表面・界面化学反応、磁性薄膜研究のERLにおける将来展望

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[1]KEK-PF, [2]慶應義塾大学

Short pulse (0.1-1 ps), High rep rate (1.3 GHz; 0.8 ns)

Outline

- 時間分解実験
  - 表面反応の高速追跡
  - 分子吸着による表面磁性の変化の追跡
  - 磁化反転過程の観測、スピントロニクス材料を見据えて
    - 透過型軟X線顕微鏡
    - 磁気小角散乱

- ちょっと提案
  - 軟X線と硬X線が同時に使えるBL

What are prospective triggers?

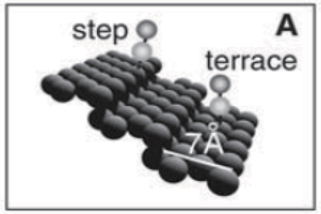
- For surface chemical reaction
  - Pulsed valve: *Widely used now, but...*
  - Laser:
    - Photo-stimulated desorption (PSD)
    - Sudden heating
- For magnetization process
  - Pulsed current
  - Pulsed magnetic field

Pulse lengths down to 10 μs

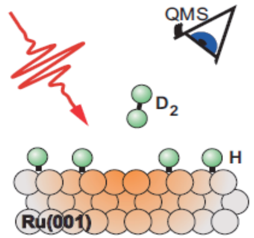
What are required time resolutions like?

<Laser-excited thermally non-equilibrium state, and ...>

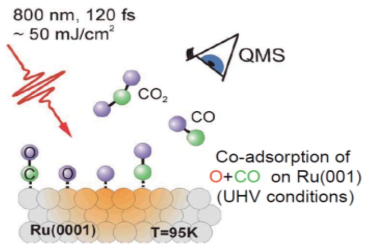
- Laser-induced Movement of CO on Pt: ~1 ps
  - E. H. J. Backus, *et al.*, Science **310**, 1790 (2005).



- Laser-induced desorption of D_2, D on Ru(0001): ~ 1 ps
  - D. N. Denzler, *et al.*, PRL **91**, 226102 (2003).



- Laser-induced CO oxidation on Ru(0001): ~ 3ps
  - M. Bonn, *et al.*, Science **285**, 1042 (1999).



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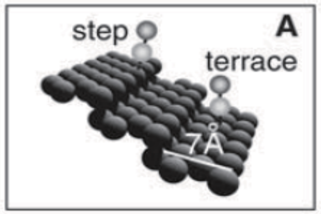
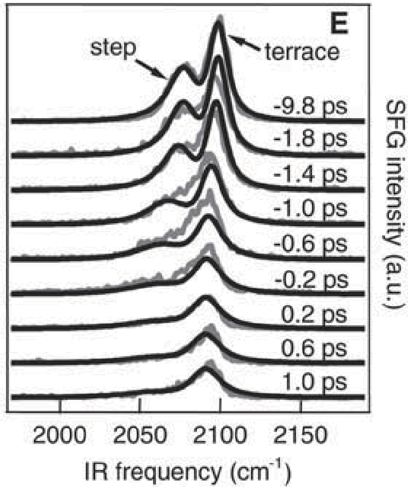
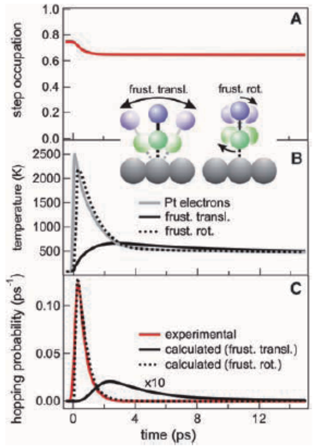
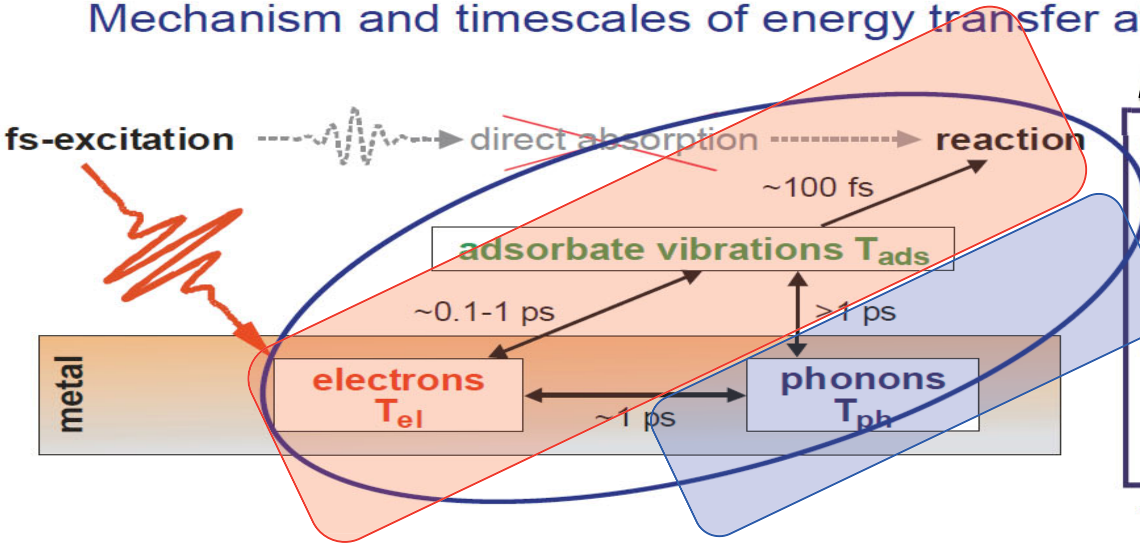


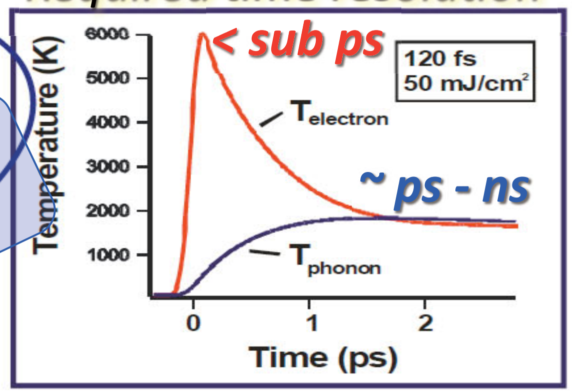




Mechanism and timescales of energy transfer after optical excitation



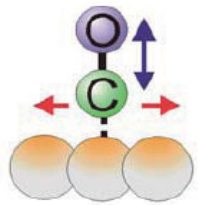
Required time resolution



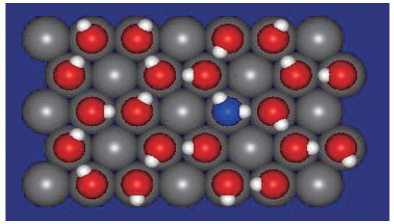
Anisimov, et al. Sov. Phys. JETP **39**, 375 (1974)

Time scales of thermally equilibrium phenomena

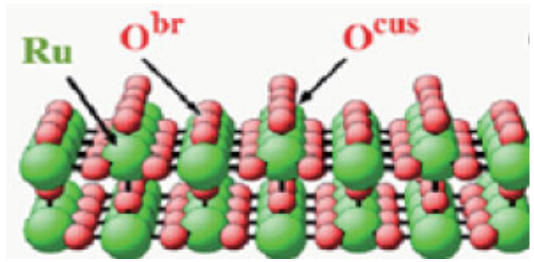
- CO site hopping on Ni(111) at 600 K: 210 ns
  - Y. R . Shen, *et al.*, PRL **61,** 2883 (1988).



- Proton transfer on Pt(111) at 150 K: 5-50 ns
  - M. Nagasaka, *et al.*, PRL **100,** 10610 (2008).

