Quantum dynamics in scattering

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Wave packet

(Erwin Schrödinger, 1926)

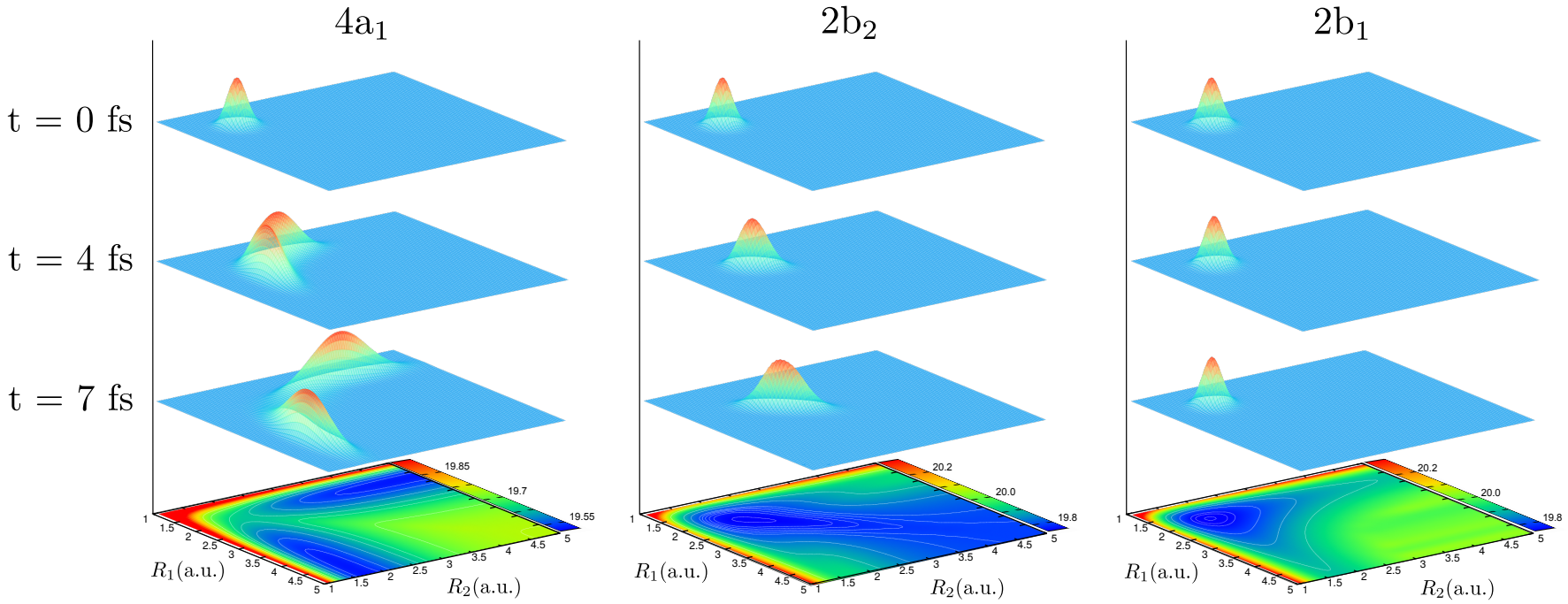
Stationary Schrödinger equation :

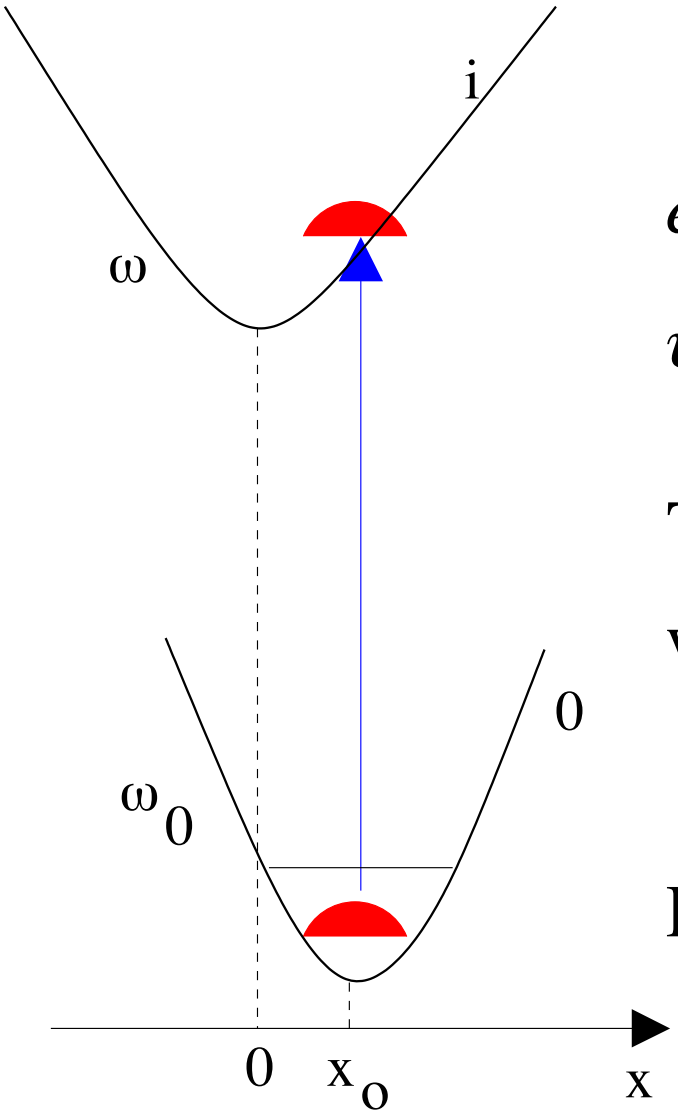
$$H\psi_n(x,t) = E_n\psi_n(x,t)$$

Wave packet

$$\iota\frac{\partial}{\partial t}\psi(x,t) = H\psi(x,t), \qquad \psi(x,t=0) = \psi(x,0)$$

$$\psi(x,t) = e^{-\iota H_i t}\psi(x,0)$$





$|0_0\rangle$ *is not eigen function of* H_i !

$$|0_0\rangle = \sum_{\nu_c} |\nu_i\rangle\langle\nu_i|0_0\rangle, \qquad \sum_{\nu} |\nu_i\rangle\langle\nu_i| = 1$$

$$e^{-\iota H_i t}|\nu_i\rangle = e^{-\iota\varepsilon_i t}|\nu_i\rangle$$

$$\psi(x,t) = e^{-\iota H_i t}|0_0\rangle = \sum_{\nu_c} e^{-\iota\varepsilon_i t}|\nu_i\rangle\langle\nu_i|0_0\rangle$$

To get the dynamics

we need to mix at least 2 states :

$$|0_i\rangle = e^{-x^2/2a^2}, \quad |1_i\rangle = x\ e^{-x^2/2a^2}$$

$$\mathrm{Re}\left(\psi(x,t)\right) \propto \left(1 + c\cdot x\cdot\cos\left(\omega_0 t\right)\right) e^{-x^2/2a^2}$$

$$\iota\frac{\partial}{\partial t}\psi(x,t)=H\psi(x,t),\quad \psi(x,t=0)=\psi(x,0)$$

$$\psi(x,t)=e^{-\iota Ht}\psi(x,0)=G\psi(x,0)$$

Green's operator

$$G=e^{-\iota Ht},\qquad \sum_n\left|\psi_n\right\rangle\left\langle\psi_n\right|=1$$

$$\psi(x,t)=\sum_n e^{-\iota Ht}\left|\psi_n\right\rangle\left\langle\psi_n\middle|\psi(x,0)\right\rangle$$

$$=\sum_n\psi_n(x)\int dx_1\psi_n^*(x_1)e^{-\iota\varepsilon_n t}\,\psi(x_1,0)$$

$$\psi(x,t)=\int dx_1 G(x,t;x_1,0)\psi(x_1,0)$$

Green's function

$$G(x,t;x_1,0)=\sum_n\psi_n^*(x_1)\psi_n(x)e^{-\iota\varepsilon_n t}\to\delta(x_1-x)$$

Wave packet in dissociative state. Free propagation.

$$H = -\frac{1}{2\mu}\frac{d^2}{dx^2}, \qquad \psi_k(x) = \frac{1}{\sqrt{2\pi}} e^{-\imath kx}, \; \varepsilon_k = \frac{k^2}{2\mu}, \; \sum_n \Rightarrow \int dk$$

$$G(x,t;x_1,0) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{\imath k(x_1-x)} e^{-\imath tk^2/2\mu}, \qquad \int_{-\infty}^{\infty} dk\, e^{-ak^2} e^{-bk} = \sqrt{\frac{\pi}{a}}\, e^{b^2/4a}$$

$$G(x,t;x_1,0) = \sqrt{\frac{\mu}{2\pi\imath t}} \exp\left(\frac{\imath\mu}{2t}(x_1 - x)^2\right), \quad \psi(x,0) = \sqrt{\frac{1}{a\sqrt{\pi}}} \exp\left(\imath k_0 x - \frac{x^2}{2a^2}\right)$$

$$P(x,t) = |\psi(x,t)|^2 = \frac{1}{a(t)\sqrt{\pi}} \exp\left(-\frac{(x - x_{cl}(t))^2}{a^2(t)}\right)$$

Center of gravity follows classical trajectory

$$x_{cl}(t) = \mathrm{v}_0 \mathrm{t}, \qquad \mathrm{v}_0 = \frac{k_0}{\mu}$$

Quantum spread of the wave packet with characteristic time, T :

$$a(t) = a\sqrt{1 + \frac{t^2}{T^2}}, \qquad T = \mu a^2$$

Wave packet in bound state. Harmonic oscillator

$$H=-\frac{1}{2}\frac{d^2}{dx^2}+\frac{\omega}{2}\frac{x^2}{a^2},\quad a=\frac{1}{\sqrt{\mu\omega}},\quad \varepsilon_n=\omega\left(n+\frac{1}{2}\right),\ \psi_n(x)=c_nH_n\left(\frac{x}{a}\right)e^{-x^2/2a^2},\ c_n=\sqrt{\frac{1}{a2^n n!\sqrt{\pi}}}$$

$$G(x,t;x_1,0)=\frac{e^{-\imath\omega t/2}}{a\sqrt{\pi}}\exp\left(-\frac{\left(x_1^2+x^2\right)}{2a^2}\right)\sum_n\frac{1}{n!}\left(\frac{e^{-\imath\omega t}}{2^n}\right)^n H_n\left(\frac{x_1}{a}\right)H_n\left(\frac{x}{a}\right),$$

$$\sum_n\frac{(z/2)^n}{n!}H_n(\nu)H_n(\mu)=\frac{1}{\sqrt{1-z^2}}\exp\left(\frac{2\mu\nu z-\left(\mu^2+\nu^2\right)z^2}{1-z^2}\right)$$

$$G(x,t;x_1,0)=\sqrt{\frac{\mu\omega}{2\pi\imath\sin(\omega t)}}\exp\left[\frac{\imath\mu\omega}{2\sin(\omega t)}\left(\left(x_1^2+x^2\right)\cos(\omega t)-2x_1x\right)\right]$$

$$\psi(x,0)=\sqrt{\frac{1}{a_0\sqrt{\pi}}}\exp\left(-\frac{\left(x-x_0\right)^2}{2a_0^2}\right),\quad a_0=\frac{1}{\sqrt{\mu\omega_0}}$$

$$P(x,t)=\left|\psi(x,t)\right|^2=\frac{1}{a(t)\sqrt{\pi}}\exp\left(-\frac{\left(x-x_{cl}(t)\right)^2}{a^2(t)}\right)$$

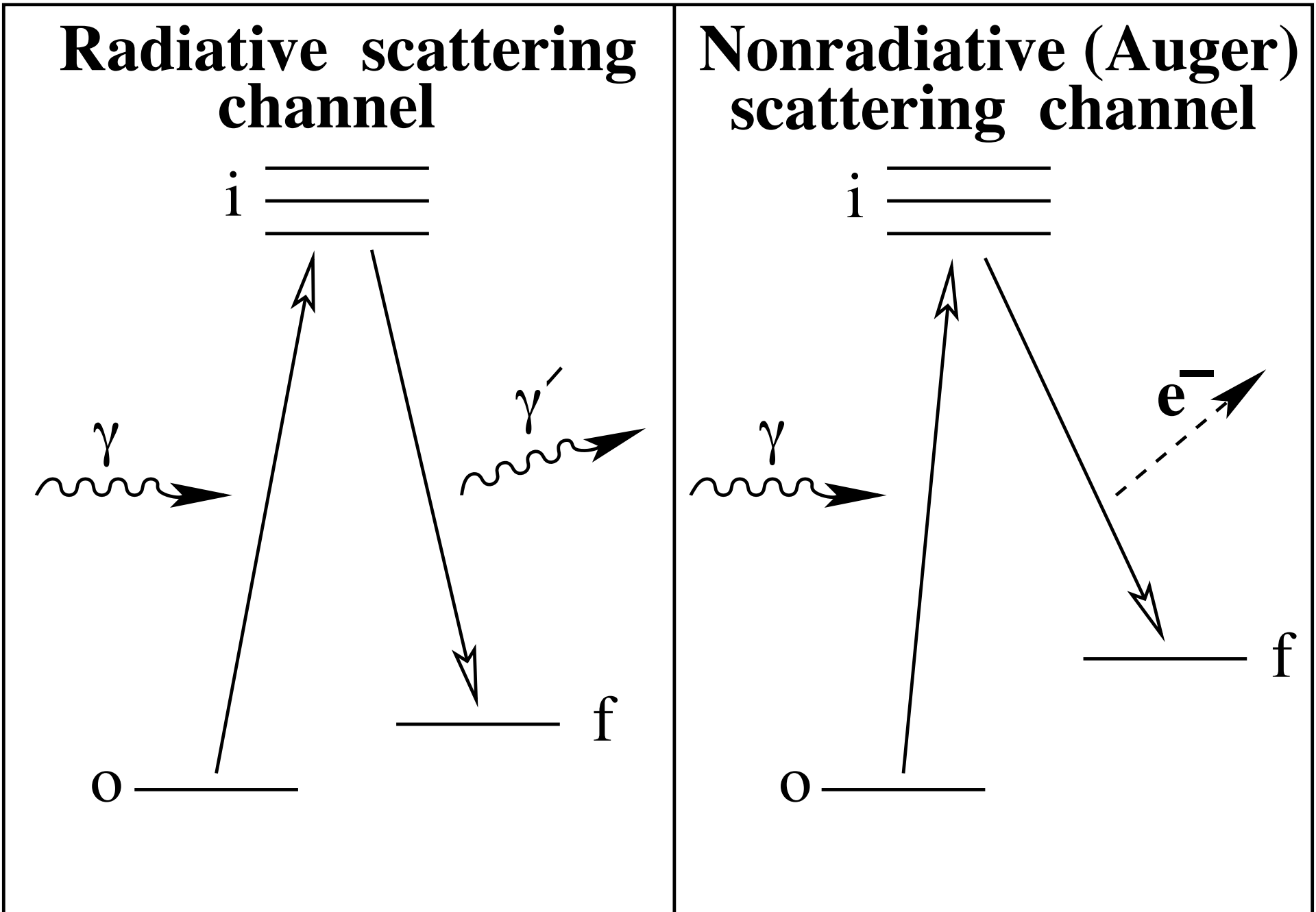
Center of gravity follows classical trajectory. No spread of wave packet

$$x_{cl}(t)=x_0\cos(\omega t),\qquad a(t)=a_0\sqrt{\cos^2(\omega t)+\frac{a^4}{a_0^4}\sin^2(\omega t)}$$

Nuclear dynamics in Resonant Raman and Auger scattering

RIXS or resonant X-ray Raman

Resonant Auger or photoemission



Resonant Raman and resonant Auger scattering

Resonant X- Raman scattering

$$\sigma(\omega',\omega) = |F|^2 \delta\left(\omega - \omega' - \omega_{f0} + \varepsilon_0 - \varepsilon_{\nu_f}\right)$$

$$F = \sum_{\nu_c} \frac{\langle \nu_f | D_{fc} | \nu_c \rangle \langle \nu_c | D_{c0} | 0 \rangle}{\omega - \omega_{c0} + \varepsilon_0 - \varepsilon_{\nu_c} + \iota\Gamma}, \qquad D_{fc} = \left(\vec{e}' \cdot \vec{d}_{fc}\right), D_{c0} = \left(\vec{e} \cdot \vec{d}_{c0}\right)$$

Raman dispersion :

$$\omega' = \omega - \omega_{f0} + \varepsilon_0 - \varepsilon_{\nu_f}$$

Resonant Auger scattering

$$\sigma(E,\omega) = |F|^2 \delta\left(\omega - E - \omega_{f0} + \varepsilon_0 - \varepsilon_{\nu_f}\right)$$

$$F = \sum_{\nu_c} \frac{\langle \nu_f | Q_{fc} | \nu_c \rangle \langle \nu_c | D_{c0} | 0 \rangle}{\omega - \omega_{c0} + \varepsilon_0 - \varepsilon_{\nu_c} + \iota\Gamma}, \qquad Q_{fc} = \left\langle f \left| \frac{1}{r_{12}} \right| c \right\rangle, D_{c0} = \left(\vec{e} \cdot \vec{d}_{c0}\right)$$

$$Q_{fc} \propto e^{\iota \vec{k} \cdot \vec{R}_n}, \qquad E = \frac{k^2}{2}, \qquad \vec{k} \text{ is the momentum of Auger electron}$$

Scattering duration

$$\sigma(\omega',\omega) = |F|^2 \, \delta\left(\omega - \omega' - \omega_{f0} + \varepsilon_0 - \varepsilon_{\nu_f}\right)$$

$$F = -\iota \langle \nu_f | \Psi \rangle, \qquad |\Psi\rangle = \iota \sum_{\nu_c} \frac{D_{fc} |\nu_c\rangle \langle \nu_c | D_{c0} |0\rangle}{\omega - \omega_{c0} + \varepsilon_0 - \varepsilon_{\nu_c} + \iota\Gamma}$$

$$\frac{1}{x + \iota\Gamma} = -\iota \int_0^\infty e^{\iota(x+\iota\Gamma)t} \, dt, \qquad D_{fc} = \left(\vec{e}' \cdot \vec{d}_{fc}\right), \; D_{c0} = \left(\vec{e} \cdot \vec{d}_{c0}\right)$$

$$F = -\iota \int_0^\infty \sum_{\nu_c} \langle \nu_f | D_{fc} | \nu_c \rangle e^{-\iota\varepsilon_{\nu_c} t} \langle \nu_c | D_{c0} | 0 \rangle e^{(i\Omega - \Gamma)t} \, dt = -\iota \int_0^\infty F(t) \, dt$$

$$F(t) = \langle \nu_f | \psi_c(t) \rangle e^{-\frac{t}{\tau}}, \qquad \psi_c(t) = D_{fc} e^{-\iota H_c t} D_{c0} |0\rangle$$

Scattering duration

$$\tau = \frac{1}{\Gamma - i\Omega}, \quad |\tau| = \frac{1}{\sqrt{\Omega^2 + \Gamma^2}}, \qquad \Omega = \omega - \omega_{c0} + \varepsilon$$

$$|\Psi\rangle = \int_0^\infty e^{\iota(\Omega+\iota\Gamma)t} \psi_c(t) \, dt, \qquad F = -\iota \langle \nu_f | \Psi \rangle$$

Pictural illustration of the X-ray shutter.

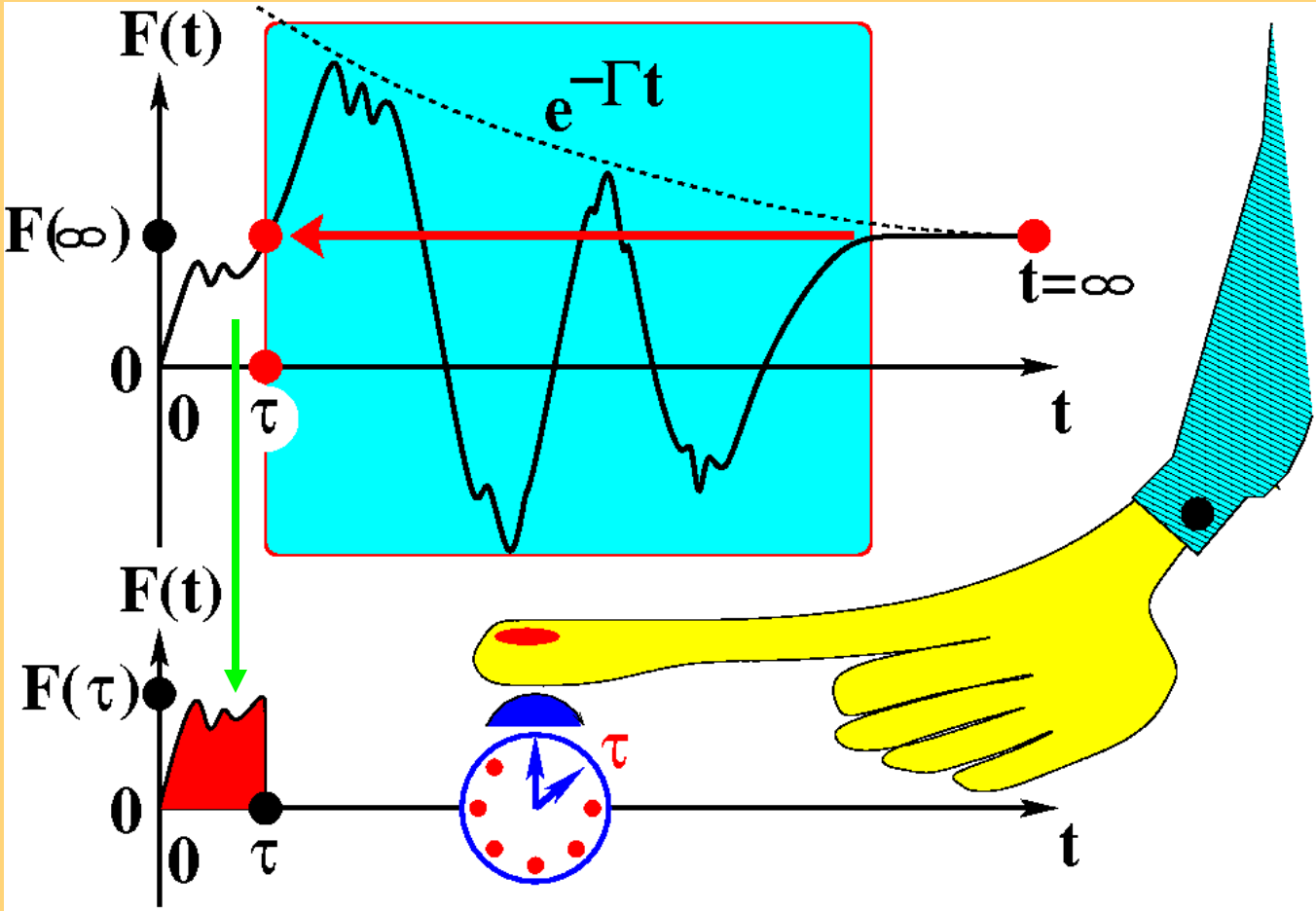
A small detuning gives a long exposure time of the process and a large detuning a short exposure time. With such a controlled X-ray shutter it is possible to select for the measurement different subprocesses on different time scales.

Only short-time contributions

$$t \le \tau = \frac{1}{\sqrt{\Omega^2 + \Gamma^2}}$$

$$\Omega = \omega - \omega_{res}$$

form the RXS amplitude because of the distructive interference for large times t.



