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UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

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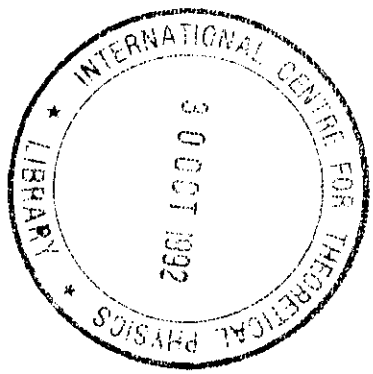
SMR. 628 - 25

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)

"HREELS and ARUPS of Physisorbed N_2"



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These are preliminary lecture notes, intended only for distribution to participants.

HREELS AND ARUPS OF PHYSISORBED N_2

MICHELE BERTOLO
SINCROTRONE TRIESTE

MEASUREMENTS PERFORMED AT
FRITZ-HABER-INSTITUT, BERLIN

K. JACOBI

M. BERTOLO
W. HANSEN
C. ASTALDI

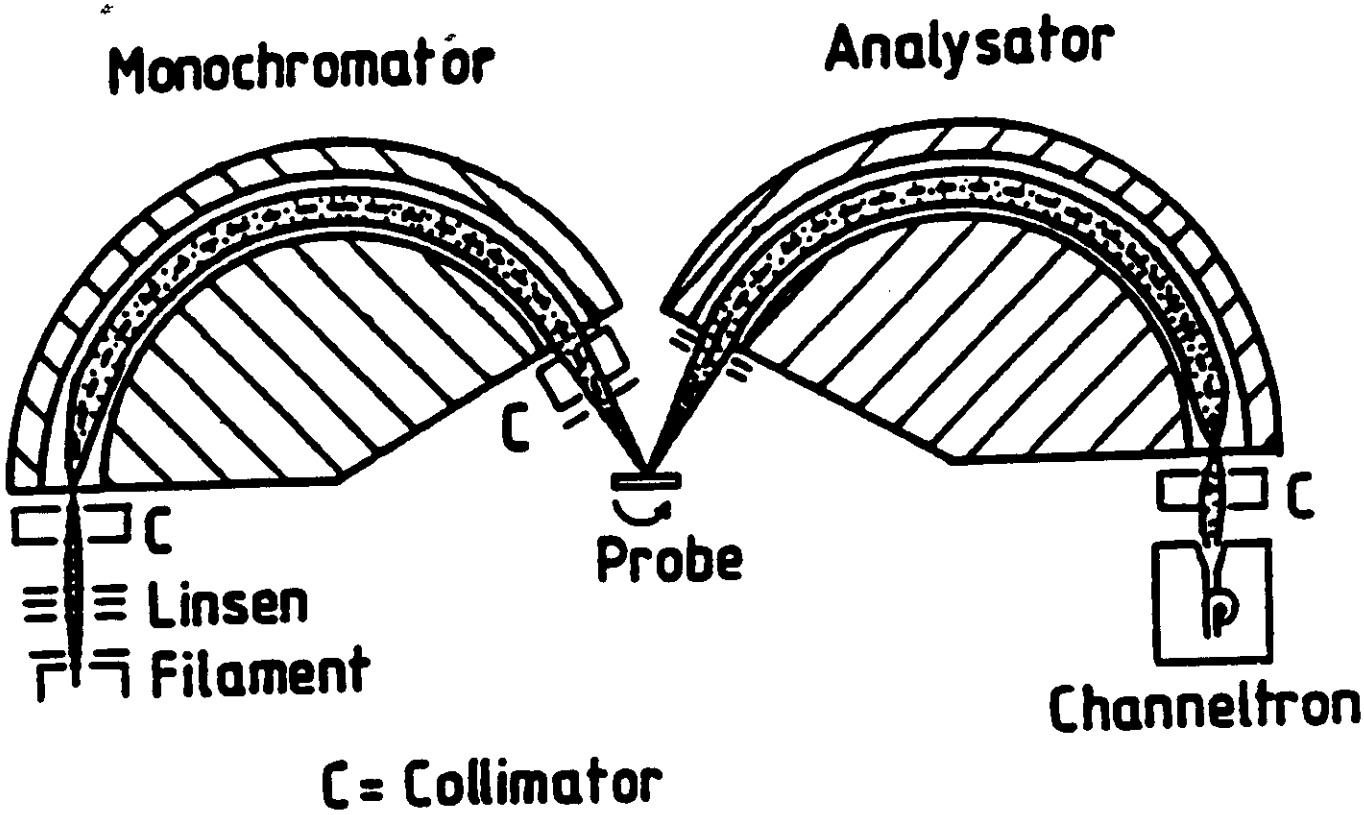
PHYSISORPTION : WEAK INTERACTION BETWEEN SURFACE AND ADSORBED SPECIES

MOTIVATION : INTERMEDIATE CASE BETWEEN ATOMIC (MOLECULAR) PHYSICS AND CONDENSED MATTER PHYSICS

HREELS (HIGH RESOLUTION ELECTRON ENERGY LOSS SPECTROSCOPY)

NEGATIVE ION RESONANCE : $N_2/Al(111)$

- RESONANCE IN E_p
- OVERTONES OF $\nu(N-N)$
- ANGULAR DISTRIBUTION
- OVERTONES OF $\nu(M-N_2)$



C = Collimator

a) RESONANCE IN E_p AND MECHANISM

 SURF. SCI. 223 (1989) 569

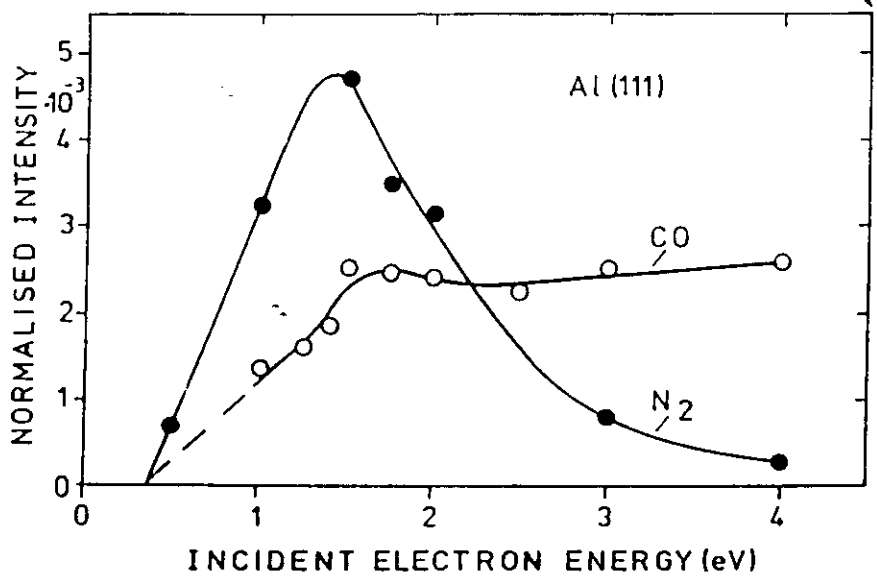
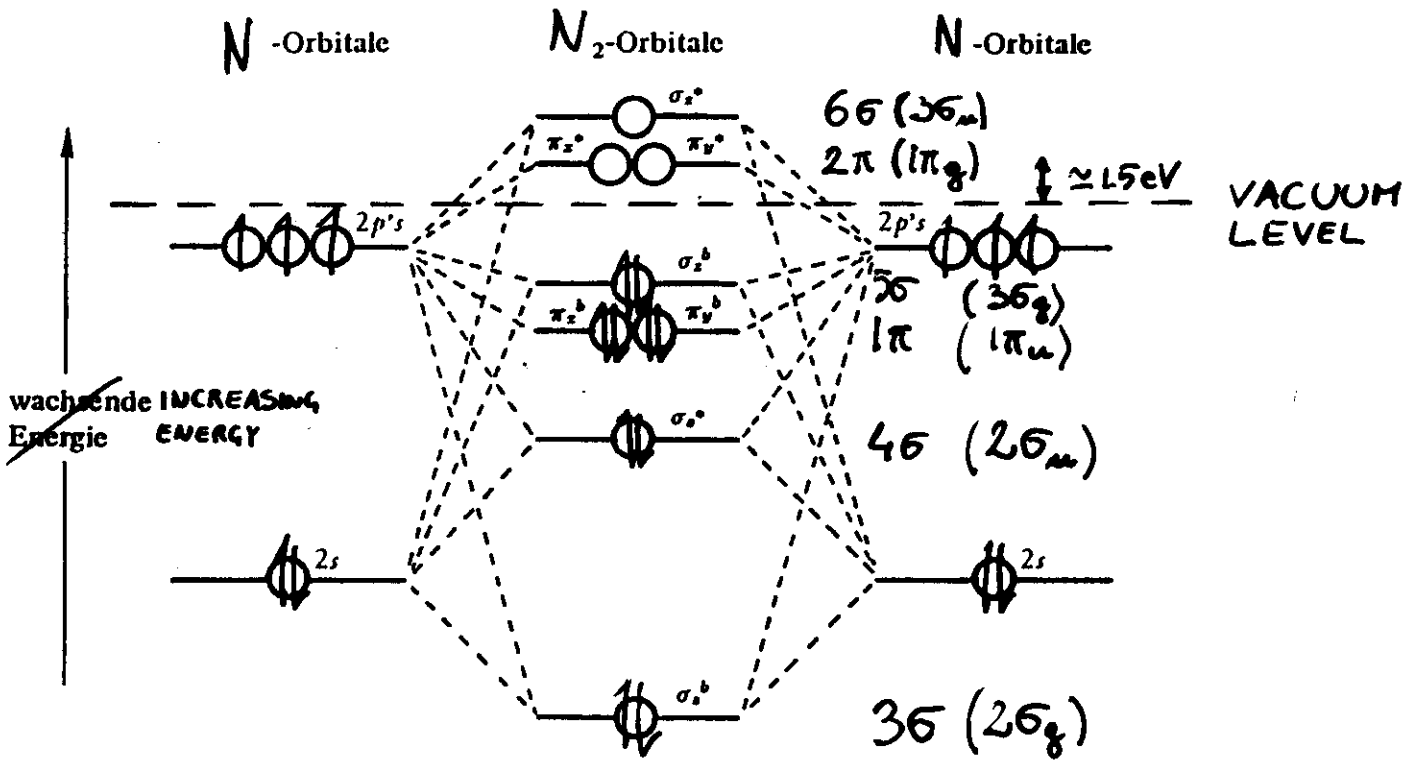
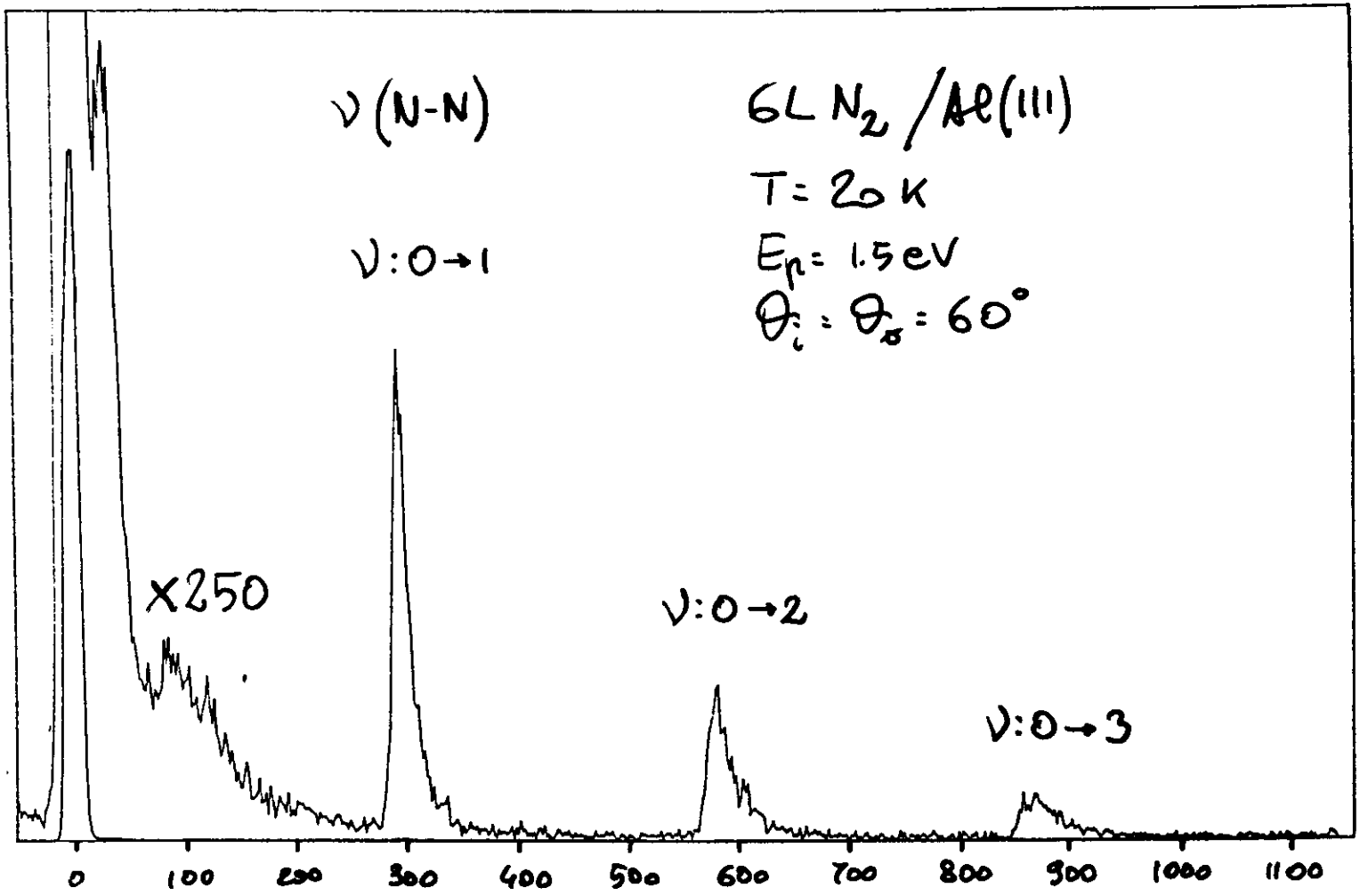
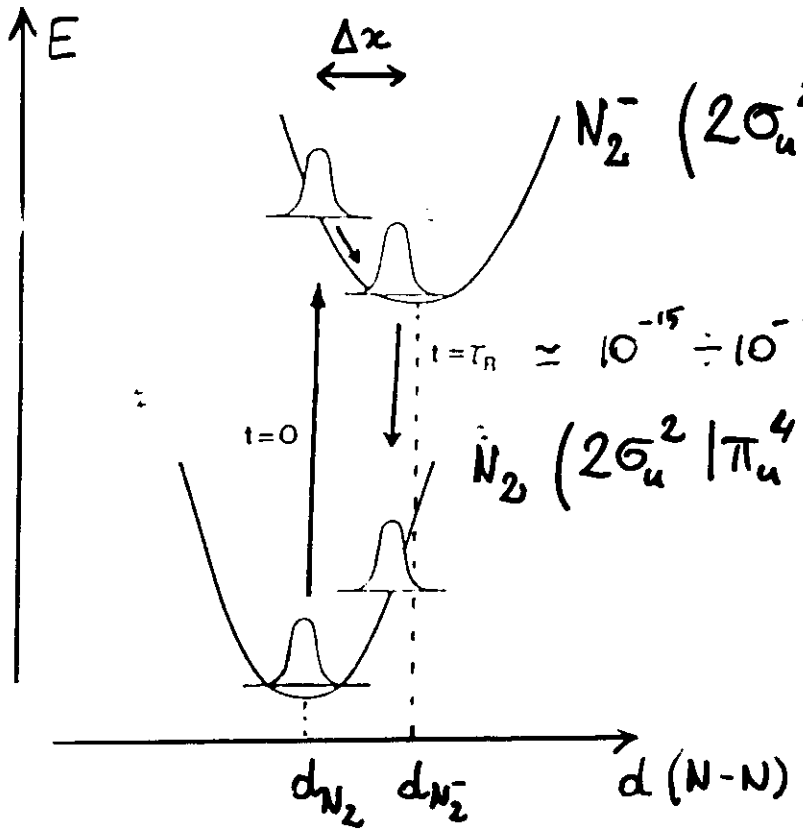