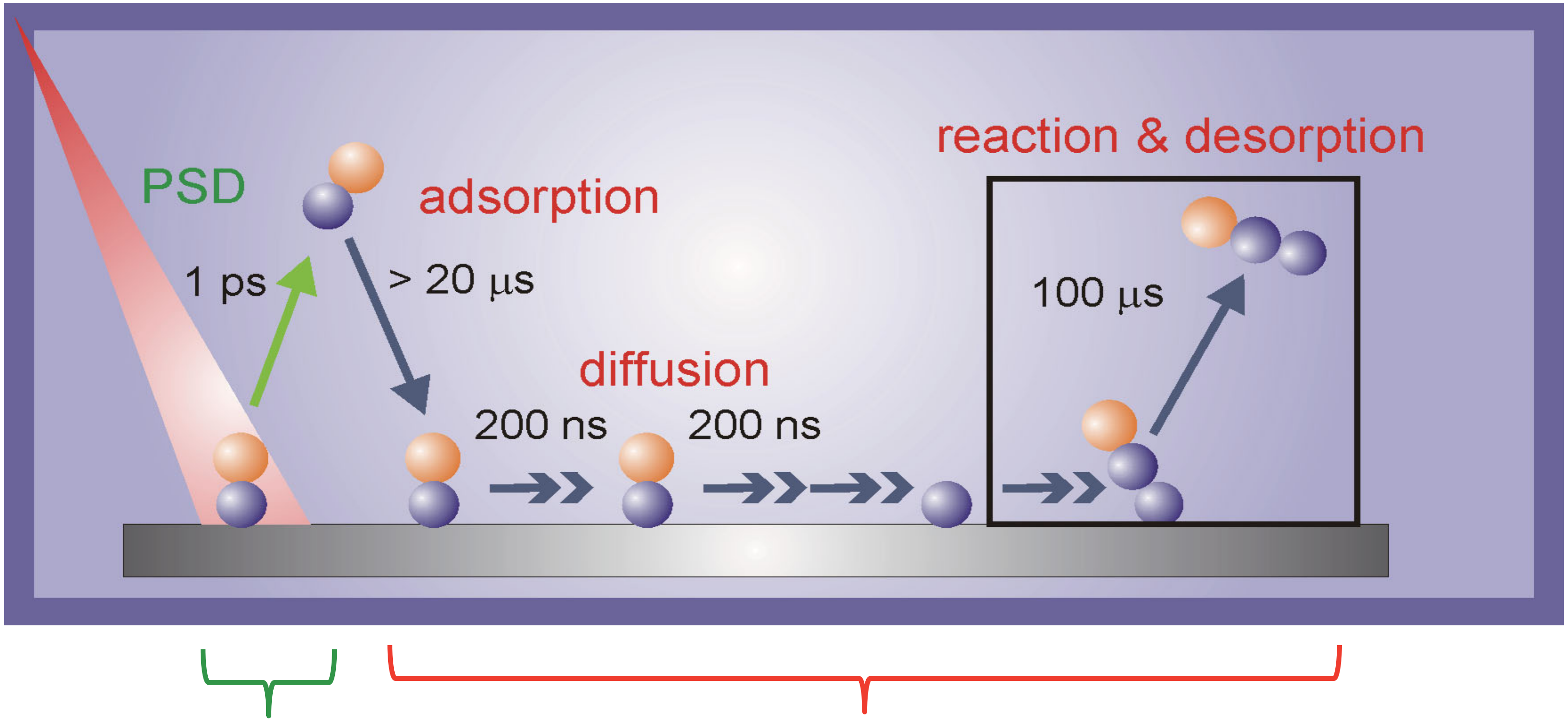


- CO desorption on RuO_2(110) at 600 K: 90 ns
- CO oxidation: 130 μs
  - K. Reuter, *et al.*, PRL **93**, 116105 (2004).



~ns snapshots:
Effective and just right to make "real time movies"

Time-resolved "pictures" of surface reaction



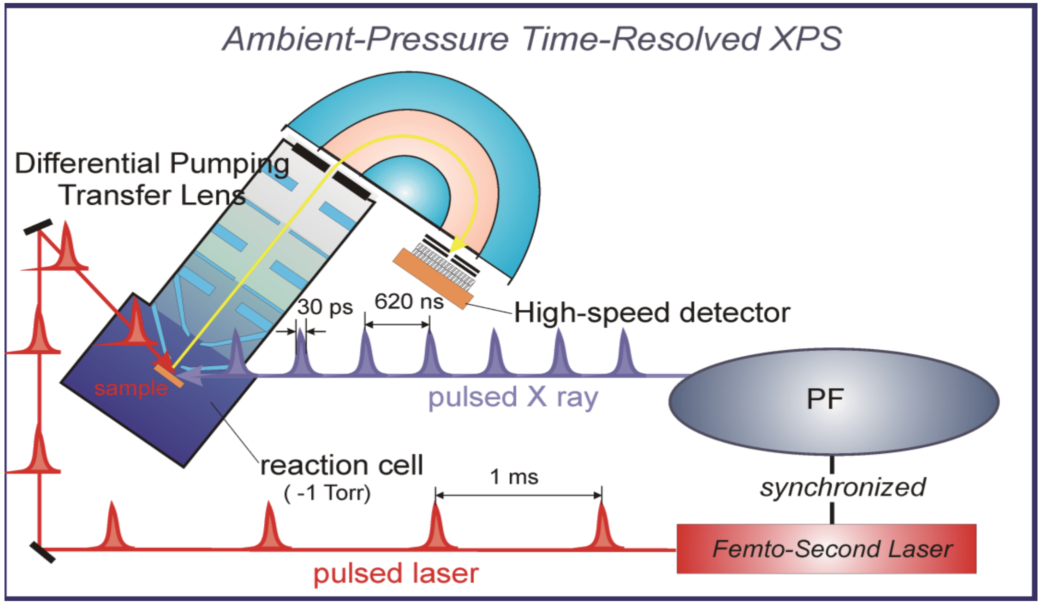
Laser pump – x-ray probe

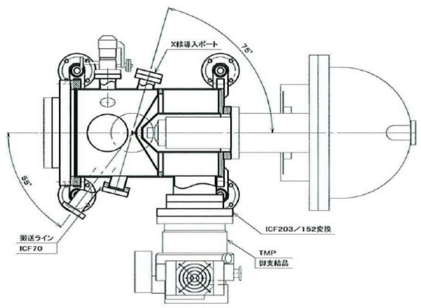
(Snapshots with delay line)

X-ray real time "movie"

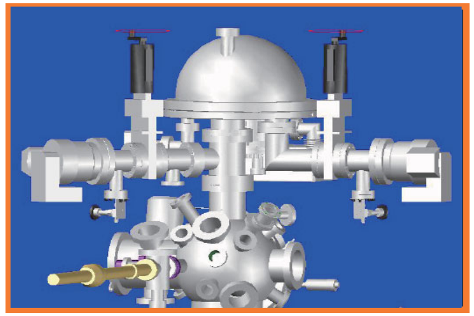
(Successive pictures)

Ambient Pressure Time-Resolved XPS





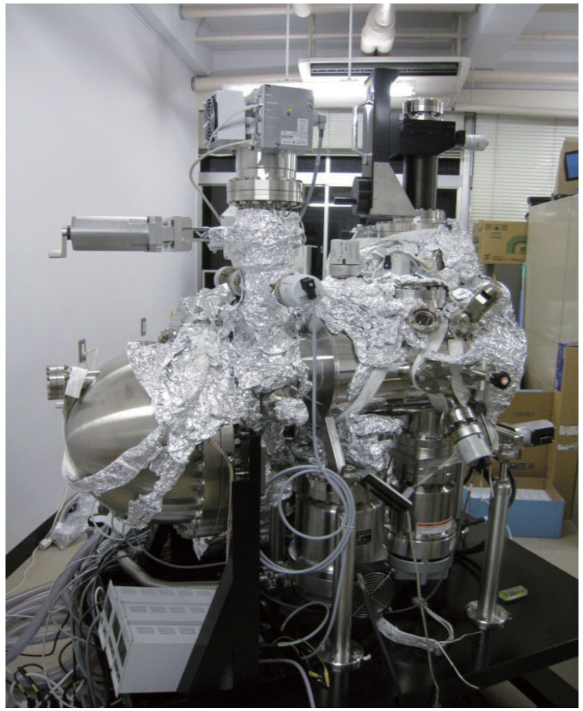
Diff. pumped Exp. chamber



Diff. pumped e^- energy analyzer

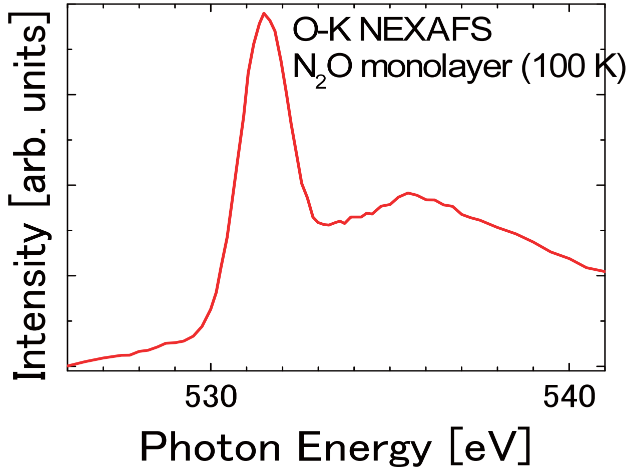
PF => ERL

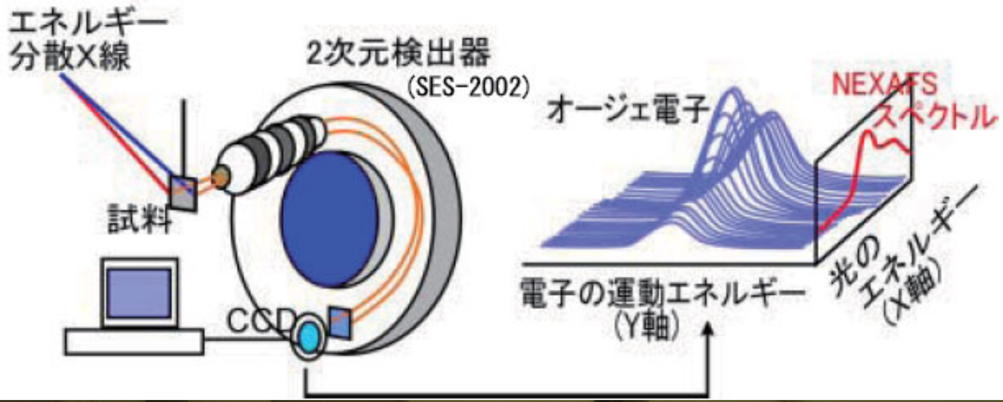
- Laser pump – x-ray probe
- Time-resolved inner shell spectroscopy
  - Time resolution: 30 ps => < 1 ps
  - Sampling rate: 620 ns/spec => 0.8 ns/spec
- Pressure controllable
  - UHV - ~1 Torr

