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SMR. 628 - 20

Research Workshop in Condensed Matter, Atomic and Molecular Physics
(22 June - 11 September 1992)

Working Party on:
"Energy Transfer in Interactions with Surfaces and Adsorbates"
(31 August - 11 September 1992)

"Inelastic Effects in Electronically Stimulated Desorption" (ESD and PSD)

(PART II)

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INELASTIC EFFECTS IN ELECTRONICALLY STIMULATED DESORPTION (ESD and PSD)

here:

SURFACE COUPLING EFFECTS IN CORE-INDUCED PHOTODISSOCIATION

D. MENZEL

(2)

Steps: (3)

see talk!

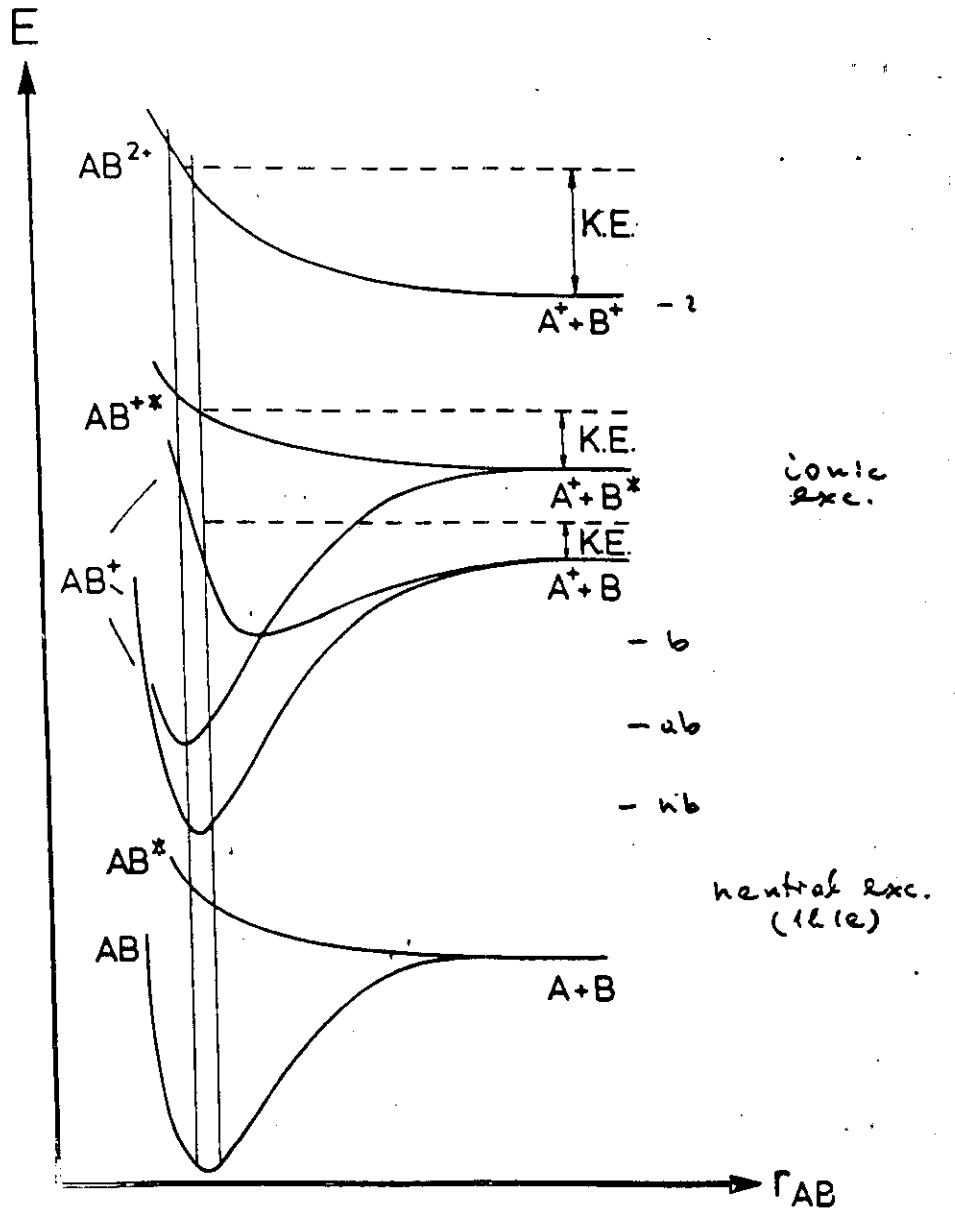
I) Excitation / Ionisation : Hole formation (by photon absorption) — Coupling to surface; Screening of charge hole

II) Deexcitation : Hole decay (electronic rearrangement) — "

III) Bond breaking: (coupling to nuclear motion) Dissociation / Desorption — Excitation transfer; Quenching

First approach:
time scales separated — stepwise

Will have to justify!



→ always at least 2 steps (more possible) with generally well-separable (≠) 3

TIME SCALES

Excitation: $> \frac{1}{\nu}$ ~ (some) 10^{-17} sec

Screening:
- Polarization (~10 eV) $\frac{1}{\nu}$ $\leq 10^{-16}$ sec
- Image charge (ω_p) $\leq 10^{-16}$ sec
- Charge transfer (>5 eV to <0.05 eV) (overlap) some 10^{-16} sec to over 10^{-14} sec !