Fig. 3. Loss intensities due to the first stretching vibrations is given as function of energy of the incoming electrons for monolayers of N_2 and CO on Al(111).



β) OVERTONES OF ν(N-N)





$$\Delta r = F \cdot \tau_R$$

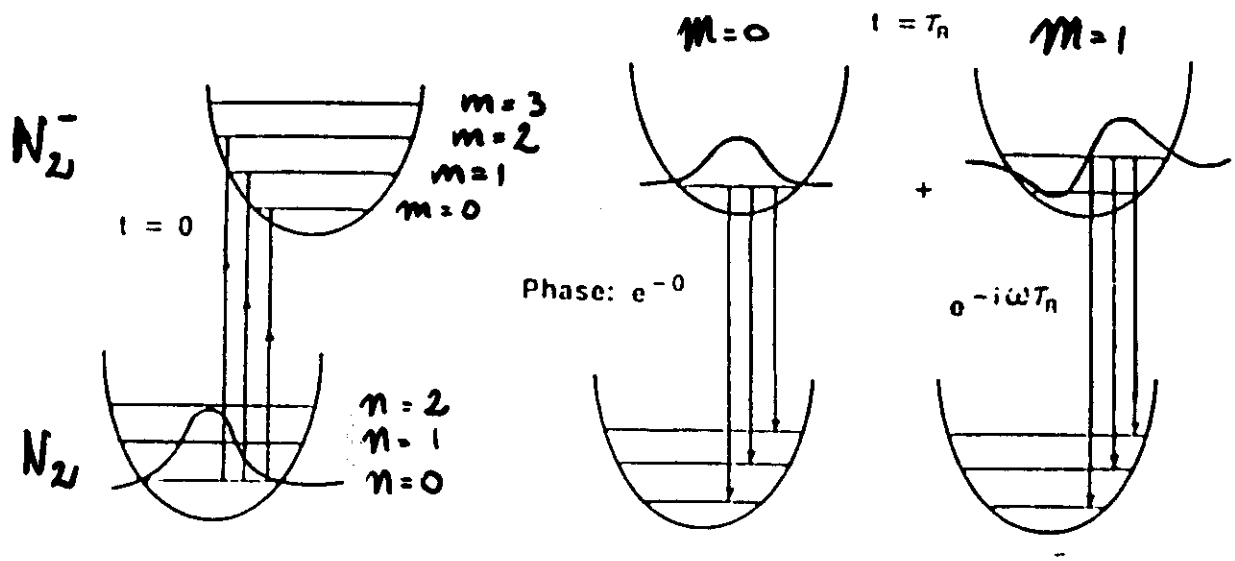
$$\Delta E = \frac{\Delta r^2}{2m} \propto \tau_R^2$$

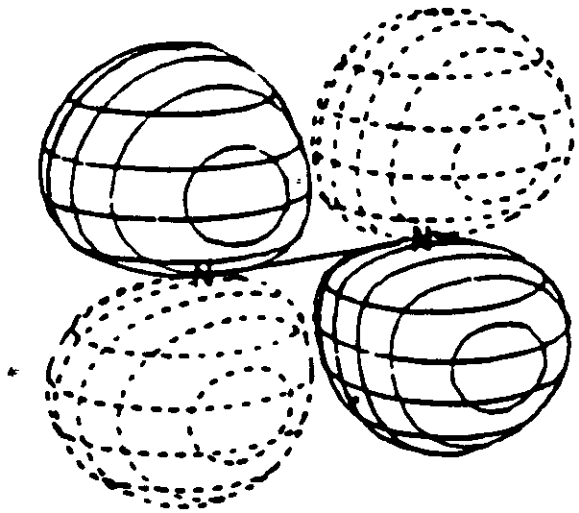
$$\beta = \frac{\Delta E}{\hbar\omega}$$

$$P_n = \frac{e^{-\beta}\beta^n}{n!}$$

$$P_n = |\langle n| e^{-i \hat{H}_{N_2^-} \tau_R/\hbar} |0\rangle|^2 = |\Sigma_m \langle n|m\rangle e^{-i\varepsilon_m \tau_R/\hbar} \langle m|0\rangle|^2$$

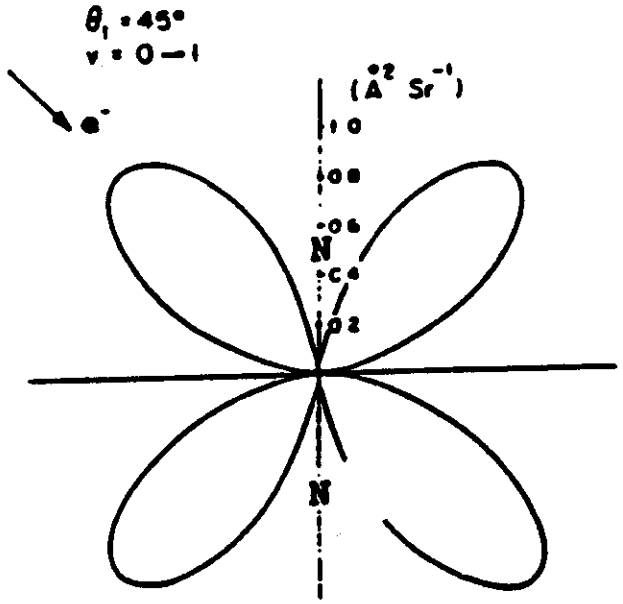
$$\tau_R = 0 \Rightarrow P_n = |\Sigma_m \langle n|m\rangle\langle m|0\rangle| = \delta_{n0}$$



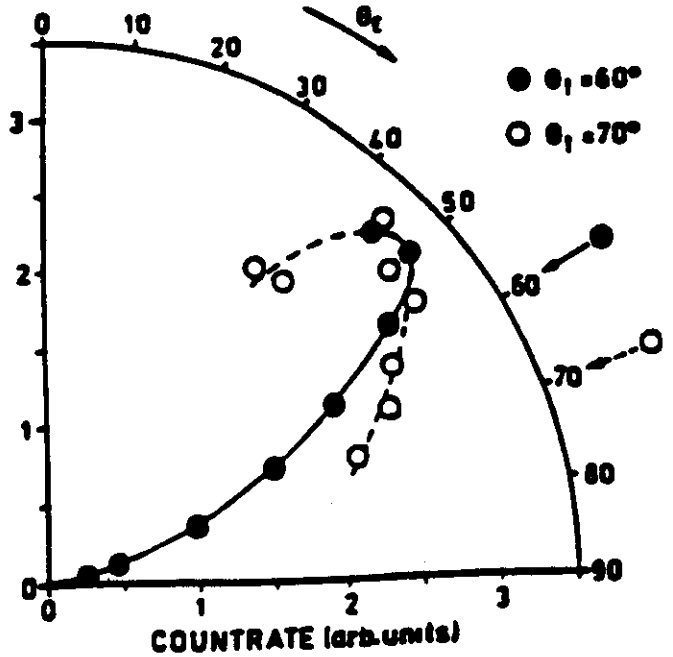


$1\pi_g$

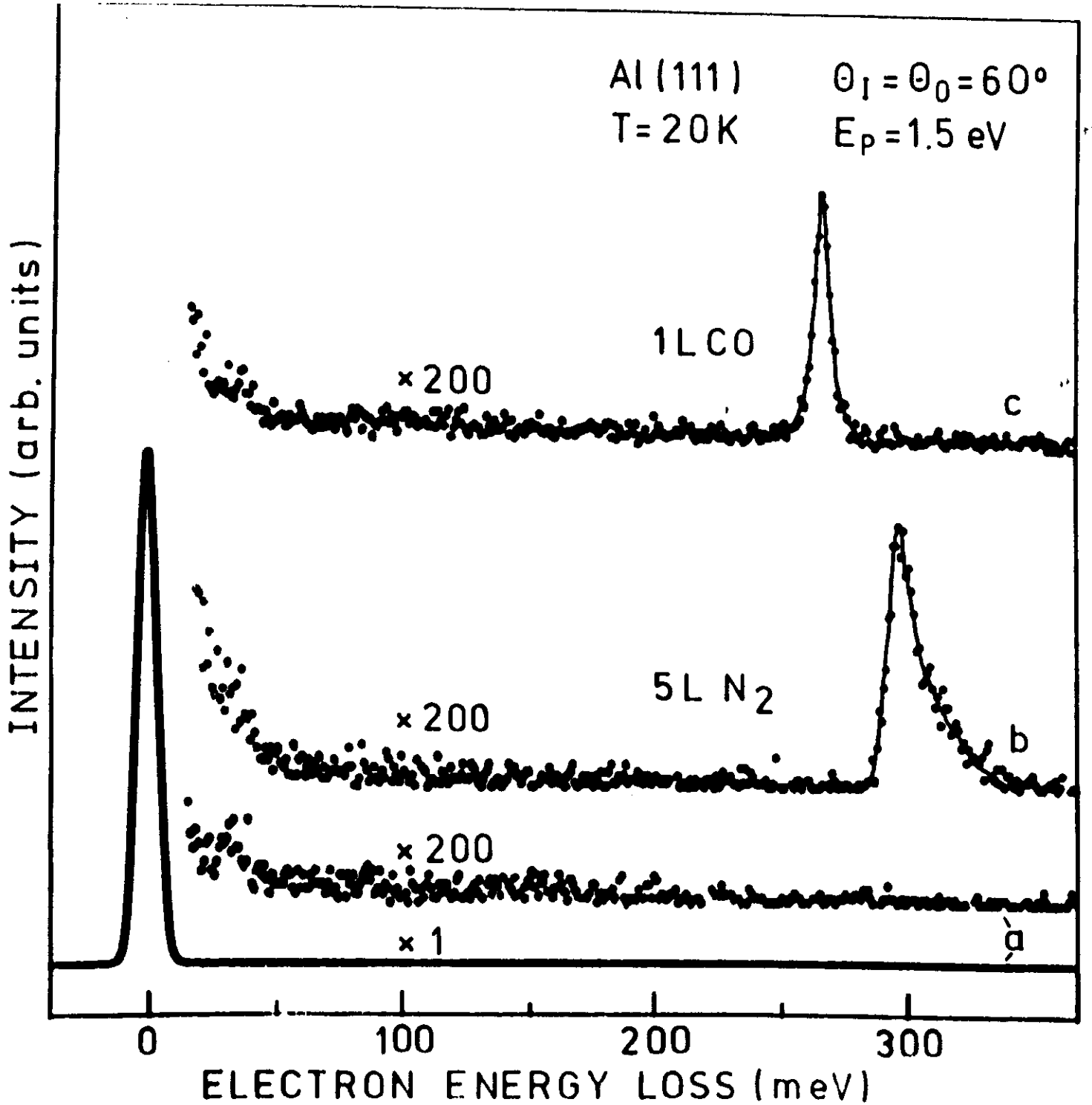
CONTOUR PLOT OF THE $1\pi_g$ STATE OF N_2



