‘08.11.8 @KEK 国際交流センター･交流ラウンジ1,2
PF研究会「PFリングのトップアップ・シングルバンチ運転利用研究と今後の発展について」

内殻共鳴励起による有機薄膜の脱離反応
-直接過程と間接過程の考察-

共同研究者

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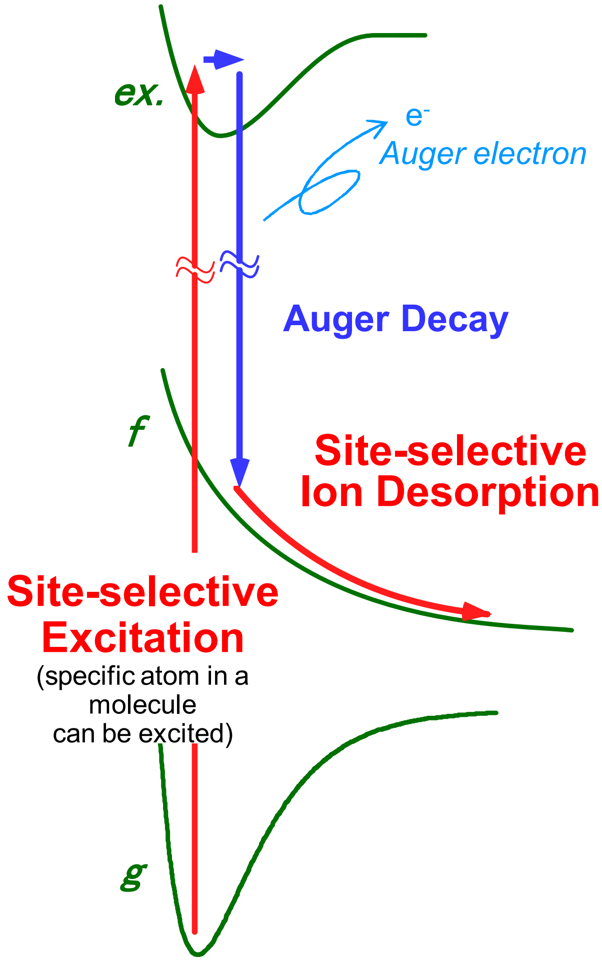
Characteristic Reaction by Core-Electron Excitation



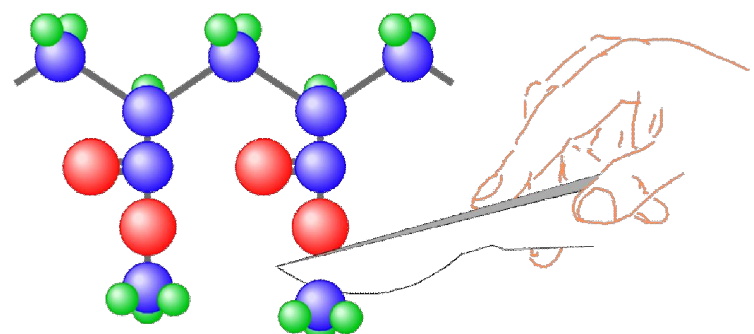
☆　内殻電子自身が分子内に局在していることから、
内殻励起は価電子励起とは異なる局所的な電子遷移である。
また束縛エネルギーはその原子の環境に強く依存している。

⇒ **サイト選択的励起**

☆　内殻励起状態は非常に速い時間領域で失活する。
Auger崩壊過程

☆　Auger終状態もまた不安定な状態であるため、
Coulomb反発が引き金となるイオン性解離の分解過程へと続く。

⇒ **選択的化学結合切断**



- 和田,田中，放射光, 18 (2005) 148.
- S. Wada et al.，J. Phys.: Condens. Matter, 18 (2006) S1629.
- K. Tanaka et al.，J. Electron Spectrosc. Relat. Phenom., 119 (2001) 255.

