

# Influence of Nuclear Motion on Electronic Properties for Small Molecules in a Field

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# Outline

- Numerical methods
- Semi-classical calculations :  $H_2^+$  (1-d & 2d) &  $H_2$  (1-d)
- Sub-Femtosecond nuclear motion of HCl

# Why & (How) molecules ?

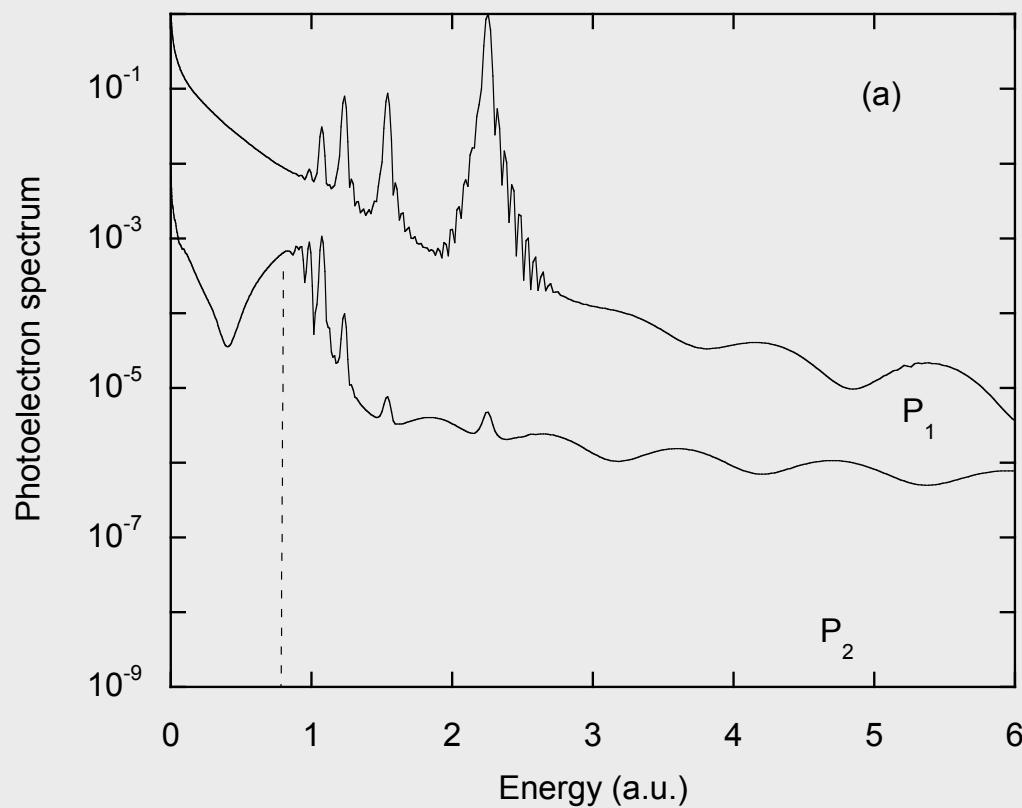
Nuclear motion → richer dynamics

World is made of molecules

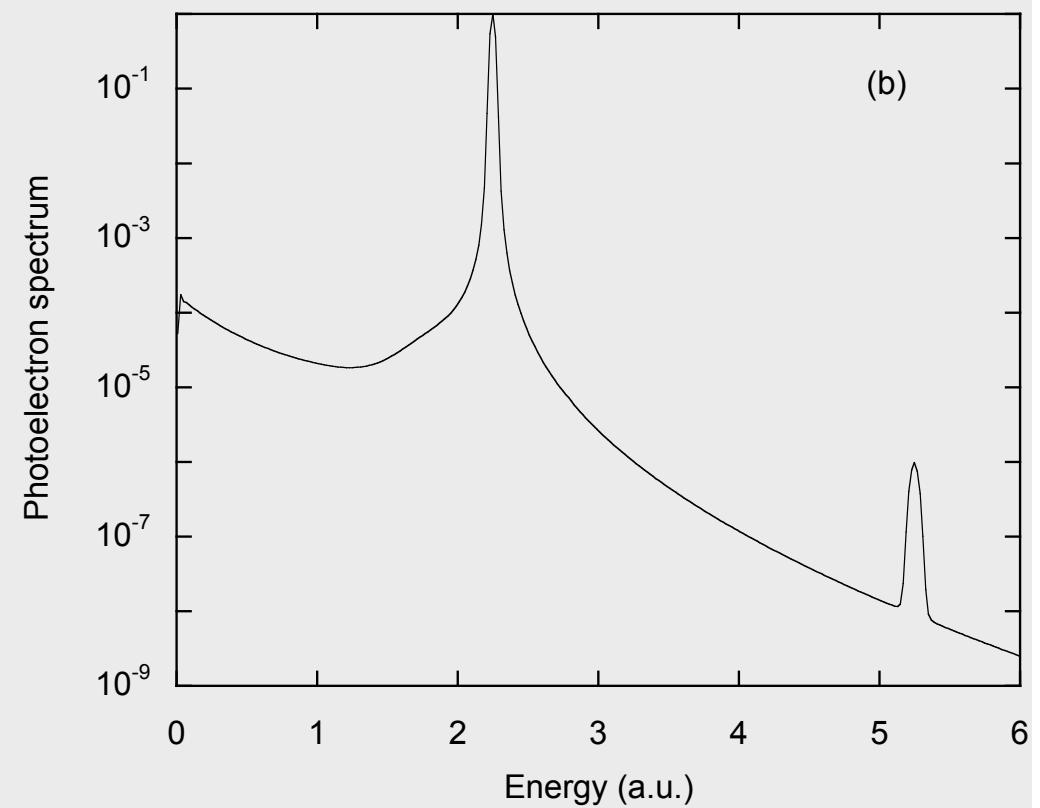
## Methods

Small Molecules	{	Born Oppenheimer: Fixed nuclei Lowest molecular states (No ionization) Full quantum Computation (moving nuclei)	Bandrauk, Ivanov, Corkum ... Weiner, Frasinski ... Bandrauk, Kulander ...
Fixed nuclei	{	TDDFT MCTDHF	Gross, Bauer Brabec, Scrinzi

(1-d, 2 e-) atom +  $\omega$  = 3 a.u.



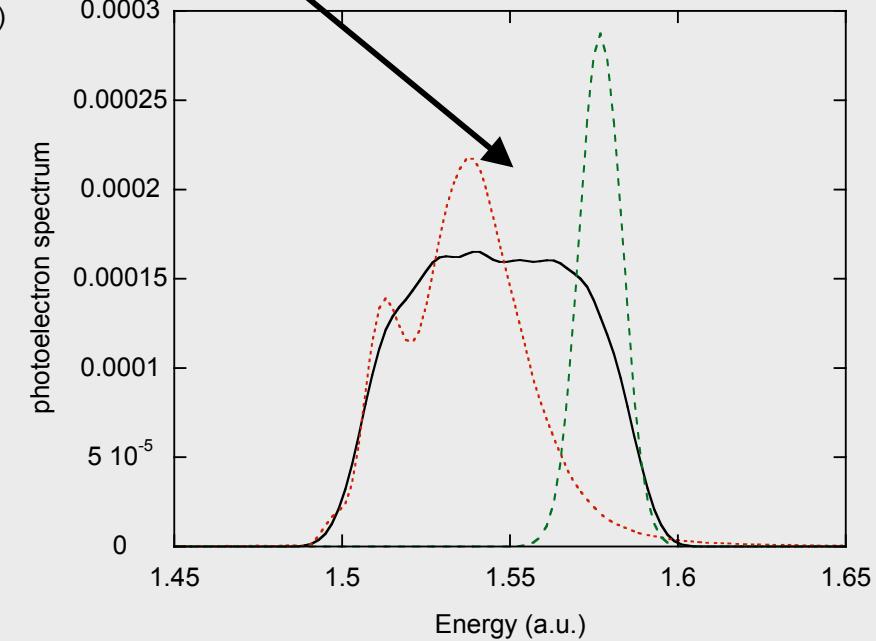
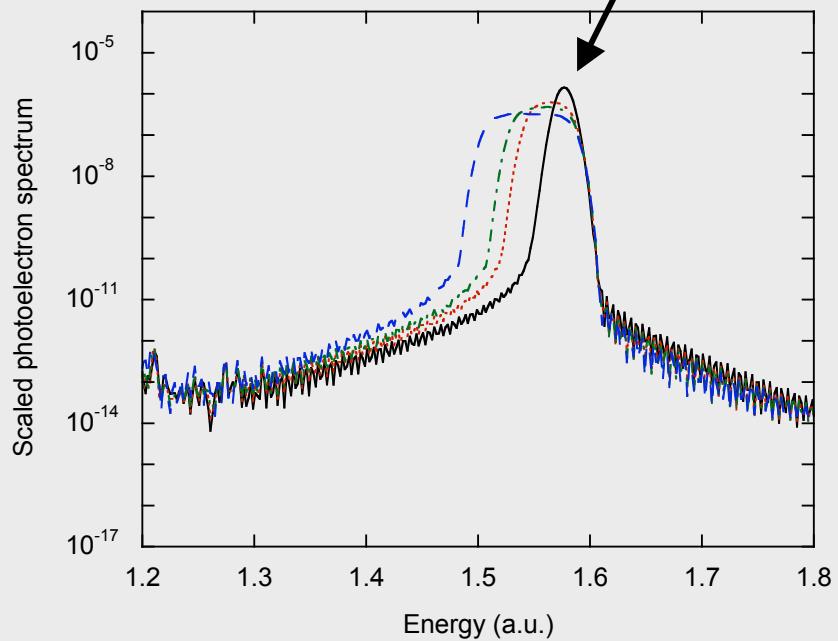
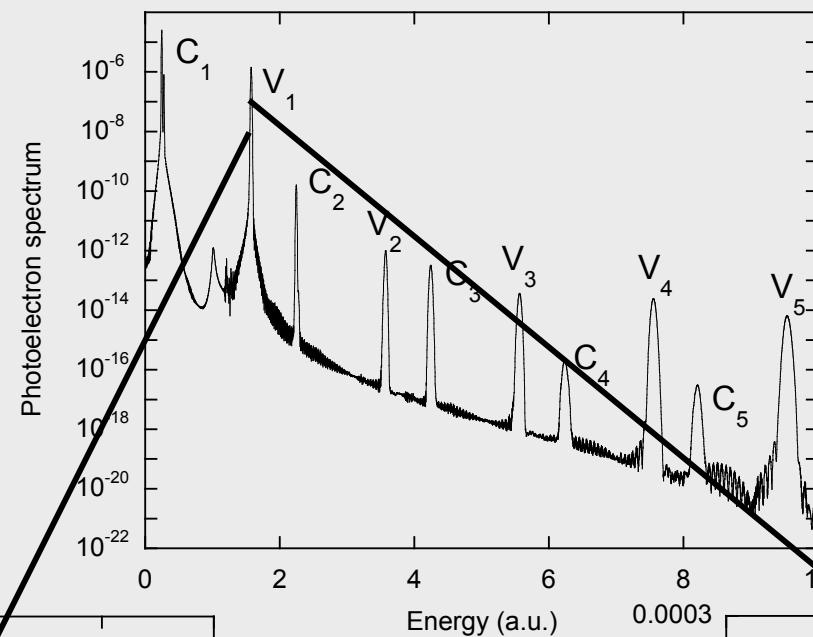
Exact solution  
+  
FFT



TDDFT  
+  
'TOF'  
 $V_e$ : HF  
 $V_c$ : Becke

(1-d, 3 e-) atom +  $\omega$  = 2a.u.

TDDFT  
+  
'TOF'  
 $V_{ec}$ : KLI



# Why & (How) molecules ?

Nuclear motion → richer dynamics

World is made of molecules

## Methods

Small  
Molecules

- { Born Oppenheimer: Fixed nuclei
- Lowest molecular states (No ionization)
- Full quantum Computation (moving nuclei)

Fixed  
nuclei

- { TDDFT
- MCTDHF

Multicomponent Density-Functional  
Theory for Electrons and Nuclei

Bandrauk, Ivanov, Corkum ...

Weiner, Frasinski ...

Bandrauk, Kulander ...

Gross, Bauer

Brabec, Scrinzi

Gross et al

## Semi-classical Approach

### Electron

$$i \frac{\partial \Psi(x,t)}{\partial t} = \left[ -\frac{\partial^2}{2\partial x^2} + V(x,t) + \frac{i}{c} A(t) \frac{\partial}{\partial x} \right] \Psi(x,t)$$

$$V(x,t) = -\frac{1}{\sqrt{a^2 + (x - X_1(t))^2}} - \frac{1}{\sqrt{a^2 + (x - X_2(t))^2}}$$

(1-D) Time Dependant  
Schrödinger Equation

### Nuclei

$$M \frac{d^2 X_i}{dt^2} = F_{j \rightarrow i}(t) + F_{e \rightarrow i}(t) + F_{laser}(t)$$