CALCULATED ANGULAR DISTRIBUTION FOR $v: 0 \rightarrow 1$ GAS PHASE N_2

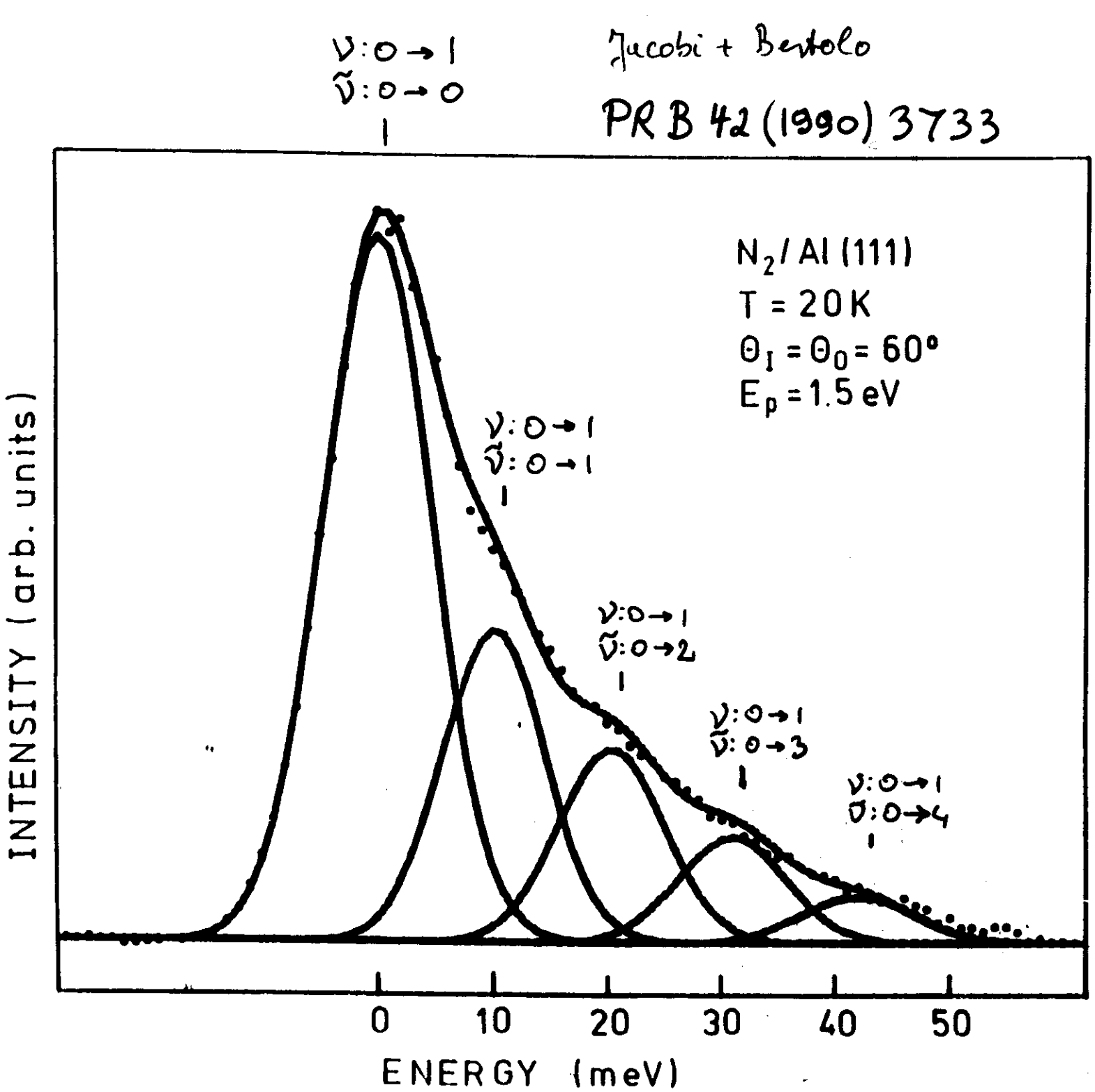


MEASURED ANGULAR DISTRIBUTION FOR $v: 0 \rightarrow 1$ $N_2/Al(111)$

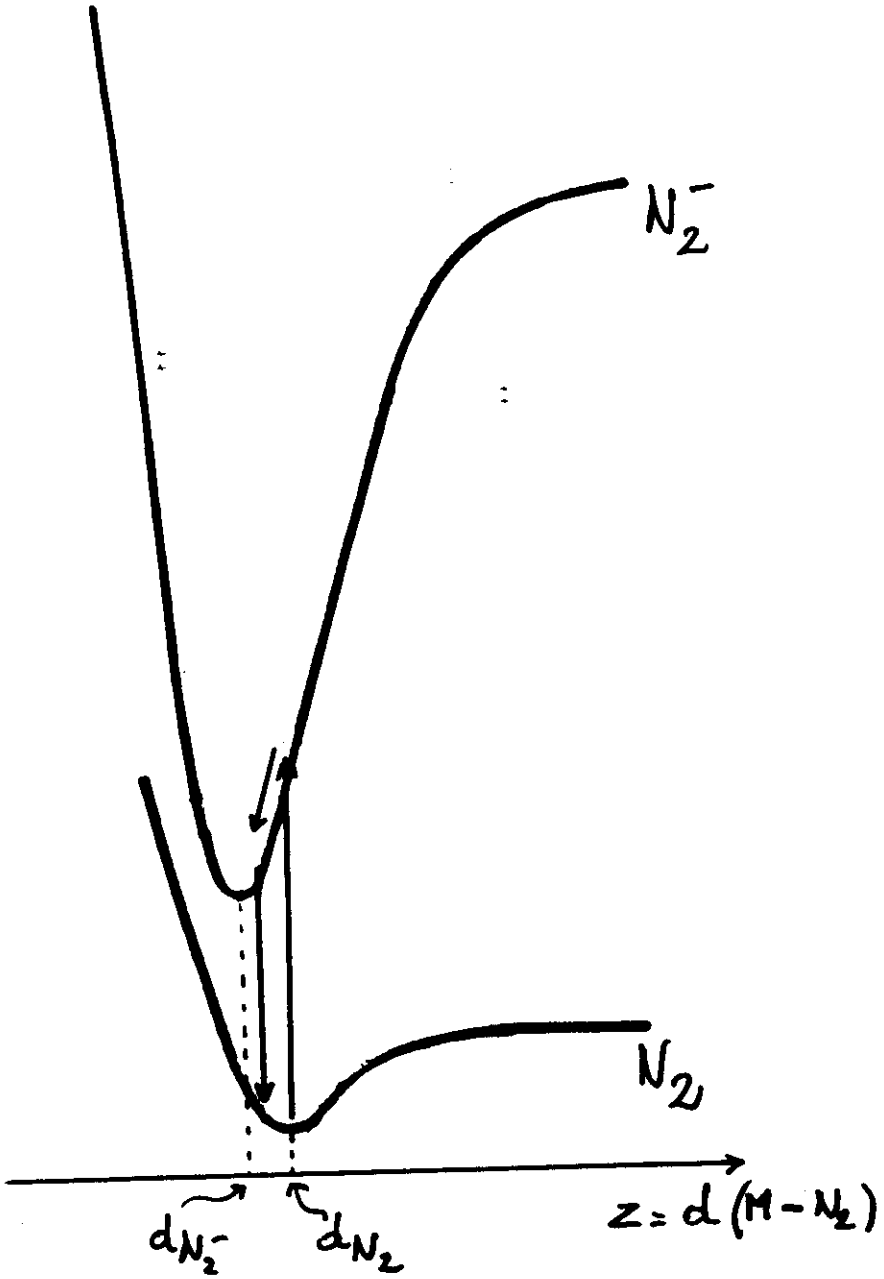

Al (111)
T = 20K
$\theta_I = \theta_0 = 60°$
$E_p = 1.5$ eV
1L CO
5L N_2
× 200
× 200
× 200
× 1
a
b
c
INTENSITY (arb. units)
0
100
200
300
ELECTRON ENERGY LOSS (meV)

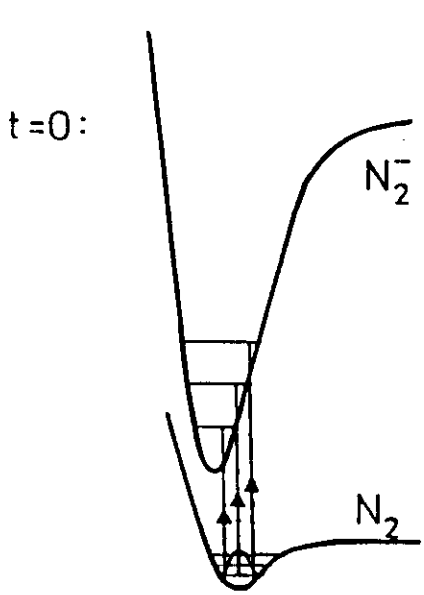
d) $\nu(M-N_2)$

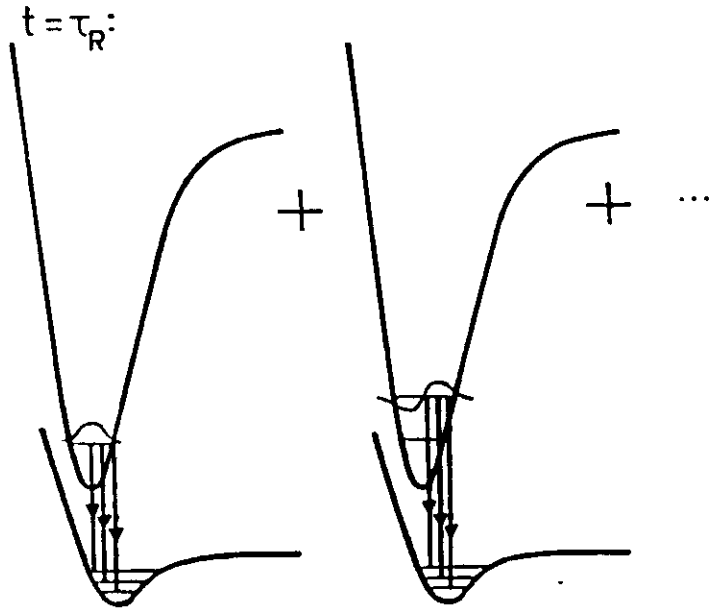
Fig. 1


ν: 0 → 1
ν̃: 0 → 0
Jacobi + Bertolo
PR B 42 (1990) 3733
N2 / Al (111)
T = 20 K
θI = θ0 = 60°
Ep = 1.5 eV
ν: 0 → 1
ν̃: 0 → 1
ν: 0 → 1
ν̃: 0 → 2
ν: 0 → 1
ν̃: 0 → 3
ν: 0 → 1
ν̃: 0 → 4
INTENSITY (arb. units)
0
10
20
30
40
50
ENERGY (meV)

$$V_{N_2^-}(z) = V_{N_2}(z) + V_0 - \frac{e^2}{4z}$$







SUMMARY HREELS

MECHANISM OF THE NEGATIVE ION RESONANCE

- OCCUPATION $(t = \tau_R)$ OF AN ANTIBONDING LEVEL OF THE MOLECULE ($1\pi_g$ IN OUR CASE)
- THE MOLECULE EXPANDS
- THE SHAPE OF THE INVOLVED LEVEL DETERMINES THE ANGULAR DISTRIBUTION OF THE SCATTERED ELECTRONS
- THE MOLECULE IS ATTRACTED TO THE SURFACE

