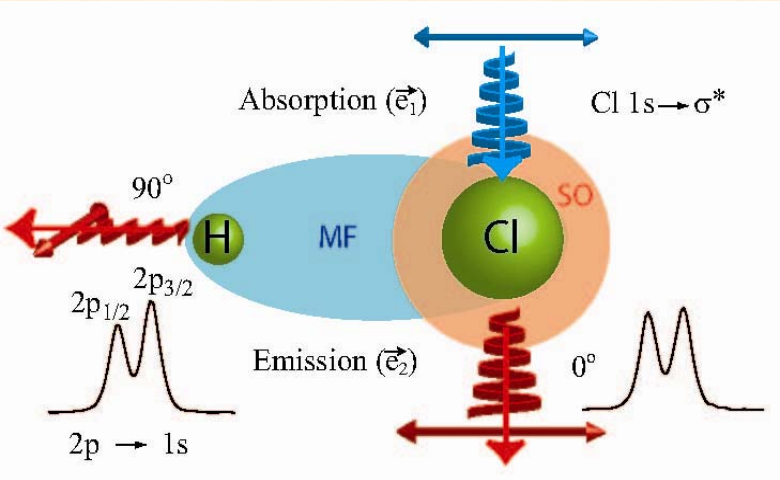
$$\sigma(\omega,\omega_1) \propto \sum_k \left| \frac{\langle f|D'|k\rangle\langle k|D|i\rangle}{\omega_1 - \omega_{kf} - i\Gamma_k} \right|^2$$

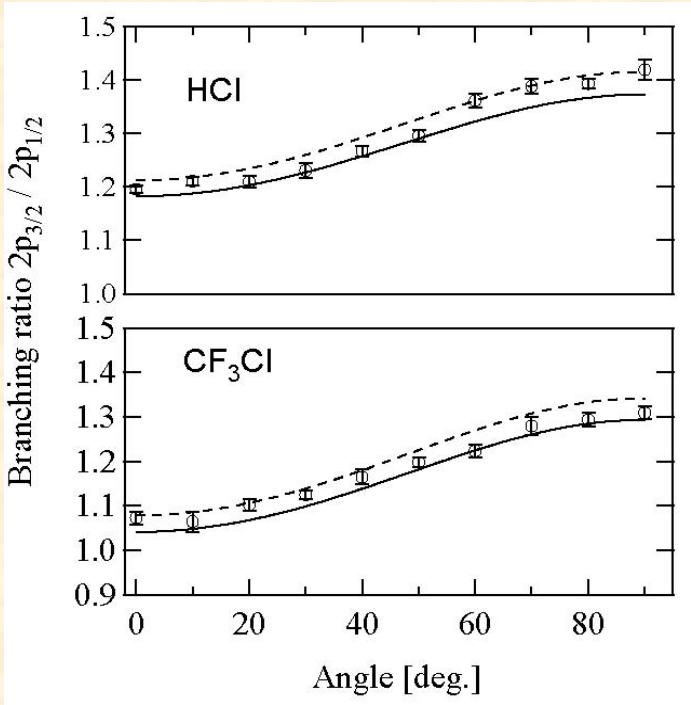
X-Ray Linear Dichroism of Molecules

Guillemin et al., PRL 101, 133003 (2008)



Absorption spectrum of HCl near the Cl 1*s* edge





Sensitive probe of spin-orbit compositions of the "2*p*" MOs

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- Higher $h\nu$ ⇨ Deeper levels ⇨ Shorter lifetimes
  - *Intrinsic femtosecond 'clock'*
  - *Ultrafast dissociation*
  - ***Resonant Inelastic X-ray Scattering (RIXS)***
- New sources ⇨ Multi-photon effects

Unique properties of LCLS radiation

Photon Energy	825 eV	8250 eV
Repetition rate	120 Hz	120 Hz
Photons per pulse	10^{13}	10^{12}
Pulse duration (rms)	137 fs	73 fs
Beam divergence	5.7 μrad	0.8 μrad
1st harmonic bandwidth	0.07%	0.03%
Peak power in 1st harmonic	4 GW	8 GW

i.e. – once operational in 2009, the LCLS will be the world's brightest x-ray source with ~100 fs long x-ray pulses over 825 – 8250 eV

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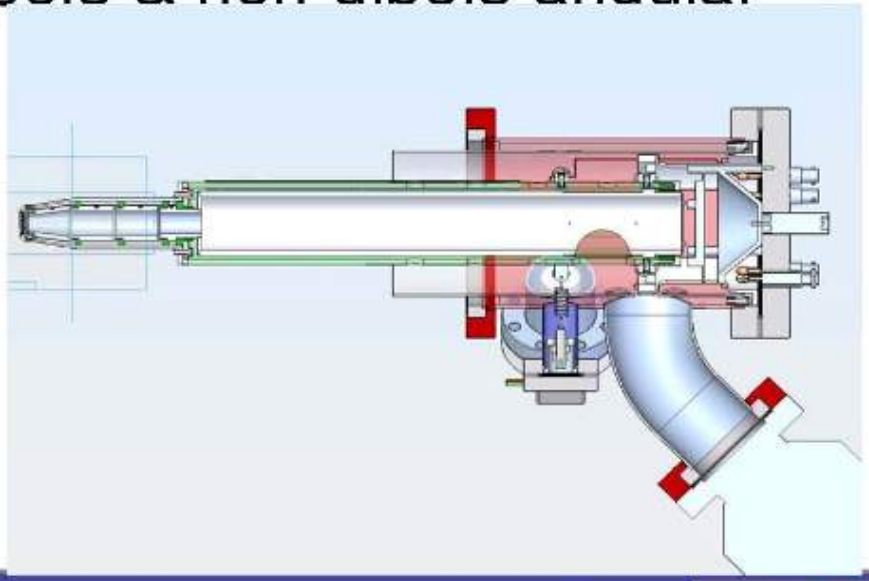
AMO Instrument Design – electron spec's

- Based on a successful time-of-flight (TOF) design used at synchrotrons (D. Lindle's group)
- Five spectrometers arrayed around interaction region to measure dipole & non-dipole angular distributions



Acknowledgements

UNLV – Current

Kyle Bowen, Iraida Demchenko, **Oliver Hemmers**, **Wayne Stolte**

UNLV – Former

Peter Glans, **Renaud Guillemin**, Amanda Hudson, Daniel Rolles, Honghong Wang, Scott Whitfield, Anna Wolska, Sung-Woo Yu

Experimental Collaborators

Loïc Journel, Maria Novella Piancastelli, **Marc Simon**

Theoretical Collaborators

Atoms: H.S. Chakraborty, K.T. Cheng, Pranawa Deshmukh, Valery Dolmatov, **Steve Manson**

Molecules: J.C. Arce, **Stephane Carniato**, **Peter Langhoff**, Jeffrey Mills, Jeff A. Sheehy, **Richard Taïeb**

Two reviews of nondipole effects in the soft-x-ray region:

Hemmers *et al.*, Rad. Phys. and Chem. **70**, 123-147 (2004)

Guillemin *et al.*, Rad. Phys. and Chem. **73**, 311-327 (2005)