Deexcitation:
- Core life time for E_B 200 – 800 eV some 10^{-15} sec

Screening: see above

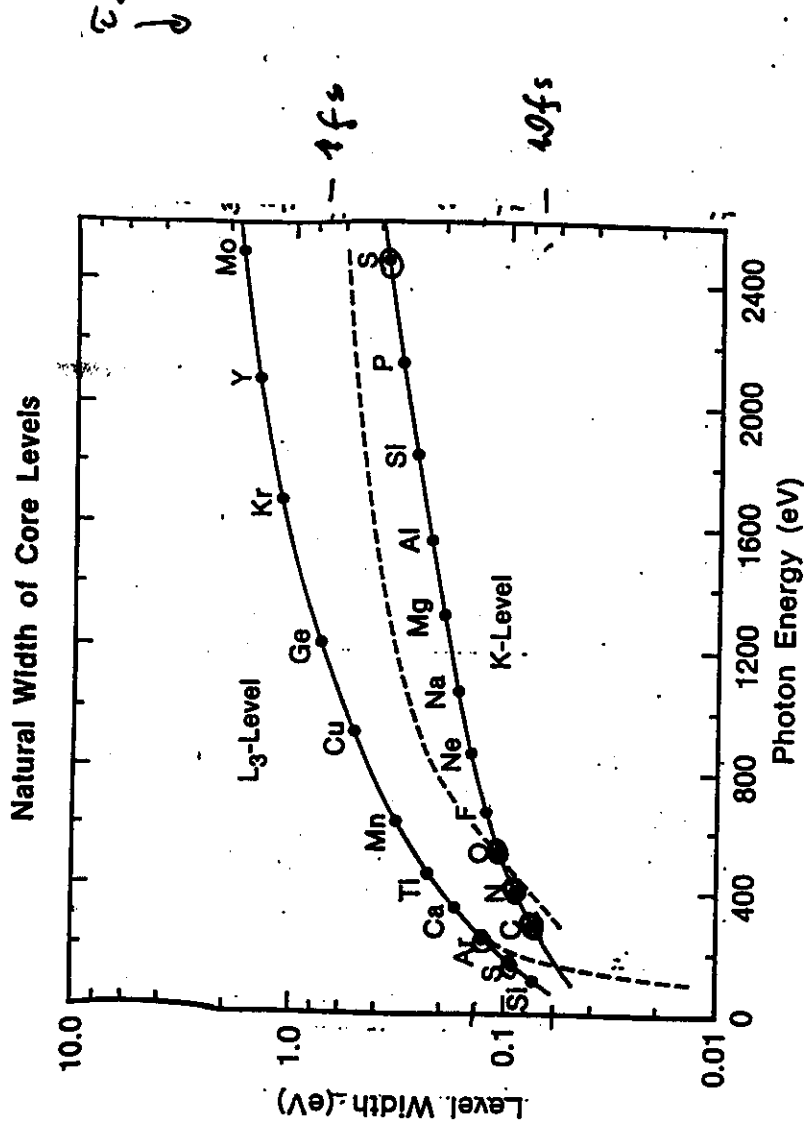
Atomic motion: Depends on mass and force (dE_p/dR) (some 10^{-15} to some 10^{-13} sec

Quenching of excitation: Overlap, best with moving atoms 10^{-16} to $> 10^{-8}$ sec

⇒ Considerable overlap of time scales ! !

⇒ No well-separated steps; competition and interference expected

Core life time



Will use examples from two classes of systems:

— Small molecules bound to metal surfaces

CO, NO, N_2, O_2, N_2O, H_2O ...

on TM single crystal surfaces (Ru, Pt, Pd, W, Ag ...); sub monos- to monolayers

Very well defined systems by surface science methods!

— Surface molecules of molecular condensates (ices)

H_2O, NH_3, CH_4, C_6H_6, H_2S ..

(and ...)

EXPERIMENTAL:

Extreme UHV (~ 10^{-11} mbar); surface science methods

Measure at SR source: TEY, PEY, AEY for excitation

Decay electron spectra for decay

"Desorbing" particles (here: fragment ions) for fragmentation

Most important coworkers:

D. Coulman
P. Feulner
G. Rocker
R. Schneider
R. Treichler
E. Umbach
W. Wurth

ADSORBATES ON METALS

EXPERIMENTAL FINDINGS:

IONS and NEUTRALS detected, but:

OVERALL STRONG DECREASE OF DISSOCIATION EFFICIENCIES ($P_D \sim 10^{-1}$ to 10^{-7})

NEUTRAL DESORPTION PRODUCTS MUCH MORE ABUNDANT THAN IONS; LOWER E_K, WIDER ANGULAR DISTRIBUTIONS

P_D depends on (e.g.)

- adsorption state (coupling)
- coverage; aperiodicity (minority states)
- adsorbate mass (isotope effect)
- primary excitation
  neutral, single $\ll$ multiple valence
  $\langle$core exc. $\ll$ core shake-up

In particular: core ionization:
~totally destructive for small isolated molecules

Surface:

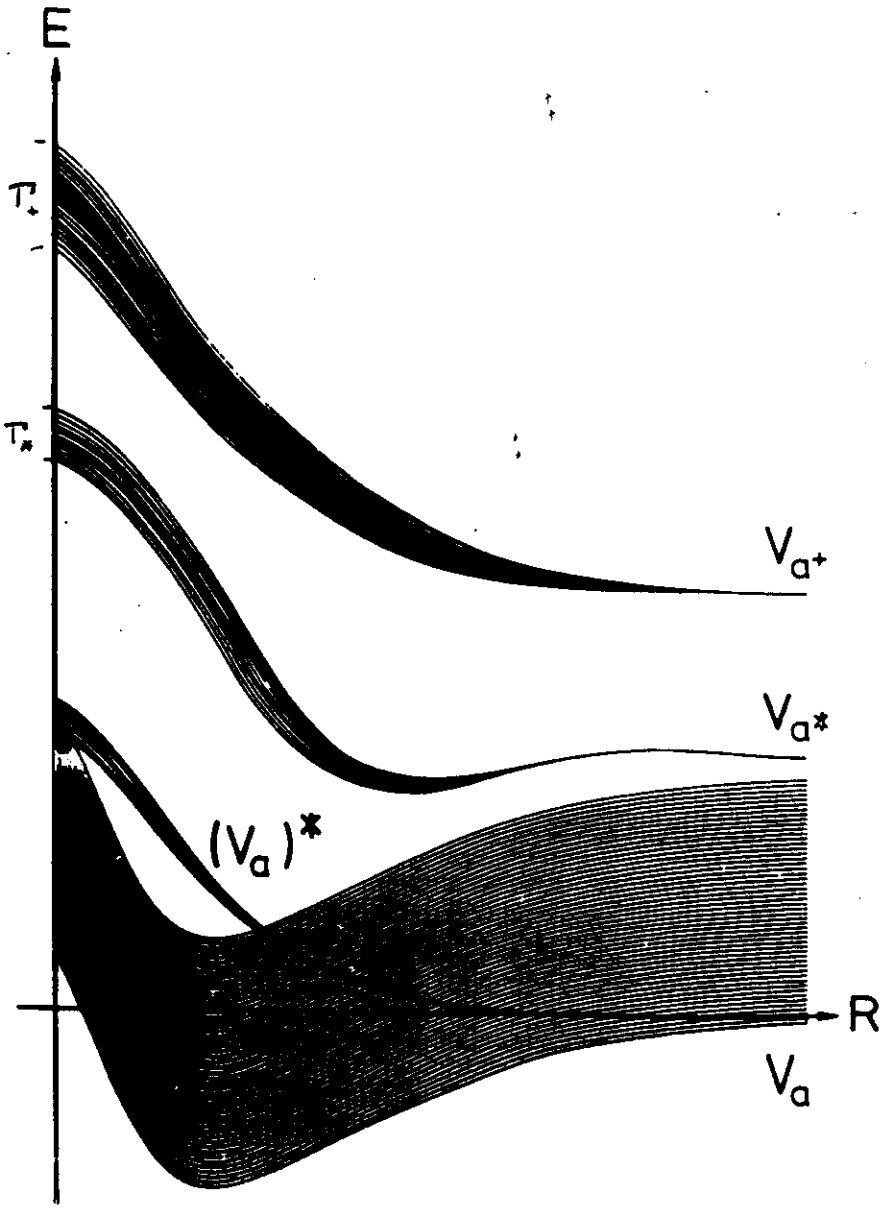
Generally:

P_D the lower, the stronger coupling
(bond strength and geometry, density, order, type of excit.)