SPECTROSCOPIC CHARACTERISTICS $(N_2/Ag(111))$

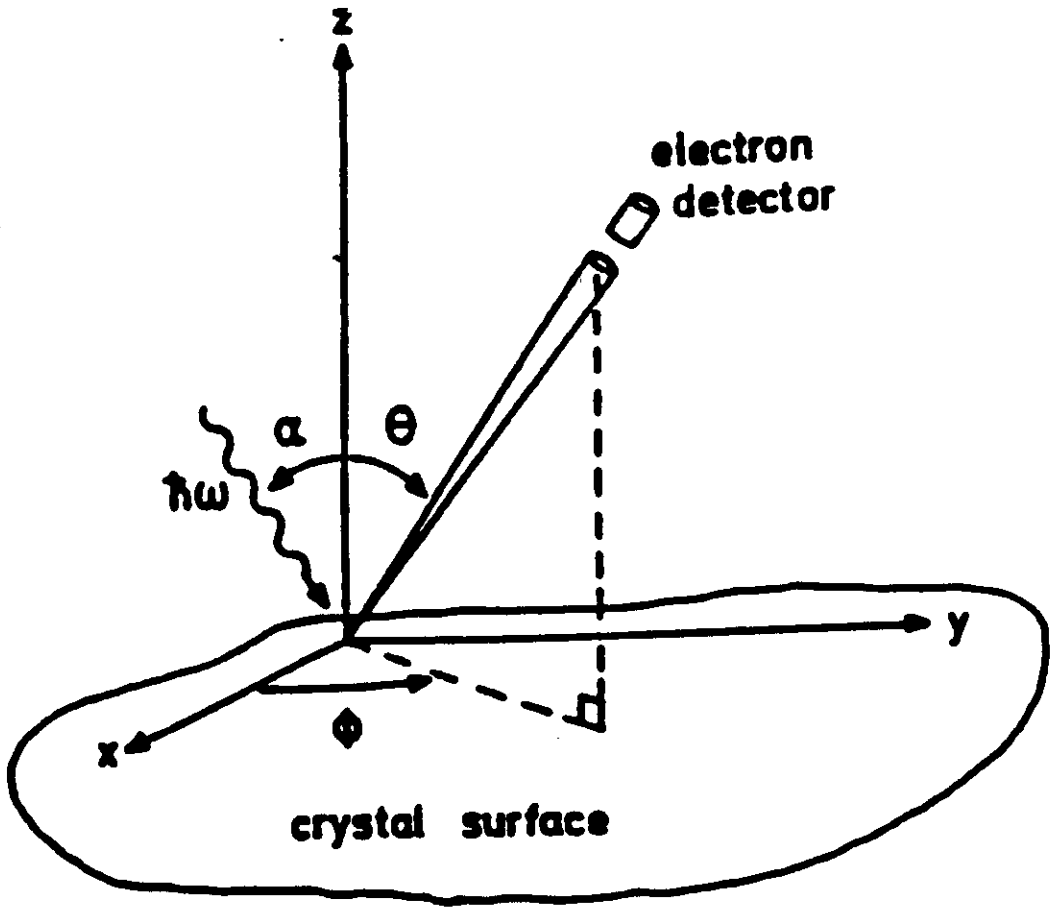
- RESONANCE IN E_i
- EXCITATION OF THE STRETCHING $\nu(N-N)$ AND OF ITS OVERTONES
- MAXIMUM OUT OF THE SPECULAR DIRECTION
- ASYMMETRIC LINESHAPE OF THE LOSSES $\nu: 0 \rightarrow n$ DUE TO SIMULTANEOUS EXCITATION OF THE $\tilde{\nu}(\pi\text{-}N_2)$ VIBRATION

UNLIKE DIPOLE SCATTERING

ARUPS (ANGLE RESOLVED ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY)

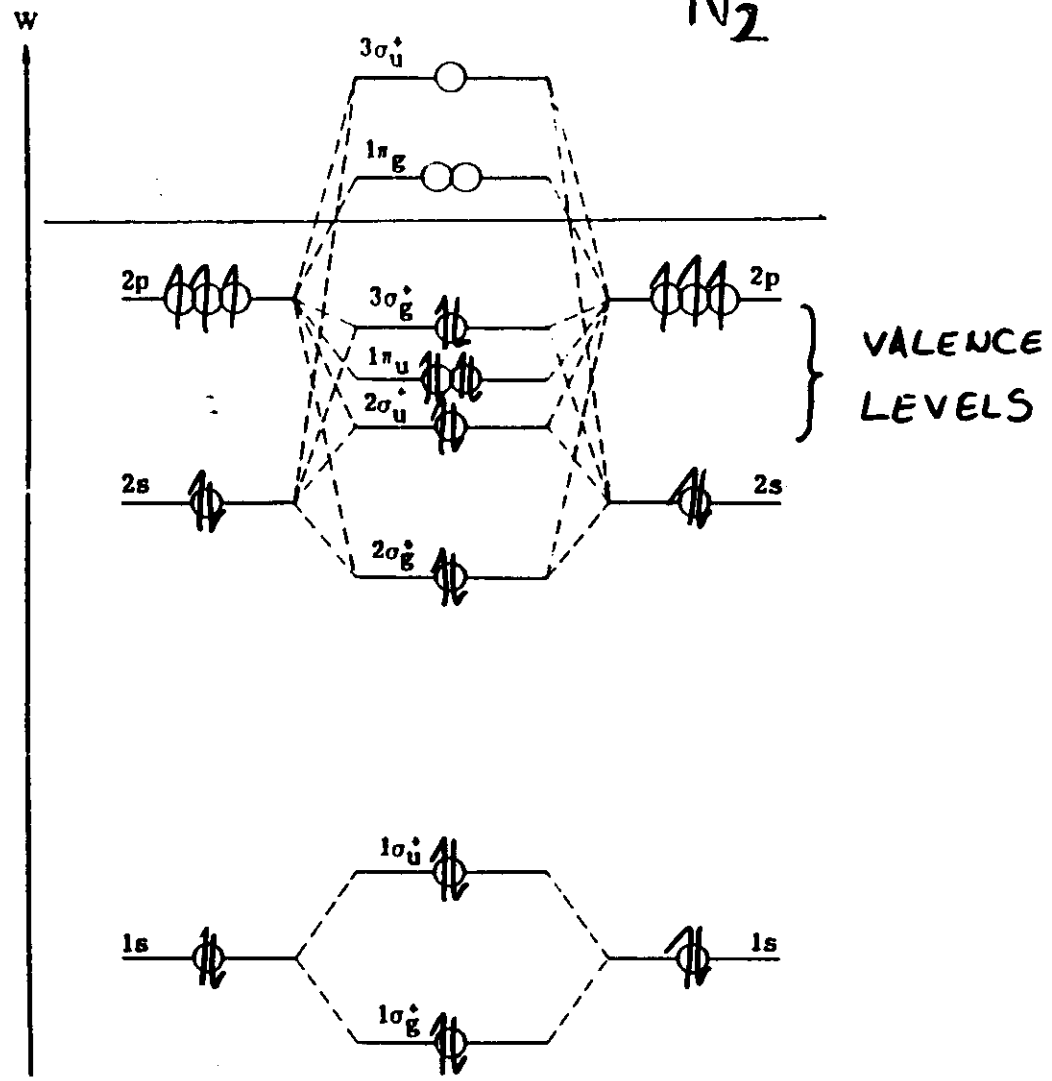
THE "INERTIA" OF THE SO CALLED FAST PHOTOEMISSION AND THE DESTINY OF THE PHOTOHOLE

- PHOTOEMISSION FROM GAS PHASE N_2: THE VIBRONIC FINE STRUCTURE
- PHOTOEMISSION FROM PHYSISORBED $N_2/Xe/Ni(111)$: THE HOPPING MODEL AND THE TWO VIBRONIC MULTIPLETS
- PHOTOEMISSION FROM PHYSISORBED $N_2/Xe/Ag(111)$ $(Pd(111))$
  - A) THE RELATIONSHIP BETWEEN HOPPING PROCESS AND BAND FORMATION
  - B) OBSERVATION OF NUCLEI MOVEMENT IN THE PHOTOEMISSION THROUGH VIOLATION OF THE SUDDEN APPROXIMATION