Proton motion treated classically

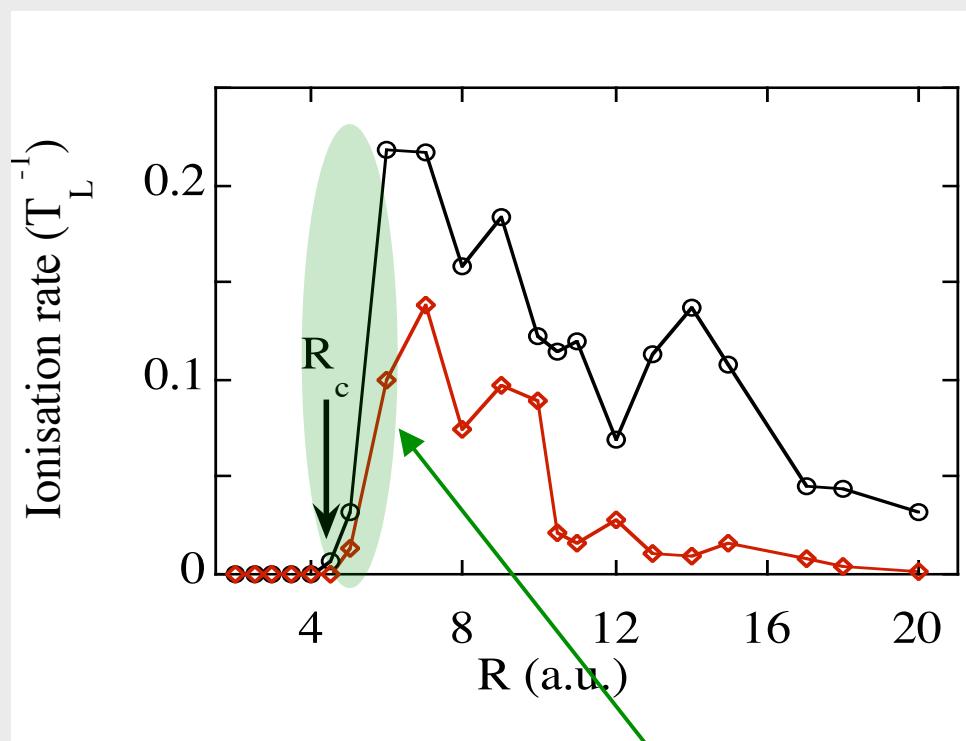
$$F_{e \rightarrow i}(t)$$

Computed using electronic density

$$|\Psi(x,t)|^2$$

# Molecular ion $H_2^+$

## 1-D Computations



Fixed nuclei

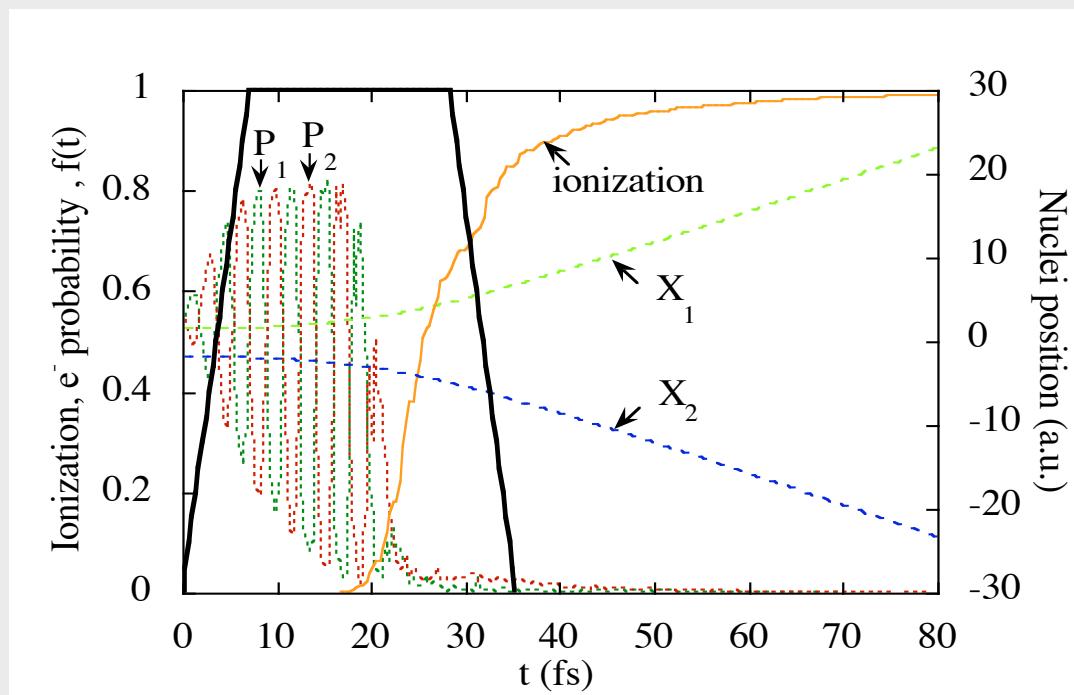
$\omega = 1.17$  eV

$I = 10^{14}$  W/cm<sup>2</sup>

$I = 5.10^{13}$  W/cm<sup>2</sup>

CREI

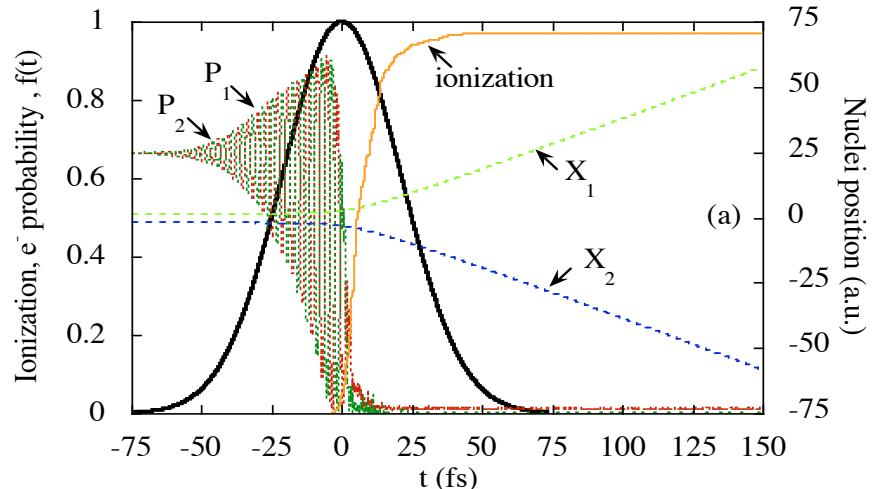
Bandrauk *et al.*  
Ivanov *et al.*



- Ionization probability
- Nuclei positions
- Electronic Density

$\omega = 1.17$  eV  
 $I = 10^{14}$  W/cm<sup>2</sup>

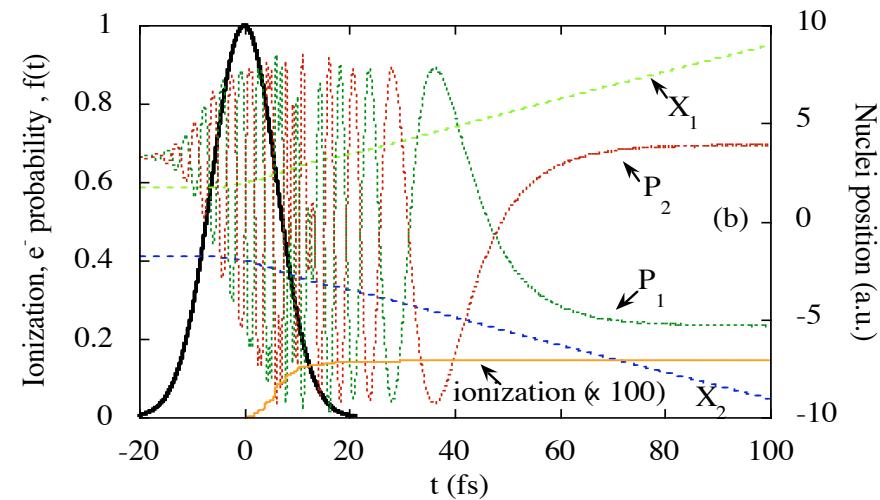
## Pulse duration role



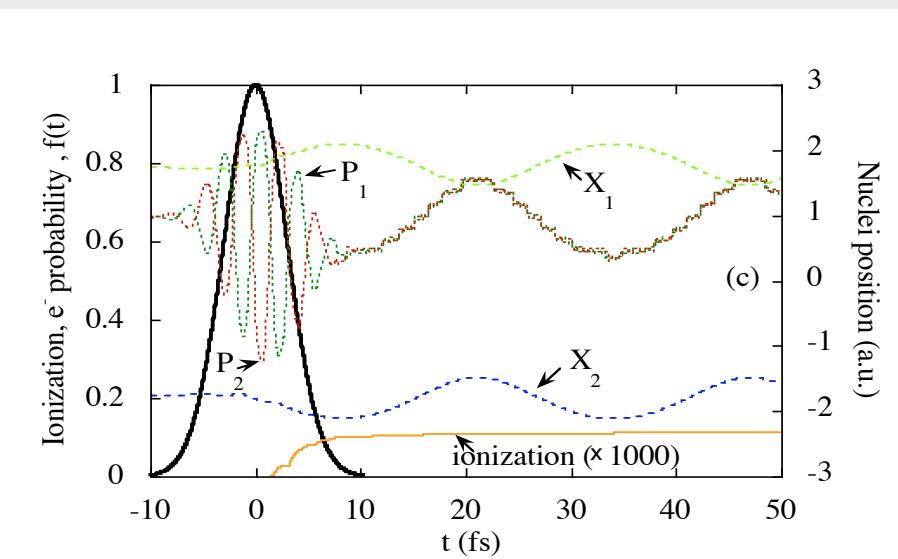
$\tau = 50\text{fs}$

**Ionization probability**  
**Nuclei positions**  
**Electronic Density**

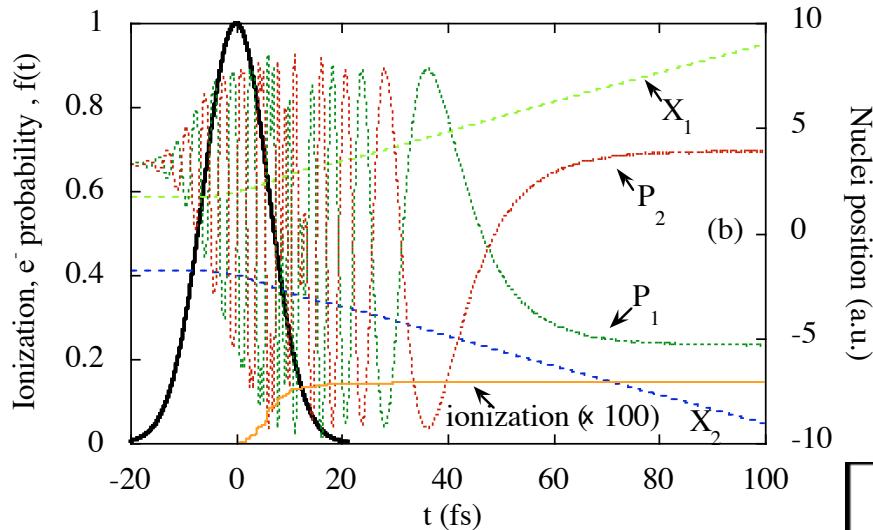
$\omega = 1.17 \text{ eV}$   
 $I = 10^{14} \text{ W/cm}^2$



$\tau = 15\text{fs}$



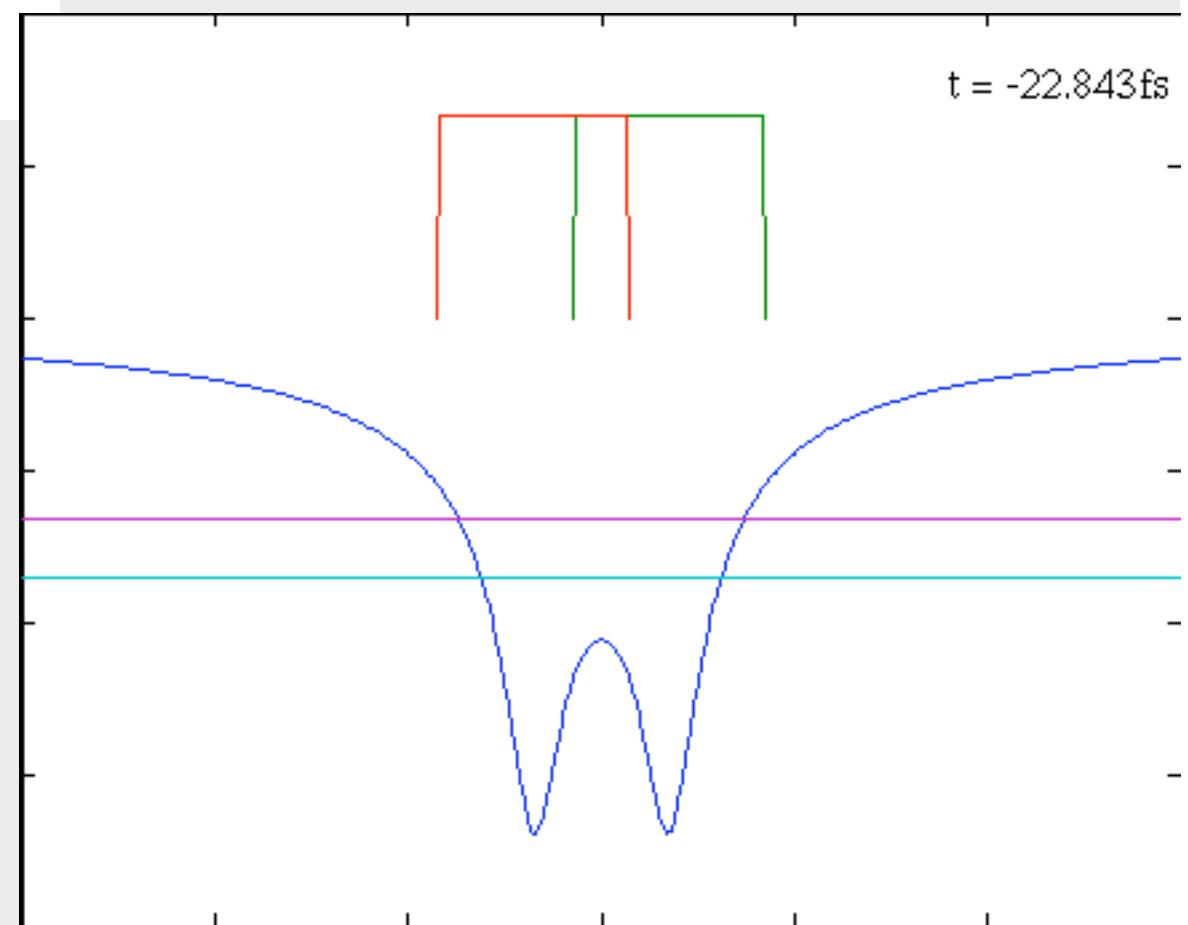
$\tau = 7\text{fs}$



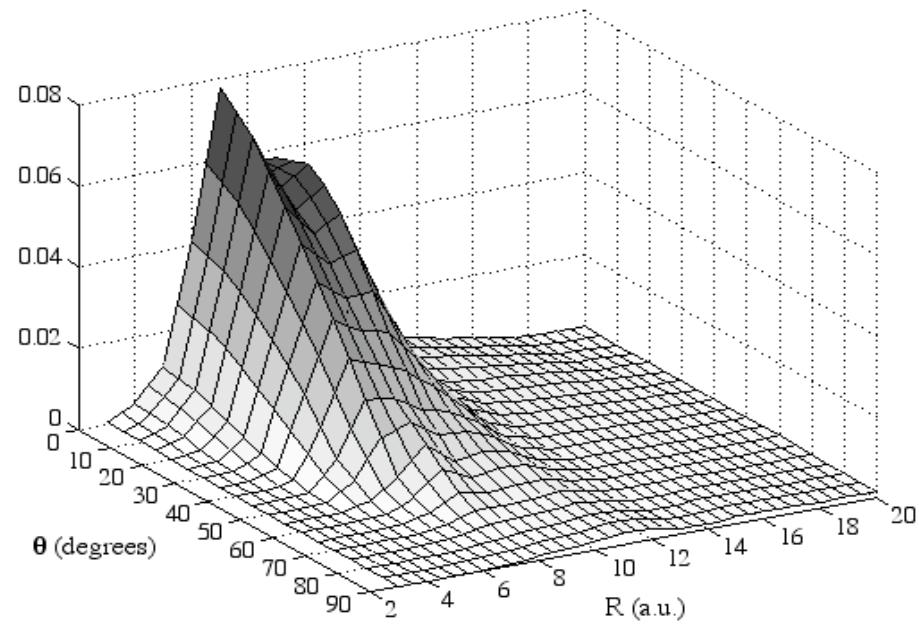
$\tau = 15\text{fs}$

Oscillations due to superposition  
of  $\sigma_g$  and  $\sigma_u$  states

cf Vrakking



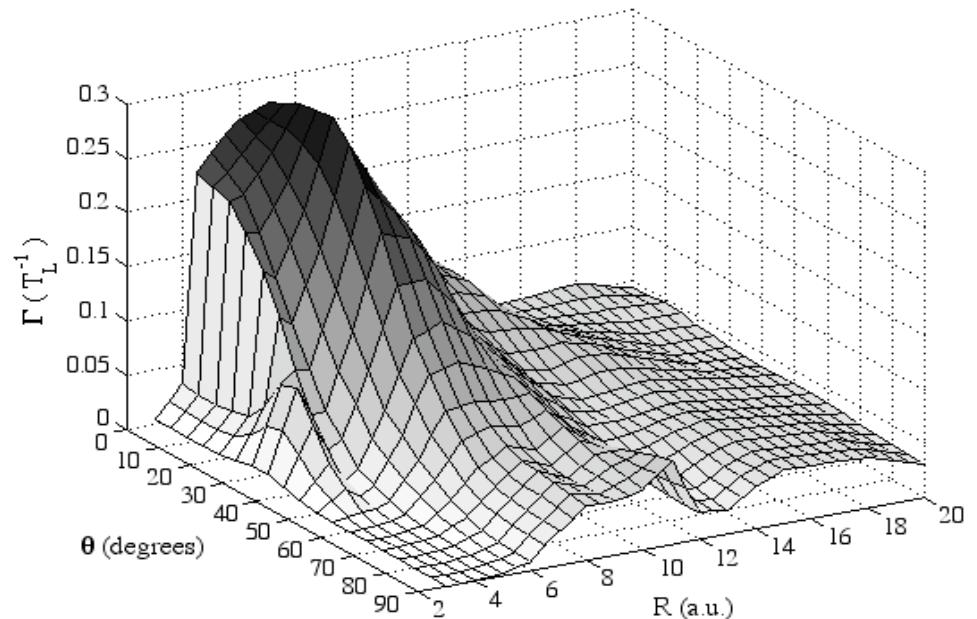
## Molecular ion $H_2^+$ 2-D Computation



$\omega = 1.55 \text{ eV}$   
 $I = 5 \cdot 10^{13} \text{ W/cm}^2$

Fixed nuclei

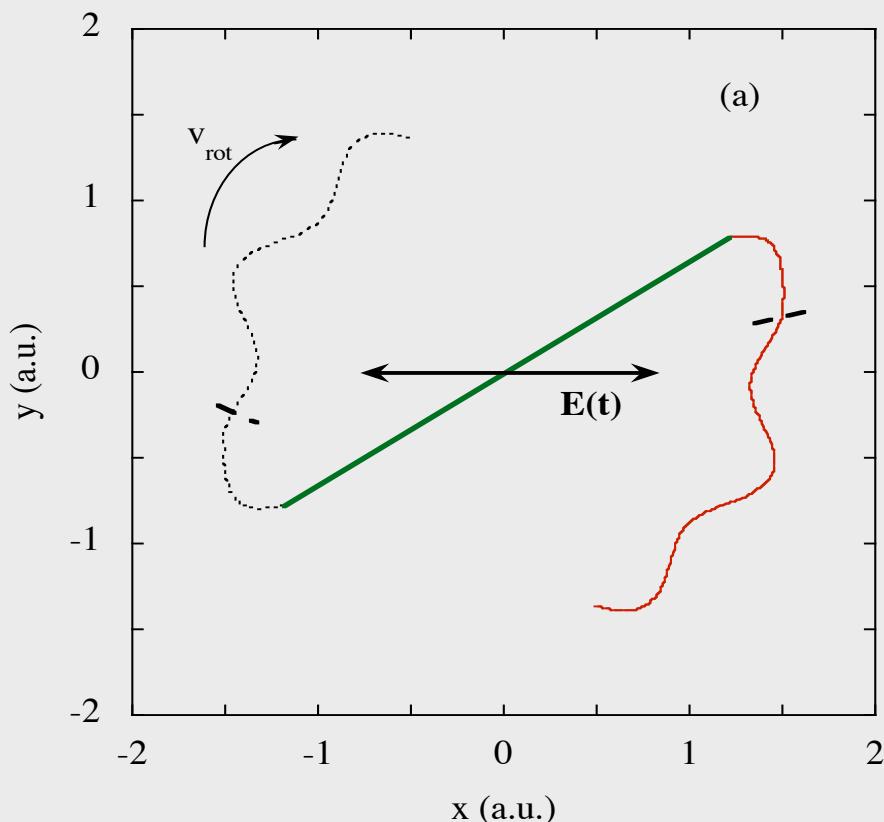
$\omega = 1.55 \text{ eV}$   
 $I = 10^{14} \text{ W/cm}^2$