" the higher, the stronger localization
(type of excitation: Coulomb localiz., disorder, "minority states")

$\Rightarrow$ "MGR" model:

DELOCALIZATION / RECAPTURE
(transfer of energy and/or charge)
in competition with atomic separation
(metal) surface as
EXCITATION SPONGE



Brenig 1976

Explanation by competition between dissociation and delocalization

⇒ the stronger the excitation is localized, the smaller is the influence of coupling to the "excitation sponge".

Cini - Sawatzki: mech. of Coulomb localization (correlation effect)

Makes the quenching sequence understandable

$h\nu < h\nu e < 2h\nu < h_c, h_{ce} \ll h_c h\nu e, h_c h_\nu$ ($h_c h_\nu 2e$)

$2h\nu$ — Spectator emission, spectator decay

$2h\nu e$

$2h\nu e$ ($3h_\nu 2e$)

$3h_\nu$

etc.

Final state considered as repulsive state.

For instance:

CO, O1s, first satellite resonance (~550 eV) Polarization dependence

see figure ←

$1s^{-1} 1\pi^{-1} 2\pi^{+2} \longrightarrow 1\pi^{-1} \nu_4^{-1} \nu_3^{-1} 2\pi^{+2}$

$(1\pi^{-1} \nu_4^{-1} 2\pi^{+1})$

Very repulsive, if ν_4, ν_3 bonding.

Barely seen in gas phase, because lower excitations suffice, if sufficient time is available (2hν, 2hνe)!

Cini - Sawatzki: localization of 2l-shake

Reason for high efficiency of 2l-shake:

$U_{eff} \leq 2h\nu$

Sequence: core excitation ⟶ Auger decay ⟶ evolution of 2e shake ($\sim 10^{-15}$ s since 10^{-15} s)

Some examples for molec/metal surf. core exc.

O^+ from CO / Ru(001)

NO / Ru(001)

- strong signal above O 1s but "delayed onset":

⇒ core – valence shake-ups i.e. multiple excit., strongly enhanced

- less than 1% signal at C 1s, N 1s; no shake-up infs.

⇒ Very strong selectivity and localiz.

- from polariz. dependence: symmetry obtainable

e.g. first triple resonance is

$O\ 1s^{-1}\ 1\pi^{-1}\ 2\pi^{+2}$

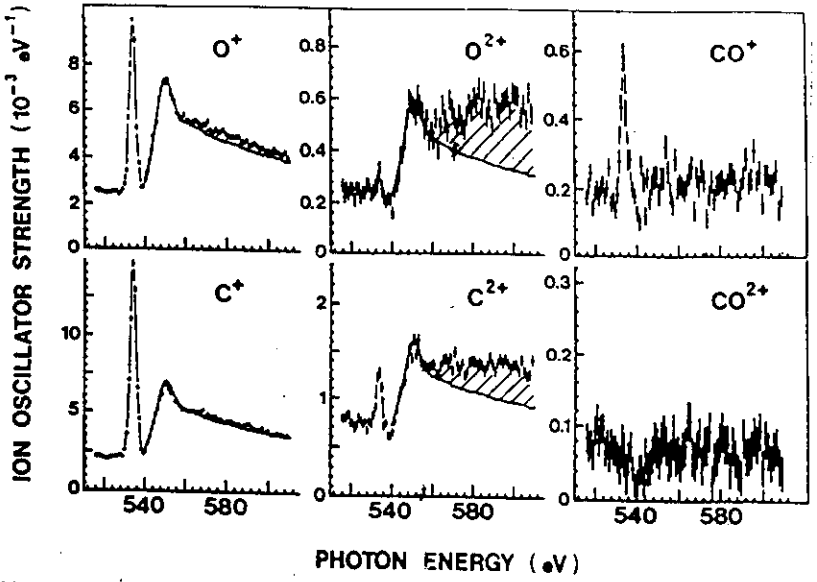
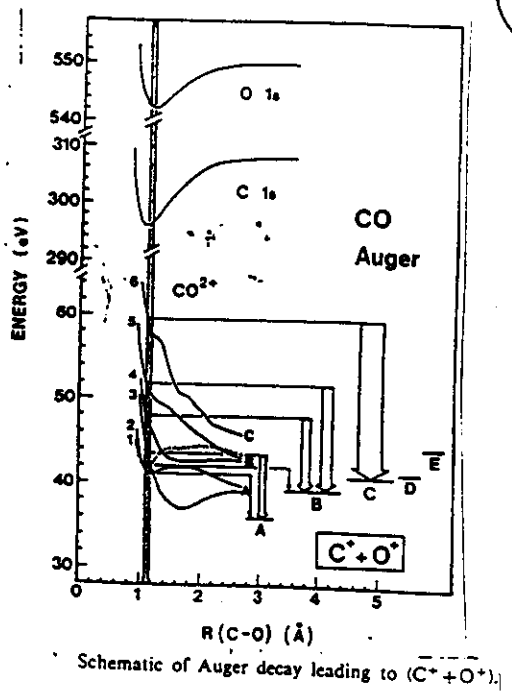


FIG. 7. Partial ion yield oscillator strengths from O 1s photoionization of CO. The absolute scales were establis tion at 565 eV to calculated atomic cross sections with a correction for dissociative multiple ionization derived fror nal. Solid lines are the total ion yield spectrum scaled to match each ion yield spectrum between 542 and 554 eV plained in Fig. 6.