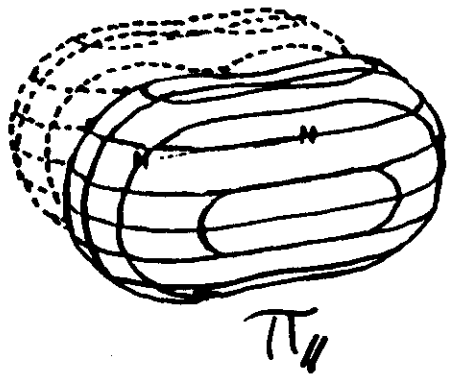


ALL MEASUREMENTS PERFORMED
AT NORMAL EMISSION $(\theta = 0)$

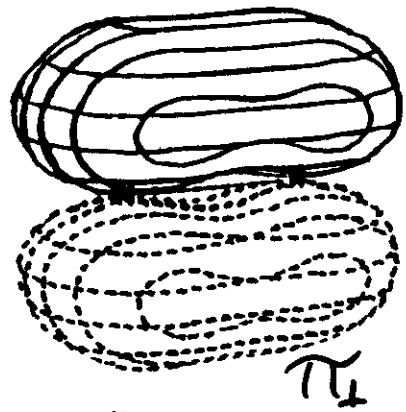
N_2



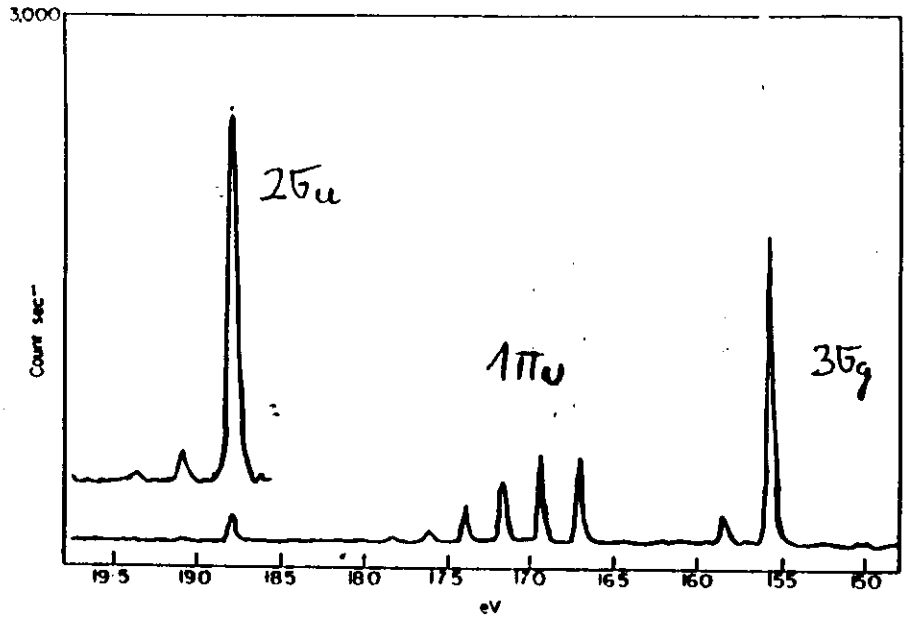
$1\pi_u$



"GOOD" OVERLAP
TENDENCY TO BAND FORMATION
"HIGH" EFFICIENCY OF THE HOPPING PROCESS

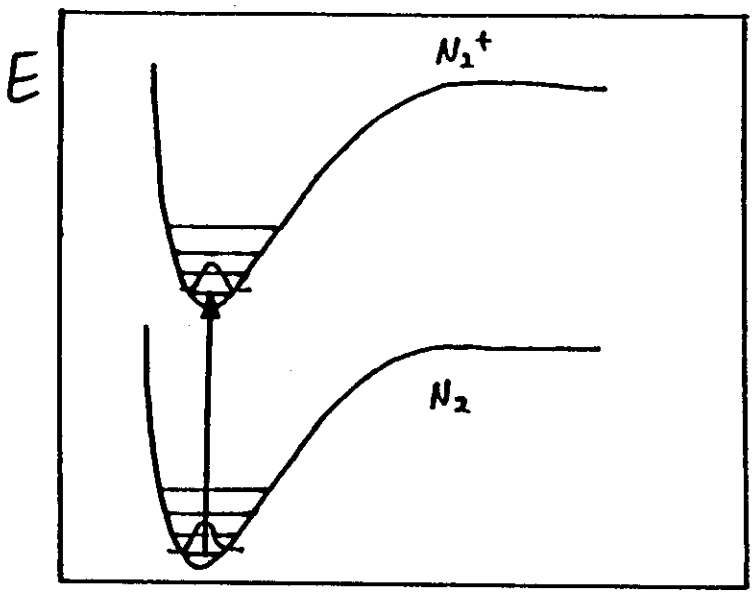


"BAD" OVERLAP
NO TENDENCY TO BAND FORMATION
"LOW" EFFICIENCY OF THE HOPPING PROCESS



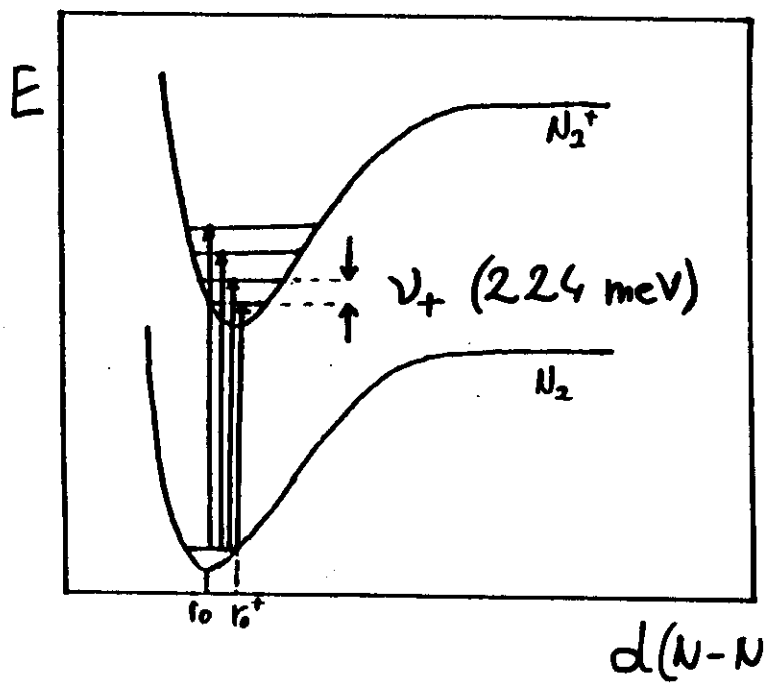
UPS

GASPHASE

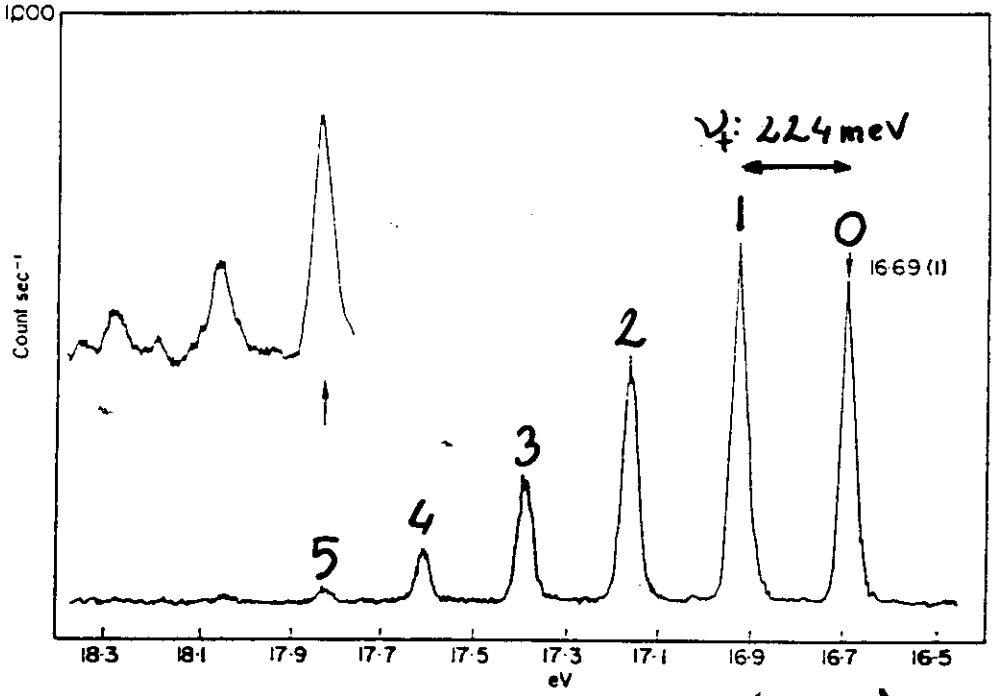


3σg

2σu



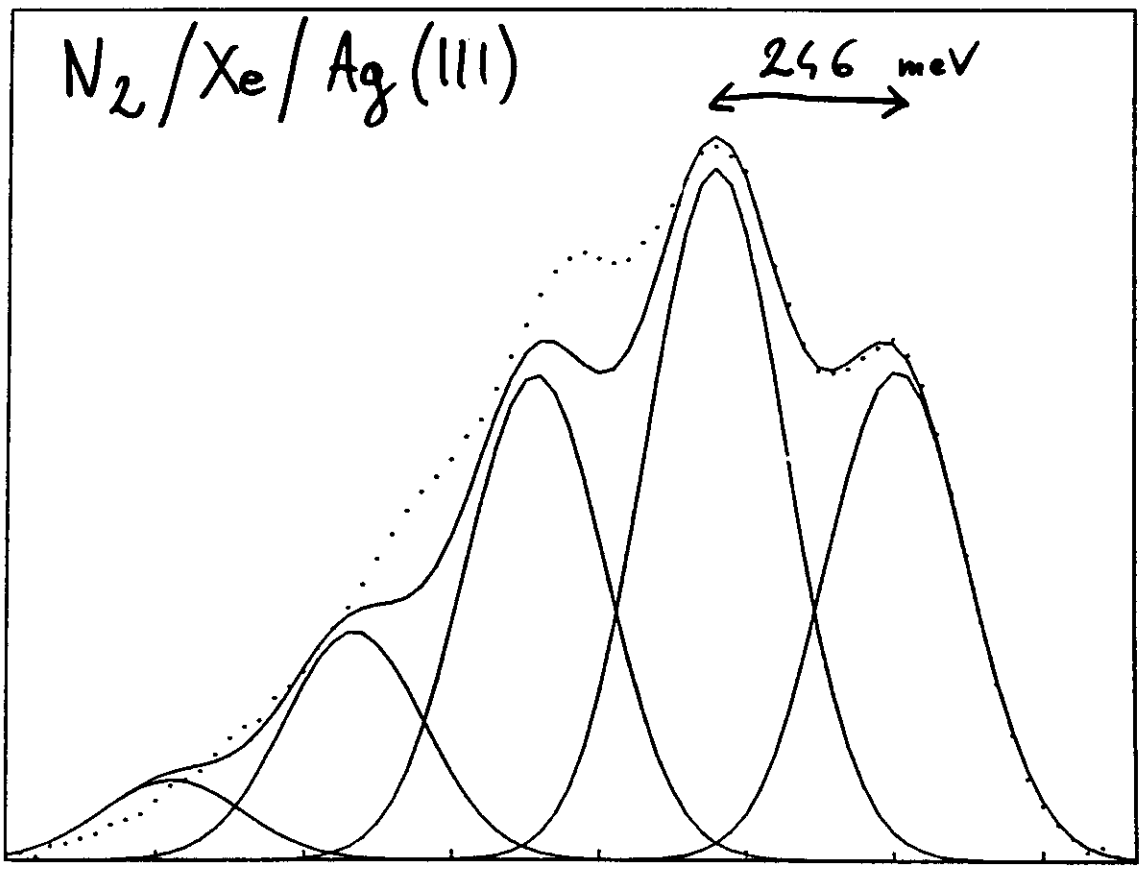
1πu



GASPHASE

$$P_n = \frac{e^{-\beta}\beta^n}{n!}$$

Figure 3.9 Nitrogen (second band) $(1\pi_u)$



(4)

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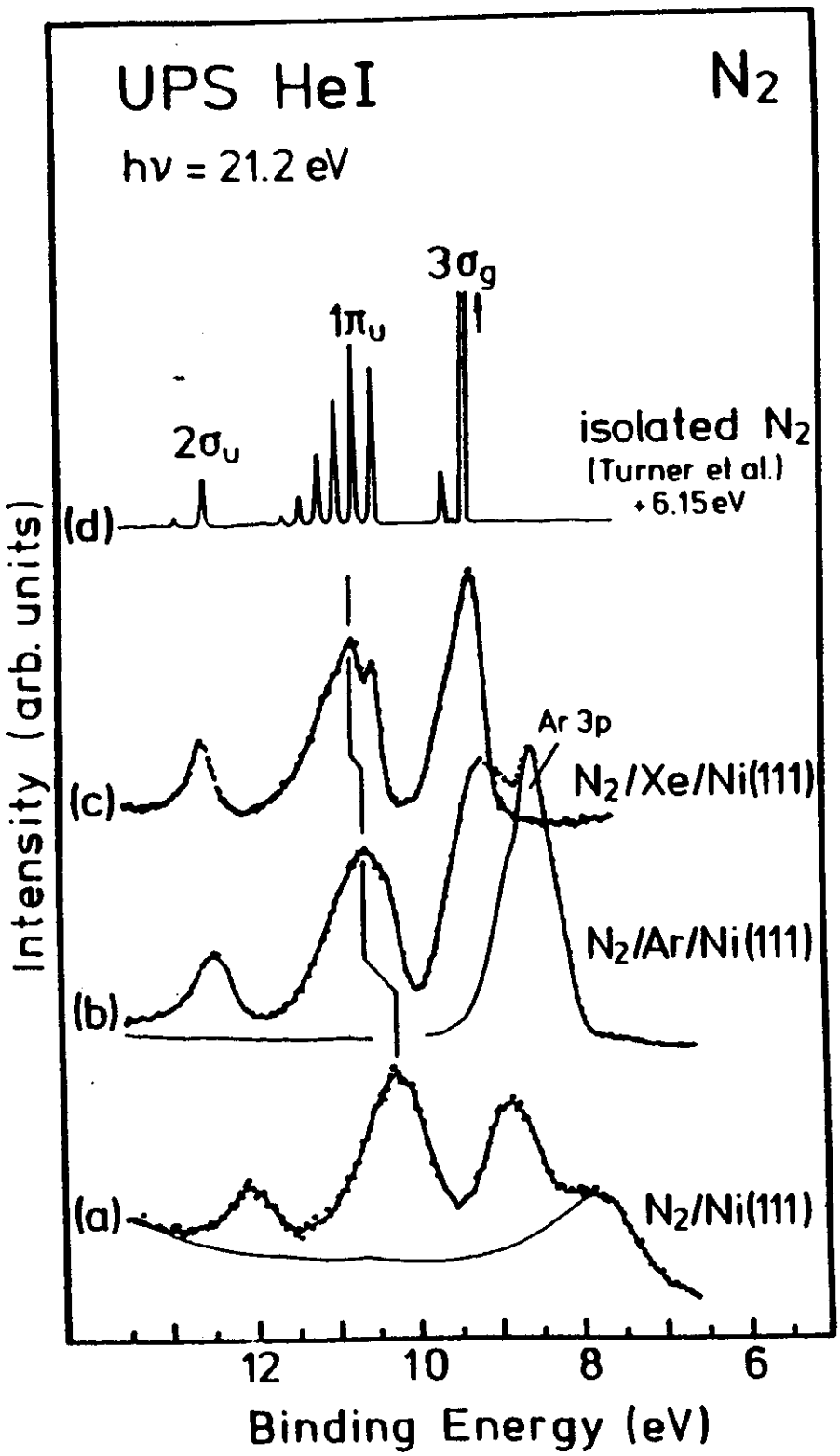
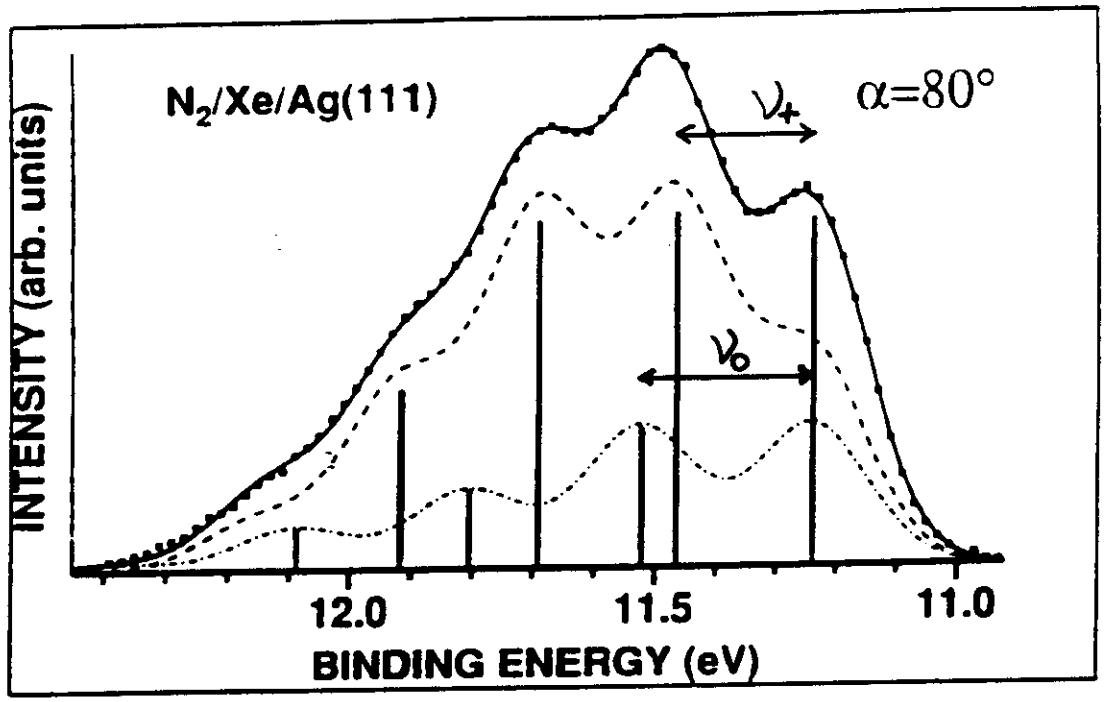


(3)



