Attosecond and strong-field electron dynamics in clusters and large molecules

Ultimate goal:
Dynamical
description
of irradiation and
response of
- electrons
- ions
- environment

Laser irradiations of free clusters
- Huge energy absorption in intense laser fields
- Production of energetic electrons, ions, photons
- Many-body « laboratory »
- Time resolved dynamics

Irradiation of solvated « bio »molecules
- Microscopic mechanisms
- Role of water environment
- Medical applications
- Society applications

Deposited/embedded species
- Shaping at nanoscale
- Defect formation
- Chromophore effects and therapy applications

Summary

I. Introduction

I.1 General context

I.2 Signals from irradiated clusters/molecules

I.3 Electronic observables

II. Theories

I.1 Theories versus dynamical regimes

I.2-4 Time Dependent Density Functional Theories et al

I.5 Some numerical considerations

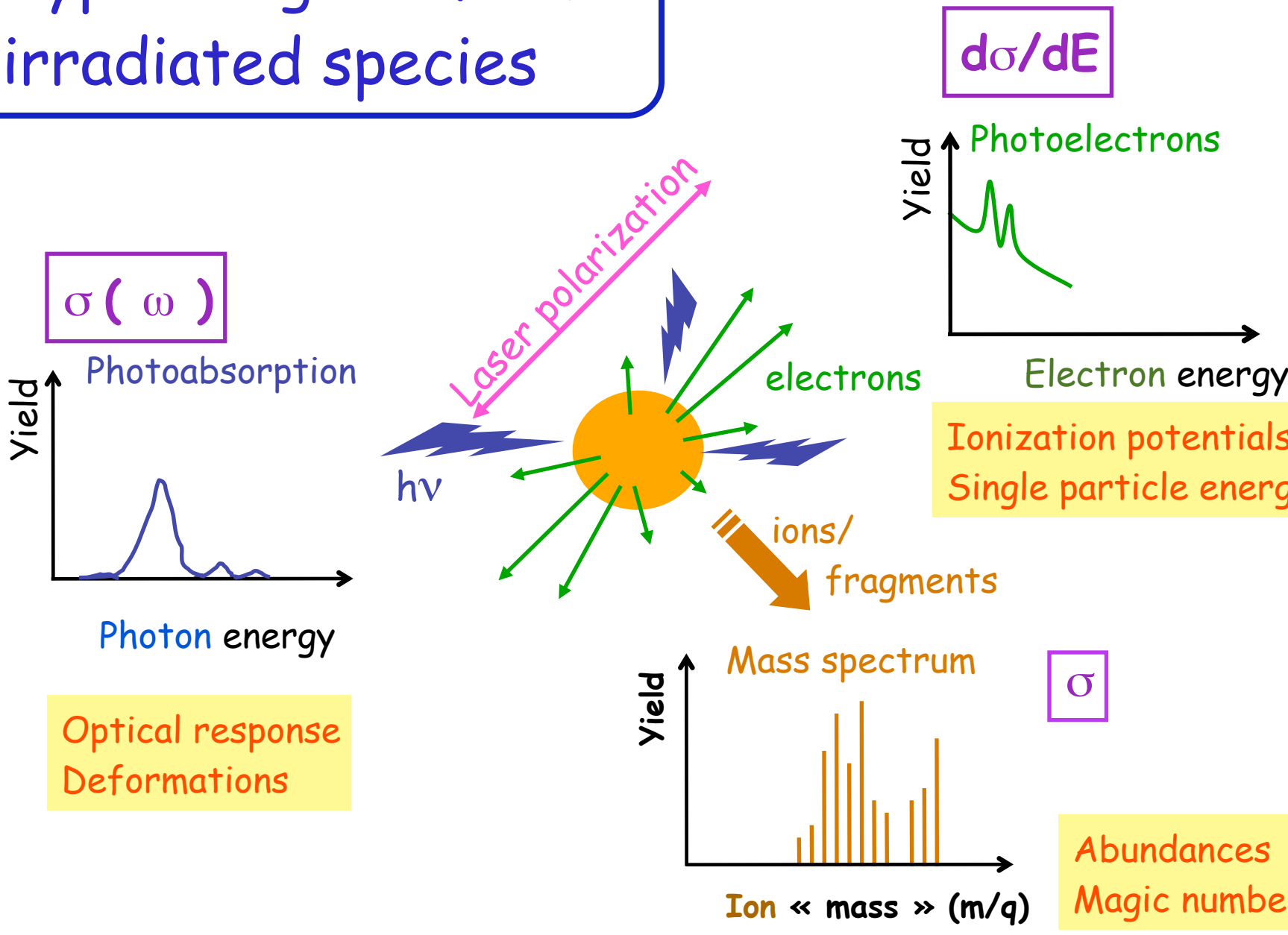
III. Examples of applications

III.1 Photo Electron spectroscopies

III.2 Electronic pump and probe dynamics probing ionic motion

III.3 Attosecond electronic dynamics

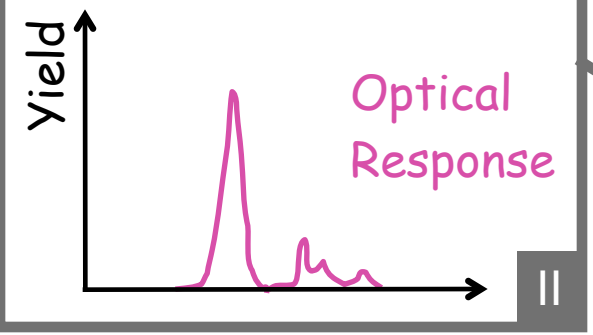
Typical signals from irradiated species



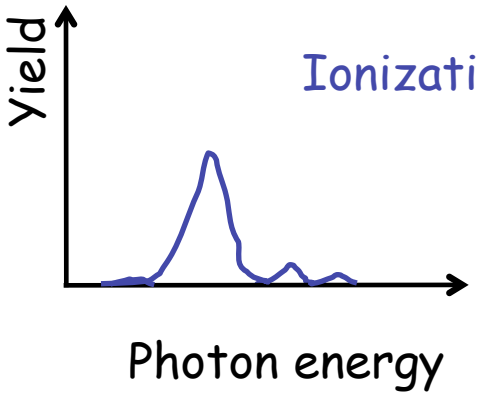
Electron emission from irradiated species

I.β

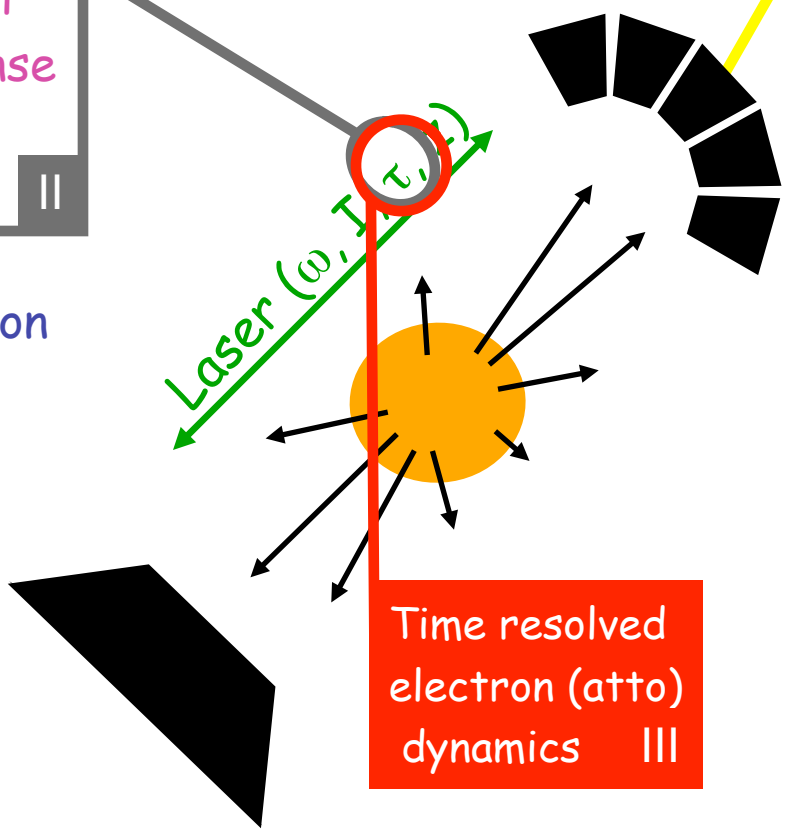
Time resolved (ion) dynam.