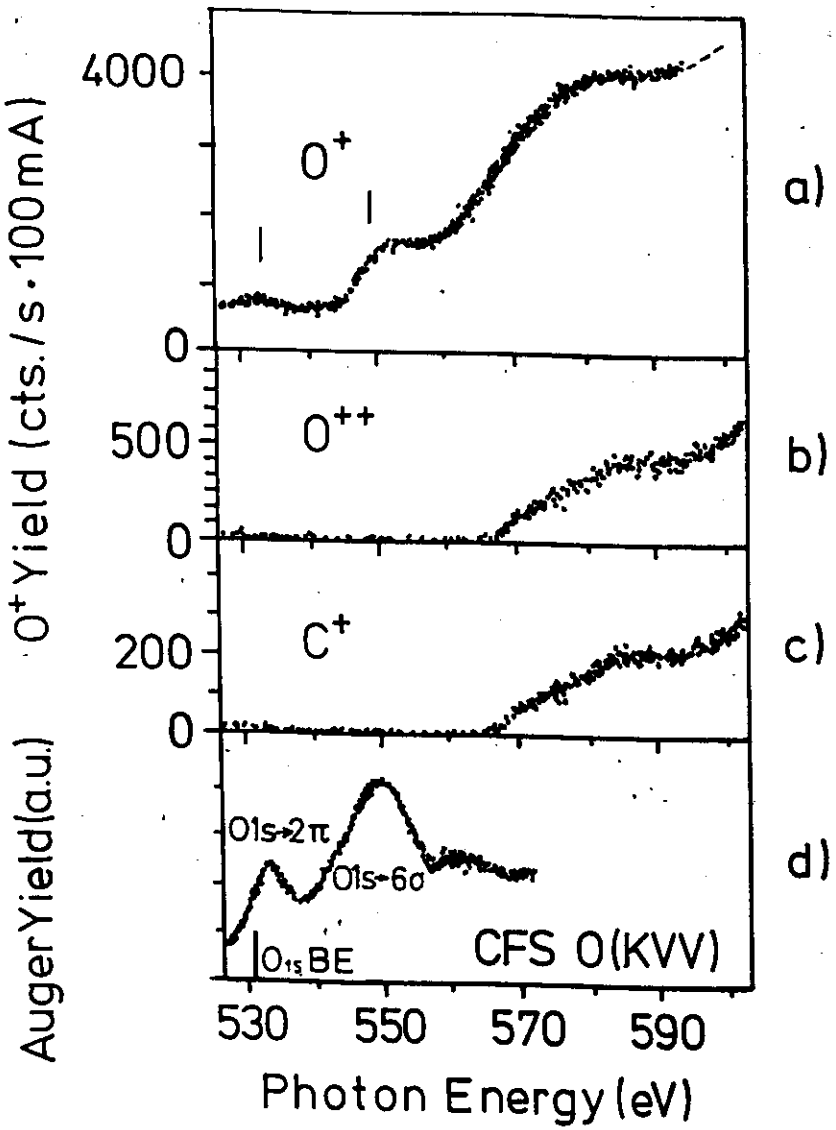
Hitchcock et al 1980

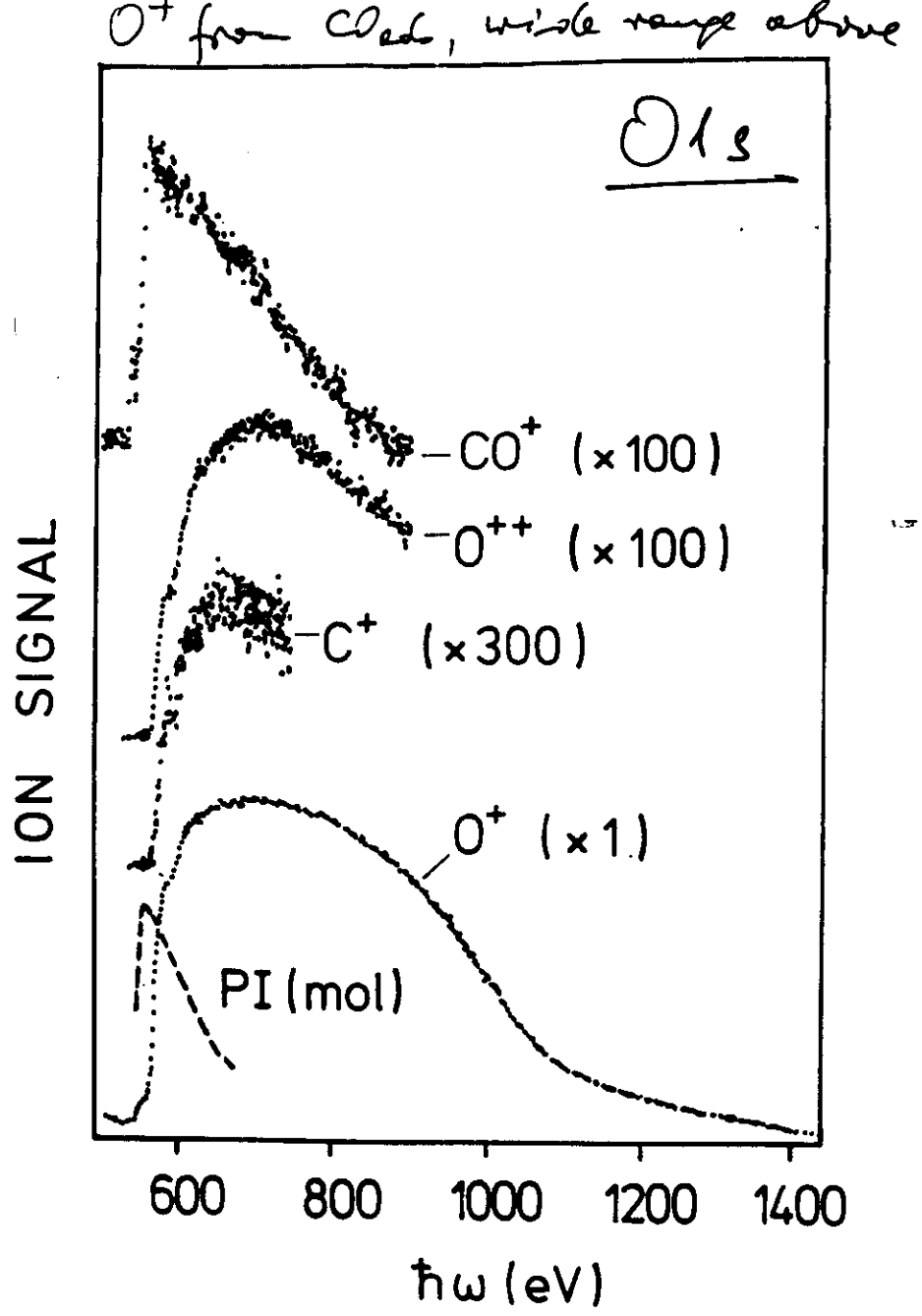
CO gas phase



Schematic of Auger decay leading to $(C^+ + O^+)$.

Process		
		single
$h\nu + CO \rightarrow CO^+$		(a)
$h\nu + CO \rightarrow C^+$	$+O$	(b)
$h\nu + CO \rightarrow C$	$+O^+$	(c)
		double
$h\nu + CO \rightarrow CO^{2+}$		(d)
$h\nu + CO \rightarrow C^{2+}$	$+O$	(e)
$h\nu + CO \rightarrow C$	$+O^{2+}$	(f)
$h\nu + CO \rightarrow C^+$	$+O^+$	(g)
		triple
$h\nu + CO \rightarrow CO^{3+}$		(h)
$h\nu + CO \rightarrow C^{3+}$	$+O$	(i)
$h\nu + CO \rightarrow C$	$+O^{3+}$	(j)
$h\nu + CO \rightarrow C^{2+}$	$+O^+$	(k)
$h\nu + CO \rightarrow C^+$	$+O^{2+}$	(l)





raichler et al.
RL 54 (85) 462
ew. Phys. 153(91)259
nface Sci. 243(91)239

CO ads. on Ru(001)
(similar : on Ni(111) Ni(111))
15 [illegible]

CO ads. on Ru(001)

Treichler et al., PRC 1985 - 16 At C1s :