Time-dependent representation for scattering cross section

$$\sigma(\omega',\omega) = \sum_{\nu_f} |F|^2 \, \delta\left(\omega - \omega' - \omega_{f0} + \varepsilon_0 - \varepsilon_{\nu_f}\right)$$

$$F = -\iota \langle \nu_f | \Psi \rangle, \quad |\Psi\rangle = \int_0^\infty e^{\iota(\Omega + \iota\Gamma)t} \psi_c(t)\, dt$$

$$\Omega = \omega - \omega_{c0} + \varepsilon \quad = \text{Detuning}$$

$$\delta(x) \Rightarrow \frac{1}{\pi} \mathrm{Re} \int_0^\infty e^{\iota(x + \iota\Gamma_f)t}\, dt,$$

$$\sigma(\omega',\omega) = \frac{1}{\pi} \mathrm{Re} \int_0^\infty e^{\iota(\omega - \omega' - \omega_{f0} + \varepsilon_0 + \iota\Gamma_f)t} \sigma(t)\, dt$$

$$\sigma(t) = \langle \Psi | e^{-\iota H_f t} | \Psi \rangle = \langle \Psi | \Psi(t) \rangle, \quad |\Psi(t)\rangle = e^{-\iota H_f t} |\Psi\rangle$$

Energy domain ➔ **Lifetime vibrational interference**

$$F = \sum_{\nu_c} \frac{\langle \nu_f | D_{fc} | \nu_c \rangle \langle \nu_c | D_{c0} | 0 \rangle}{\omega - \omega_{c0} + \varepsilon_0 - \varepsilon_{\nu_c} + \iota\Gamma}, \qquad \sigma(\omega', \omega) = |F|^2 \, \delta\left(\omega - \omega' - \omega_{f0} + \varepsilon_0 - \varepsilon_{\nu_f}\right)$$

Time domain(wave packet) ➔**Scattering duration** ➔ **Dynamics**

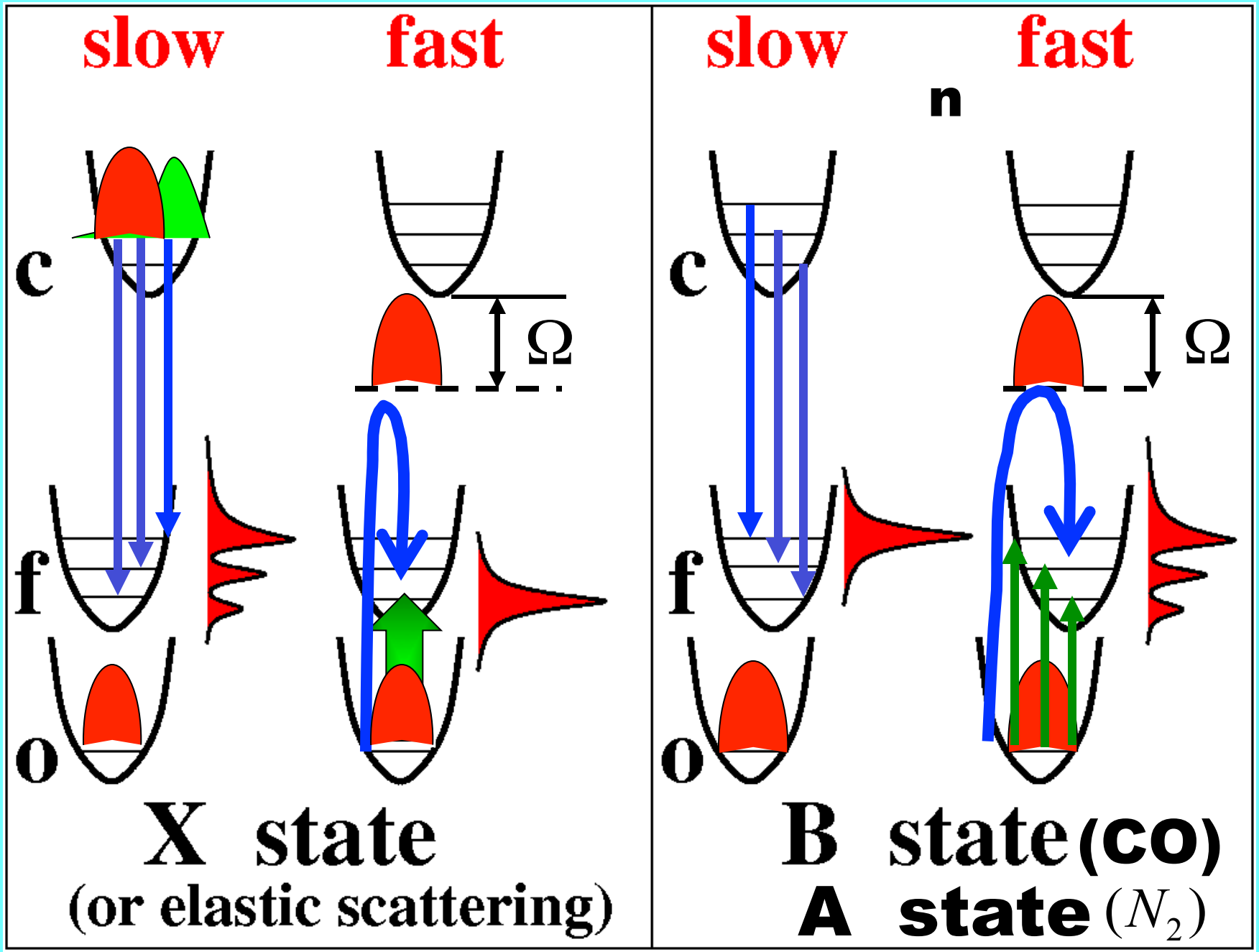
$$F = -\langle \nu_f | \Psi \rangle, \qquad |\Psi\rangle = \int_0^\infty e^{\iota(\Omega + \iota\Gamma)t} \psi_c(t) \, dt = \int_0^\infty \psi_c(t) e^{-\frac{t}{\tau}} \, dt,$$

$$\tau = \frac{1}{\Gamma - \iota\Omega}, \qquad |\tau| = \frac{1}{\sqrt{\Omega^2 + \Gamma^2}}, \qquad \psi_c(t) = D_{fc} e^{-\iota H_c t} D_{c0} |0\rangle$$

Collapse of vibrational structure

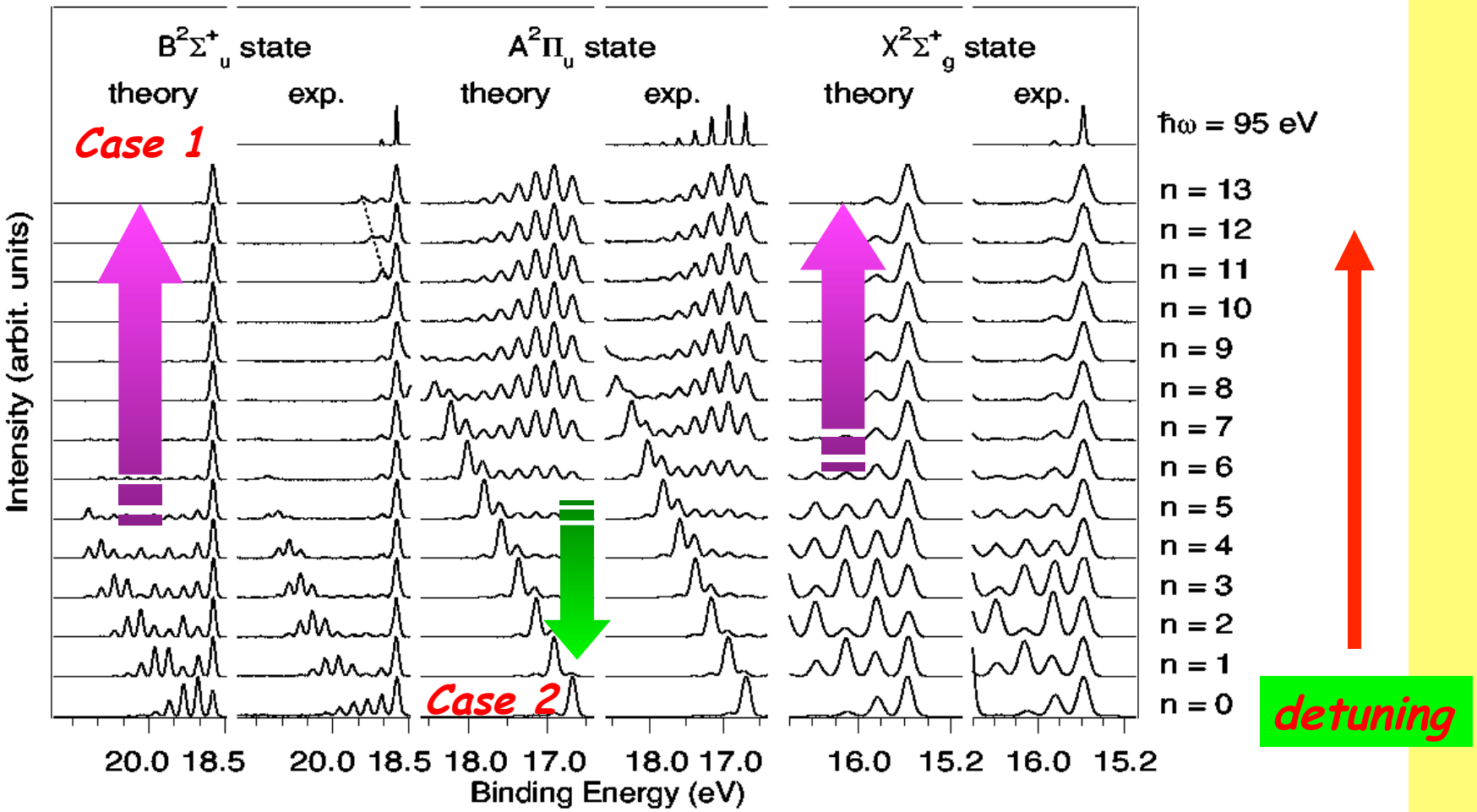
Phys Rev A 56(1997)256,
Phys Rev Lett 79(1997) 1451

Collapse of vibrational structure



Collapse of vibrational structure in N_2. Positive detunings

$$U_f = U_0 \qquad U_c = U_f \qquad U_f = U_0$$



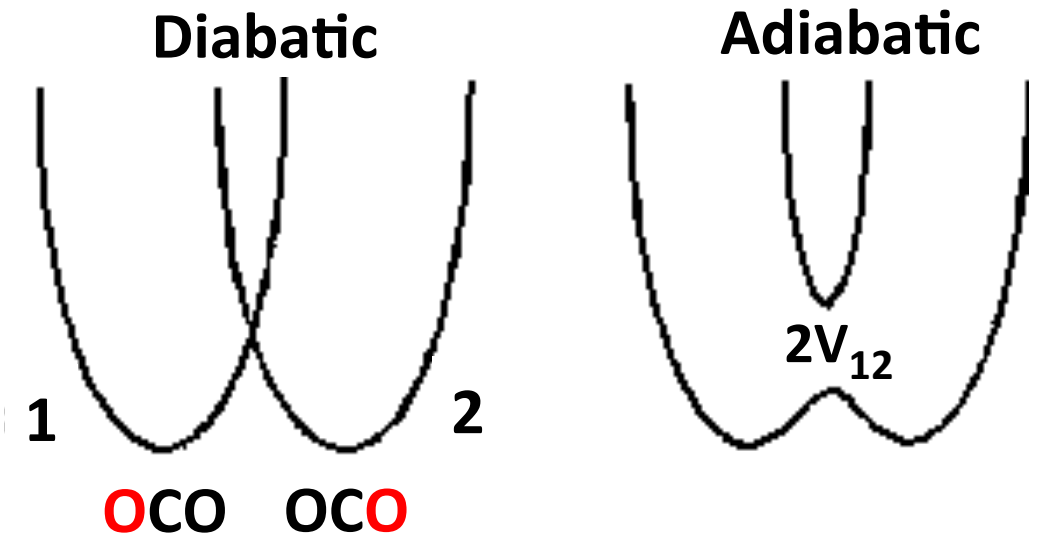
R. Feifel et al

Vibronic coupling

Avoided crossing

Breakdown of Born-Oppenheimer approximation

Vibronic coupling. Diabatic vs adiabatic pictures



$$\Psi(r,R,t)=\sum_n \psi_n(R,t)\phi_n^{el}(r,R), \quad \iota\frac{\partial}{\partial t}\psi_n=\sum_m\left\langle\phi_n^{el}\middle|K+h_{el}\middle|\phi_m^{el}\right\rangle\psi_m$$

Diabatic representation is better :

$$\left\langle\phi_n^{el}\middle|K\middle|\phi_m^{el}\right\rangle\approx K\delta_{nm}; \quad K=-\frac{1}{2\mu}\frac{d^2}{dR^2}, \quad E_n(R)=\left\langle\phi_n^{el}\middle|h_{el}\middle|\phi_n^{el}\right\rangle, \quad V_{nm}=\left\langle\phi_n^{el}\middle|h_{el}\middle|\phi_m^{el}\right\rangle$$

$$\iota\frac{\partial}{\partial t}\psi_n=\sum_m H_{nm}\psi_m, \qquad H_{nm}=\delta_{nm}\left(K+E_n(R)\right)+\left(1-\delta_{nm}\right)V_{nm}$$

Vibronic coupling in core-excited state (CO_2 : O1s RIXS)

Real localization of core hole

Phys Rev Lett 77(1996) 5035

Restoration of electronic selection rules in RIXS.

Fast scattering

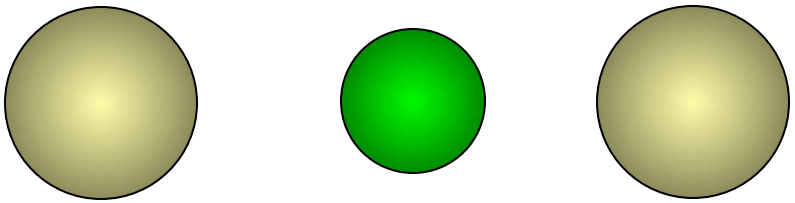
(large detuning)

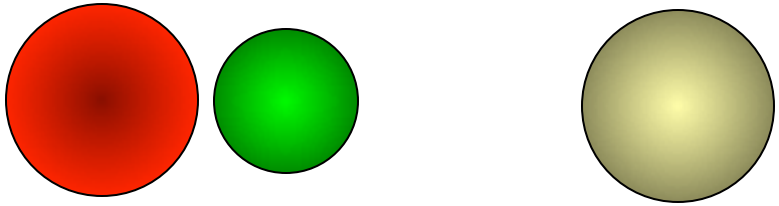
$$\tau\,\omega_{vib} << 1$$

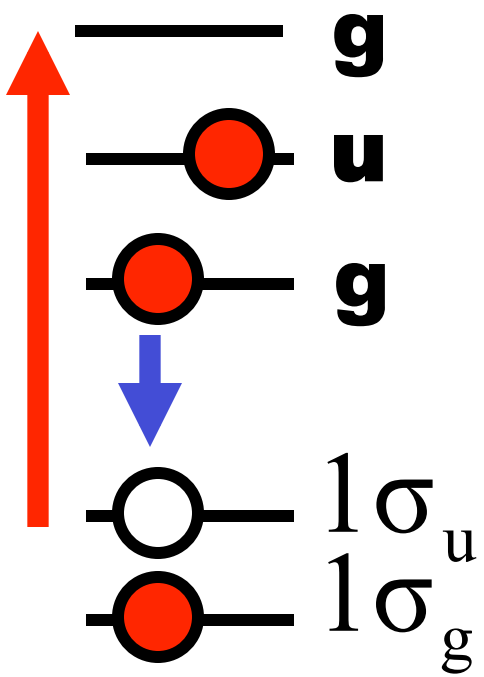
Slow scattering

(small detuning)

$$\tau\,\omega_{vib} >> 1$$

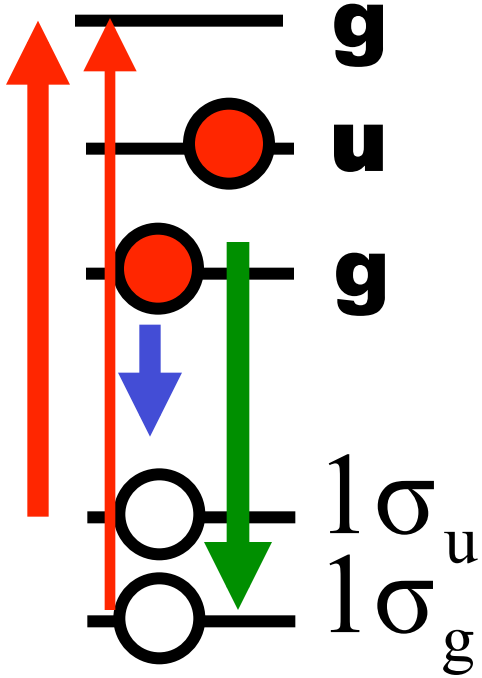






$$\tau = \frac{1}{\sqrt{\Omega^2 + \Gamma^2}}$$

$$\Omega = \omega - \omega_{res}$$



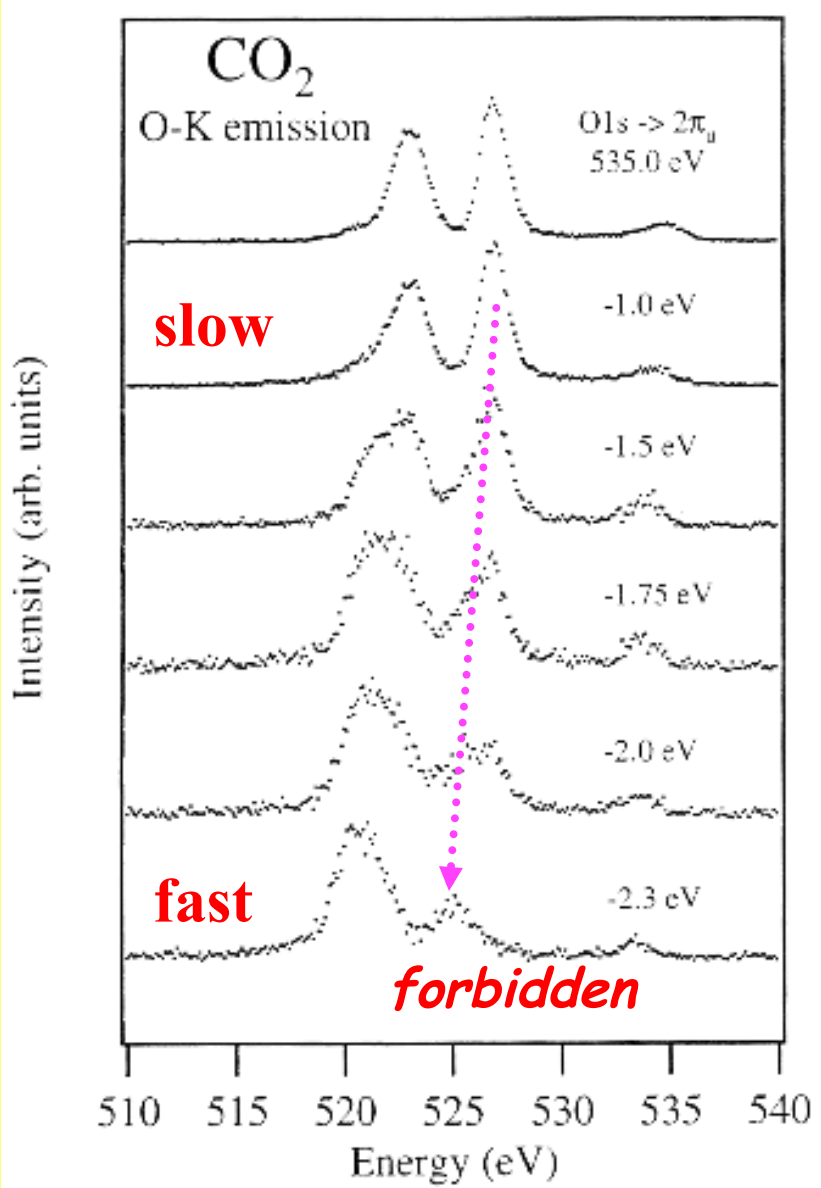
We have real localization of core hole in the course of symmetry breaking vibrations according to equation

$$\Psi(r,R,t) = \sum_n \psi_n(R,t)\phi_n^{el}(r,R)$$

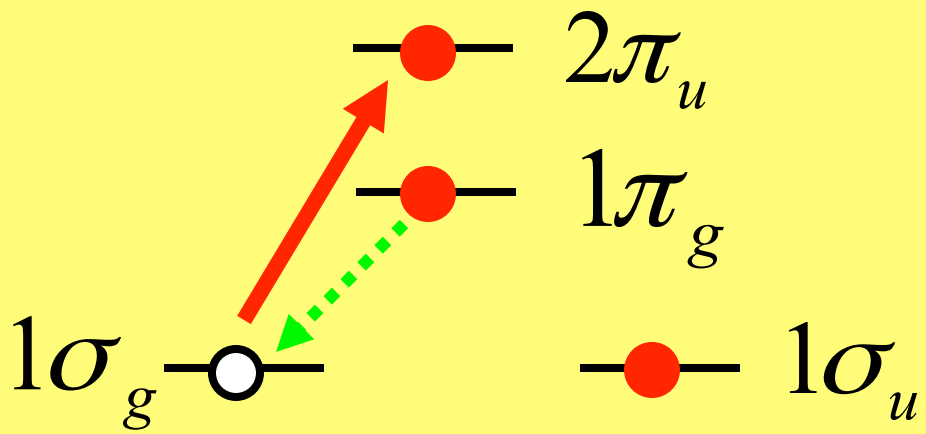
$$= \psi_g(R,t)\phi_g^{el}(r,R) + \psi_u(R,t)\phi_u^{el}(r,R)$$

Restoration of selection rules.

Radiative RXS of CO_2



Symmetry forbidden (SF) RXS



The vibronic coupling of the close lying gerade and ungerade core excited states breaks down the symmetry of electronic state. The SF transition is now allowed.

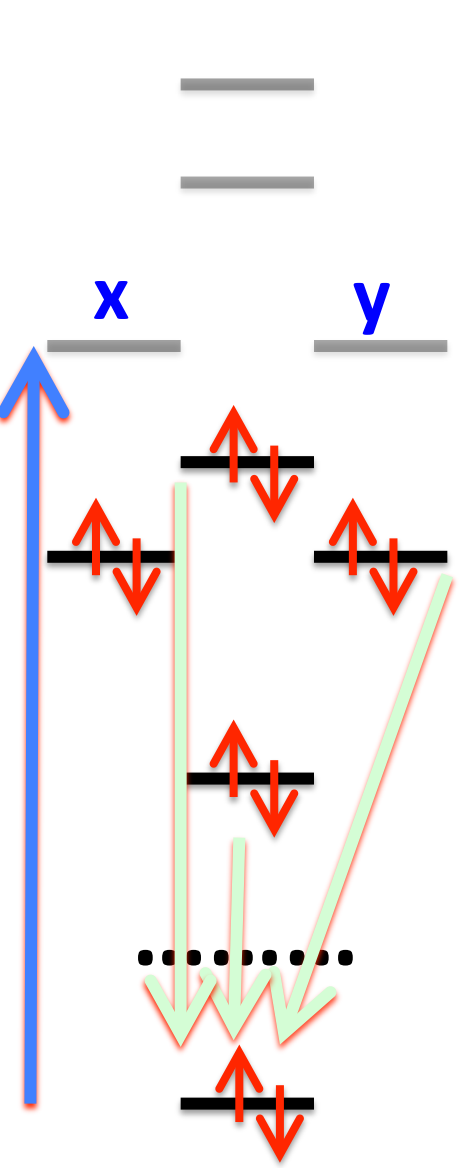
The selection rules are restored when the scattering is fast.

Vibronic coupling in final state

(CO : O1s RIXS)