## Typical nuclei trajectories

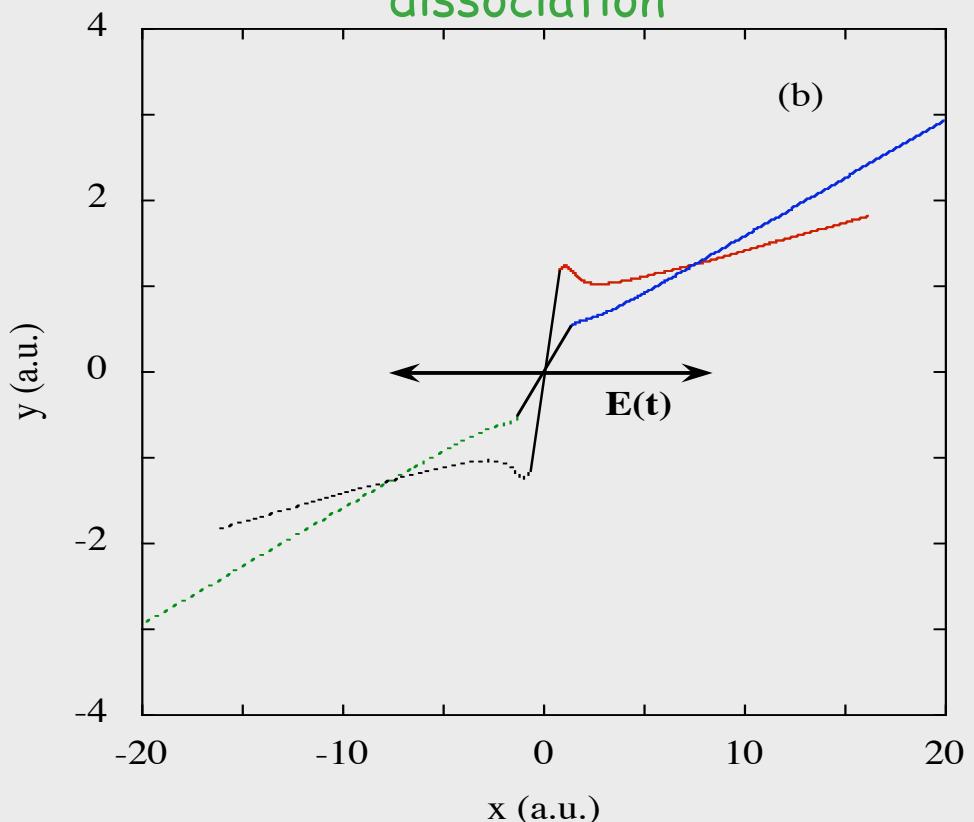
$\omega = 1.55 \text{ eV}$ ,  $I = 9.10^{13} \text{ W/cm}^2$   
 $\theta_{\text{ini}} = 33^\circ$

Rotation (alignment)



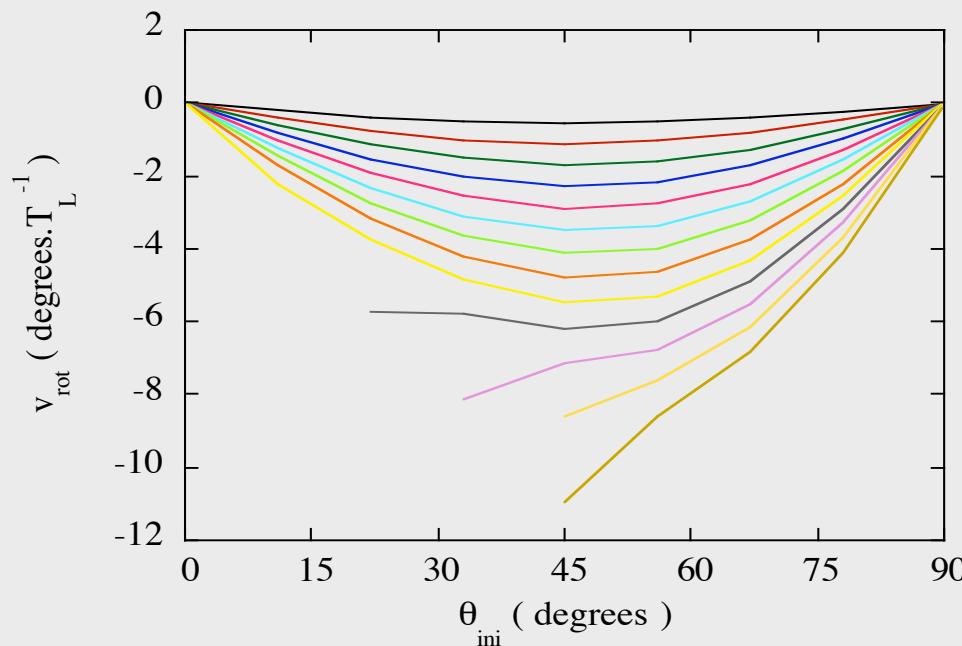
$\omega = 1.55 \text{ eV}$ ,  $I = 2.10^{14} \text{ W/cm}^2$   
 $\theta_{\text{ini}} = 22^\circ$ ,  $\theta_{\text{ini}} = 56^\circ$

Ionization + Coulomb explosion  
or  
dissociation



## « Observables »

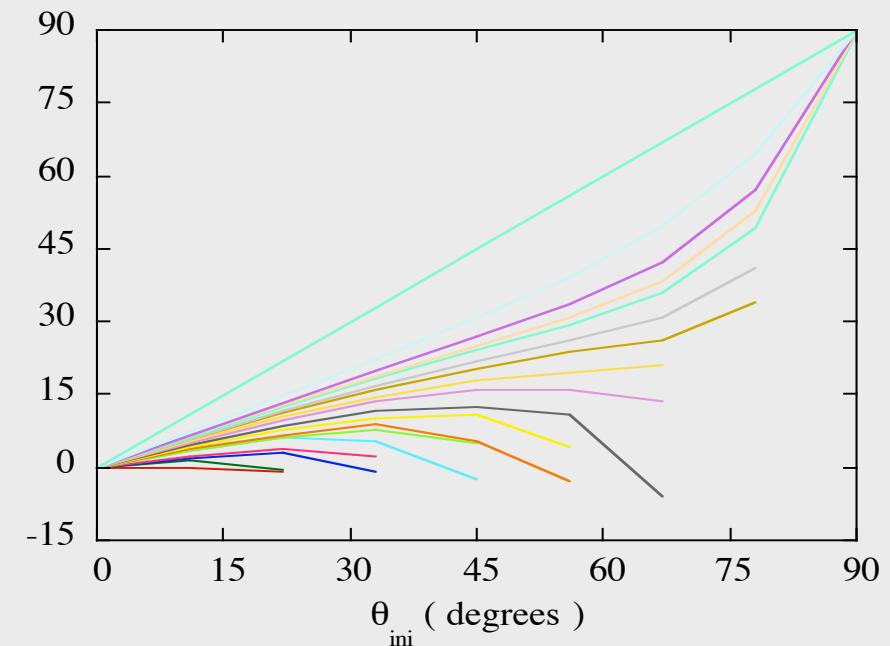
$10^{13} < I < 5 \cdot 10^{14} \text{ W/cm}^2$



Rotation velocity  
of the molecule

$$V_{\text{rot}} \quad \xrightarrow{\text{when } I} \quad V_{\text{rot}} \propto \sin 2\theta$$

$\omega = 1.55 \text{ eV}$



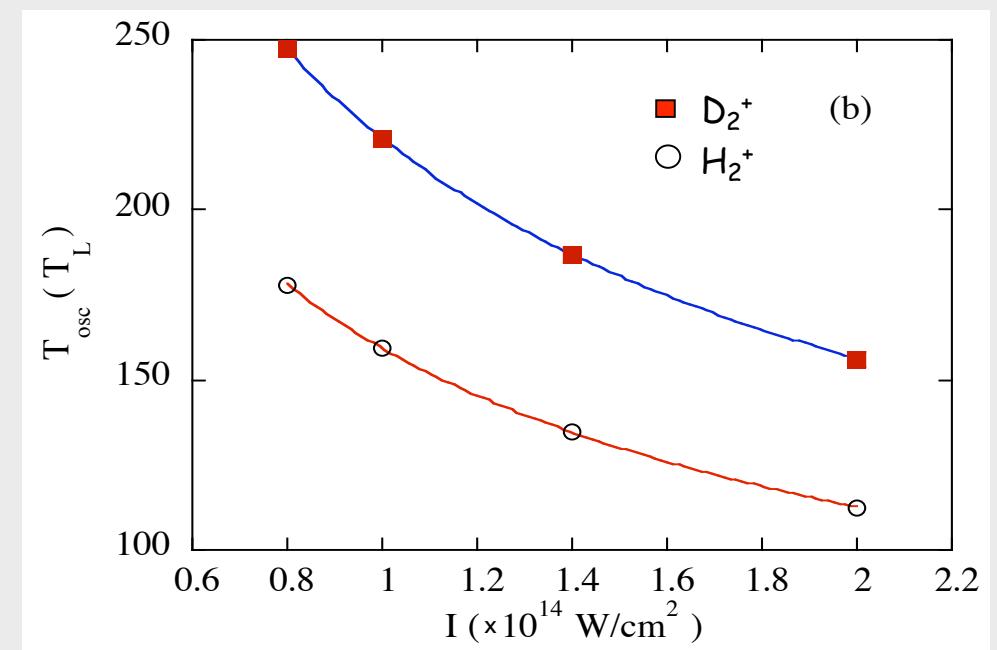
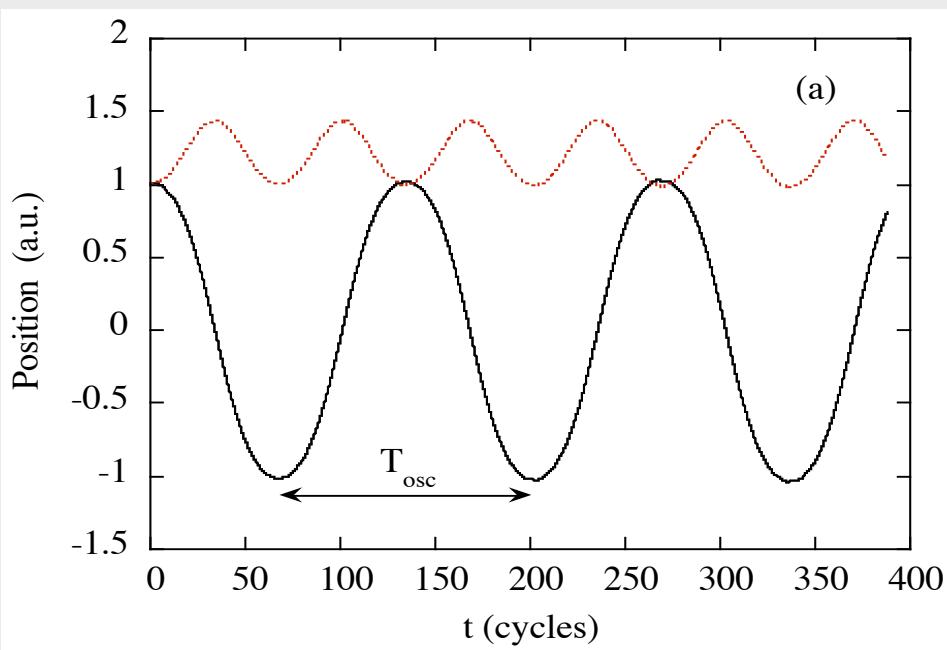
Detection angle  
of the fragments

$$\theta_{\text{dect}} \quad \xrightarrow{\text{when } \theta_{\text{ini}}} \quad \theta_{\text{dect}} \rightarrow \theta_{\text{ini}} \quad \xrightarrow{\text{when } I}$$

## « Observables »

$\omega = 1.55 \text{ eV}$ ,  $I = 10^{13} \text{ W/cm}^2$

$\theta_{\text{ini}} = 45^\circ$



$$\omega_{\text{osc}} = \frac{2\pi}{T_{\text{osc}}} \propto \sqrt{\frac{I \cos \theta_{\text{ini}}}{\mu}}$$

## Comparison Quantum vs Semi-classical

- Electron + Nuclei

$$i \frac{\partial \Psi(x, R, t)}{\partial t} = \left[ -\frac{\partial^2}{2\partial x^2} - \frac{1}{M} \frac{\partial^2}{\partial R^2} + V(x, R, t) + \frac{i}{c} A(t) \frac{\partial}{\partial x} \right] \Psi(x, R, t)$$

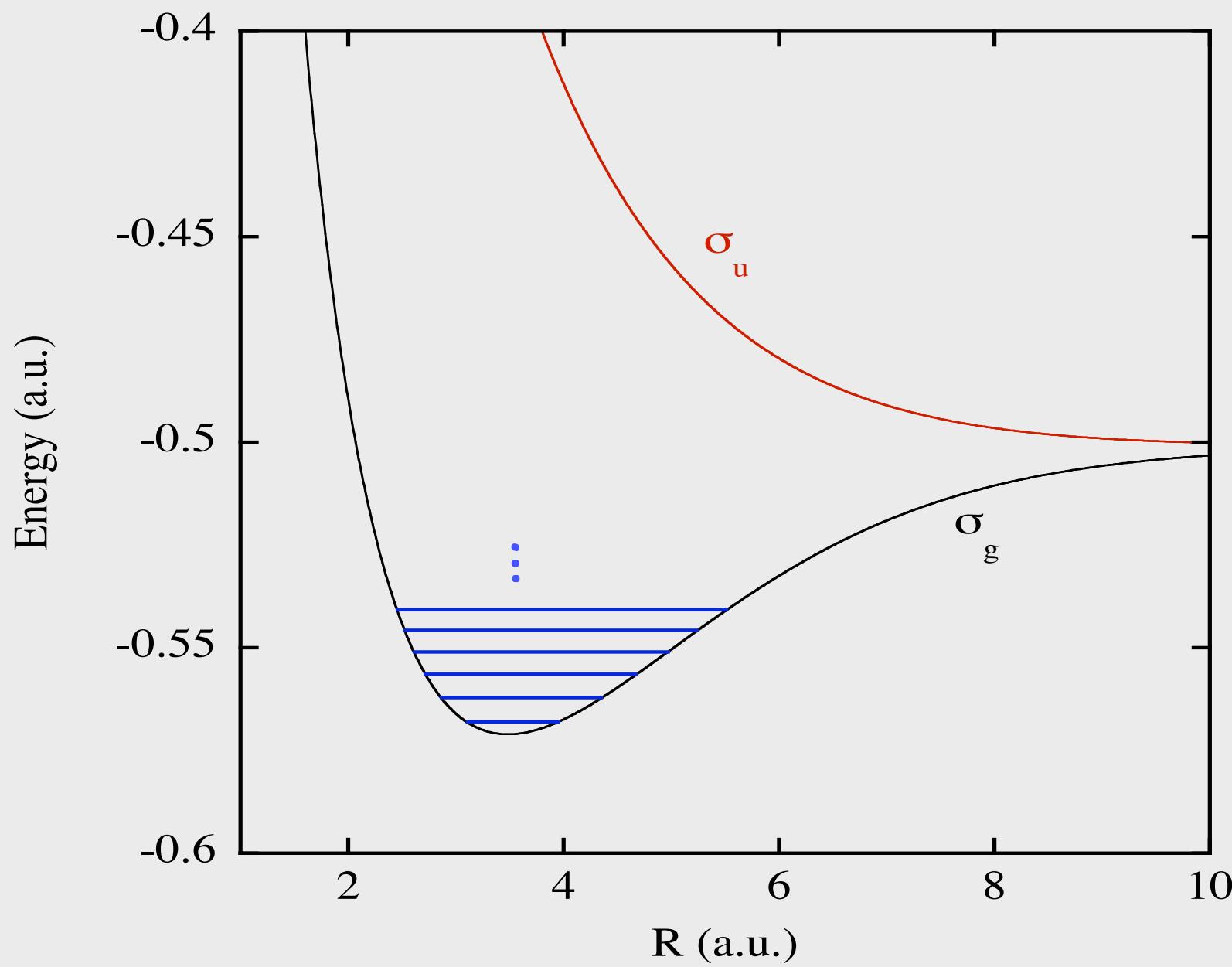
$$V(x, R, t) = -\frac{1}{\sqrt{a^2 + (x - R/2)^2}} - \frac{1}{\sqrt{a^2 + (x + R/2)^2}} + \frac{1}{\sqrt{q + R^2}}$$

