Surface Reactions induced by XUV Laser Radiation

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Thanks to: J. Feldhaus[2] and the FLASH team

Introduction

Reaction dynamics on interstellar dust particles


horsehead nebula


protoplanetary disc

Introduction

Reaction dynamics on interstellar dust particles

molecular hydrogen formation (Salpeter, 1963, 1970)

reviews, e.g., by D.A. Williams, E. Herbst, Surf. Sci. **500**, 823 (2002)

E. Herbst, J. Phys. Chem. A **109**, 4017 (2005)

Dust particles: graphitic, olivines, ice-covered (H_2O, CO, CO_2) cores

formation of **H_2** on amorphous ice/graphite:

thermal at low T: L. Hornekær et al., Science **302**, 1943 (2003)

S.D. Price et al., J. Chem. Phys. **124**, 114701 (2006)

Photon-induced reactions

desorption of **H atoms**, formation of **H_2, CO, H_2O, CO_2, NH_3**

Introduction

Femtosecond hot electron induced reactions:

laser desorption: **NO / Pd(111), O_2 / Pt(111)** — T.F. Heinz and coworkers, PRL, **64**, 1537 (1990); F. Budde et al., PRL, **66**, 3024 (1991)

CO / Pt(111)
CO / Cu(111) — F.J. Kao et al., PRL, **71**, 2094 (1993); L.M. Struck et al., PRL, **77**, 4576 (1996)

NO / NiO(100) — G. Eichhorn et al., Chem. Phys. Lett. **289**, 367 (1998)

laser induced diffusion: **O / Pt(111) ; CO / Pt(111)** — J. Güdde et al., PRL, **94**, 236103 (2005); M. Bonn and coworkers, Science **310**, 1790 (2005)

laser induced reactions: **O + CO / Ru(0001)** — G. Ertl and coworkers, Science, **285**, 1042 (1999)

D + D / Ru(0001) — D.N. Denzler et al. , PRL, **91**, 226102 (2003); S. Wagner et al., Phys. Rev. B, **72**, 205404 (2005)

metal substrates and large band gap systems

electronic excitations are central

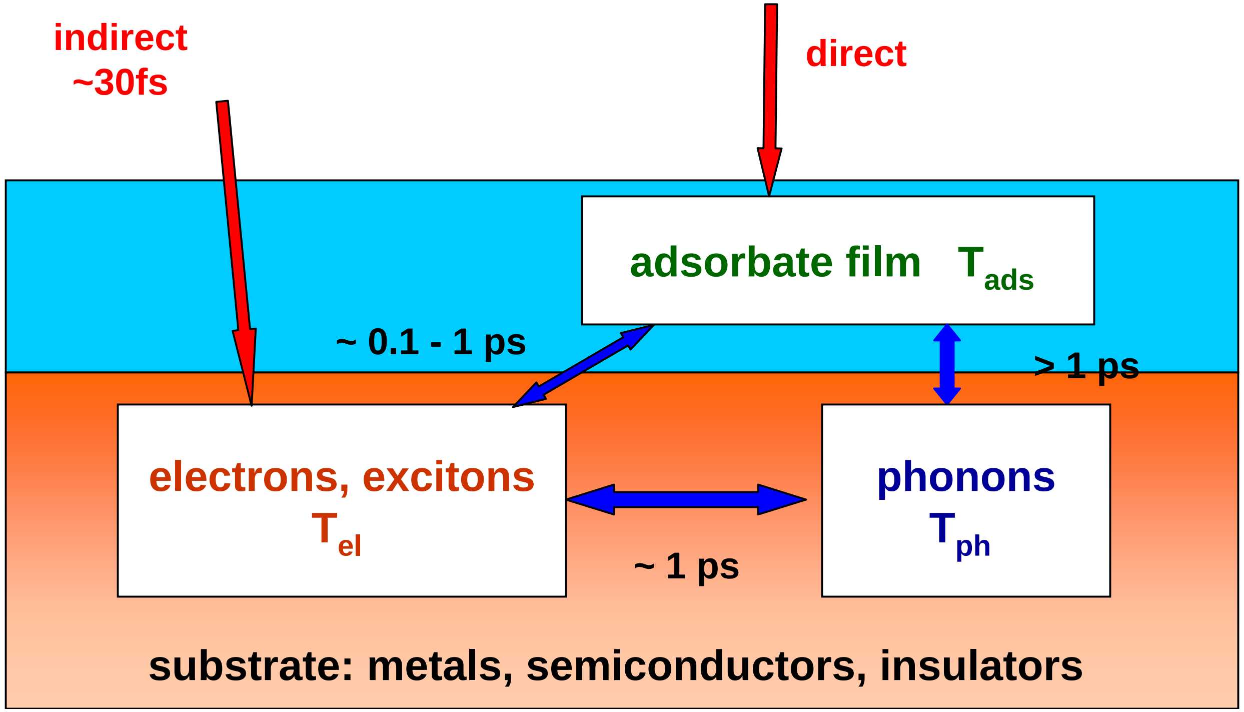
Introduction

nearly all experiments on metallic surfaces

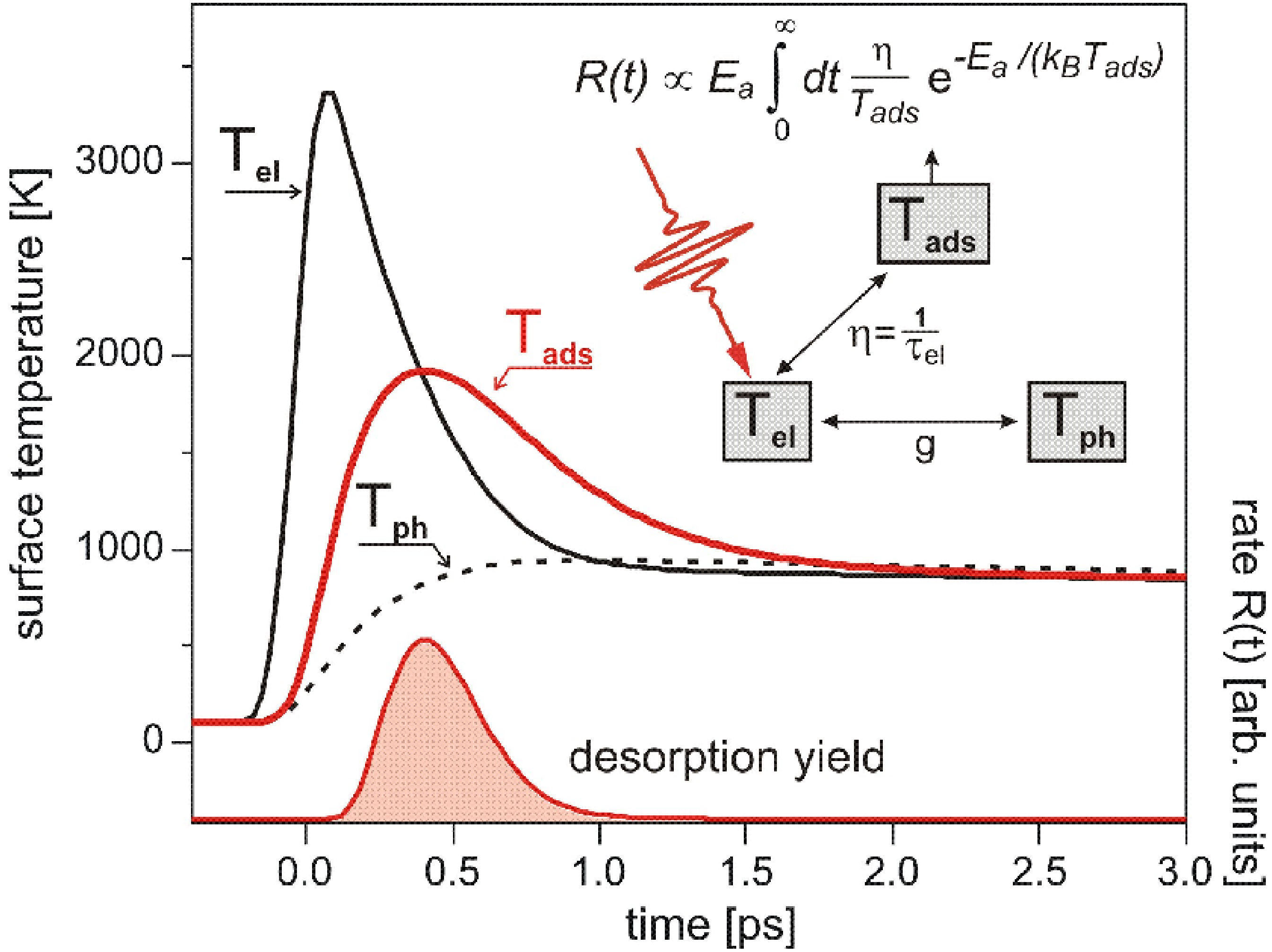
low-lying excitations: near IR wavelength of the inducing laser