Scientific Reports, 6(2016) 20947

Genealogy of multi-electronic states in CO



$3d_\pi$

$3p_\pi$ **Rydberg**

2π

5σ **Valence**

1π

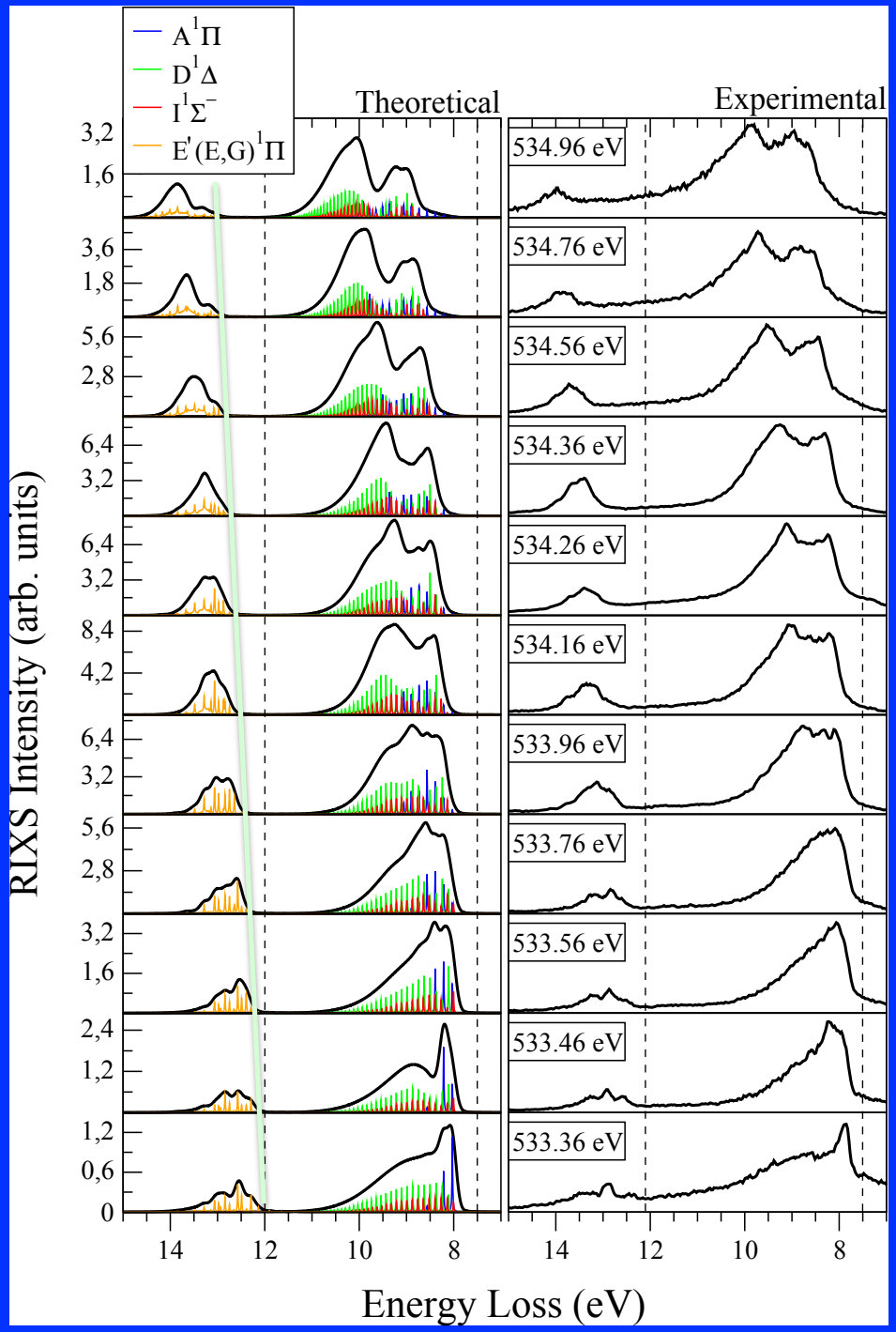
4σ

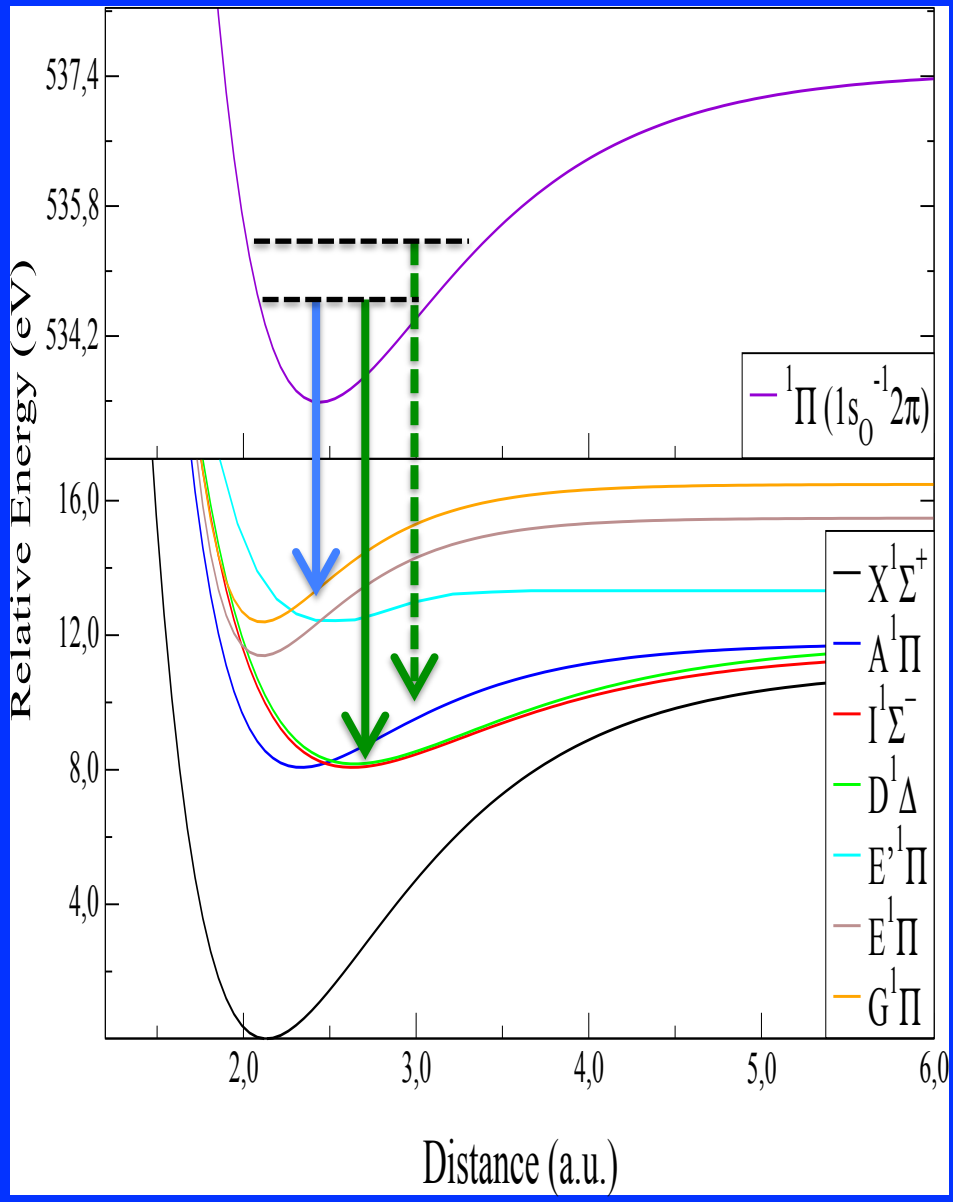
$1s$

$$8\text{ eV}: \begin{cases} \left|5\sigma^{-1}2\pi^{1}\right\rangle \rightarrow A^{1}\Pi \\ \left|1\pi^{-1}2\pi^{1}\right\rangle \rightarrow \begin{cases} I^{1}\Sigma^{-} \\ D^{1}\Delta \end{cases} \end{cases}$$

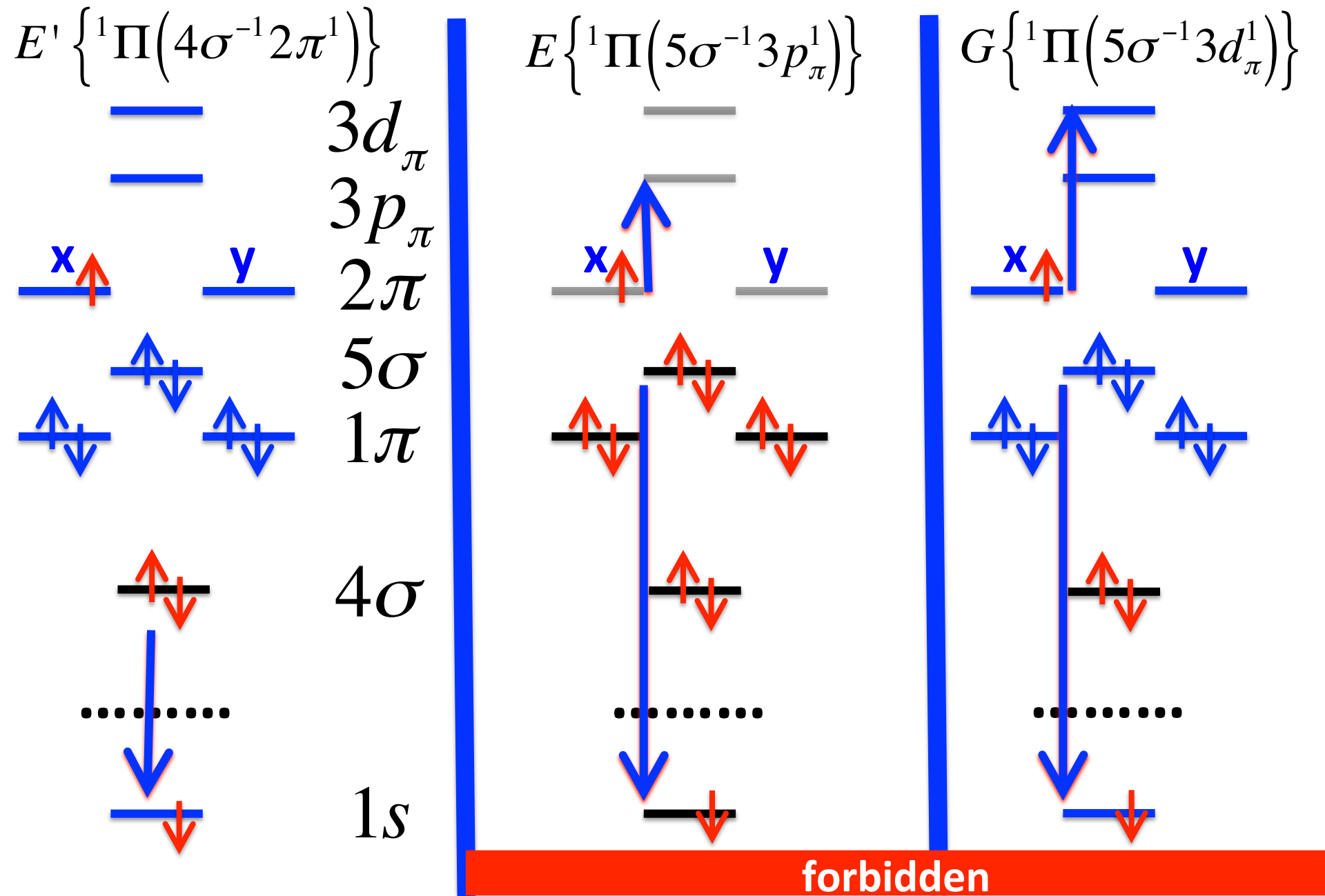
$$13\text{ eV}: \begin{cases} E'\left\{^{1}\Pi\left(4\sigma^{-1}2\pi^{1}\right)\right\} \\ +E\left\{^{1}\Pi\left(5\sigma^{-1}3p_{\pi}^{1}\right)\right\} \\ +G\left\{^{1}\Pi\left(5\sigma^{-1}3d_{\pi}^{1}\right)\right\} \end{cases}$$

RIXS circular polarization (non-Raman dispersion)

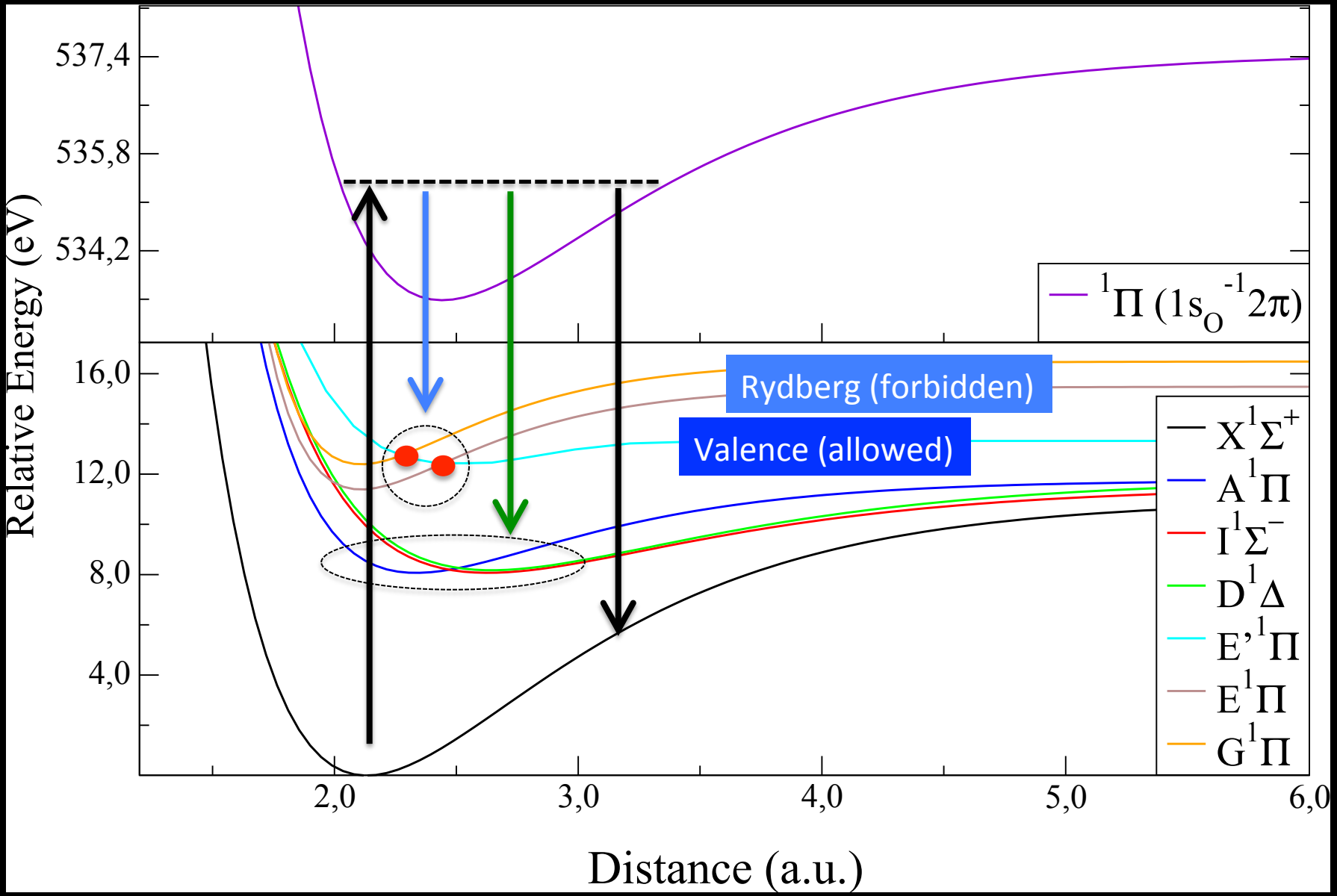




Enhancement of two-electron one-photon transitions in CO



Potentials of core excited, final and ground states



Cross section of electron-vibrational RIXS

$$\mathrm{H}_f = \begin{pmatrix} h_{E'} & V_{E'E} & V_{E'G} \\ V_{EE'} & h_E & 0 \\ V_{GE'} & 0 & h_G \end{pmatrix}$$

$$h_n = -\frac{1}{2\mu}\frac{d^2}{dR^2} + E_n(R)$$

$$\vec{d} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

$$\sigma(\omega',\omega) = \int \sigma_f^{(o)}\left(\omega_1',\omega\right)\Phi\left(\omega_1' - \omega'\right)d\omega_1'$$

$$\sigma_f^{(o)}(\omega',\omega) = \xi\sigma(f)\sigma_f^{\mathrm{vib}}(\omega',\omega),$$

$$\xi = r_0^2\frac{\omega\omega'^3}{30}D^2\left(X^1\Sigma^+, {}^1\Pi_x\right)$$

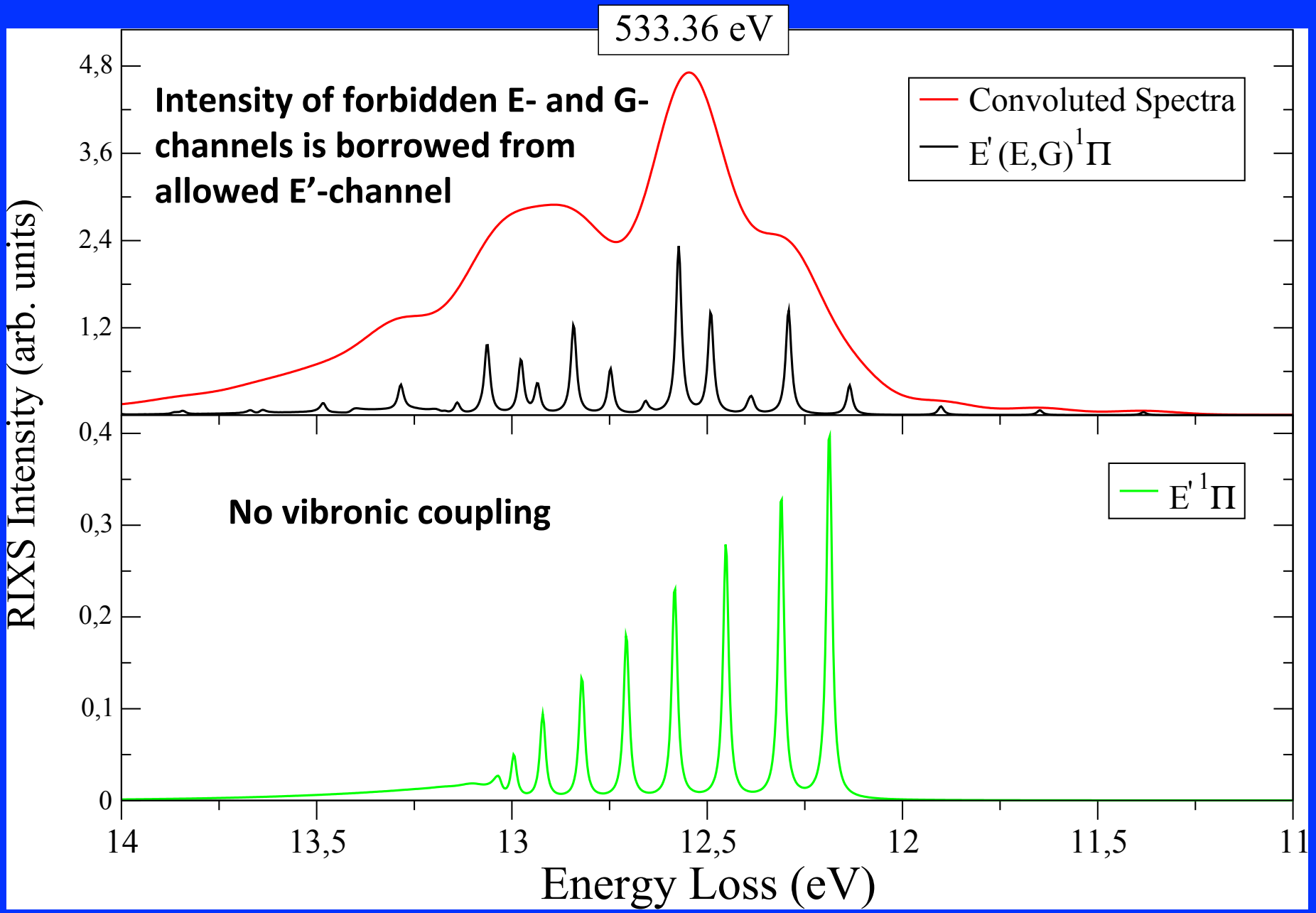
$$\sigma_f^{\mathrm{vib}}(\omega',\omega) =$$

$$= \frac{1}{\pi}\mathrm{Re}\int_0^\infty \sigma(\tau)\, e^{\iota\left(\omega-\omega'-\omega_{f0}+\iota\Gamma_f\right)\tau}d\tau$$

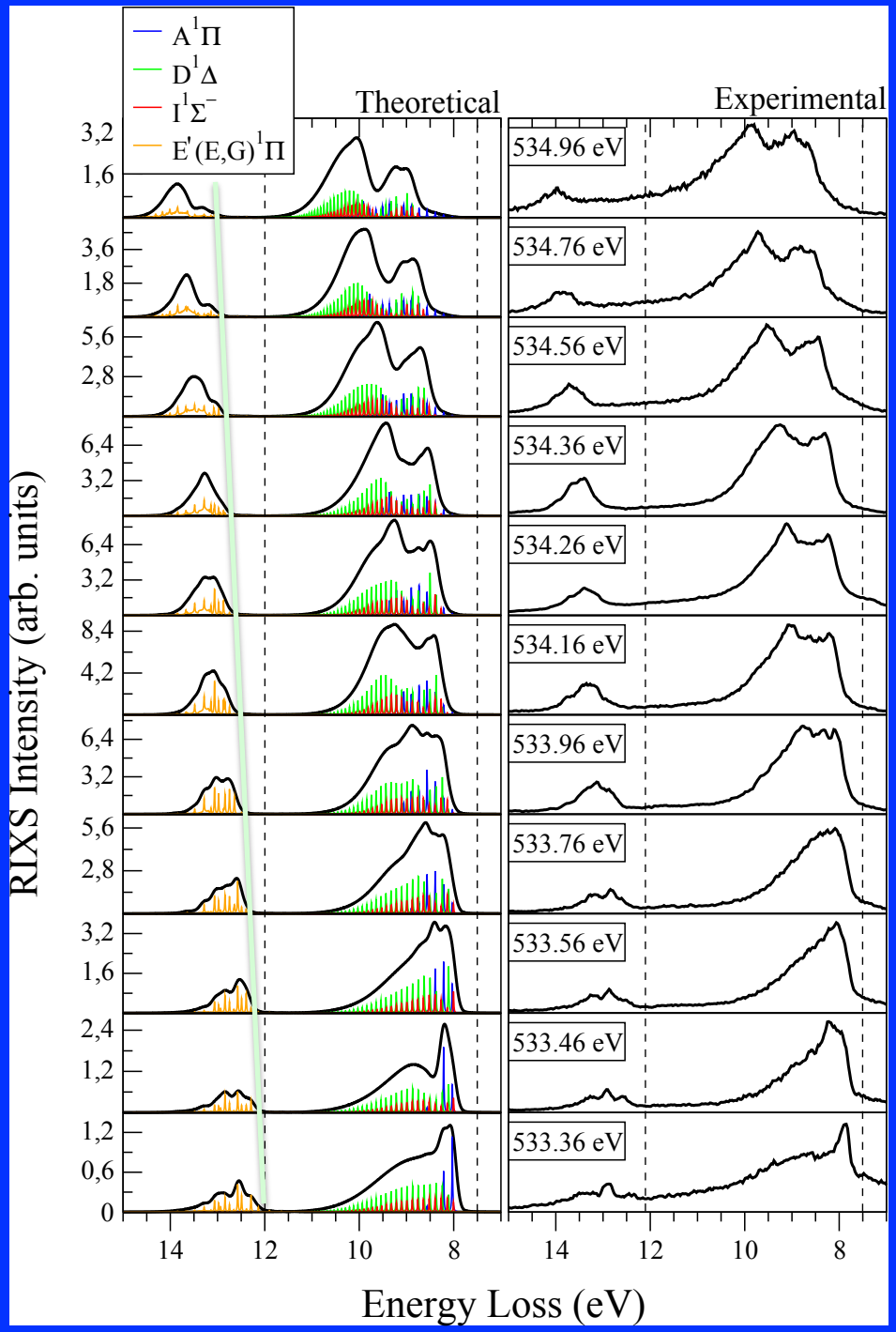
$$\sigma(\tau) = \left\langle\Psi\middle|\vec{d}_f^{+}e^{-\iota \mathrm{H}_f\tau}\vec{d}_f\middle|\Psi\right\rangle$$

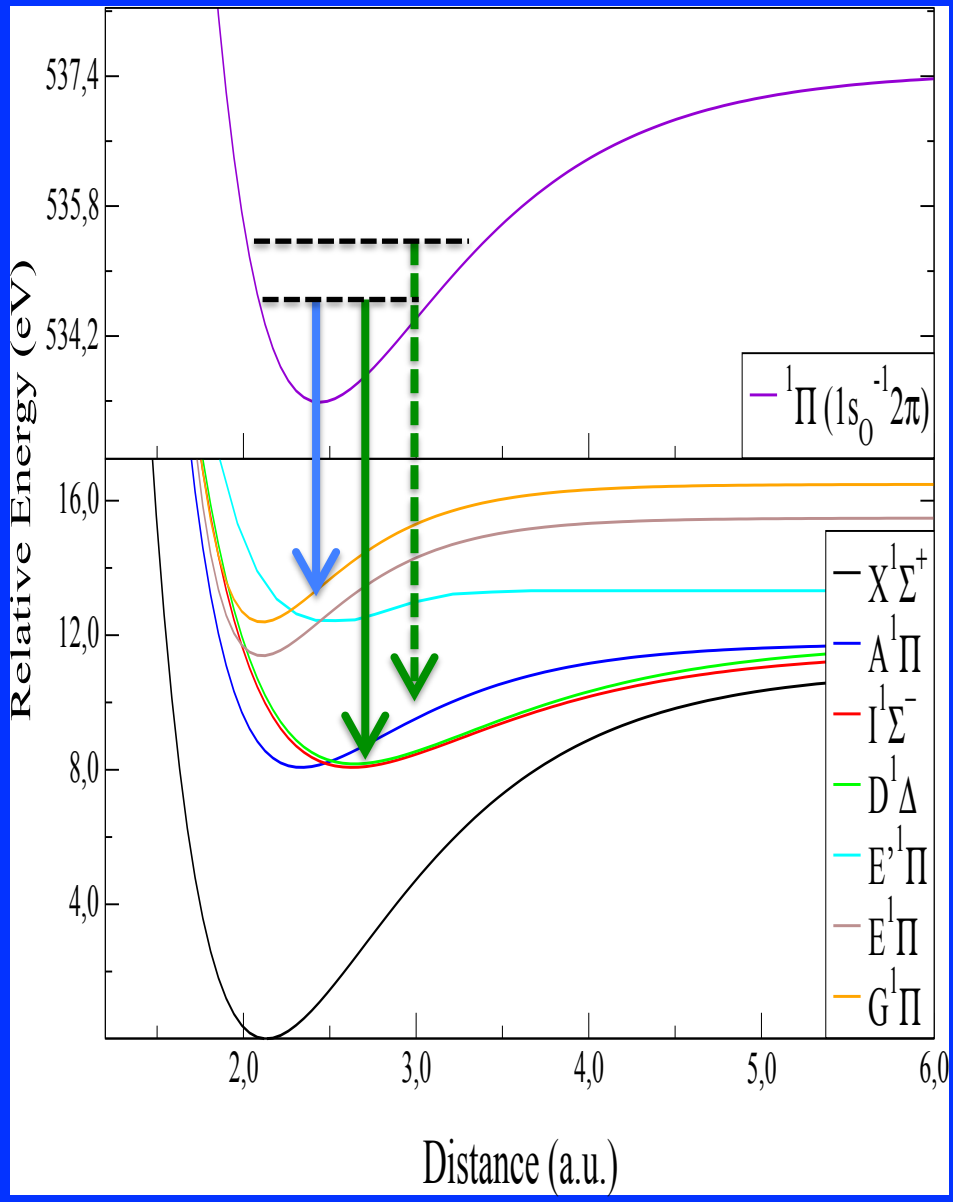
$$\left|\Psi\right\rangle = \int_0^\infty e^{-\iota\left(h_c+\omega_{c0}-\omega-\iota\Gamma_f\right)\tau}\left|0\right\rangle d\tau$$