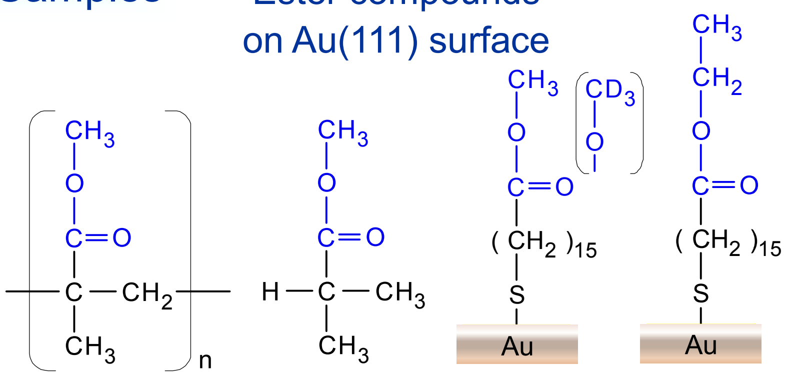
Experimental - Ion Detection

Light Source

- KEK, Photon Factory BL7A
  (Single bunch)

Samples

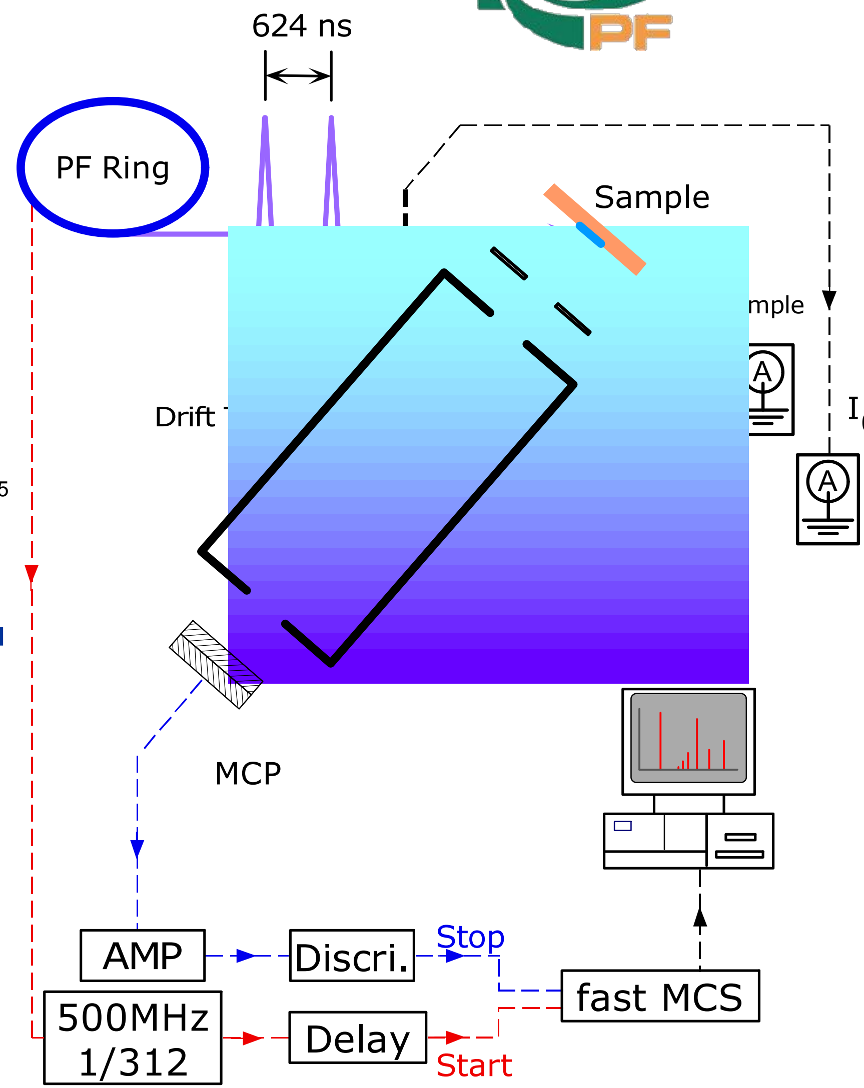
Ester compounds on Au(111) surface



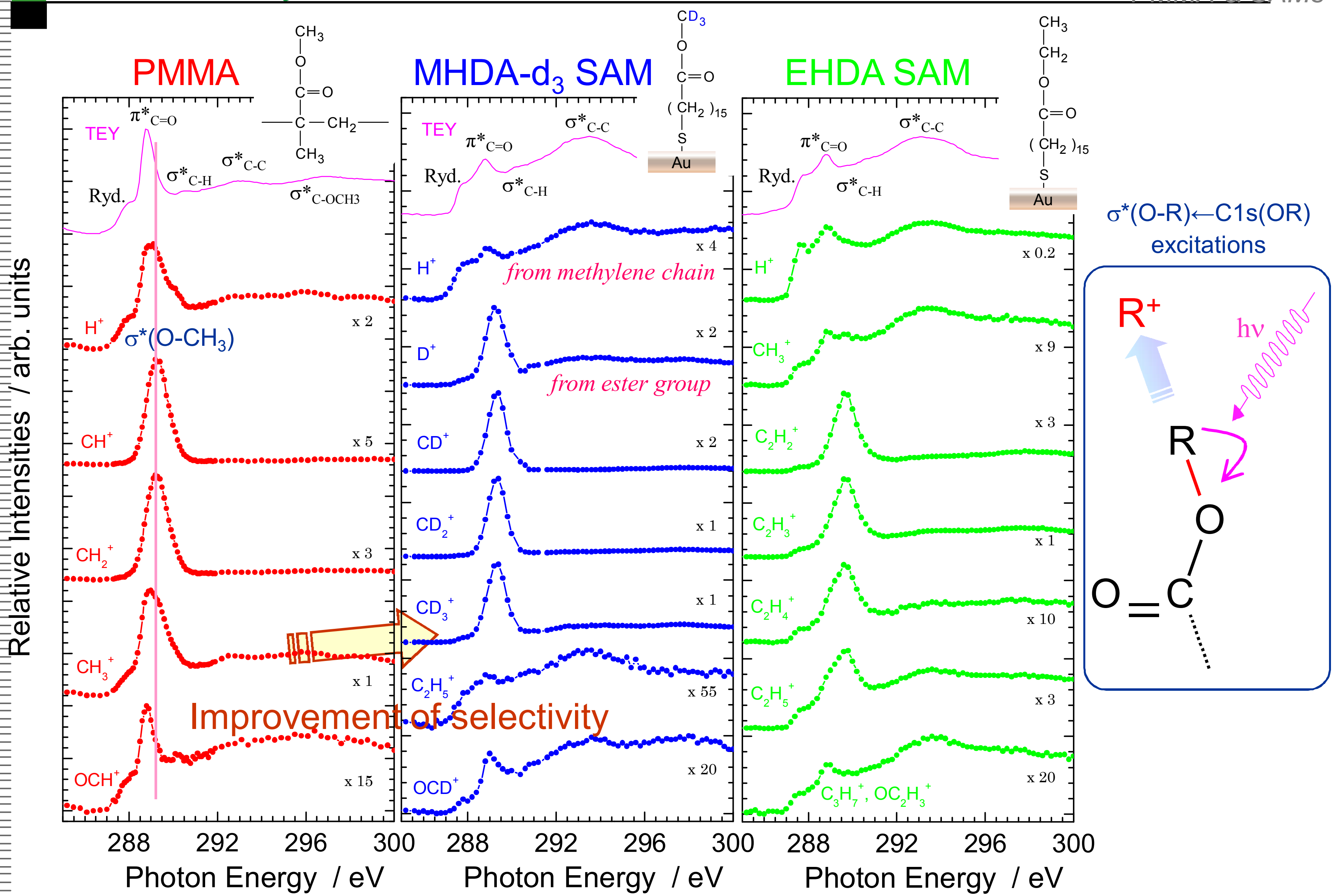
PMMA **MIB** **MHDA SAM (MHDA-d_3 SAM)** **EHDA SAM**