two-temperature model for electron and phonon excitation

electronic friction for electronic coupling to the adsorbate molecules



Three temperature model



S. Wagner et al., Phys. Rev. B, **72**, 205404 (2005)

XUV photons

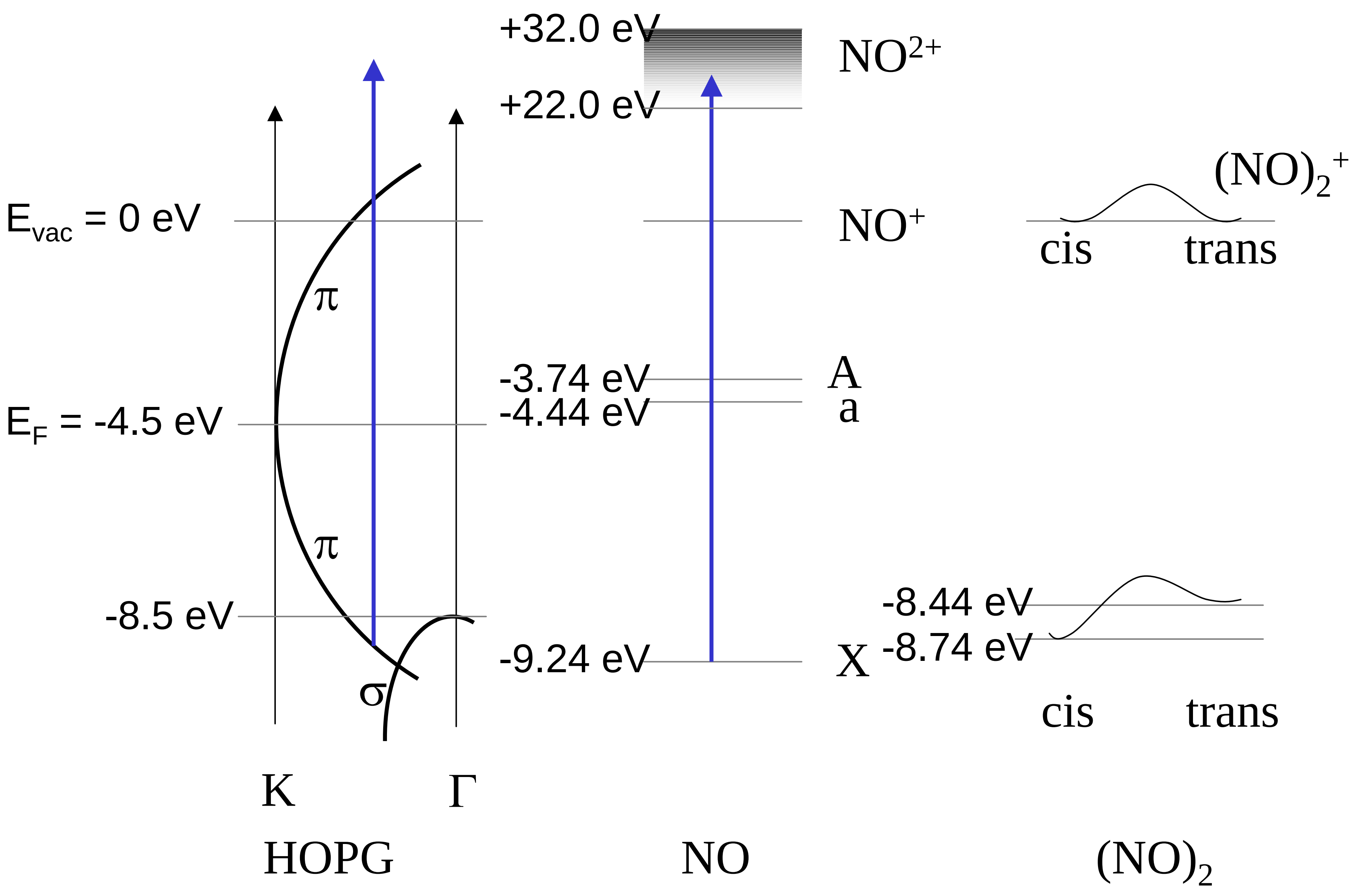
Reactions of molecules and atoms at surfaces
at high photon energies :

- ? substrate mediated ?
- ? direct excitation of the adsorbate ?
- ? excitation of the substrate – adsorbate complex ?

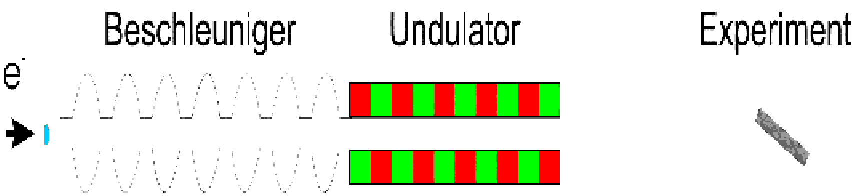
- ? participation of inner shell states ?

Model systems: NO / graphite ; H (D) / graphite

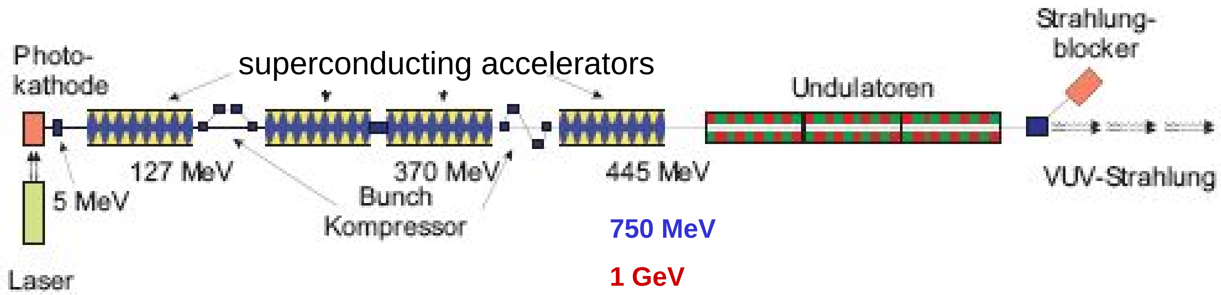
Graphite with NO



XUV Laser system



XUV Free Electron Laser (FLASH)

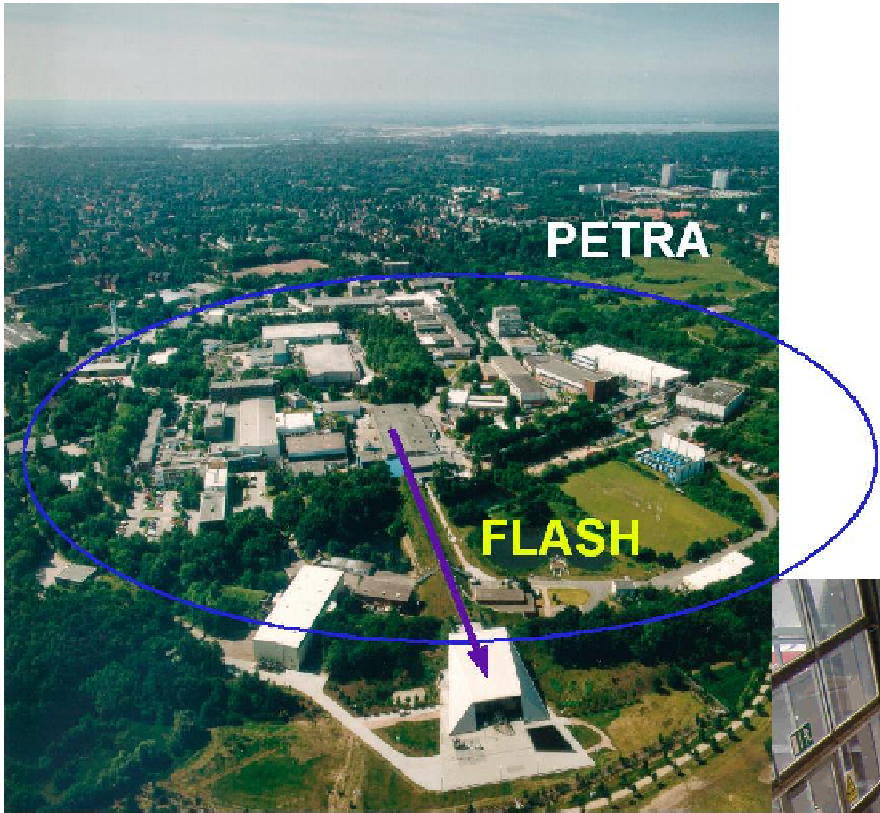


h? = 25 to 206 eV

Third harmonic ~ 600 eV

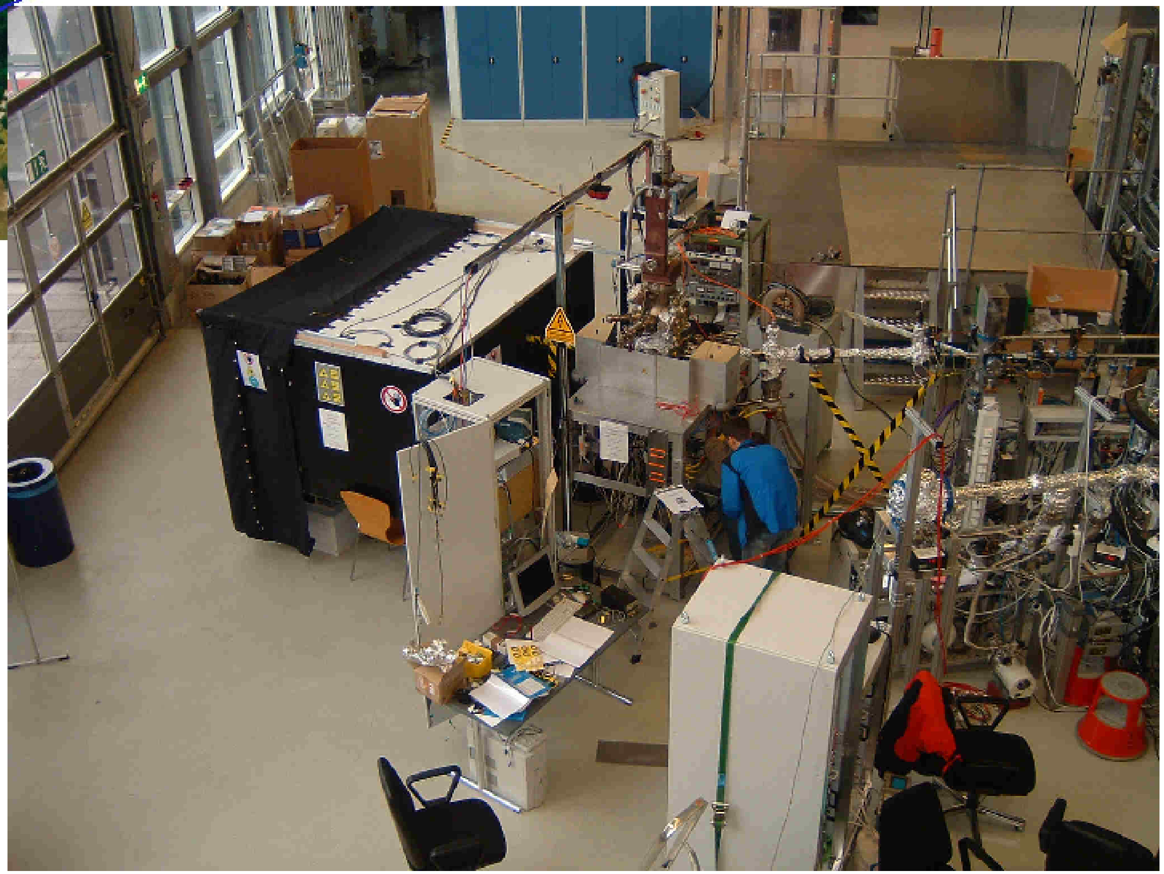
Current parameters:

wavelength	50 to 13 (6) nm
photon energy	25 to 95 (206) eV
pulse energy	~ 50 µJ
repetition rate	5 Hz
bunches	Single to ~ 30
pulse length	20 to 30 fs