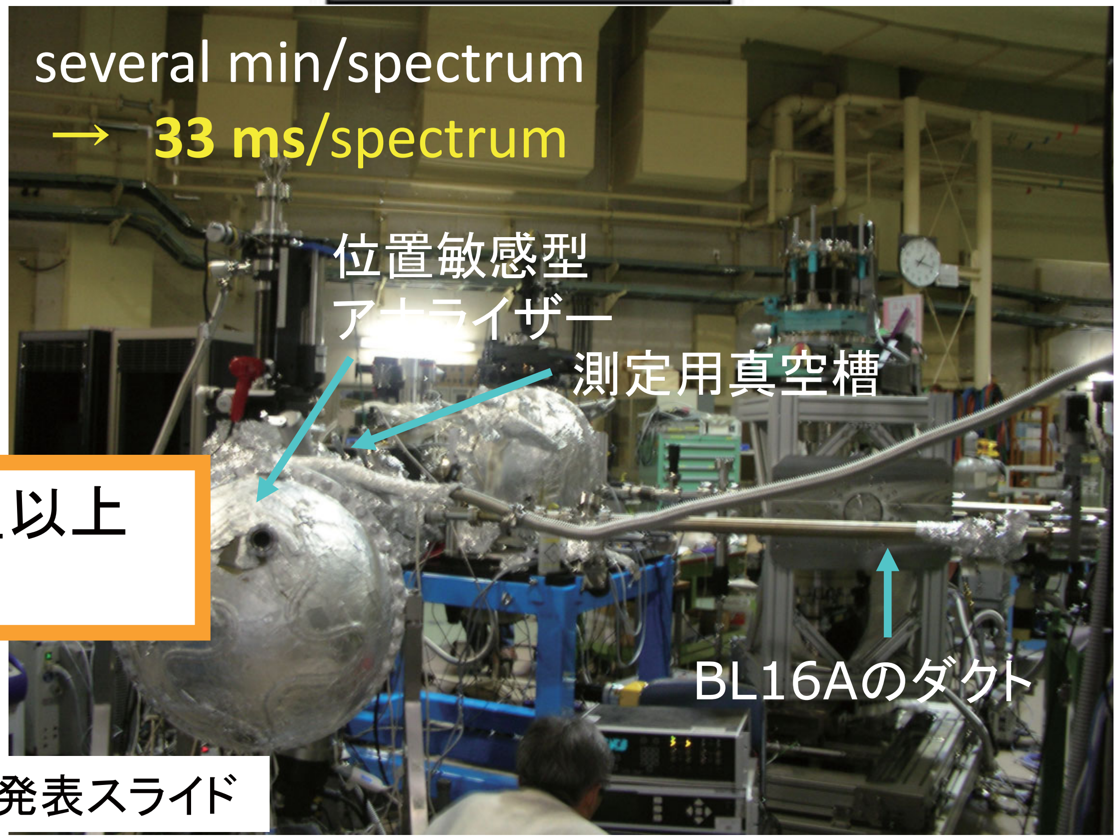


Current status of our time-resolved experiment

Disp-NEXAFS







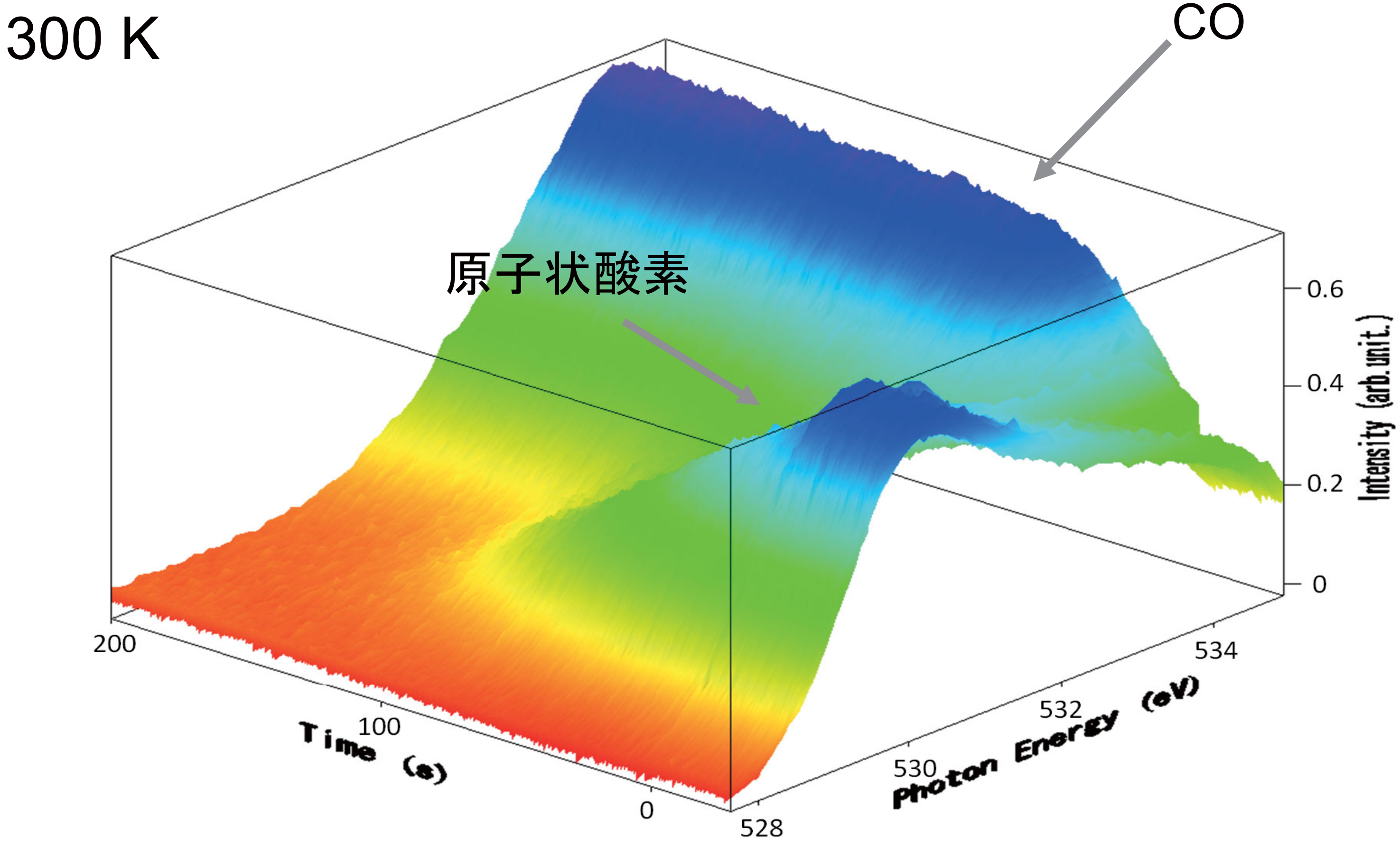
→ 反応が速い室温以上でも
追跡可能に！ [*]