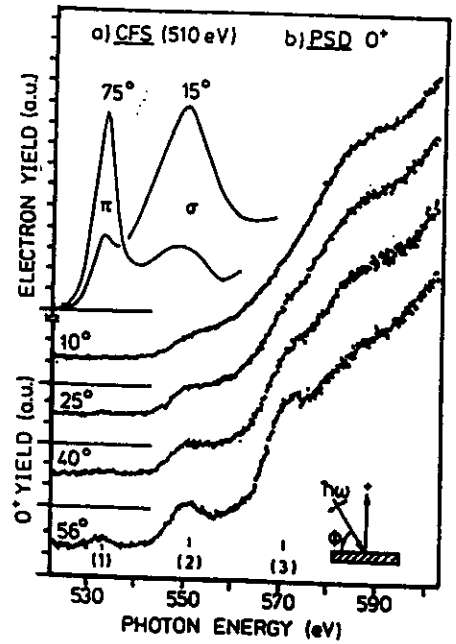


Fig. 9. Comparison of polarization dependences of a) the total ionization cross section (CFS) and b) the O^+ yield above O1s for CO/Ru(001), as a function of photon energy (from ref. [29], with permission). Contrary to the behaviour for total yields, the O^+ yield shows π-type resonances at 550 and 573 eV.

from Treichler et al., PRL 1985

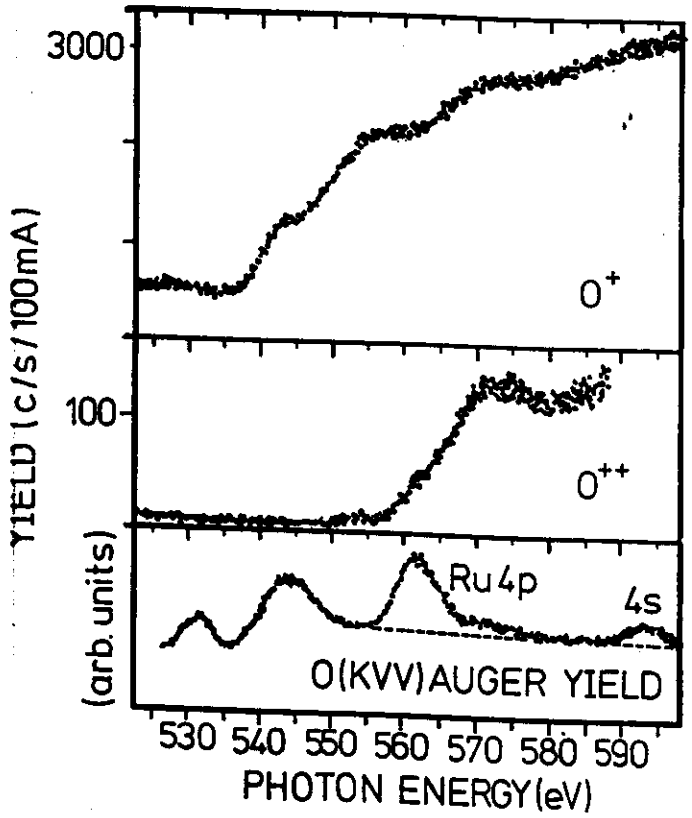
→ peak (2) is not shape resonance, as this would be σ symm.; but is π - symm.

⇒ threshold res. of $1\sigma^{-1}\,1\pi^{-1}\,2\pi^{+2}$ shake-up

similar: NO / Ru(001)

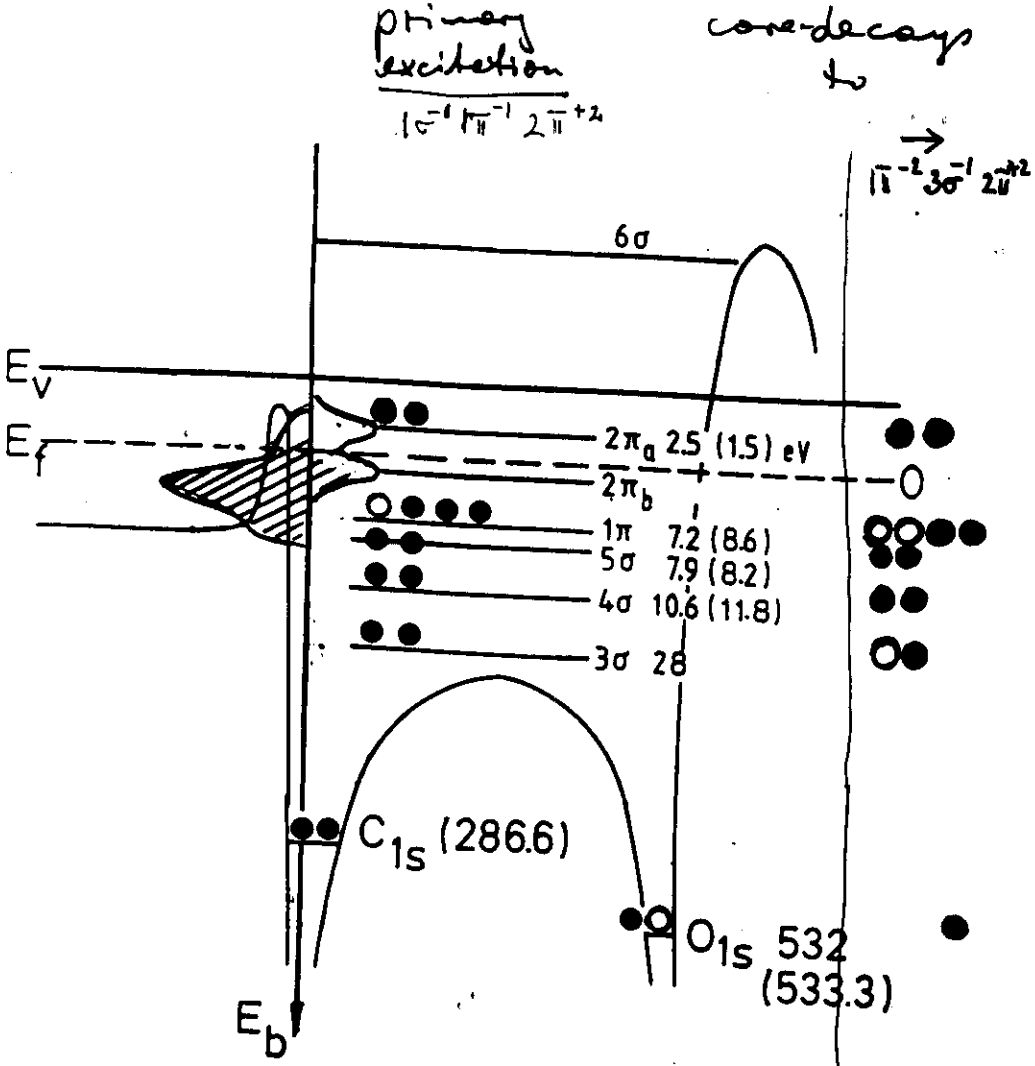
V_2 - NO $Ru-Ru-\overset{O(\pi^*)}{\underset{|}{N}}$

V_1 - NO $-Ru\,Ru-\overset{O(\pi^*)}{\underset{|}{N}}$



O^+ at N 1s : less than 1% signal (only res.)