Role of vibronic coupling of (E,G) and E’ final states

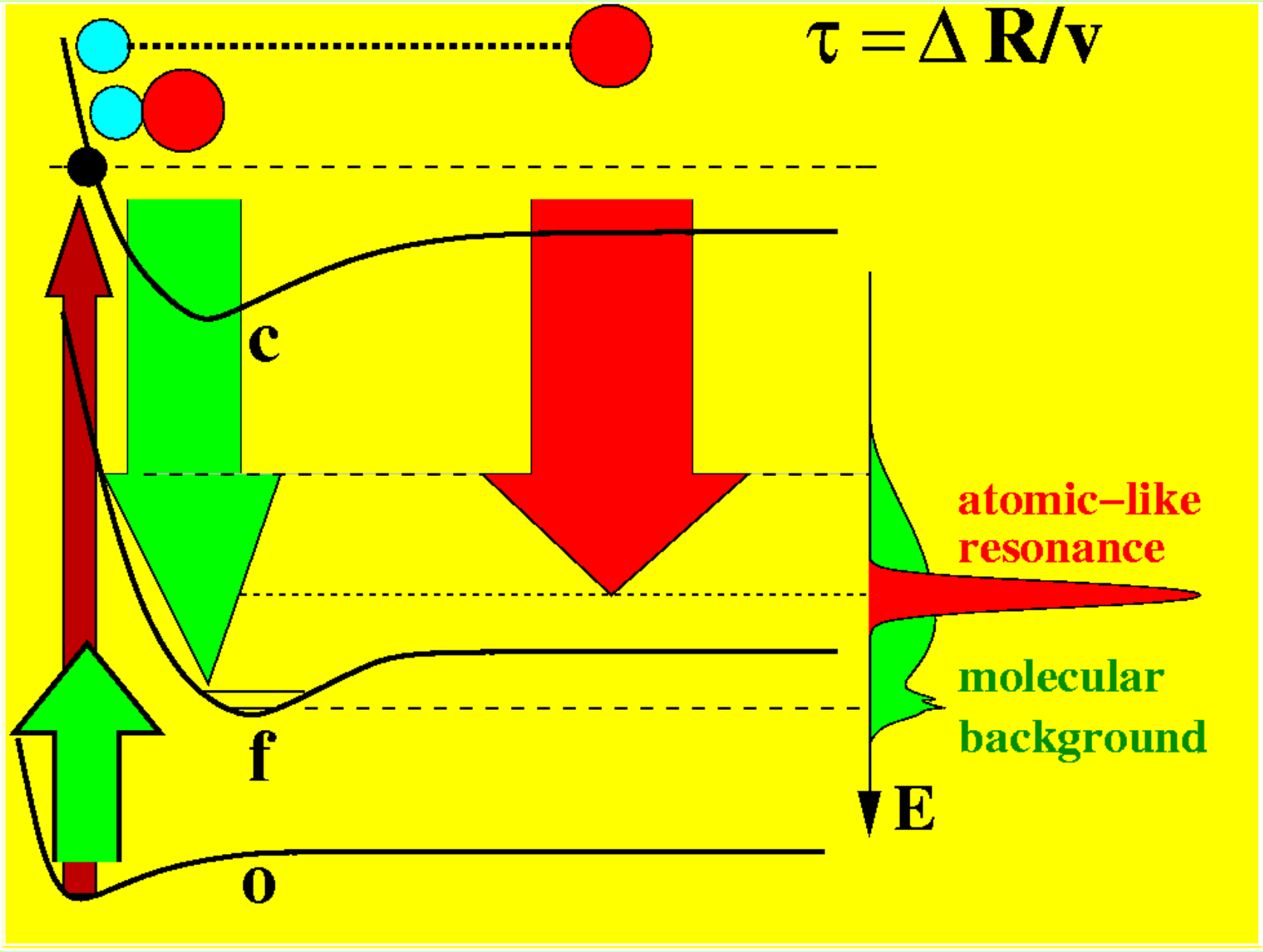


RIXS circular polarization (non-Raman dispersion)





Scattering through dissociative state. Atomic-like resonance and molecular band



Atomic peak and hole

Phys Rev Lett 56(1986) 1913
Phys Rev A 59(1999)1147,
Phys Rev Lett 85(2000) 3133

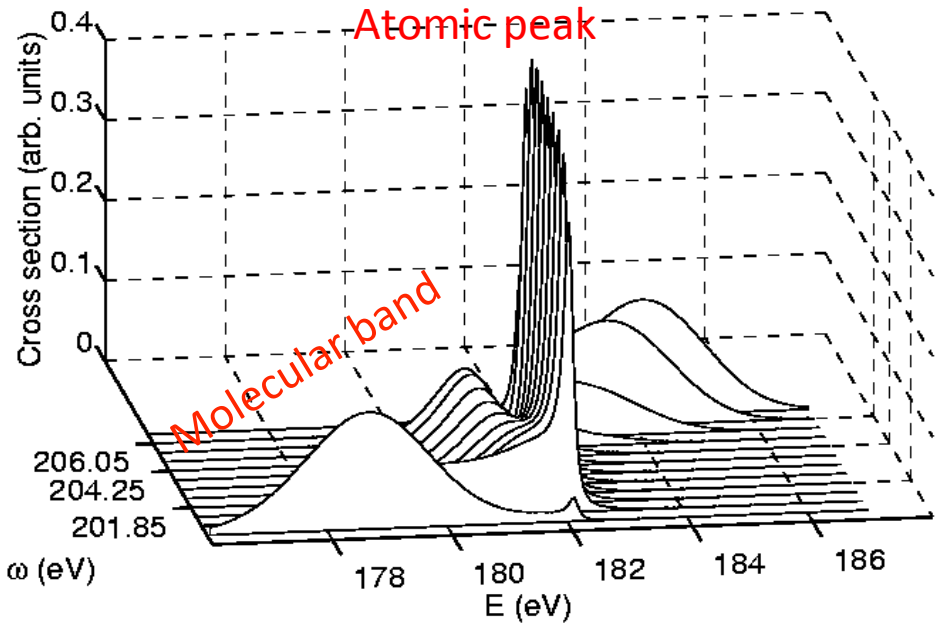
Spectral shape of RXS for unbound final state of HCl

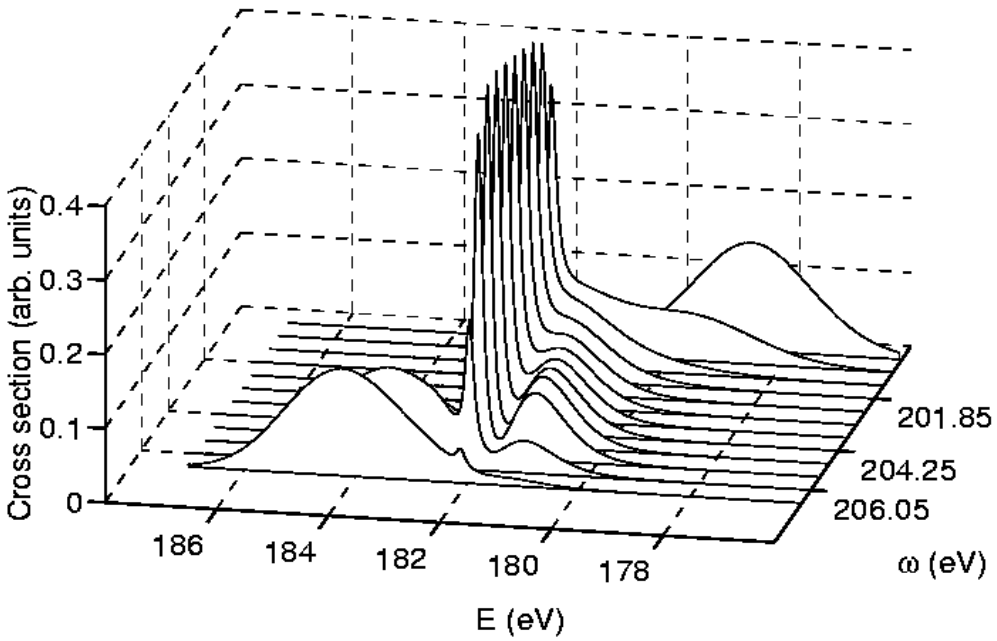
$$^2\Sigma^-$$

The position of narrow atomic resonance (contrary to broad molecular band (MB)) does not depend on the photon frequency.

The atomic peak intensity decreases faster than MB for large detunings due to small scattering duration:

$$\tau = \frac{1}{\sqrt{(\Omega^2 + \Gamma^2)}}$$





Atomic hole

The scattering amplitude consists of a broad molecular and a sharp atomic contributions

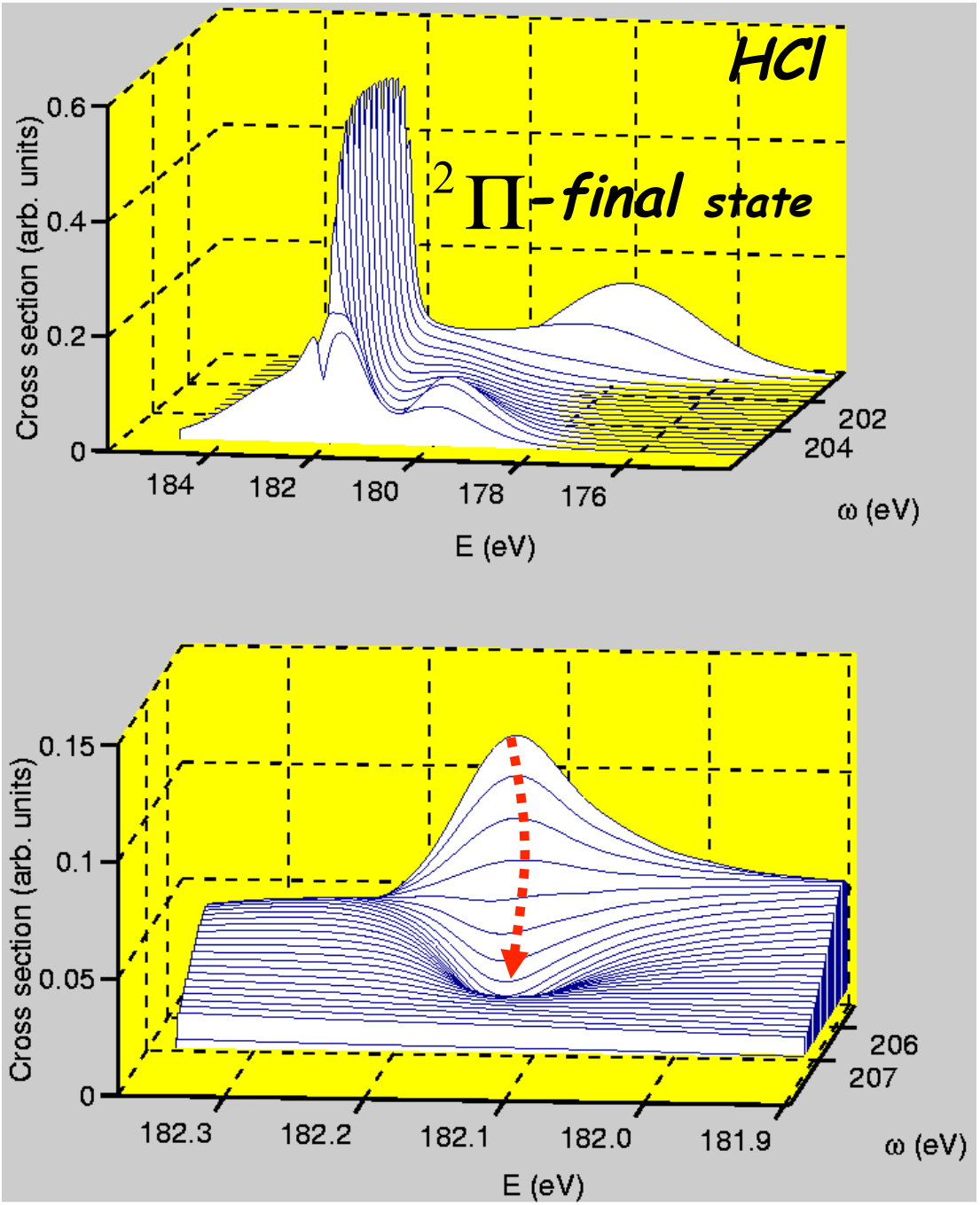
$$F = F_{mol}(\Omega, E) + F_{atom}(\Omega, E)$$

$$F_{atom} = \frac{\eta}{E - E_{atom} + i\Gamma}$$

Continuum-continuum interference between atomic and molecular channels

$$|F|^2 = |F_{mol}|^2 + |F_{atom}|^2 + 2\,\mathrm{Re}\,(F^*_{mol} F_{atom})$$

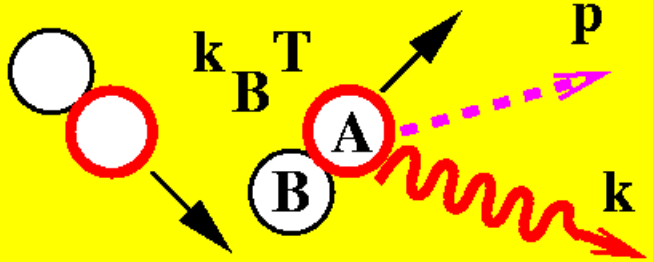
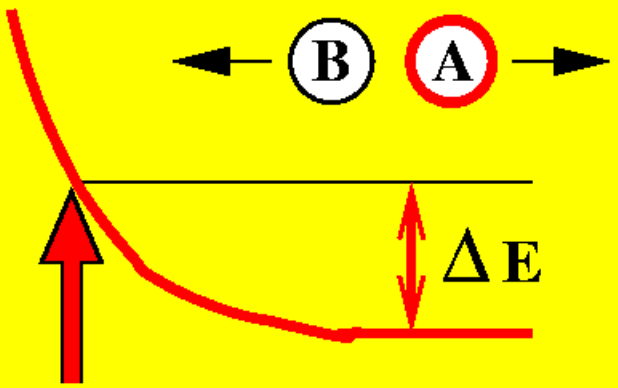
When the molecular background moves across the narrow atomic resonance, the atomic peaks develops into a hole.



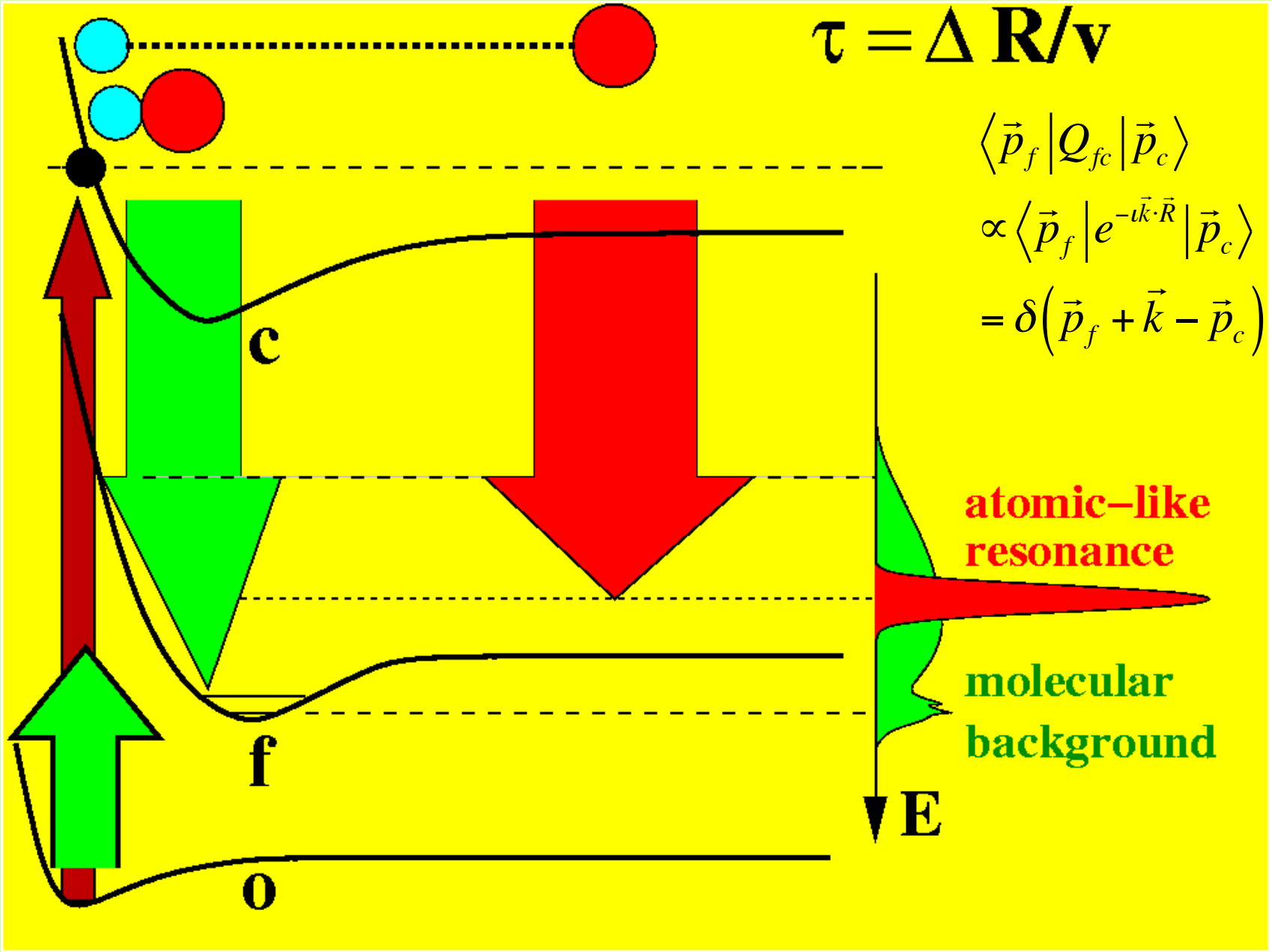
Electronic Doppler effect in resonant Auger scattering

Phys Rev A 57(1998)2511,
Phys Rev Lett 84(2000) 2826

Classification of Doppler effects

	Photon Doppler effect	Electron Doppler effect
thermal motion 	Doppler broadening $\bar{v} = \sqrt{\frac{2 k_B T}{M}}$ $k\bar{v} \sim 10^{-3}$ eV	$k_B T = 0.03$ eV $p\bar{v} \sim 10^{-2}$ eV
dissociation: atomic–like resonance 	$v_A = \frac{\sqrt{2\mu\,\Delta E}}{m_A}$ $kv_A \sim$ 0.01–0.05 eV	$\Delta E \sim$ 1–10 eV $pv_A \sim$ 0.1–0.5 eV

The reason for the Doppler shift is the momentum exchange between molecule and Auger electron



$$\sigma(E,\omega) = \int d\hat{\vec{R}} \frac{\left(\vec{e}\cdot\vec{d}_{oc}\right)^2}{\left(E-\omega_{fc}-\vec{k}\cdot\vec{v}\right)^2+\Gamma^2}$$

Absorption probability $\left(\vec{e}\cdot\vec{d}_{oc}\right)^2$ takes maximum when $\vec{e}\parallel\vec{d}_{oc}$.

Thus, in spite of molecules are randomly oriented in ground state, they are alligned preverentially along $\vec{d}_{oc}$

$1s \Rightarrow \sigma^*$

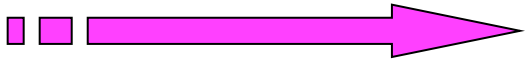
$\vec{d}_{oc}\parallel\vec{R}, \qquad \vec{v}\parallel\vec{R}$

We controle in experiment the directions of $\vec{e}$ and $\vec{k}$:

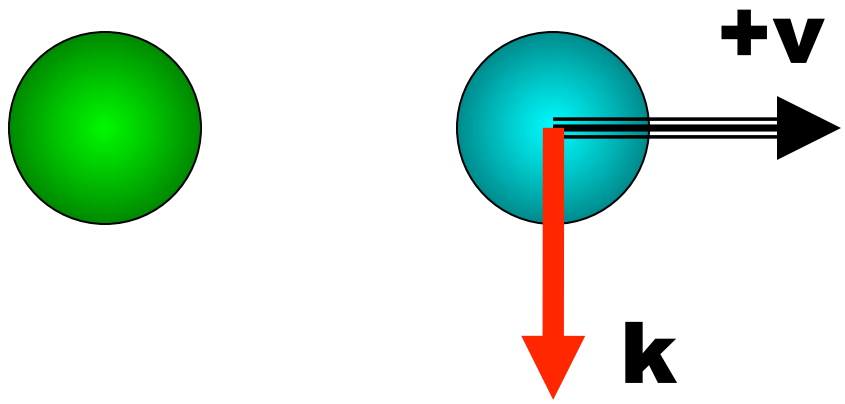
$\vec{e}\parallel\vec{k}$ or $\vec{e}\perp\vec{k}$

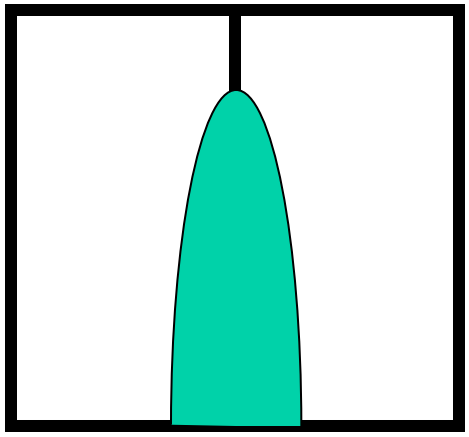
Doppler splitting of atomic line: σ-excitation

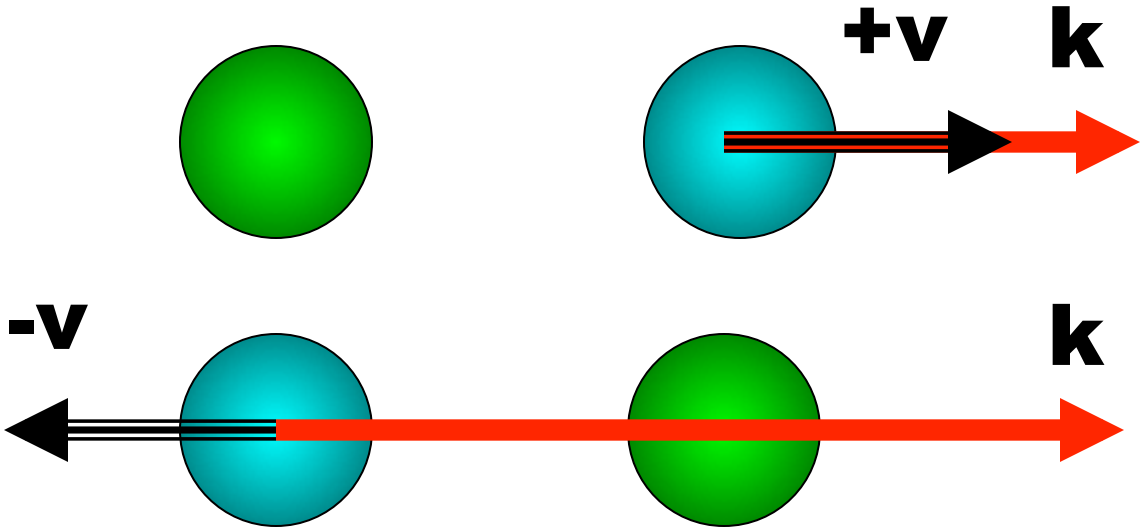
Polarization vector aligns core-excited molecules:

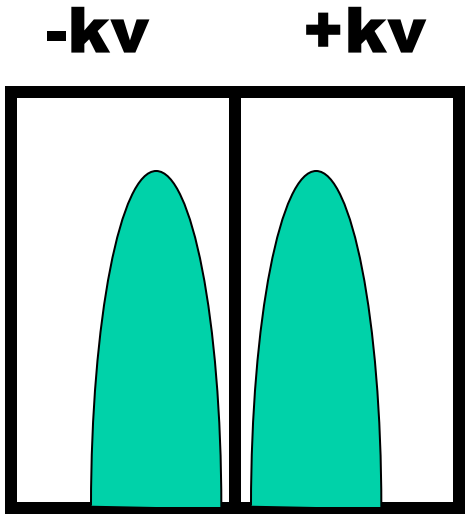


$$\vec{k} \bullet \vec{v} = 0$$







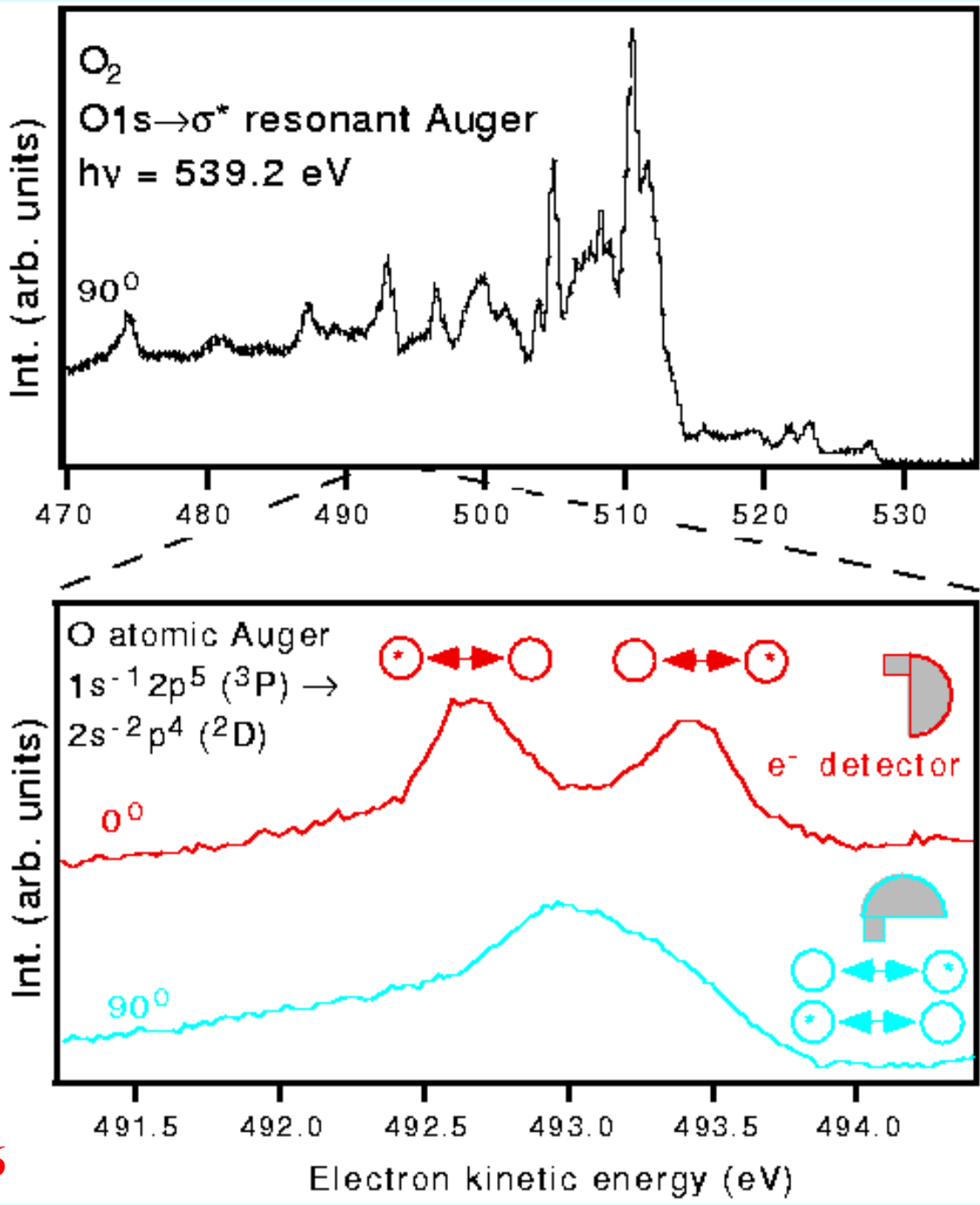


The Auger-Doppler effect in Oxygen

Photoexcitation near

$$O\ 1s \Rightarrow 3\sigma_u$$

resonance



O.Bjorneholm et al PRL 84 (2000) 2826

Einstein-Bohr recoiling double-slit gedanken experiment performed at the molecular level - complementarity unveiled by decoupling coupled slits

