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Miramare - Trieste, Italy

Long-lived excited states in adsorbate/metal surface systems

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Long-lived excited states in adsorbate/metal surface systems

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ICTP, Trieste, 11-15 Sept. 2000

There exists a variety of excited electronic states at surfaces that are involved in many different processes:

Energy transfer with a solid surface
with an adsorbate/substrate system
(photon, electron and heavy particle impact)
Relaxation of the above energy transfer
Reaction intermediate : An excitation induces an evolution of the surface system.

For example, an **electron capture** by an adsorbed molecule induces an internal evolution of the molecule (contraction or stretching) that can lead to a transformation of the chemical bonds on the surface and thus to the following processes

Desorption (DIET) of ions or neutrals
Dissociation of adsorbates
Vibrational excitation of adsorbates
Reactivity ...

The efficiency of the above processes depends in a crucial way on the life time of the excited state on the surface : its should not be too short !

Decay of excited electronic states on a metal

- One-electron transfer

The excited electron localised at the surface (e.g. on an adsorbate) is transferred into the bulk

Resonant Charge Transfer (RCT) process

Very fast : lifetime below 1 fs

Ex. Alkali/Al (Lang and Williams, 1978)

- Inelastic electron-electron interaction

The excited electron can suffer **inelastic collisions with bulk electrons**, leading to two hot bulk electrons. This process is a priori favoured by a large penetration of the electron wavefunction into the bulk.

Ex. ●Lifetime of hot electrons in metals

Cu, $\tau \sim 5$ fs for e^- 2 eV above the Fermi level

(Knoesel et al Surf.Sci. 368 (1996) 76)

(in free electron gas, $\tau \propto (E-E_F)^{-2}$)

●Lifetime of image states at surfaces

Cu(100) n=1 image state

Theory $\tau \sim 30$ fs ; Experiment $\tau \sim 40$ fs

(Chulkov et al PRL 80(1998)4947; Höfer et al Science 277(1997)1480)

- Electron-phonon scattering

Thermalisation of the electron gas with the phonon bath

Slower than the above processes, except for the e-e interaction close to the Fermi level.

- Electron defect scattering: usually neglected

For excited electrons at surfaces, the Γ decay rates ($\Gamma=1/\tau$) are usually such that:

$\Gamma_{RCT} > \Gamma_{ee} > \Gamma_{ep}$ **(when they exist)**

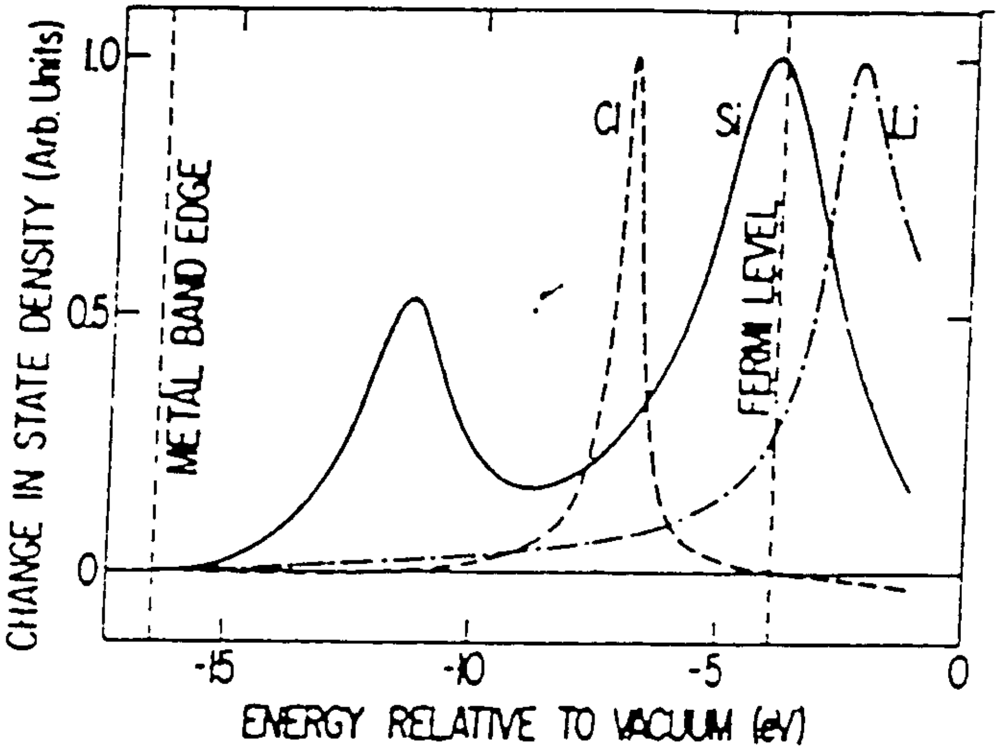


FIG. 2. Change in state density $\delta n(E)$ due to chemisorption. Curves correspond to metal-adatom distance d which minimizes the total energy (Table I). High-density ($r_s = 2$) substrate. Note that the lower Si resonance corresponds to the 3s level of the atom; for Cl this is a discrete state below the band edge.

(Lang and Williams

Phys. Rev B 18(1978) 616

Experimental studies of Cs/Cu(111) by Time Resolved 2-Photon-Photo-emission TR-2PPE

(Bauer et al 1997, Ogawa et al 1999)

→ very long lived states

15 ± 6 fs (300K) Bauer et al
~ 50 fs (50K) Ogawa et al

→ Photon induced desorption of the Cs adsorbate

(H.Petek et al, Science 288 (2000) 1402)

-Theoretical studies on alkali/free electron metal surfaces

(Lang and Williams, Phys.Rev.B 18 (1978) 616; Nordlander and Tully, Phys.Rev.B 42 (1990) 5564; Borisov et al Phys.Rev.B 54 (1996) 17166)

→very fast decay by one electron transfer (Resonant Charge Transfer, RCT)

$\Gamma_{RCT} \sim 900$ **meV**
$\tau \sim 0.7$ **fs**

-Interpretation :

Very long lived states in alkali/Cu(111) are due to the strong modifications (blocking) of the Resonant Charge Transfer, RCT, induced by the peculiarities of the Cu band structure (projected band gap along the surface normal).

Contents

- Treatment of the RCT process by the **Wave Packet propagation (WPP)** method
  - Case of a **free-electron metal**
  - Case of a metal surface with a **projected band gap**

- Application to the **Cs/Cu(111)** system
  - Why is it so stable ?
  - Effect of the **electron-electron interaction**
  - Comparison between **Cu(111) and Cu(100)**
  - Effect of the **adsorbate coverage**

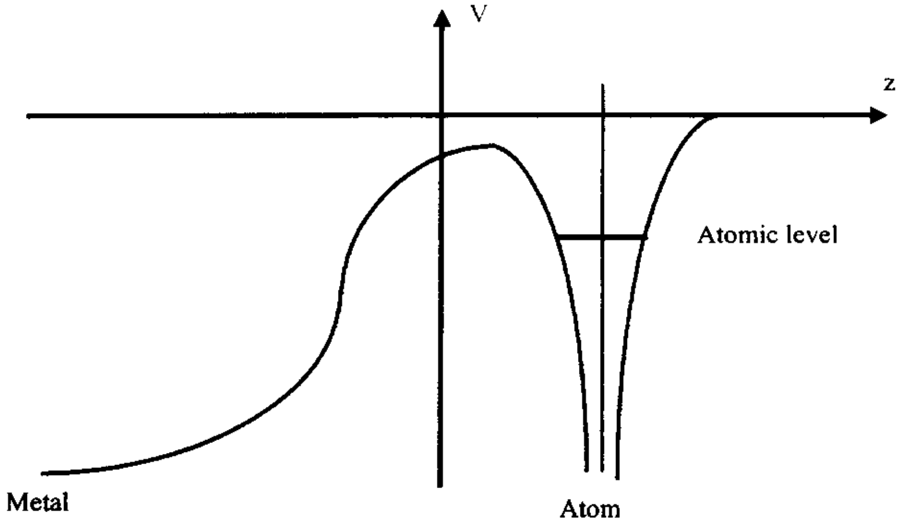
- Consequences on scattering experiments
  - **Time dependence** of the process
  - Relative roles of the **2D** surface state and **3D** bulk propagating states

- **Other systems**
  - Is the Cs/Cu(111) unique ?
  - **H^-/Cu(111)**
  - **F^-/Ag(111), F^-/Cu(111)**
  - **CO($2\pi^*$)/Cu(111)**

- **Conclusions**

- Resonant Charge Transfer (RCT) process

(free-electron metals/jellium)



Potential 'felt' by the active electron along the normal to the surface that goes through the adsorbate centre (1D picture)

The electron can tunnel through the potential barrier

→ **Width** of the level : charge transfer rate

→ **Energy** E of the level : direction of the charge transfer

(metal ↔ adsorbate)

Resonant Charge Transfer (RCT) process

(free-electron metals/jellium)

Determination of **energies and widths** for atomic levels interacting with a free electron metal :

-**Complex scaling** : P.Nordlander and J.C.Tully Phys.Rev. Lett. 61 (1988) 990

-**Scattering approach (CAM)** : D.Teillet-Billy and J.P.Gauyacq Surf.Sci. 239 (1990) 343

-**Stabilisation** : S.A.Deutscher, X.Yang and J.Burgdörfer Phys.Rev. A 55 (1997) 466; F.Martin and M.F.Politis Surf. Sci. 356 (1996) 247

-**Wave-packet propagation** : Ermoshin and Kazansky, Phys. Lett. A218 (1996) 99

-**Chemi-sorption approach** : Merino J., Lorente N., Pou P. and Flores F. Phys.Rev. B 54 (1996) 10959

-**Self-energy** : Kürpick P., Thumm U. and Wille U. Nucl.Inst. Meth. B 125 (1997) 273

General idea of the wave-packet propagation approach

- One only considers the active electron in the RCT
- Study of the time evolution of the electron wave-packet in the compound potential :

$$V_{e\text{-surf}} + V_{e\text{-atom}} + \Delta v_{e\text{-surf}}$$

- The atom-metal surface distance is fixed (Static calculation)

Electron-atom interaction

-model potential function of the electron-atomic core distance (e^--H, Li^+, Na^+, Cs^+ … interactions)