⇒ extreme selectivity



$1\sigma^{-1}\ 1\pi^{-1}\ 2\pi^{+2}$

satellite "threshold resonance

But is this all ?

- Exp.: Direct $2h\nu$ excitations and $h_c \rightarrow 2h\nu$ exct. are <u>not</u> equivalent !
- Gen.:
  - Core life time is quite <u>long</u> ($\sim 5\times 10^{-15}$ s)
  - Reversed argument: ultrafast channels <u>need no</u> localisation !

$\Rightarrow$ Is there a contribution from dissociation <u>during</u> core life time?

"ULTRAFAST", "non-F.C." - CHANNELS (see Hering + Nenner)

Appears possible for steep repulsive pot. curve.
Evidence from autoionisation (decay from relaxed core state)

Exp.: Should be more obvious for <u>light</u> fragments (H^+, D^+)

DISSOCIATION BY CORE-TO-BOUND RESONANCES

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For really fast processes: molecular properties should dominate.

Two general cases:

1) $\bar{c}\,v^*$ repulsive
2) $\bar{c}\,v^*$ bound → see figure

TIME SCALES:

(simple light molecules such as CO, N_2, H_2O, CH_4...

core decay (τ_c)	: 1 - 10 fs
vibrations	: ~ 50 fs
screening	: 0.1 - 1 fs
charge transfer	: < 1 to 100 (?) fs
dissociation	: ? fs to ns
on surface	: to 0.1 ps (restrict to direct disso

On potential with slope 5eV/Å, an H atom moves (classically) about 0.6 Å in 5 fs and picks up 3eV.

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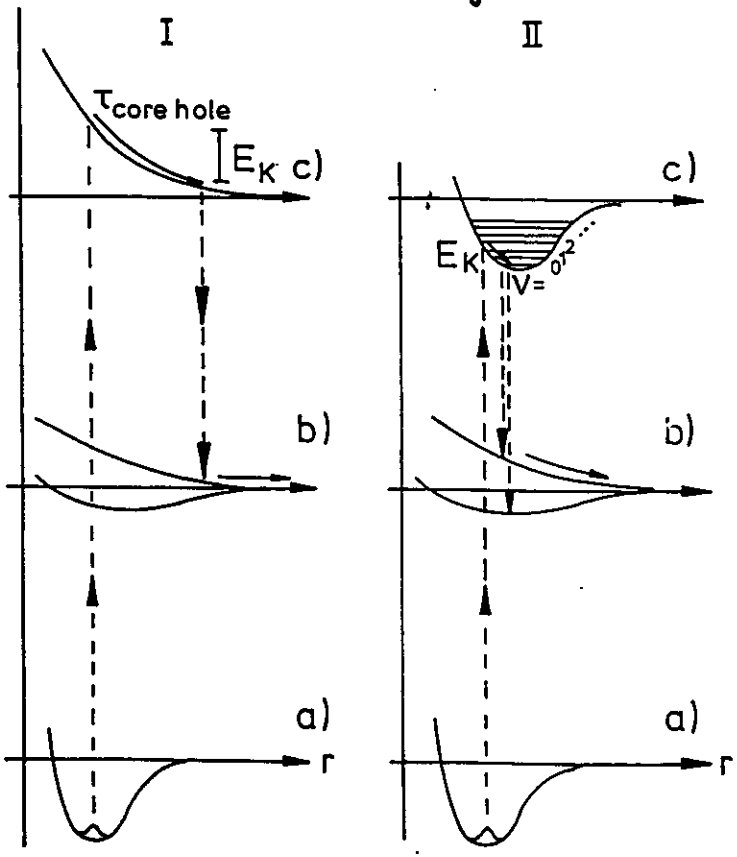
Resonant excitation to

repulsive | bound

$\bar{a}\,v^*$ state

time evolution (very schematic)



If $\tau_d < \tau_c$: certainly "ultrafast"

If $\tau_d > \tau_c$: still possibly "

(in decay state)

Case 1) Repulsive core-excited state:

If strongly repulsive, dissociation in τ_c feasible for light atoms. otherwise essentially as case 2)

First example: Gas phase HBr, Br 3d exc.
Decay spectrum of Br atom observed (Morin + Nenner, 1986)

Possible clues:

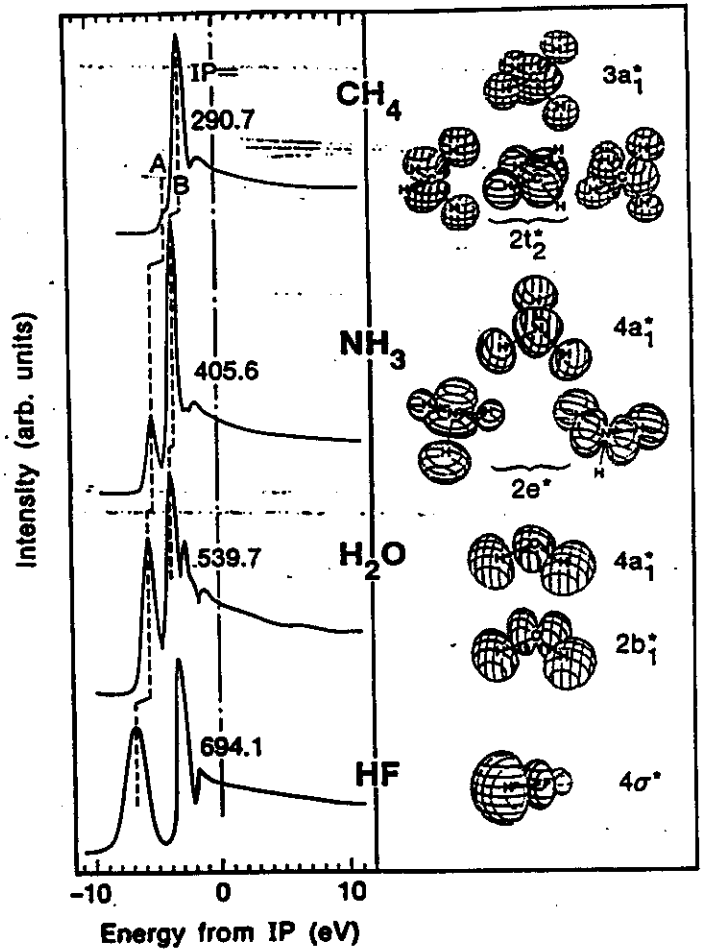
- Strong enhancement of dissoc. in certain σ^* state(s)
  Observed for: H_2O, NH_3, H_2S, C_6H_6
  not CH_4
  Could still be due to $\overline{v_1}$ $\overline{v_2}$ ν^* states (ion observed!)

