Wave packet dynamics

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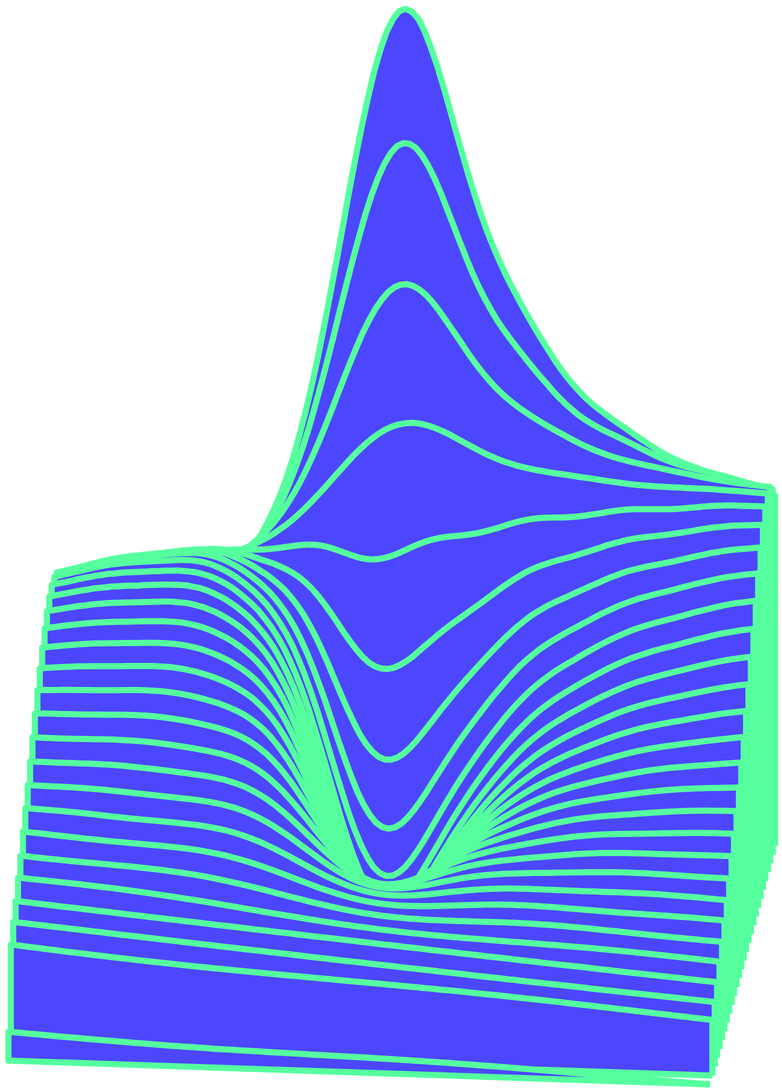
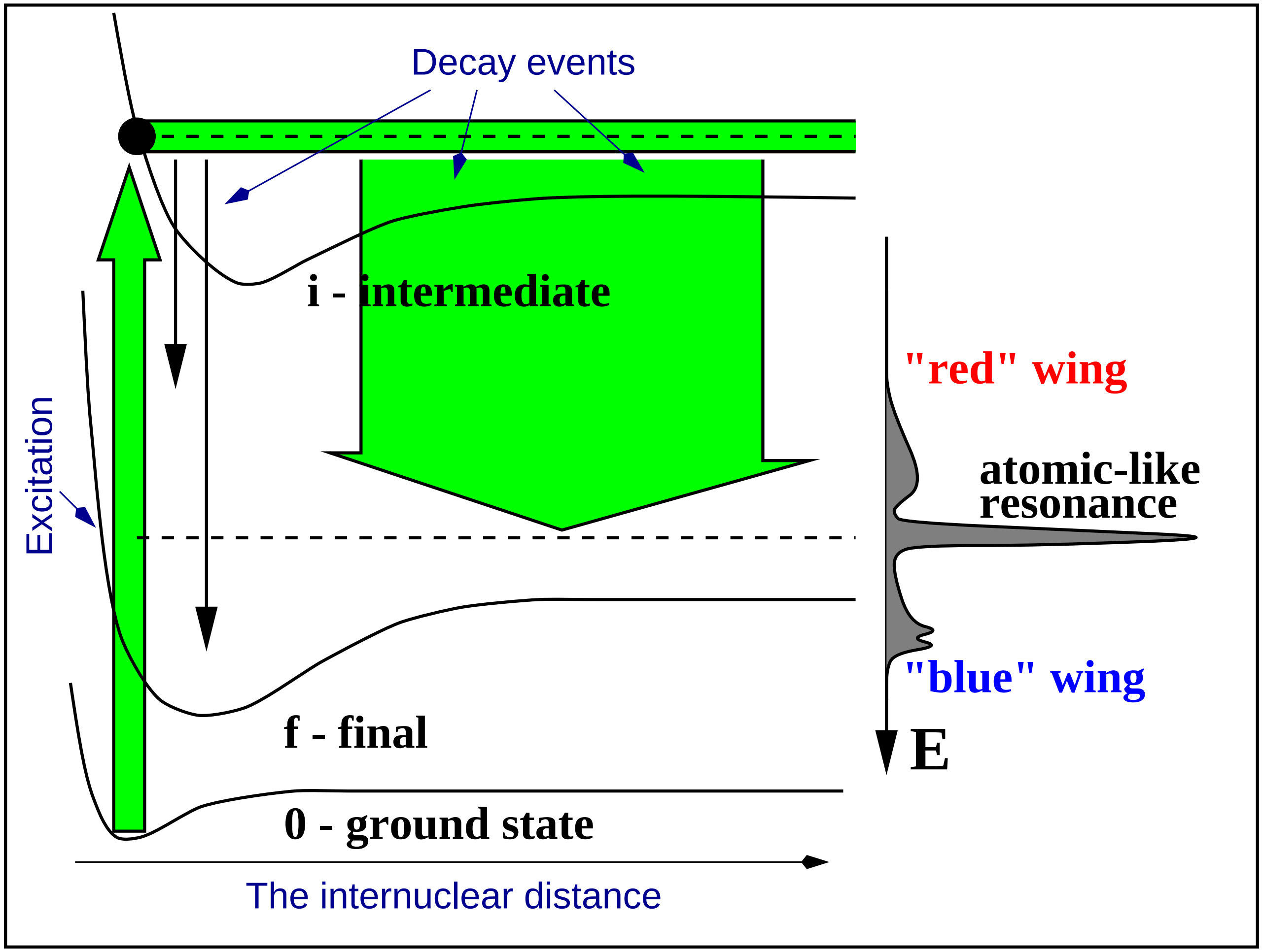


Presentation outline

- Wave packets in RXS: phenomena, theory and experiment.
- Aspects of the theory: duration time. Direct and resonant channels.
- Generalized FC: Doppler effect and photoelectron spectroscopy.
- Numerical method: ground state, wave packet evolution. Oscillating integrands.
- Discovered or explained effects:
  - The atomic hole
  - N_2 spectrum flattening
  - Dynamical suppression
  - Doppler effect

Resonant X-ray scattering

- Slow decay and dissociation in the core-excited state → atomic peak at constant energy.
- fast decay → molecular background moving on incident photon energy change (Raman law).