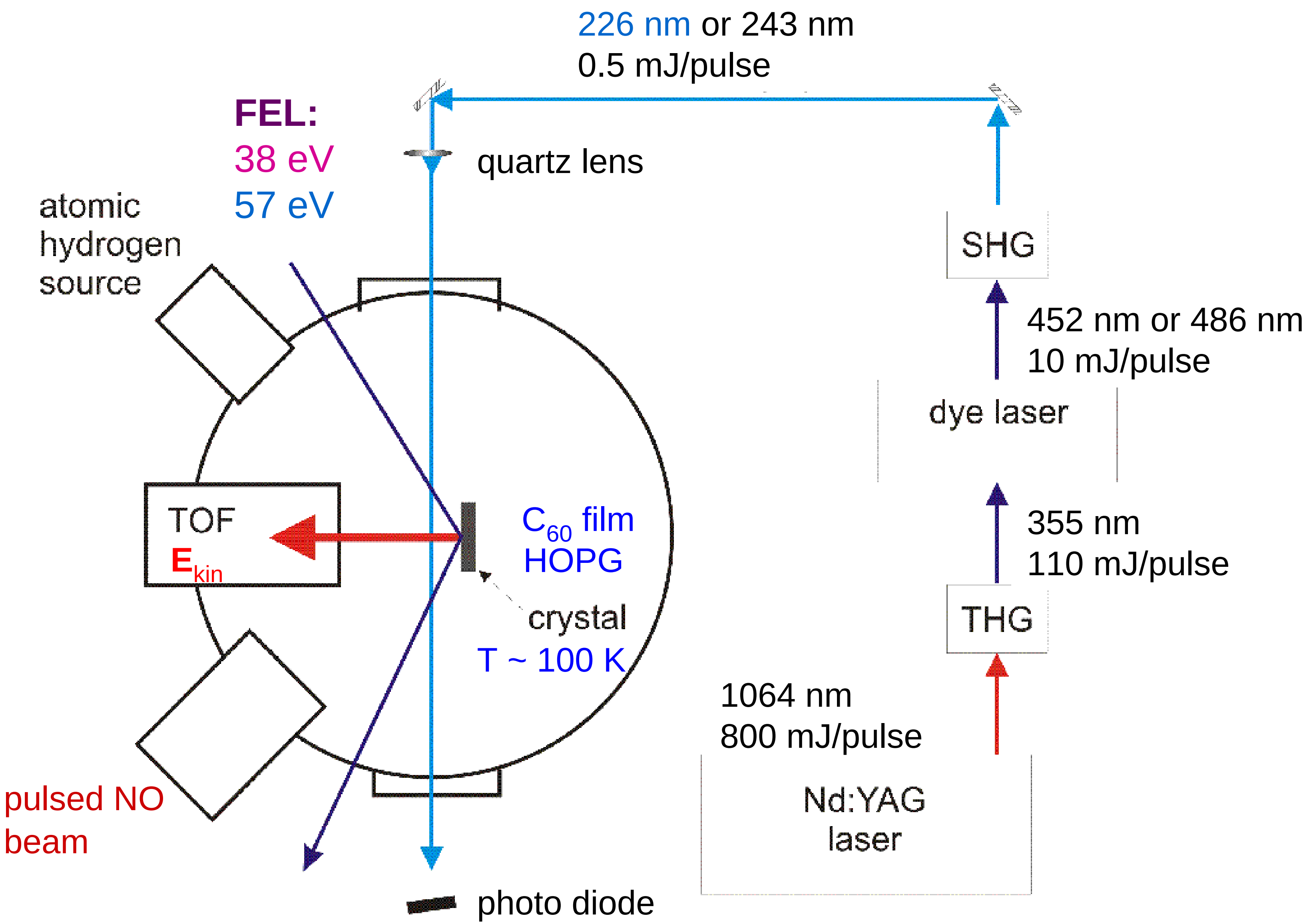


DESY area in Hamburg

Experimental hall

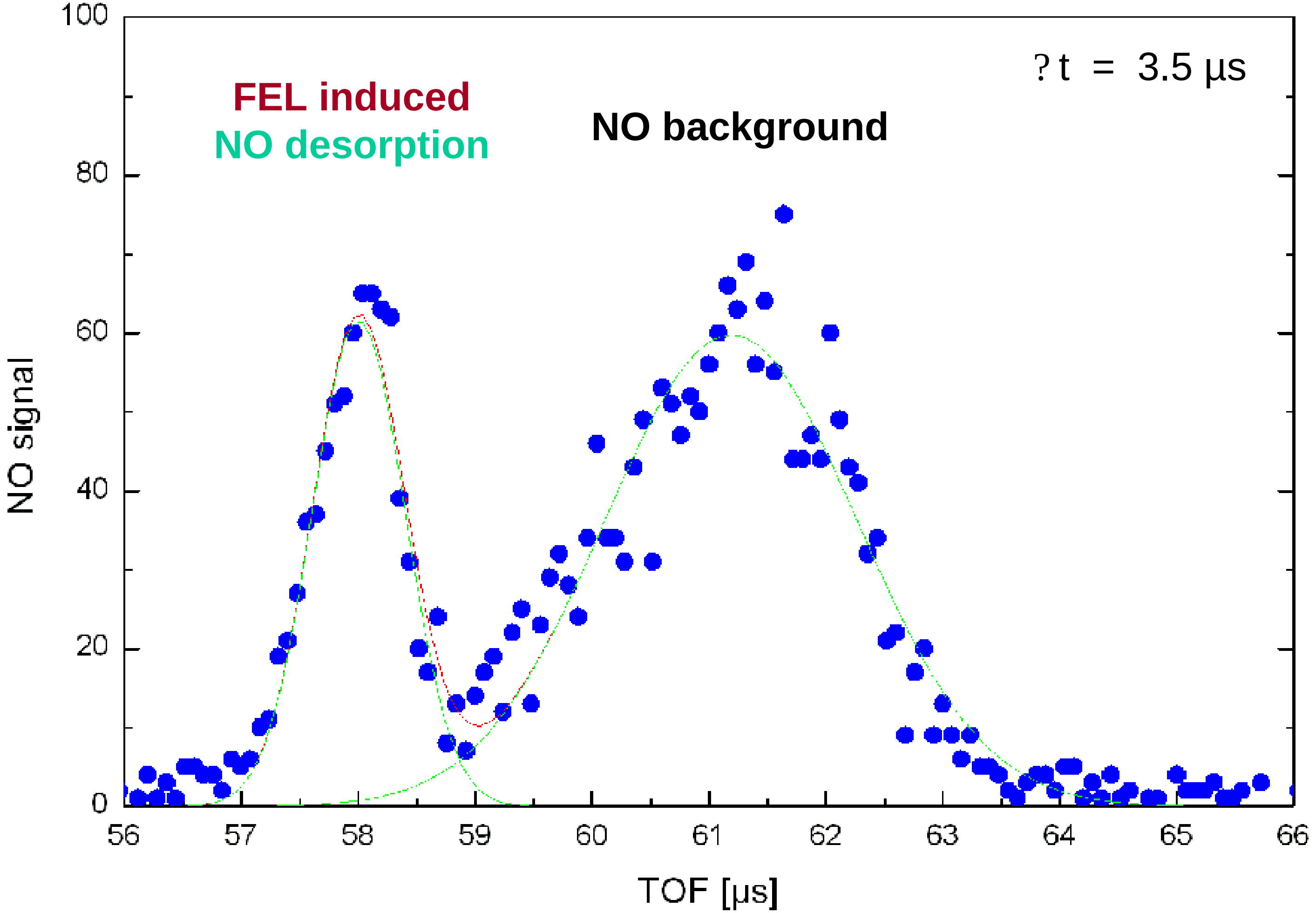


Experimental set-up



NO/graphite: double resonance

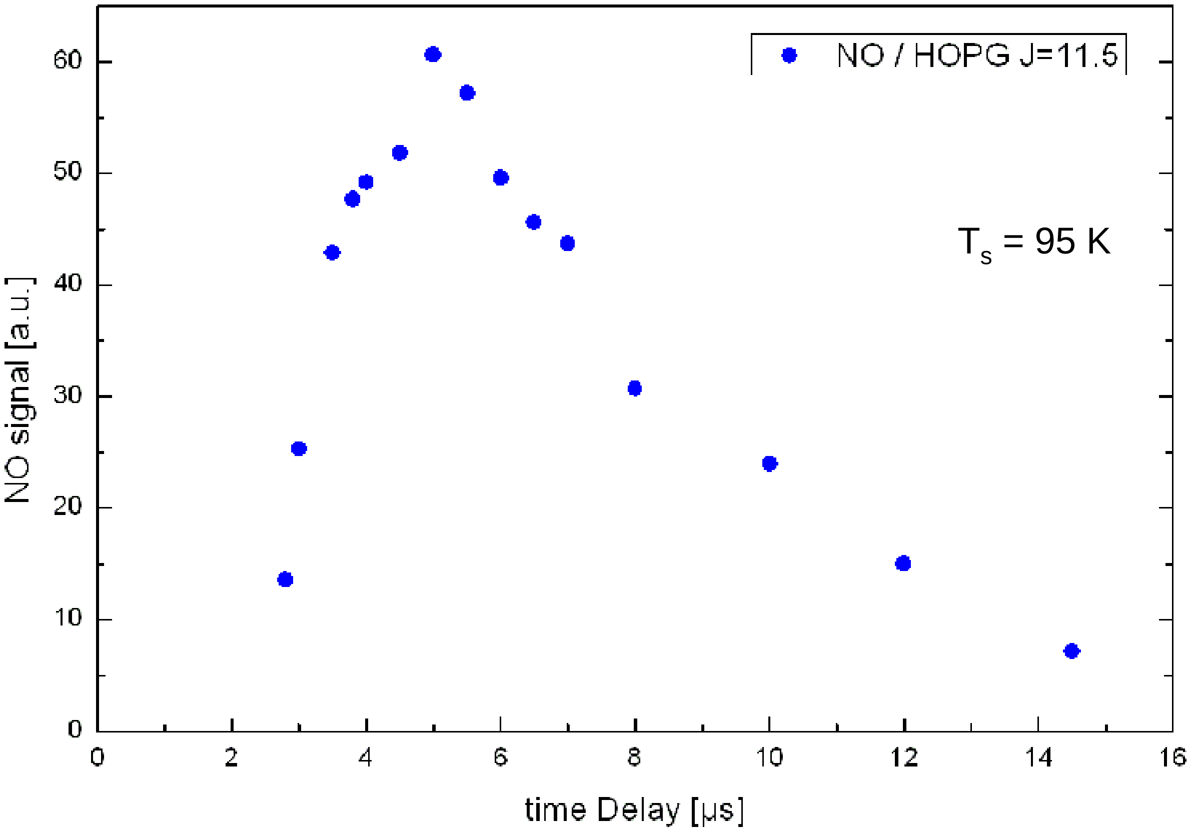
FEL: 32.0 nm (38 eV)