II

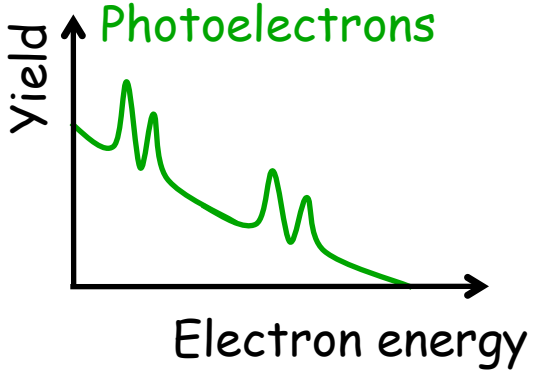


$\sigma(\omega)$

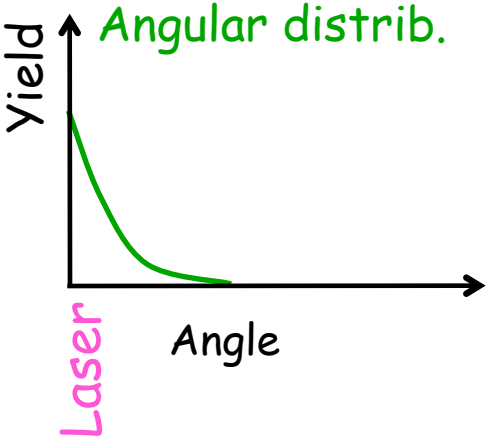


Time resolved electron (atto) dynamics III

$d\sigma/dE$



$d\sigma/d\Omega$



Energy resol. angul. distri.

Which theory for which situations ?

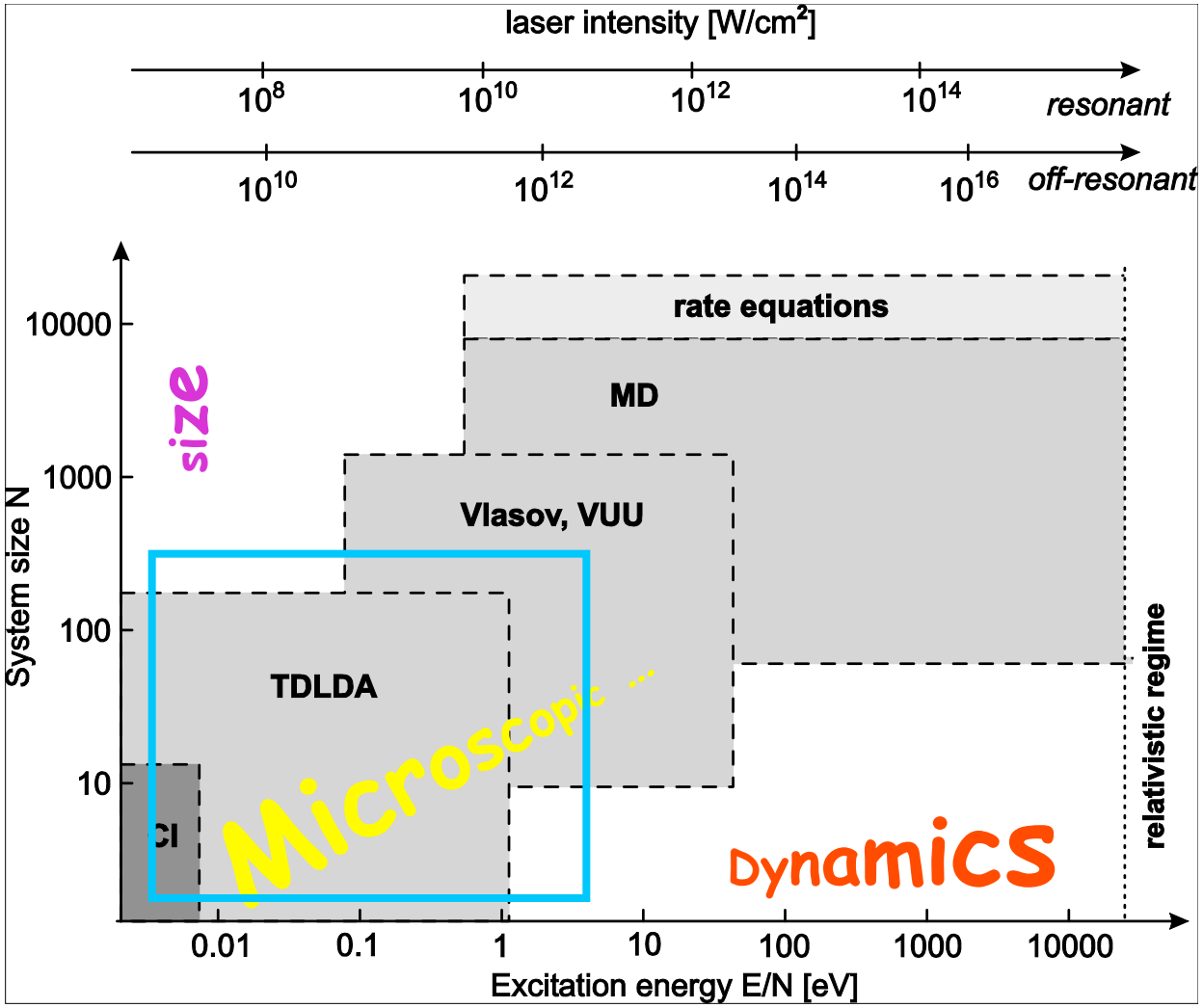
Electrons

Requirements

- Size
- Dynamics
- Microscopic …

Compromises

- No « final » Theory yet…
- Boundaries to explore …



Model (cluster/molecule)

➢ Electrons

- Time Dependent Density Functional Theory (TDDFT)

  Ensemble of orbitals (1 electron) / no correlation $\{\phi_i(\mathbf{r}), i = 1, ...\}$

  One body density $\rho(\mathbf{r}) = \sum_j |\phi_j(\mathbf{r})|^2$

  Effective mean field theory (Kohn-Sham)

$$i\hbar \frac{\partial \phi_i}{\partial t} = h[\rho]\phi_i \qquad h[\rho] = -\frac{\hbar^2}{2m}\Delta + U_{\mathrm{KS}} + U_{\mathrm{ext}}(\mathbf{r}, t)$$

Kohn-Sham potential — Ions + ext.

$$U_{\mathrm{KS}} = U_{\mathrm{H}} + U_{\mathrm{xc}}[\rho]$$

Coulomb direct — Exch. + Corr.

- Local Density Approximation (LDA)

+ Self Interaction Correction (SIC) ...

- Semi-classical theory available (Vlasov, VUU)