- This is well adapted for low adsorbate coverage

Electron surface interaction

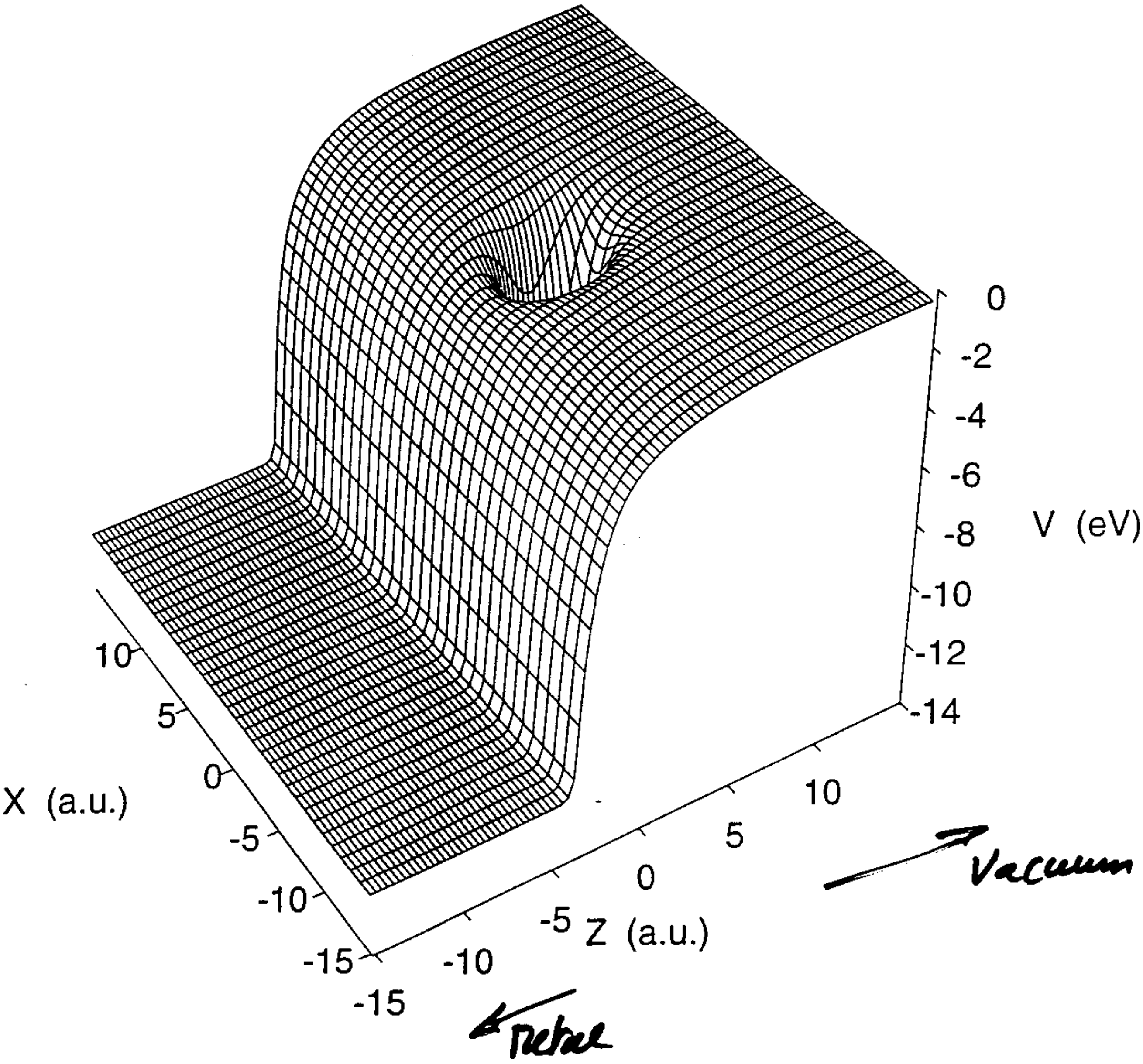
-Two models : **free-electron and model Cu(111)**

Free-electron Cu model

$V_{e\text{-surf}}$: local potential function of z the electron-surface distance

$$
\begin{aligned}
V_{e-surf} &= -\frac{1}{4z}(1-e^{-az}) \quad z>0 \\
V_{e-surf} &= -V_0\,(1+Ae^{Bz}) \quad z<0
\end{aligned}
$$

(Jennings et al, Phys.Rev B 37(1988) 3113)



Potential "felt" by the active electron

(H^- – Jellium Cu)

Wave-packet propagation approach of the RCT

-Use of **cylindrical co-ordinates** : z, ρ and ϕ

→propagation of **2D** wave-packets (z, ρ)

-Propagation method:

- Hamiltonian : (case of a local V_{e-A} potential)

$$H = T_z + T_\rho + V_{e-A}(z,\rho) + V_{e-surf}(z) + \Delta V_{e-surf}$$

- **Split operator** propagation (T_ρ and $H - T_\rho$) and Cayley propagation scheme

$$e^{(A+B)dt} = e^{Adt/2} e^{Bdt} e^{Adt/2} + 0(dt^3)$$

- **Change of variables** : $\rho = x^2$
- **Finite difference** expressions for T_z and T_ρ
- **Initial wave packet** equal to the bound state of the free atom $\Psi(t=0) = \Phi_0$
- **Optical potential** close to the box edge to remove the wave-packet reflections

References:

Ermoshin and Kazansky, Phys. Lett. A218 (1996) 99
A.G.Borisov, A.K.Kazansky and J.P.Gauyacq Phys.Rev.Lett. 80 (1998) 1996; Phys.Rev. B 59 (1999) 10935; Surf.Sci. 430 (1999) 165

-**Propagation in the static case** (fixed atom-surface distance):

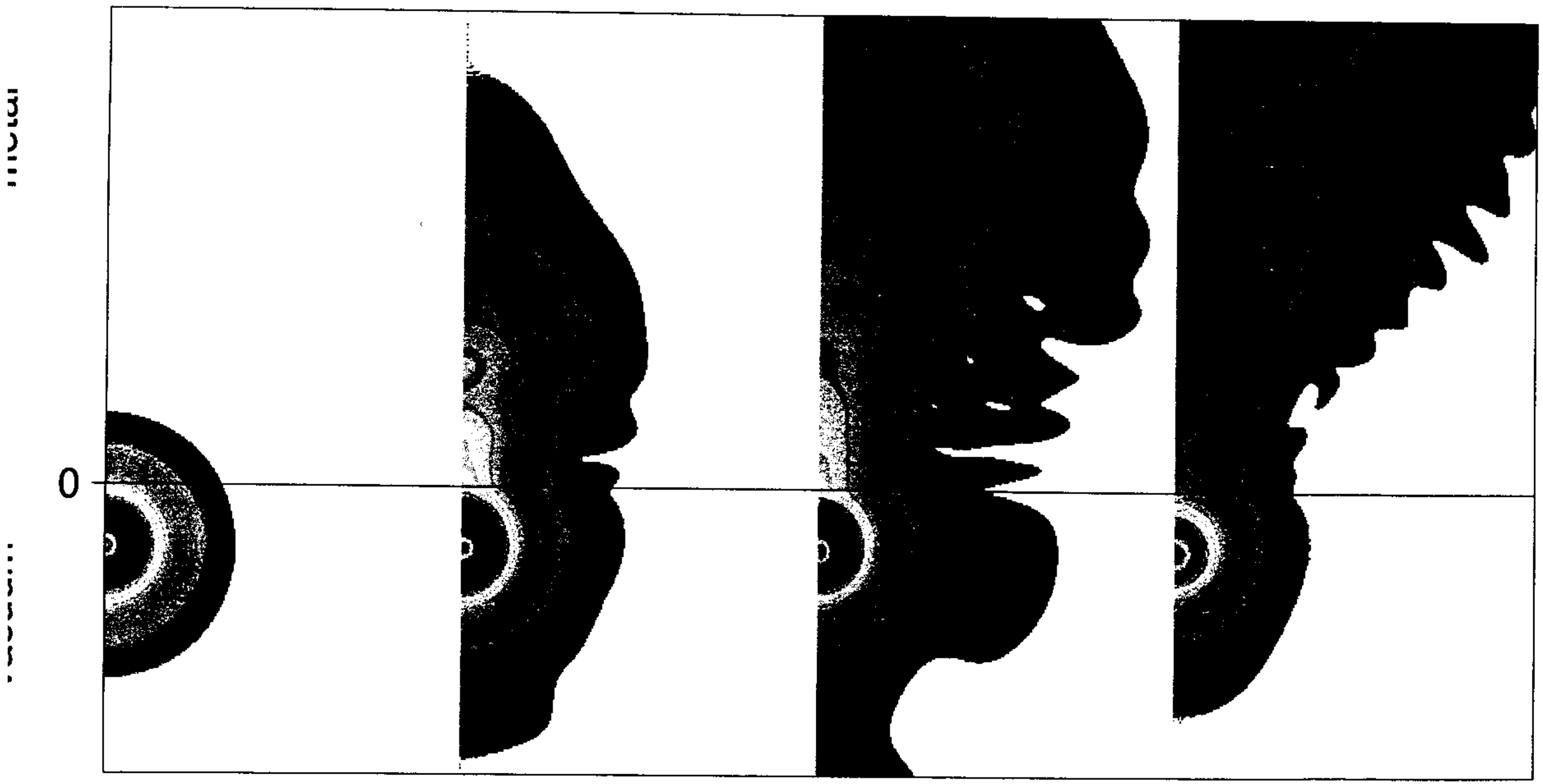
- **Survival amplitude :** $A(t) = \langle \Phi_0 | \Psi(t) \rangle$
- **Projected density of states :**

$$S(\omega)=\frac{1}{\pi}Re\left(\int_0^{\infty} A(t)e^{i\omega t}\,dt\right)$$

- The analysis of $A(t)$ and $S(\omega)$ yields the **energy and width** of the atomic levels.