Wave packets

Formalism based on time-dependent Schrödinger equation:

$$H\psi(t) = i\frac{\partial}{\partial t}\psi(t) \quad \Leftrightarrow \quad \psi(t) = e^{-iHt}\psi(0)$$

- properties expressed in terms of correlation functions $\langle\psi(0)|\psi(t)\rangle$
- no need to construct explicitly eigenstates of the Hamiltonian $\rightarrow$ handy when dealing with systems of continuous density of states
- time evolution operator $\exp(-iHt)$ – substantial element of the theory.

Duration time

$$\sigma(\omega, E) \sim \sum_f \left| \sum_c \frac{\langle f|c\rangle\langle c|0\rangle}{\Omega + i\Gamma} \right|^2 \delta(E + E_f - E_0 - \omega) \ , \qquad \Omega = \omega - (E_c - E_0)$$

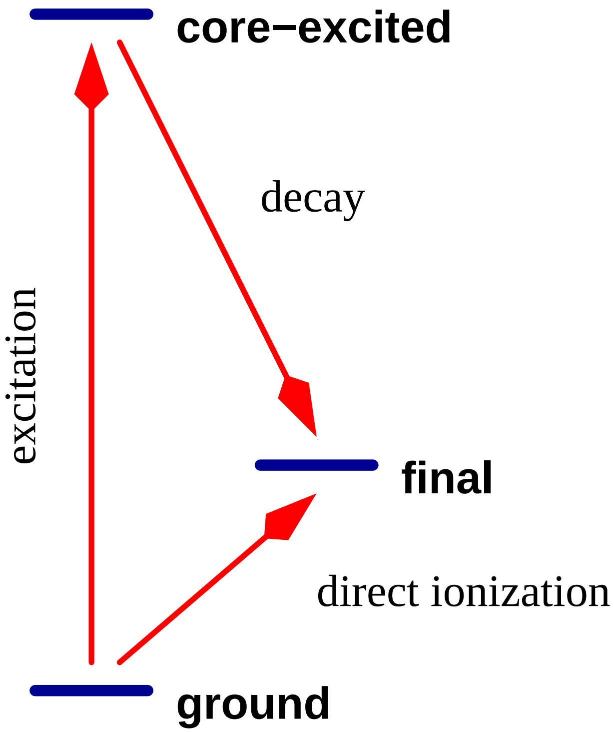
- off-resonant spectra resemble fast-scattering spectrum $\rightarrow$ there exists a relationship between duration time of the scattering process and detuning.

$$\sigma(\omega, E) \sim \frac{1}{\Omega^2} \sum_f |\langle f|0\rangle|^2 \delta(E + E_f - E_0 - \omega)$$

- the duration time of the scattering process

$$T = \frac{1}{\sqrt{\Gamma^2 + \Omega^2}}$$

Theory: Direct and resonant terms



Entire wave packet evolution on core excited PES:

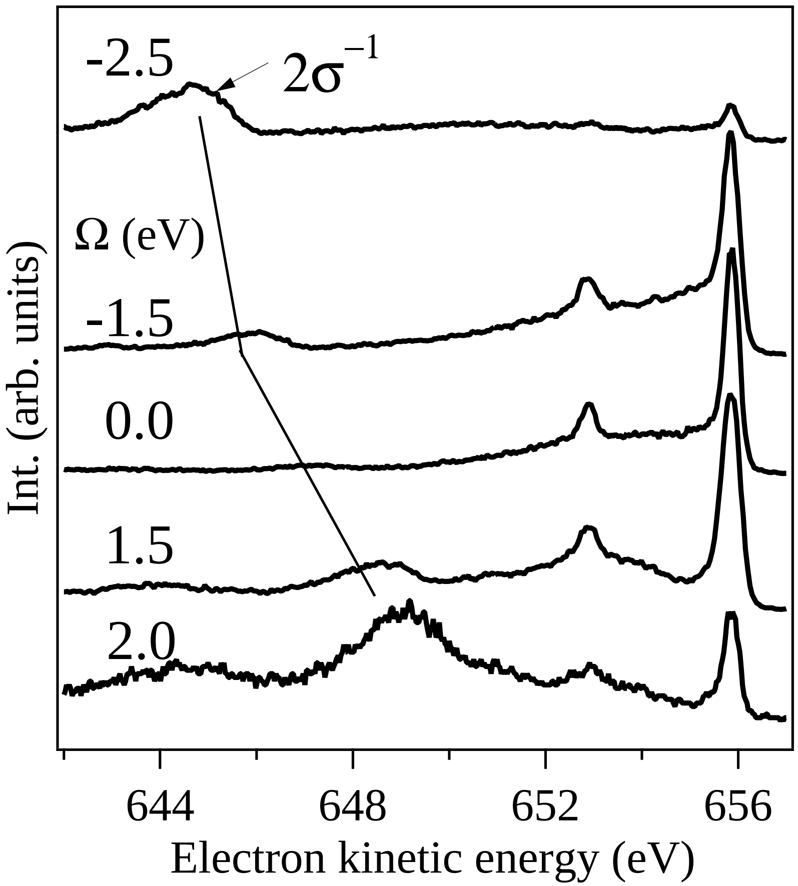
$$|\Psi(0)\rangle = \hat{Q}\int_0^\infty e^{-i(\hat{H}_c - E_0 - \omega)t}\hat{V}|0\rangle e^{-\Gamma t}\,\mathrm{d}t$$

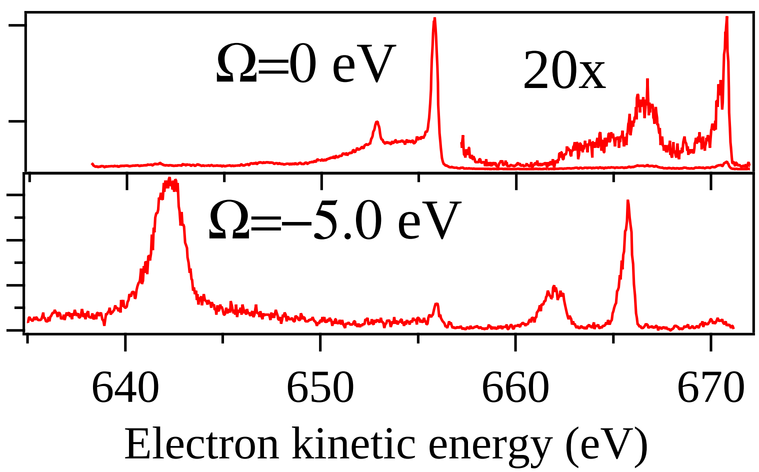
Fourier transform:

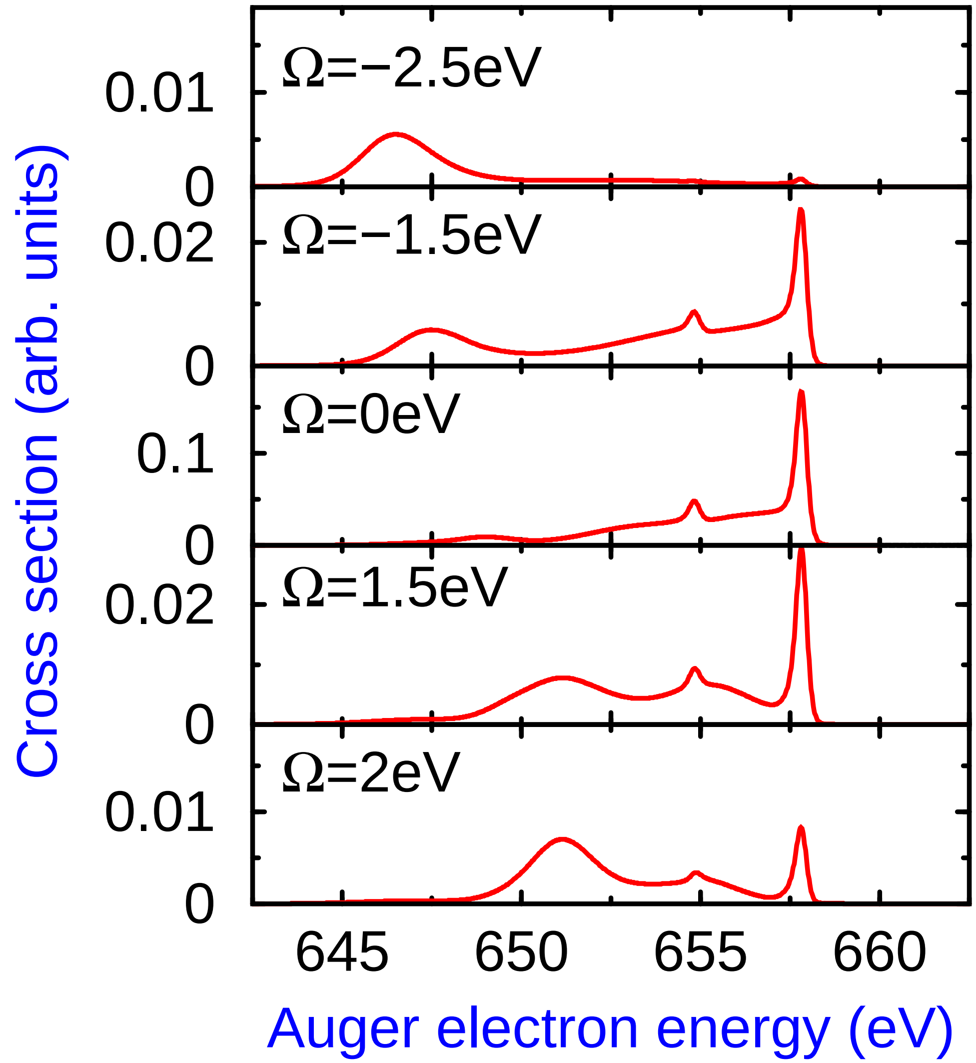
$$\sigma_0(\omega, E) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty \sigma(\omega,\tau)e^{i(\omega-E)\tau}\,\mathrm{d}\tau$$

The correlation function:

$$\begin{aligned}\sigma(\omega,\tau) = {} & \langle\Psi(0)|e^{-i(\hat{H}_f - E_0)\tau}|\Psi(0)\rangle \\ & +\langle 0|\hat{Z}^\dagger e^{-i(\hat{H}_f - E_0)\tau}\hat{Z}|0\rangle \\ & +i\{\langle\Psi(0)|e^{-i(\hat{H}_f - E_0)\tau}\hat{Z}|0\rangle \\ & \quad -\langle 0|\hat{Z}^\dagger e^{-i(\hat{H}_f - E_0)\tau}|\Psi(0)\rangle\}\end{aligned}$$


-2.5
$2\sigma^{-1}$
Ω (eV)
-1.5
0.0
1.5
2.0
Int. (arb. units)
644
648
652
656
Electron kinetic energy (eV)


Ω=0 eV
20x
Ω=−5.0 eV
640
650
660
670
Electron kinetic energy (eV)


Ω=−2.5eV
Ω=−1.5eV
Ω=0eV
Ω=1.5eV
Ω=2eV
0.01
0
0.02
0
0.1
0
0.02
0
0.01
0
Cross section (arb. units)
645
650
655
660
Auger electron energy (eV)

Generalized Franck-Condon factors

- The Auger decay transition moment $Q(R)$ includes a phase factor

$$\hat{Q}(R) = \hat{Q}_0 e^{-i\alpha \mathbf{k}\cdot\mathbf{R}} \quad (1)$$

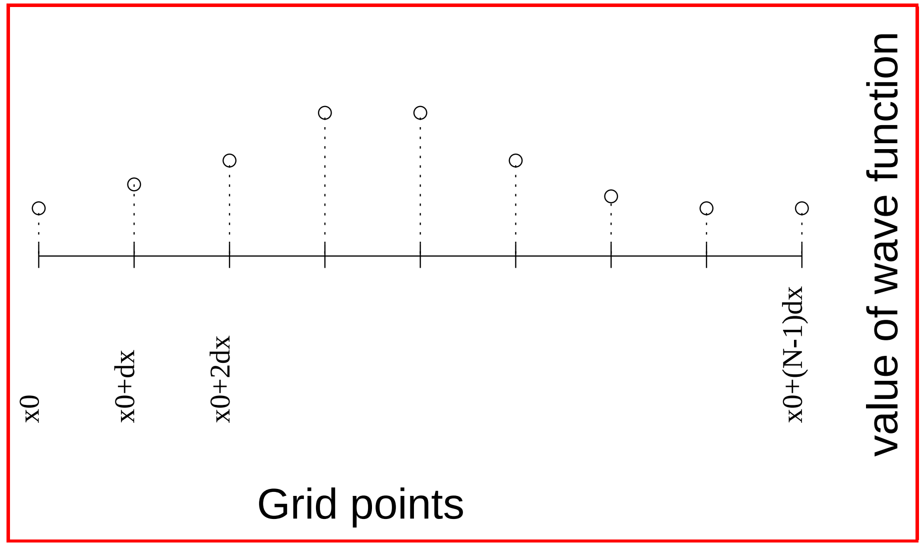
- $Q(R)$ operator modifies overlap between $|f\rangle$ and $|c\rangle$