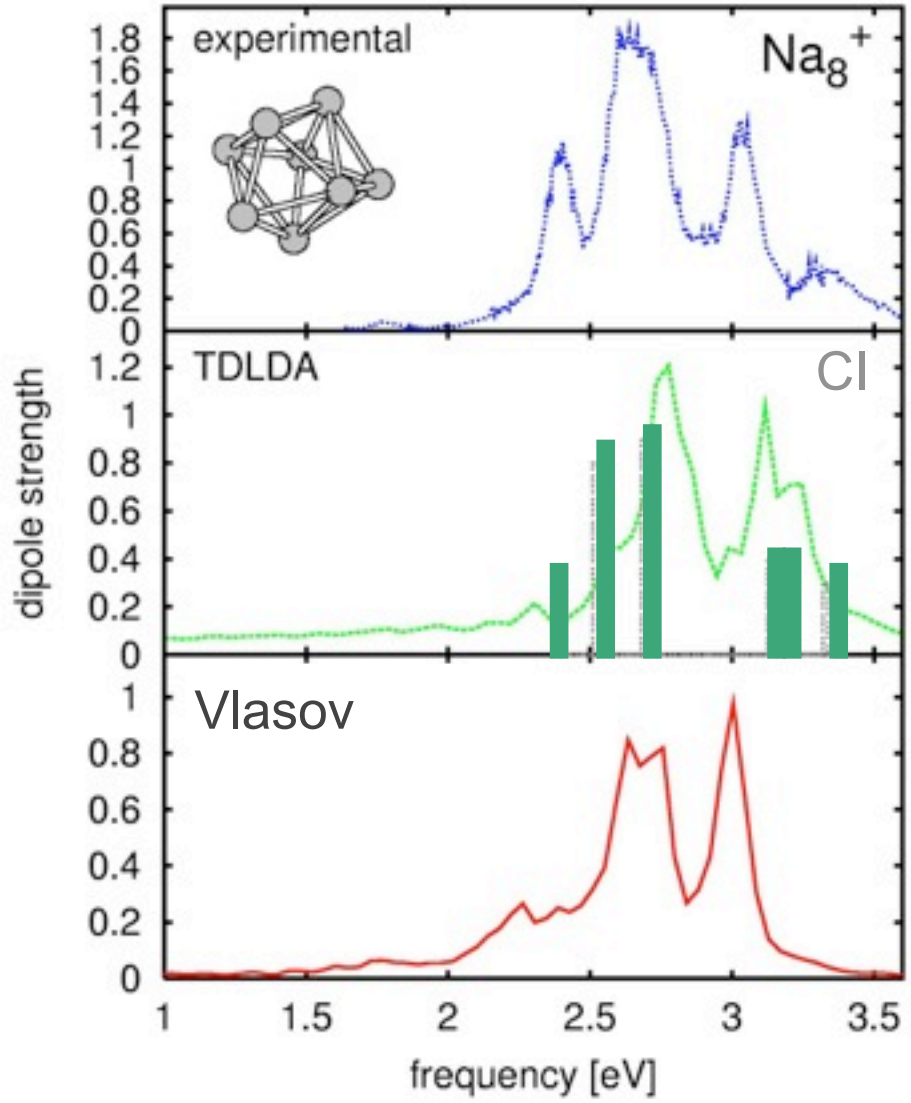
➢ Ions

- Explicit ions via pseudo potentials
- Detail of structure + ionic Molecular Dynamics (MD)

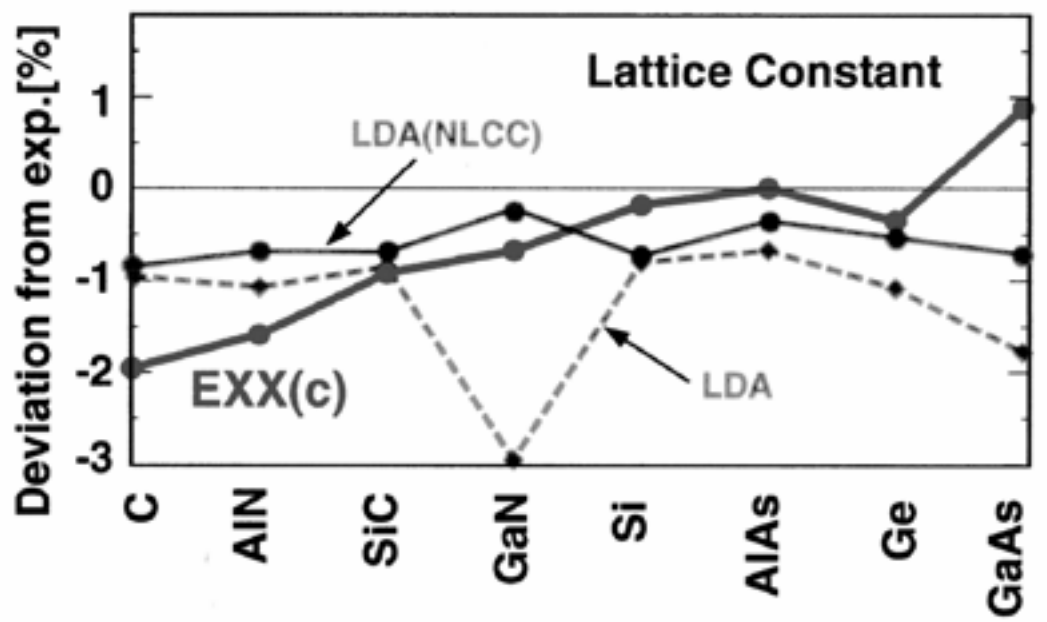
Coupled non adiabatic electrons (fs) + ions (ps) dynamics

Local Density Approximation (LDA)

Optical response



Local Density Approximation (LDA)



Local Density Approximation (LDA)

Table 8.2 LSD Spectroscopic Constants for Diatomic Molecules[a]

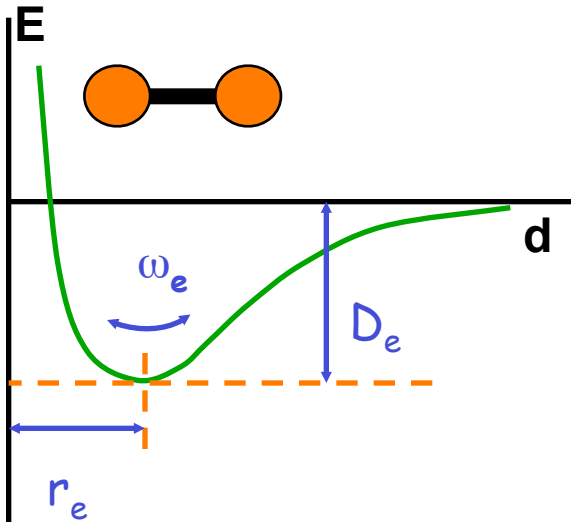
	r_e (bohrs)		D_e (eV)		ω_e (cm^{-1})	
	Expt.	LSD	Expt.	LSD	Expt.	LSD
H_2	1.40	1.45	4.8	4.9	4400	4190
Li_2	5.05	5.12	1.1	1.0	350	330
B_2	3.00	3.03	3.0	3.9	1050	1030
C_2	2.35	2.35	6.3	7.3	1860	1880
N_2	2.07	2.07	9.9	11.6	2360	2380
O_2	2.28	2.27	5.2	7.6	1580	1620
F_2	2.68	2.61	1.7	3.4	890	1060
Na_2	5.82	5.67	0.8	0.9	160	160
Al_2	4.66	4.64	1.8	2.0	350	350
Si_2	4.24	4.29	3.1	4.0	510	490
P_2	3.58	3.57	5.1	6.2	780	780
S_2	3.57	3.57	4.4	5.9	730	720
Cl_2	3.76	3.74	2.5	3.6	560	570

[a] From Becke (1986a).