$\nu_+ = \nu(N-N)$ IN N_2^+ $(2\sigma_u^2 1\pi_u^3 3\sigma_g^2)$

GAS PHASE VALUE = 224 meV

$\nu_0 = \nu(N-N)$ IN N_2 $(2\sigma_u^2 1\pi_u^4 3\sigma_g^2)$

GAS PHASE VALUE = 289 meV

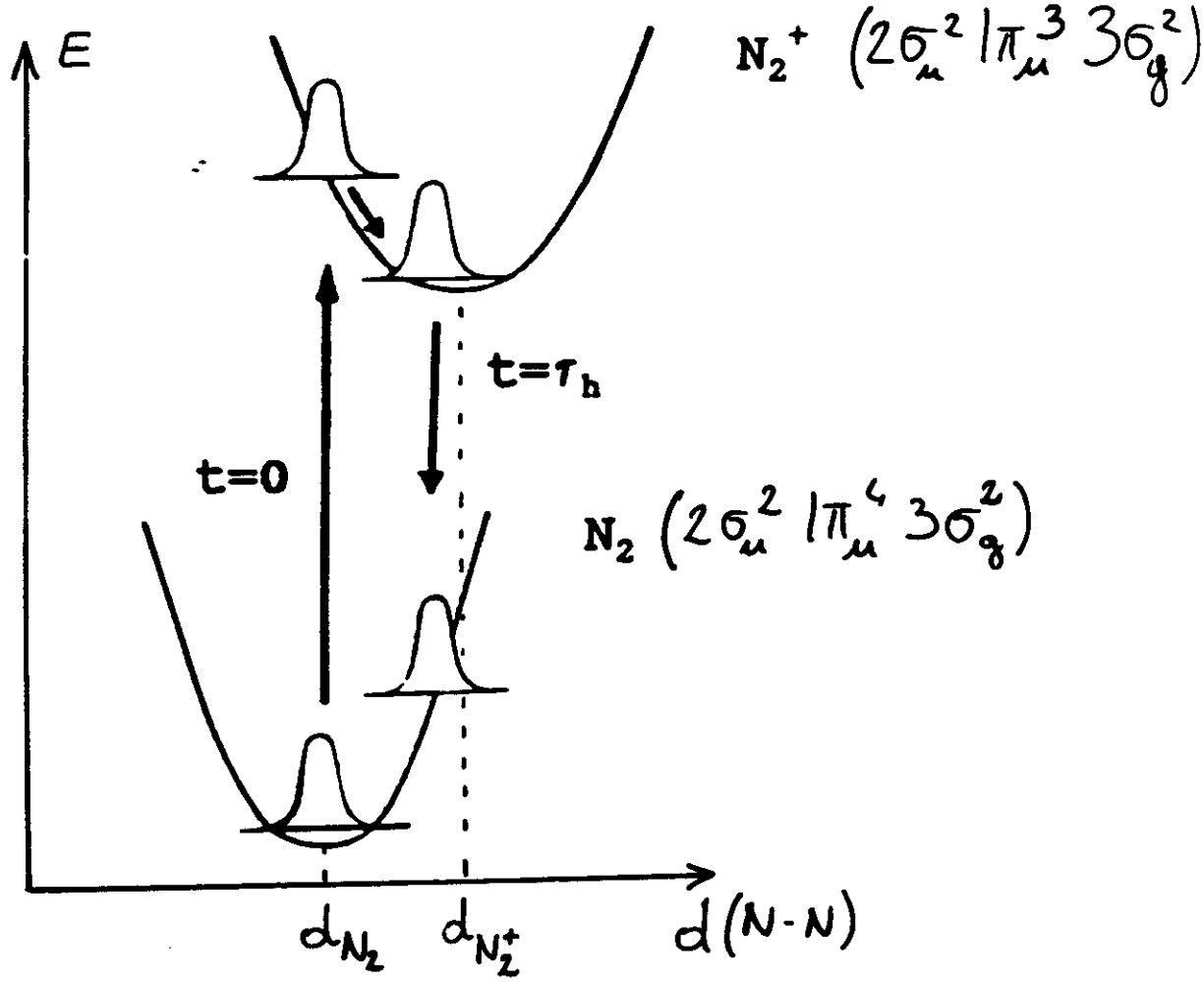
$$P_{\nu_+}(0 \to m) = I_+ \frac{e^{-\beta_+} \beta_+^m}{m!}$$

$$P_{\nu_0}(0 \to m) = I_0 \frac{e^{-\beta_0} \beta_0^m}{m!}$$

PARAMETERS:

$\beta_+, \beta_0, \nu_+, \nu_0, I_+/I_0$

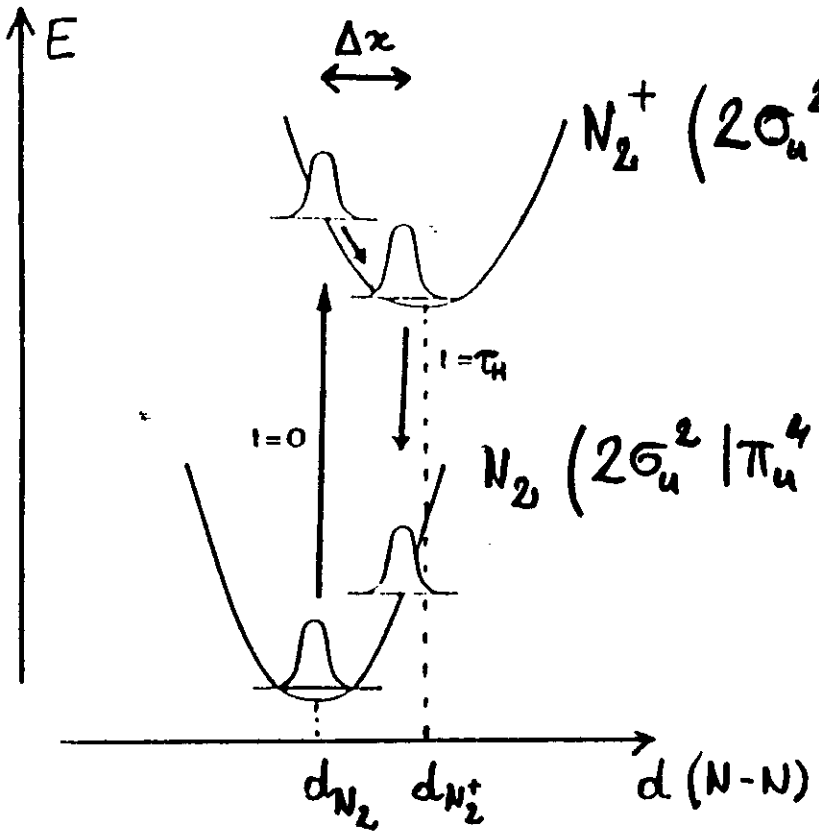
THE HOPPING PROCESS:
THE DELOCALIZATION OF THE PHOTOHOLE



$$\tau_H = 2-3 \times 10^{-15} \; s$$

THE DELOCALIZATION PROCESS TAKES PLACE : ν_0

THE DELOCALIZATION PROCESS DOES NOT TAKE PLACE : ν_+



$$\Delta r = F \cdot \tau_H$$

$$\Delta E = \frac{\Delta r^2}{2m} \propto \tau_H^2$$

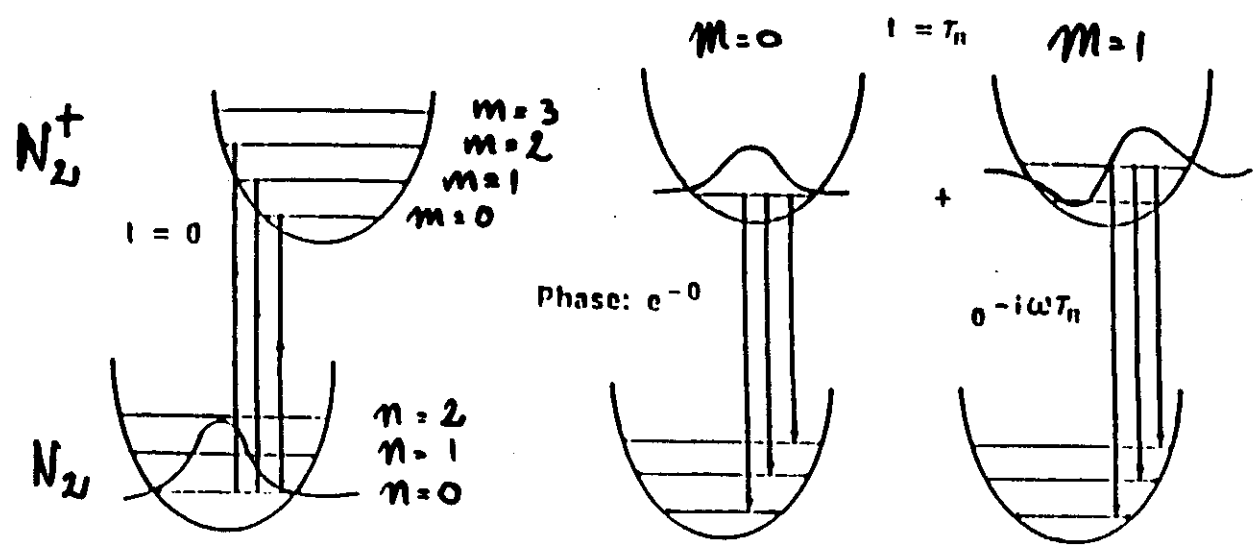
$$\beta_0 = \frac{\Delta E}{\hbar\omega}$$

$$P_n = \frac{e^{-\beta}\,\beta_0^n}{n!}$$

$$\tau_H \simeq 2 \div 3 \times 10^{-15}\ s$$

$$P_n = |\langle n| e^{-i \hat{H}_{N_2^+} \tau_H/\hbar} |0\rangle|^2 = \left|\sum_m \langle n|m\rangle e^{-i E_m \tau_H/\hbar} \langle m|0\rangle\right|^2$$

$$\tau_H = 0 \Rightarrow P_n = |\Sigma_m \langle n|m\rangle\langle m|0\rangle| = \delta_{n0}$$



(6)

GROUND STATE

GAS PHASE
LOCALIZED WAVE FUNCTION

$\psi_{1\pi}(\vec{r}-\vec{R}_i)$

CONDENSED PHASE
BLOCH WAVE

$\psi_{1\pi(\vec{k})}(\vec{r}) = \sum_i e^{i\vec{k}\cdot\vec{R}_i}\psi_{1\pi}(\vec{r}-\vec{R}_i)$

PHOTOEMISSION

GAS PHASE
LOCALIZED PHOTOHOLE

$\psi_{1\pi}(\vec{r}-\vec{R}_i)$

CONDENSED PHASE

$t=0$ { LOCALIZED PHOTOHOLE
$\psi_{1\pi}(\vec{r}-\vec{R}_i)$

$t=\tau_H$ { DELOCALIZED PHOTOHOLE
$\psi_{1\pi(\vec{k})}(\vec{r}) = \sum_i e^{i\vec{k}\cdot\vec{R}_i}\psi_{1\pi}(\vec{r}-\vec{R}_i)$

TIME EVOLUTION OF THE PHOTOHOLE:

$\Psi(t=0) = \psi_{1\pi}(\vec{r}-\vec{R}_i)$

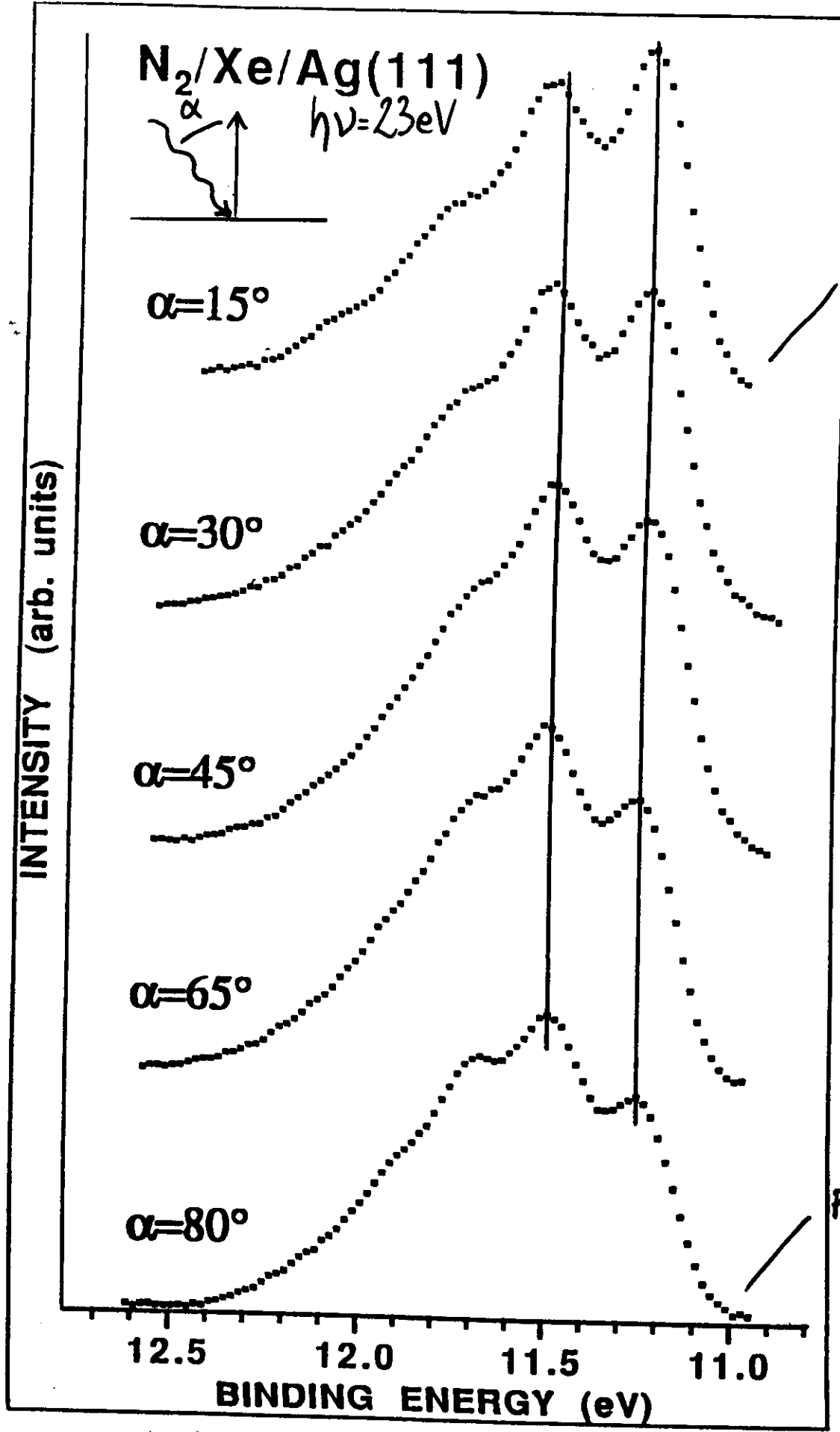
$\Psi(t): \exp(-\frac{i}{\hbar}\hat{H}t)\Psi(t=0) = (1-\frac{i}{\hbar}\hat{H}t)\Psi(t=0)$