2-particles (1-D) Time Dependant Schrödinger Equation

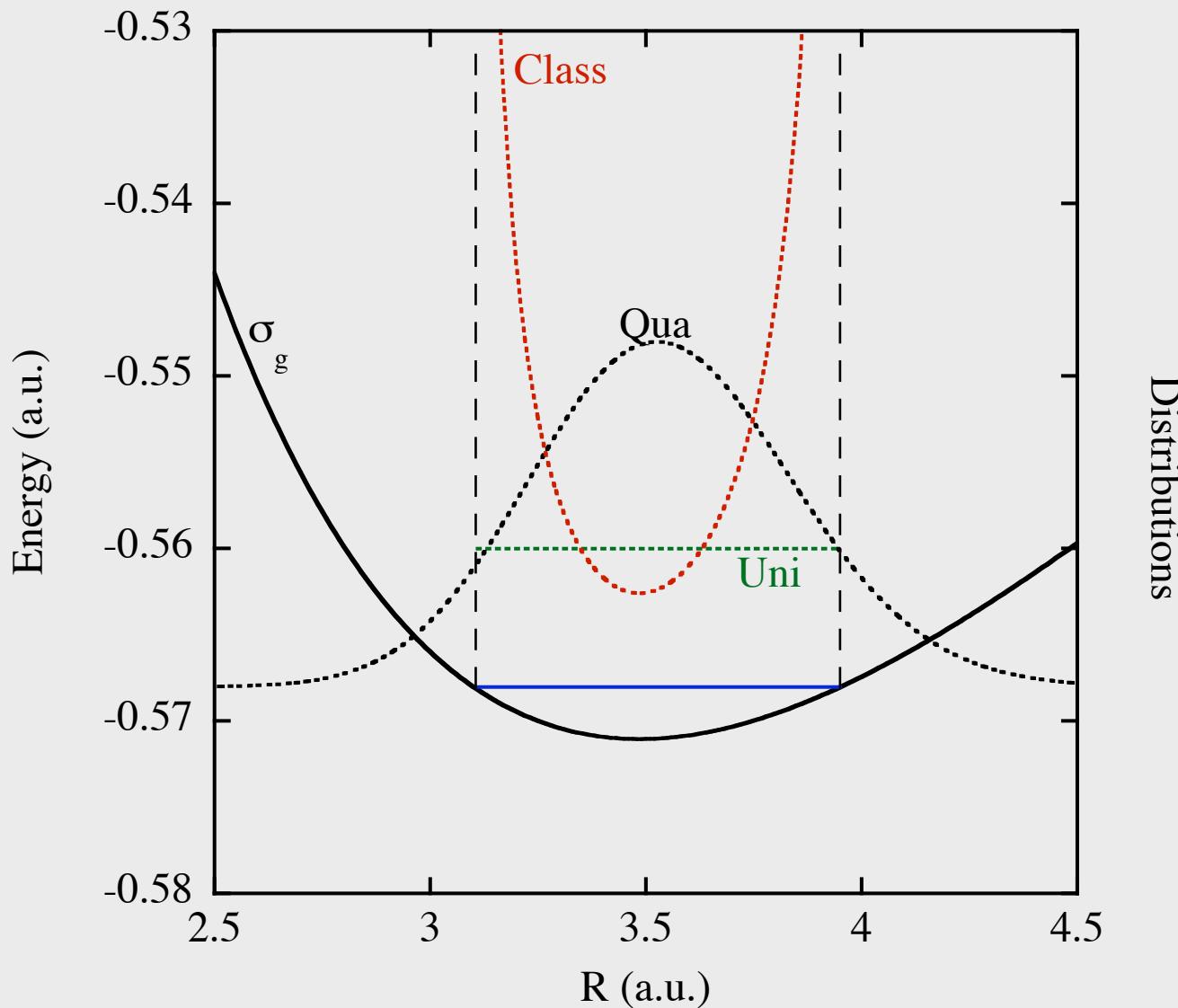
- Initial distribution for the positions and the velocities of the nuclei

"CTMC approach"