Dispersive NEXAFS法を用いて室温以上
での反応を表面分光法で調べる

[*] 小宇佐友香（慶應大、近藤研），修士論文発表スライド

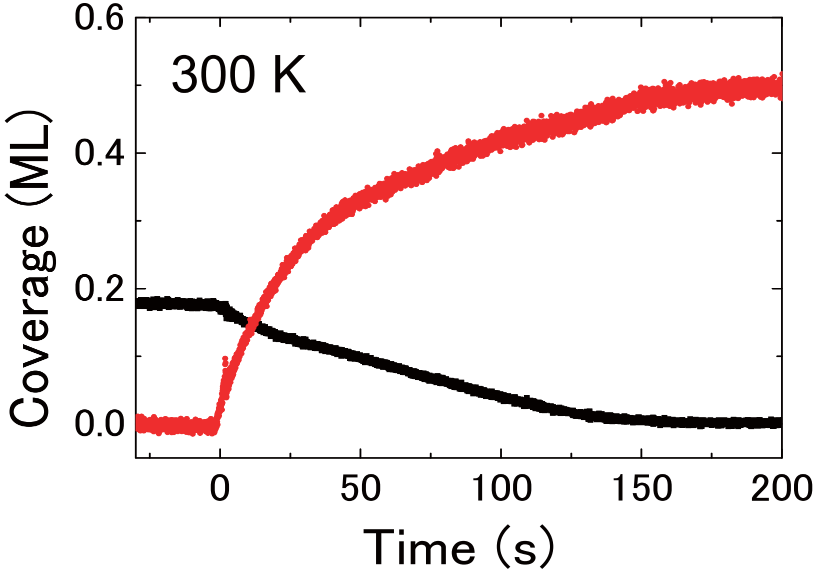
3Dプロット

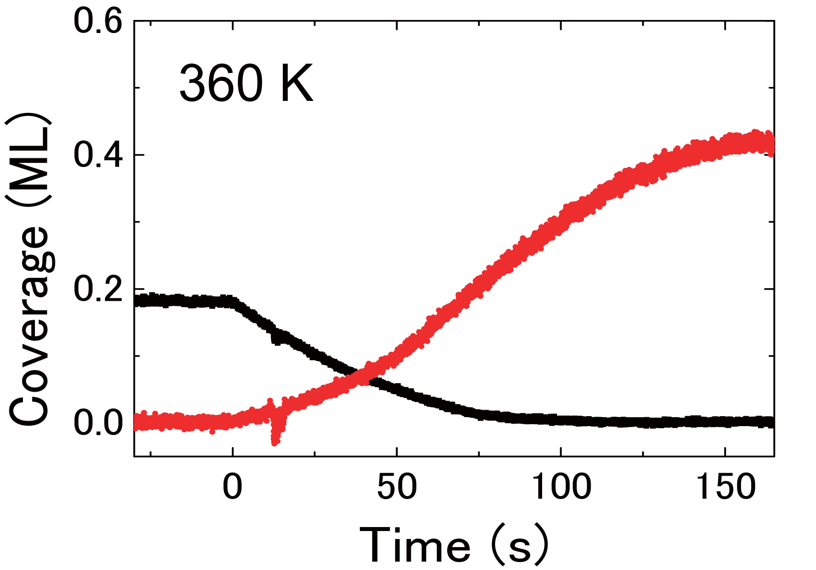
測定したO-*K*吸収端NEXAFSスペクトルを時間で並べたもの

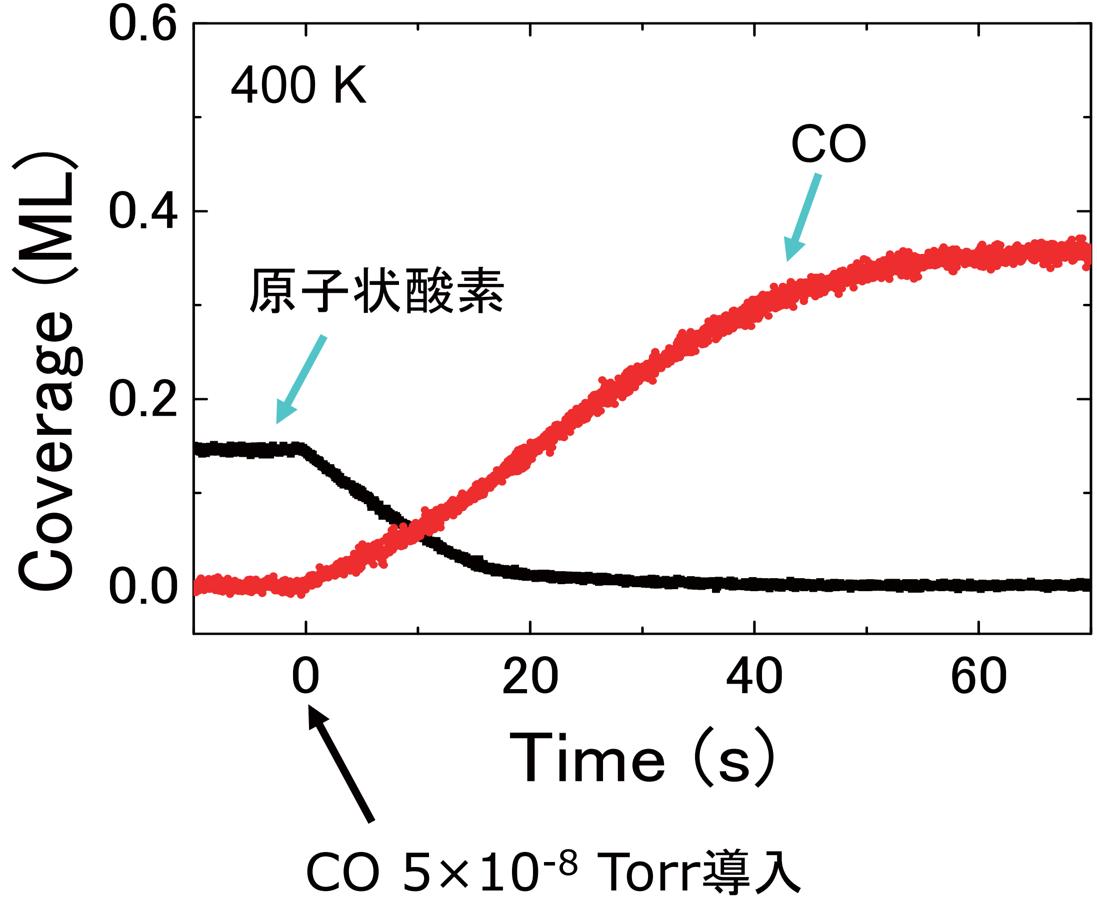


* 小宇佐友香(慶應大、近藤研)，修士論文発表スライド

被覆率の時間変化







* 小宇佐友香(慶應大、近藤研), 修士論文発表スライド

Available time resolution & possible study

	Acquisition Rep rate	Period of real time observable reaction	Ratio (Period/Rep rate)
Current status: 16A at PF	**33 ms** (Video rate of the camera)	~**100 s**	$\sim10^{3\text{-}4}$
Future: ERL	**0.8 ns** (Pulse interval)	**(~100 ns)- 1 -10 μs**	$\sim10^{3\text{-}4}$

Real time observations of catalysts at very working temperature

For example... — *How suitable!! Perfect!!*

...maybe (^^;)

CO oxidation on Pt(111)