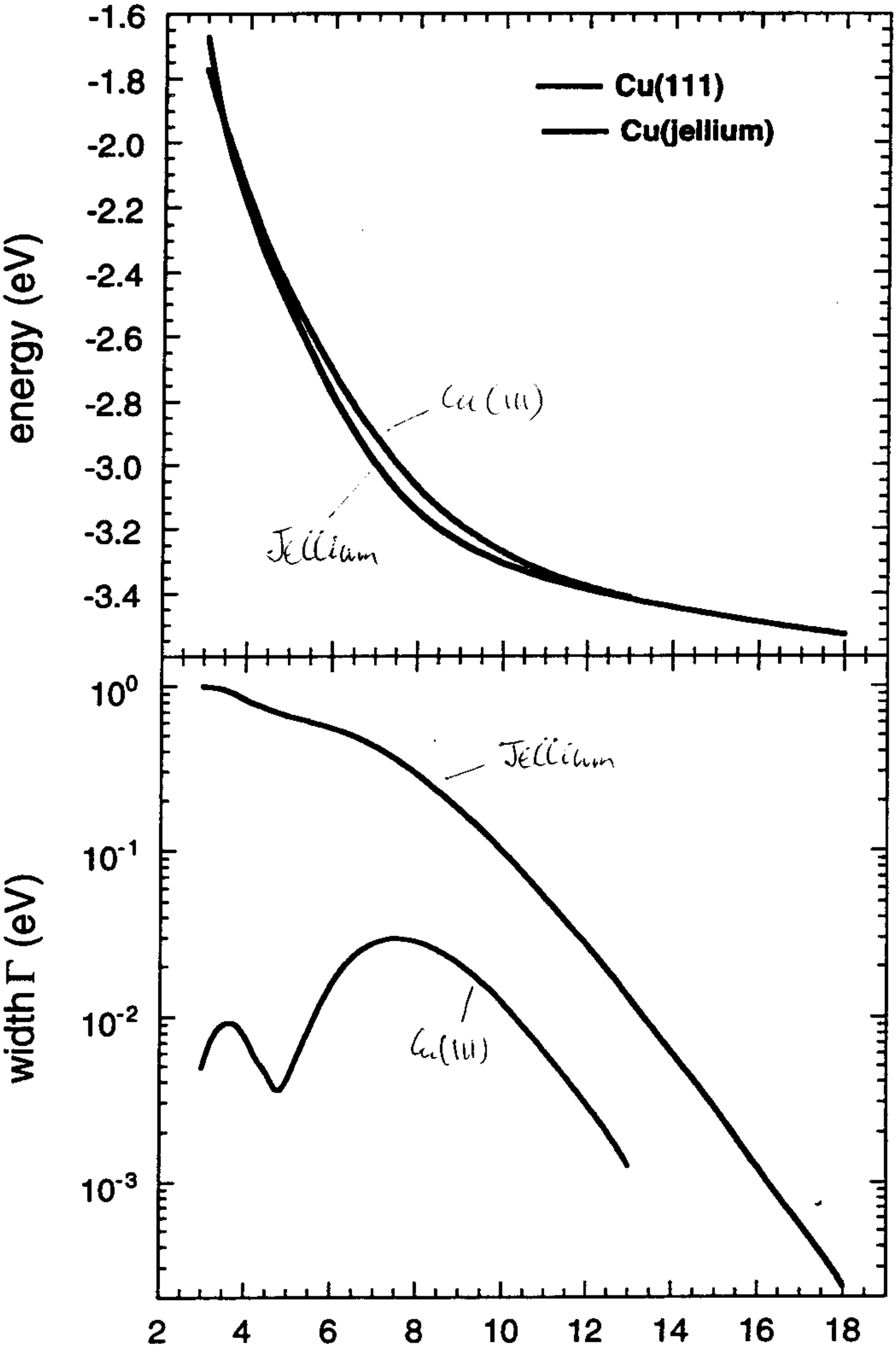
- **Excellent agreement** between the wave-packet propagation and the Coupled Angular Mode results for ‘jellium’ surfaces. Also with self-consistent studies using an LDA approach and a jellium metal (Lang and Williams, Phys.Rev.B 18 (1978) 616)

Cs(6s)/Jellium Metal. The Cs atom is placed at Z=10 a.u. from the image plane.



t=0 a.u. t=50 a.u. t=100 a.u. t=500 a.u.

Energy and width of the Cs(6s) level as a function of the atom-surface distance (measured from the image plane). Model Cu(111) case and Jellium metal case.



Results for the Cs/free electron Cu system

(see Borisov et al Phys.Rev. B 54 (1996) 17166 for other alkalis)

- **Energy of the level** function of Z, the adsorbate-surface distance

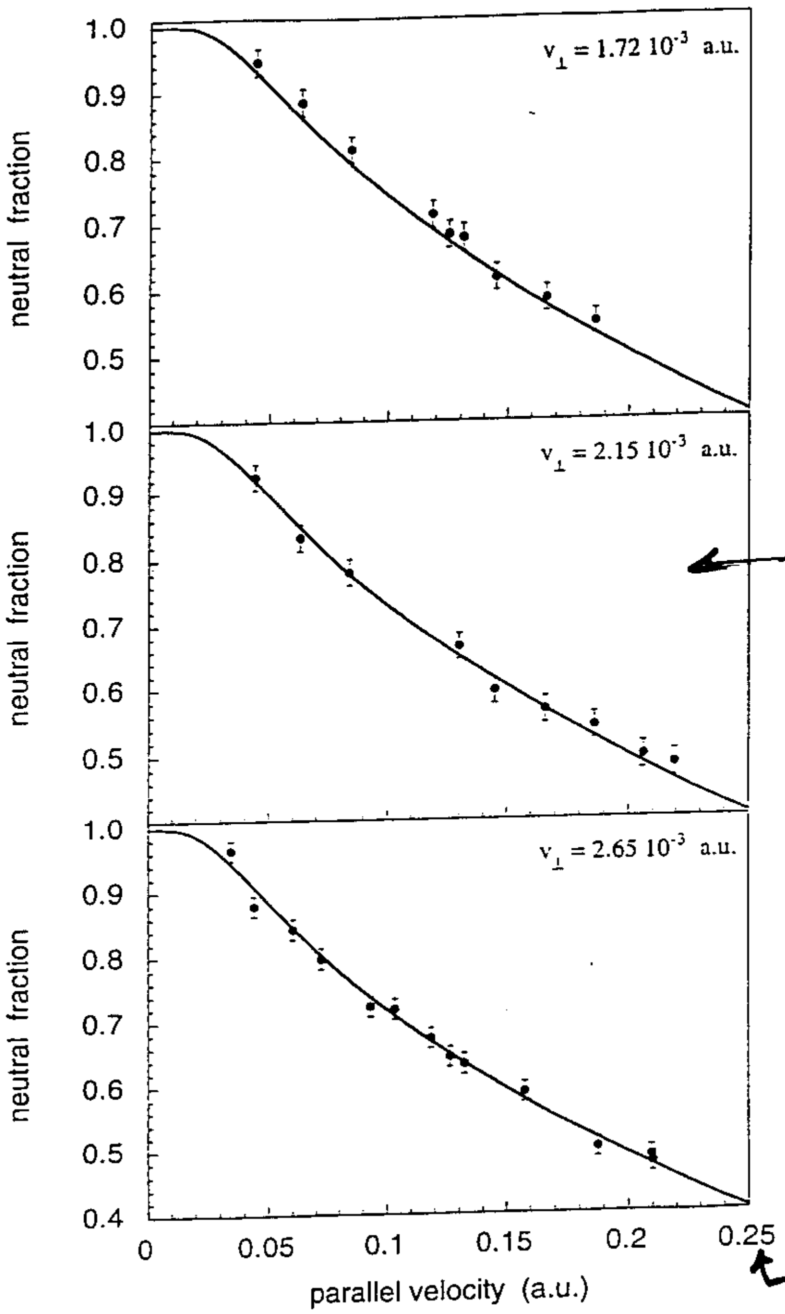
  Variation close to 1/4Z, **following the image charge interaction**

- **Width of the level**

  Exponential behaviour with Z, saturating around 1 eV at small Z

  (width of 1 eV ↔ lifetime of 0.66 fs)

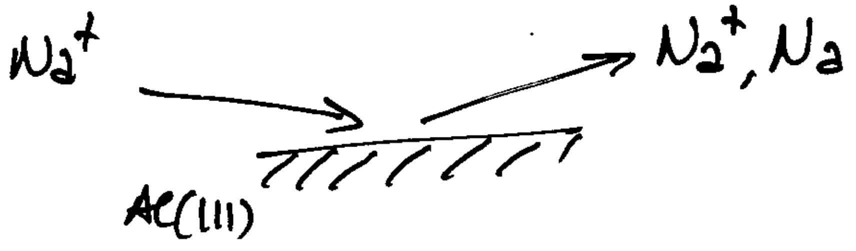
- **Very usual behaviour** for an atom(ion)-surface system



$E_\perp \simeq 2.6$ eV

$E_\parallel \simeq 36$ keV

Neutralisation probability of Na^+ on Al(111) in grazing collisions



Cu(111) model

(E.V.Chulkov, V.M.Silkin and P.M.Echenique, Surf.Sci. 437 (1999) 330)

→ **Inside Cu** :

$$V = V_0 + V_G \cos(Gz + \Phi)$$

(G : reciprocal lattice vector along z)

With V_0 = -11.895eV and V_G = 2.57eV, there exists a **band gap** (-5.83 eV,-0.69 eV) for the z motion.