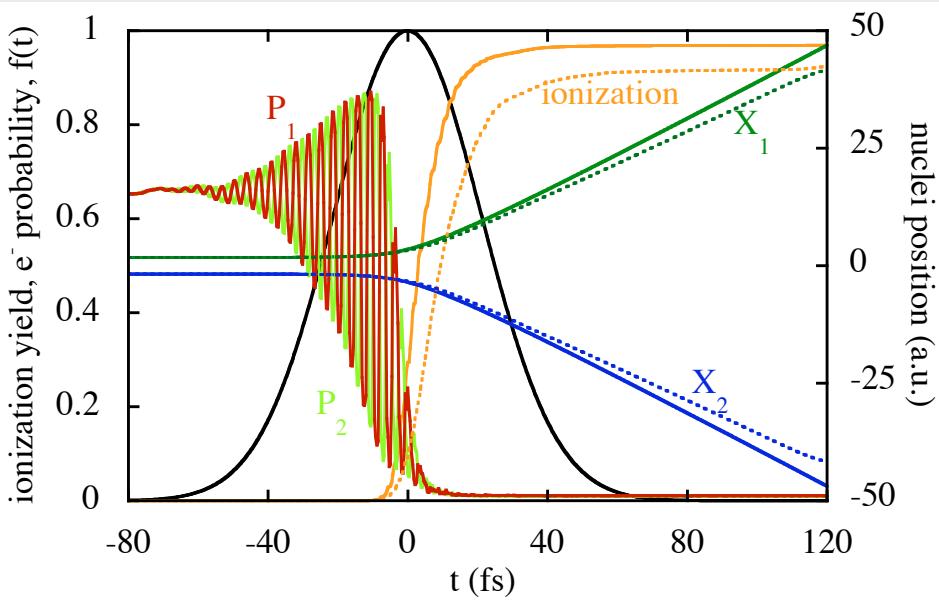
## Nuclear initial distribution



## Nuclear initial distribution



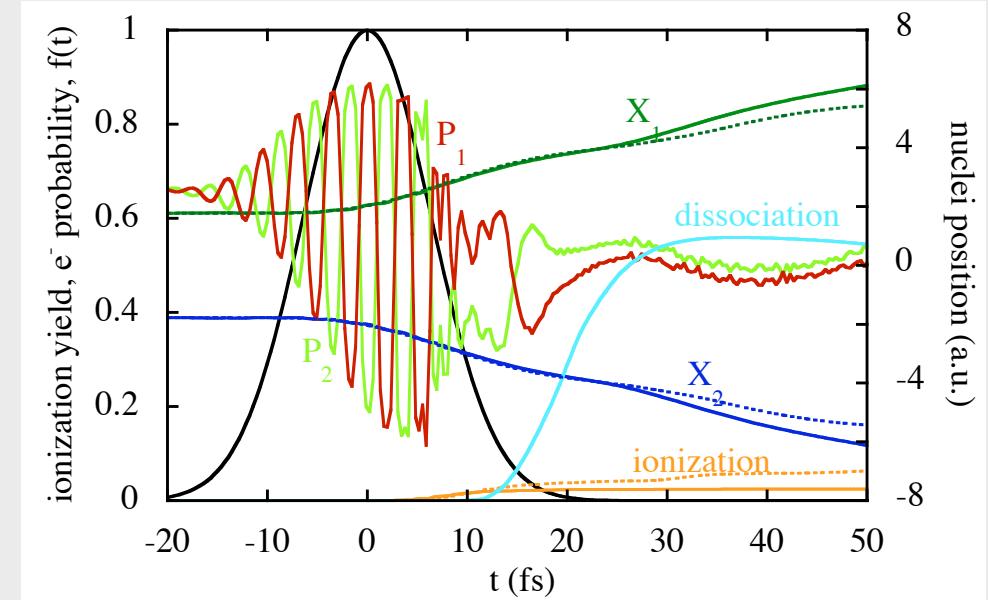
## Comparison Quantum vs Semi-classical



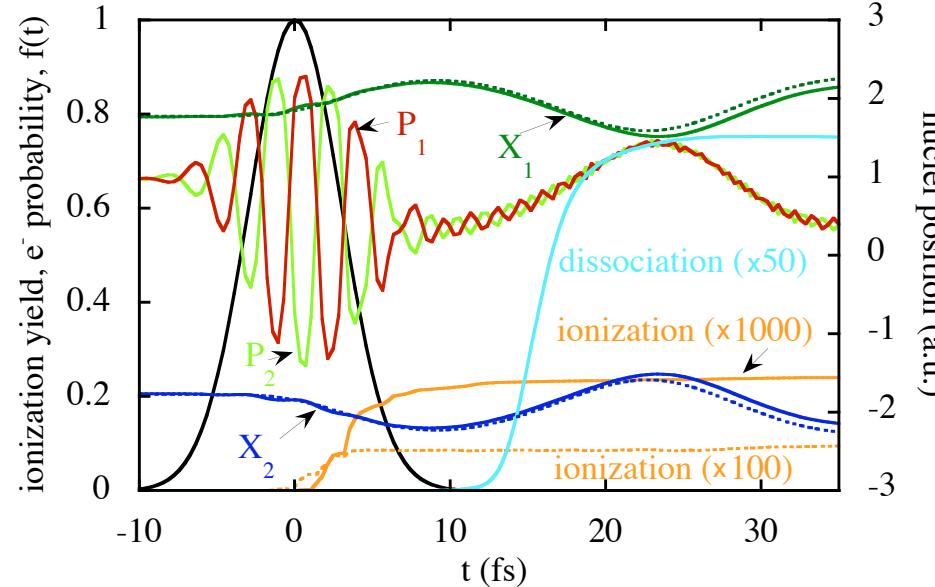
$\tau = 50\text{fs}$

Ionization probability  
Nuclei positions  
Electronic Density

$\omega = 1.17 \text{ eV}$   
 $I = 10^{14} \text{ W/cm}^2$

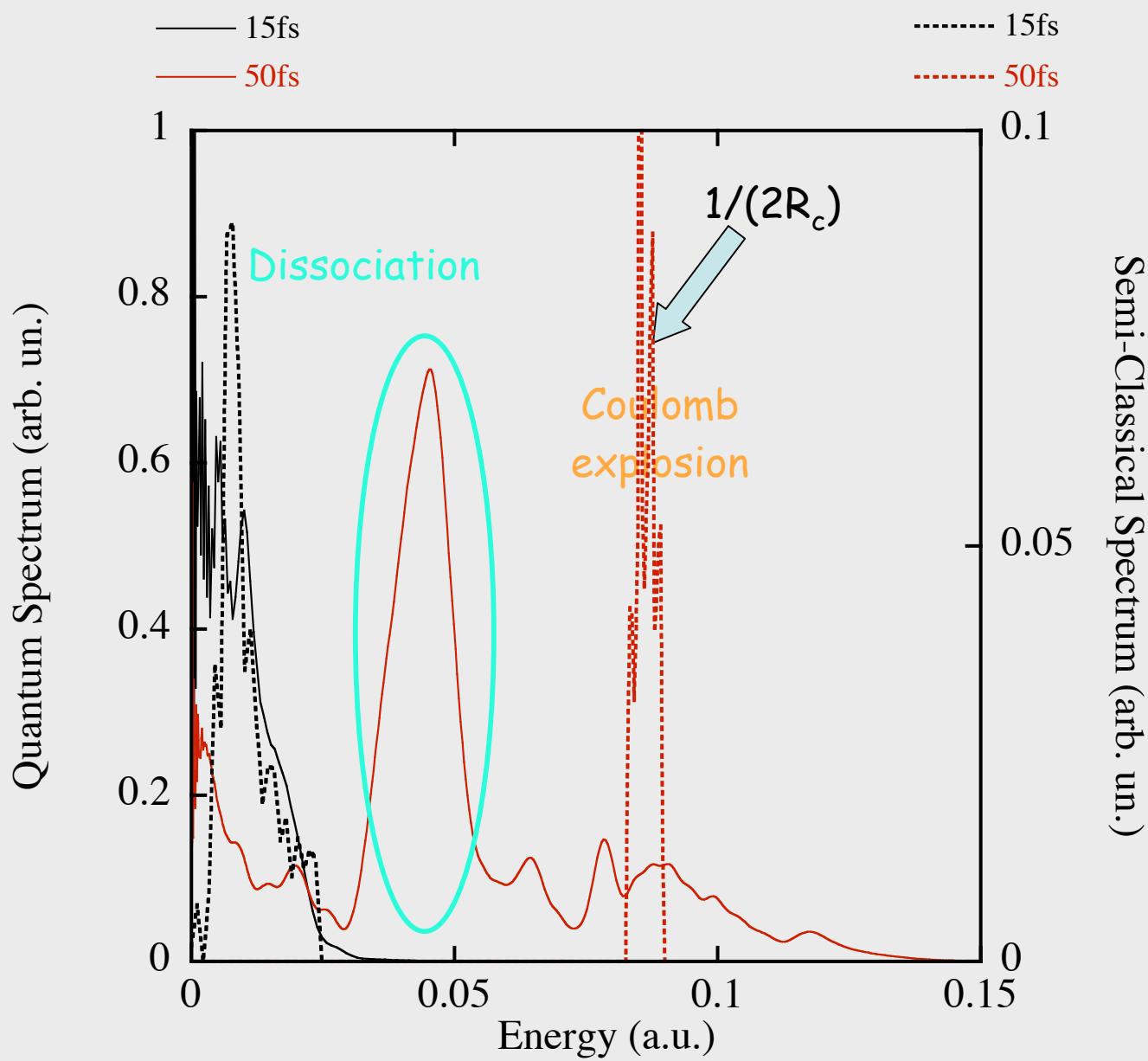


$\tau = 15\text{fs}$

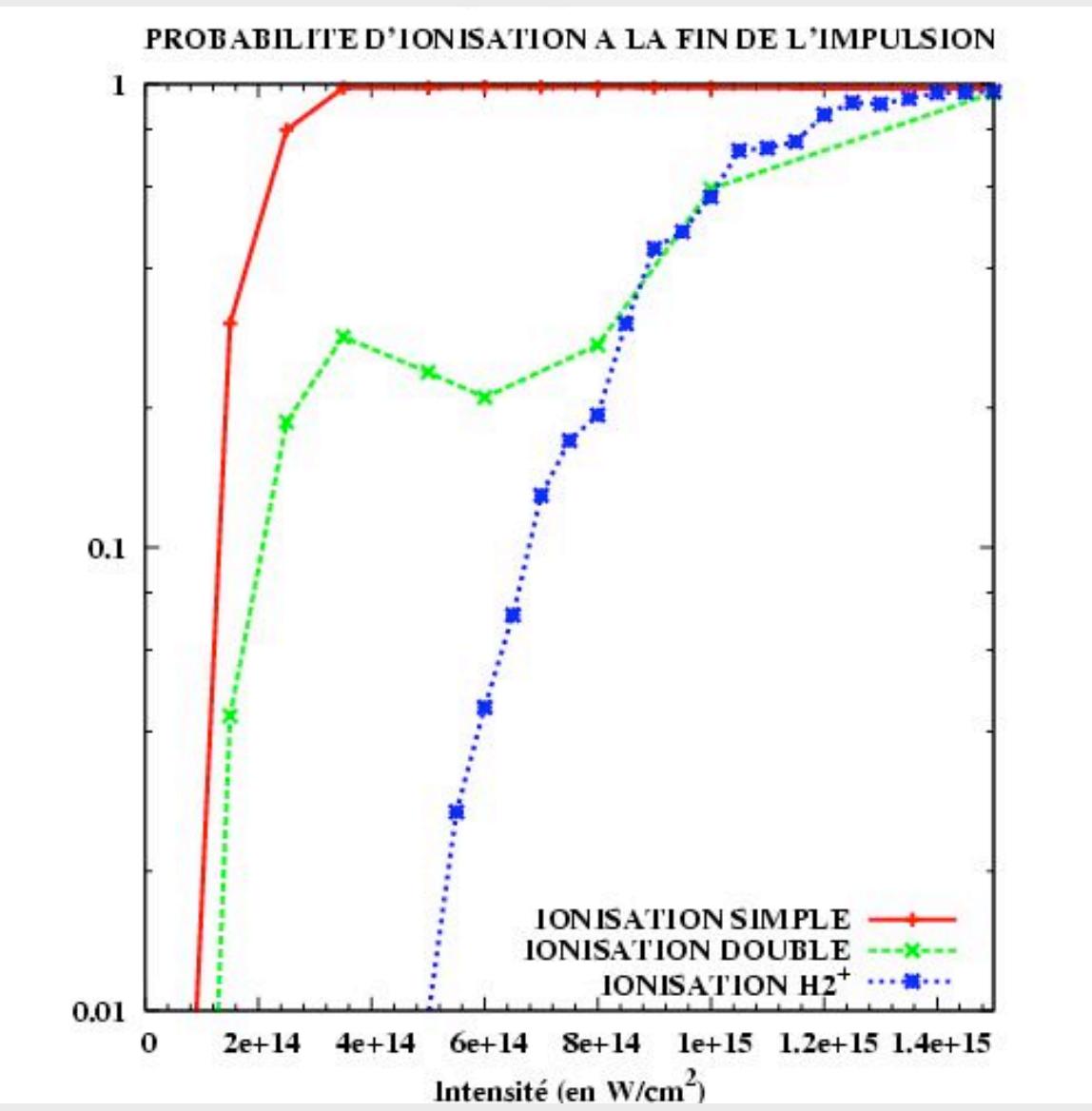


$\tau = 7\text{fs}$

## Comparison Quantum vs Semi-classical



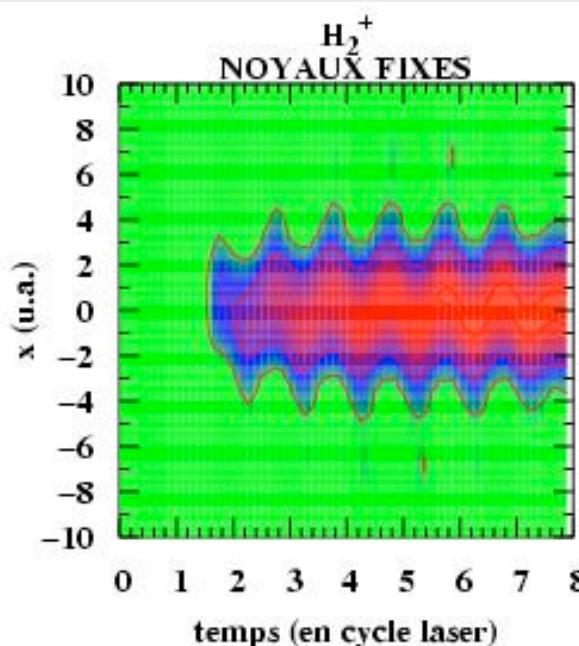
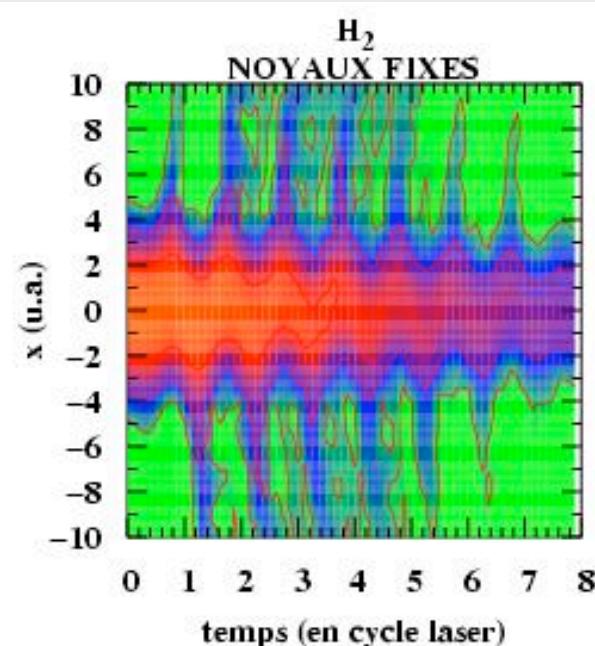
## H<sub>2</sub> : 1-D Computations



Fixed Nuclei

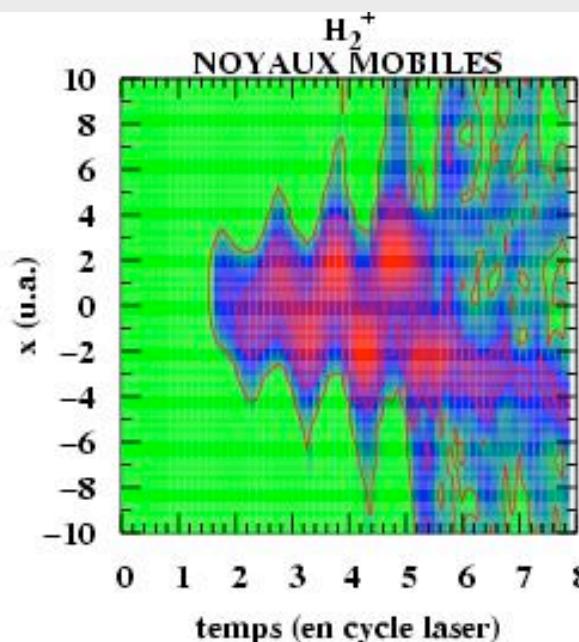
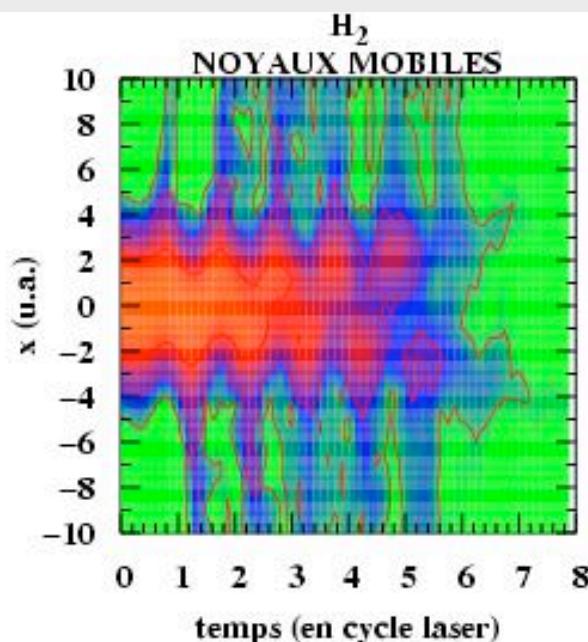
$\omega = 1.55$  eV

## H<sub>2</sub> : 1-D Computations



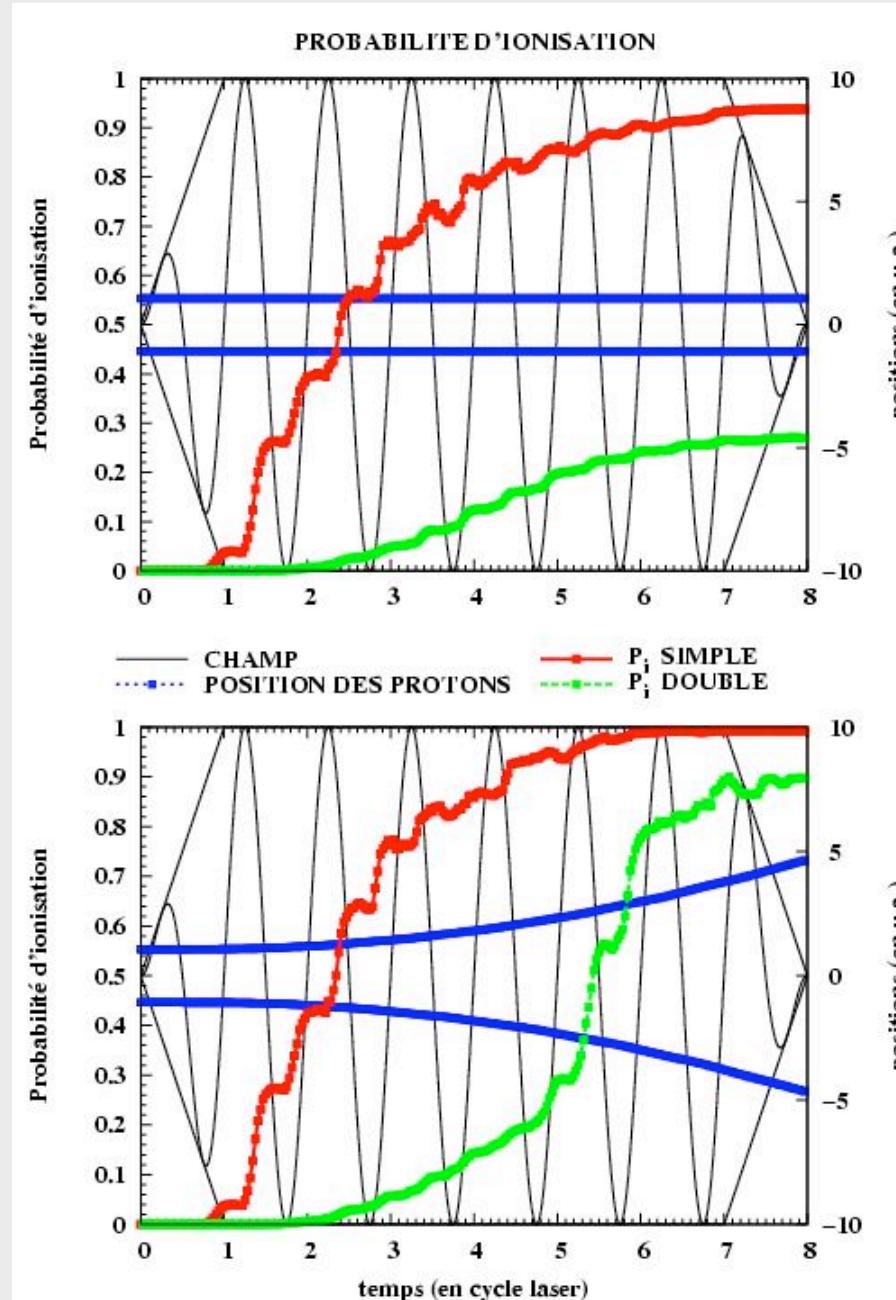
Fixed Nuclei

$\omega = 1.55 \text{ eV}$   
 $I = 3 \cdot 10^{14} \text{ W/cm}^2$



Moving Nuclei

## H<sub>2</sub> : 1-D Computations

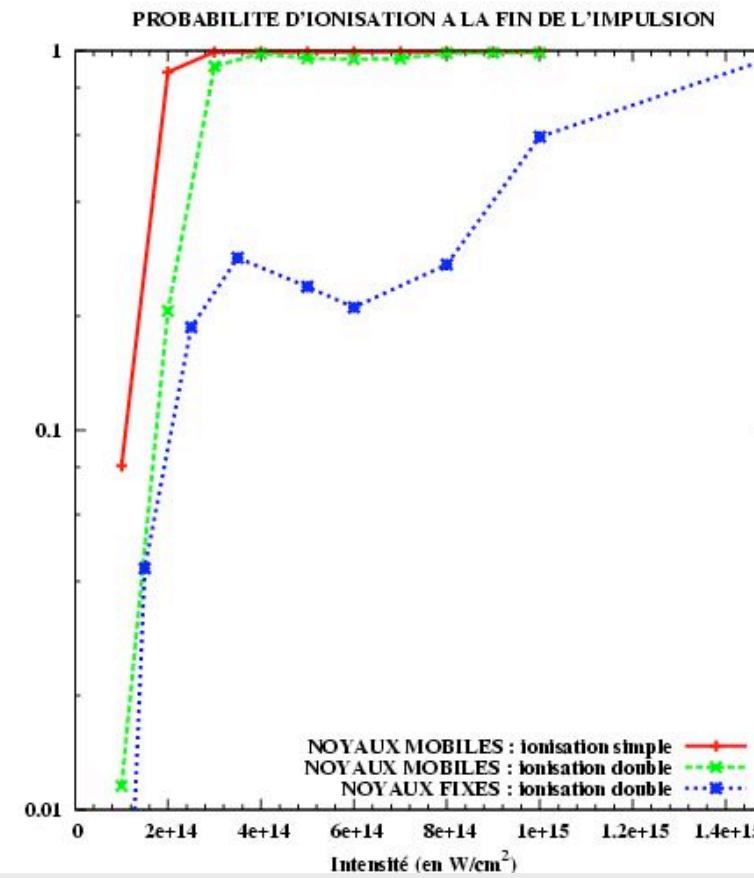
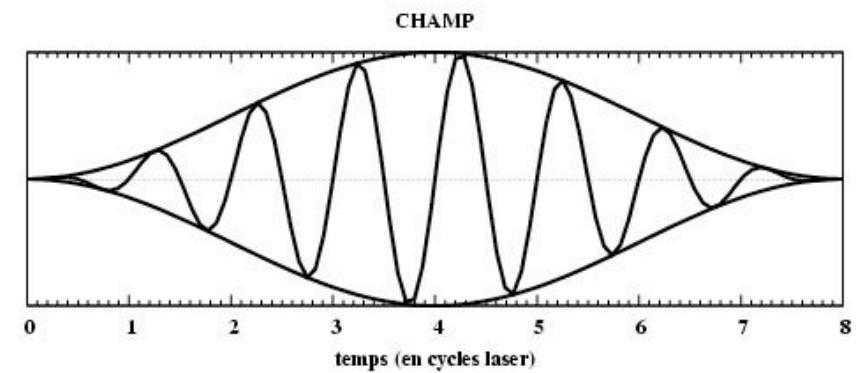
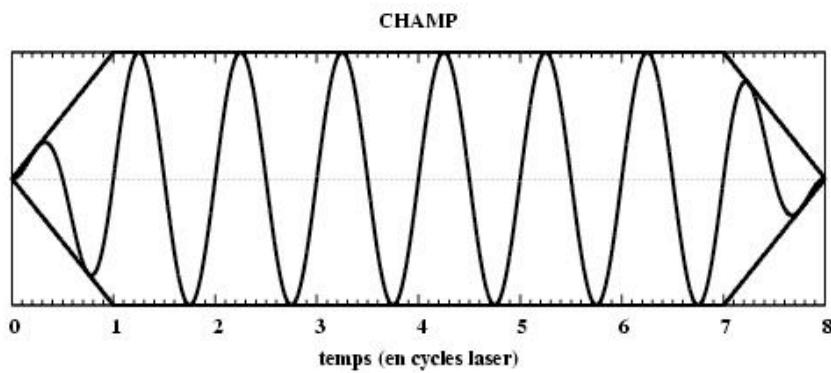


Fixed Nuclei

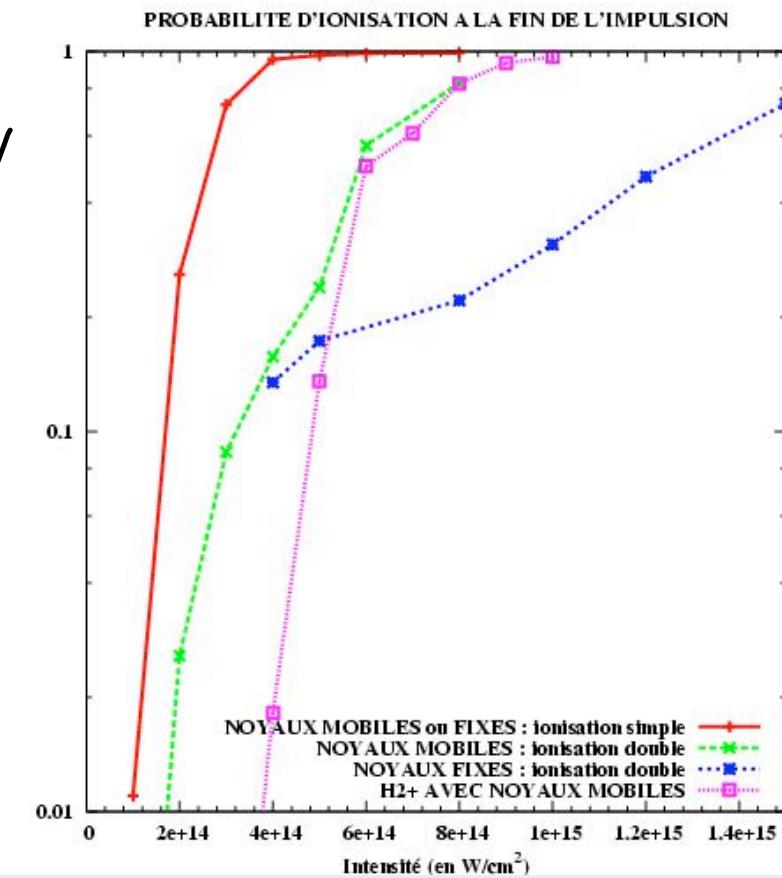
$$\omega = 1.55 \text{ eV}$$
$$I = 3 \cdot 10^{14} \text{ W/cm}^2$$