24%

1%

3%



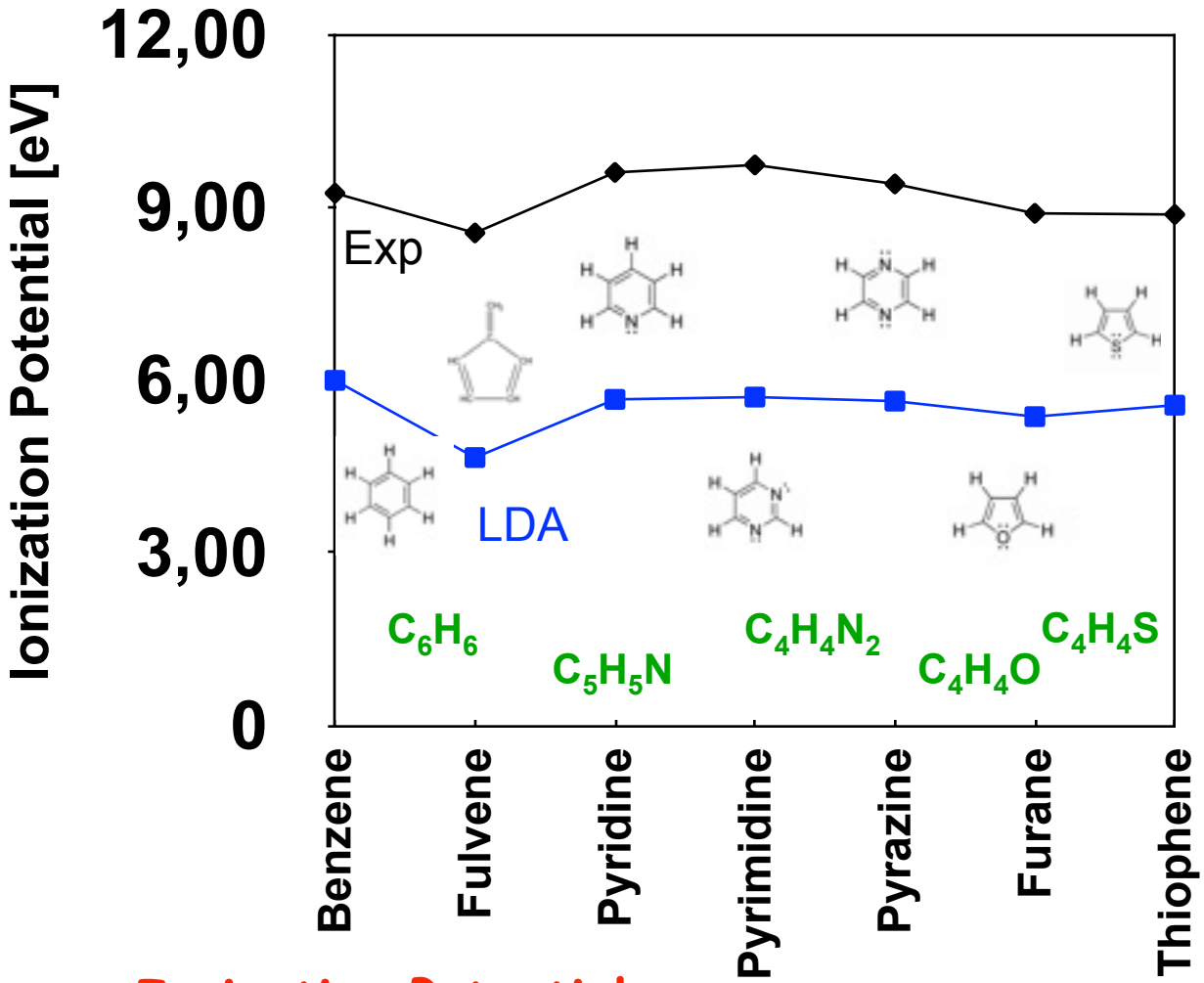
The Ionization Potential Problem

Example of organic molecules:

Benzene-like cyclic structures:
H → N, O, S

Neutral species
Covalent bond

50% error on IP !



LDA : Totally wrong Ionization Potential

Vlasov and VUU

- Vlasov provides a sound basis for complementing mean-field by dynamical correlations (« Boltzmann-like » collision term)

$$i\hbar\dot{\rho} = [h, \rho]$$ TDHF/TDDFT

$$\dot{f} = \{h, f\}$$ Vlasov

$$\dot{f} = \{h, f\} + I_{coll}[f]$$ VUU/BUU

- Semi classical kinetic equation (plasmas, nuclear physics…)
- Collision integral

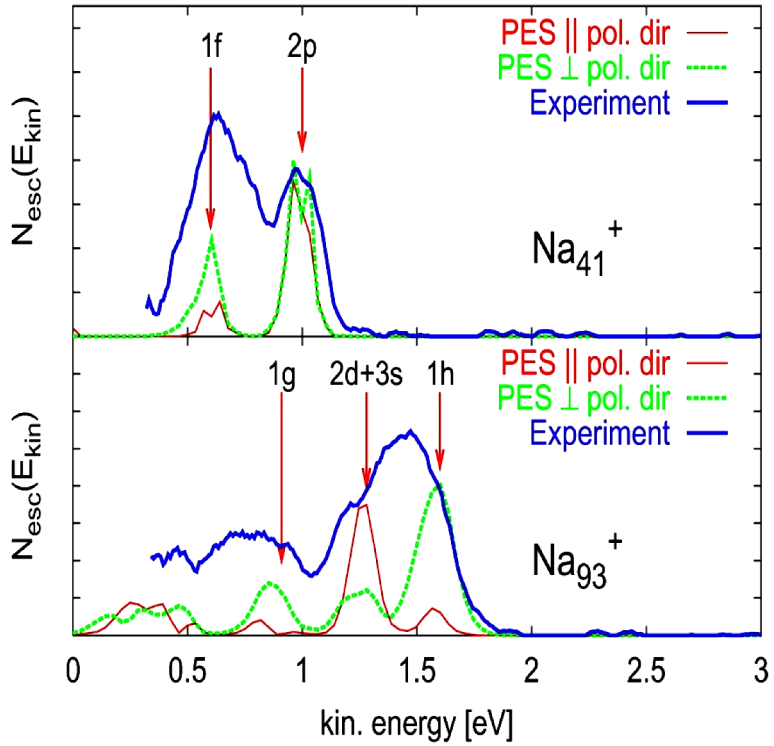
$$I_{coll}[f] \sim \int d\mathbf{p}_2 d\mathbf{p}_3 d\mathbf{p}_4 \delta(\sum \mathbf{p}_i)\delta(\sum \epsilon_i)\frac{d\sigma}{d\Omega}\{f_1 f_2(1-f_3)(1-f_4) - ...\}$$

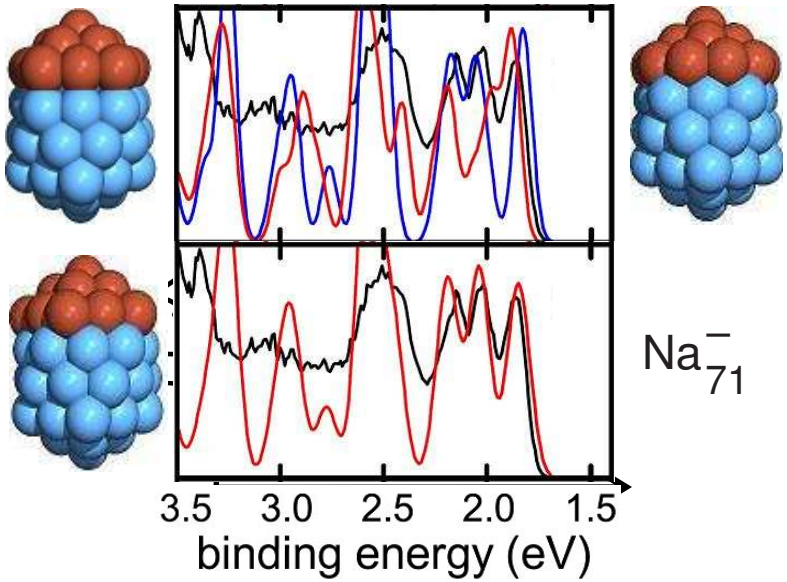
In medium cross section/
Screened Coulomb

Pauli blocking

Numerics : test particles

Photoelectron Spectroscopy (PES)