→ **Free electron motion along the x and y co-ordinates**

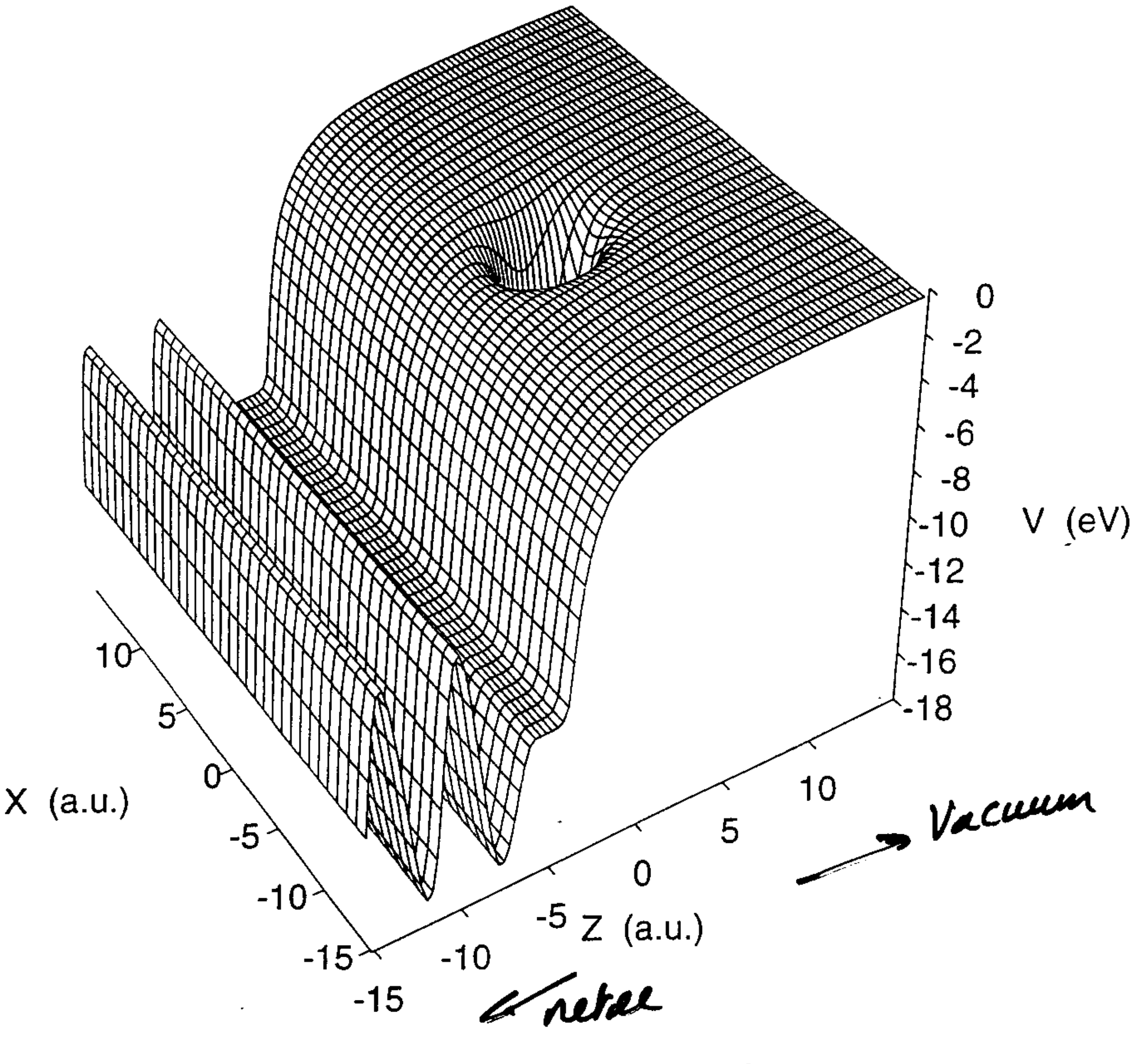
→ This potential is joined to a '**Jennings type**' **potential outside.** It is adjusted from an ab initio DFT study (Chulkov et al 1999). With this potential, the surface state and the first image state are located at -5.33 eV and -0.82 eV, with respect to vacuum.

References

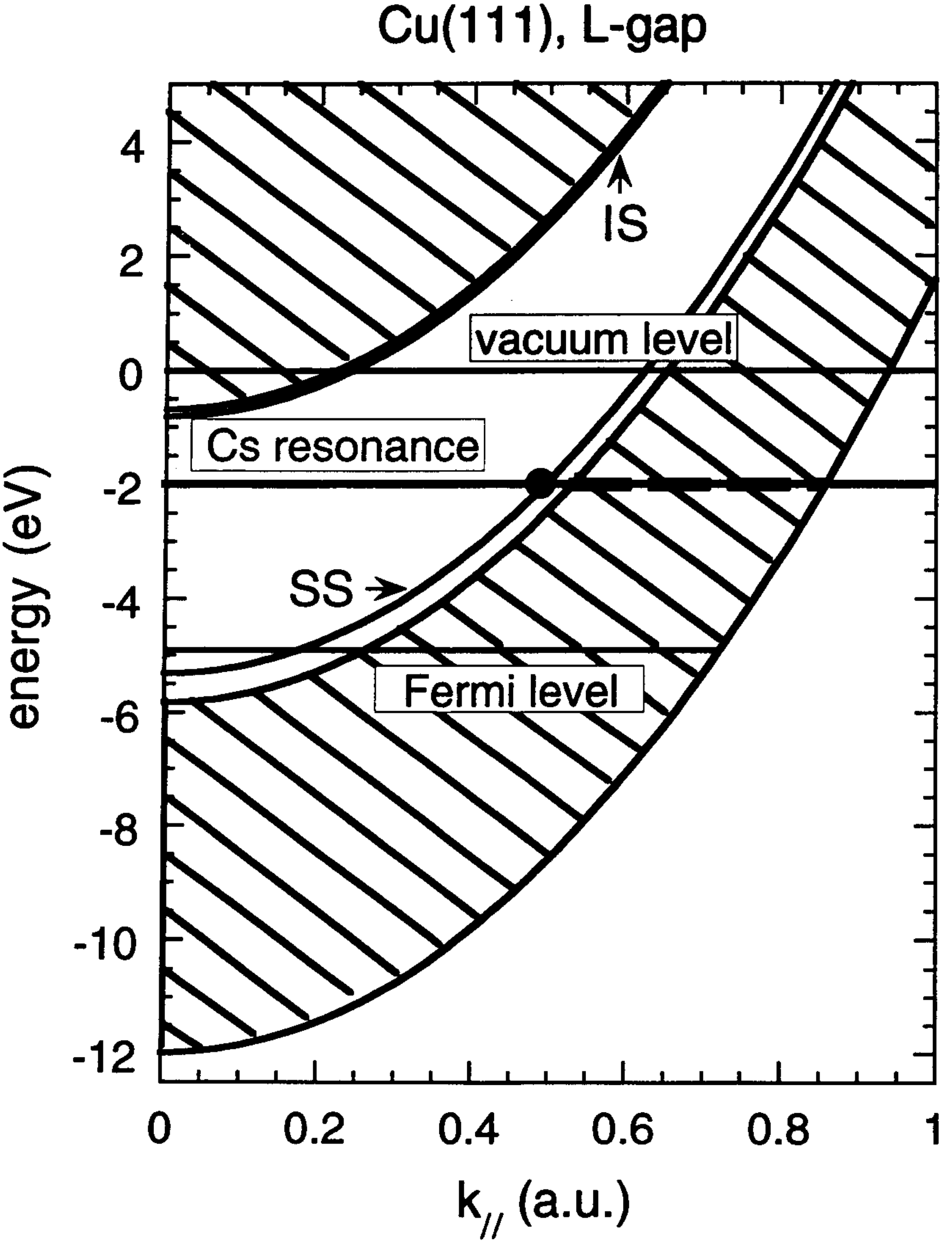
-M.C.Desjonquères and D.Spanjaard, Concepts in Surface Science, 1993, Springer.

-P.M.Echenique and J.B.Pendry, Prog.Surf.Sci. 32(1990)111.

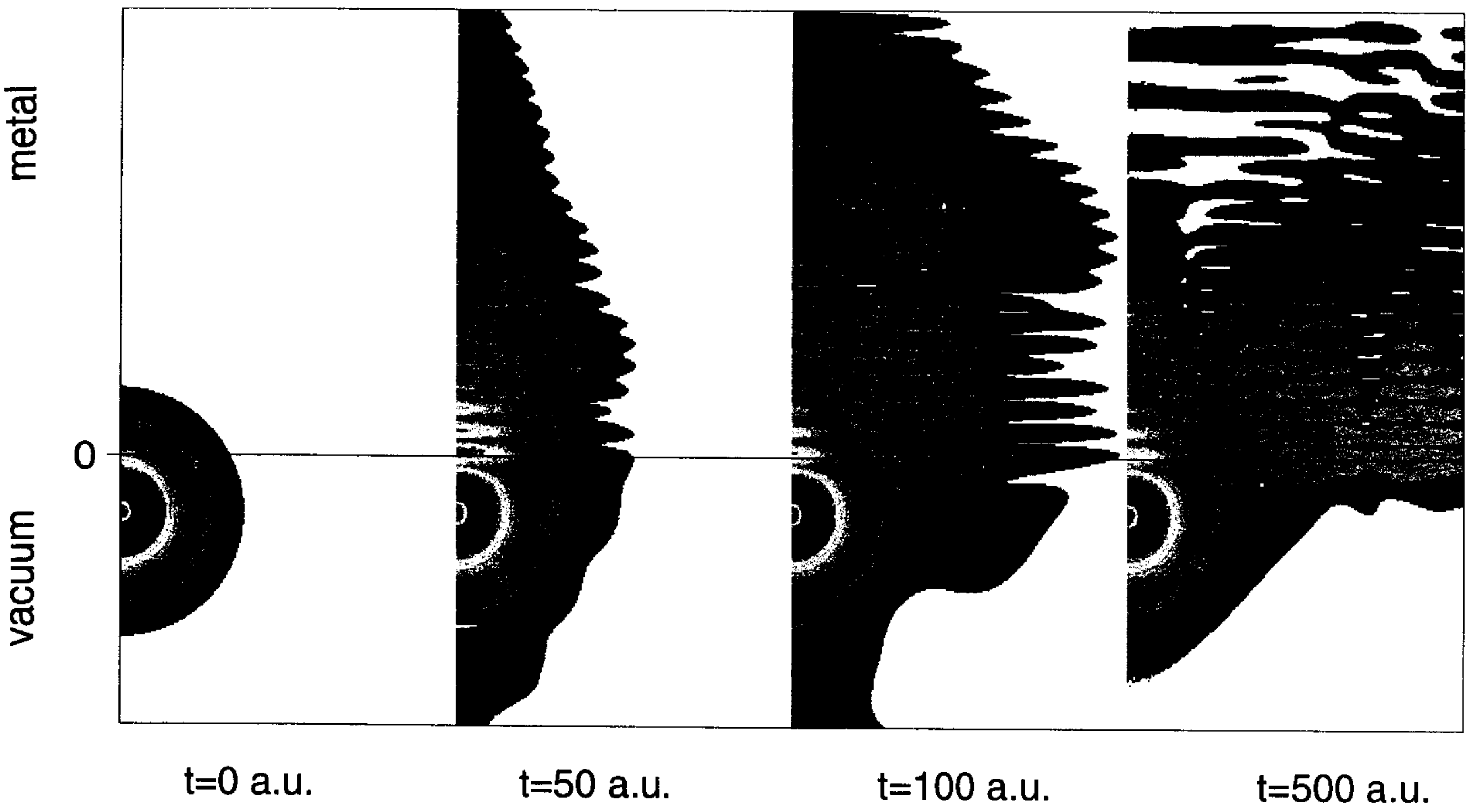
-E.V.Chulkov, V.M.Silkin and P.M.Echenique, Surf.Sci. 437 (1999) 330 and private communication.