Moving Nuclei

# H<sub>2</sub> : 1-D Computations



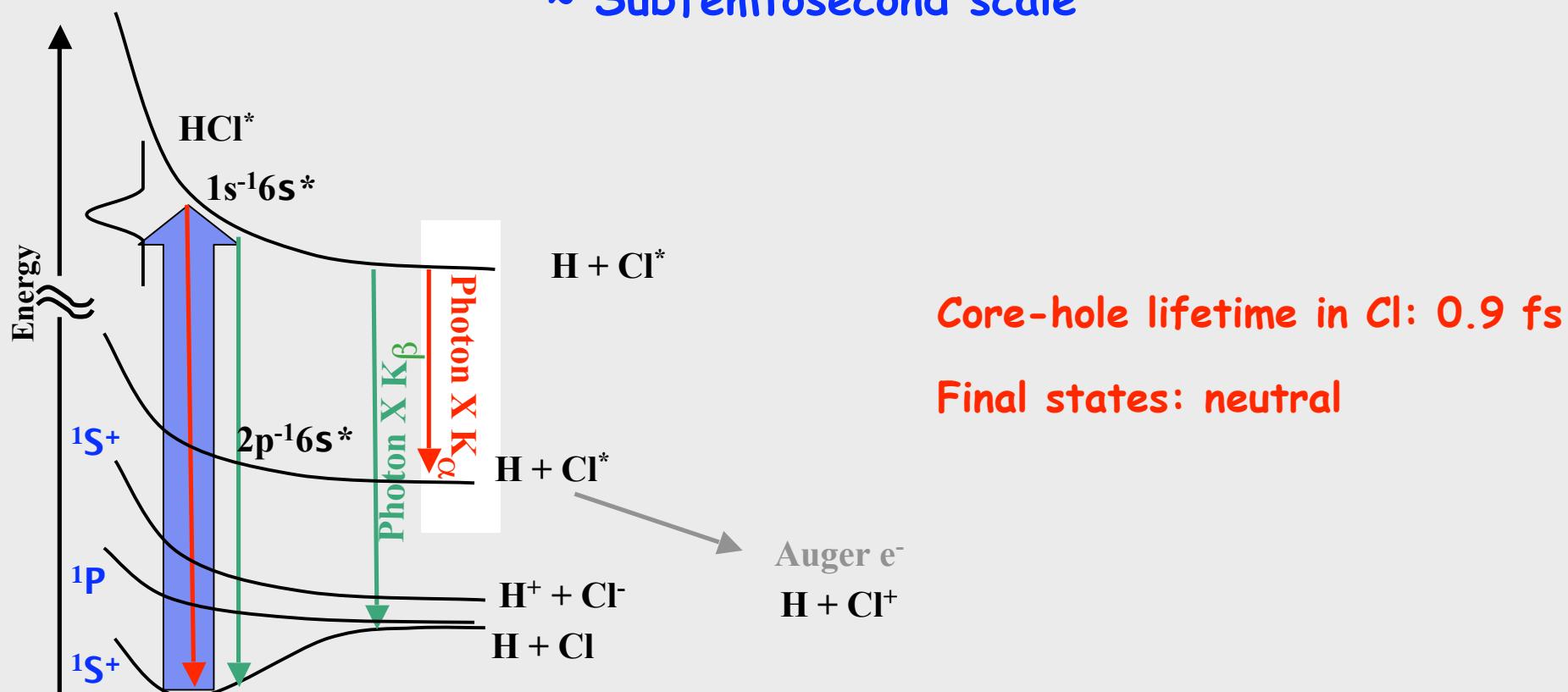
$\omega = 1.55 \text{ eV}$



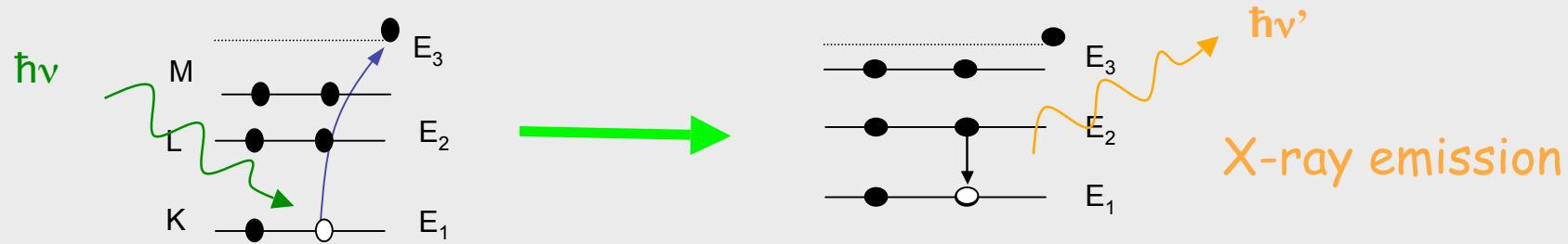
# Femtosecond nuclear motion of HCl probed by resonant x-ray Raman scattering in the Cl 1s region

Competition between nuclear motion and core-hole relaxation:

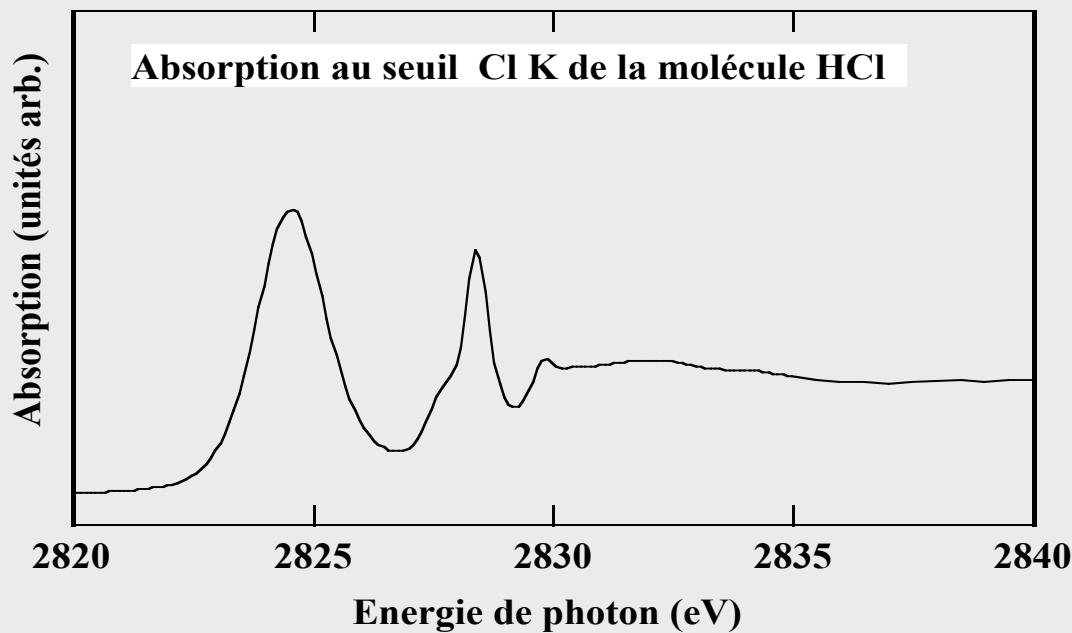
~ Subfemtosecond scale



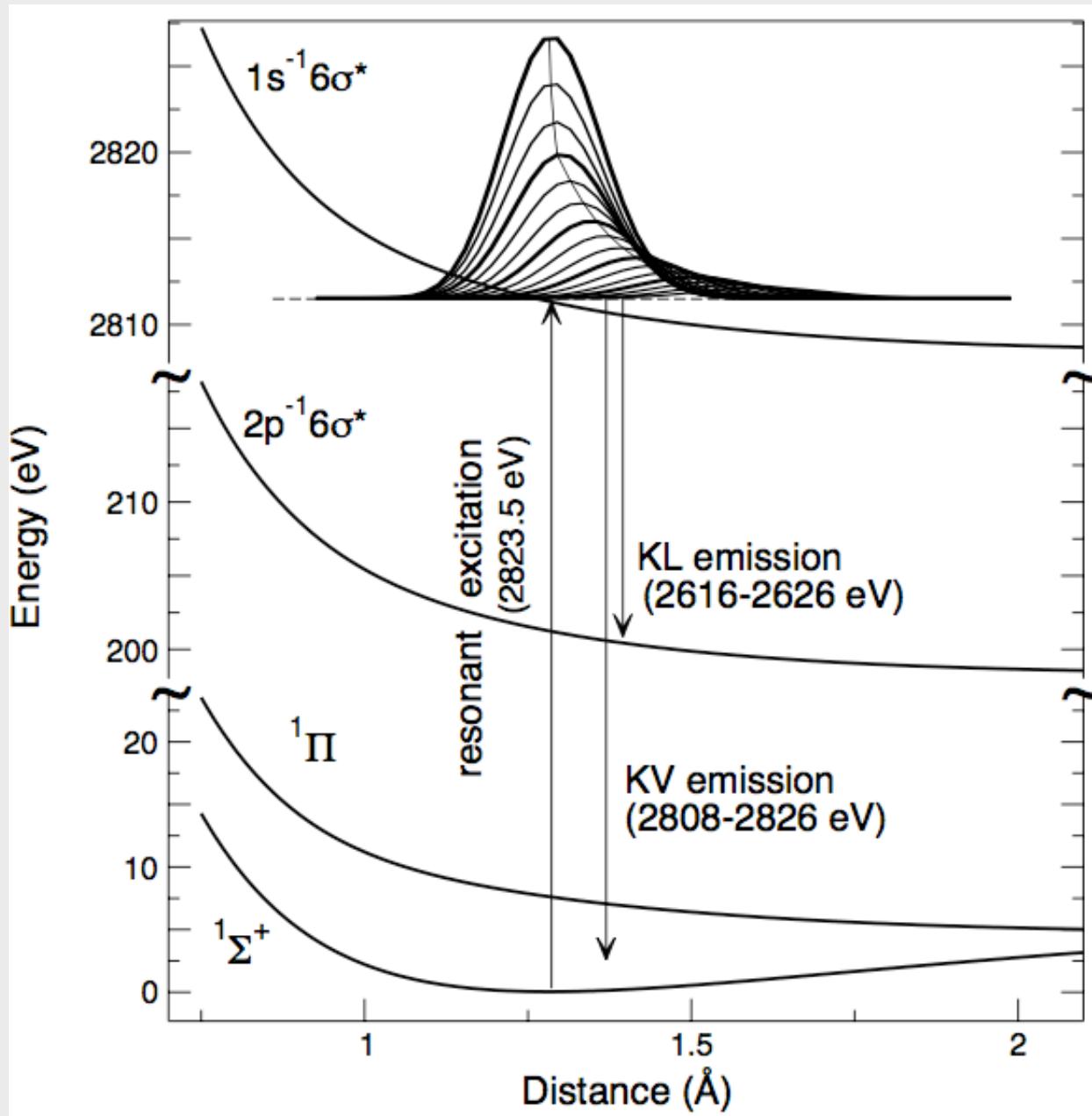
# RIXS : Resonant Inelastic X-ray Scattering



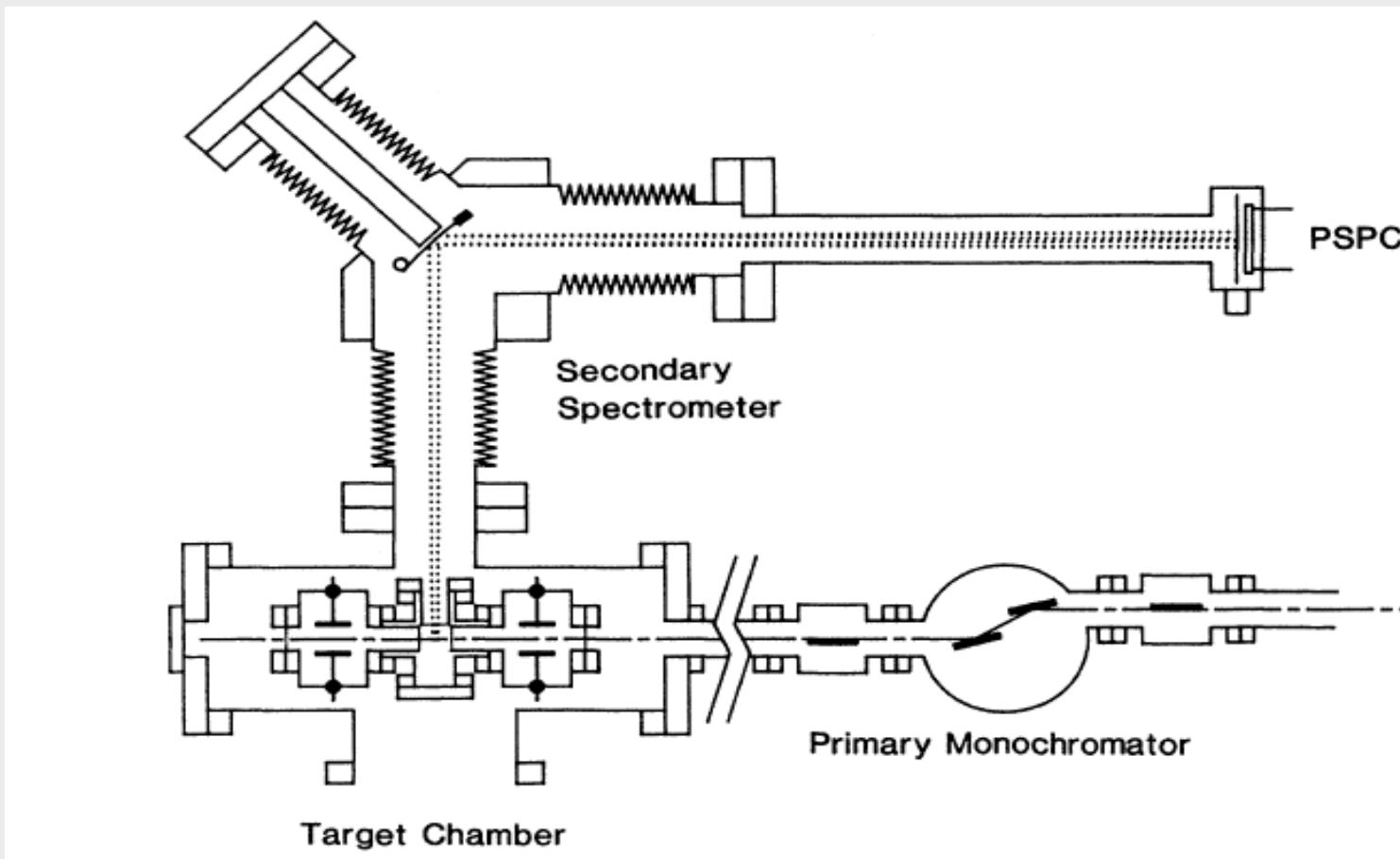
Resonant photoexcitation



Can we see that motion?

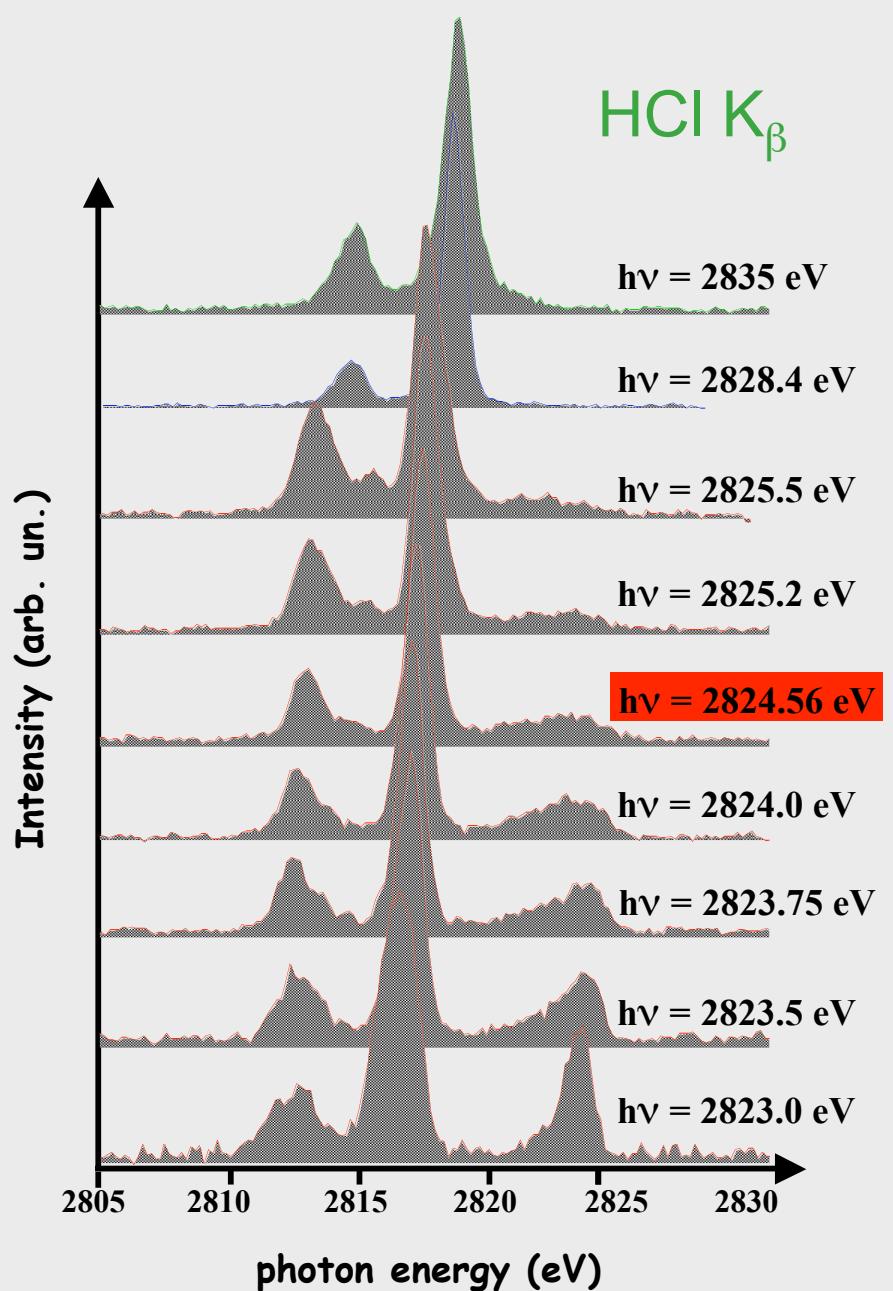
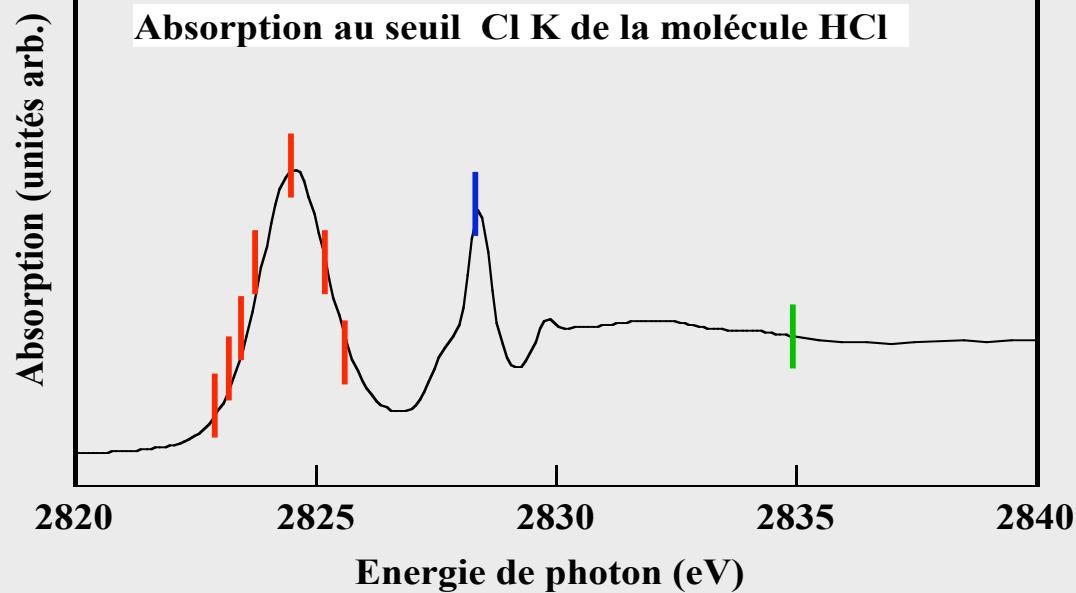