NO/graphite: arrival distribution

probe delay scan on NO (v“ = 0, J“ = 11 ½) :

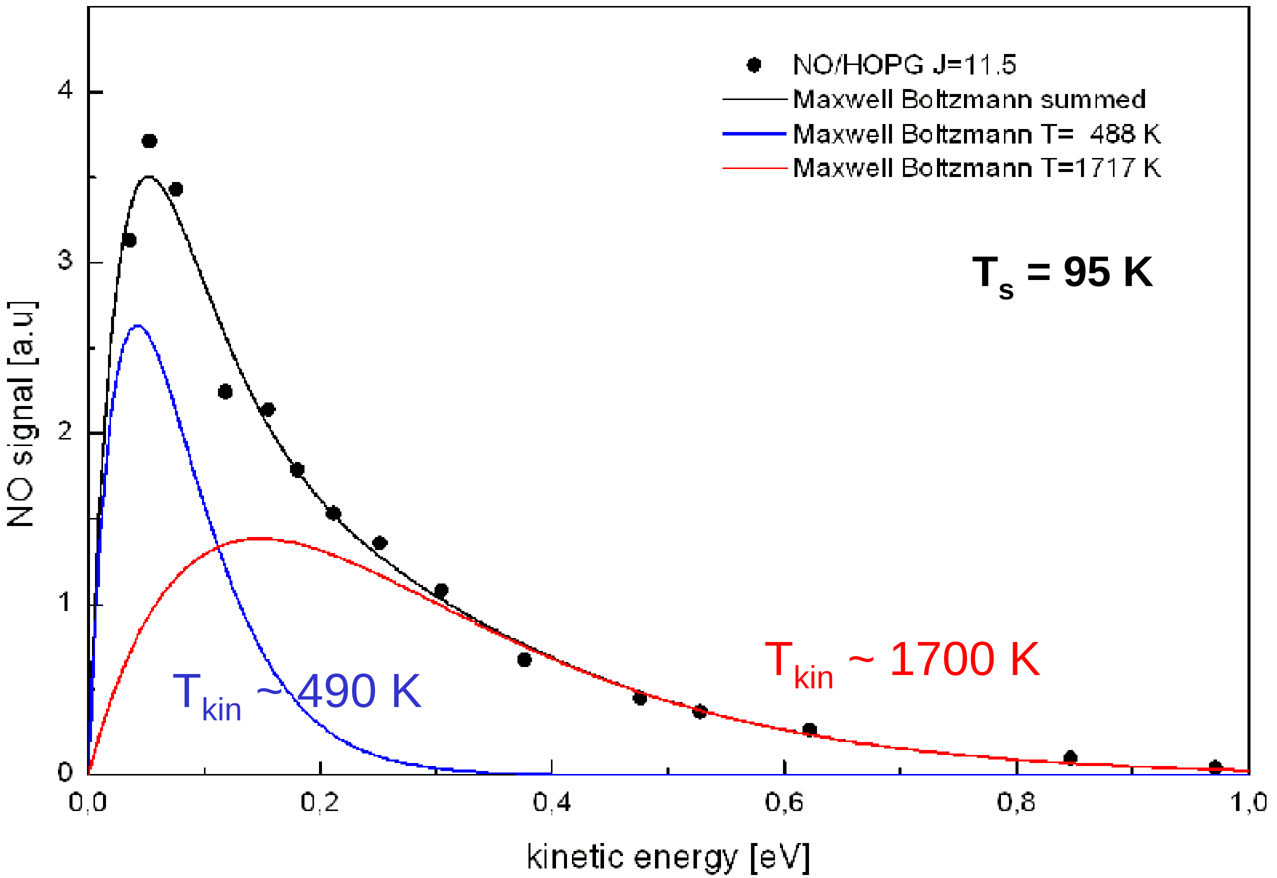
FEL: 32.0 nm (38 eV)



kinetic energy distribution

NO / graphite(0001):

FEL: 32.0 nm (38 eV)



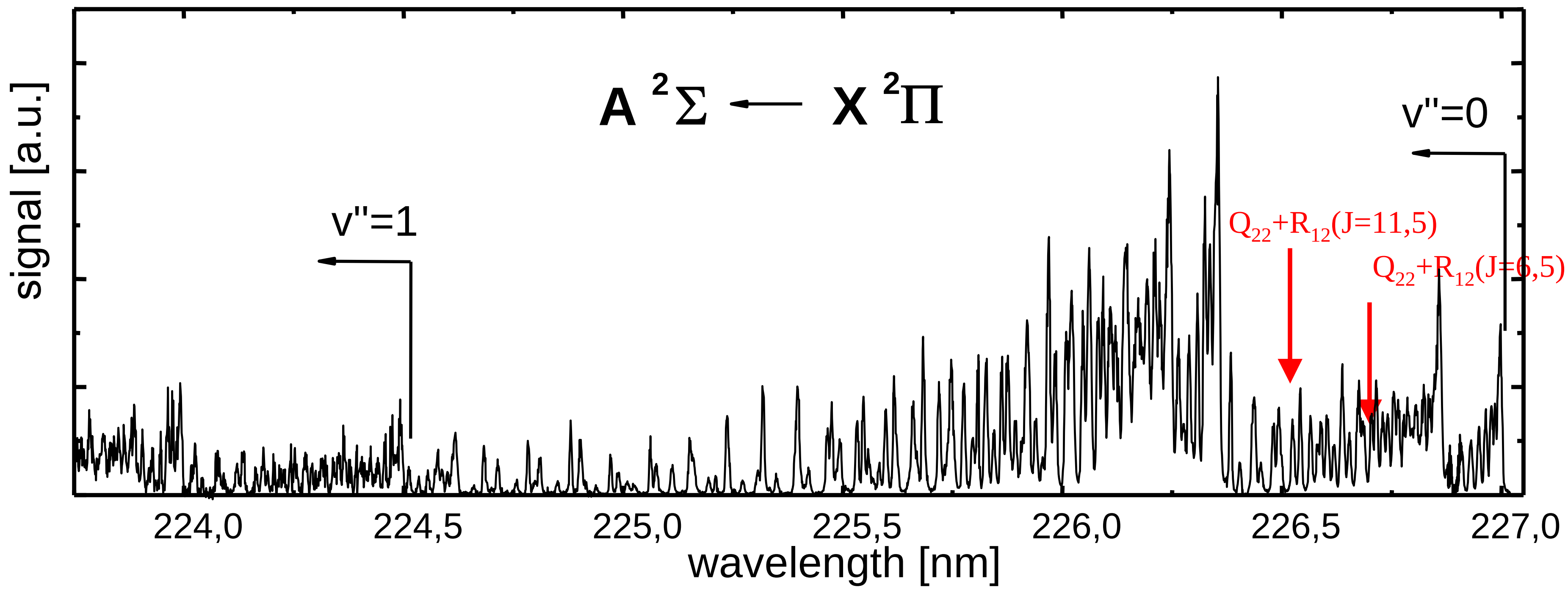
average energy: ~ 170 meV

for other J": similar distributions

NO/graphite

NO: adsorbes at T = 100 K as $(NO)_2$

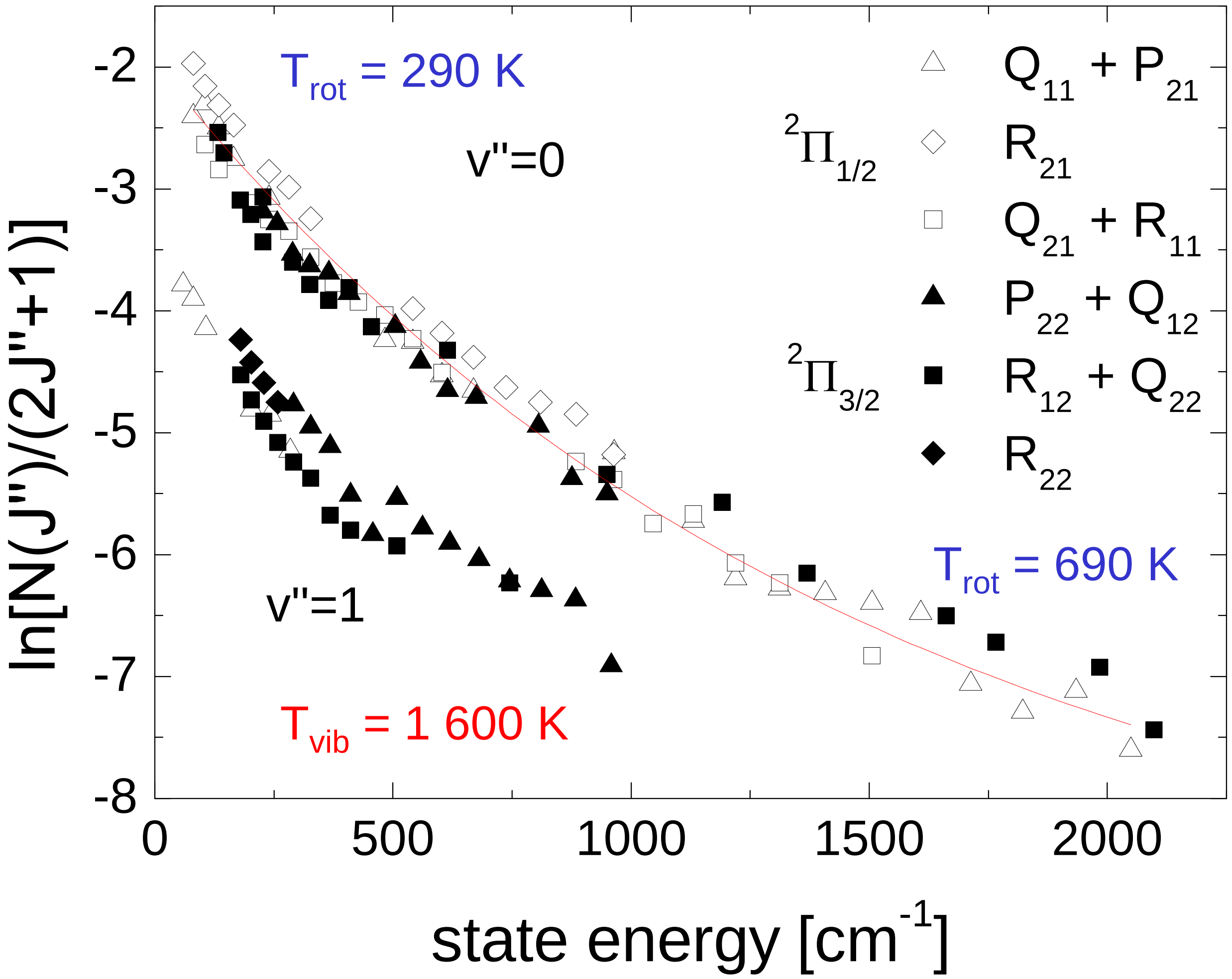
detection via (1 + 1) REMPI at λ ~ 226 nm
very sensitive, rotationally and vibrationally state selective