Positive proof:

- Decay spectra
  not applic. to H_2O, NH_3, H_2S cond. or ads.
  (but free H_2S: Akselsson et al.)
  C_6H_6: selectively dissociating peaks has different decay spectrum
- No vibrational structure in absorption:
  not applicable for the above (interactional broadening?)
  But in isolated molecules: H_2O, NH_3;
  not CH_4 (Rondelez et al.)
- Enhancement persists in adsorbates:
  H_2O, H_2S

Ultrafast processes ($\tau_d < \tau_c$) expected for

- long-lived core holes
- strongly repulsive excitations
- fast-moving fragments

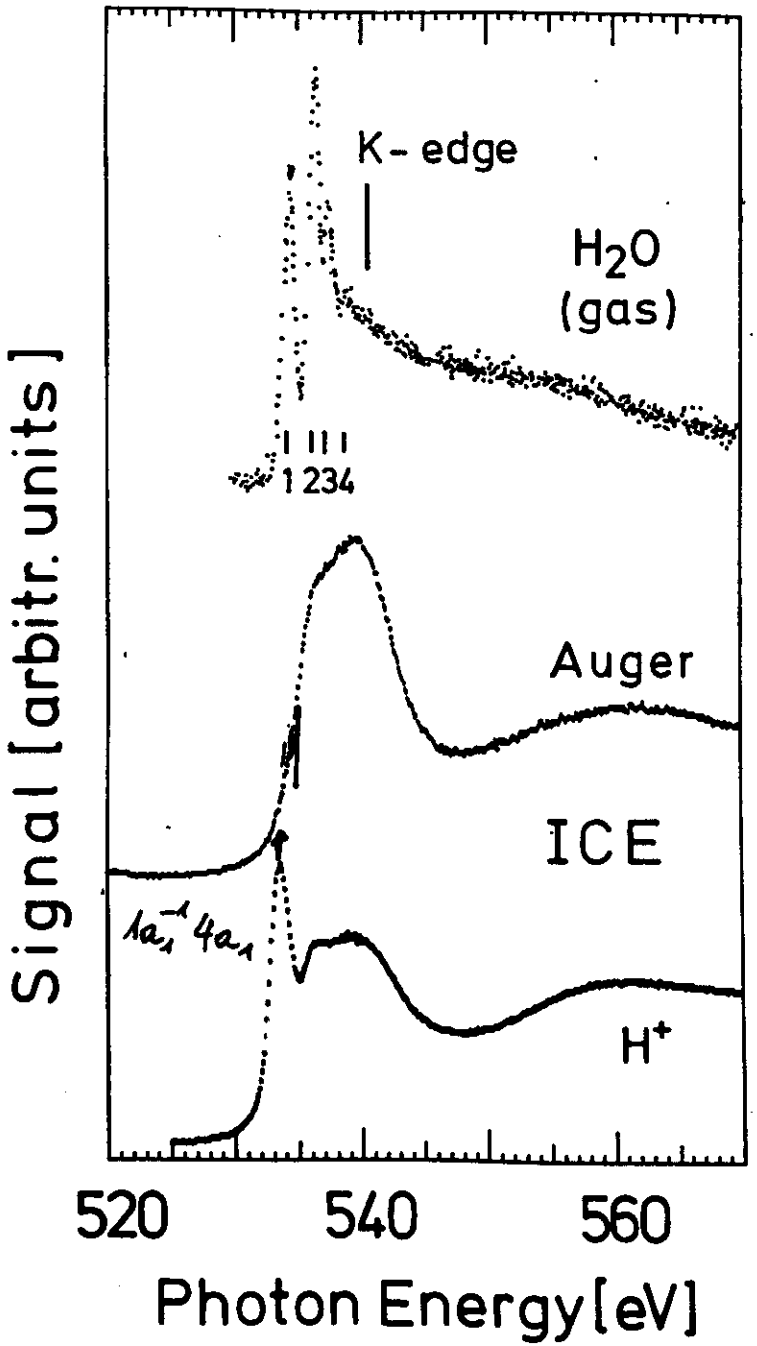


C 1s: $\tau_c \approx 10\text{-}13$ fs

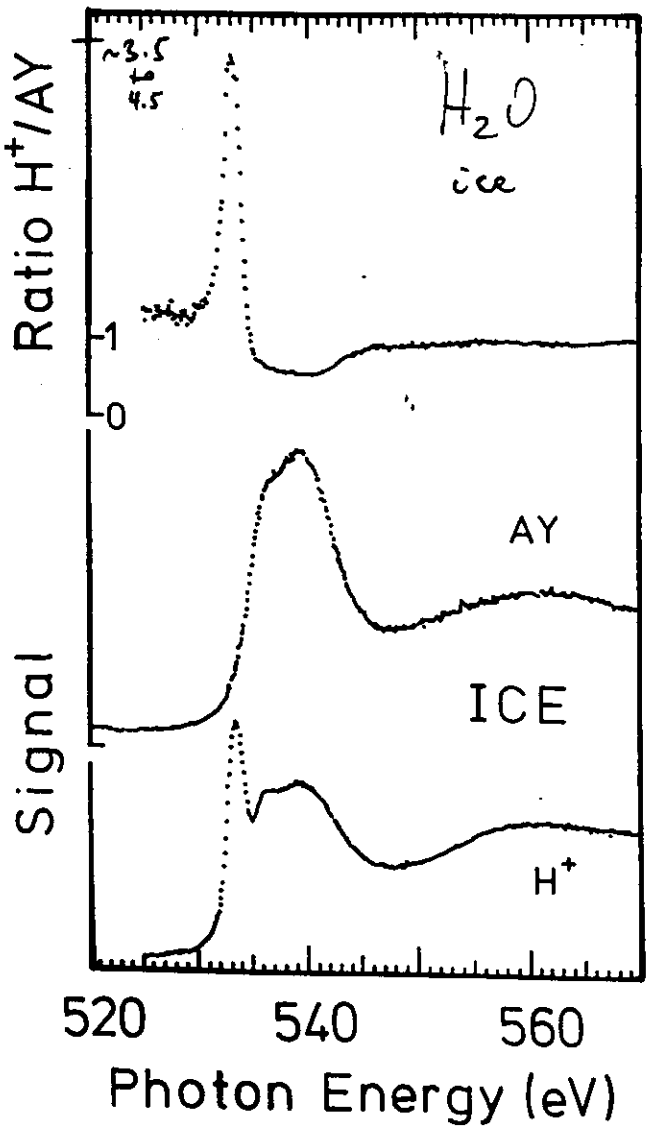
N 1s: $\tau_c \approx 7\text{-}11$ fs

O 1s: $\tau_c \approx 4\text{-}6$ fs

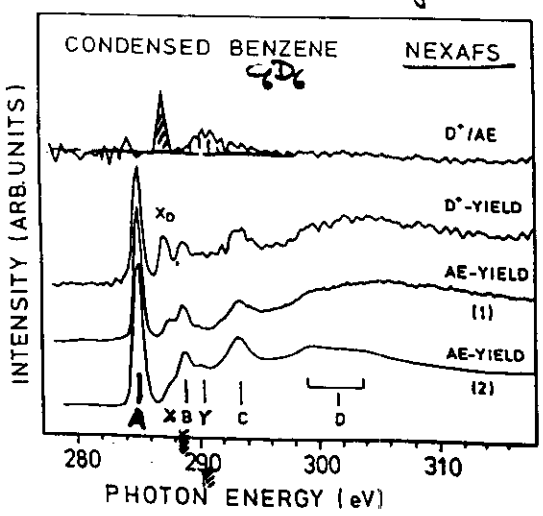
Signature 1: selective enhancement of dissociation