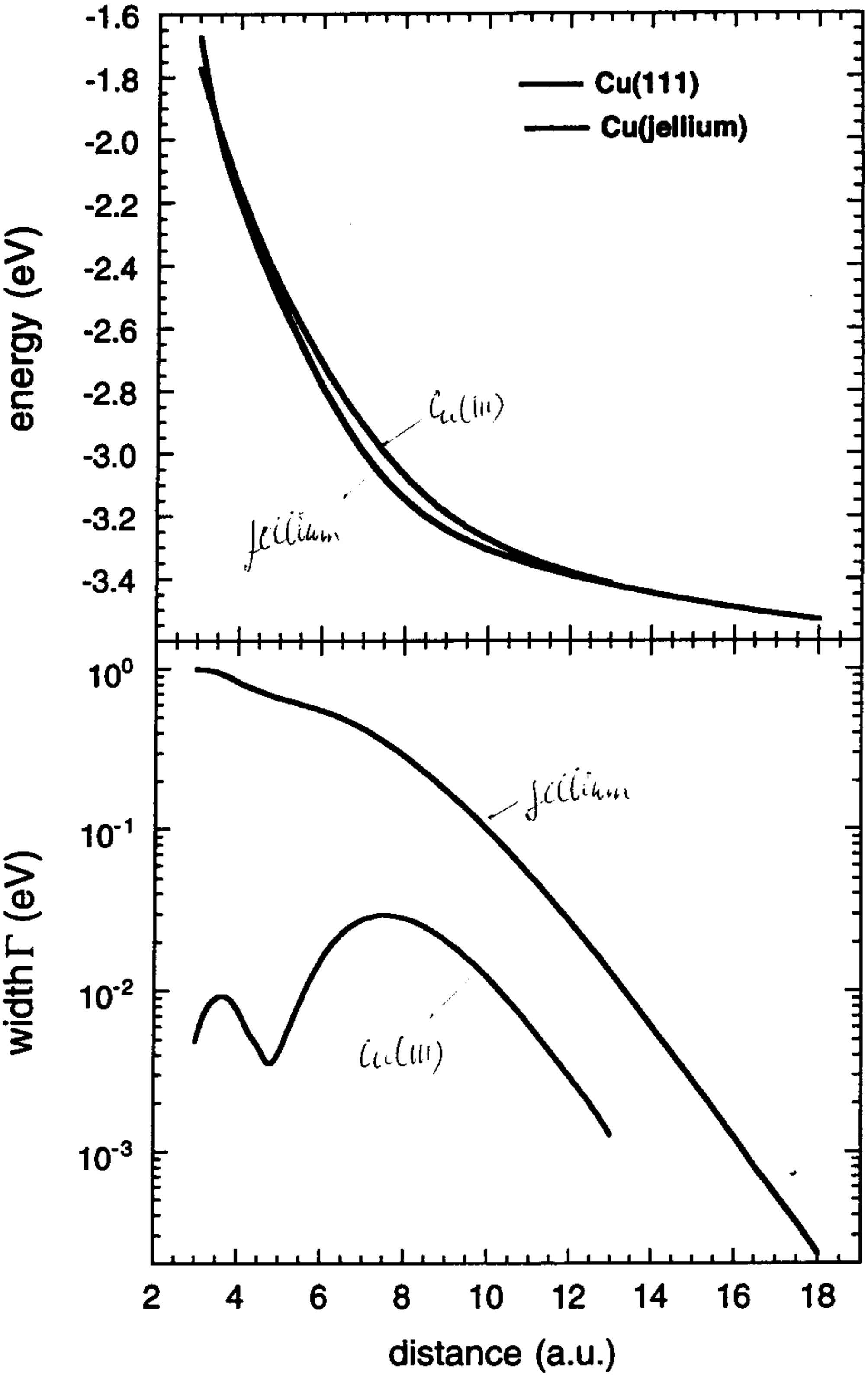
Model Cu(111) surface


Cu(111), L-gap
IS
vacuum level
Cs resonance
SS
Fermi level
energy (eV)
4
2
0
-2
-4
-6
-8
-10
-12
0
0.2
0.4
0.6
0.8
1
$k_{//}$ (a.u.)

Cs(6s)/Cu(111). The Cs atom is placed at Z=10 a.u. from the image plane.



Energy and width of the Cs(6s) level as a function of the atom-surface distance (measured from the image plane). Model Cu(111) case and Jellium metal case.



Comparison between Cs/free electron Cu and Cs/Cu(111) systems

(Borisov et al Surf.Sci. 430 (1999) 165)

- **Energy** of the level unperturbed

- Drastic decrease of the **level width**, in particular at small Z (adsorption at 3.5 a_0) : blocking of the RCT !

- **Wave-packet at Z = 3.5 a_0**
  - -Polarisation of the atomic wave-function
  - -No decay along the surface normal
  - -Decay to the 3D bulk states with a finite $k_{\parallel}$
  - -Decay to the surface state very weak

The very **efficient blocking of the RCT comes from the interplay of the band gap and polarisation effects**, which results in the suppression of the decay to the 3D bulk states around ($k_{\parallel} = 0$) and to the quasi-suppression of the decay to the surface state.

Effect of the electron-electron interactions

Since the 1e$^-$-effect on the evolution (RCT) is weak, one should look at the 2e$^-$-effects.

- **Combined study of the RCT and 2e$^-$ interactions**

(Borisov, Gauyacq, Kazansky, Chulkov, Silkin and Echenique, to be published)

The electron wave packet taking into account the RCT is used as the initial state for the treatment of the 2e$^-$-interactions in a **many-body self energy approach** (See P.Echenique talk)

→ **The 2e$^-$-interactions are dominating the decay in the Cs/Cu(111) case**

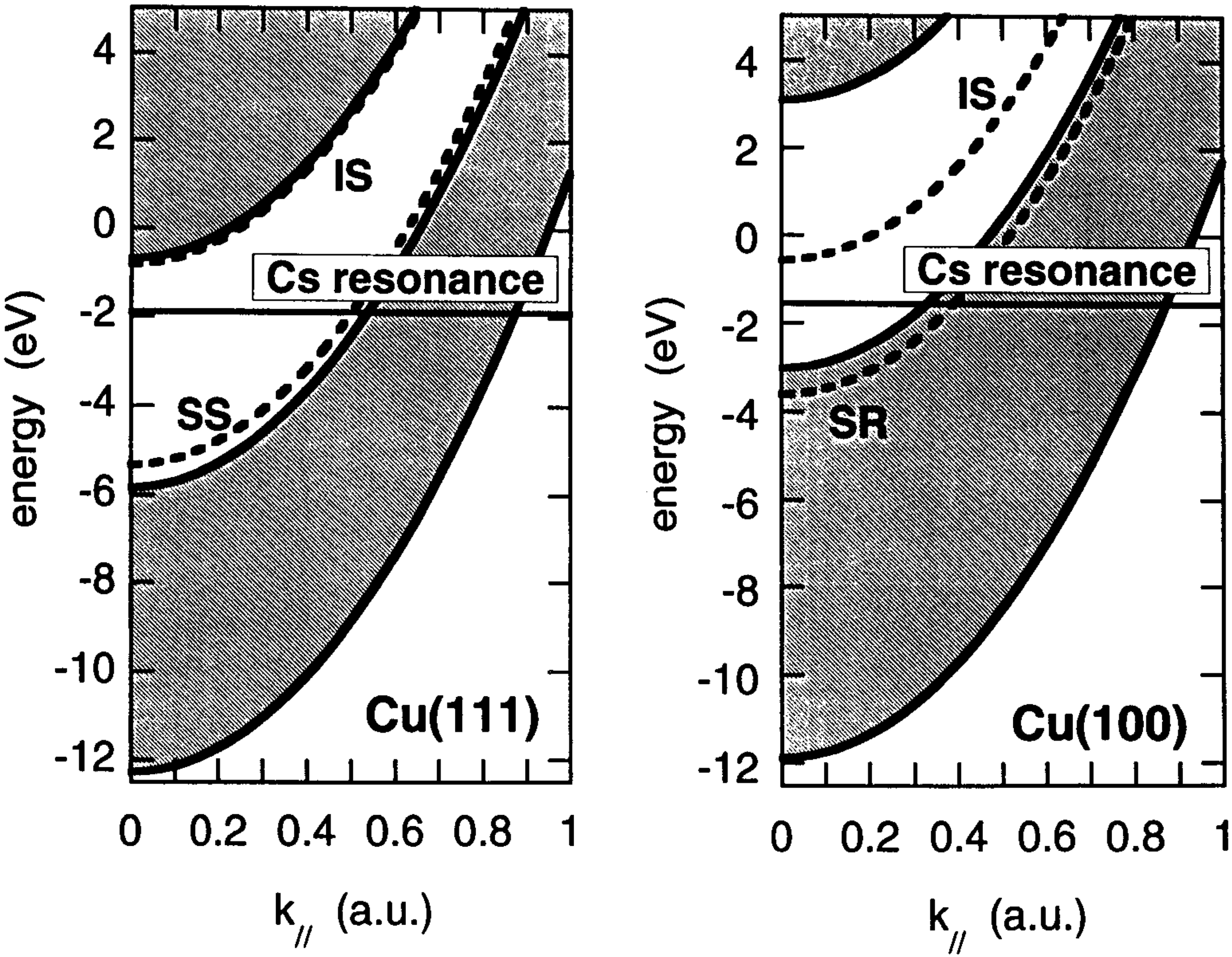
→ The RCT blocking is less efficient and the **RCT is dominating the decay in the Cs/Cu(100).**