FEL: 21.7 nm (57.1 eV)

Results: NO/HOPG

FEL: 21.7 nm (57.1 eV)

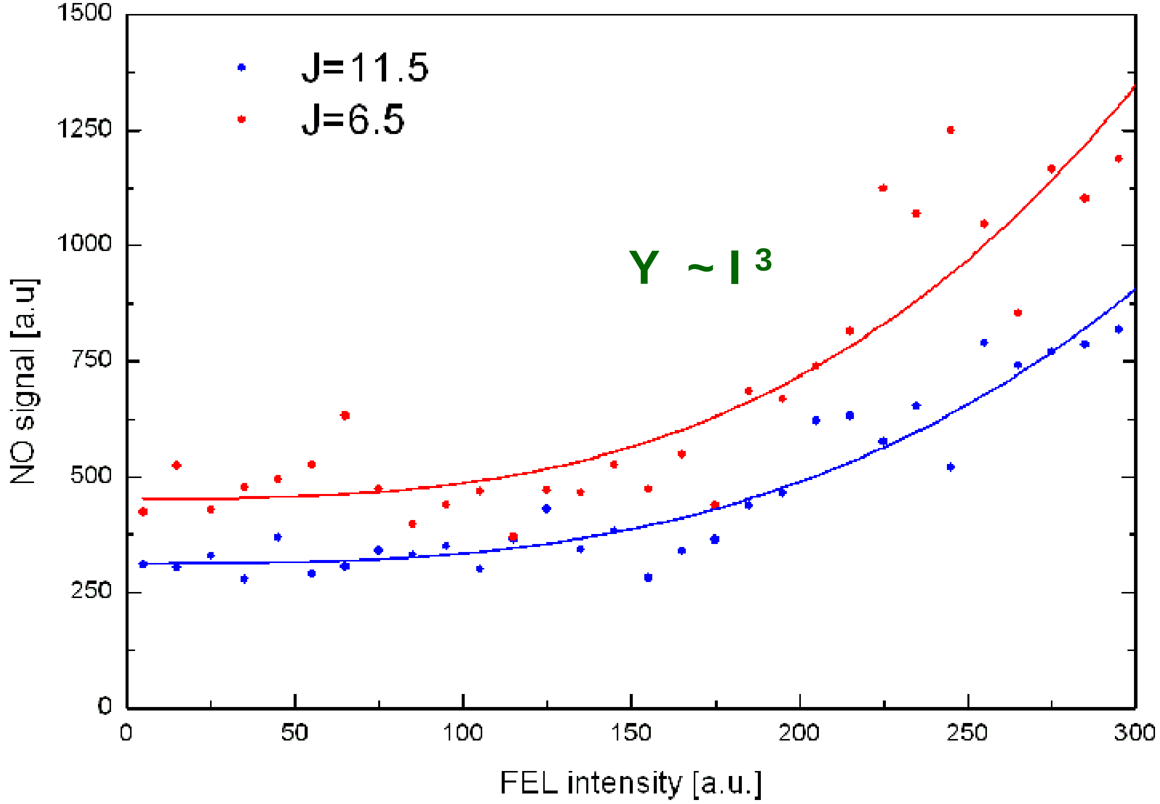


vibrational population ~ 18 %

Intensity dependence

FEL: 32.0 nm (38 eV)

double resonance peak



similar intensity dependence for FEL at 21.7 nm (57.1 eV) : $Y \sim I^{1.4-1.6}$

non-linear surface photochemistry in the soft x-ray regime

NO / graphite

- high rotational excitation: T_{rot} ~ 700 K ; $<E_{rot}>$ ~ 42 meV
- high vibrational excitation: T_{vib} ~ 1 600 K

  gas phase $(NO)_2$ dissociation yields only very low rotational excitation

  (M.P. Casassa, J.C. Stephenson, D.S. King, J. Chem. Phys. **89**, 1966 (1988))
- NO velocity distribution peaks around 1000 m/s , $< E_{kin} >$ ~ 170 meV

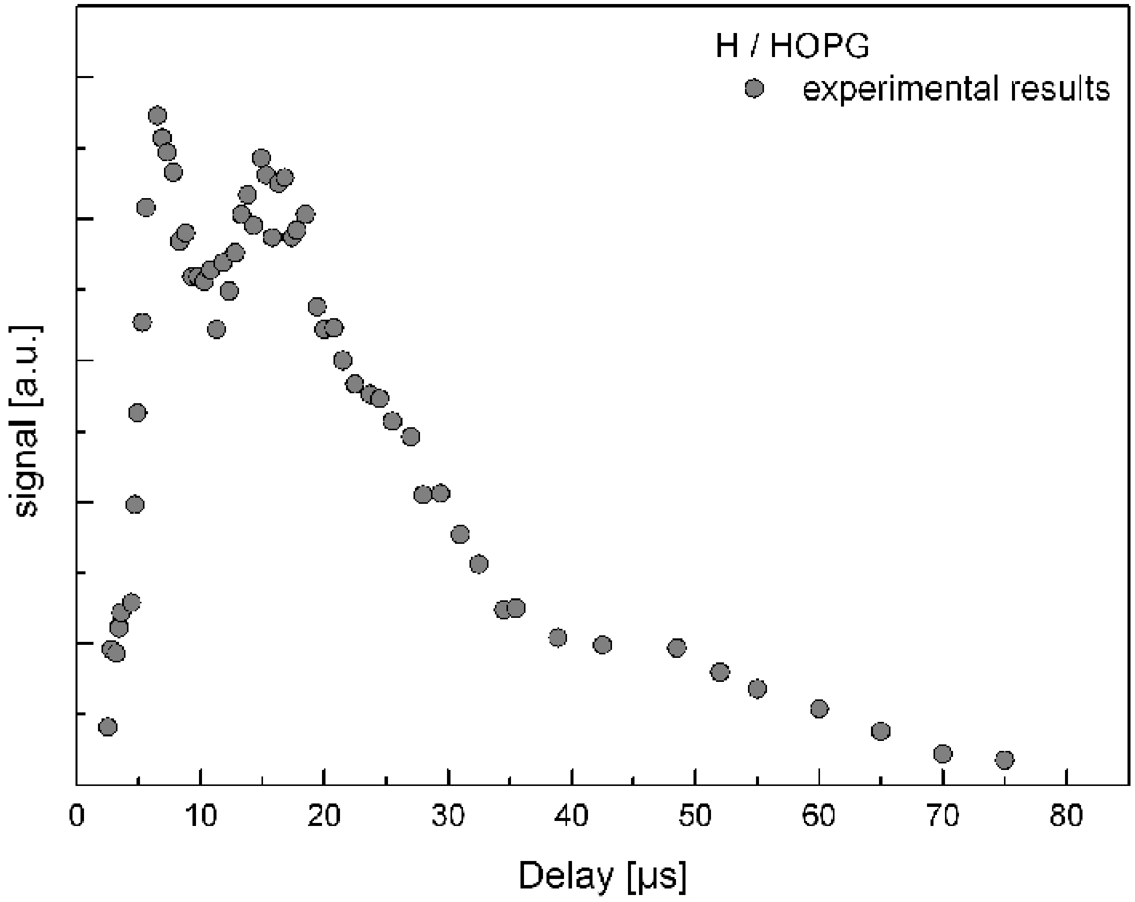
- huge desorption cross section (~ 1 x 10^{-17} cm^2)
- **non-linear yield** dependence for NO from $(NO)_2$ / graphite