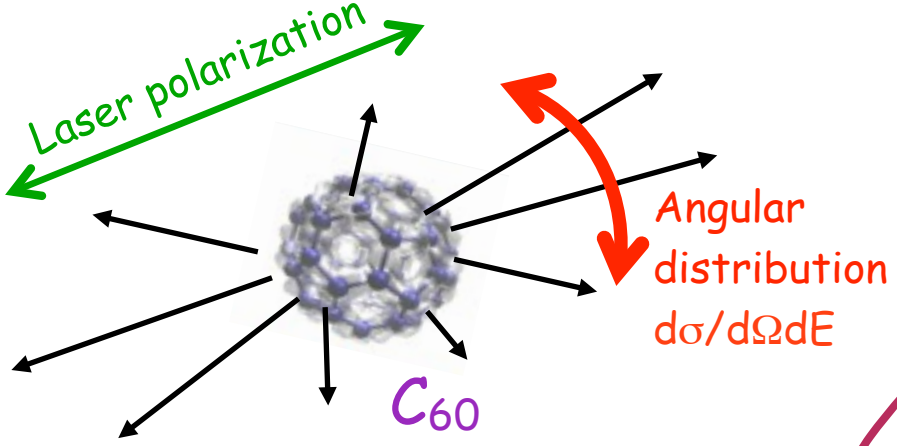


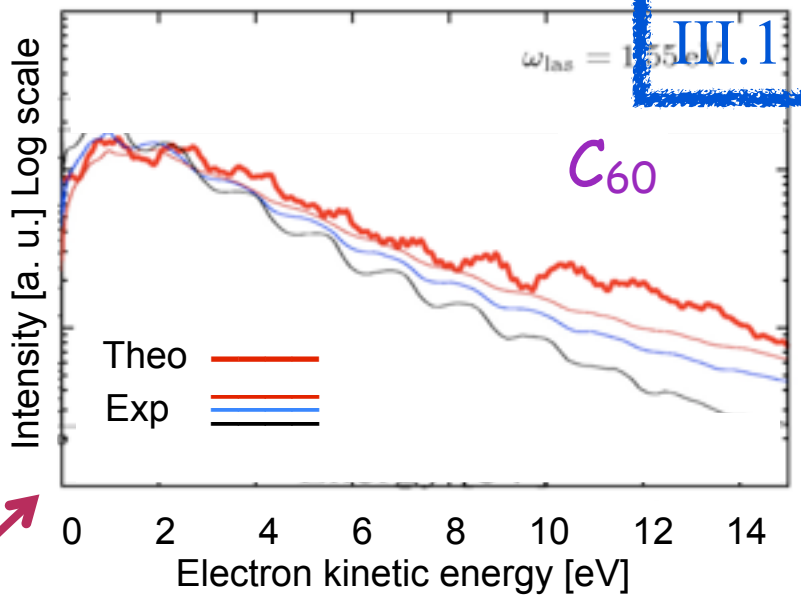
Pohl et al, PRA 2003 Exp. Freiburg

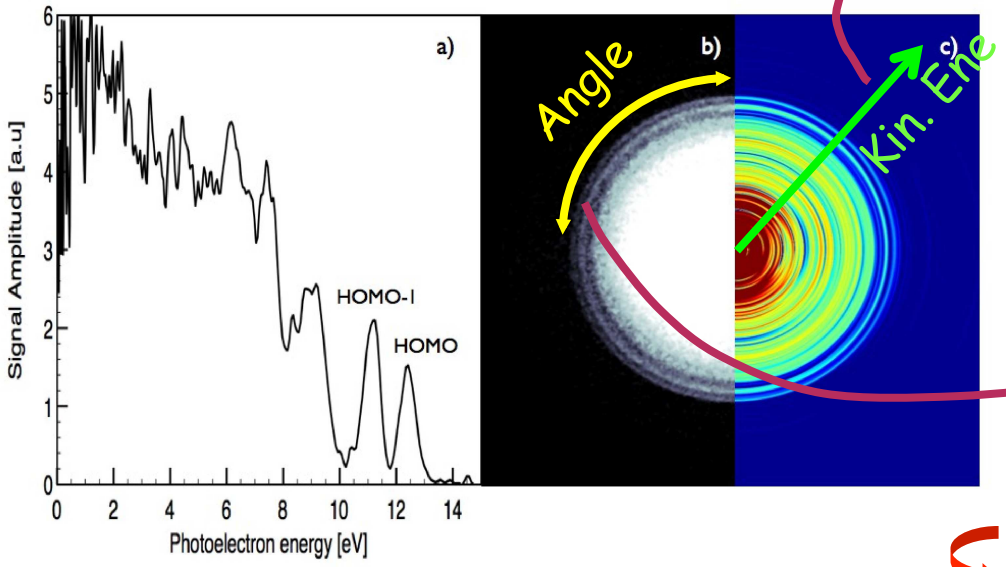
- **Access to photoelectron spectroscopy**
- **Angular distributions**
- **Dynamical features**