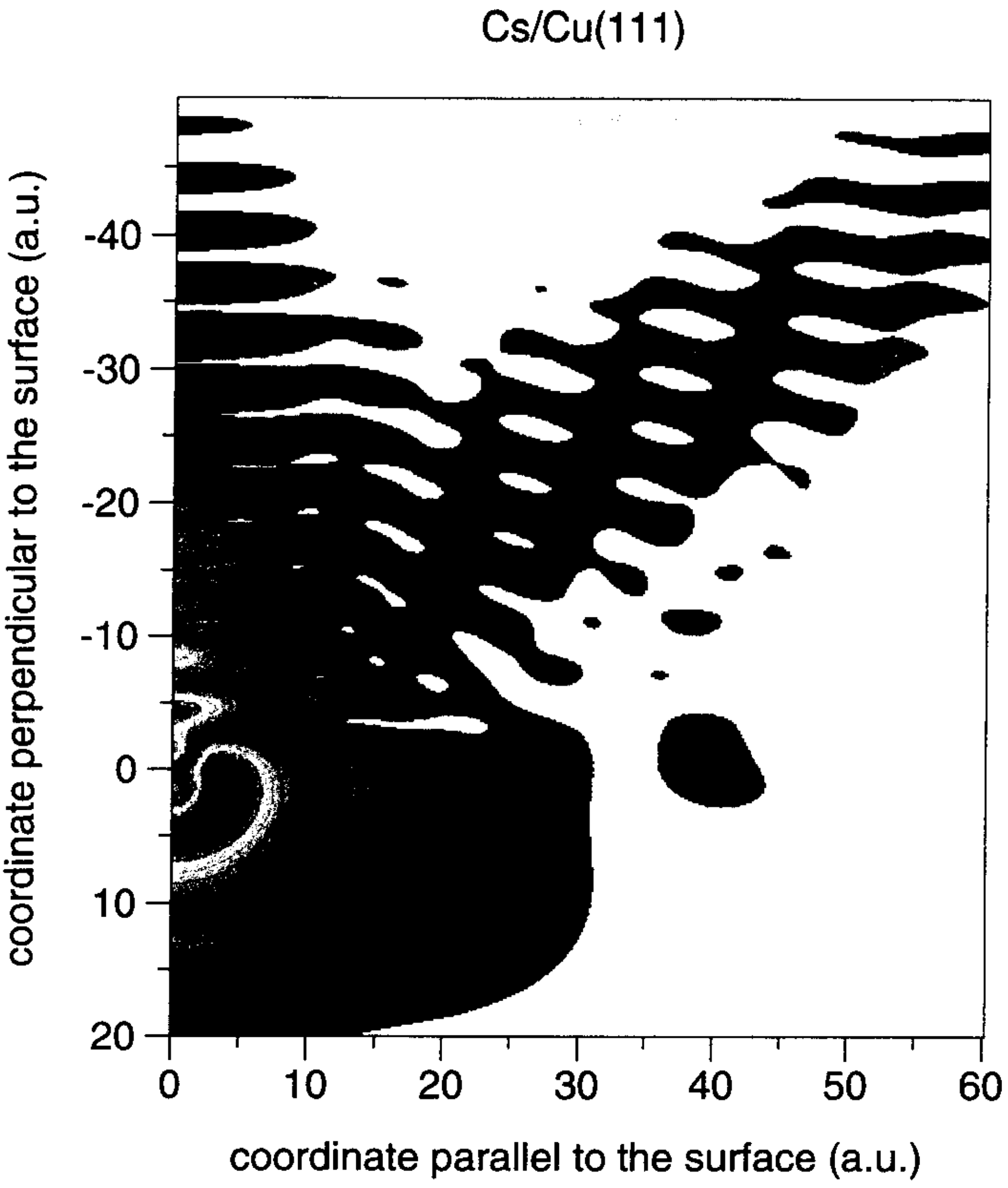
→ The difference between the two surfaces is attributed to the different positions of the Cs level in the band gap that results in different RCT blocking effects (the blocking is weaker when the level is low in the gap and the role of the surface state is different)

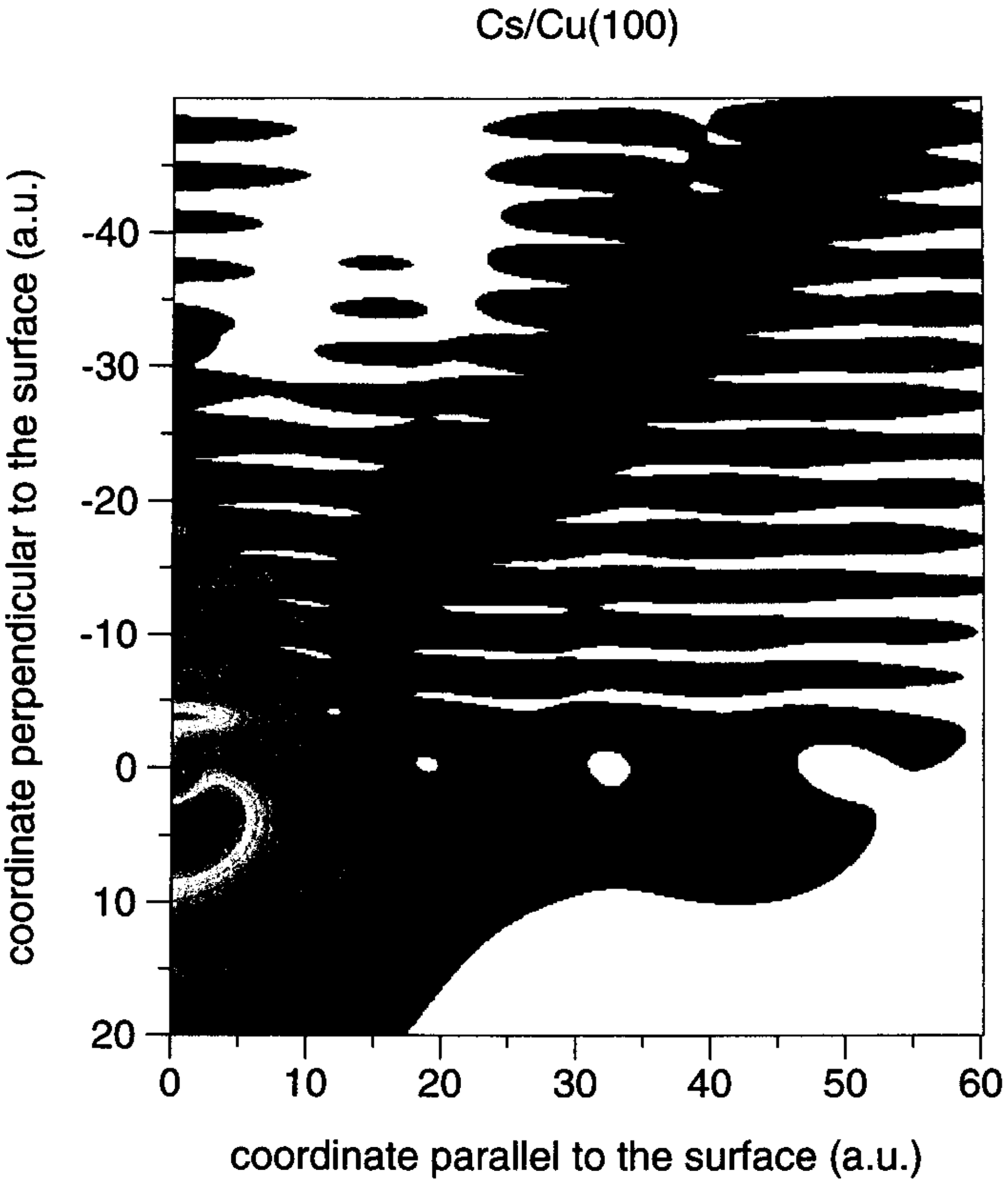
Decay rates

for the Cs/Cu(111) and Cs/Cu(100) systems

	Cs/Cu(111)	Cs/Cu(100)
EXPERIMENTS		
Transient state life-time, Bauer et al Phys.Rev.B 55 (1997) 10040	**15 ± 6 fs**	**6 ± 4 fs**
Transient state life-time, Ogawa et al Phys.Rev.Lett. 82 (1999) 1931	**50 fs**	
THEORETICAL RESULTS		
Free electron metal, Γ_{RCT} ($1/\Gamma_{RCT}$)	**900 meV** (0.7 fs)	**900 meV** (0.7 fs)
Cu, Γ_{RCT}, **one electron decay**	7 meV	112 meV
Cu, Γ_{ee}, **inelastic electron-electron decay**	16.5 meV	20 meV
Cu, $\Gamma_{T} = \Gamma_{RCT} + \Gamma_{ee}$, **Total decay rate**	23.5 meV	132 meV
Cu, **Transient state life time** ($1/\Gamma_T$) (Borisov, Gauyacq, Kazansky, Chulkov, Silkin and Echenique, to be published)	**28 fs**	**5 fs**


energy (eV)
4
2
0
-2
-4
-6
-8
-10
-12
IS
Cs resonance
SS
Cu(111)
0
0.2
0.4
0.6
0.8
1
$k_{//}$ (a.u.)
energy (eV)
4
2
0
-2
-4
-6
-8
-10
-12
IS
Cs resonance
SR
Cu(100)
0
0.2
0.4
0.6
0.8
1
$k_{//}$ (a.u.)


Cs/Cu(111)
coordinate perpendicular to the surface (a.u.)
-40
-30
-20
-10
0
10
20
0
10
20
30
40
50
60
coordinate parallel to the surface (a.u.)


Cs/Cu(100)
coordinate perpendicular to the surface (a.u.)
-40
-30
-20
-10
0
10
20
0
10
20
30
40
50
60
coordinate parallel to the surface (a.u.)