Coulman et al., J. Chem. Phys. 93(90)58



Also: NH_3, H_2S



A : π^* (e_{2u})

X : $3s / \sigma^*_{C-D}$

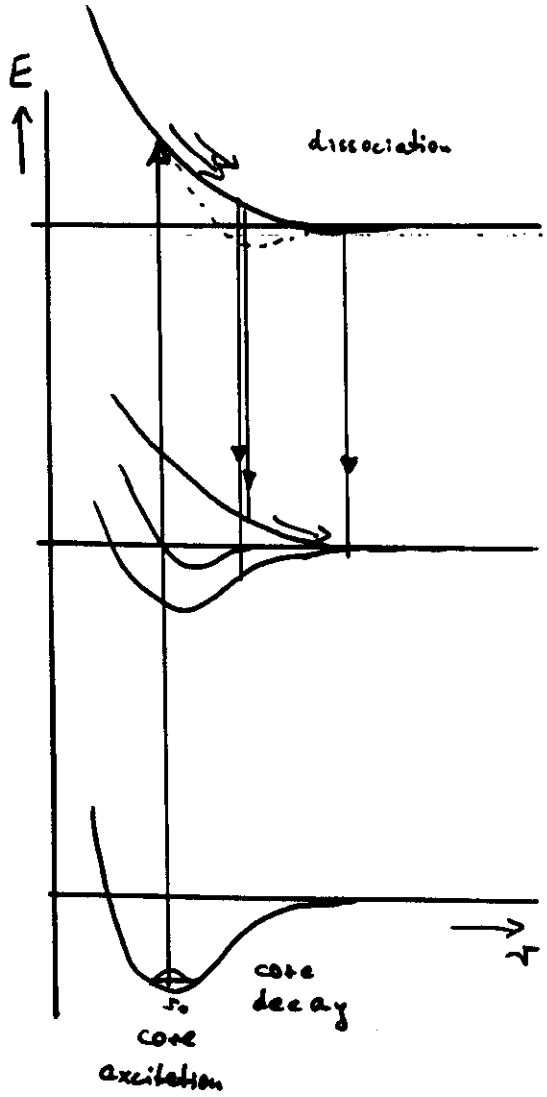
B : π^* (b_{2g})

Y : σ^*_{C-D}

C : σ^*_{C-C} + shape res.

D : shape res.

Resonant core excitation and dissociation :



$\tau_c \gtrless \tau_d$

Primary excitation by resonant core absorption to electronically bound, but repulsive molecular states :

$AB + h\nu \rightarrow AB^{c*}$

where $c^* : (c^{-1} v_a^{+1})$

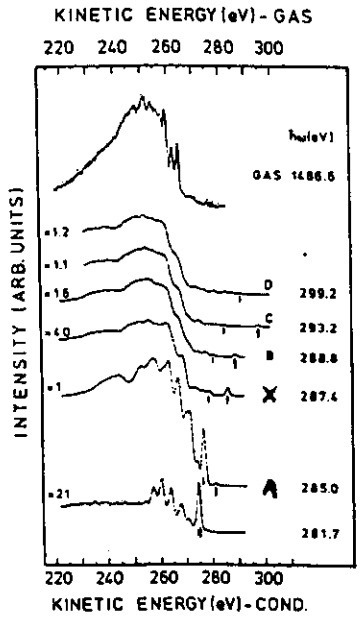
Depending on $\tau_c(r)$, electronic decay leads to

$v_a^{-1} v_b^{-1} v_a^{+1}$ (spectral decay of AB^{**}

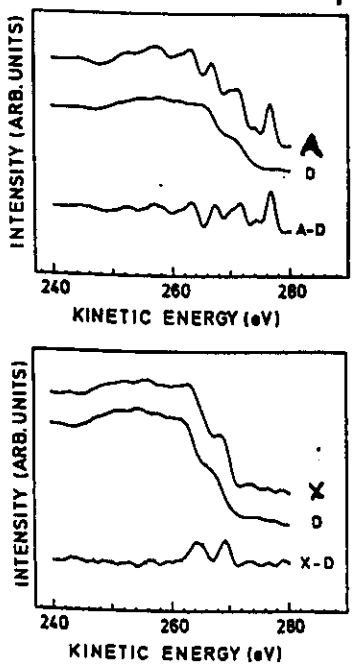
AB^{**} at $r > r_0$

$A^+ + B^*$

Decay spectra



extraction of autoionic. feature



Case 2) : Stable core-excited state

Example : N_2

Vibrational resolution of $N1s \rightarrow 1\pi_g$ <u>persists</u> in thick and thin condensates, in physisorbed monolayer, for N_2 in Ar matrix, and for N_2 on Xe spacer layer

<u>But</u> changes by environment (cage effect)

Also : Dissociation and desorption signals show vibrational structure which differs → different predissociation

Simplest case : thin N_2 layer on N_2/Xe
Absorption (PY) as in gas phase.
N^+ : possible slight enhancement of high vib. states → dynamics leading to dependence of weighting of decay channels on vib. state (or excess energy) ?

3) <u>In all cases</u> :
Use of dipole selection rules allows selection of certain channels
e.g. Rydberg exc. of N_2
Broken symmetry of CH_4 on surface

CONCLUSIONS :
(direct dissoc. by core-to-bound exc.)

1) Very fast dissociation processes <u>do</u> exist.
Distinction between $\tau_e \gtrless \tau_N$ difficult.

2) Even for somewhat slower processes (<u>bound</u> $c^1 v_2^{+1}$), electronic and nuclear time scales are comparable

Need coupled treatment ?

→ Together with conclusion from core excitation / deexcitation studies:

Screening, charge transfer, electronic decay, nuclear motion on similar

CONCLUSIONS:

1) Molecules strongly coupled to metal surfaces:
Dissociation events requiring long times are efficiently <u>quenched</u>. "Long" means times below ps (depending on coupling)

10^{-14} to 10^{-12} s

⇒ only DIRECT dissociation seen.

COMPETITION between DISSOCIATION and DELOCALISATION limits desorption

2) There are also ULTRAFAST dissociation processes (i.e. on time scales of some fs). They eliminate the need for localisation so that DISSOCIATION ALWAYS WINS.

10^{-15} to 10^{-14} s

⇒ seen equally in isolated molecules (to be proved directly), in condensed and in adsorbed layers.

3) The time scales of screening, charge transfer, electronic evolution and decay and nuclear motion CAN BE COMPARABLE.