E_a = 0.5 – 0.7 eV

RT => 600 - 900 K

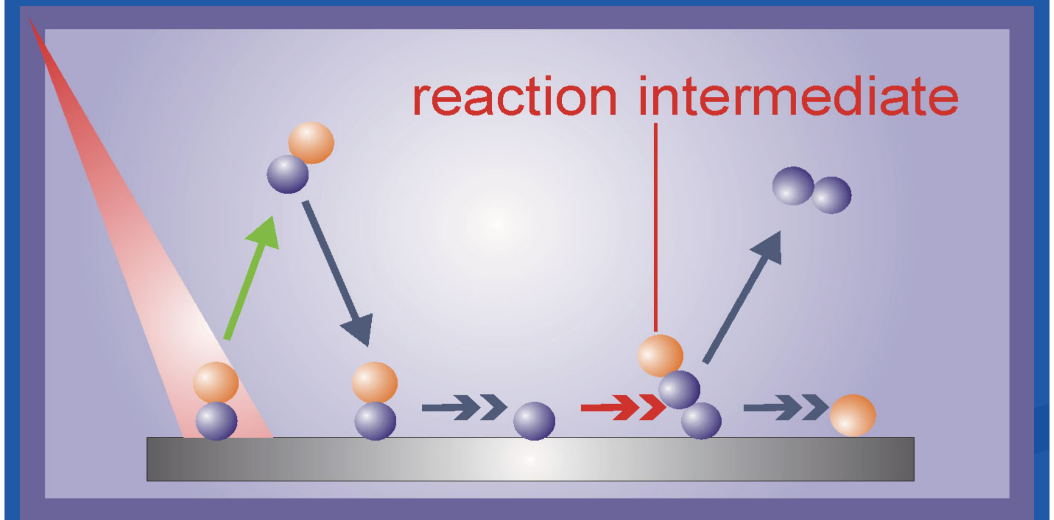
(Ratio of *k*) = $\mathbf{10^4 – 10^8}$

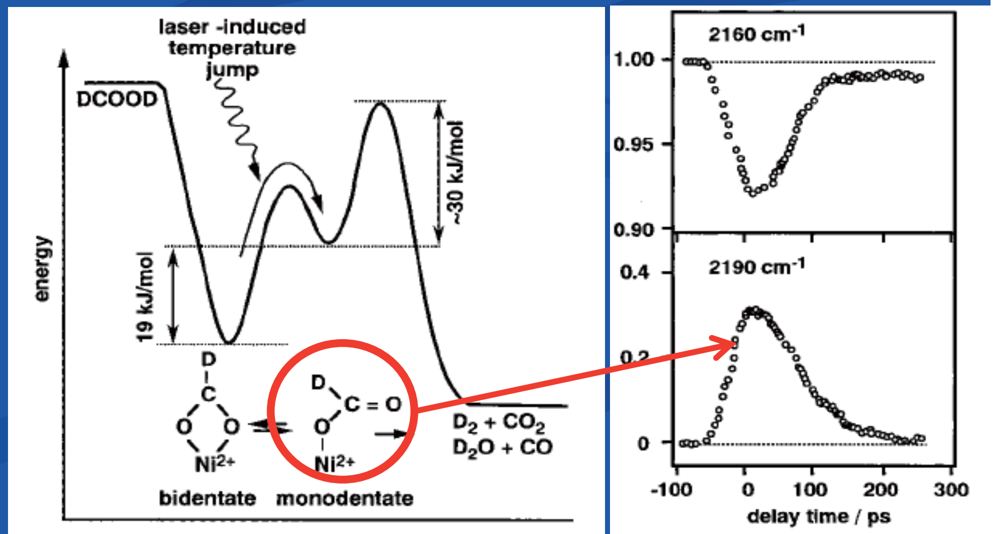
ERL光源による超高速反応モニタリング

- 100 fs ～ 1 psのパルス幅
- 1.3 GHz（0.8 ns間隔）のパルストレイン

100 fs～1 psの時間分解能　→　短寿命反応中間体を捉えられる？

0.8 ns間隔でｻﾝﾌﾟﾘﾝｸﾞ　→　それが何時生成するかを調べられる

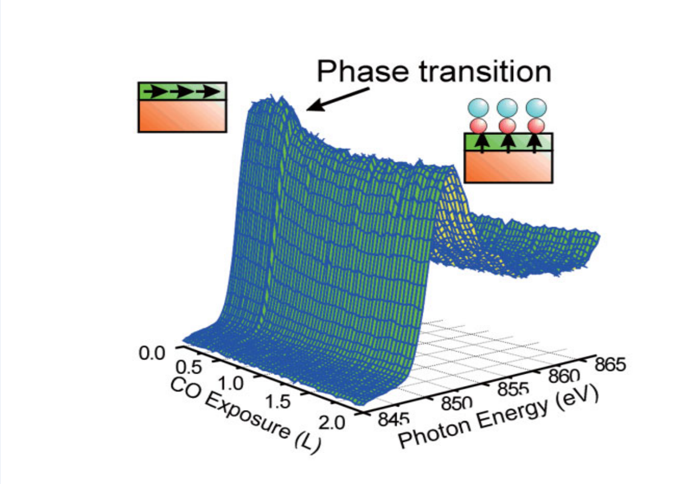




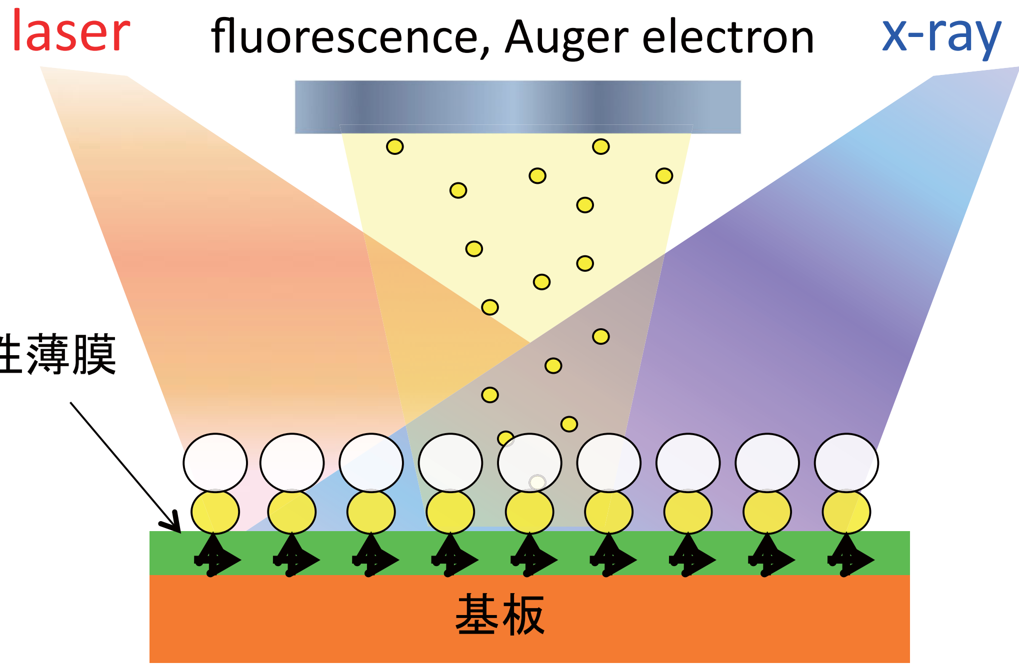
A. Bandara et al. *J. Phys. Chem.* B 102, 5951 (1998).

磁性薄膜での雰囲気制御時間分解測定

分子吸着誘起スピン再配列転移(SRT)



雰囲気制御時間分解XMCD, EXAFS



PSDによる磁性薄膜表面からの分子の脱離

ps-ns

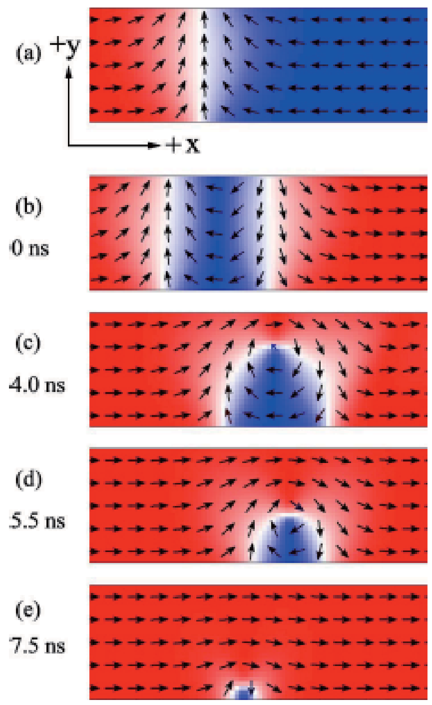
分子脱離による　SRT
薄膜構造の変化

分子再吸着による
薄膜構造の再変化
元の状態へのSRT

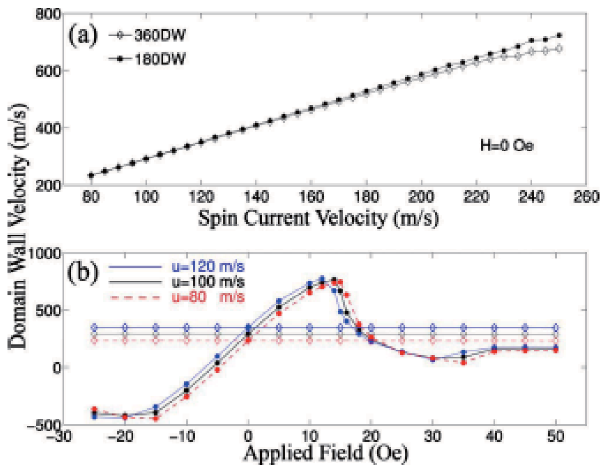
Observation of Magnetic Reversal Process

Magnetic reversal process
Domain wall (DW) movement

typical period: ~ns



Velocity
- several m/s [強磁性体の物理]
- ~$10^{2\text{-}3}$ m/s [Science, PRB]



ERL光
- パルス幅1 ps
- パルス間隔 0.8 ns

工夫も必要だが
ERLを用いた実験に適した現象ではないか

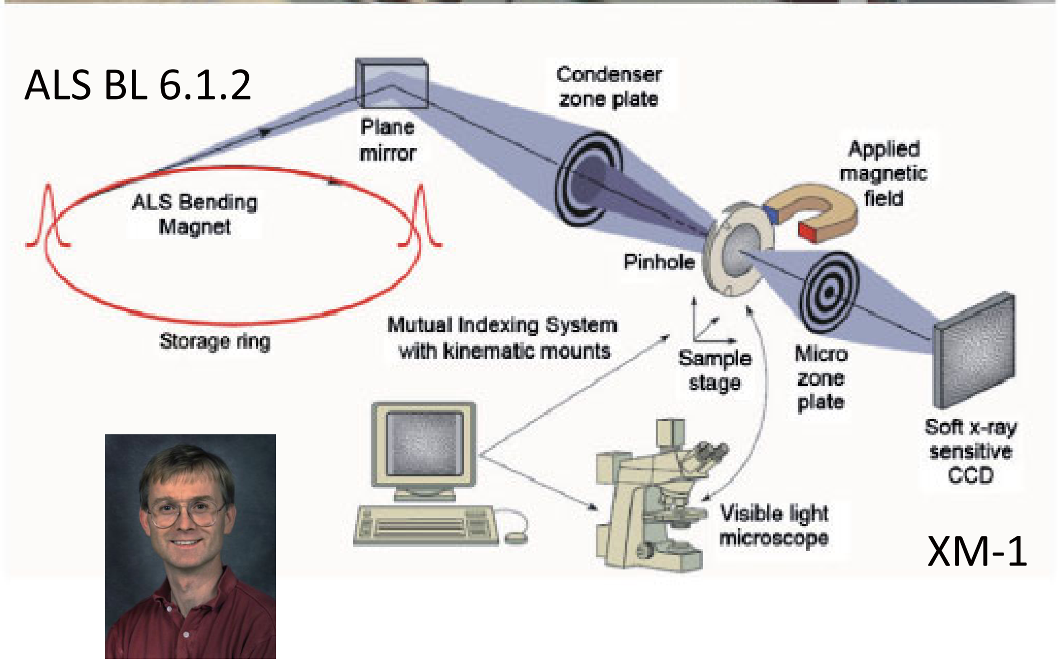
Magnetic transmission soft x-ray microscopy
（磁気透過型軟X線顕微鏡）

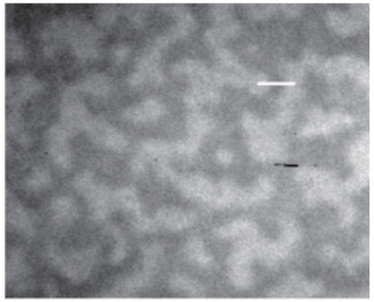
Magnetic soft x-ray small angle scattering
（磁気軟X線小角散乱）

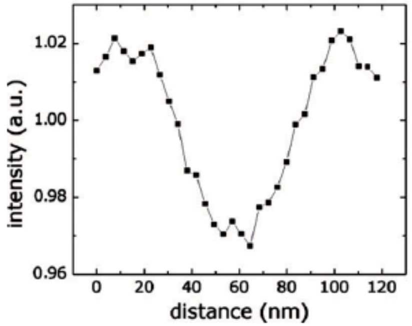
Mark D. Mascaro and C. A. Ross, PRB 82, 214411 (2010)

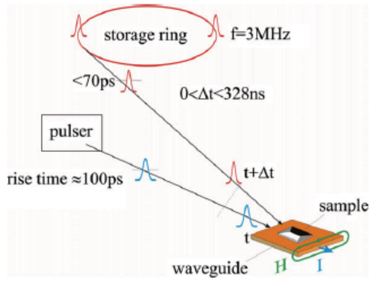
Magnetic transmission soft X-ray microscopy