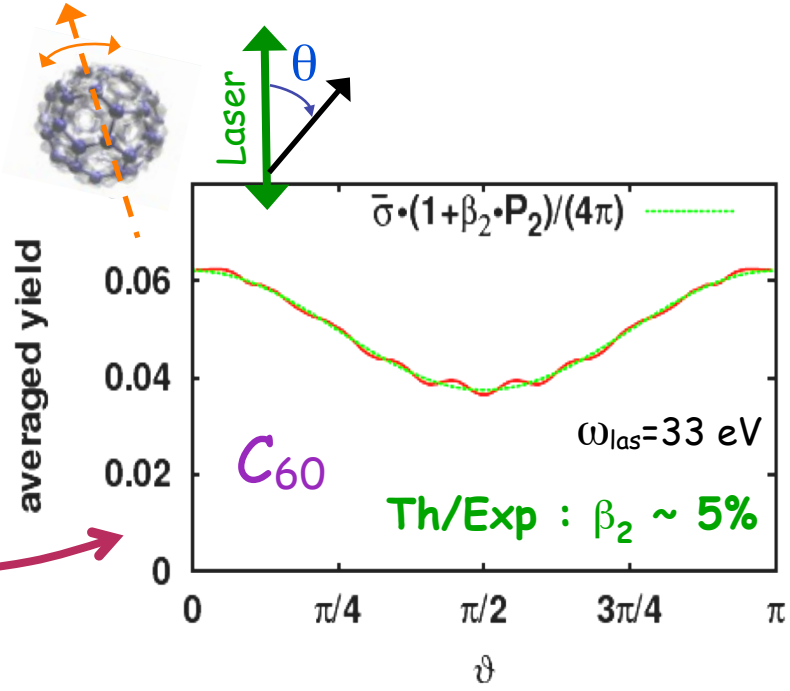
Energy/angle resolved distributions

III.1



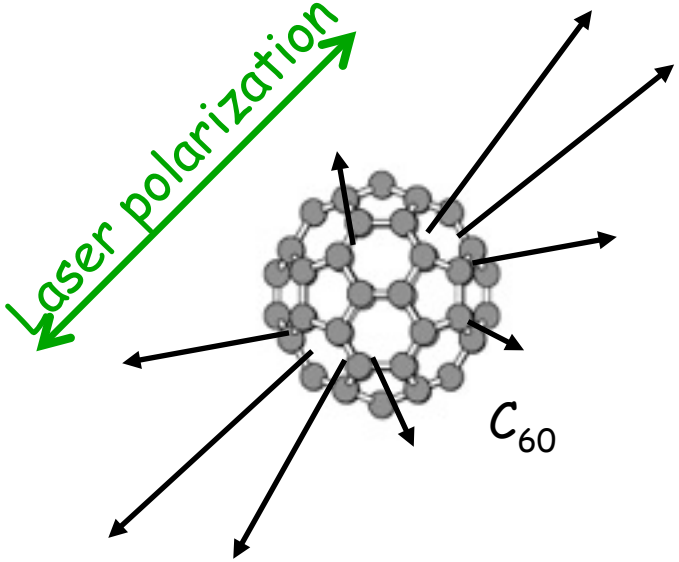


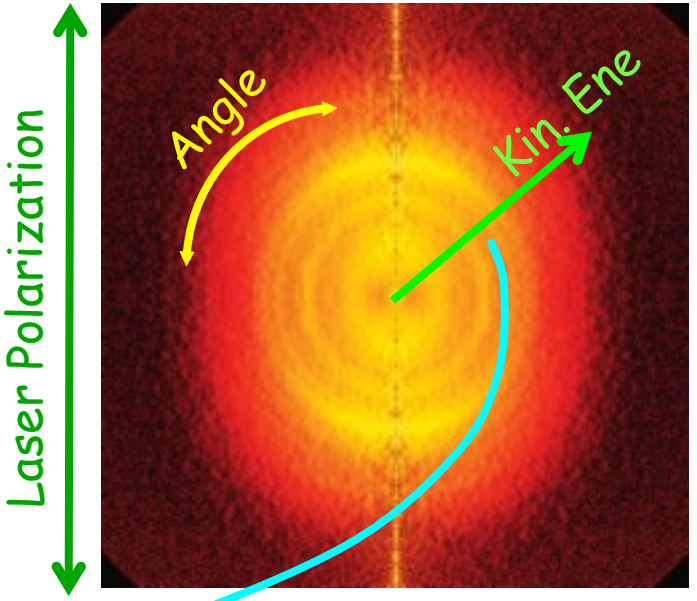


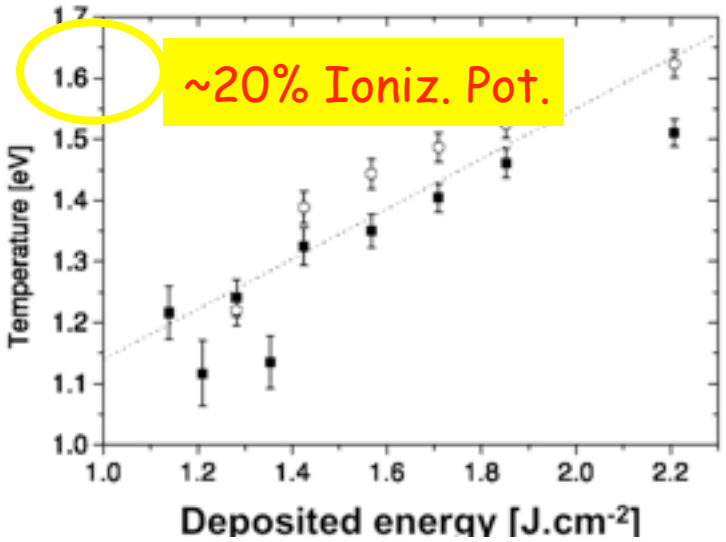


Access to dynamical effects

Angular distributions and temperature







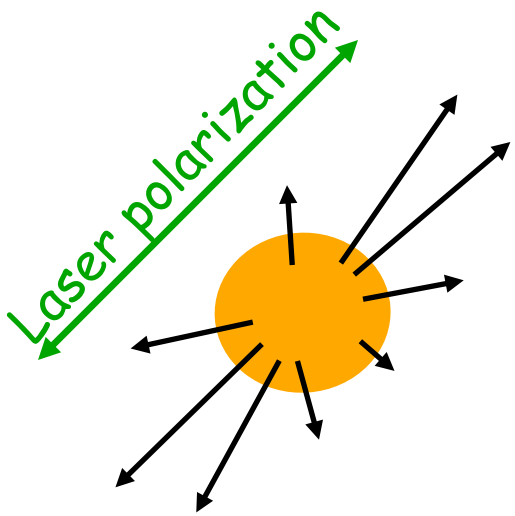
Thermalization

Dissipation:

collective (laser) → thermal

... isotropic emission?

Angular distributions and (thermo)dynamics



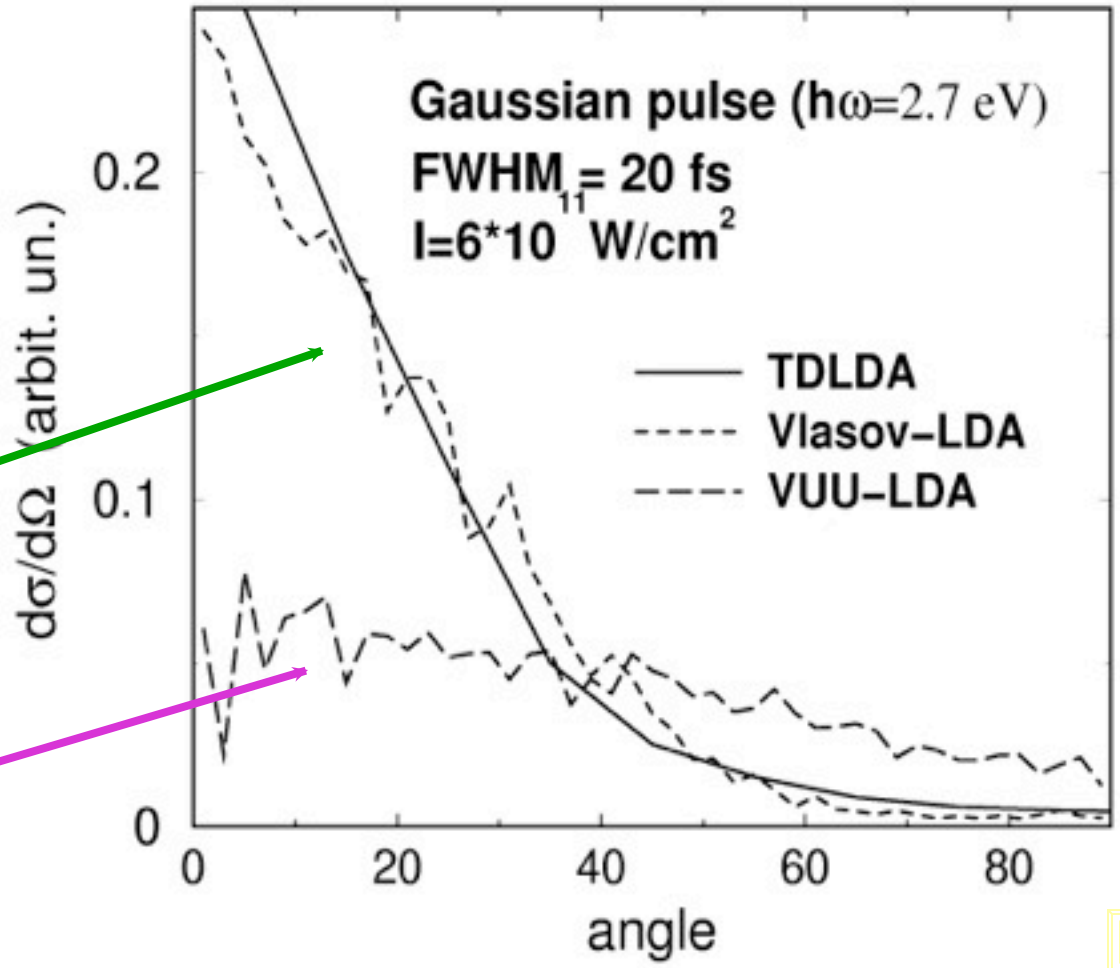
Laser polar.

Mean field:

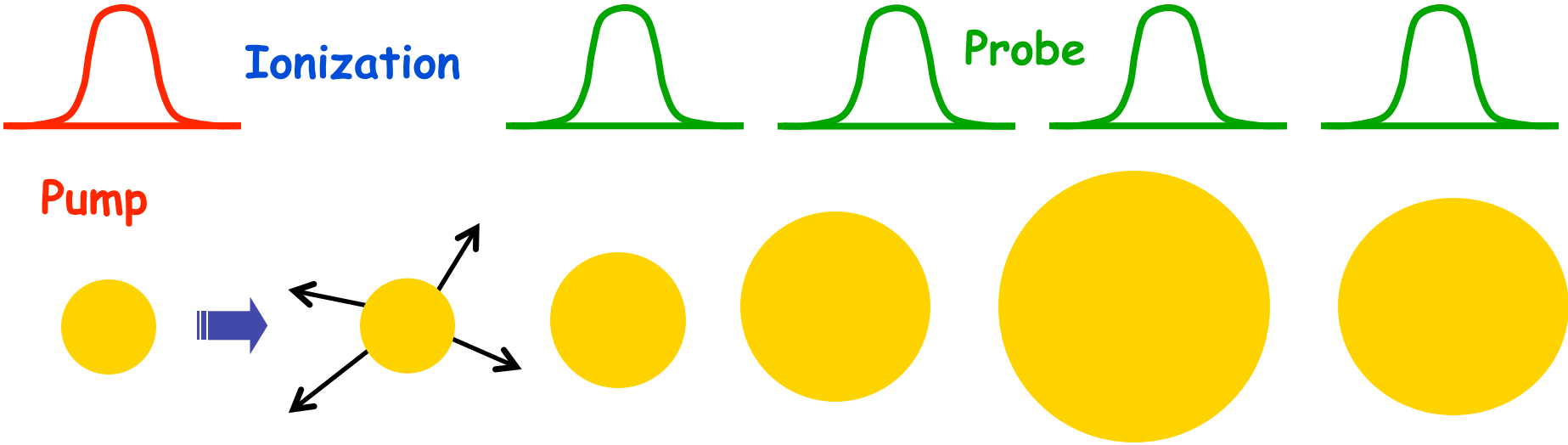
Directed emission

Mean-field + colls :