$$\sigma(\omega, E) = \sum_f \left| \sum_c \frac{\langle f|\hat{Q}|c\rangle\langle c|\hat{V}|0\rangle}{E - E_c + E_f + i\Gamma} \right|^2 \Phi(E + E_f - \omega - E_0, \gamma) \quad (2)$$

where $\mathbf{k}$, $\mathbf{R}$, $\alpha = m_B/(m_A + m_B)$ is the mass ratio coefficient equal to $\frac{1}{2}$ for a homonuclear molecule and $\mathbf{R}$ is the radius vector.

Numerical method

- DVR: discrete variable representation.
- choose sufficiently wide interval
- the equidistant spacing dense enough to represent momenta appearing during the evolution.

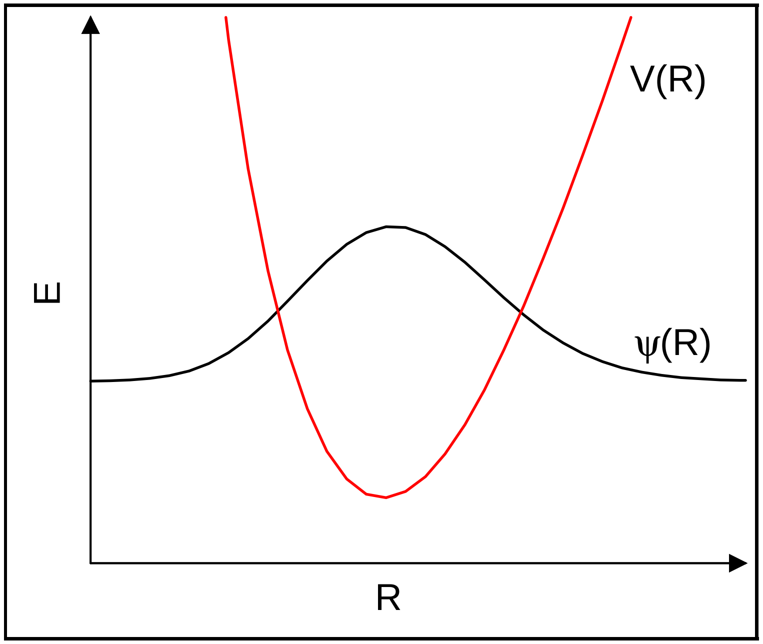


Operator representation

- local operators translate to a diagonal matrix (example: the potential $\hat{U}$). Scaling $\propto N$.
- non-local operators translate generally to full matrices. Scaling $\propto N^2$.
- in the case of the kinetic energy, Fast Fourier transform can be used to reduce the scaling to $\propto N \log N$.

Time-indepentent Schrödinger equation reduced to a matrix eigenproblem.

- the potential represented by a diagonal matrix.
- Nth order approximation by Miller & Collbert: The kinetic energy operator is represented by a full matrix $\mathbf{K} = (k_{ij})$



$$k_{ij} = \frac{(-1)^{i-j}}{2\mu\Delta x^2} \begin{cases} \pi^2/3, i = j \\ \dfrac{2}{(i-j)^2}, i \neq j \end{cases}$$

Full matrix diagonalization scales $\propto N^3$: The state of interest localized in space $\rightarrow$ computation time negligible.

Wave packet evolution: Lanczos method

- Find for each time step a subset of K Hamiltonian eigenfunctions

$$\Phi(x) = \sum_{n=1}^{K} a_n f_n(x)\,, \qquad \hat{H} f_n(x) = \lambda_n f_n(x) \tag{3}$$

- This finite expansion convergent only in a limited time radius.

- matrix $\mathbf{U}^{(t)} = \{f_n(x)\}$ transforms from the DVR space to the energy subspace

$$\psi^{(t+\tau)} = \sum_{n=1}^{K} \mathbf{U}^{(t)} \underbrace{\exp(-i\lambda_n^{(t)}\tau)}_{\text{time-evolution operator}} (\mathbf{U}^{(t)})^\dagger \psi^{(t)}\,. \tag{4}$$

- $\mathbf{U}^{(t)}$ is not necessarily an optimal vector set at time $t+\tau$.

INTEGRALS

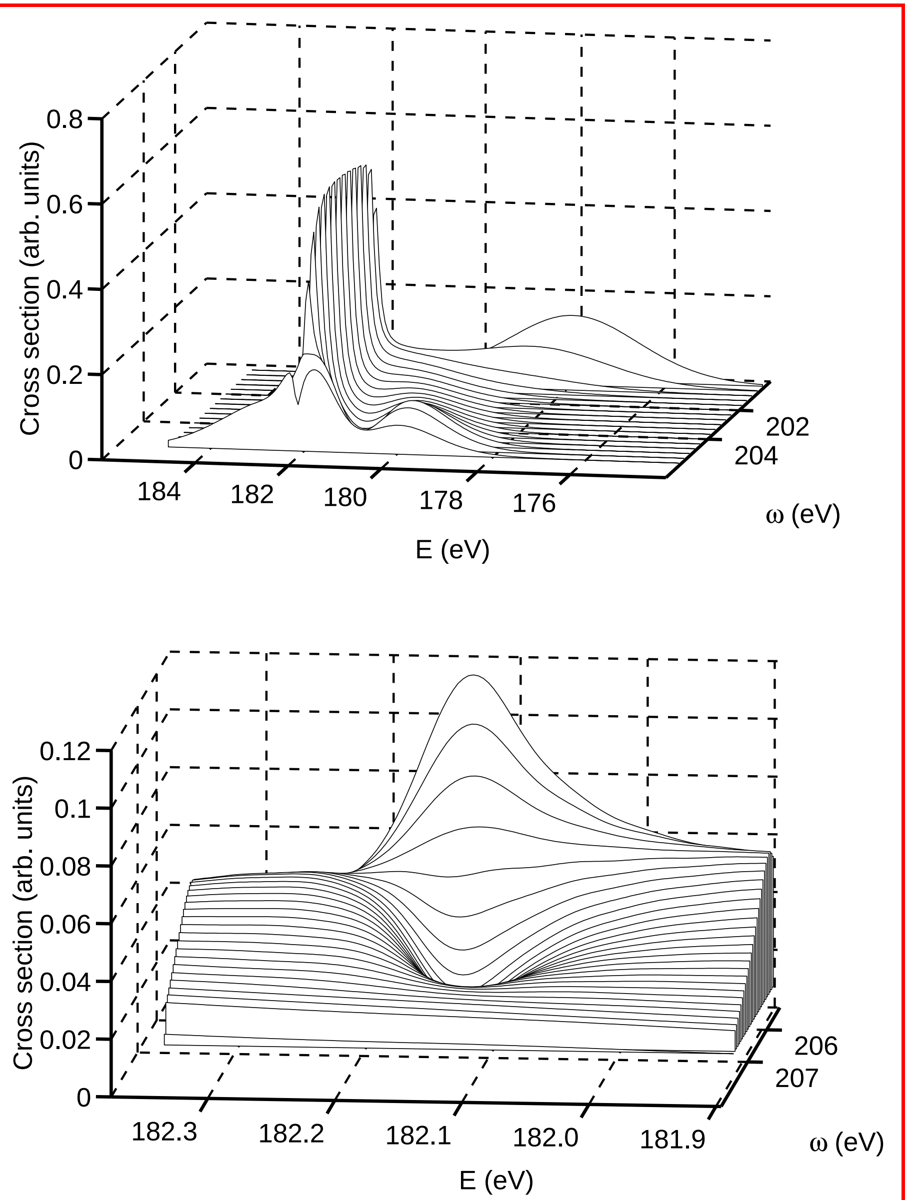
$$|\Phi(0)\rangle = \int_0^\infty e^{-i\mathcal{H}_c t}\hat{V}|0\rangle e^{-\Gamma t}\,\mathrm{d}t \tag{5}$$