Model study of the effect of the coverage

-Treated using the **model** of Goryunov et al (Surf.Sci. 401 (1998) 206)

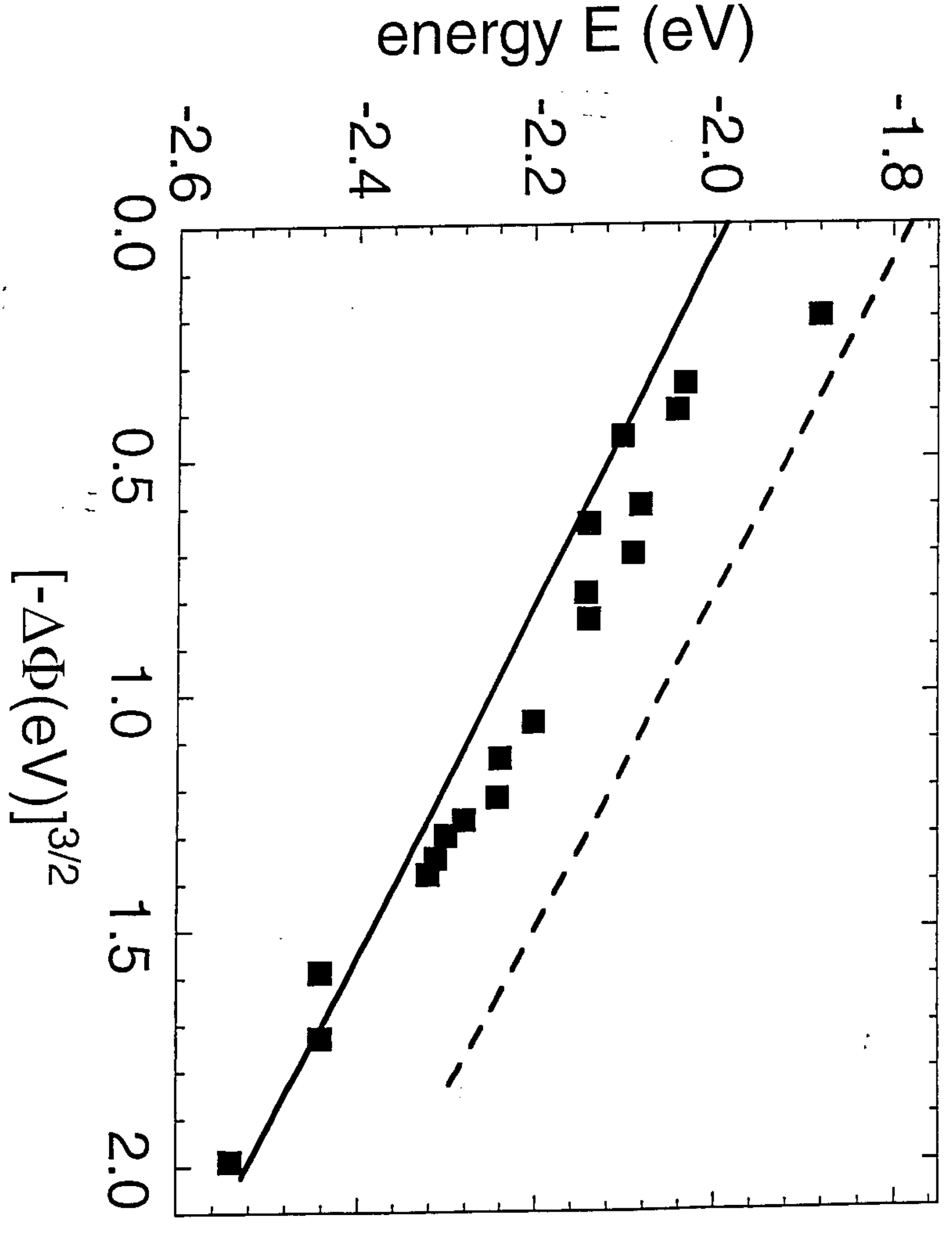
It introduces the **electrostatic interaction** between a given adsorbate and the others as the **dipole potential** created by the adsorbates (related to the surface work function change). The adsorbates being rather far one from the other, the electrostatic potential is then represented as that of a **dipolar plane.**

Results:

-Little effect on the RCT decay rate

-Change of the level energy roughly linear in $\Delta\Phi^{3/2}$ ($\Delta\Phi$: change of the surface work-function)

-Good agreement with the experimental results of Bauer et al (1997)


energy E (eV)
-1.8
-2.0
-2.2
-2.4
-2.6
0.0
0.5
1.0
1.5
2.0
$[-\Delta\Phi(\mathrm{eV})]^{3/2}$

Consequences in scattering experiments

Charge transfer in ion(atom)-metal surface scattering

Changes in the charge transfer rates should lead to differences between collisions on surfaces with or without projected band gap !

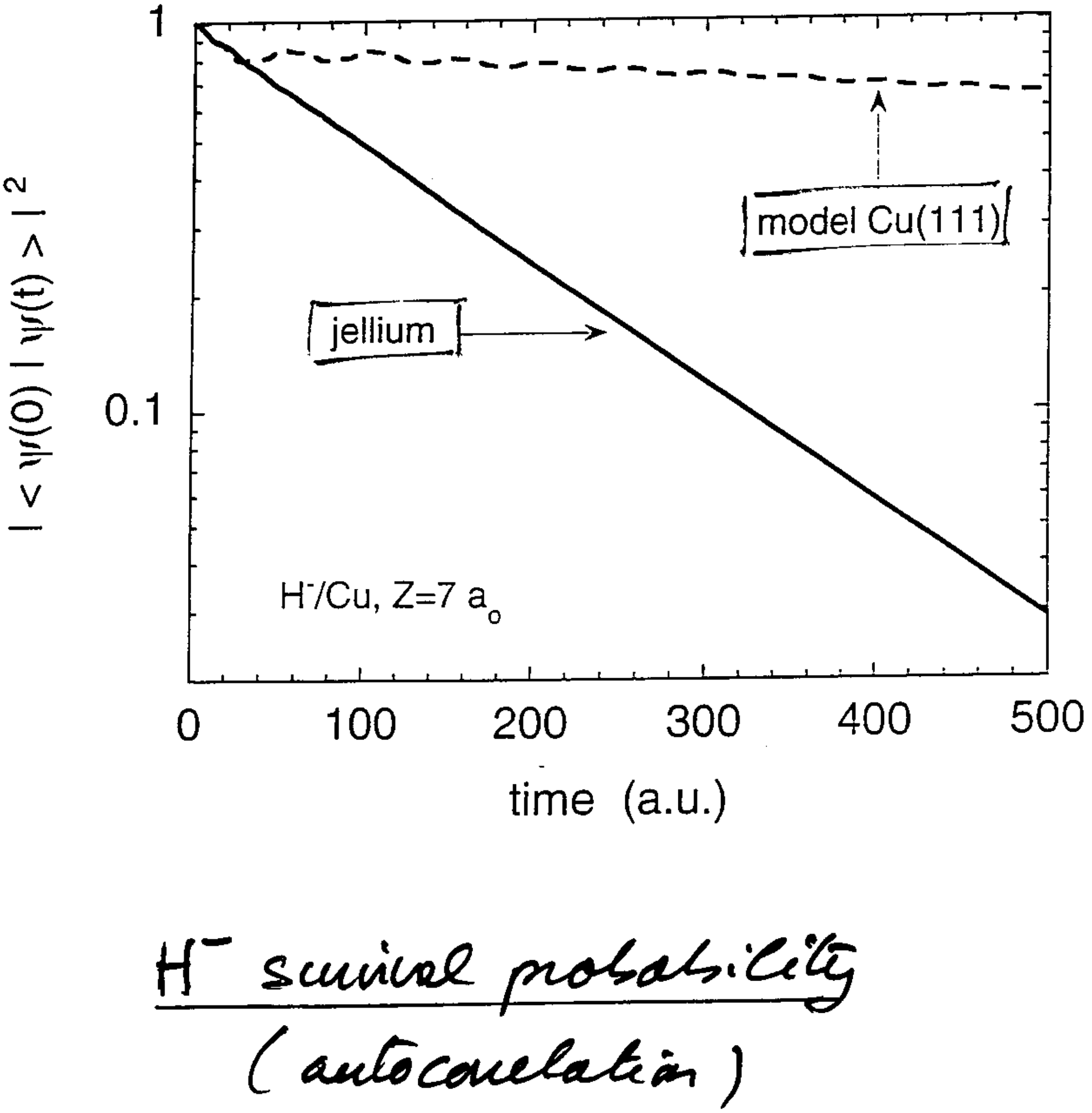
Two special aspects:

- The RCT blocking effect of the projected band gap is **time dependent,** it is not present on short time scales.

(A.G.Borisov, A.K.Kazansky and J.P.Gauyacq Phys.Rev.Lett. 80 (1998) 1996; Phys.Rev. B 59 (1999) 10935; Experiment : L.Guillemot and V.A.Esaulov Phys.Rev.Lett. 82 (1999) 4552)

- The role played in the RCT by the **2D surface state continuum** is different from that played by the **continuum of 3D propagating bulk states.** This is quite visible in **grazing angle scattering**

(T.Hecht, H.Winter, A.G.Borisov, J.P.Gauyacq and A.K.Kazansky, Phys.Rev.Lett. 84 (2000) 2517)



H⁻ survival probability

(autocorrelation)

How general is the stabilisation effect observed in Cs/Cu(111)?