Isotropic emission



Pump – probe for vibration

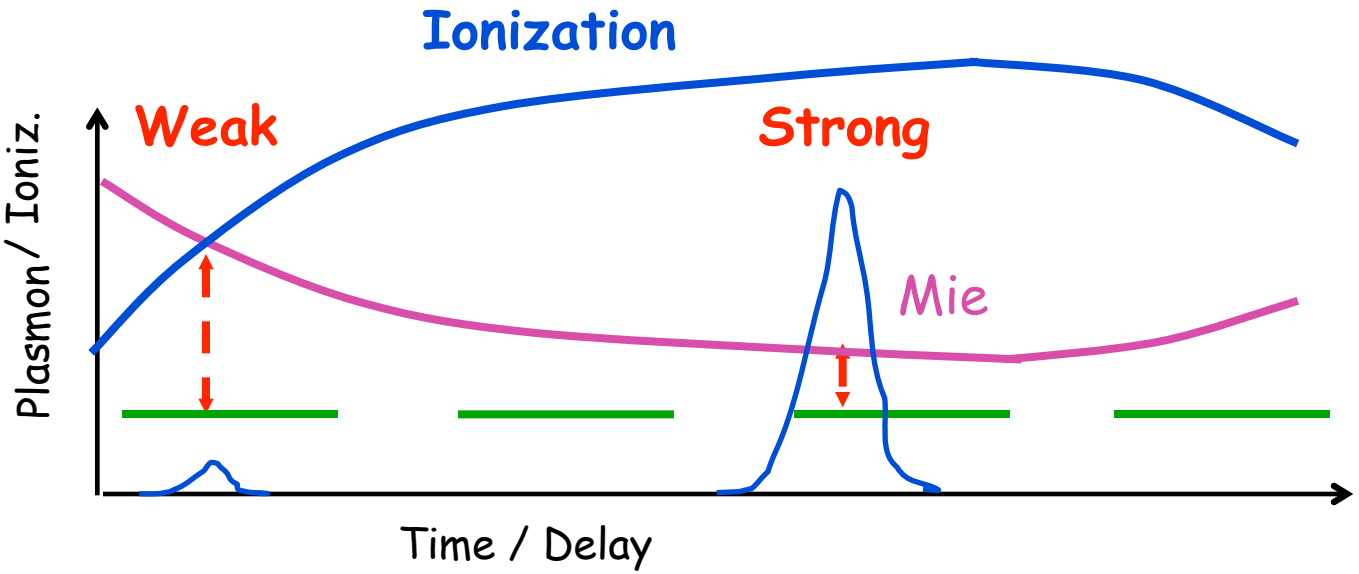


$\omega^2_{Mie} \sim 1 / R^3$

Ionization

maps

Vibrations

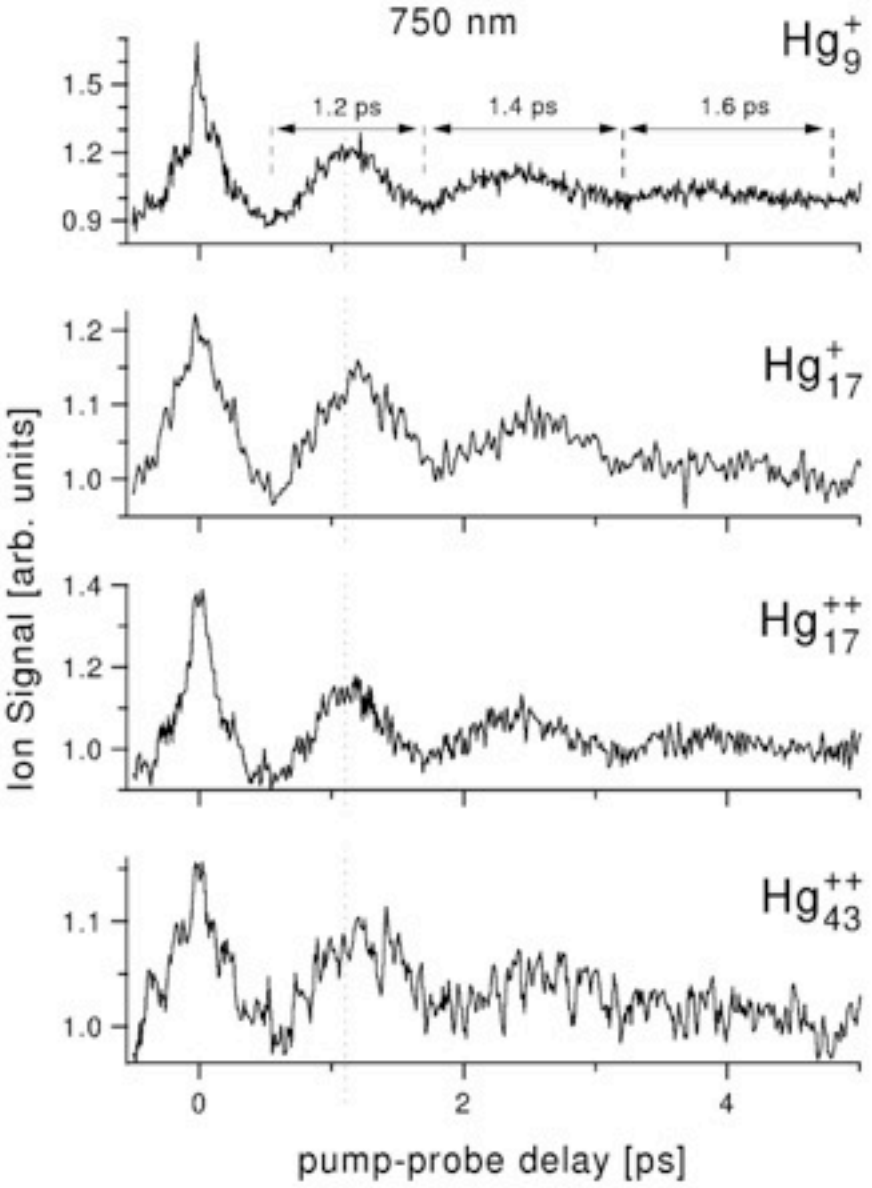


Monopole « Pump – Probe » Dynamics

Ionization as a function of delay between pump and probe laser pulses

- **Ionic vibration period**
- **Expansion rate**

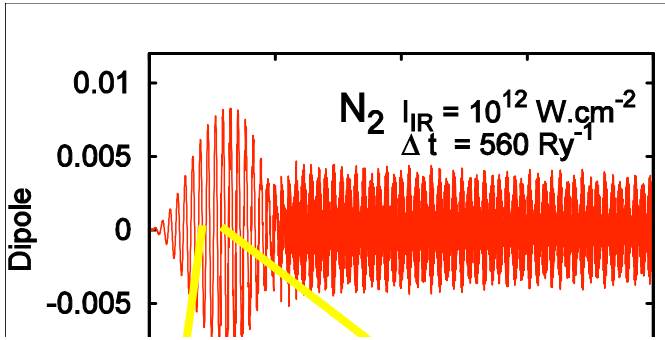
Structure (vibrations…)
Dynamics (viscosity…)