- Oscillating integrand $\rightarrow$ numerical integration tricky.
- The integral (5) expressed through a sum of contributions I_l

$$|\Phi(0)\rangle = \sum_l I_l = \sum_l \sum_{k=1}^{K} \frac{e^{-\Gamma t_l}}{i\lambda_k + \Gamma}\left[1 - e^{(-i\lambda_k - \Gamma)\tau_l}\right] \mathbf{U}_{:,k}^{(t_l)} z_{1,k}^{(t_l)*} \; .$$

- contribution I_l expressed through a sum of basis vectors $\mathbf{U}^{(t_l)}$ with appropriate prefactors.
- $\langle\Psi(0)|\Phi(0)\rangle$ proportional to the absorption cross section of the core-excited state at a given incident photon frequency ω.

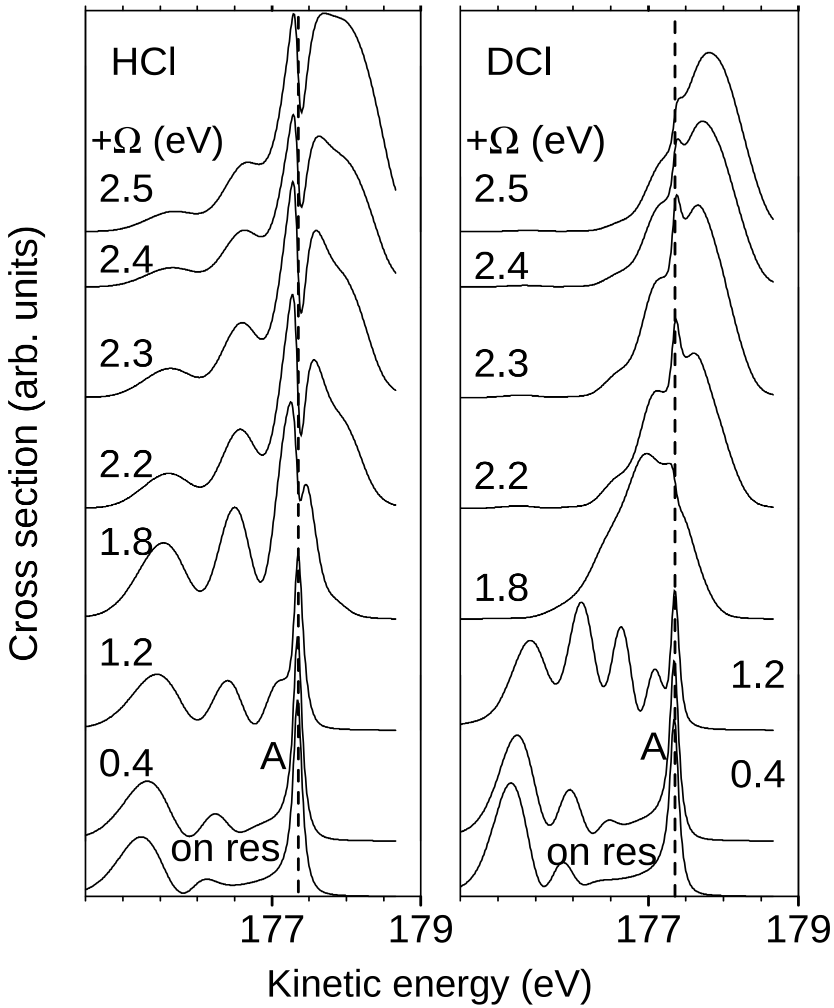
The hole, and isotope effects



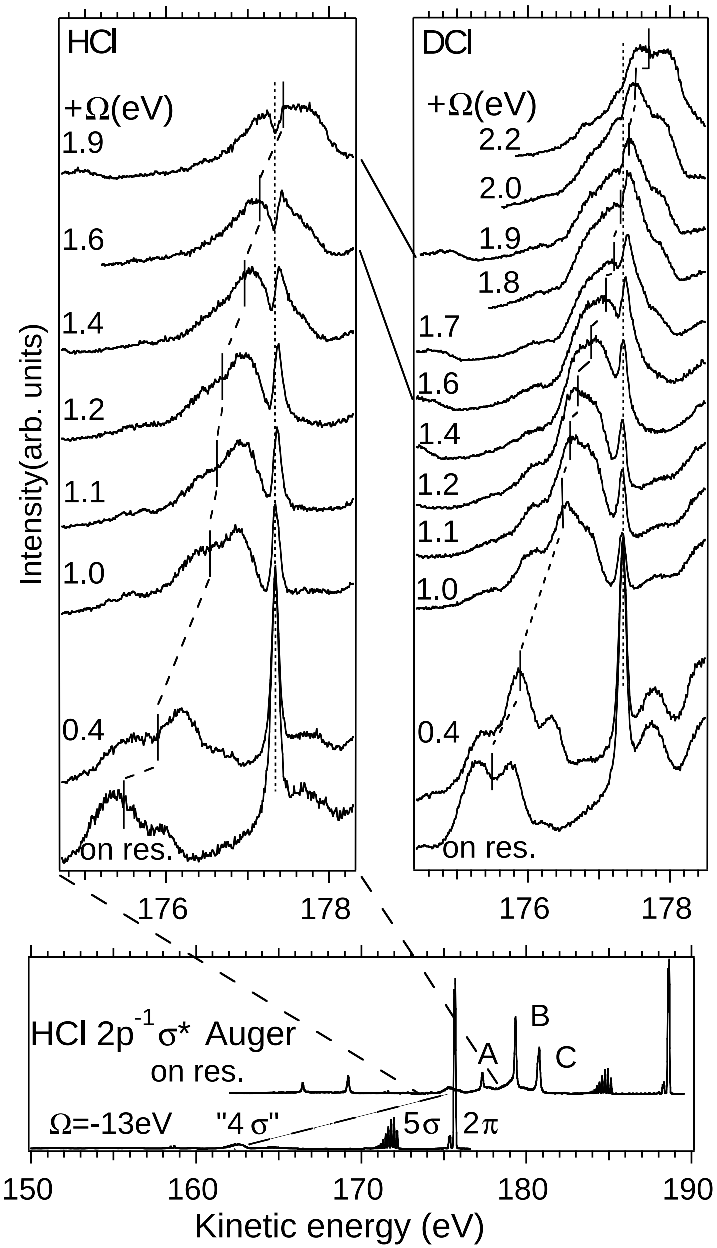
Formation conditions:

- dissociative core-excited state
- sufficently long core-excited state lifetime with respect to the dissociation speed.
- dissociative final state separated in the energy space from other states.
- the only electronic state associated with given atomic limit.
- Dissociation speed in "proper" range (DCl-HCl).

The isotope effect:



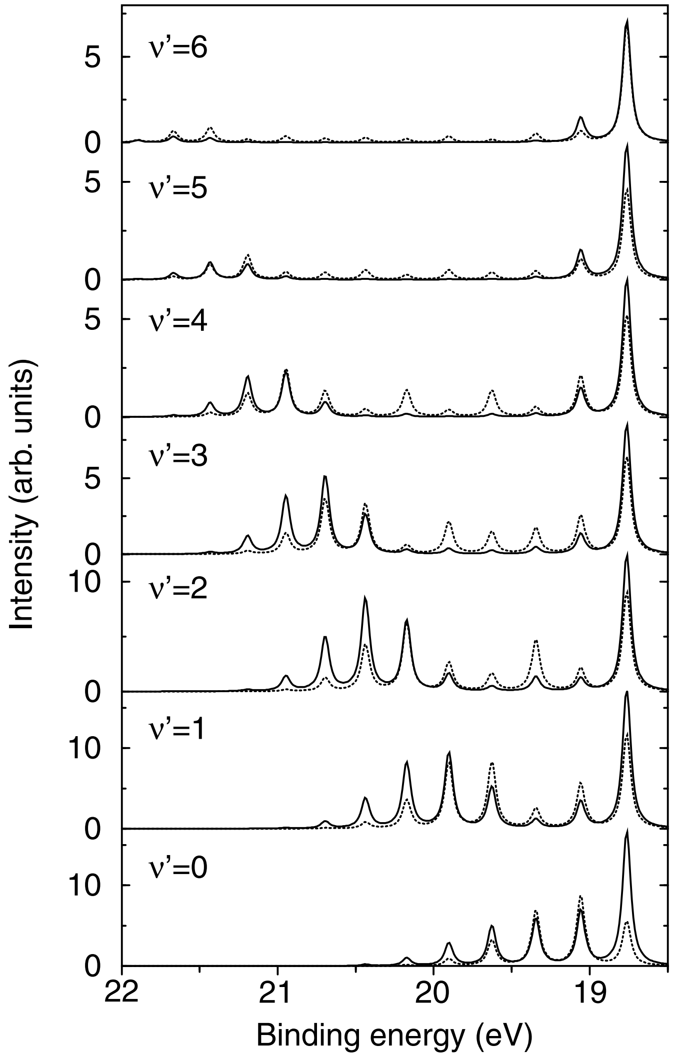
Theoretical calculations.



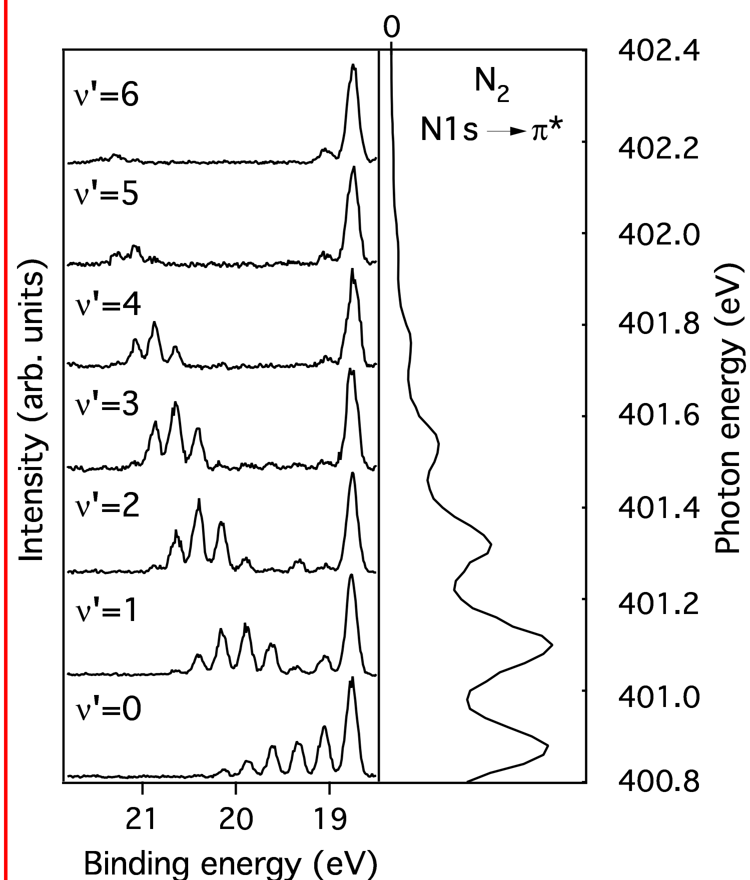
Measured cross section.