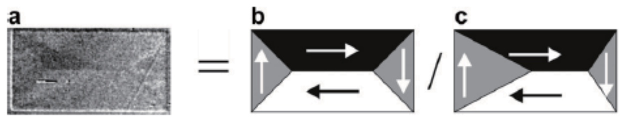
（磁気）透過型軟X線顕微鏡











Spatial resolution: max. ~15 nm

Temporal resolution: max. ~70 ps

P. Fischer, *et al.*, Surf. Sci. **601**, 4680 (2007)

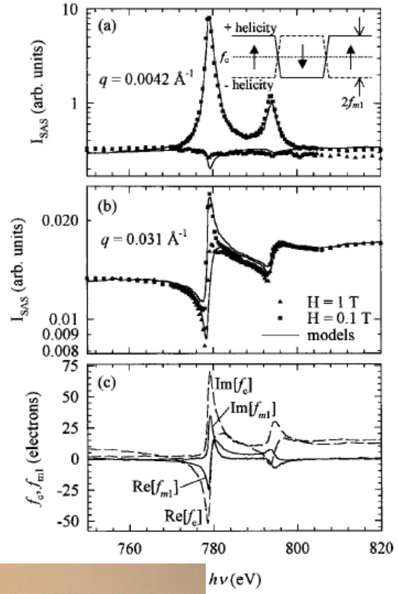
Magnetic SX-SAS

磁気軟X線小角散乱

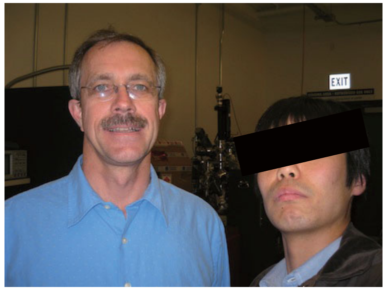
$$f=(\mathbf{e}_f^*\cdot\mathbf{e}_0)f_c+i(\mathbf{e}_f^*\times\mathbf{e}_0)\cdot\mathbf{m}f_{m1}+(\mathbf{e}_f^*\cdot\mathbf{m})(\mathbf{e}_0\cdot\mathbf{m})f_{m2}$$

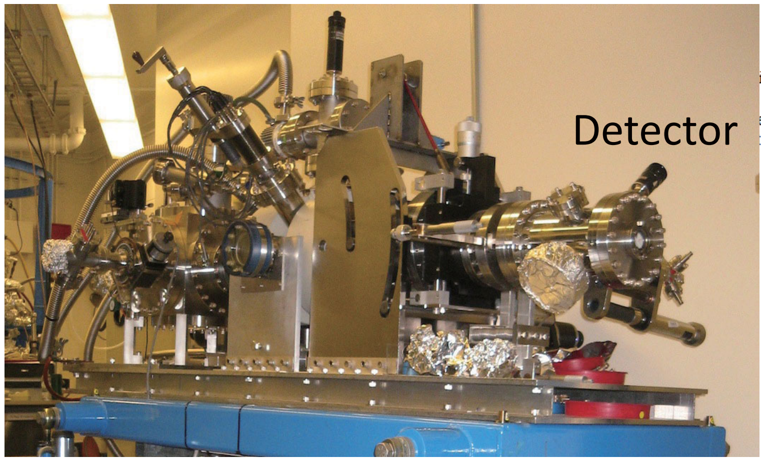
charge — 1st order magnetic (MCD) — 2nd order magnetic (MLD)

$$f_{\pm}=f_c \pm f_{m1}$$



at saturation and 0.1 T measured in (a) and (b), respectively. Real charge (f_c) and magnetic (f_{m1}) e used to model the spectra in (a) for details).





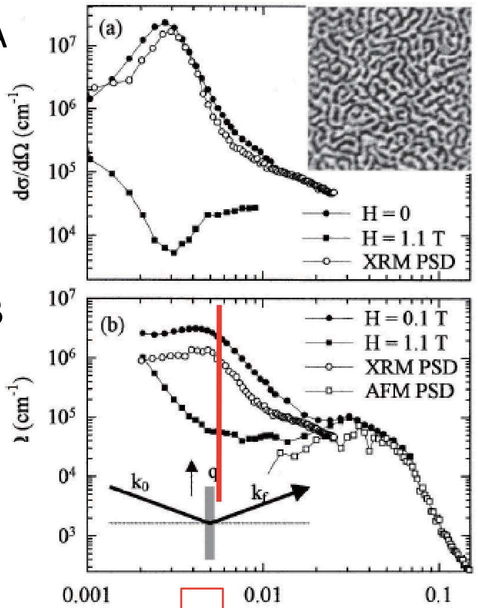
Pt(20 nm)/[Co(t_{Co})/Pt(t_{Pt})]$_{50}$/Pt(3 nm)

sample A

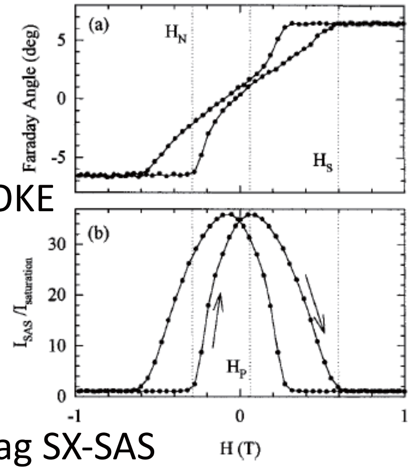
t_{Co} = 0.4 nm, t_{Pt} = 0.7 nm

sample B

t_{Co} = 0.6 nm, t_{Pt} = 0.4 nm



MOKE



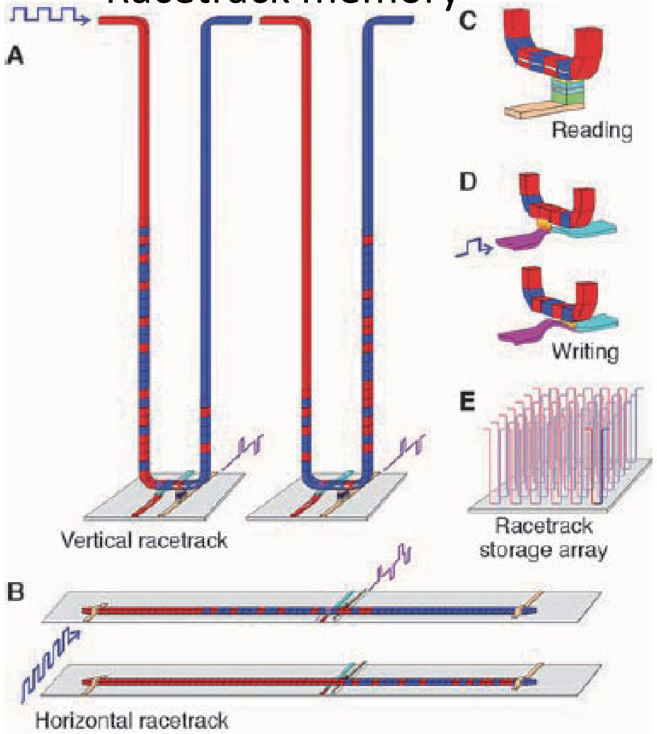
Mag SX-SAS

J. B. Kortright, *et al.*, PRB, **64**, 092401 (2001)

Racetrack memory: Magnetic thin films in Spintronics

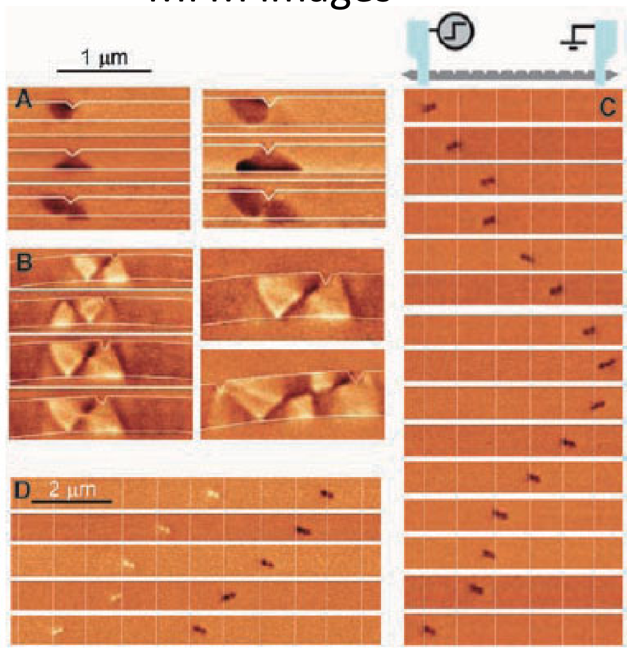
Stuart Parkin, *et al.* (IBM Almaden)

Racetrack memory



S.S.P. Parkin, *et al.*, Science **320**, 190 (2008)

MFM images

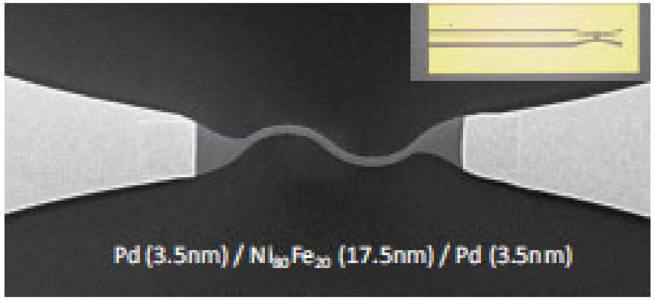


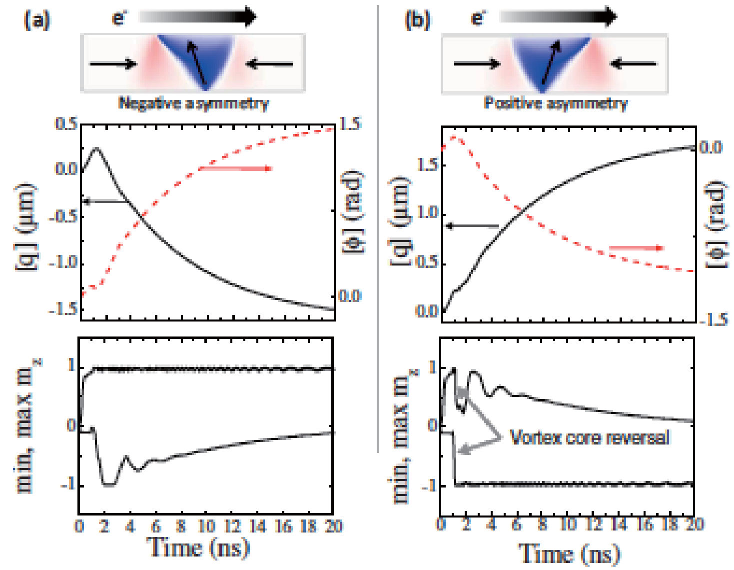
Domain wall velocity ~100 m/s (100 nm/ns)