$\langle\psi_{1\pi}(\vec{r}-\vec{R}_j)|\Psi(t)\rangle = -\frac{i}{\hbar}t\underbrace{\langle\psi_{1\pi}(\vec{r}-\vec{R}_j)|\hat{H}|\psi_{1\pi}(\vec{r}-\vec{R}_i)\rangle}_{\text{HOPPING INTEGRAL } H_{ij}}$

$\tau_H \propto \frac{1}{H_{ij}}$

BAND WIDTH $\propto H_{ij}$

} HOPPING PROCESS AND BAND FORMATION AS COMPLEMENTARY ASPECTS



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$\nu_+ = 210 - 239$ meV

$\nu_0 = 271 - 300$ meV

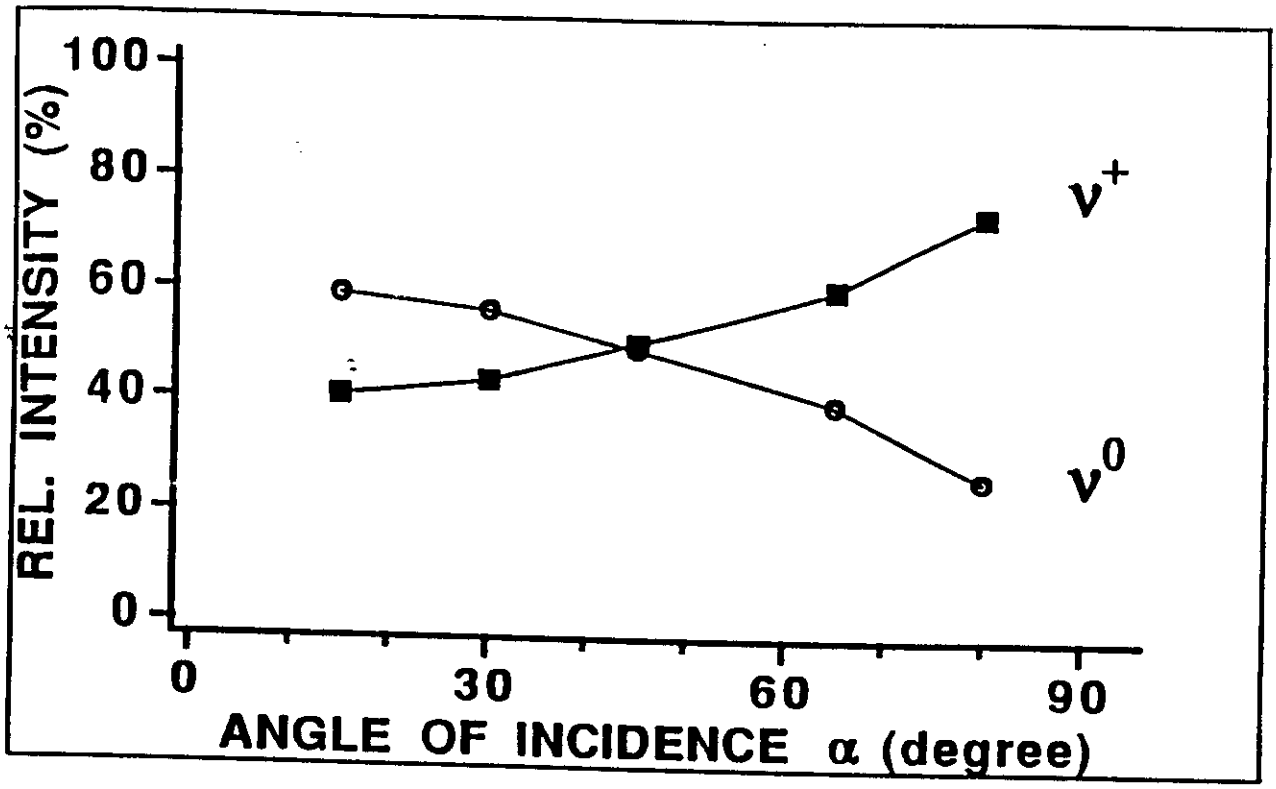
$\beta_+ = 1.6 - 2.2$

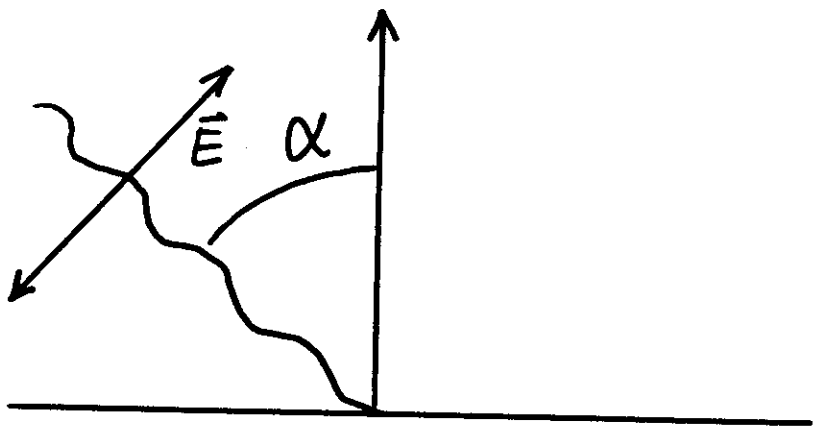
$\beta_0 = 0.6 - 1.0$

$$P_n = \frac{e^{-\beta}\beta^n}{n!} \Rightarrow P_0 = e^{-\beta}$$

$\alpha = 15^\circ$: HIGHER ν, LOWER $\beta \Rightarrow \nu_0$

$\alpha = 80^\circ$: LOWER ν, HIGHER $\beta \Rightarrow \nu_+$





$\alpha = 15° \Rightarrow E_{//} \Rightarrow \pi_{//} \Rightarrow$ BAND FORMATION

$\alpha = 15° \Rightarrow \nu_0 \Rightarrow$ HOPPING ⇄

$\alpha = 80° \Rightarrow E_{\perp} \Rightarrow \pi_{\perp} \Rightarrow$ "NO" BAND FORMATION

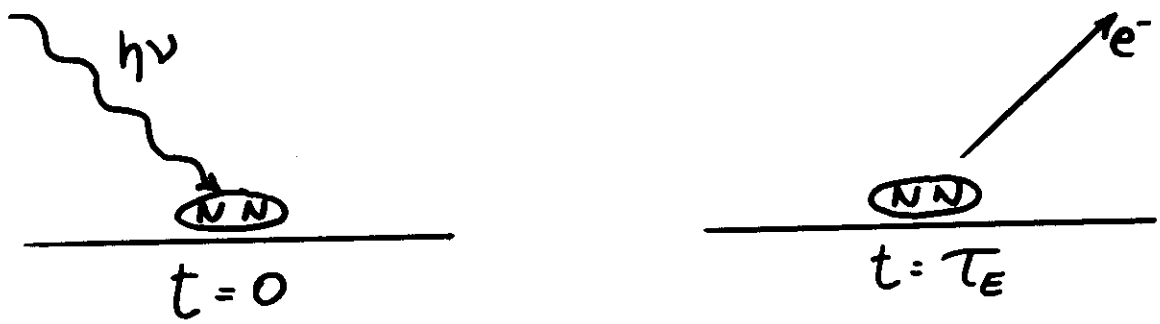
$\alpha = 80° \Rightarrow \nu_+ \Rightarrow$ "NO" HOPPING ⇄

$$T = \frac{h}{E} = \frac{4.14 \cdot 10^{-12}\ \text{meV}\cdot\text{s}}{224\ \text{meV}} = 1.85 \cdot 10^{-14}\ \text{s}$$

τ_H: FRACTION OF T $\Rightarrow$ $2-3 \cdot 10^{-15}$ s

τ_H DETERMINES β_0

ASSUMPTION $\tau_H \sim \tau_E$ (E FOR "ESCAPE")



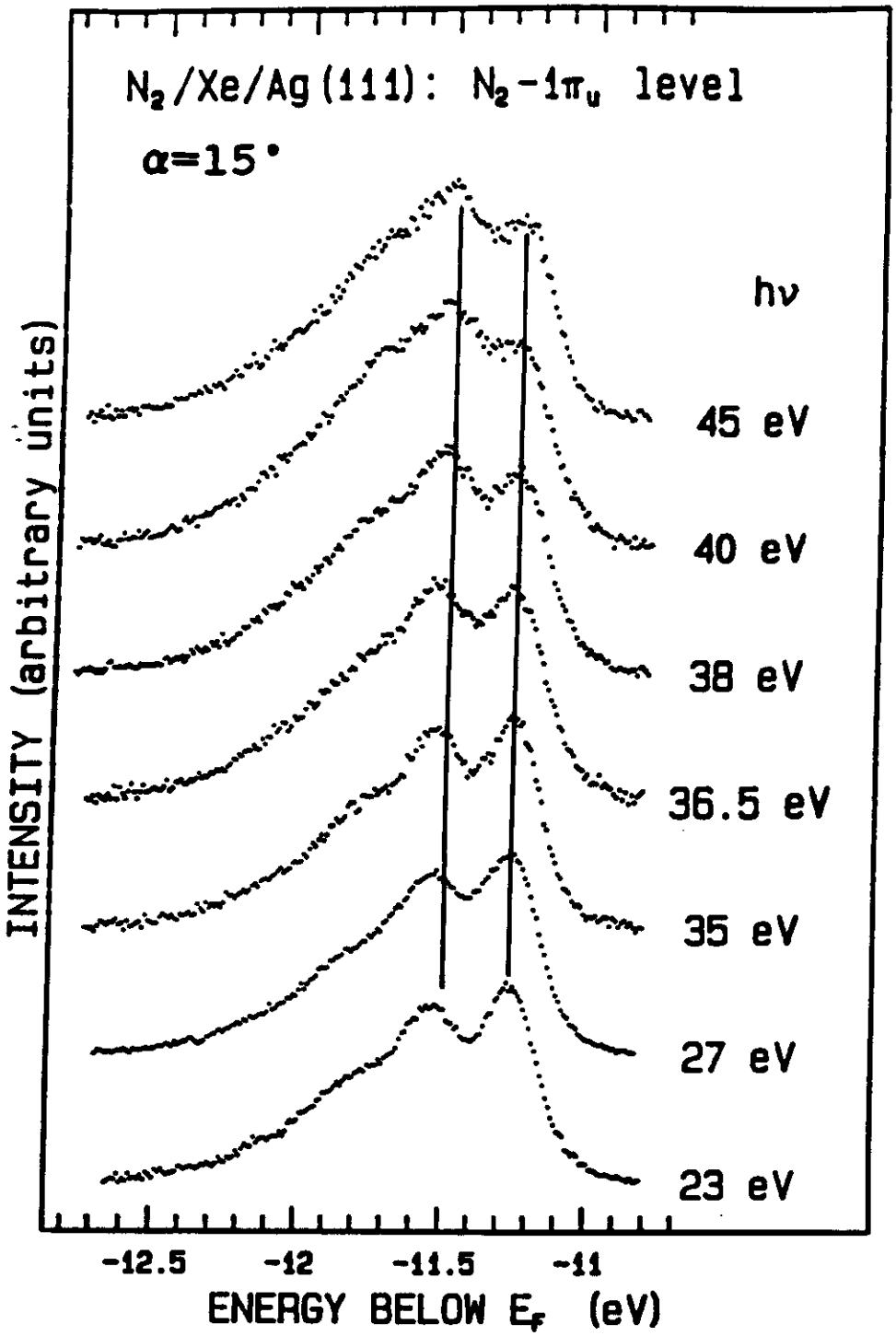
$\tau_E \neq 0 \Rightarrow$ VIOLATION OF THE SUDDEN APPROXIMATION