N_2 SPECTRUM FLATTENING

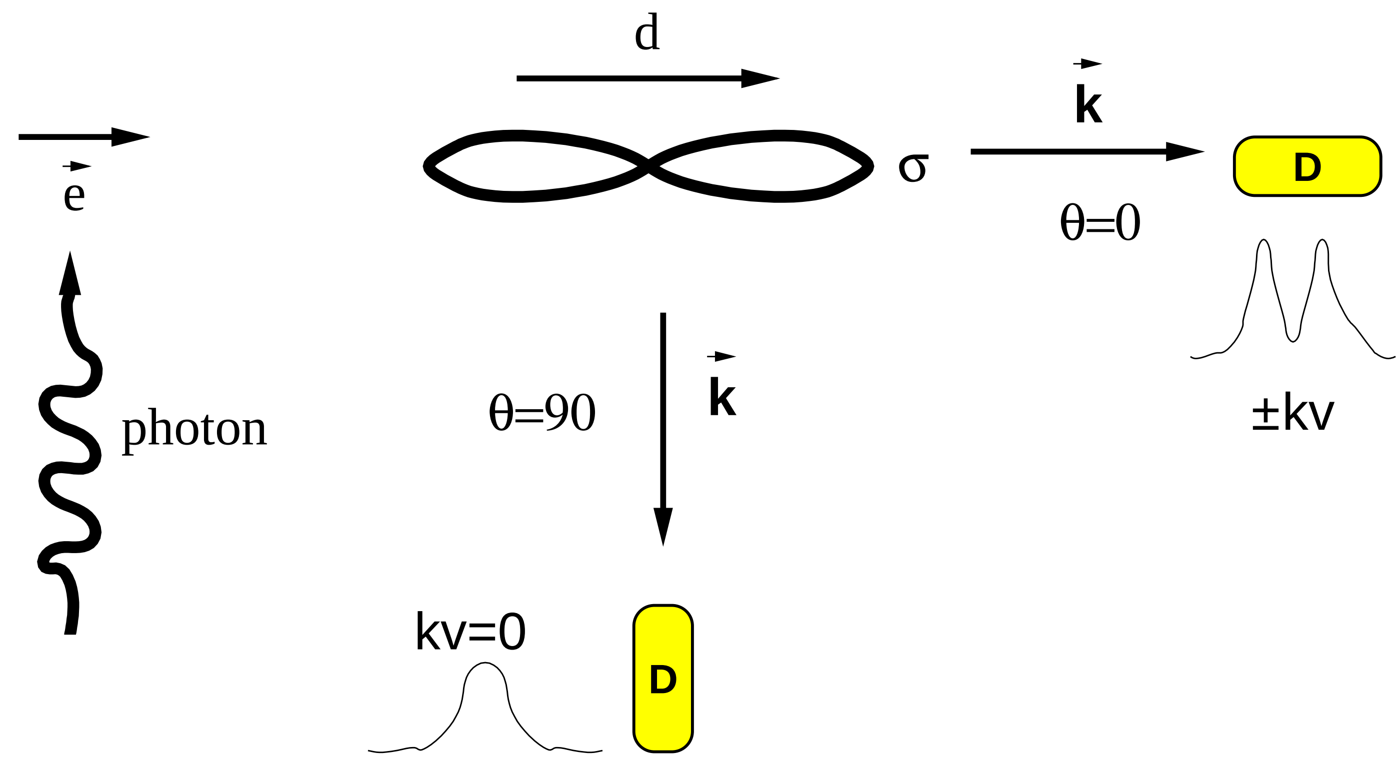
LVI and LVI + $Q(R)$



The experiment



Doppler effect and related phenomena

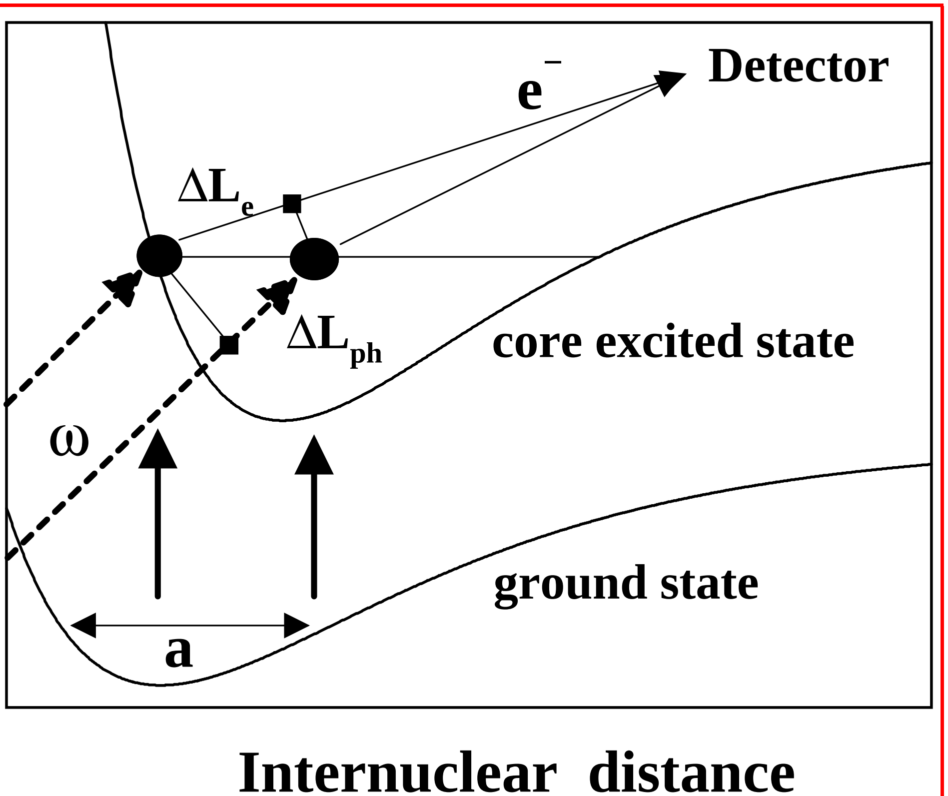


- selective excitation $(\mathbf{e} \cdot \mathbf{d})^2$
- the Auger electrons captured by the spectrometer have different energies depending on the direction of motion of the emitting atoms.