Nature Photonics 9, 120–125 (2015)

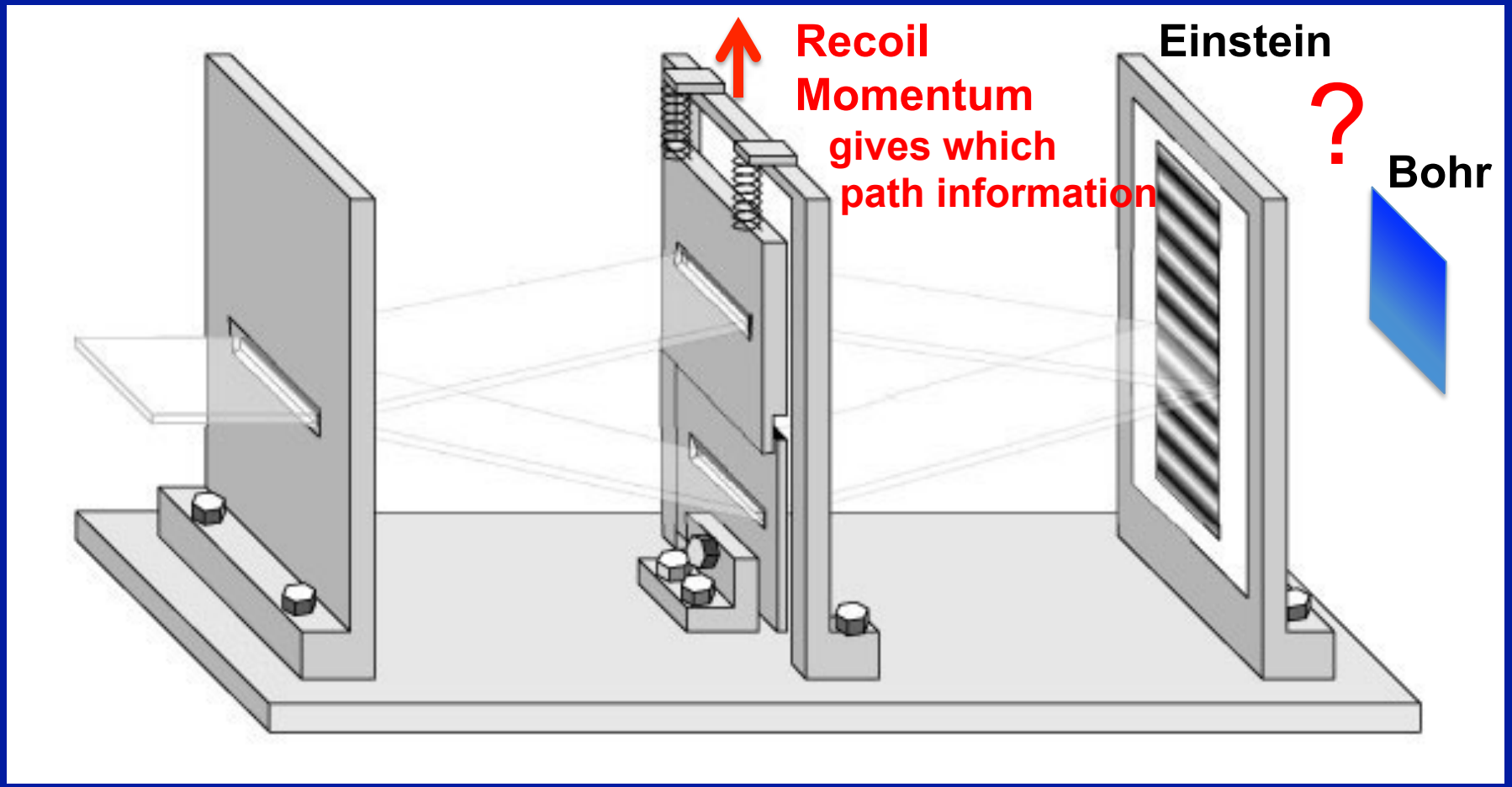
Einstein's :

the measurement of the recoil of slit after the particle passed can not influence the process. Therefore the measurement of the momentum of the wall does not affect the position of the well and hence the YDSE pattern is preserved !

Bohr's response:

Due to the uncertainty principle the measurement of the recoil momentum erases YDSE pattern

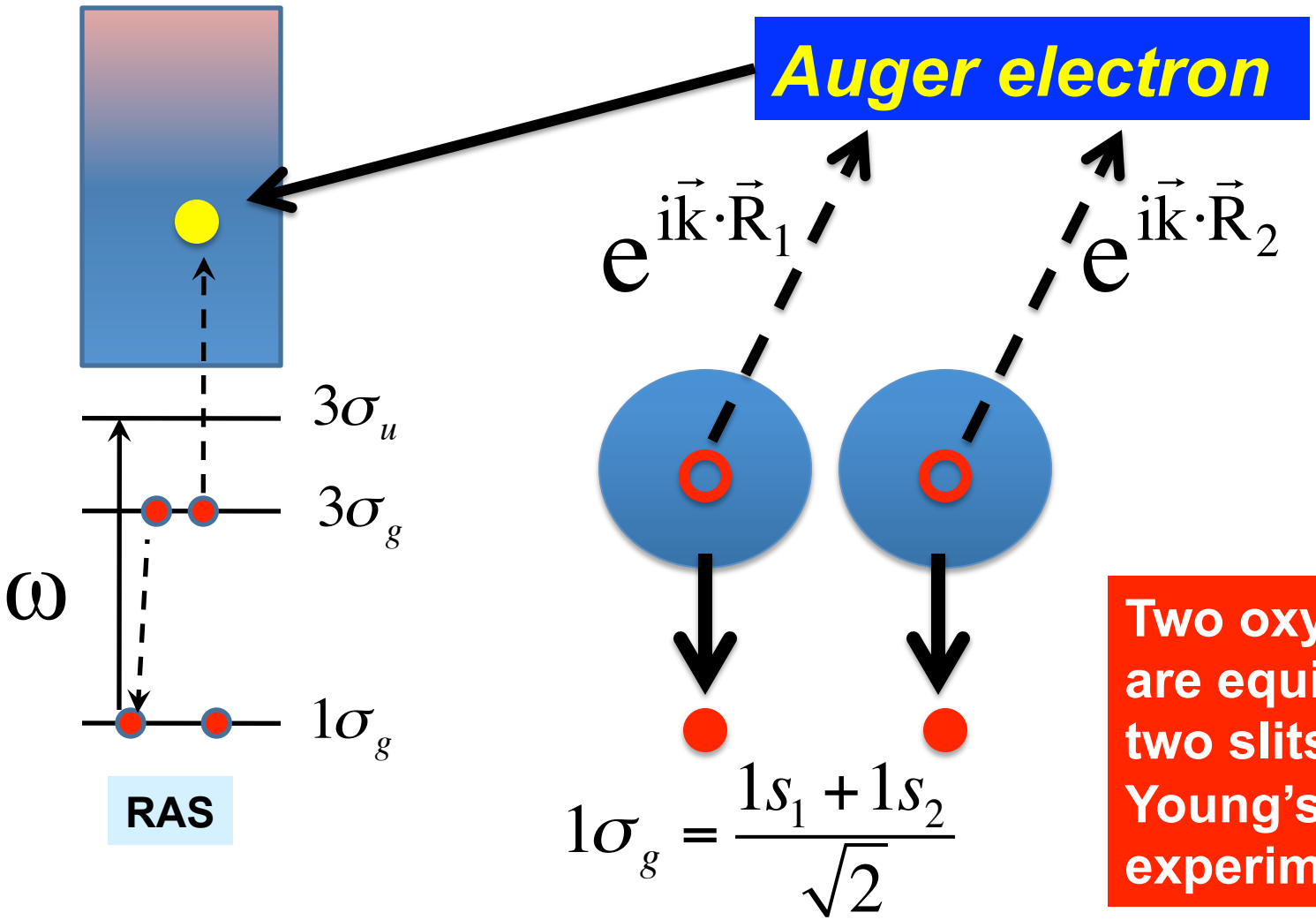
Recoiling slit, adapted from Bohr



Resonant Auger scattering

O_2

$$|\text{final state}\rangle = (OO)^+ = O^+O \pm OO^+$$

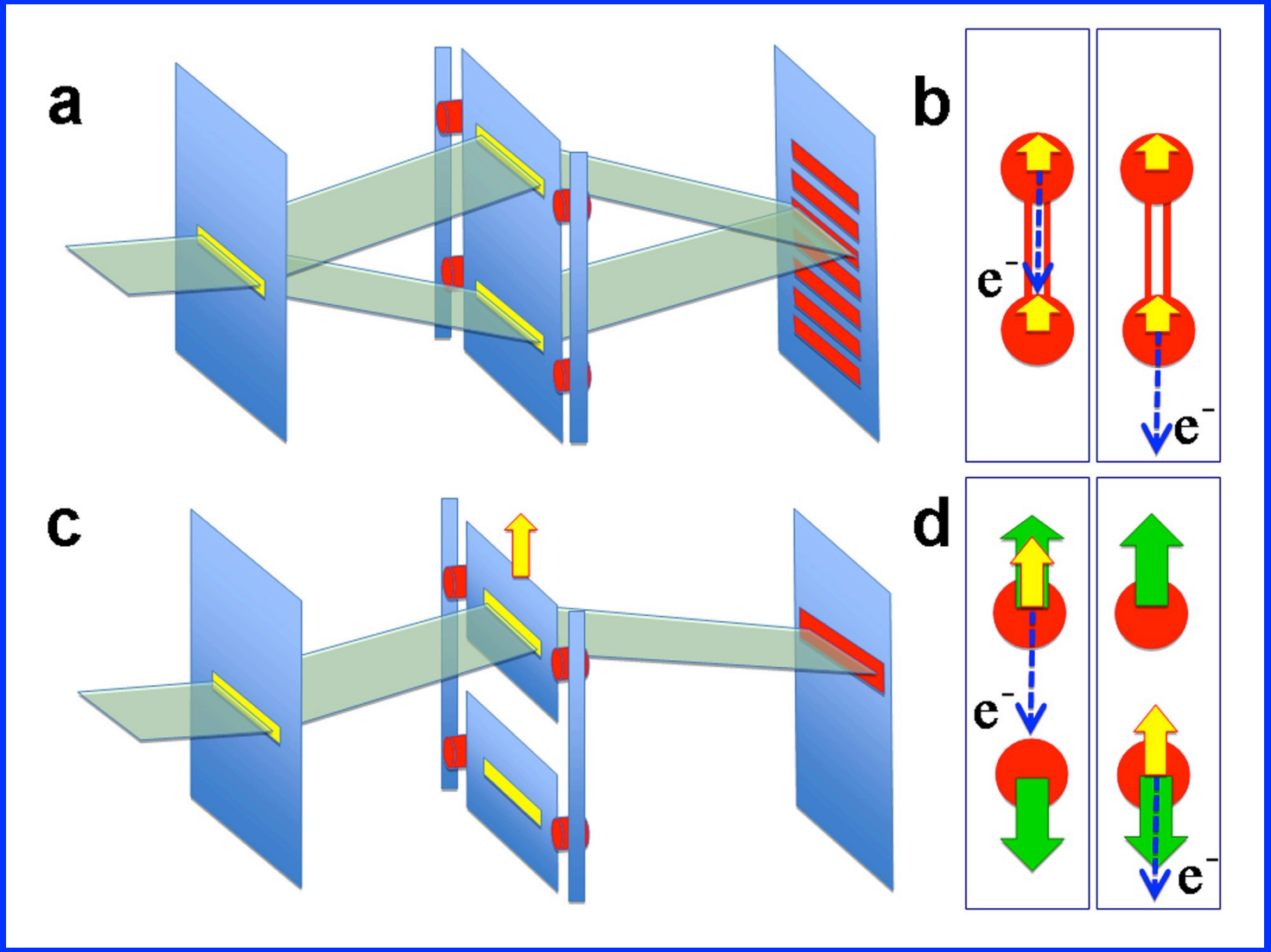


Two oxygen atoms are equivalent to two slits in Young's Double Slit experiment

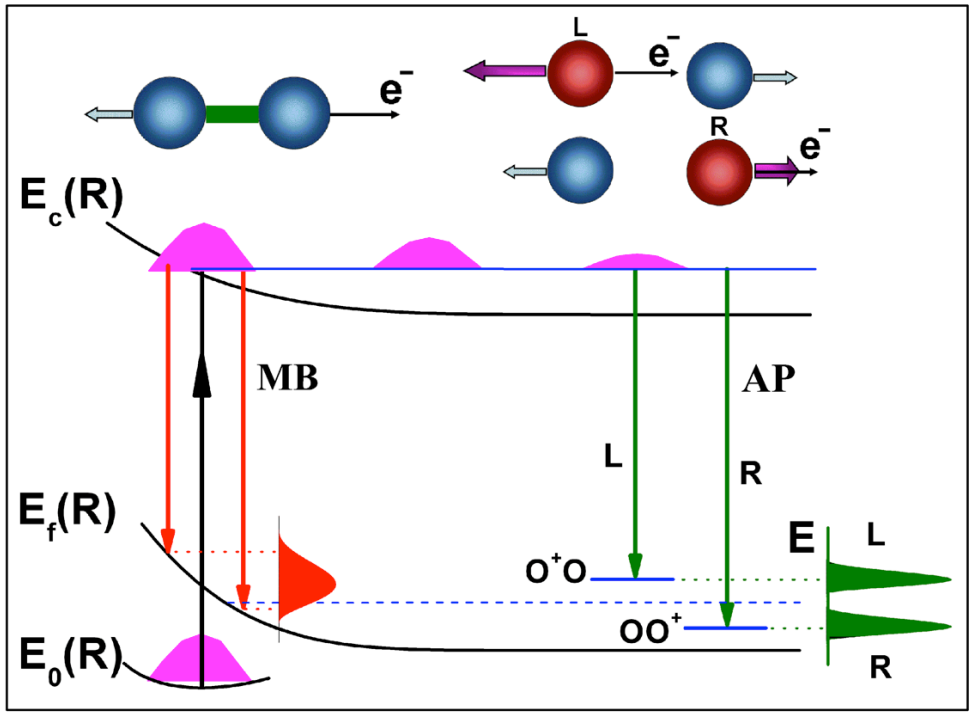
Molecular realization of Einstein-Bohr recoiling slit experiment

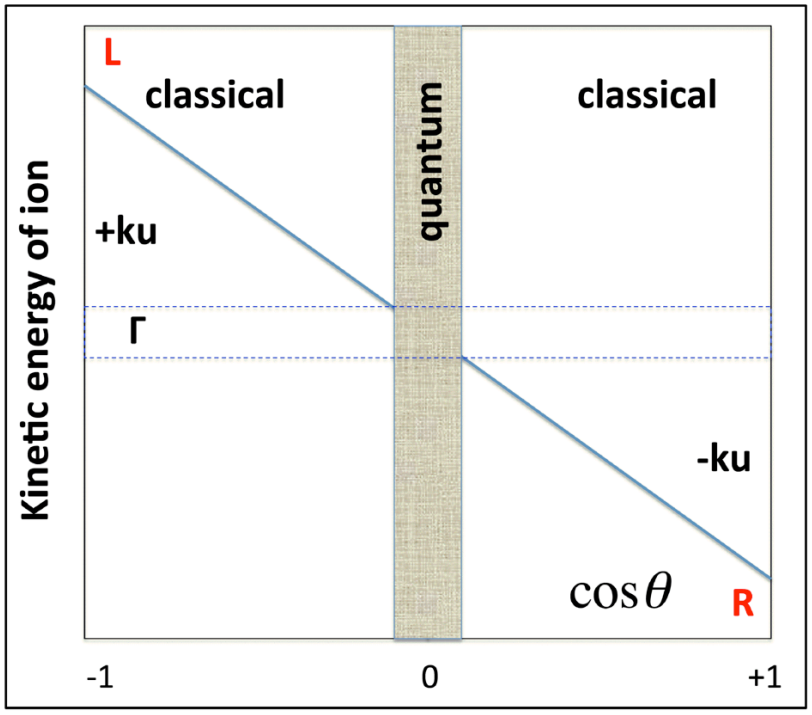
Coupled slits (mol.band)

Uncoupled slits (atom. peak)



Momentum exchange near the equilibrium differs qualitatively from one in the dissociation region





$$\text{mol}: \quad E_{dis}^{OO^+} = E_{dis}^{O^+O}$$

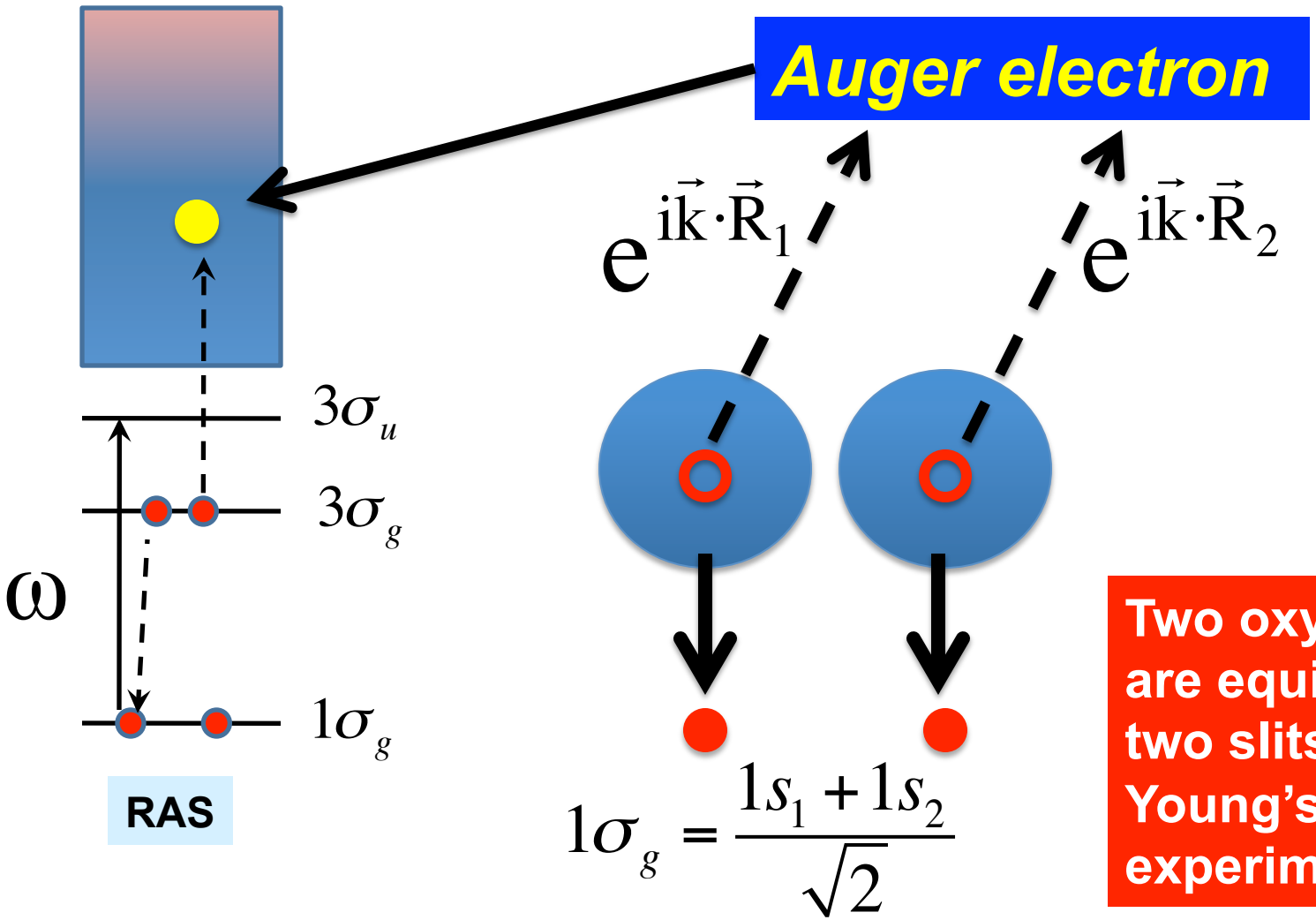
$$\text{atom}: \quad E_{dis}^{OO^+} = \text{const} - ku\cos\theta, \quad E_{dis}^{O^+O} = \text{const} + ku\cos\theta$$