  for both h? = 38 and 57 eV

two – pulse correlation experiments with the FEL

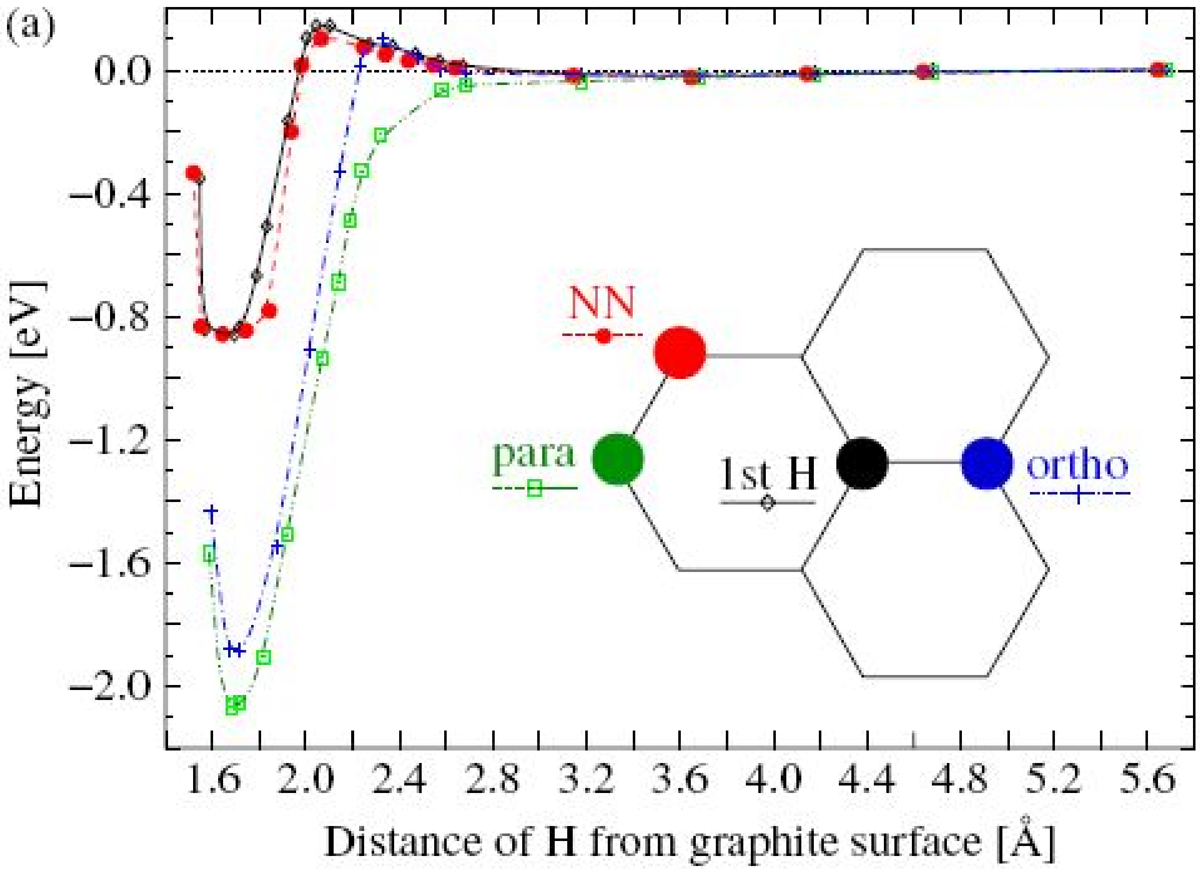
H atom detection

FEL at 32 nm detected by (2+1)REMPI via the 2s ? 1s transition at 243nm



desorption cross section ~ 1.3 x 10 $^{-19}$ cm^2

Hydrogen / graphite



barrierless adsorption for the para position

L. Hornekær et al., Phys. Rev. Lett. **97**, 186102 (2006)
N. Rougeau, D. Teillet-Billy, V. Sidis, Chem. Phys. Lett. **431**, 135 (2006)

Hydrogen / graphite

- extremely late arrival times

  → very low kinetic energy of neutral **H** and **D** atoms

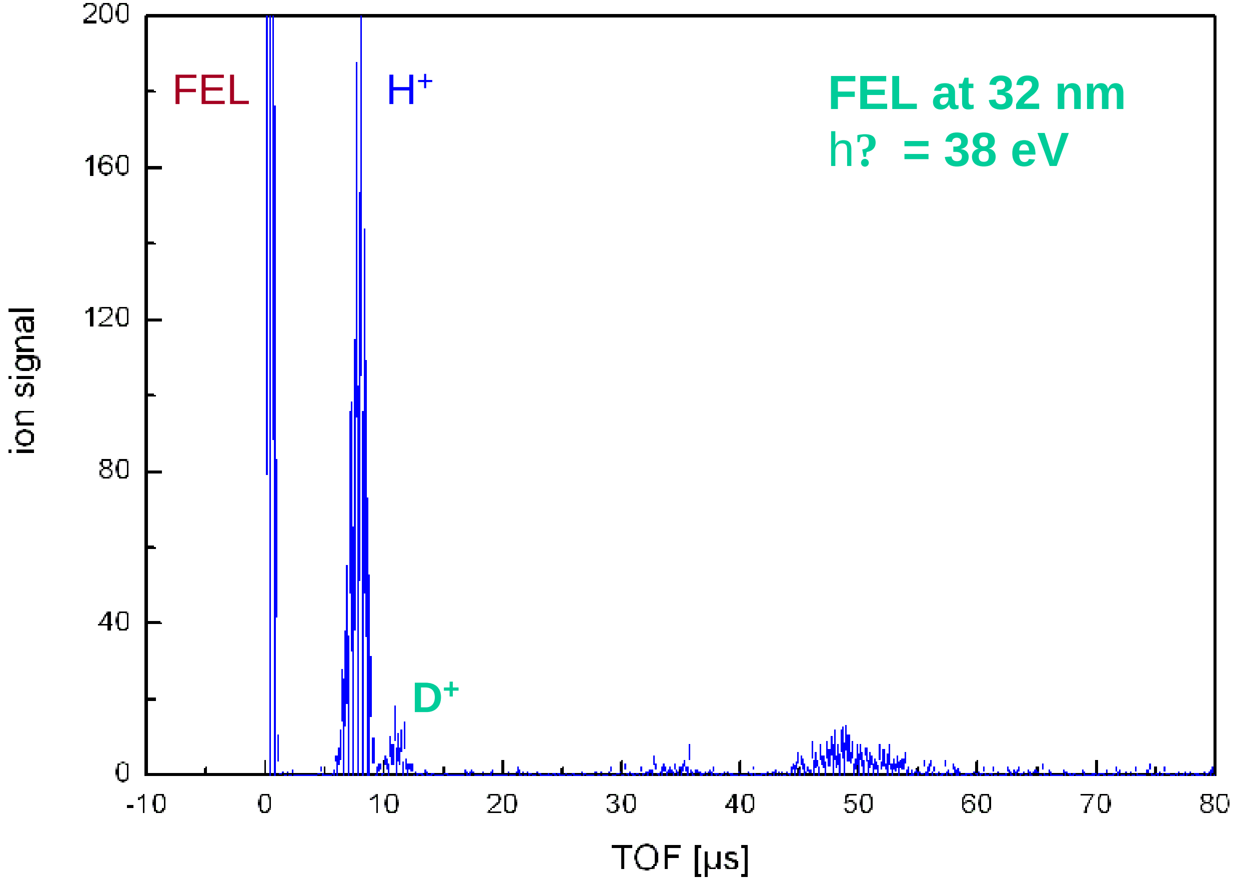
- low desorption cross section (1.3 x 10^{-19} cm^2) for neutral **H**

H^+ ion detection

FEL induced desorption after dosing with neutral H and D atoms

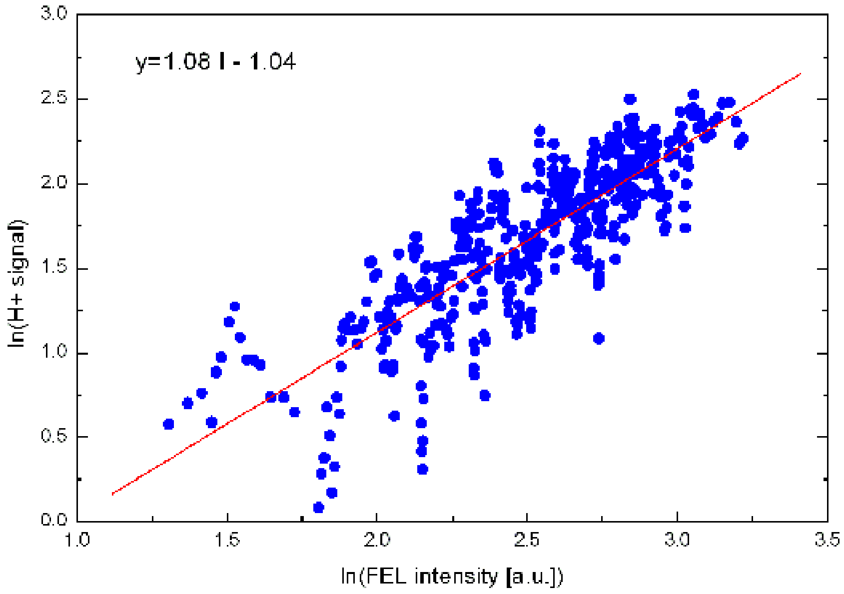
time-of-flight mass spectrum with kinetic energy resolution