# Experimental Set-up



R Guillemin, D. Lindle UNLV, ALS

LCPMR Ideal Resolution (200 meV)



## Theoretical treatment of RIXS (2<sup>nd</sup> order Perturbation Theory)

$$\sigma(E, \omega') = \int d\omega \sigma(E, \omega) e^{-\frac{(\omega - \omega')^2}{\Delta\omega^2}}$$

Spectral bandwidth of excitation:  $\Delta\omega \sim 0.25\text{eV}$

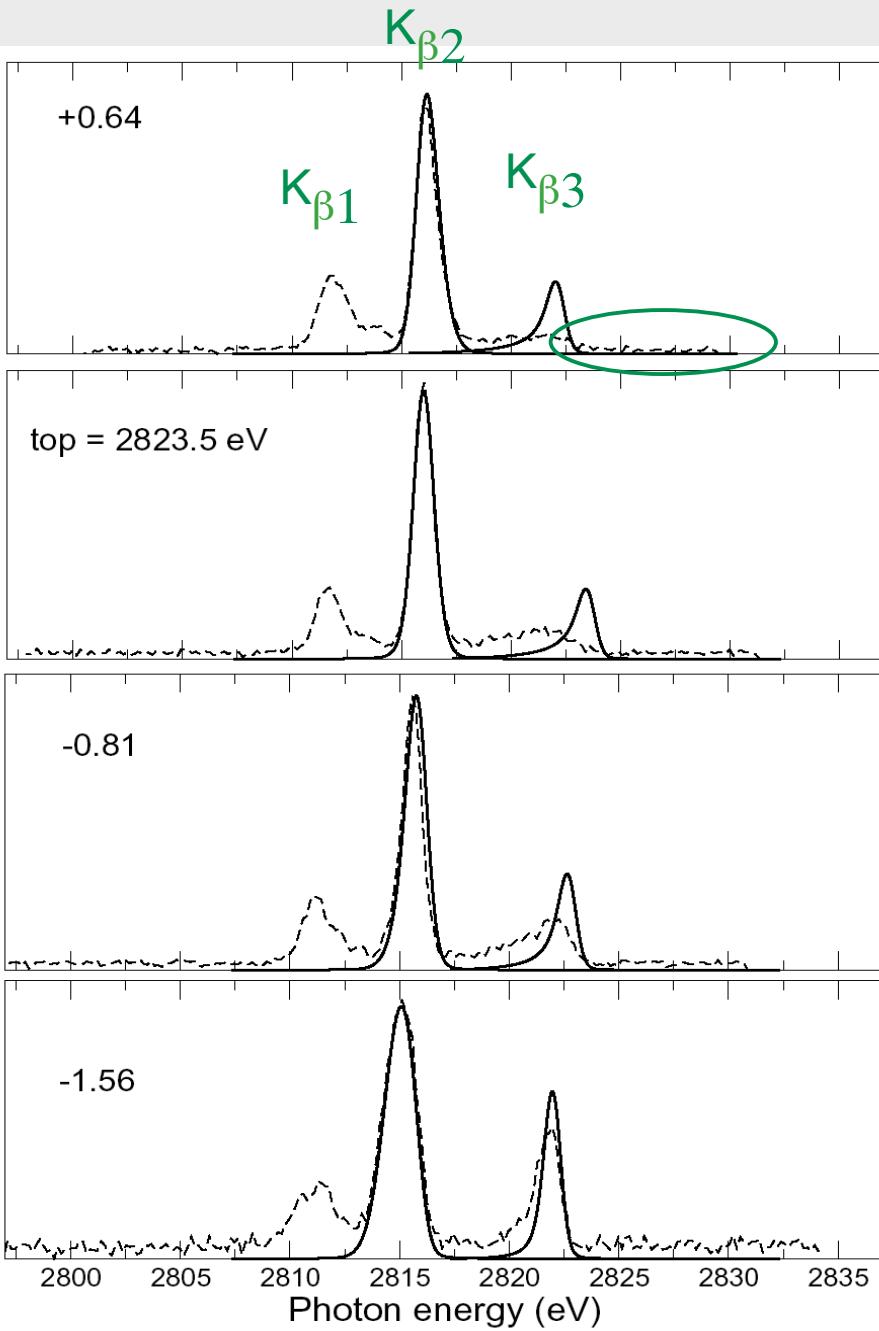
$$\sigma(E, \omega) \propto \sum_f |F_f|^2 \underbrace{\frac{\Gamma_f^2}{[E + E_f - (E_0 + \omega)]^2 + \Gamma_f^2 / 4}}$$

lifetime of final state  $f$  ( 0 for elastic peak  $\approx$  energy conservation)

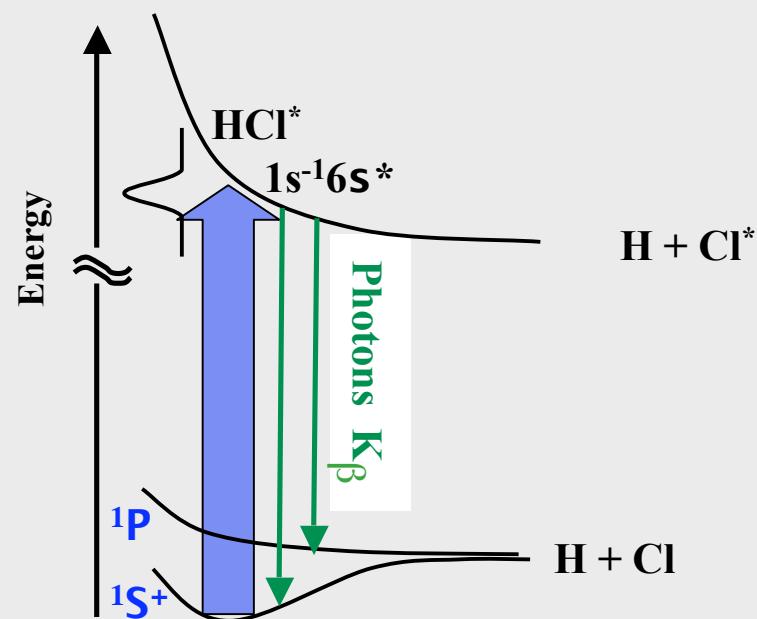
$$F_f = \sum_c \frac{\langle f | D | c \rangle \langle c | D | 0 \rangle}{E_0 + \omega - E_c + i \frac{\Gamma_c}{2}}$$

2<sup>nd</sup> order matrix element  
 $c$  : core-hole state  
 $D$  : dipole operator

Intensity (arb. units)