Doppler shift of the energy of the "source" of the electron wave

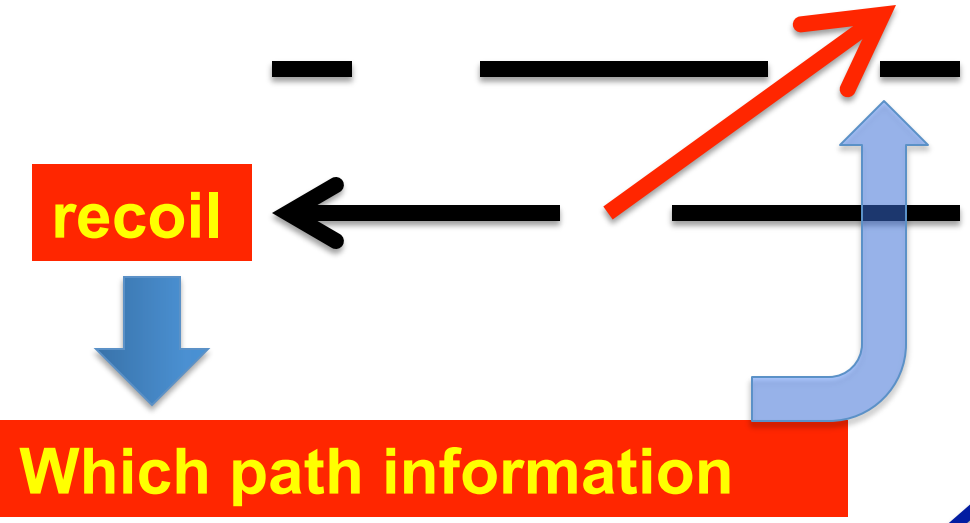
Resonant Auger scattering

O_2

$$|\text{final state}\rangle = (OO)^+ = O^+O \pm OO^+$$



Two oxygen atoms are equivalent to two slits in Young's Double Slit experiment



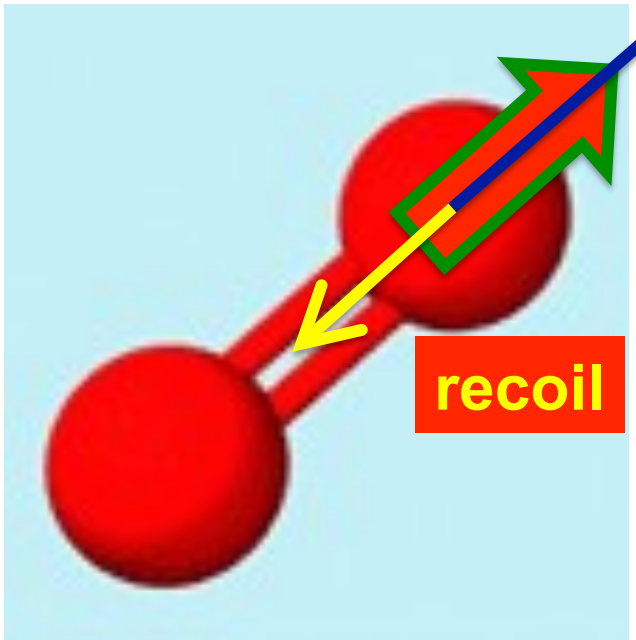
Einstein's recoiling slit

Which path information

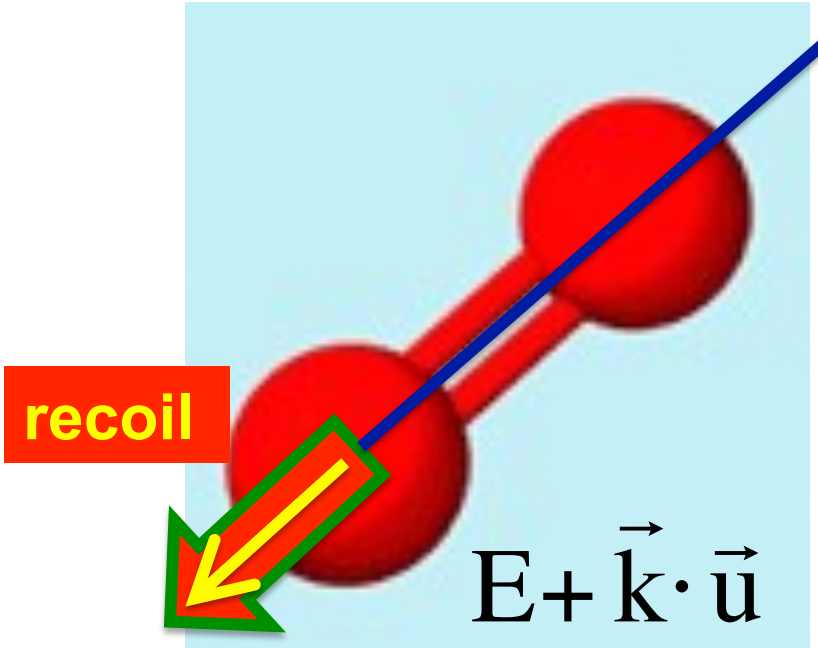
Site specific Doppler shift gives which path information about ionization site/slit

e^-

$E - \vec{k} \cdot \vec{u}$

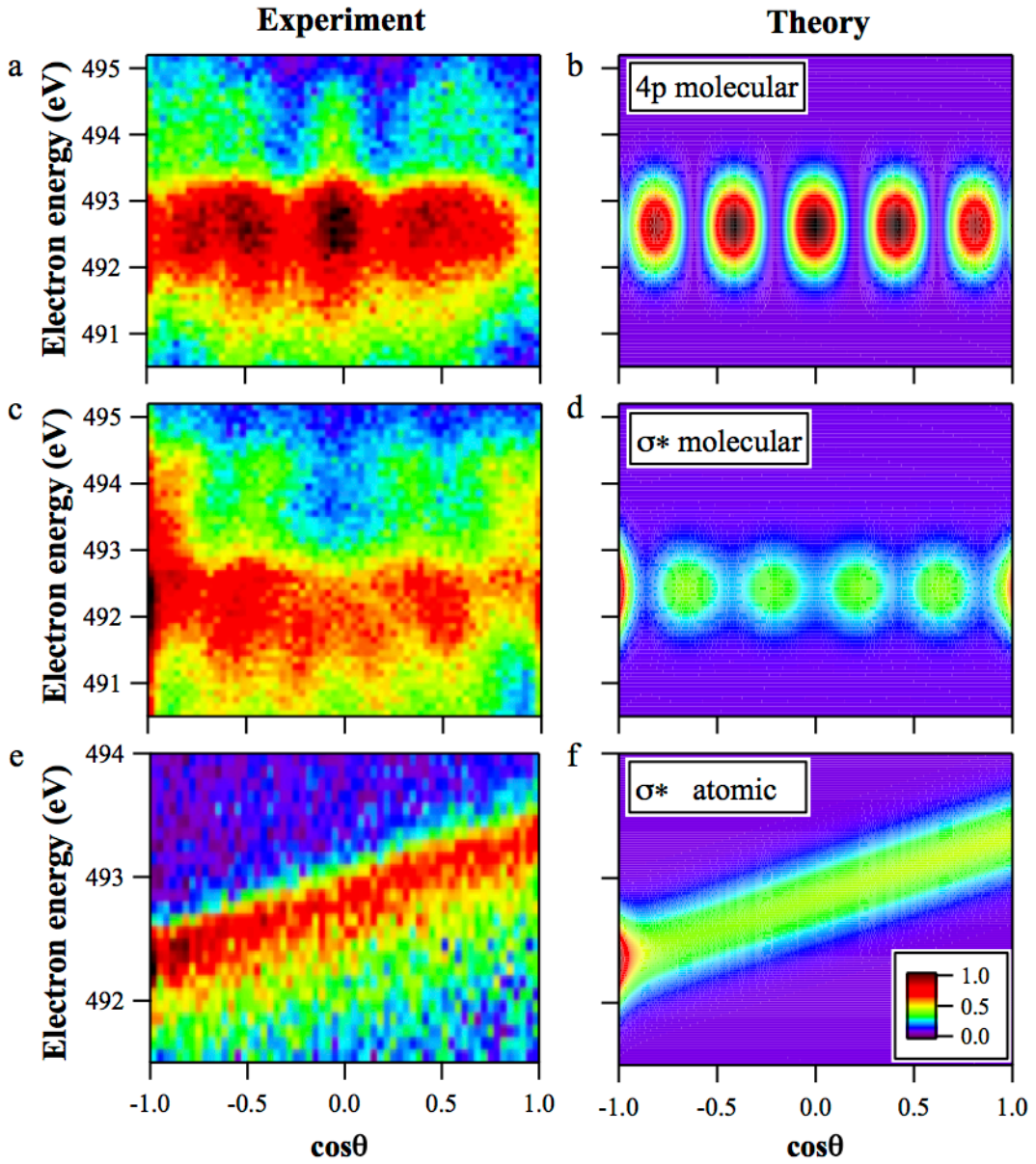


e^-

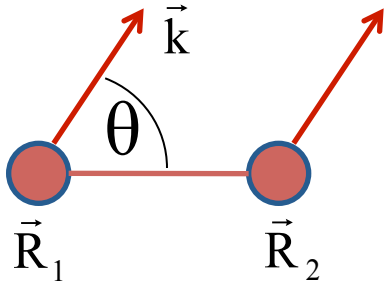


$E + \vec{k} \cdot \vec{u}$

Young's double slit pattern

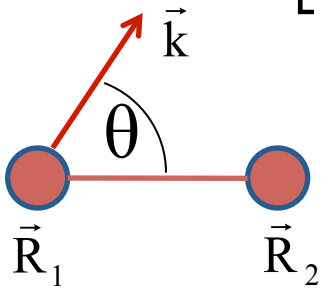


Molecular band: symmetry is preserve



$$\sigma_{mol} = \sigma_0 \left[1 \pm \cos\left(kR\cos\theta\right)\right]$$

$$\sigma_{at} = \sigma_0 \left[1 \pm \cos\left(kR\cos\theta\right)\right]$$

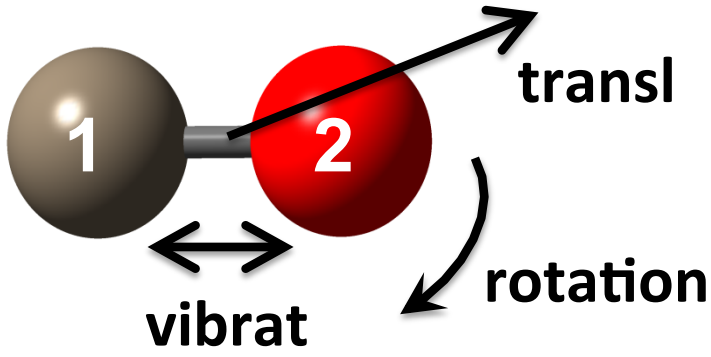


Atomic peak: symmetry is broke

Rotational dynamics

Rotational recoil and Doppler effects

Phys. Rev. A 82, 052506 (2010)
Phys. Rev. Lett. 2011, 106, 193009.
Nature Communications, 8, 3816 (2014)
J. Phys. Chem. Lett. 6, 1568−1572 (2015)



Analogy	
tran	rot
M	I
V	w
P	J

$$E = E_{tr} + E_{vib} + E_{rot}$$

$$E_{tr} = \frac{MV^2}{2} = \frac{P^2}{2M}, \quad E_{vib} = \frac{\mu \dot{x}^2}{2} + \frac{\kappa x^2}{2} \Rightarrow \omega_{vib}\left(v + \frac{1}{2}\right)$$

$$M = m_1 + m_2, \quad \mu = \frac{m_1 m_2}{M}, \quad R = R_0 + x, \quad v = 0,1,2,\ldots$$

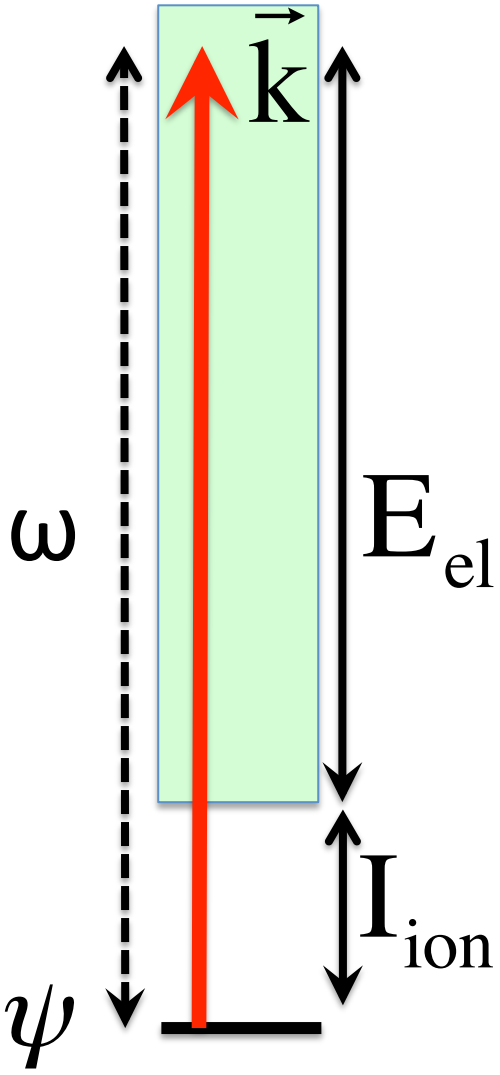
$$E_{rot} = \frac{Iw^2}{2} = BJ^2 \quad \Rightarrow \quad E_J = BJ(J+1), \quad J = 0,1,2,\ldots$$

$$B = \frac{1}{2I} = \text{rotational constant}, \quad I = \mu R^2 = \text{mom. of inertia}$$

$$\text{Classical mechanics}: w = \dot{\varphi} = \text{angular velocity}$$

$$J = Iw = \text{classical angular momentum}$$

Recoil and translational Doppler effect in X-ray photoionization



$$\vec{k}_{ph} + \vec{p} = \vec{p}' + \vec{k}, \quad \vec{p}' = \vec{p} - \vec{k}$$

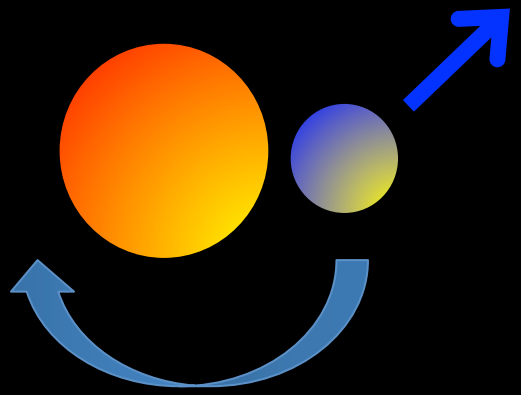
$$\omega + E_0 + \frac{p^2}{2M} = E^{ion} + \frac{p'^2}{2M} + E_{el}$$

$$E_{el} = \omega - I_{ion} + \vec{v}\cdot\vec{k} - \Delta_{rec},$$

$$\Delta_{rec} = \frac{k^2}{2M} = E_{el}\frac{1}{M}, \qquad E_{el} = \frac{k^2}{2}$$

Rotational Doppler effect in X-ray photoelectron spectroscopy

SOLEIL (Paris) – Stockholm-China collaboration

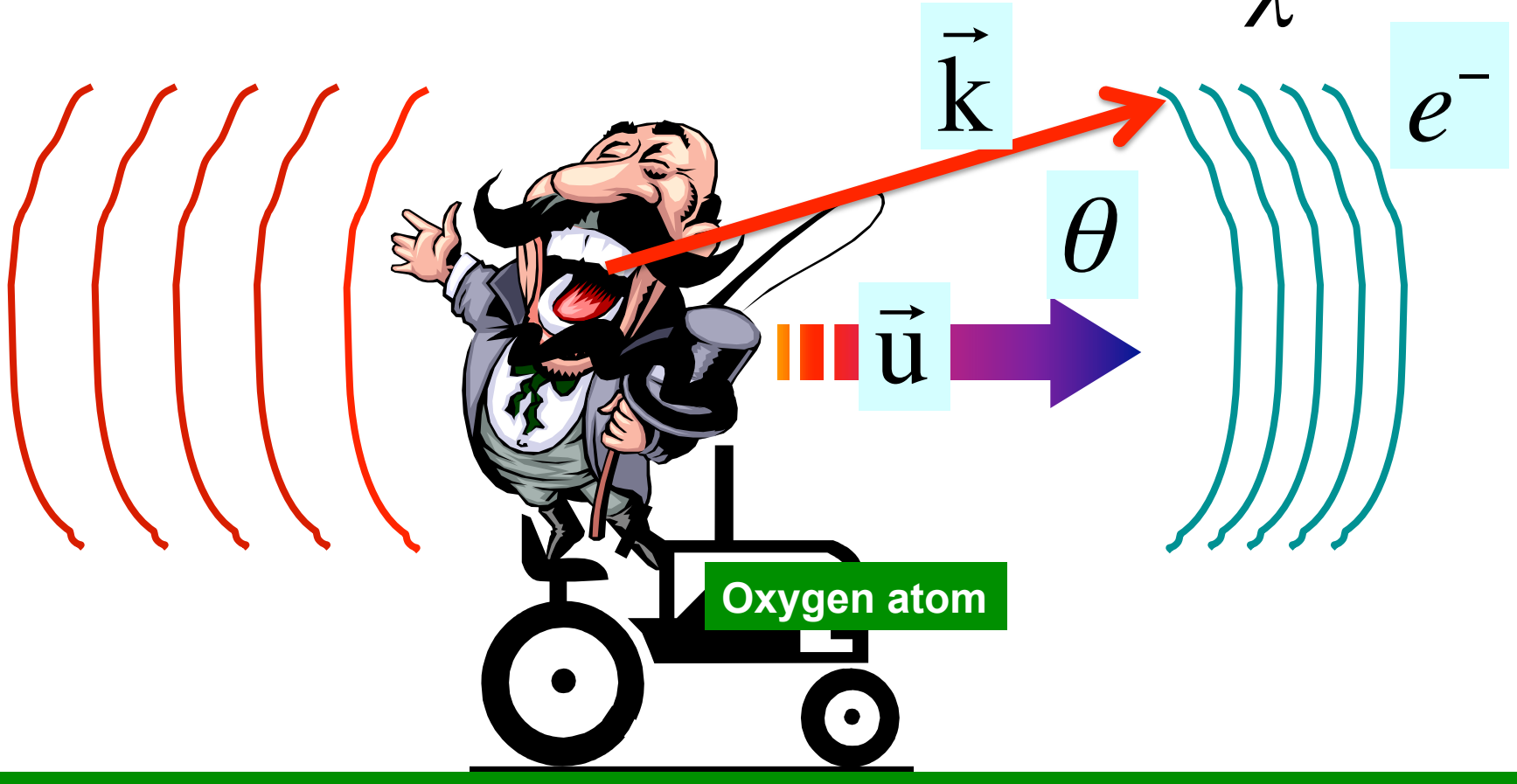


Prediction: Y.-P. Sun, C.-K- Wang, and F. Gel'mukhanov, Phys. Rev. A 82, 052506 (2010)

Experimental proof: T.D. Thomas et al Phys. Rev. Lett.106, 193009 (2011);

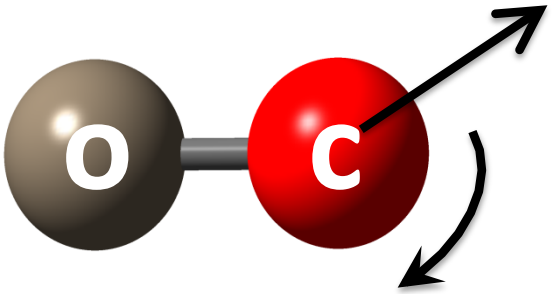
Translational Doppler shift: D=ku

$$E \Rightarrow E - \vec{k}\cdot\vec{u} = E - ku\cos\theta; \qquad k = \frac{2\pi}{\lambda}$$

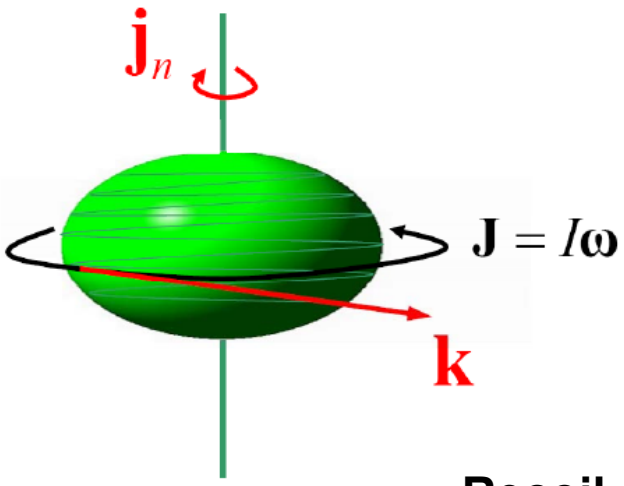


The translational Doppler shift:

$$D_{tr} = \mathbf{k} \cdot \mathbf{v}$$



The close analogy between translational and rotational degree of freedom:



Translation : m, $\mathbf{v}$, $\mathbf{k}$

Rotation : I, $\boldsymbol{\omega}$, $\mathbf{j}$

Recoil angular momentum: $\vec{\mathbf{j}} = \alpha\left[\vec{R} \times \vec{k}\right],\ \alpha = \dfrac{m_O}{M}$

Translational shift

$$D_{tr} = \mathbf{k} \cdot \mathbf{v}$$

Rotational shift

$$D_{rot} = \mathbf{j} \cdot \boldsymbol{\omega}$$

Shift and broadening of the resonance

$$\mathrm{E_{el}} = \omega - \mathrm{I_{ion}} + D_{tr} + D_{rot} - \Delta_{\mathrm{tr}}^{\mathrm{rec}} - \Delta_{\mathrm{rot}}^{\mathrm{rec}},$$

$$D_{tr} = \vec{\mathrm{v}} \cdot \vec{\mathrm{k}}, \quad D_{tr} = \vec{\mathrm{w}} \cdot \vec{\mathrm{j}}$$

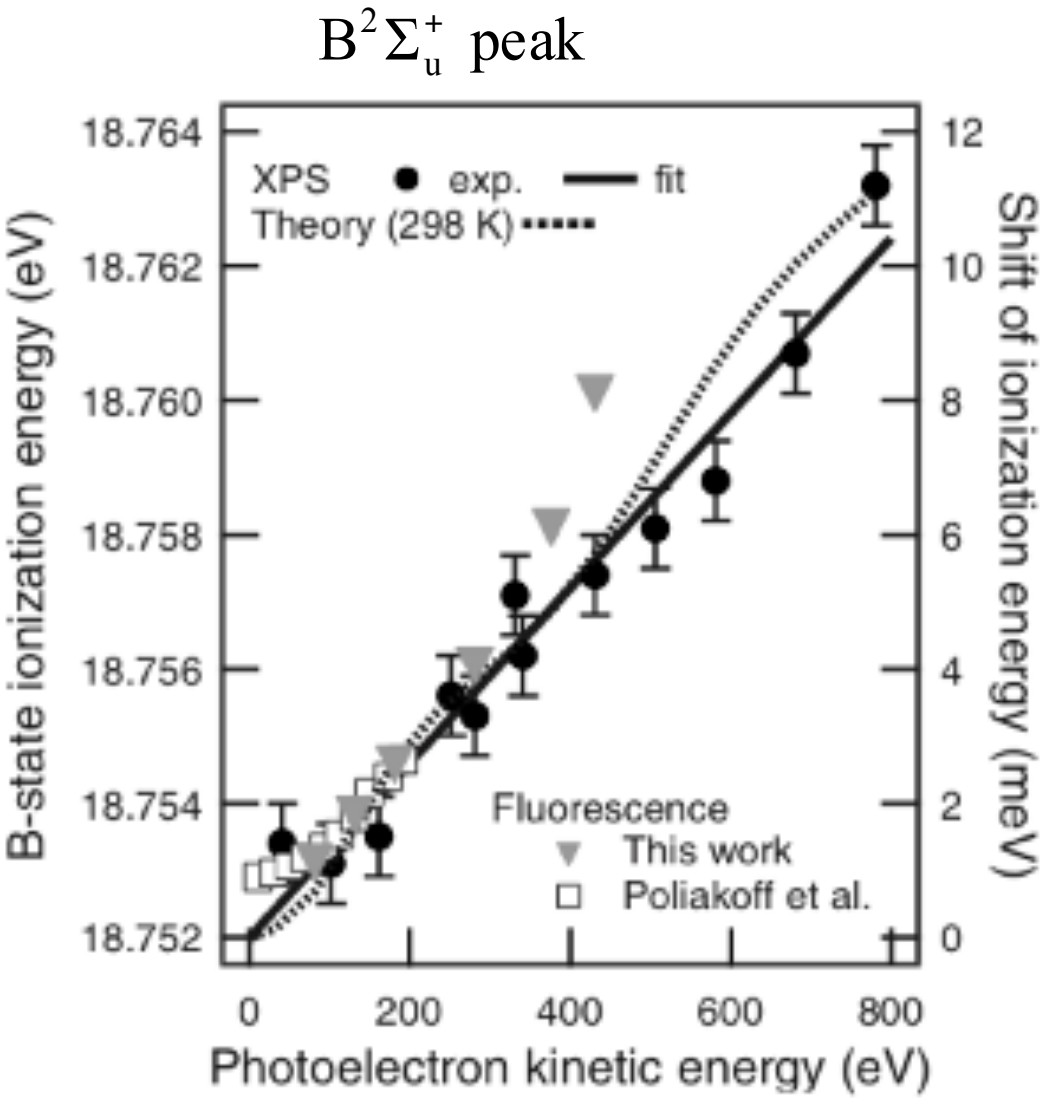
$$\Delta_{\mathrm{tr}}^{\mathrm{rec}} = \frac{\mathrm{k}^2 m_e}{2\mathrm{M}} = \mathrm{E_{el}} \frac{\mathrm{m_{el}}}{\mathrm{M}}, \quad \Delta_{\mathrm{rot}}^{\mathrm{rec}} = \frac{j^2}{2I} \approx \mathrm{E_{el}} \frac{\mathrm{m_{el}}}{\mathrm{M}}$$

Recoil effect $\Rightarrow$ shift of resonance

Doppler effects $\Rightarrow$ broadening of resonance

$$\langle D_{tr} \rangle = \langle D_{rot} \rangle = 0; \qquad \langle D_{tr}^2 \rangle \neq 0, \langle D_{rot}^2 \rangle \neq 0$$

Recoil-induced shift of x-ray photoelectron line



$$\left\langle \vec{v} \cdot \vec{k} \right\rangle = 0$$

Doppler shift gives broad.