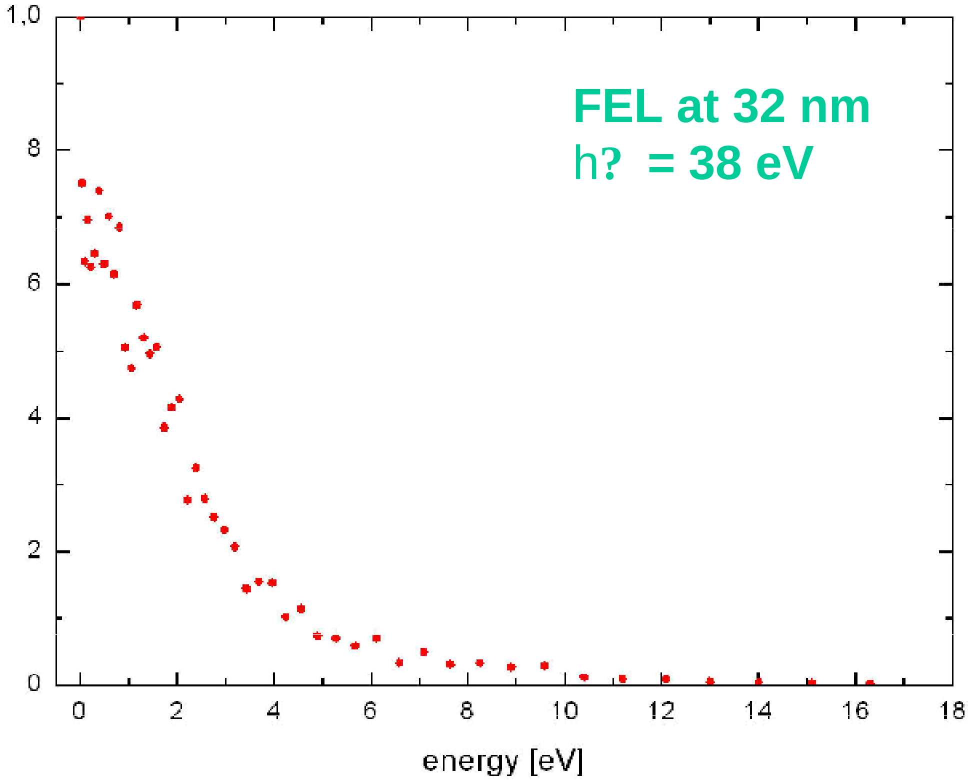
low FEL intensity



H^+ Desorption

H^+ yield dependence





linear intensity dependence

? **DIET process**

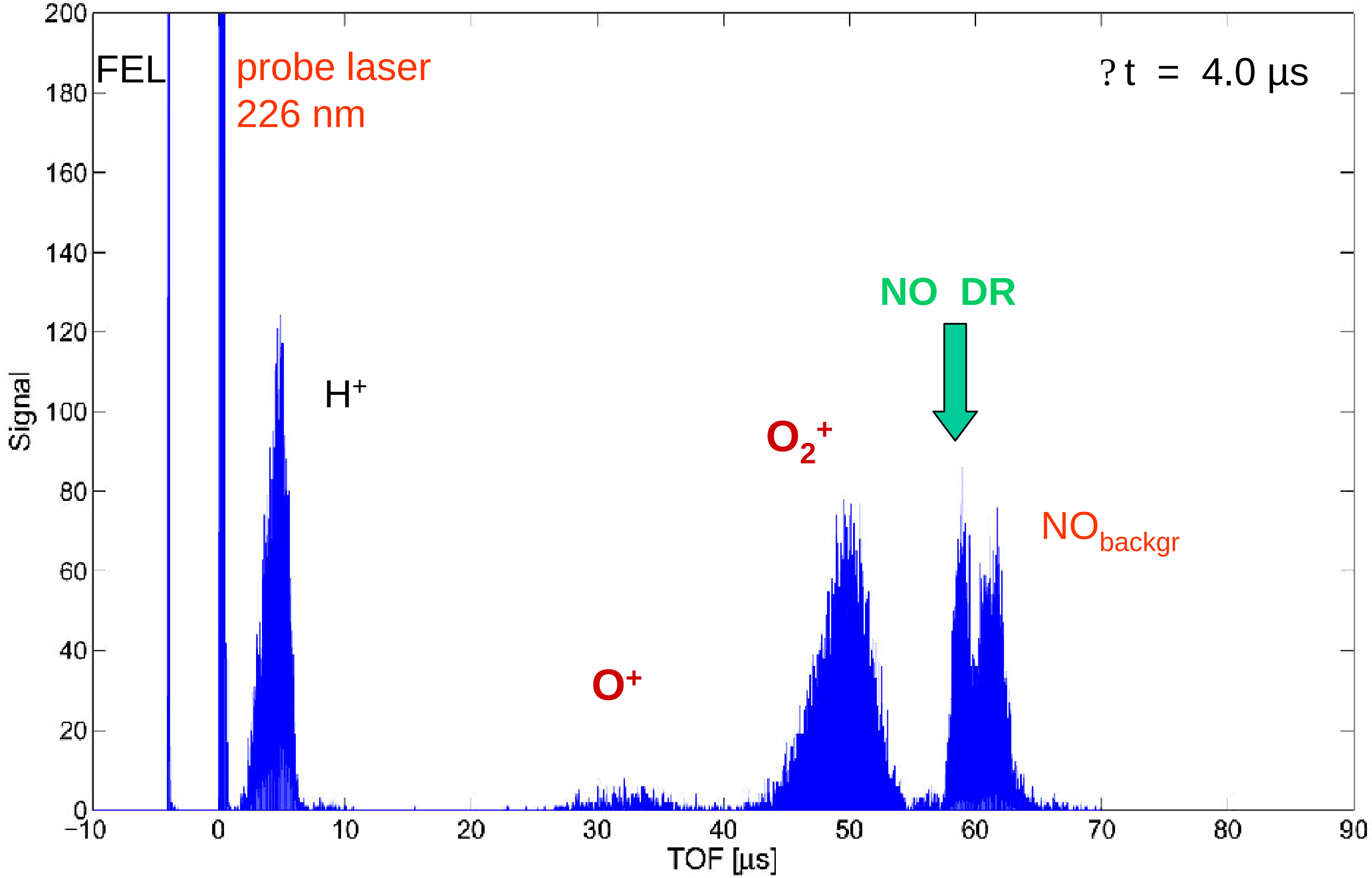
Kinetic energy distribution of H^+ directly desorbed from graphite by the FEL pulse

Average energy: 2.5 eV

NO/graphite

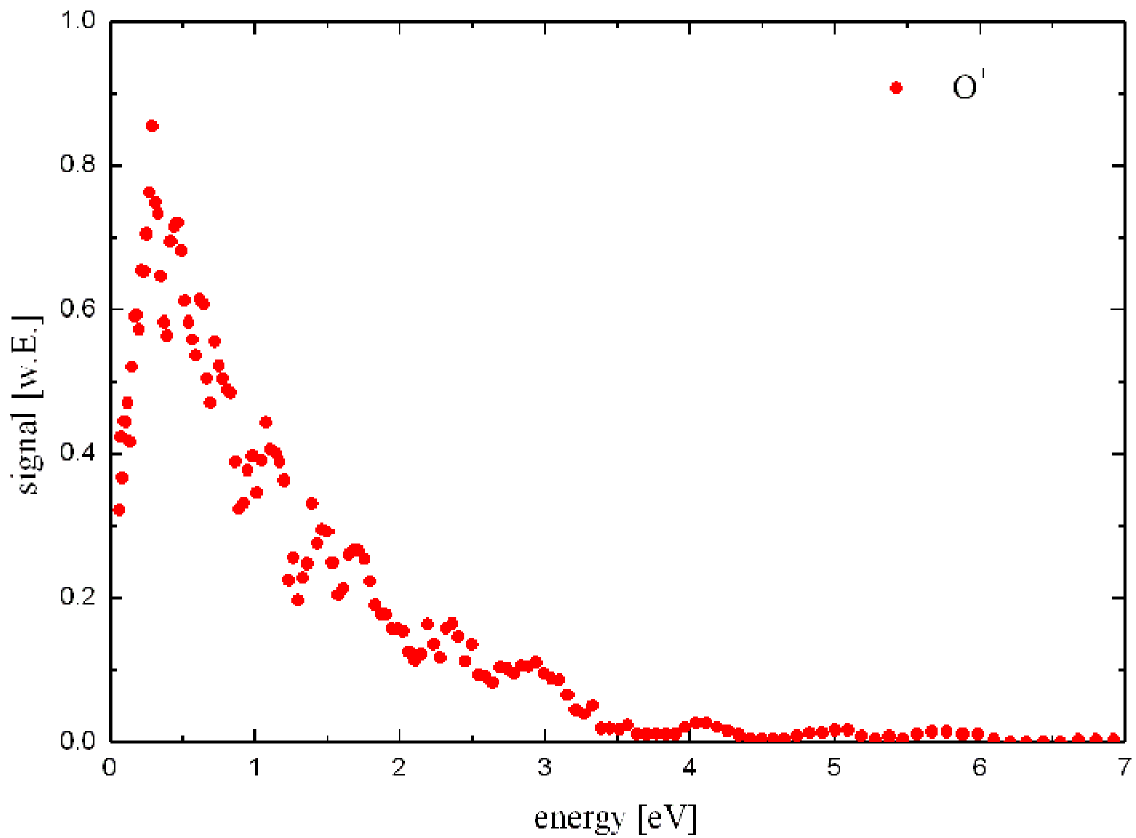
kinetic energy resolving mass spectrum:

FEL: 32.0 nm (38 eV)



O+ kinetic energy

FEL at 32 nm (38.7 eV)