まさに動いているところが見えるのでは

DW displacement

SEM image





~ns phenomena

MFM image

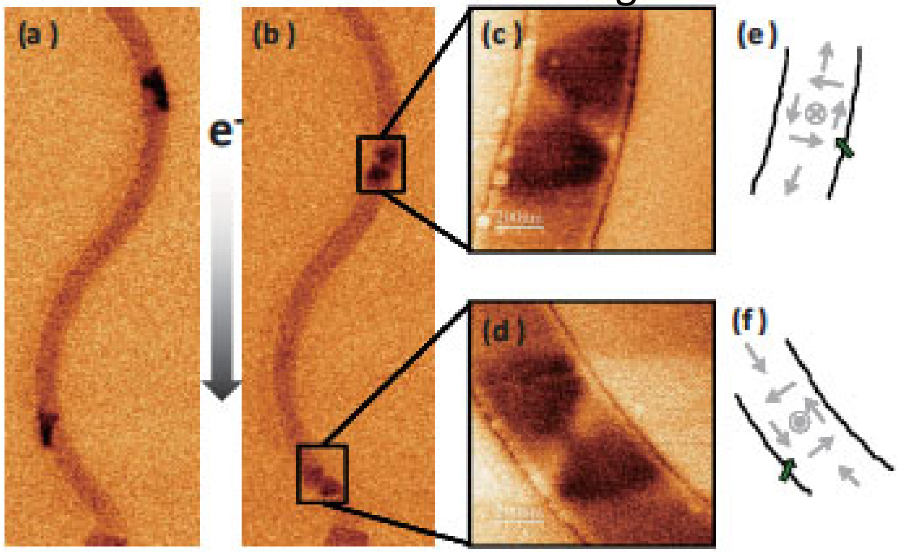


FIG. 3. (Color online) (a) MFM image of the initial magnetic state of the entire S-shaped nanostrip showing two ATWs. (b) Final magnetic state with two VWs displaced by 1.5 and 1.7 μm after transforming under a 1 ns current pulse of 3.6 TA/m^2 amplitude. [(c) and (d)] Zoom on the VWs, with schematics shown in (e) and (f), the bigger arrows indicating the vortex injection path.

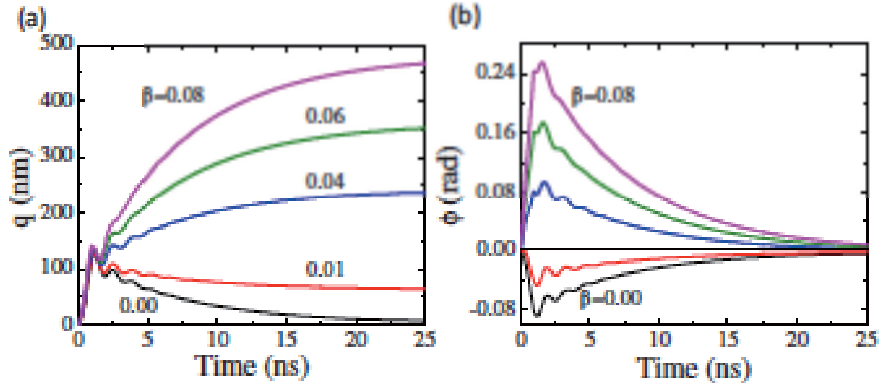


FIG. 8. (Color online) Micromagnetic simulations for a VW under a pulsed current of 1 ns and 3.8 TA/m^2 amplitude (u =133 m/s) for different values of β (α=0.02). The graphs show (a) the wall position q and (b) the generalized wall angle Φ.

J.-Y. Chauleau, *et al.*, PRB **82**, 214414 (2010)

ここからちょっと提案

- Soft x-ray + Hard x-ray

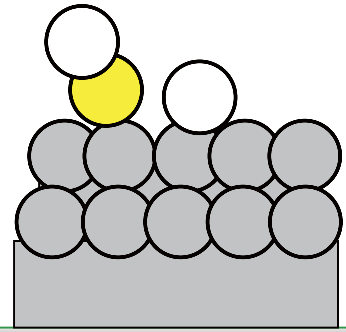
Soft x-ray + Hard x-ray

両方使えるビームラインがあったら何か面白いことができないか？

軽元素と重金属元素 – 同時（双方）測定実験

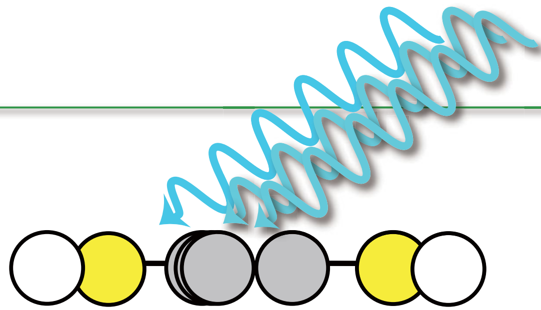
ex) CO酸化反応 on Pt 触媒

有機物のNEXAFS, XPSと貴金属触媒のEXAFS



軟X線ポンプ – 硬X線プローブ実験

ex) 有機金属錯体



軟X線で励起・イオン化

引き続く構造変化を中心金属のXAFSで追跡する

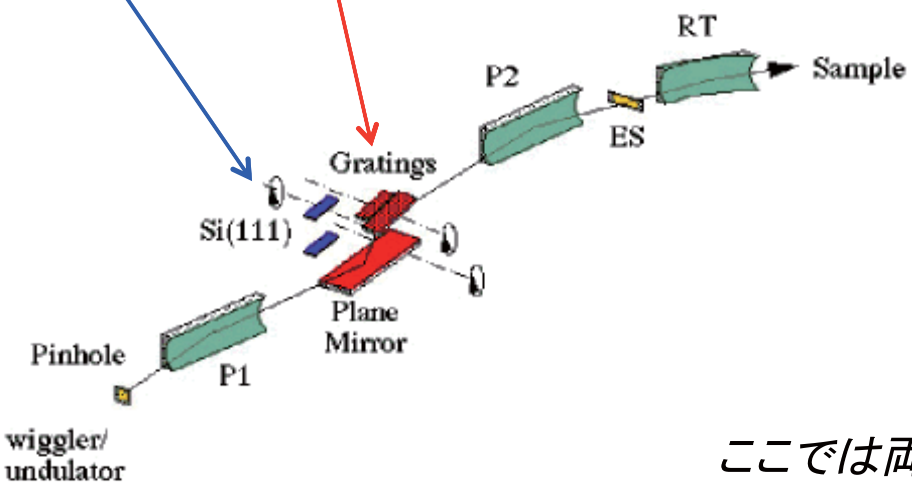
BL 7.2, Elettra

The parallel light beam impinges on the energy dispersing device which can be selected to be

a plane mirror - plane grating for the low energy range (120-2000 eV)

or

Si channel cut for the high energy range (2800 to 8000 eV).

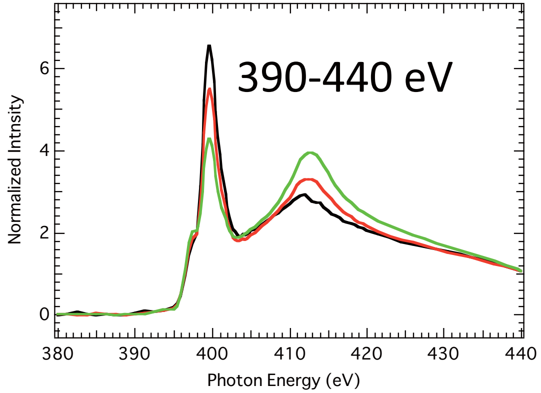


ここでは両方は使えるけど、同時には使えない

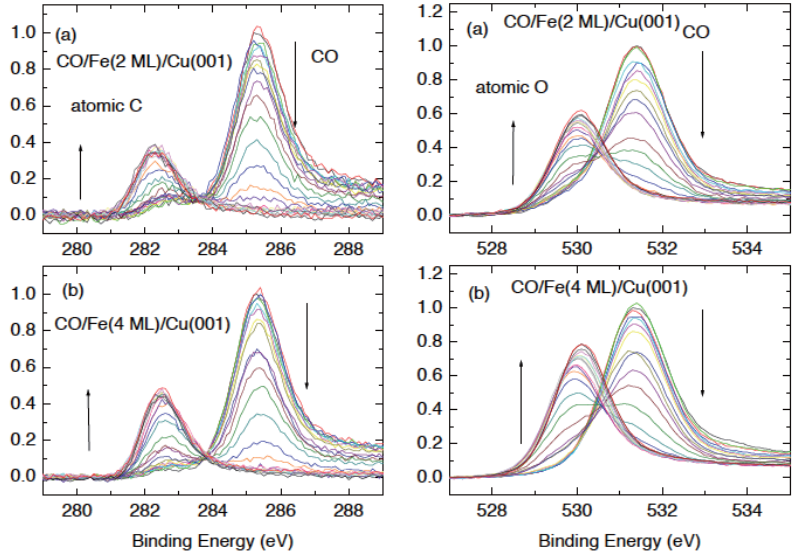
http://www.elettra.trieste.it/experiments/beamlines/aloisa/index.html