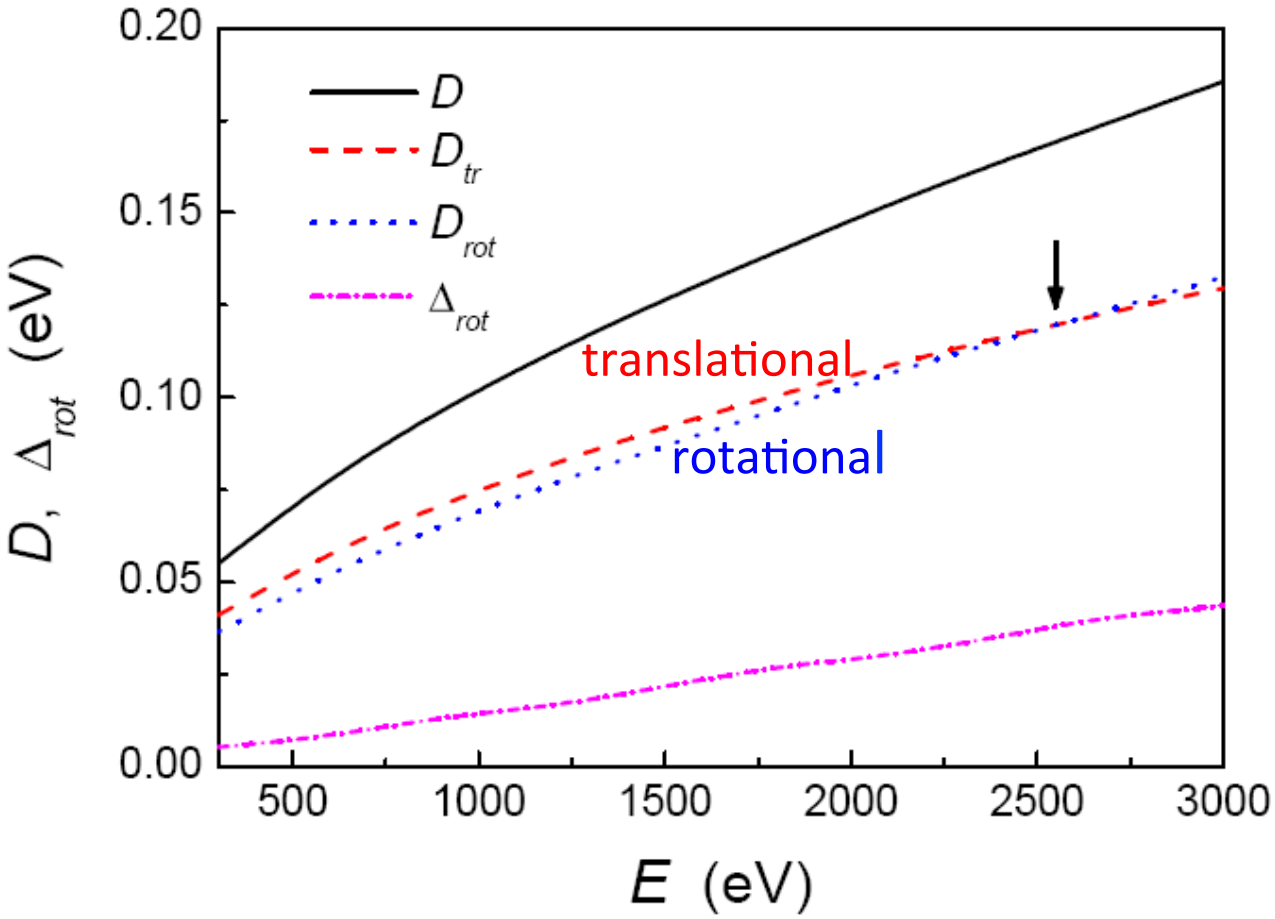
$$E_{el} = \omega - I_{ion} - E_{rec},$$

N_2

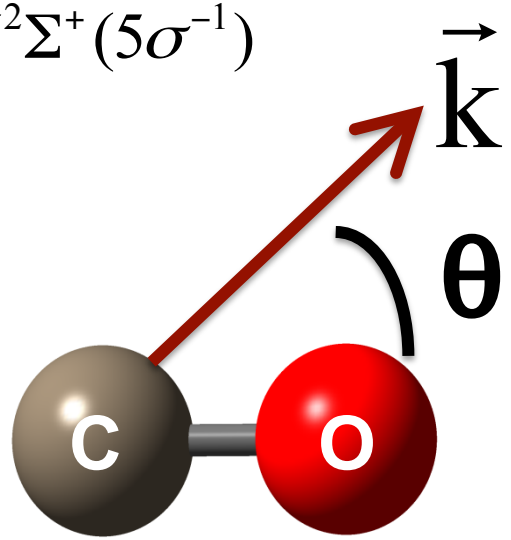
T.D. Thomas et al
Phys. Rev. A 79, 022506 (2009)

Rotational Doppler shift has the same order of magnitude as the translational Doppler shift: CO

Rotational Doppler shift >> translational Doppler shift: HCl



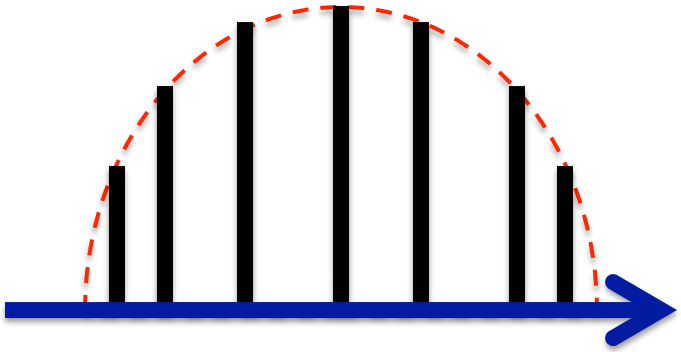
$X^2\Sigma^+(5\sigma^{-1})$



$$D_{rot}^{(1)}(\theta) = D_{tr}\sqrt{\frac{m_2}{m_1}}\sin\theta$$

Quantum versus classical theory of rotational excitation

Quantum



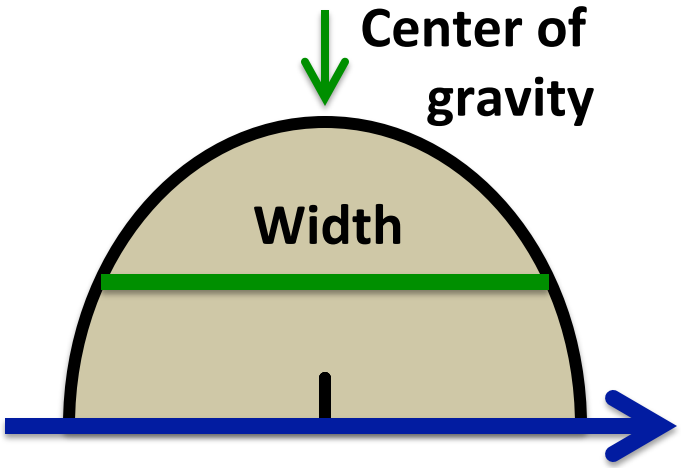
Photon's spin

Recoil angular momentum from electron

$$\langle J_0 M_0 | \left(\vec{e}\cdot\vec{d}\right) e^{i\alpha\vec{k}\bullet\vec{R}} | JM \rangle$$

$$E_J = BJ(J+1)$$

Classical: J>>1



$$\vec{j} = \alpha \vec{R} \times \vec{k}$$

Angular recoil shift

$$= \Delta = \frac{j^2}{2I}$$

Rotational Doppler shift

$$= D = \vec{j} \bullet \vec{\omega}$$

Translational Doppler shift

$$D_{tr} = \mathbf{k} \cdot \mathbf{v}$$

Rotational Doppler shift

$$D_{rot} = \mathbf{j} \cdot \boldsymbol{\omega}$$

Thermal velocity and thermal angular velocity

$$\bar{v} = \sqrt{\frac{2 k_B T}{M}}, \qquad \bar{\omega} = \sqrt{\frac{2 k_B T}{I}}$$

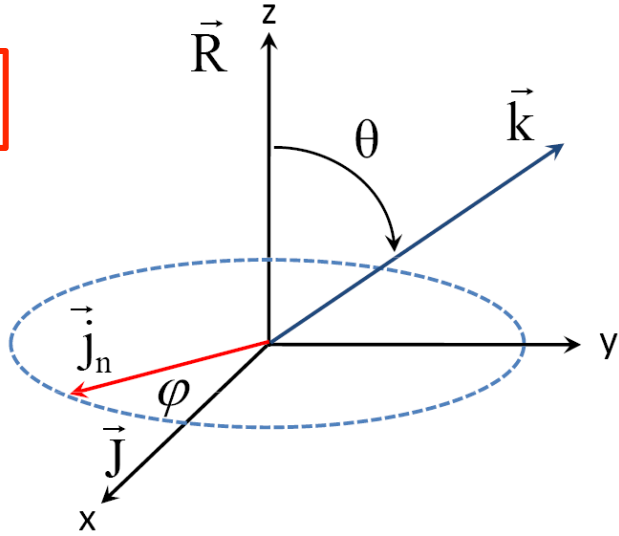
Valence ionization: $\Gamma << D$

Classical limit:

$$\sigma_n = \sigma_n^{(ph)} \int_0^{\pi} d\theta \frac{\sin\theta}{D_n(\theta)} \exp\left(-\frac{\left[\Delta E + \Delta_n(\theta)\right]^2}{D_n^2(\theta)} \right) \left(\vec{e}\cdot\vec{d}\right)^2$$

photon

electron



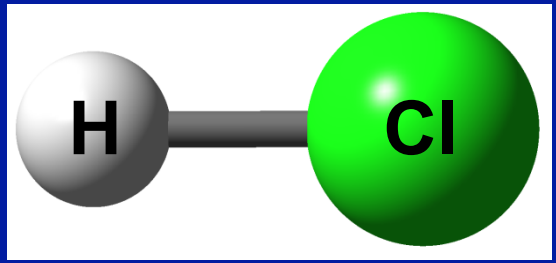
Recoil shift: $\Delta_n(\theta) = \Delta_{tr} + \Delta_{rot}^{(n)}(\theta), \quad \Delta_{tr} = \frac{k^2}{2M}, \quad \Delta_{rot}^{(n)}(\theta) = \frac{j_n^2}{2I} = \frac{\alpha_n^2 k^2 R^2}{2I}\sin^2\theta$

Doppler broadening:

$$D_n(\theta) = \sqrt{D_{tr}^2 + D_{rot}^{(n)2}(\theta)}, \quad D_{tr} = k\bar{v}, \quad D_{rot}^{(n)}(\theta) = j_n\bar{\omega} = \alpha_n kR\bar{\omega}\sin\theta$$

Rotational Doppler effect depends on angle and it is sensitive to the ionization site

Site-selective photoemission from delocalized valence shells induced by molecular rotation



Thermal angular velocity !

$$D_n = j_n w, \qquad j_n = \alpha_n k R \sin\theta$$

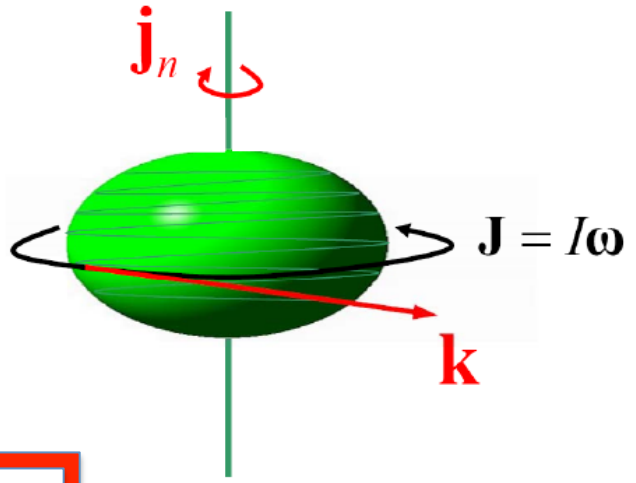
$$\alpha_H = \frac{m_{Cl}}{m_{Cl} + m_H} \approx 1 >> \alpha_{Cl} = \frac{m_H}{m_{Cl} + m_H}$$

(Soleil:PLEADES+Stockholm)
Nature Commun. 5, 3816 (2014)

Rotational Doppler shift depends on ionization site: D= jw

$$\Delta J_{\text{phot}} = \pm 1, 0: \qquad \text{photon spin}\left(\vec{e}\cdot\vec{d}\right)$$

$$\Delta J^{(H)}_{elect} = j = \alpha_H kR\sin\theta \approx 10: \quad \text{electron}\left(e^{i\alpha\vec{k}\cdot\vec{R}}\right)$$



$$5\sigma \approx C_{1s}\,1s^{H} + C_{3p}\,3p^{Cl}_{\sigma} + \ldots$$

Site selectivity :

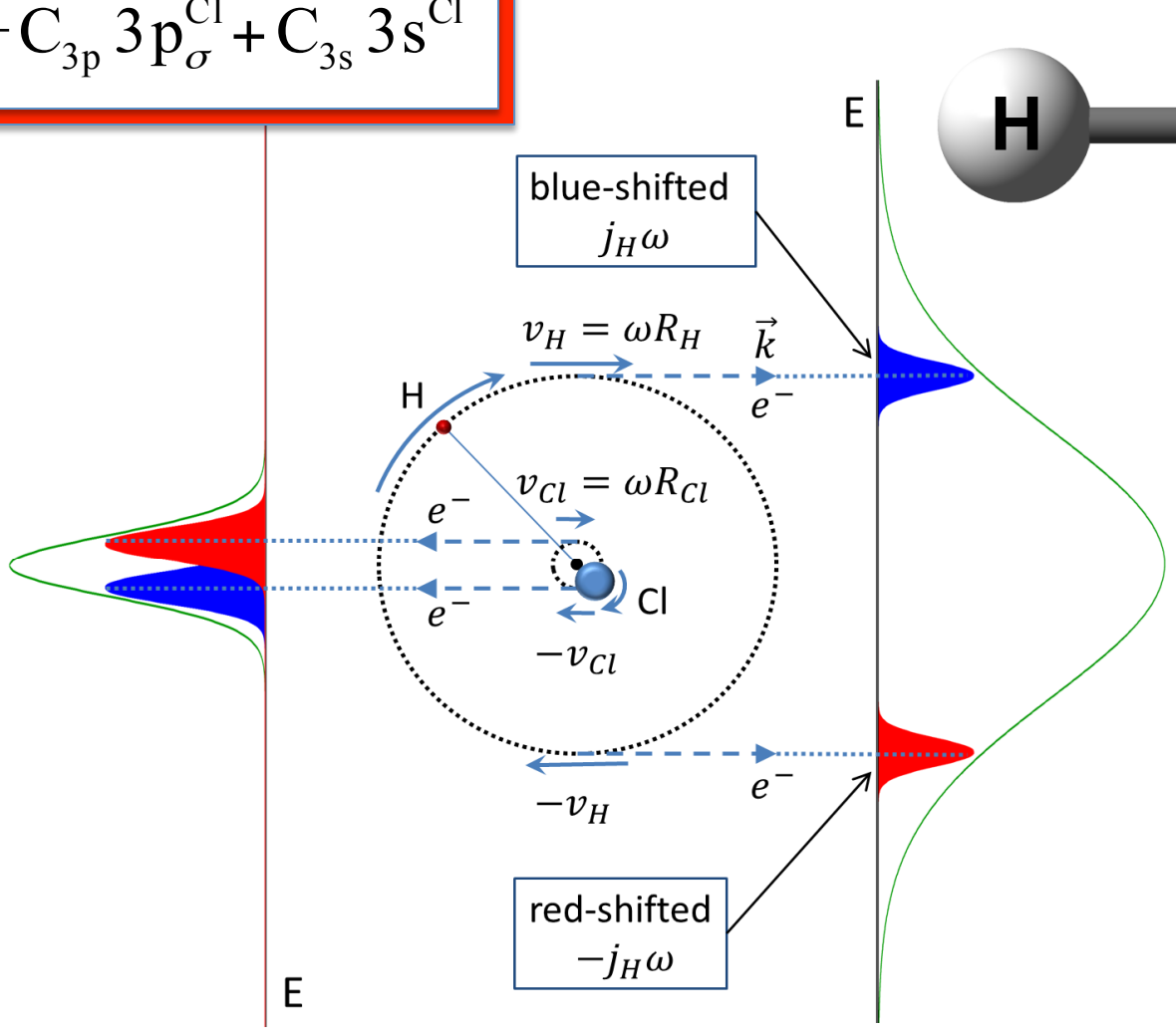
$$\alpha_H = \frac{m_{Cl}}{m_{Cl}+m_H} \approx 1 >> \alpha_{Cl} = \frac{m_H}{m_{Cl}+m_H}$$

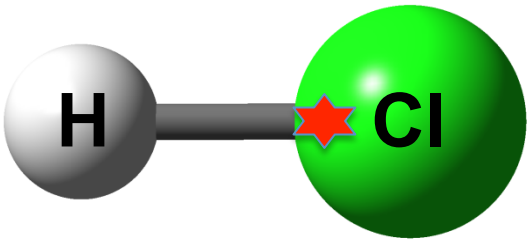
Site selective valence ionization caused by Rotational Doppler effect

$$5\sigma \approx C_{1s}\,1s^{H} + C_{3p}\,3p_{\sigma}^{Cl} + C_{3s}\,3s^{Cl}$$

HCl

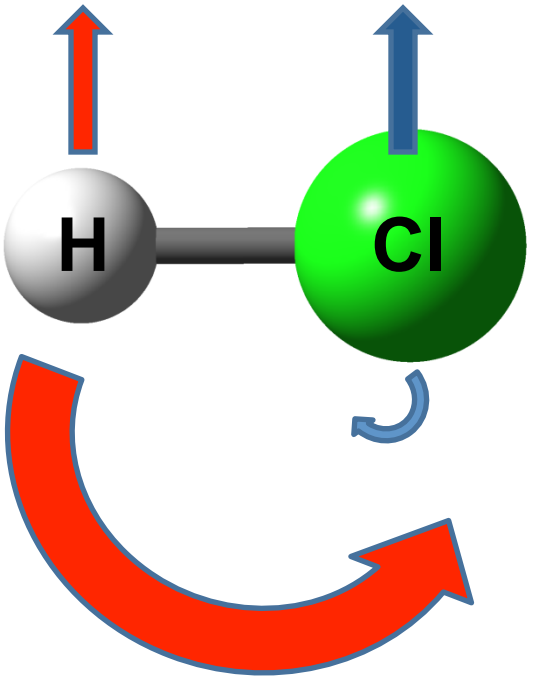
Heavy chlorine



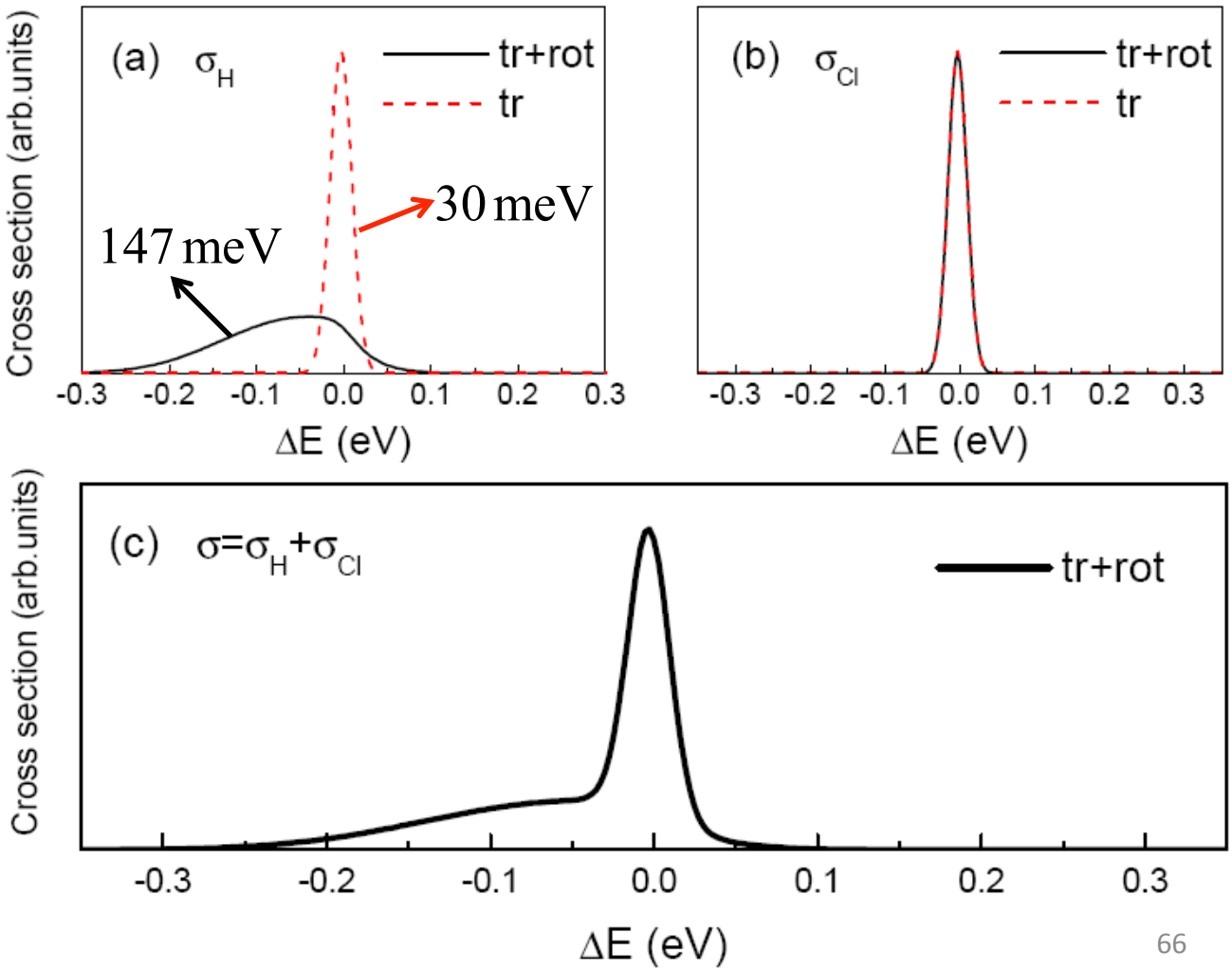


Light hydrogen

Rotational broadening versus molecular orbital (site selectivity: light/heavy atom effect)



$$5\sigma \approx C_{1s}\,1s^{H} + C_{3p}\,3p_{\sigma}^{Cl} + C_{3s}\,3s^{Cl}$$



$E = 200\,eV$

Yu- Ping Sun. Thesis Stockholm, 2011

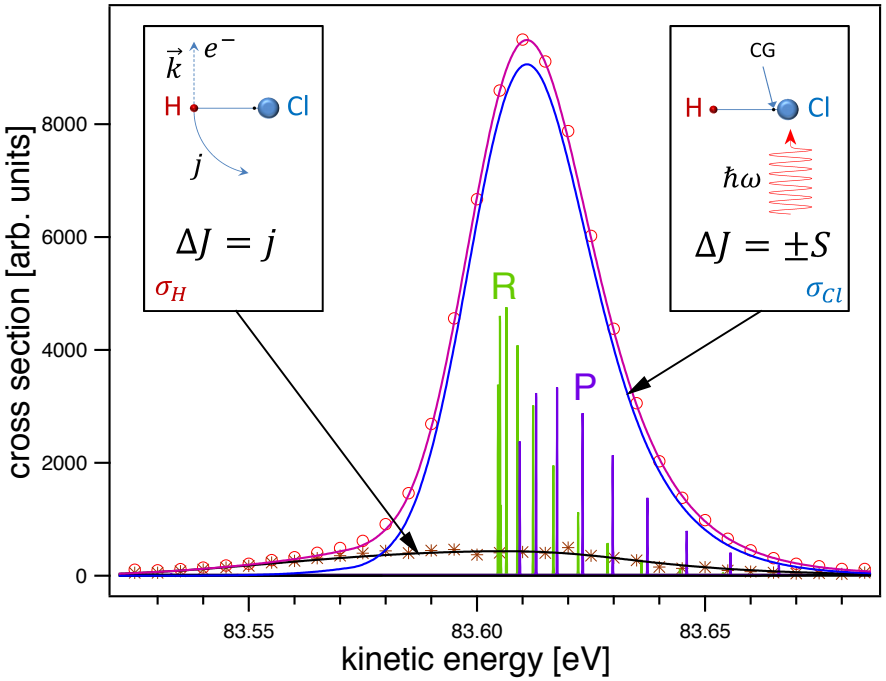
Rotational heating: Photon angular momentum versus angular recoil momentum

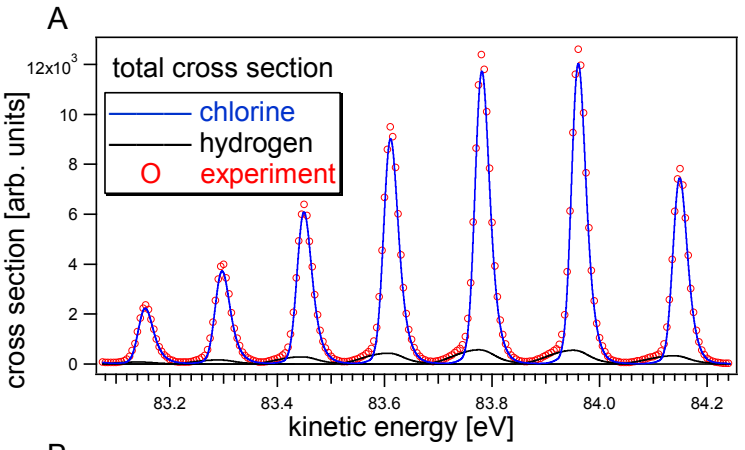
FWHM=88 meV, and 83 meV on the way from v = 0 to v = 6.