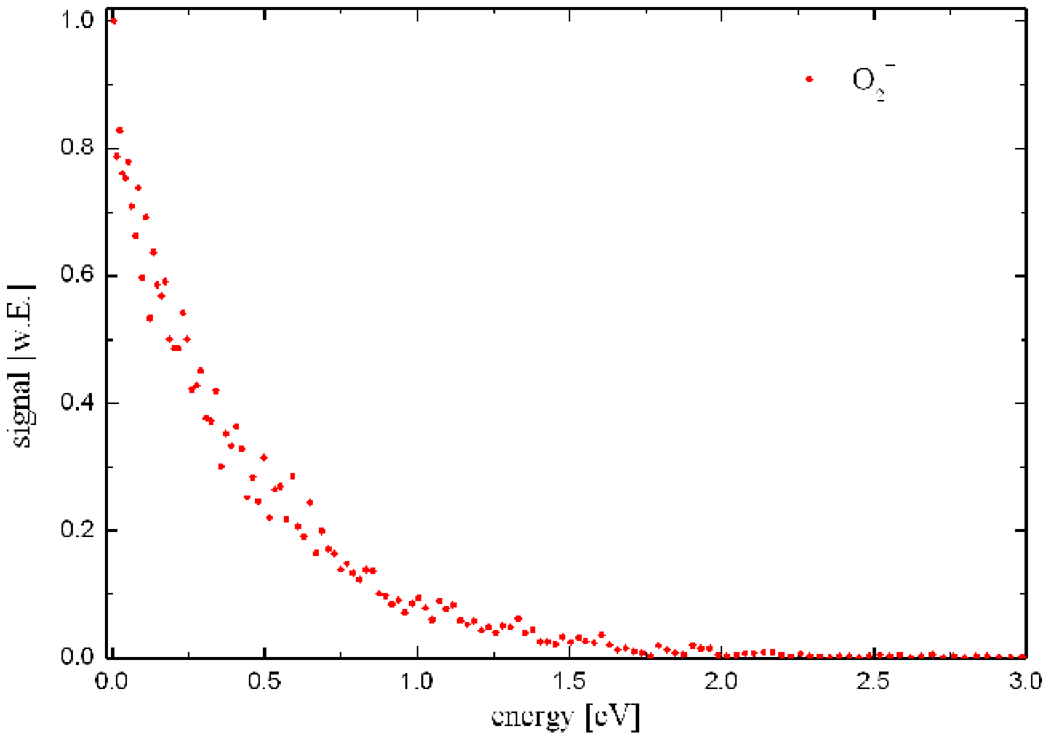


average energy: ~ 1.1 eV

linear dependence
on FEL intensity ? DIET process

O_2^+ kinetic energy

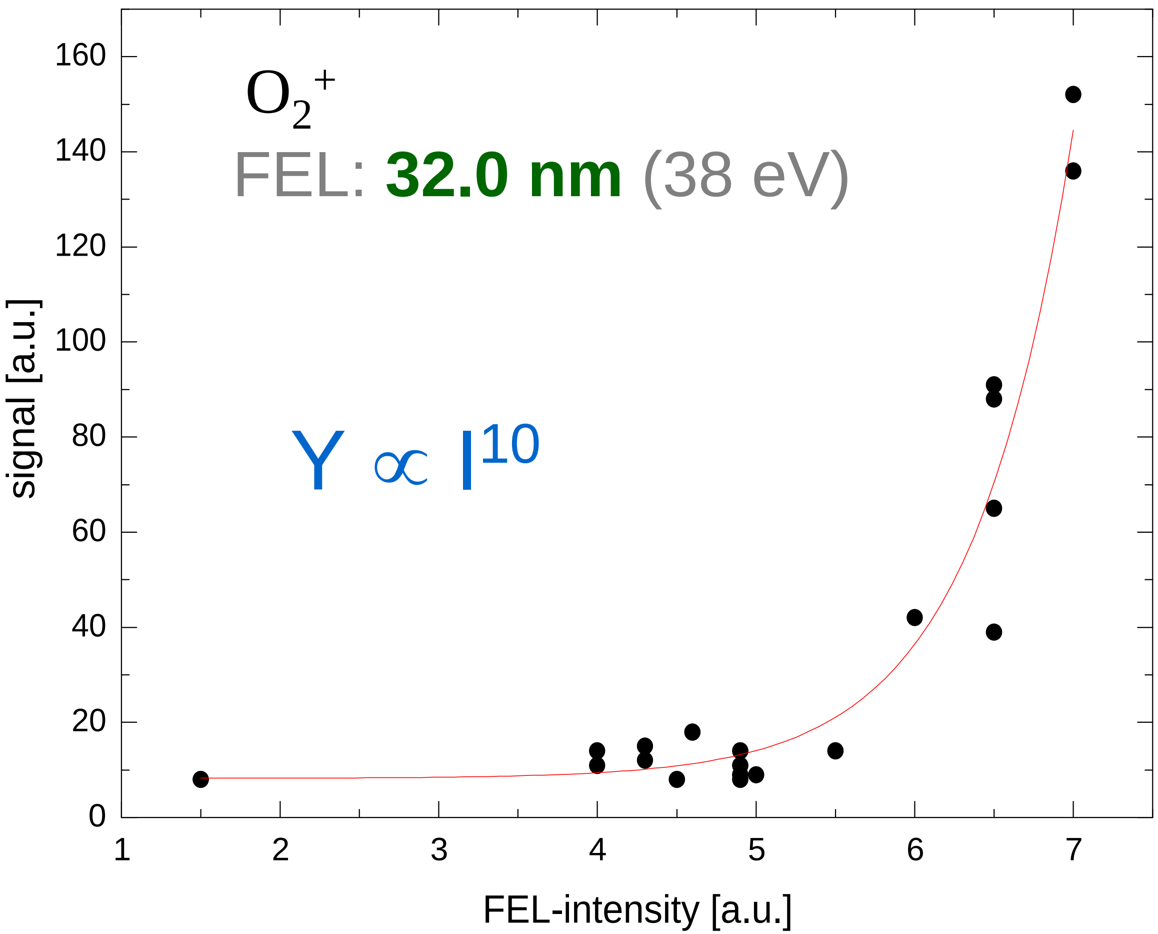
FEL at 32 nm (38.7 eV)



average energy: ~ 430 meV

NO / graphite

O_2^+ desorption from $(NO)_2$ / graphite induced by FLASH



highly non-linear yield

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Conclusion

DESY

? first laser induced desorption and reaction in the XUV
using the **Free Electron Laser FLASH**

? strong internal excitation of NO: electronic processes

? surprisingly slow neutral H atoms

? fast ions (H^+, D^+, O^+) with linear yield

? nonlinear yields (NO, O_2^+)

in the future: experiments at low surface temperature
with time-correlated FEL pulses

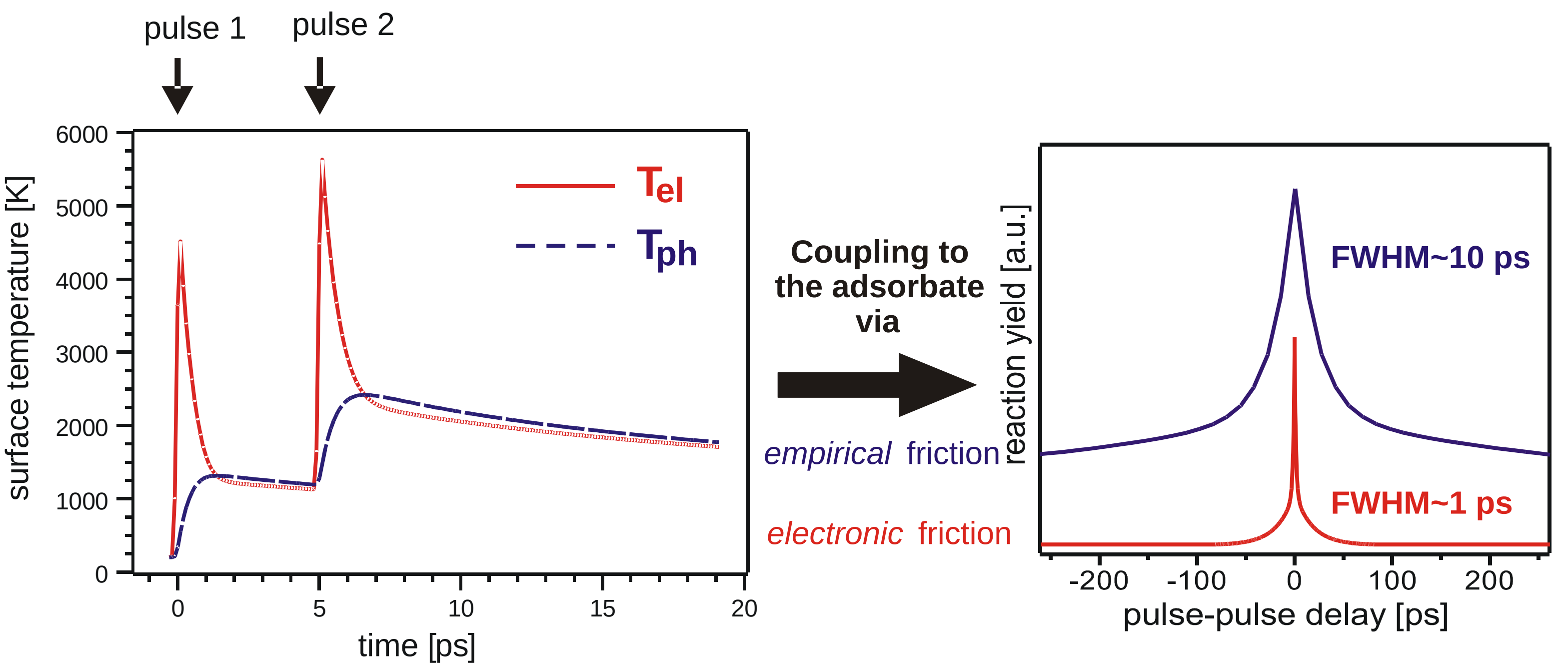
Outlook

•**non-linear yield** dependence for NO from $(NO)_2$ / graphite for both

h? = 38 and 57 eV

•**non-linear yield** dependence for O_2^+ from $(NO)_2$ / graphite

two – pulse correlation experiments with the FEL



F. Budde et al., Phys. Rev. Lett. **66**, 3024 (1991)

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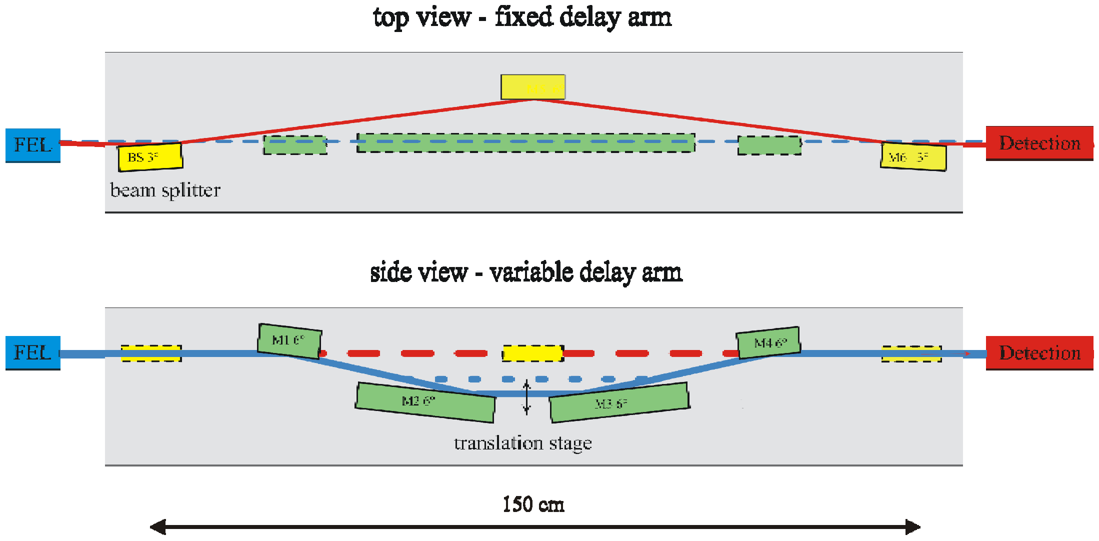
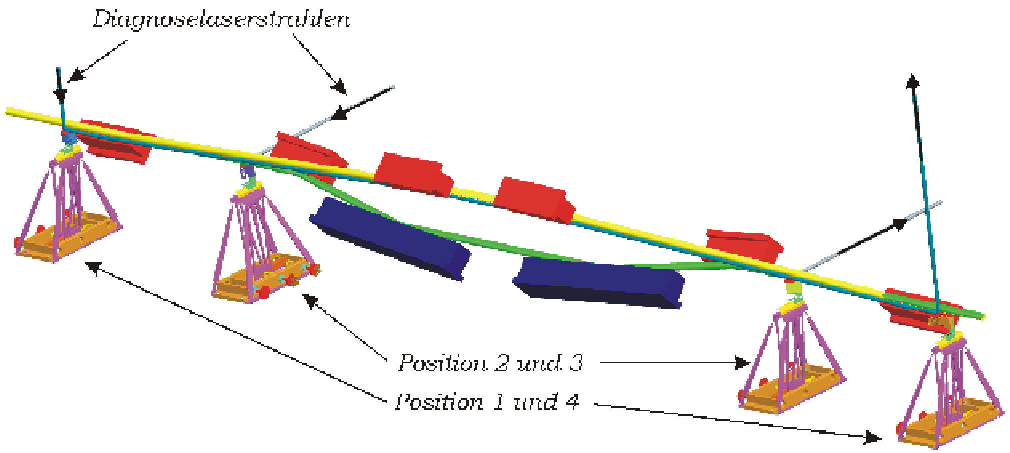
Two – pulse correlator

BESSY



Time-resolved experiments directly with the FEL pulses

FEL beam



built together with BESSY for the FEL

R. Mitzner, M. Neeb, T. Noll, N. Pontius, W. Eberhardt, Proc. SPIE, 59200D (2005)

ready to be tested at the FEL in a few months