Experiments

Alkali on metal surfaces with a projected band gap

Cs/Cu(111)	15-50 fs
Cs/Cu(100)	6 fs
Rb/Cu(111)	20 fs
Cs/Ag(111)	> 7 fs
Na/Cu(100)	> 4 fs

(Bauer et al Phys Rev B 60 (1999) 5016 ; Ogawa et al Surf.Sci. 451 (2000) 22)

($2\pi^*$) CO/Cu(111) 0.8-5 fs (free CO : 0.8 fs)

(Bartels et al PRL 80(1998)2004; E.Knoesel et al CPL 240(1995)409)

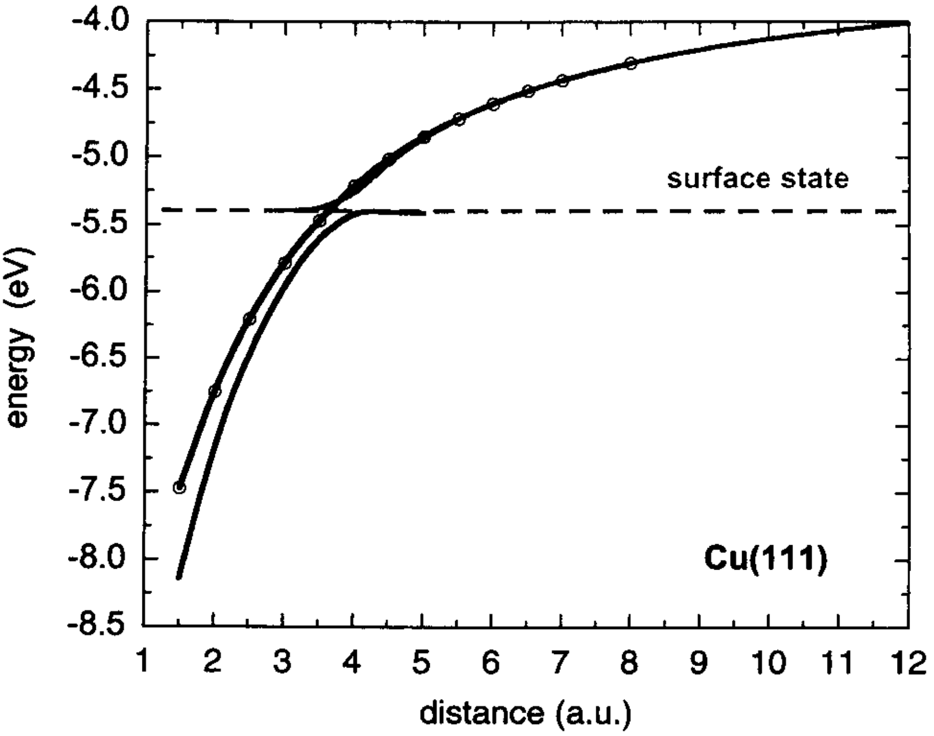
Theory

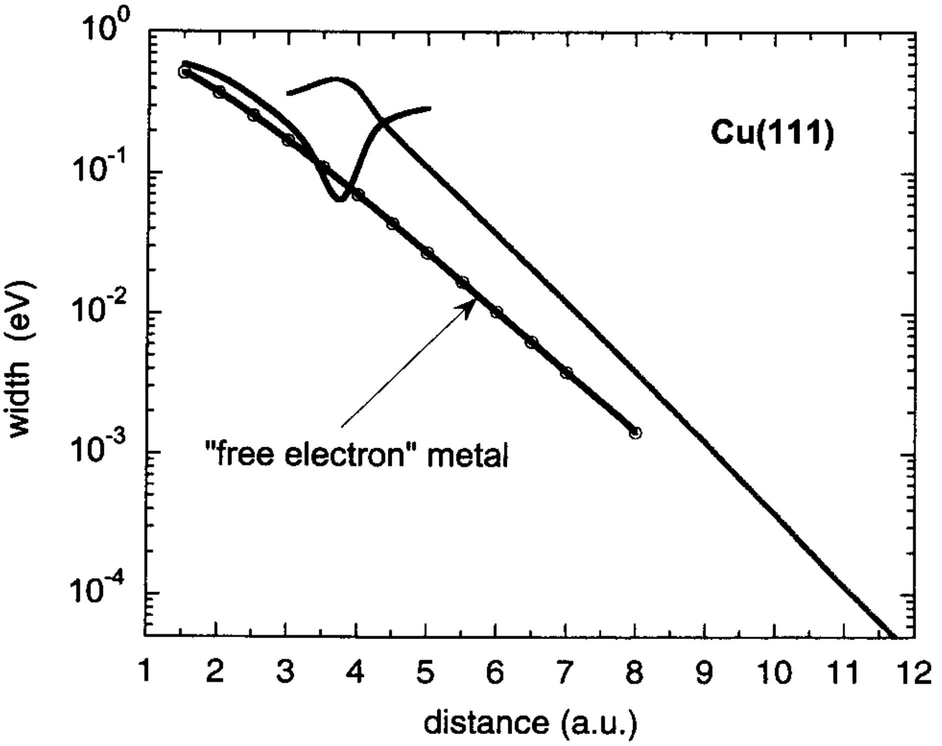
- **stabilisation for the alkalis (Li, Na, K, Cs) compared to the free electron metal surface case;** Cs exhibits the strongest effect : 28 fs on (111) and 5 fs on (100)
- **H^-/Cu(111)** : stabilisation at large ion-surface distance
- **F^-/Cu(111), Ag(111)** : strong perturbation by the band gap but no stabilisation
- **($2\pi^*$)CO/Cu(111) and Cu(100)** : stabilisation at large molecule surface distance, none at the adsorption distance.

($2\pi^*$)CO/Cu(111) **τ~0.26 fs ; E ~ 4 eV** (above Fermi level)

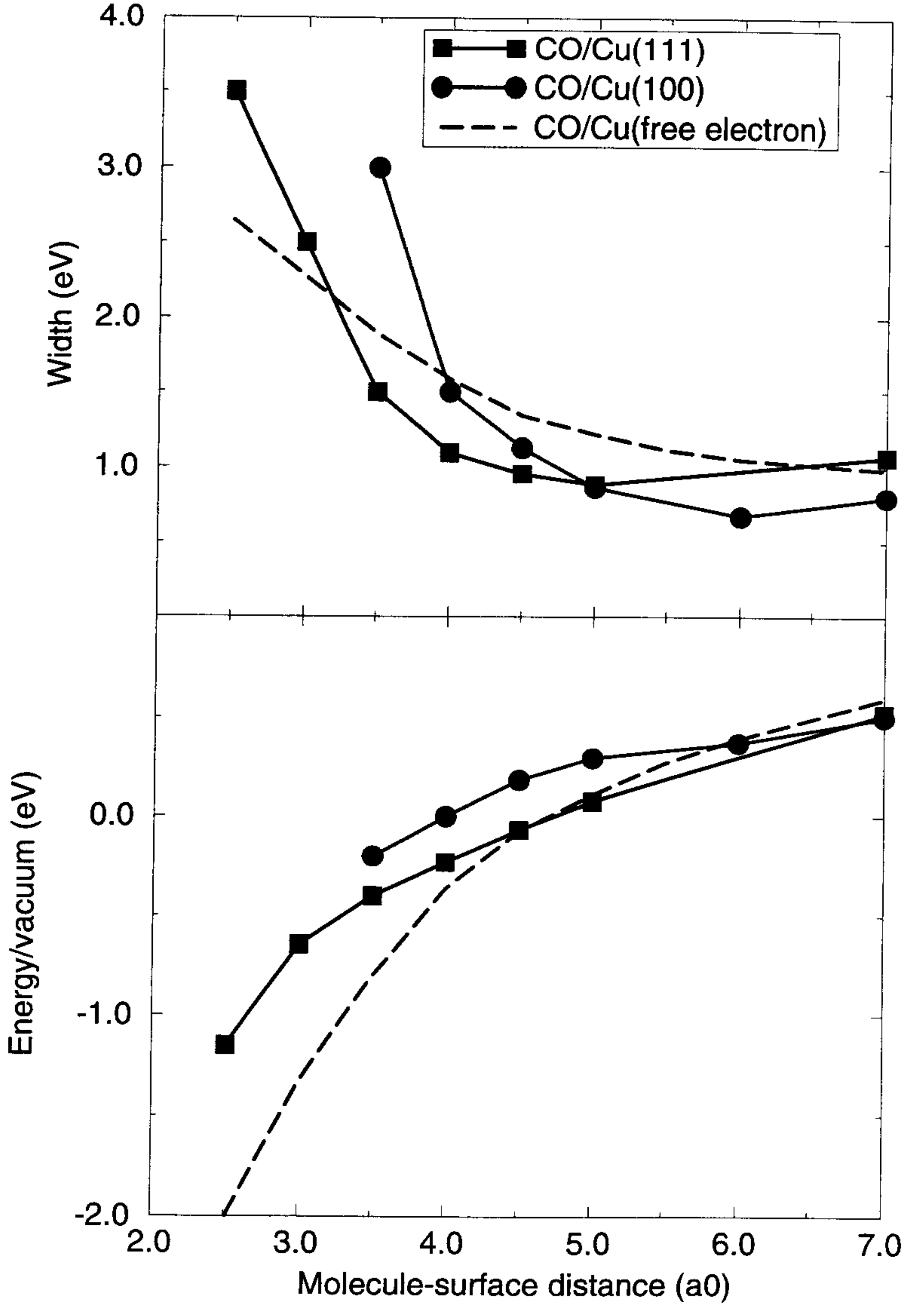
τ~0.3 fs for a free electron metal

F⁻/Cu(111)


energy (eV)
-4.0
-4.5
-5.0
-5.5
-6.0
-6.5
-7.0
-7.5
-8.0
-8.5
surface state
Cu(111)
1
2
3
4
5
6
7
8
9
10
11
12
distance (a.u.)


width (eV)
10^0
10^-1
10^-2
10^-3
10^-4
Cu(111)
"free electron" metal
1
2
3
4
5
6
7
8
9
10
11
12
distance (a.u.)

CO on Cu surfaces



(J.P. Gauyacq, A.G. Borisov and G. Raseev, to be published)

Differences between the CO(2π*)/Cu(111) and Cs/Cu(111) systems

	CO(2π*)	Cs
	Negative ion	**Neutral**
Polarisation effect	**Electron attracted toward the surface**	**Electron repelled from the surface**
Free species	**Unstable ion**	**Stable atom**

CONCLUSIONS

- Study of the **Resonant Charge Transfer** process in the adsorbate/metal surface system
    - ➧determination of the **energy and lifetime of excited electronic states at surfaces.**

- The **Wave Packet Propagation** method is very efficient in this context
    - ➧characteristic of the adsorbate levels
    - ➧**analysis of the process via the wave packet pictures.**

- The **RCT process can be blocked** by the presence of a projected band gap (ex.: Cu(111) surface)
    - ➧very low RCT decay rate
    - ➧importance of the e^--e^- interactions

- In the **Cs/Cu(111)** system, this leads to **very long lived states** in the few 10's fs range.

- The blocking is due to **an interplay between the band gap, the adsorbate polarisation and the role of the surface state.** It is not a general feature.
    - ➧It can lead to important consequences in the sense that it can help **promote excited state mediated reactions at surfaces.**