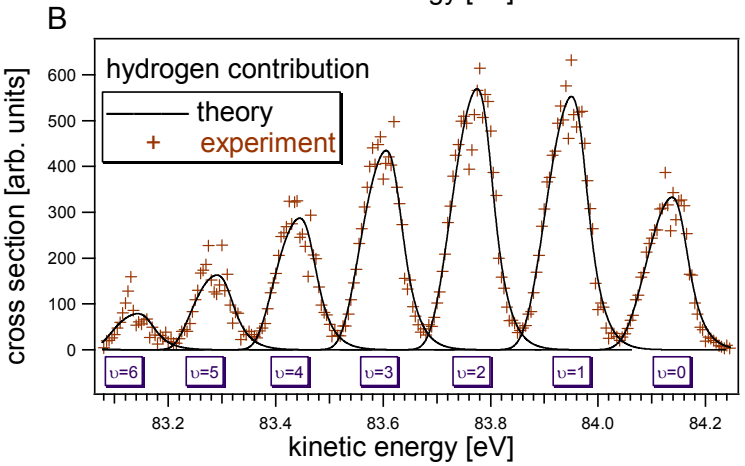
$$\sigma_n = \sigma_n^{(ph)} \int_0^{\pi} d\theta \frac{\sin\theta}{D_n(\theta)} \exp\left(-\frac{\left[\Delta E + \Delta_n(\theta)\right]^2}{D_n^2(\theta)} \right) \left(\vec{e}\cdot\vec{d}\right)^2$$

$$\Delta J_{phot} = \pm 1, 0: \quad \text{photon}$$

$$\Delta J_{electr} = \frac{m_{Cl}}{m_{Cl} + m_H} kR\sin\theta: \quad \text{electron}$$

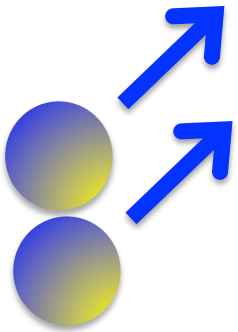






Nature Commun. 5, 3816 (2014)

Rotational Doppler broadening versus molecular orbital, polarization, Young's double slit interference

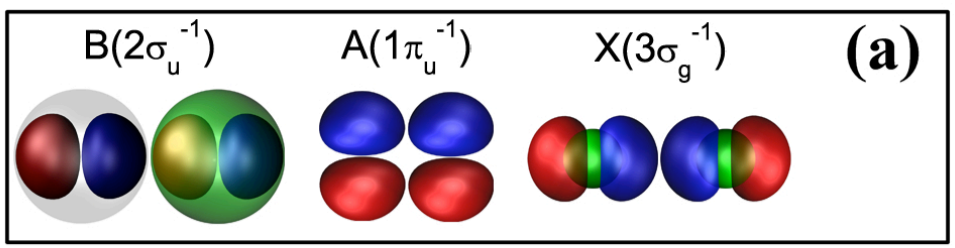


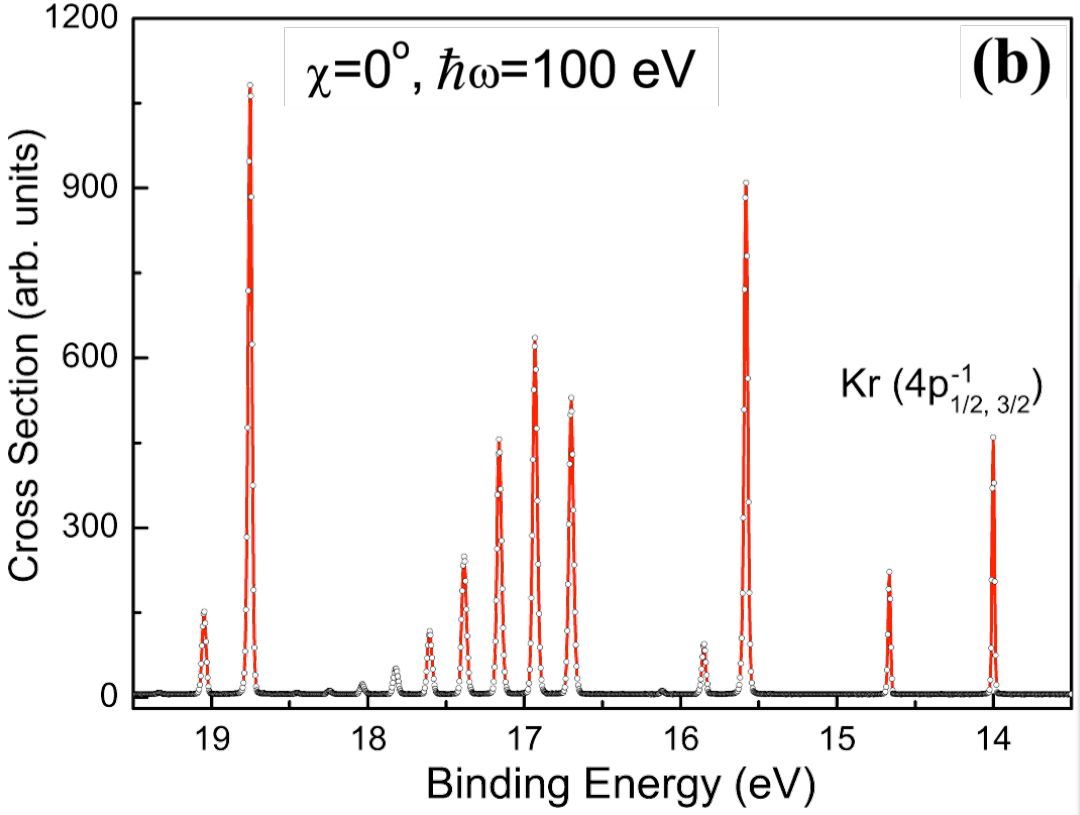
Nitrogen molecule

$$\sigma_n = \sigma_n^{(ph)} \int_0^{\pi} d\theta \frac{\sin\theta}{D_n(\theta)} \exp\left(-\frac{\left[\Delta E + \Delta_n(\theta)\right]^2}{D_n^2(\theta)} \right) \left(\vec{e} \cdot \vec{d} \right)^2$$

(Soleil:PLEADES+Stockholm)

Q. Miao et al J. Phys. Chem. Lett. 6 (2015) 1568





$$\chi = \angle\left(\vec{e},\vec{k}\right)$$

$$\psi_i = a_i\left(2s^{(1)} \pm 2s^{(2)}\right) + b_i\left(2p_z^{(1)} \mp 2p_z^{(1)}\right)$$

Role of polarization

$$\left(\vec{e}\cdot\vec{d}^{\,2s}\right) \propto \left(\vec{e}\cdot\vec{k}\right)$$

$$\left(\vec{e}\cdot\vec{d}^{\,2p_z}\right) \propto \left(\vec{R}\cdot\vec{k}\right)\left(\vec{e}\cdot\vec{k}\right) - \frac{\left(\vec{e}\cdot\vec{R}\right)}{3}$$

$$\vec{R} \Updownarrow \vec{e}$$

$$\sigma_n = \sigma_n^{(ph)} \int_0^{\pi} d\theta \frac{\sin\theta}{D_n(\theta)} \exp\left(-\frac{\left[\Delta E + \Delta_n(\theta)\right]^2}{D_n^2(\theta)}\right)\left(\vec{e}\cdot\vec{d}\right)^2$$

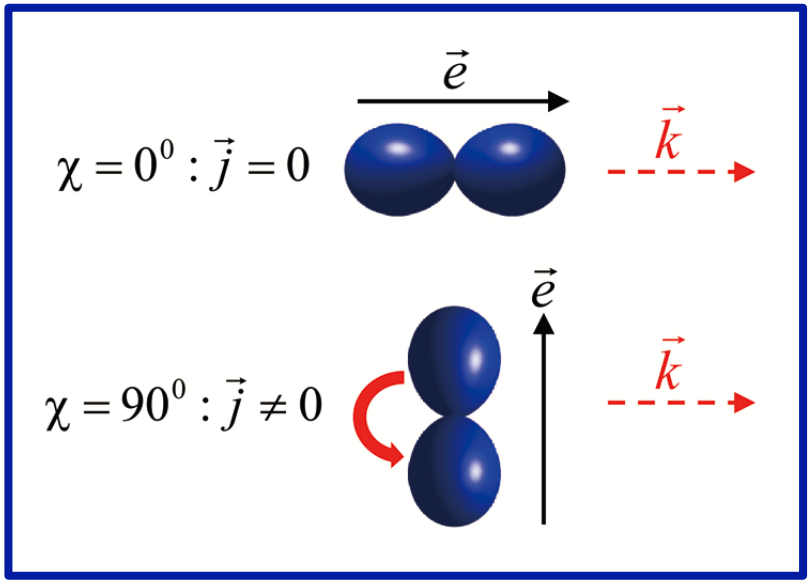
Rotational Doppler broadening (exp/theor)

$$\chi = \angle\left(\vec{e}, \vec{k}\right)$$

$$\omega = 200 \ eV$$

Dependence on polarization : $\chi = \angle\left(\vec{e}, \vec{k}\right)$

$$D_{dop}^{2\sigma_u}\left(90^o\right) - D_{dop}^{2\sigma_u}\left(0^o\right) = \text{exp/ the} = 12.5 / 8.7 meV$$



Dependence on molecular orbital : $\chi = 0^o$

$$D_{dop}^{2\sigma_u}\left(0^o\right) - D_{dop}^{3\sigma_g}\left(0^o\right) = 4.9 / 4.5 \ meV$$

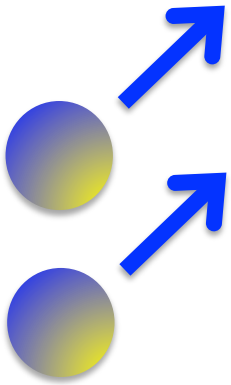
Young's double slit interefence

$$\chi = 90^o$$

$$\left(\vec{e}\cdot\vec{d}^{2s}\right) = \left(\vec{e}\cdot\vec{k}\right) = 0$$

$$D_{dop}^{2\sigma_u}\left(90^o\right) - D_{dop}^{3\sigma_g}\left(90^o\right) = 5.9 / 3.9 \ meV$$

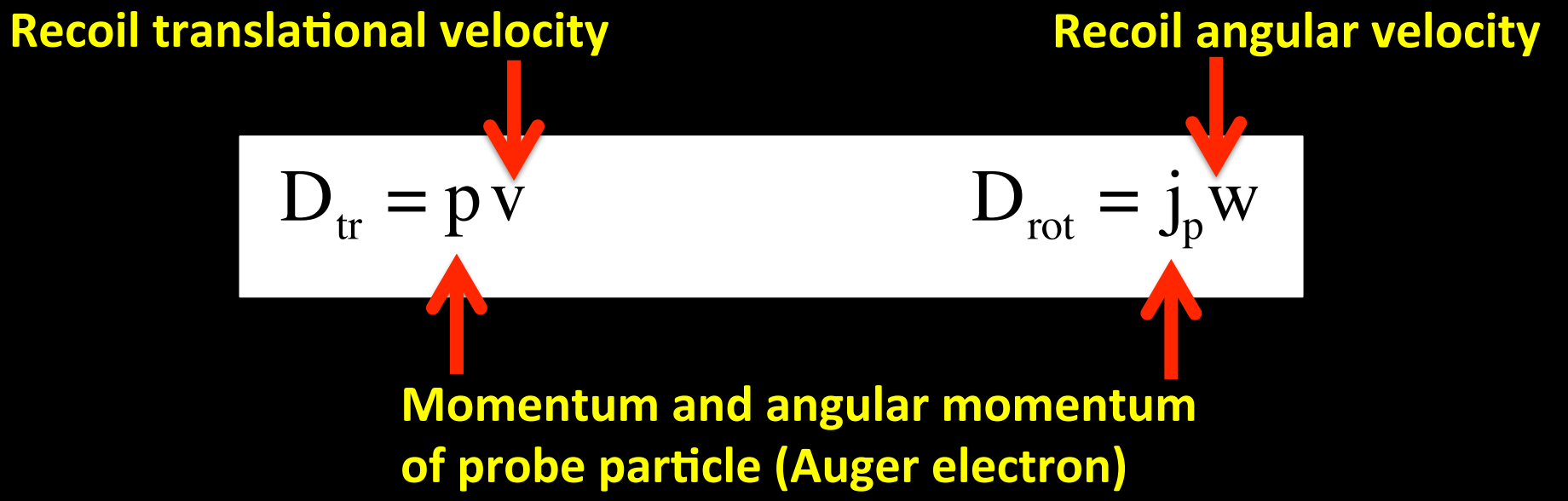
$$\psi_{g,u} = 2p_z^{(1)} \mp 2p_z^{(2)}$$



$$D = \left\langle D(\theta) P(\theta) \right\rangle$$

$$P(\theta) = \frac{1 \mp \cos\left(\alpha k R \cos\theta\right)}{1 \mp \dfrac{\sin\left(\alpha k R\right)}{\alpha k R}}$$

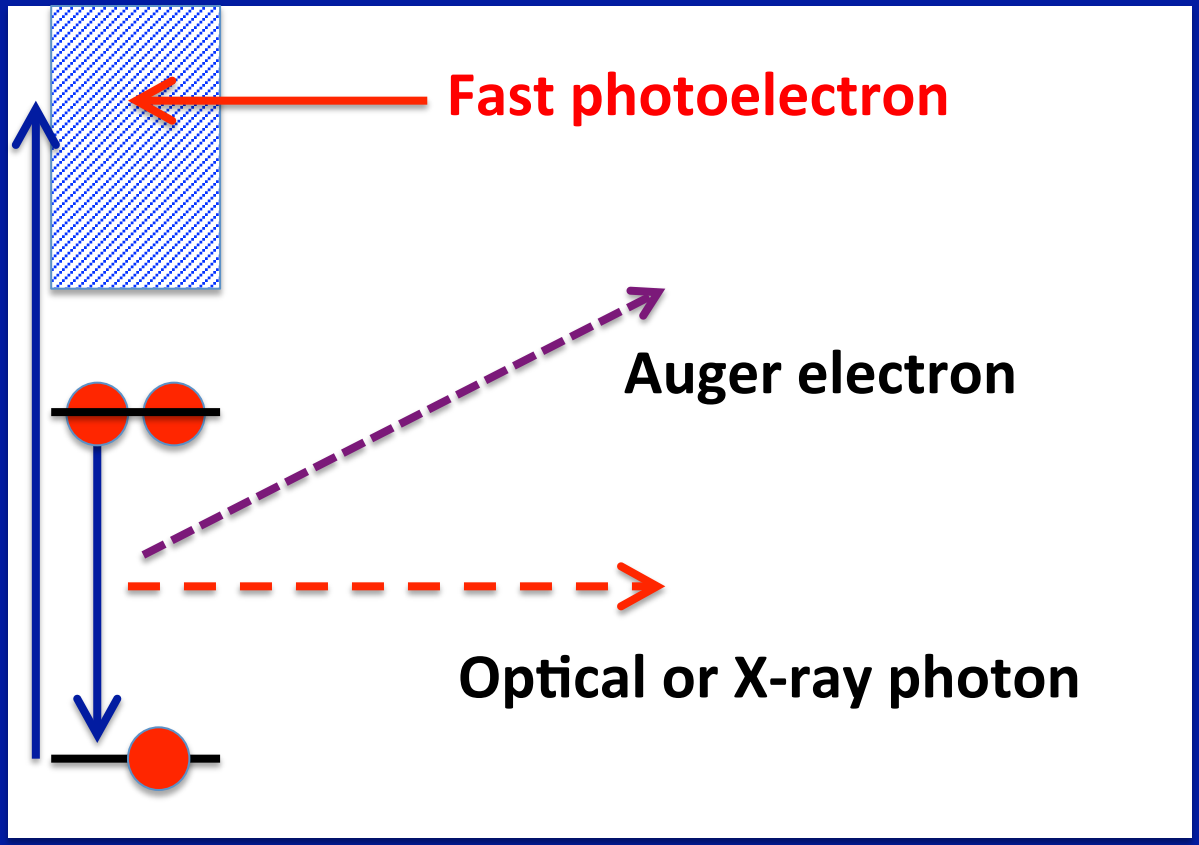
Doppler effect in scattering:
X-ray ionization followed by fluorescence or Auger decay



Recoil induced splitting of X-ray or optical resonances

1: Optical or X-ray fluorescence induced by X-ray ionization

2: Auger spectroscopy

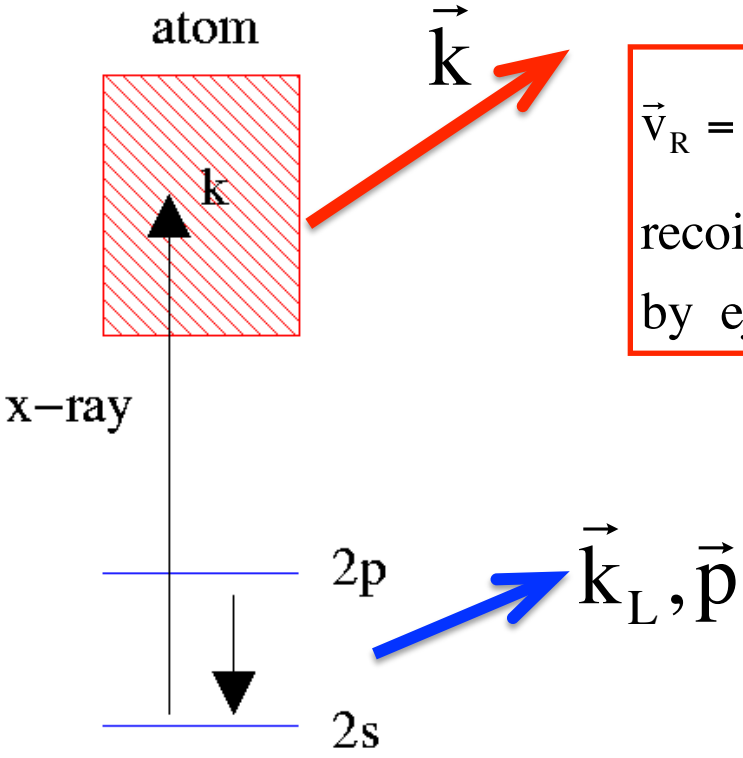


S. Gavrilyuk, Y.-P. Sun, S. Levin, H. Ågren, and F. Gel'mukhanov, Phys. Rev. A 81 035401 (2010).

M. Simon et al, Nature Commun. 5, 4069 (2014)

Recoil splitting of x-ray induced optical fluorescence

Probability of ionization is anisotropic: $\left(\vec{e}\cdot\vec{d}_{2s,k}\right)^2 \propto \left(\vec{e}\cdot\vec{k}\right)^2 \propto \cos^2\theta$

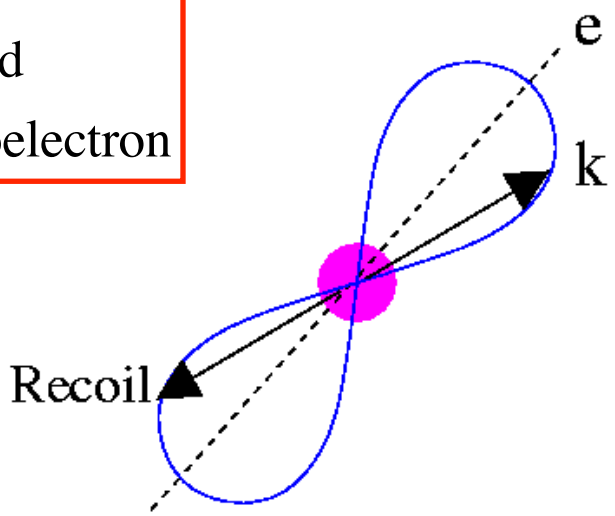


$\vec{k}$

$\vec{k}_L, \vec{p}$

$$\vec{v}_R = -\frac{\vec{k}}{M}, \qquad k = \sqrt{2E}$$

recoil velocity caused by ejection of photoelectron

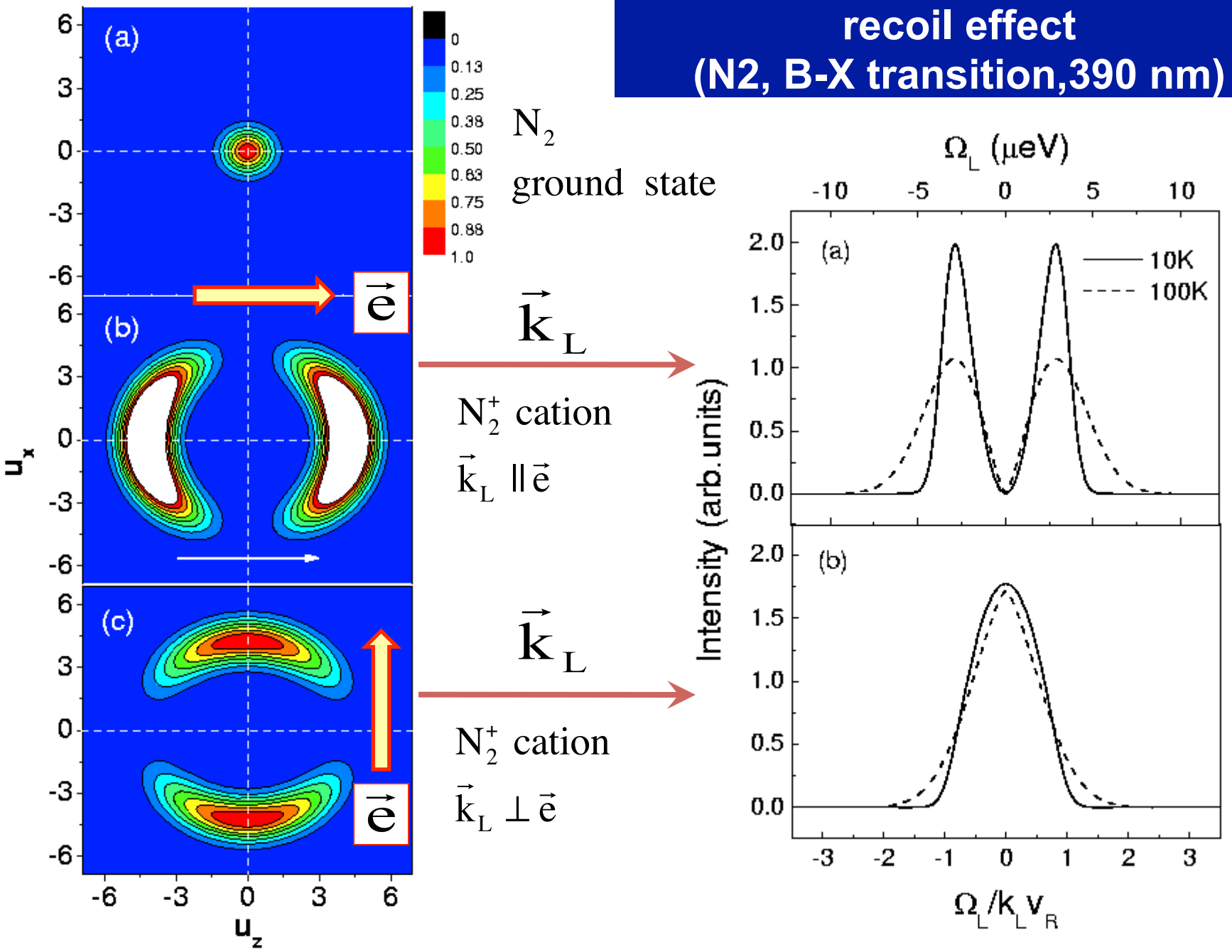


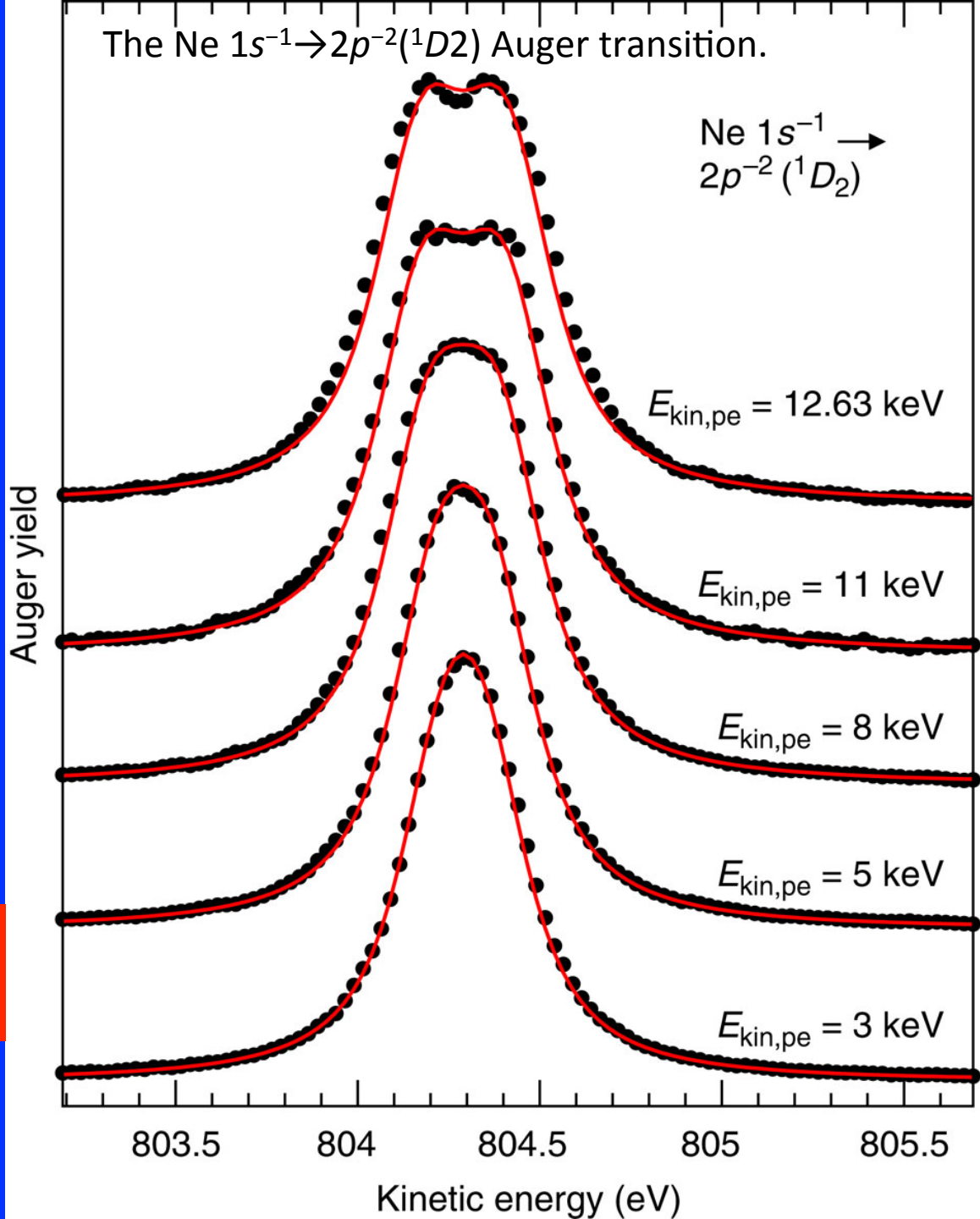
Probability of optical fluorescence/absorption:

$$P_{fluor} \propto \int d\hat{\vec{k}} \frac{\left(\vec{e}\cdot\vec{k}\right)^2}{\left(\Omega_L - \vec{k}_L\cdot\vec{v}_R\right)^2 + \Gamma^2} \propto \begin{cases} 2\left(\Omega_L/k_L v_R\right)^2, & \vec{e}\parallel\vec{k}_L \\ 1-\left(\Omega_L/k_L v_R\right)^2, & \vec{e}\perp\vec{k}_L \end{cases}$$

$\Omega_L = \omega_L - \omega_{res}$

Doppler splitting caused by the recoil effect (N2, B-X transition,390 nm)





Marc Simon et al,
Nat. Commun. 5, 4069 (2014)

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