### $K_{\beta}$ Lines



$K_{\beta 2}$

Looks like

$K_{\alpha}$

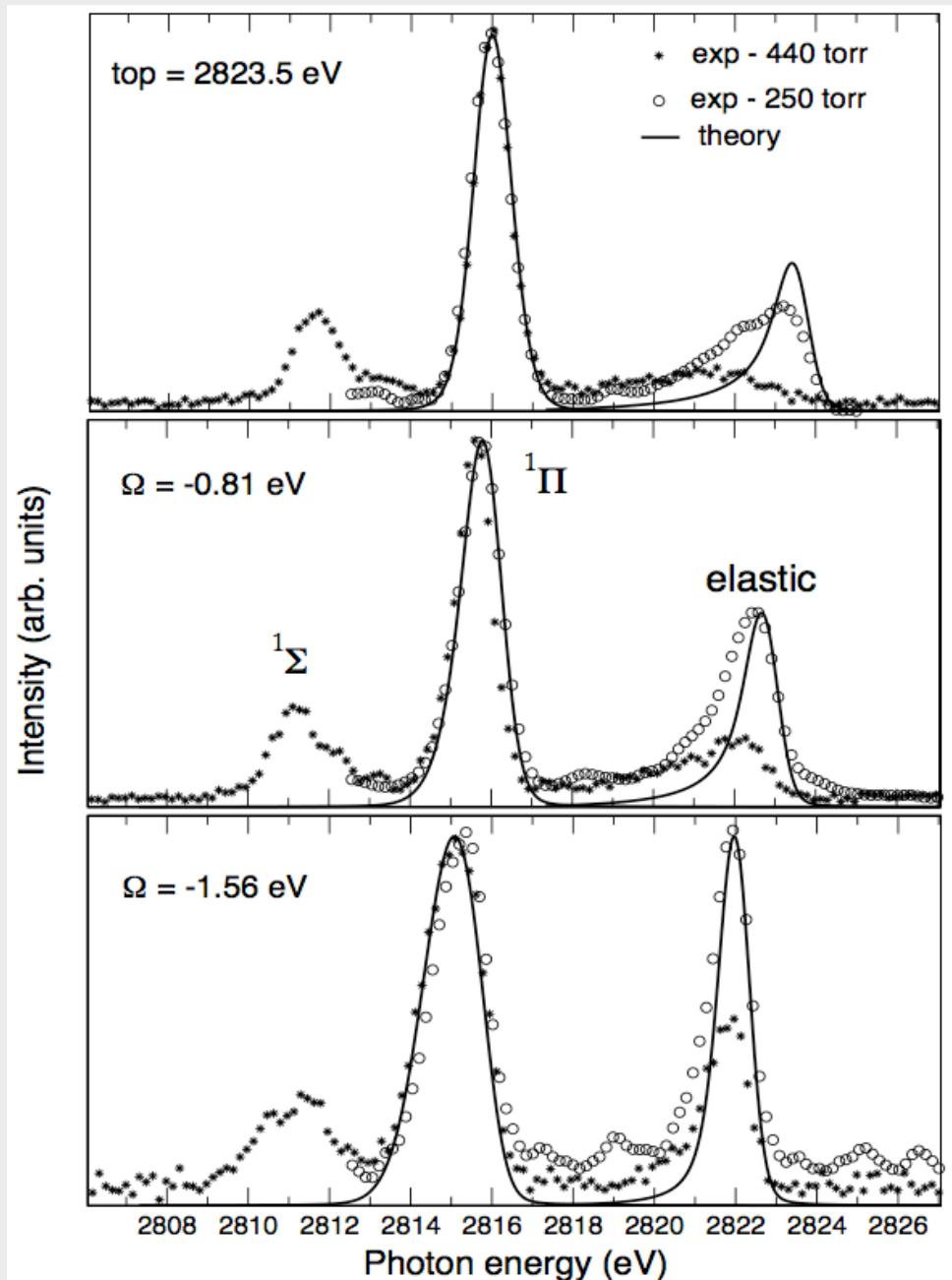
$K_{\beta 1}$

'Weird' shape: many  
excited states

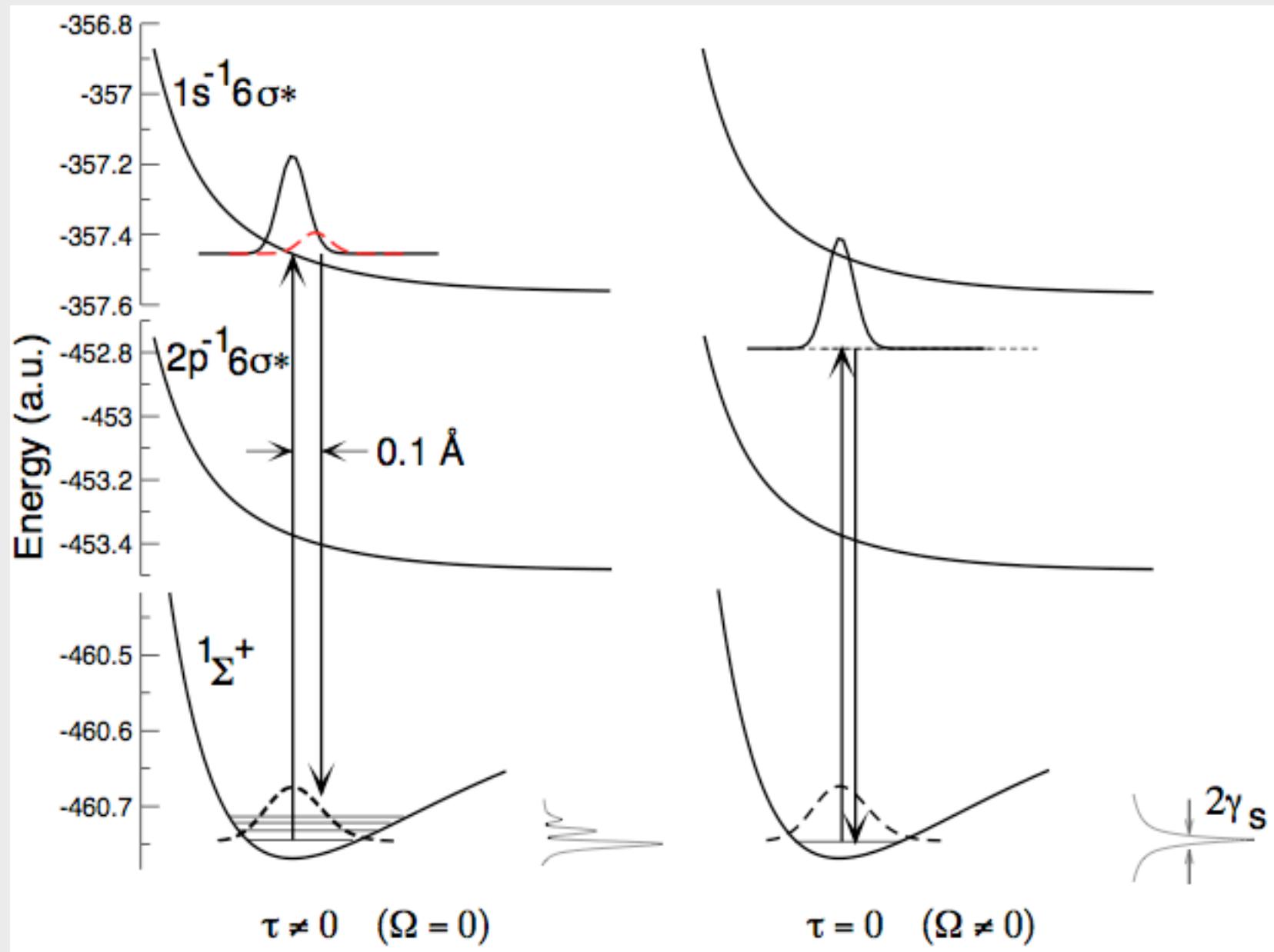
$K_{\beta 3}$

high absorption : high Pressure

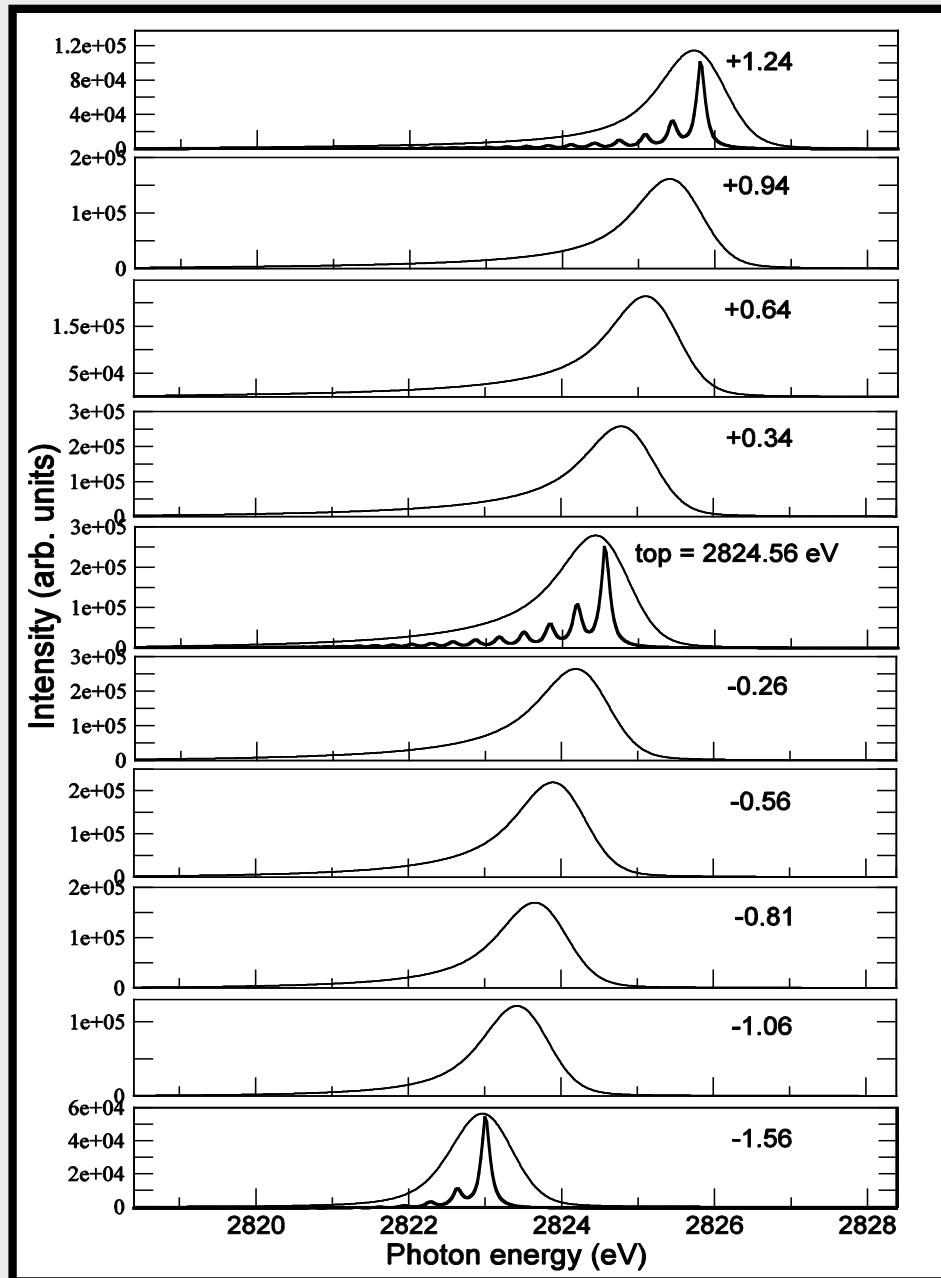
# Pressure Effect



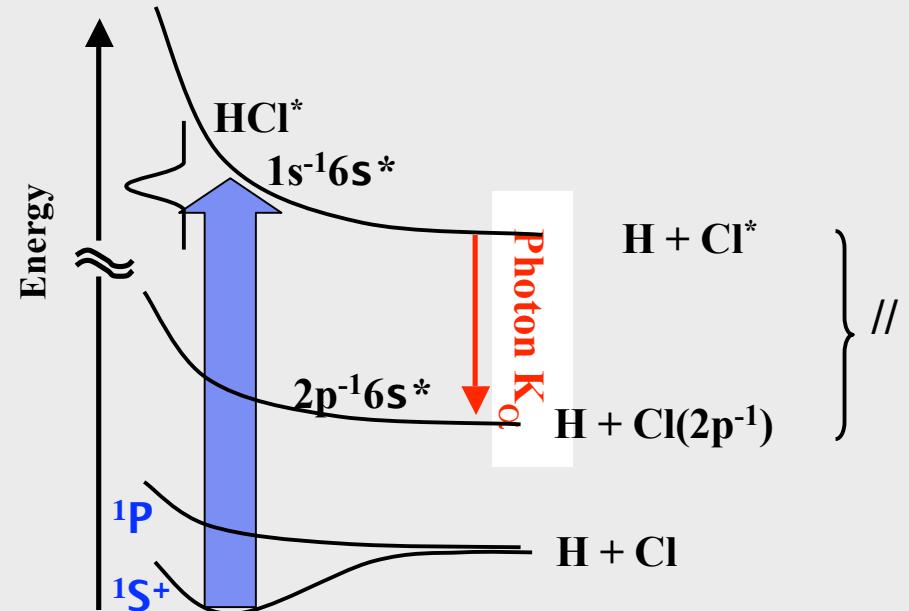
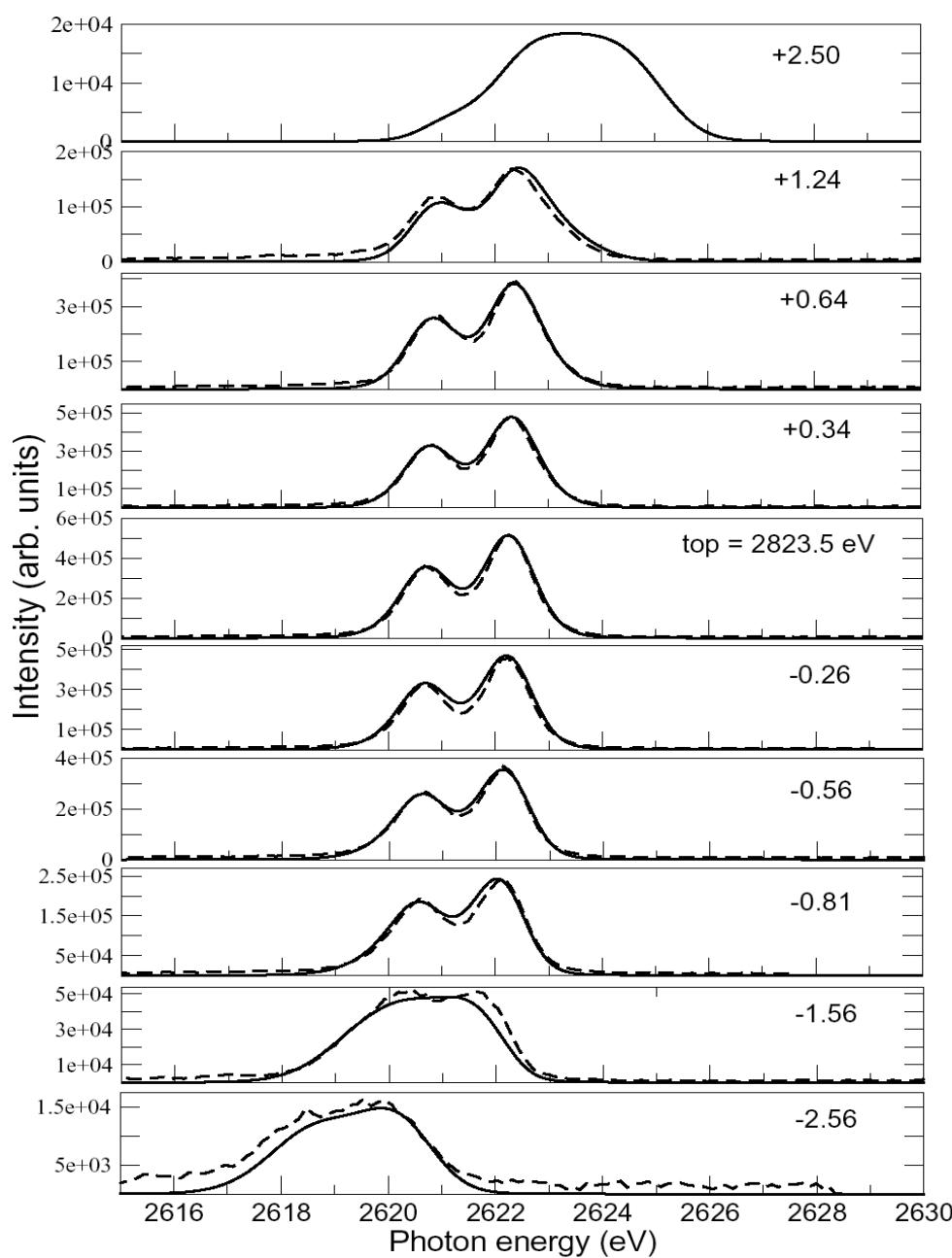
## K $\beta$ line : Elastic peak



# K $\beta$ line : Elastic peak



## K $\alpha$ Line



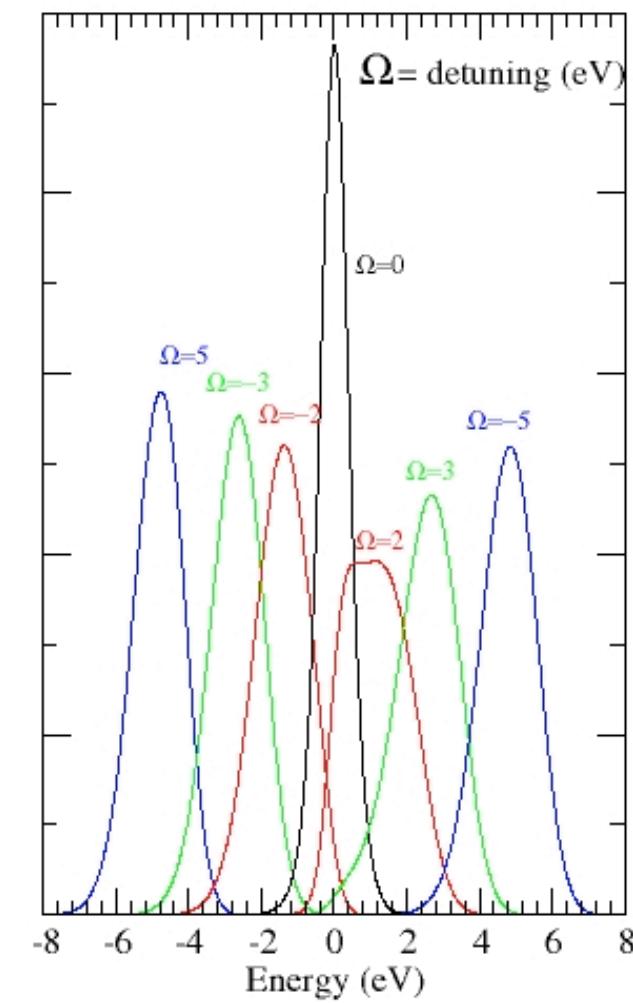
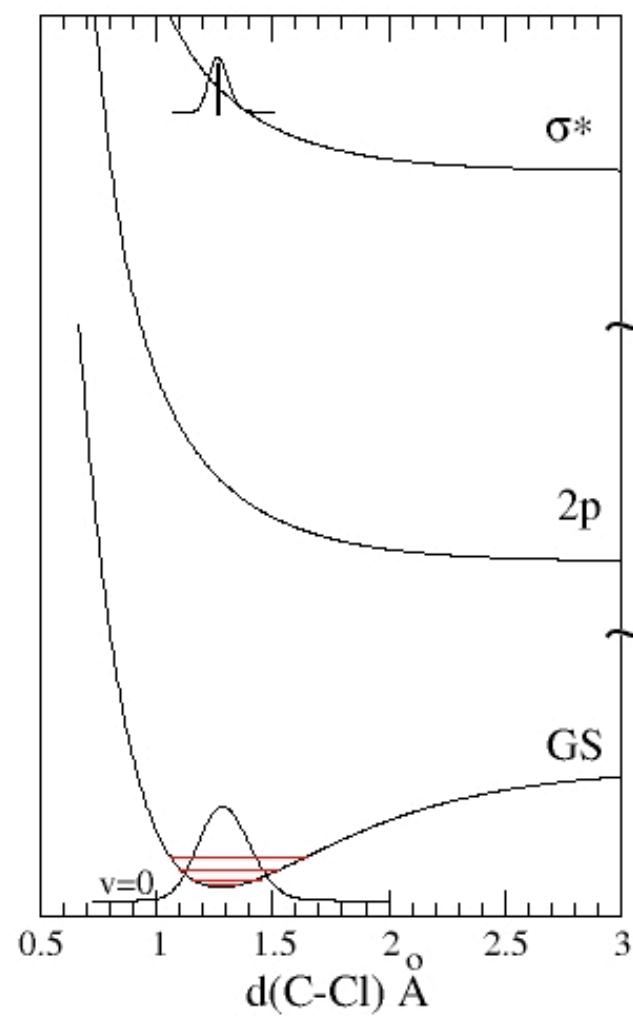
$$\sigma(E, \omega) \propto \frac{\exp\left(-\frac{([E - \omega_{cf}(\infty)] - \Omega)^2}{\Delta^2}\right)}{(E - \omega_{cf}(\infty))^2 + \Gamma^2/4}$$

$$\propto \frac{1}{(E - \omega_{cf}(\infty))^2 + \Gamma^2/4} \quad |\Omega| < \Delta$$

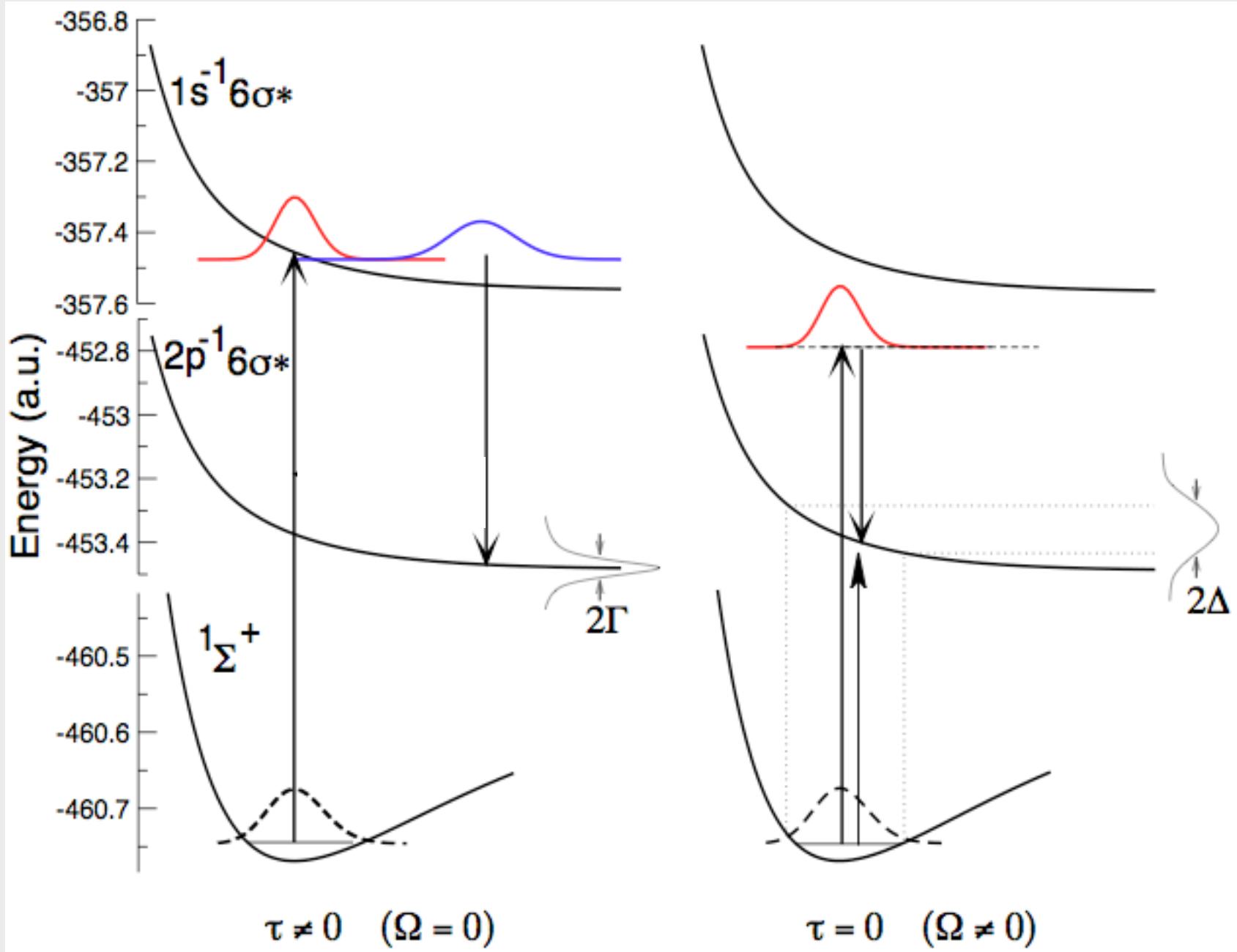
$$\propto \frac{\exp\left(-\frac{([E - \omega_{cf}(\infty)] - \Omega)^2}{\Delta^2}\right)}{\Omega^2} \quad |\Omega| > \Delta$$

## HCl K <sub>$\alpha$</sub> line

1s-(v=0)  $\rightarrow$   $\sigma^*$



## K $\alpha$ line



# Theory vs experiment