Soft & Hard x-rays to observe chemical reactions

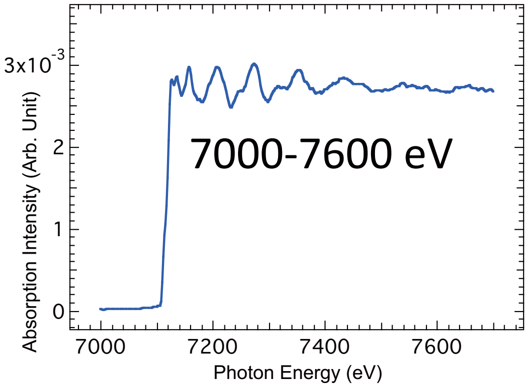
N *K*-edge NEXAFS



C, O 1*s* XPS
280-290, ~530 eV



Fe *K*-edge XAFS



cf. Pt L_1; 11.6 keV

反応種（有機物）のNEXAFS, XPS:　250-600 eV
触媒金属のEXAFS (XANESも):　数 keV以上

Soft & Hard x-rays 両方使えたら

反応種を分光法で直接観察しつつ、
触媒金属の構造、電子状態を直接観察できる

The CO + NO Reaction over Pd: A Combined Study Using Single-Crystal, Planar-Model-Supported, and High-Surface-Area Pd/Al_2O_3 Catalysts

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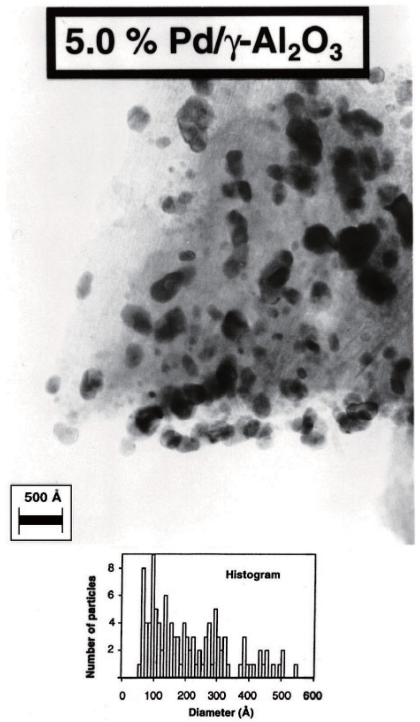
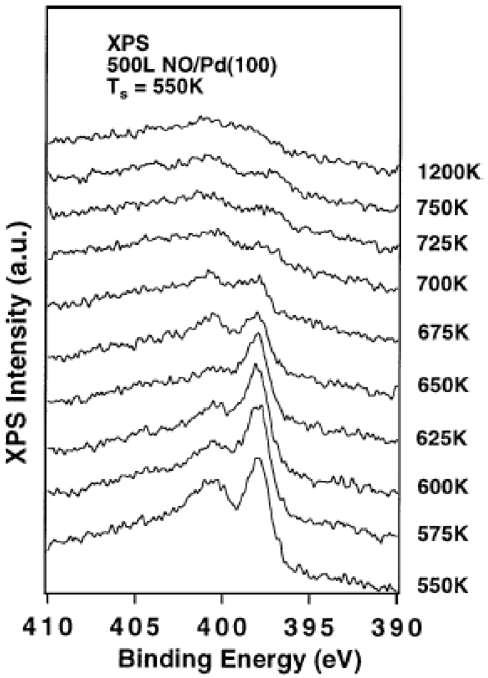


FIG. 2. TEM image and particle size histogram for a 5% Pd/γ-Al_2O_3 powder catalyst prepared by incipient wetness impregnation.



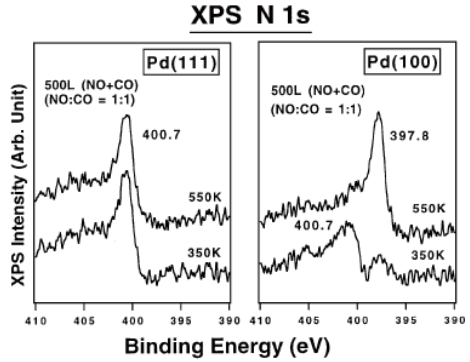


FIG. 7. XPS of the N1*s* peak on Pd(111) and (100) after a 500-langmuir exposure to CO + NO (1 : 1) at 350 K and 550 K.

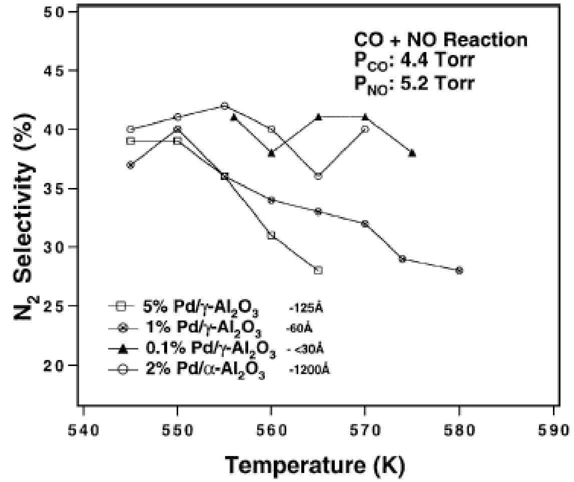


FIG. 11. N_2 selectivity vs temperature for the CO + NO reaction over each powder catalyst.

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Effect of Oxygen Adsorption on the Chiral Pt{531} Surface

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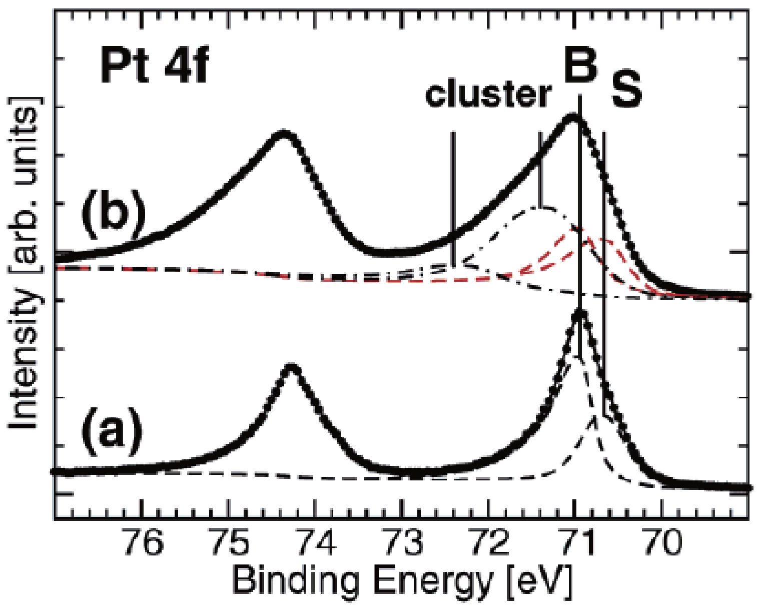

Figure 2. Pt 4f signal for (a) the clean Pt{531} surface and (b) the surface covered with oxide clusters. Filled circles represent the data points, fitted curves are shown as dashed (single peaks) and solid lines (sum of all peaks). For clarity only the peaks fitted to the Pt $4f_{7/2}$ line are shown. ($h\nu$ = 162 eV (a), 650 eV (b); normal emission).

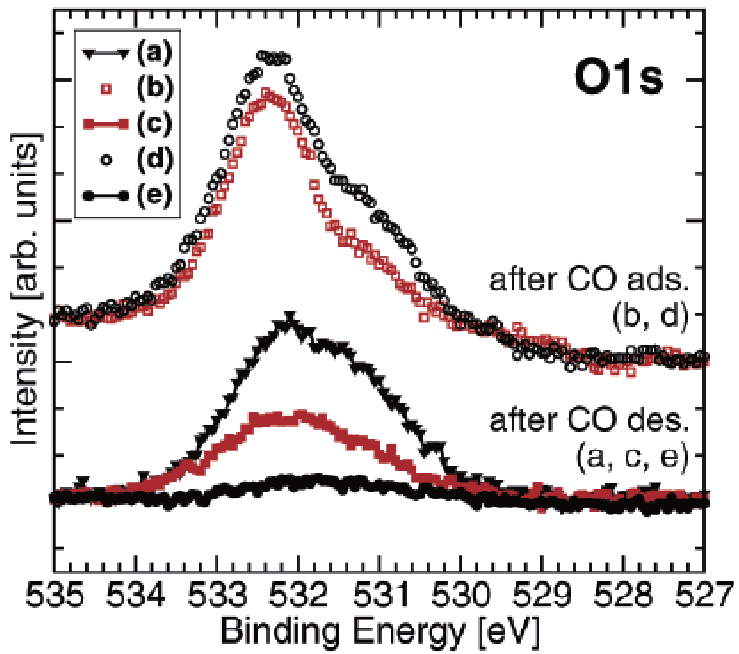

Figure 3. O 1s spectra (a) after oxygen treatment of the Pt{531} surface, (b) after first CO adsorption (45 L at 315 K), (c) after CO desorption (anneal to 620 K), (d) after second CO adsorption (45 L at 315 K), and (e) after second CO desorption (anneal to 620 K). See text for details. ($h\nu$ = 650 eV; normal emission).

Summary

ERLでの表面反応、磁性薄膜の時間分解実験

- Laserをトリガーとして
  - 電子温度とカップルする分子の挙動のPump-Probe時間分解測定
  - 昇温で反応開始する表面反応のReal time時間分解測定
  - 分子再吸着による表面反応の時間分解測定
  - 分子脱離、再吸着による磁性薄膜のSRT過程の時間分解測定
- パルス磁場、電流をトリガーとする磁化反転過程の観測
  - 透過型軟X線顕微鏡
  - 磁気小角散乱
- ERLでのちょっとした新展開の可能性提案
  - 軟X線と硬X線が同時に使えるBL