IF $\tau_E = 0 \Rightarrow I_0 = 0$

$\Rightarrow I_0/I_+$ IS A MEASURE FOR THE VIOLATION OF THE SUDDEN APPROXIMATION

$$\tau_E \sim \frac{l}{v} \propto \frac{l}{\sqrt{E_K}}$$

$$I_0/I_+ \sim \frac{1}{h\nu}$$



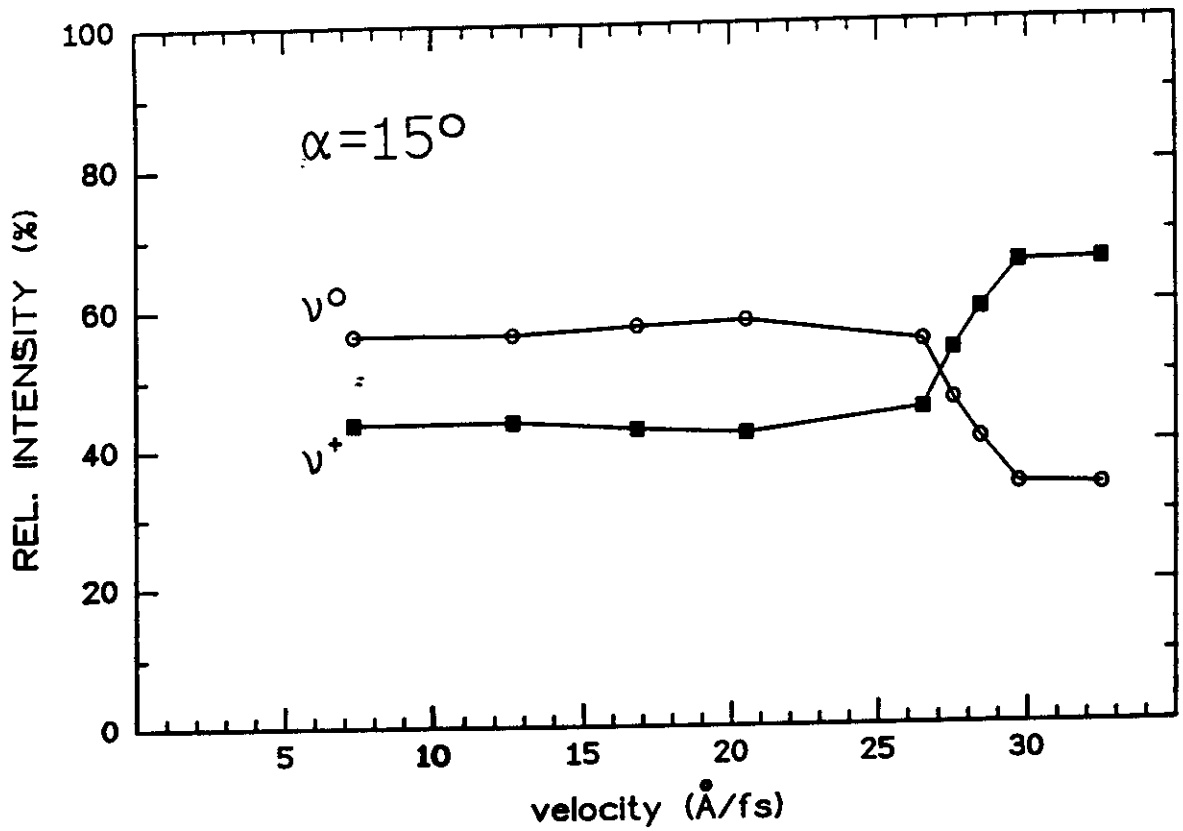
$\alpha = 15° \Rightarrow \pi_{//}$

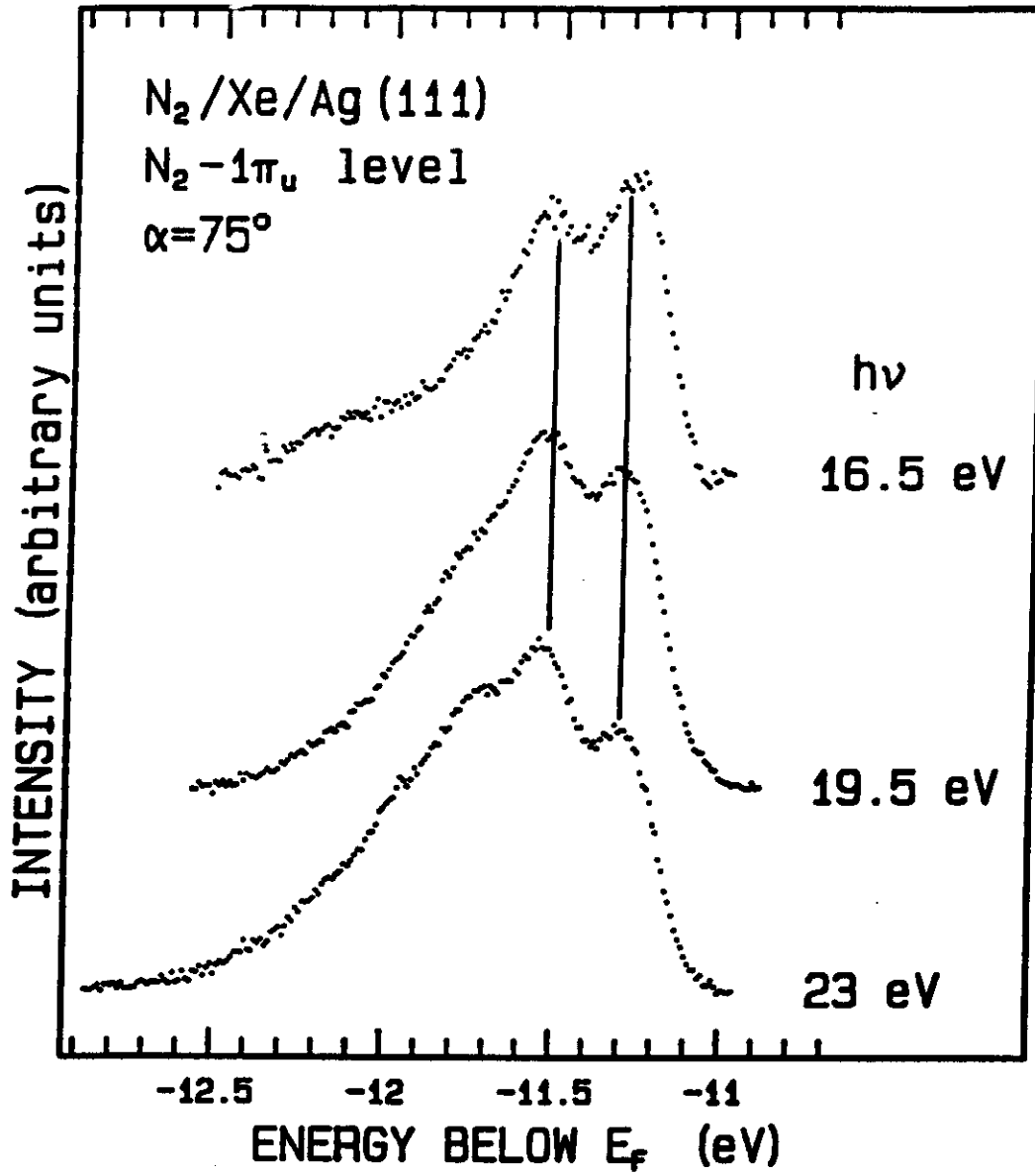
AT $h\nu = 23eV$ $I_0 > I_+$

$h\nu \nearrow$ $v \nearrow$ $\tau_e \searrow$ $I_0 \searrow$

BETTER VALIDITY OF THE SUDDEN APPROXIMATION

M. BERTOLO ET AL. CHEM. PHYS. LETT., IN PRESS


α=15°
ν°
ν⁺
REL. INTENSITY (%)
velocity (Å/fs)
0
20
40
60
80
100
5
10
15
20
25
30

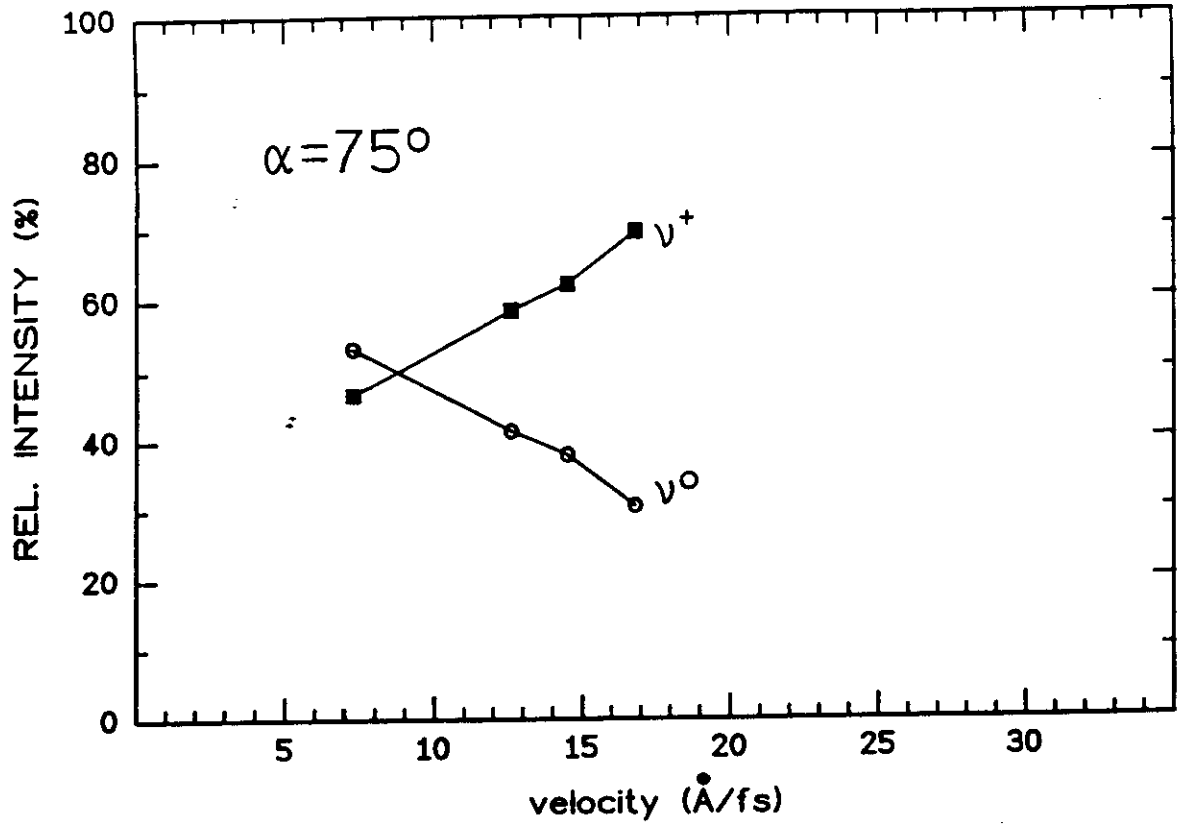


$\alpha = 75^\circ \Longrightarrow \pi_\perp$

AT $h\upsilon = 23$ eV $\quad I_0 < I_+$

$h\nu \searrow \quad \upsilon \searrow \quad \tau_\epsilon \nearrow \quad I_0 \nearrow$

BIGGER VIOLATION OF THE SUDDEN APPROXIMATION



$\pi_\perp$: DISPERSION $\sim$ 0 (< 10 meV)

NEVERTHELESS $\tau_H \sim \tau_E$

USUAL CASES : DISPERSION $\geq$ 1eV

$\Rightarrow \tau_H << \tau_E$

$\Rightarrow$ PHOTOHOLE DELOCALIZED BY THE TIME τ_E

$\Rightarrow$ CORRECTNESS OF THE DESCRIPTION THROUGH BLOCH WAVES

SUMMARY ARUPS

SYSTEM : PHYSISORBED $N_2/Xe/Ag(111)$ $\left(Pd(111)\right)$

PHOTOEMISSION IN THE CONDENSED PHASE

- THE PHOTOHOLE IS LOCALIZED AT $t=0$ (NO BLOCH WAVE)
- THE PHOTOHOLE DELOCALIZES WITH $\tau_H \propto \frac{1}{\text{BAND WIDTH}}$ (HOPPING PROCESS)
- THE DELOCALIZATION IS OBSERVED THROUGH VIOLATION OF THE SUDDEN APPROXIMATION : $\tau_E \neq 0$
- THE PHOTOEMISSION IS "SLOW" ENOUGH TO HAVE $\tau_H \sim \tau_E$ FOR π_1 (DISPERSION ~ 0)
- PHOTOEMISSION FROM VALENCE BAND OF METALS

  $\tau_H << \tau_E \Rightarrow$ THE PHOTOHOLE IS DELOCALIZED