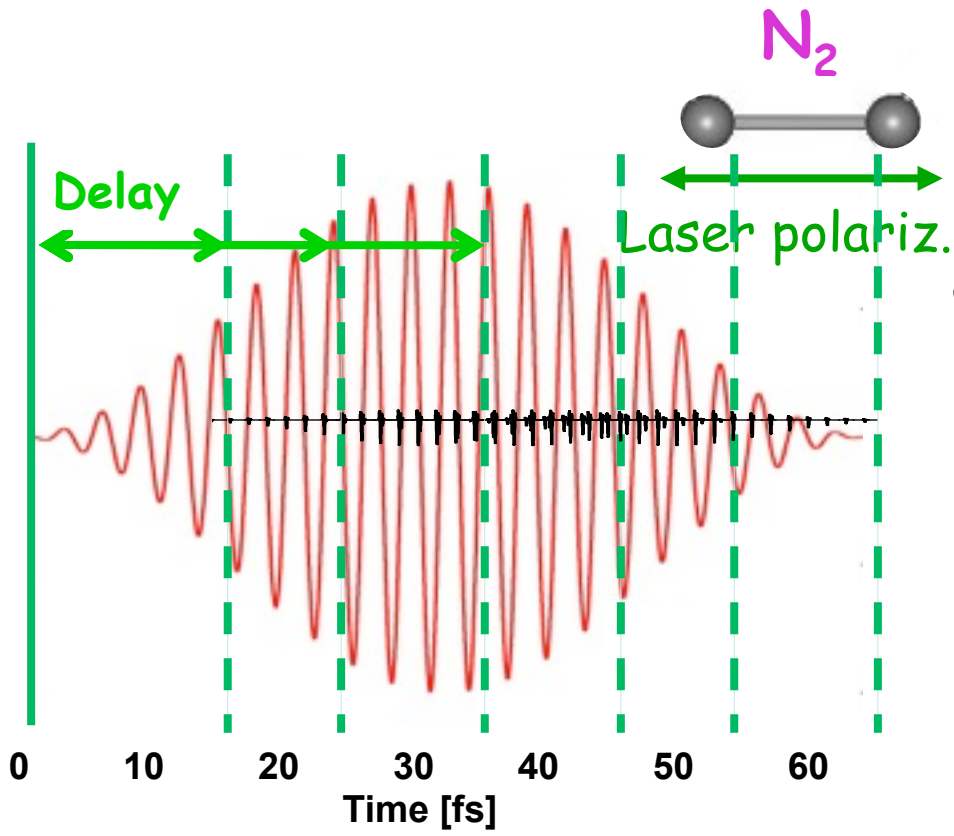


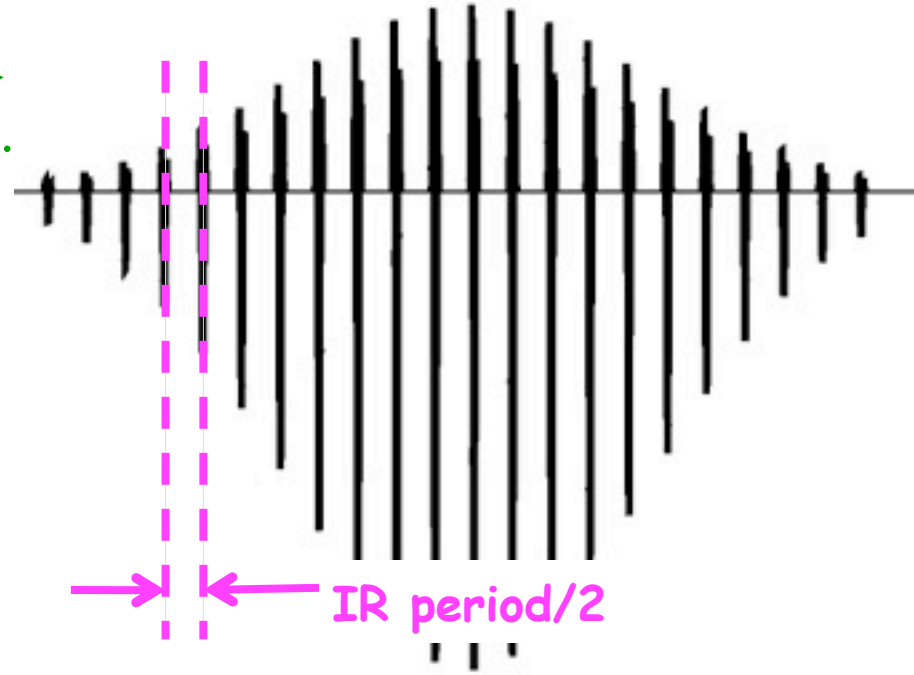
Exp. Gerber

A simple example

Dipole response



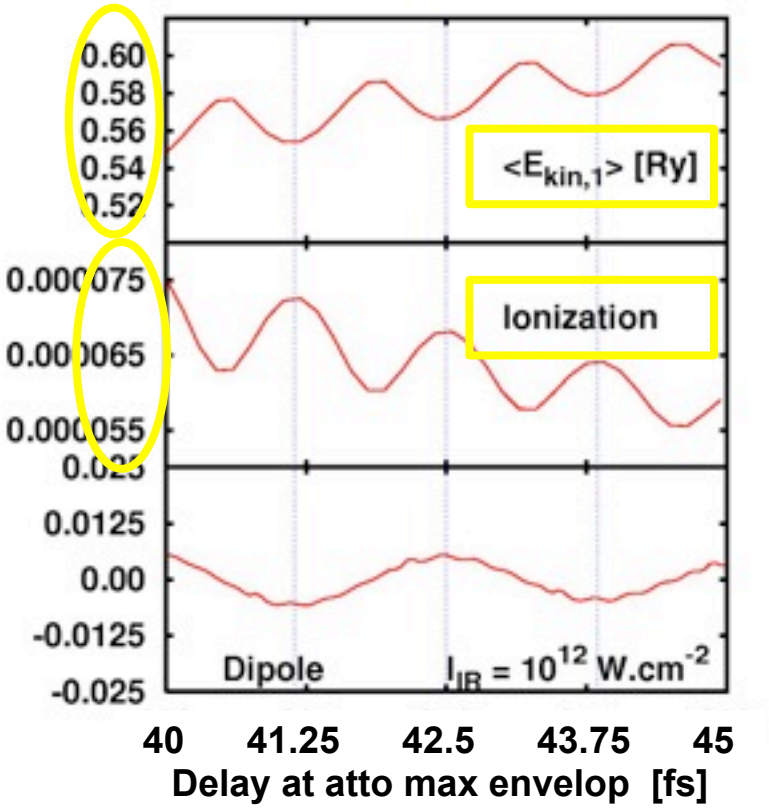




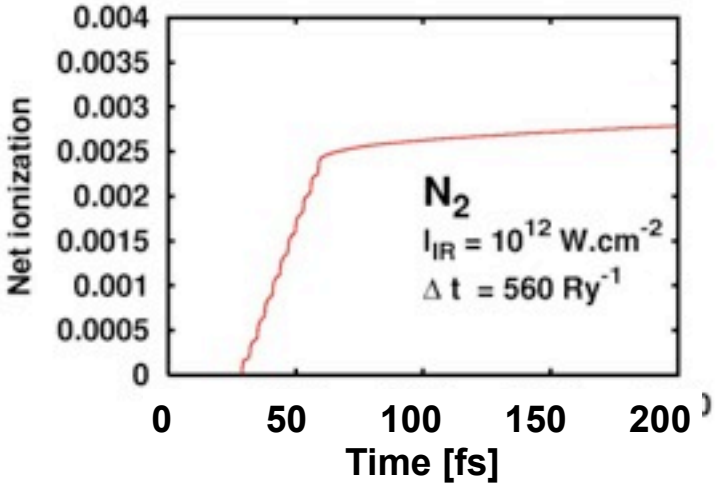
IR 60 fs, 0.11 Ry @ 10^{12} W.cm^{-2}

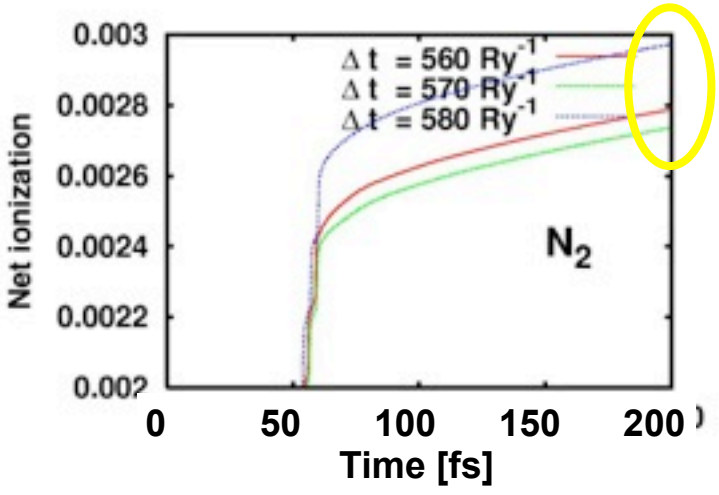
Atto train 30 fs, 1.5 Ry @ 10^{10} W.cm^{-2}

Ionization characteristics



Net ionization





Strong effects and correlation

Attosecond and strong-field electron dynamics in clusters and large molecules

Dynamics of ionization in TDDFT
- Self Interaction problem (SIC)
- Benchmark TDSIC calculation done
- Boundary conditions in the oven
- Dynamical correlations in near future (electronic transport) in quantum TDDFT

Ultimate goal:
Dynamical description of irradiation and response of
- electrons
- ions
- environment

Time resolved dynamics
- Key importance of non adiabatic electron/ion couplings
- Photoelectron spectroscopy energy, angle done/ in the oven
- Pump and probe scenarios done
- FEL laser domain mostly in future
- Ionization cross sections in near future
- Atto laser domain in the oven

A few references

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Rev. Mod. Phys. **82** (2010) 1793