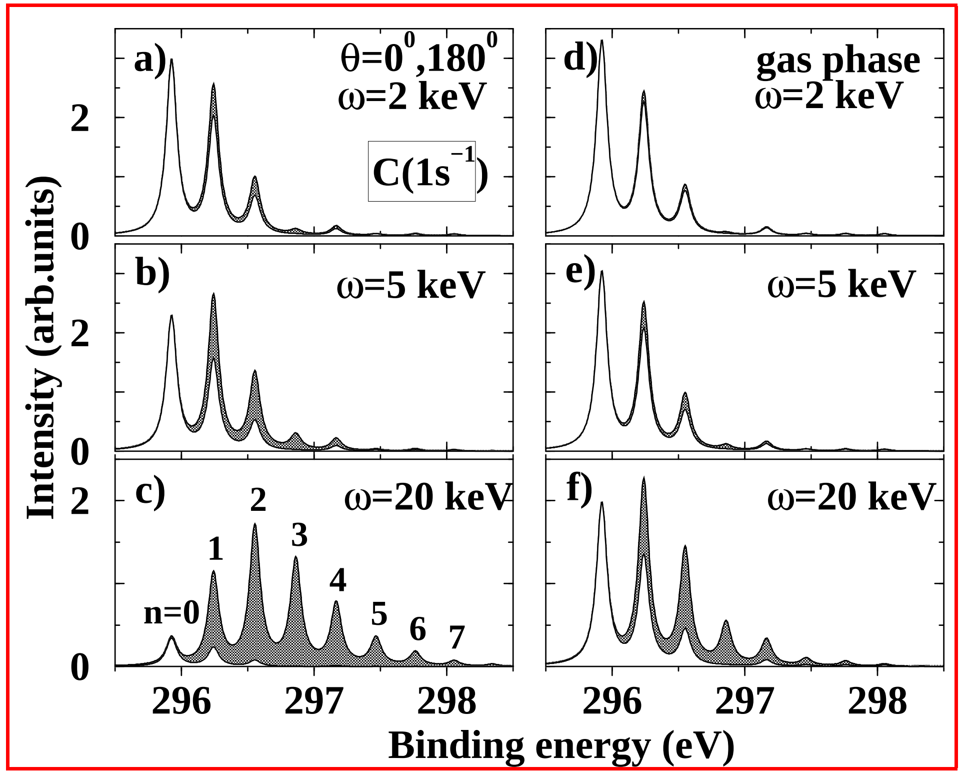
GFC in photoelectron spectroscopy

The cross section:

$$\sigma \sim \sum_f \left| \langle f | \hat{D} e^{-i\alpha \mathbf{k}\cdot\mathbf{R}} | 0 \rangle \right|^2$$

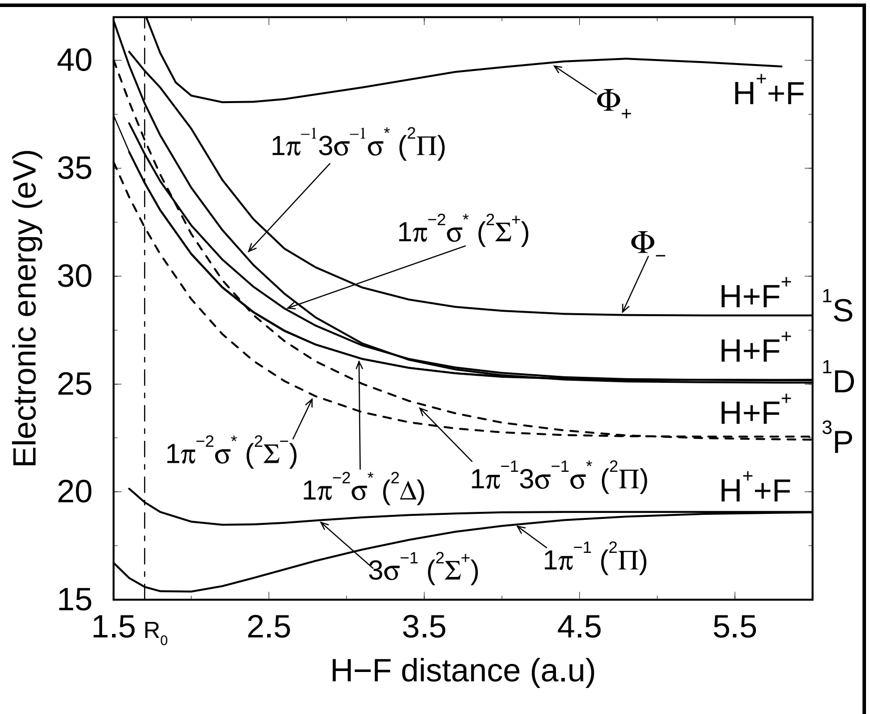


The scheme



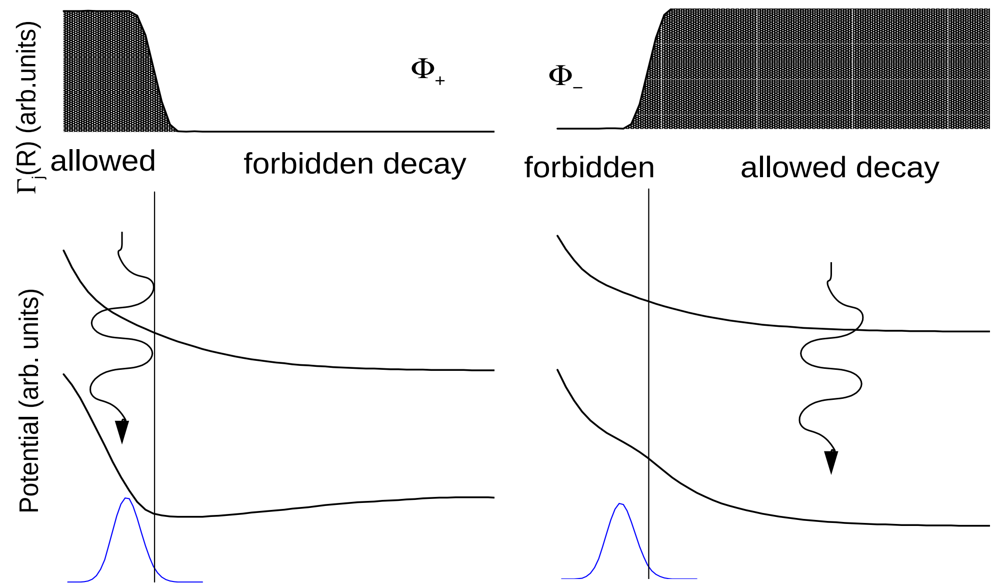
The simulated spectra

Dynamical suppression



RXS on HF: Potential curves of final states.

Avoided crossing of $2\sigma^{-1}$ and $3\sigma^{-1}\sigma^{*}$ configurations.



- electronic configuration switching
- inhibited atomic peak associated with a state which has substantial Auger decay ratio at the equilibrium geometry – but very small in the dissociative region.

Collaborators

Theory

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Svante Svensson
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Ingela Hjelte
Martin Magnusson
Conny Såthe
Joseph Nordgren

Summary

- wave packets – time-dependent approach to RXS – natural description of a dynamic system.
- merge of the electronic structure theory with nuclear dynamics.
- Interference effects: The atomic hole.
- R-dependent transition moments: N_2 spectrum flattening, dynamical suppression.
- Doppler effect