Measurements

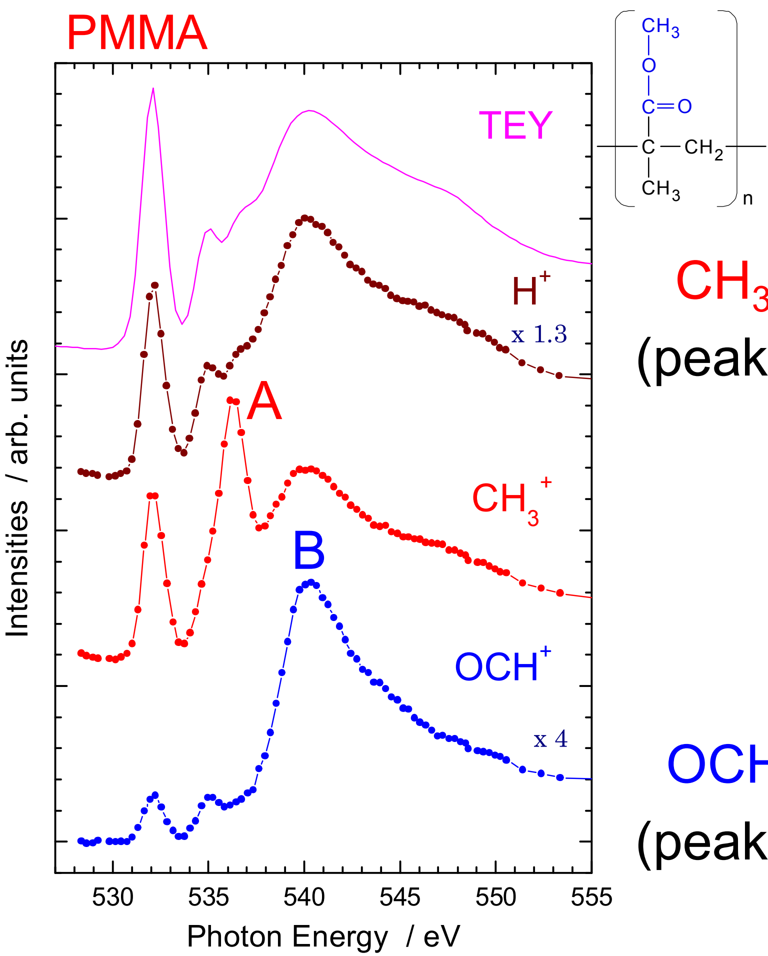
- Total Electron Yield (TEY) Spectrum
  = Absorption spectrum
- Total Ion Yield (TIY) Spectrum
- Partial Ion Yield (PIY) Spectrum
  Time-of-flight (TOF) measurement
  by pulsed SR (single-bunch operation)

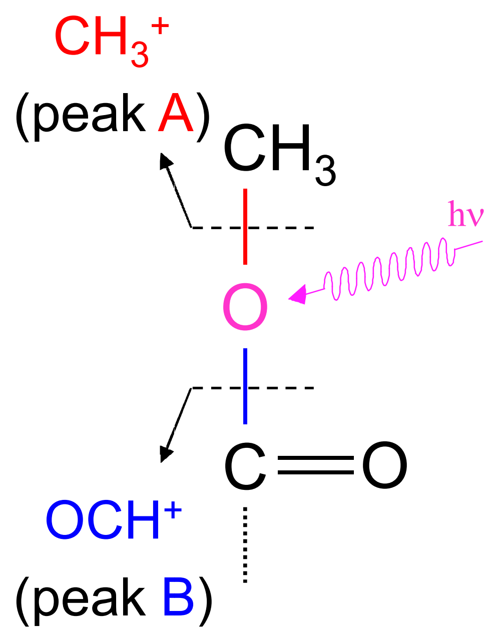


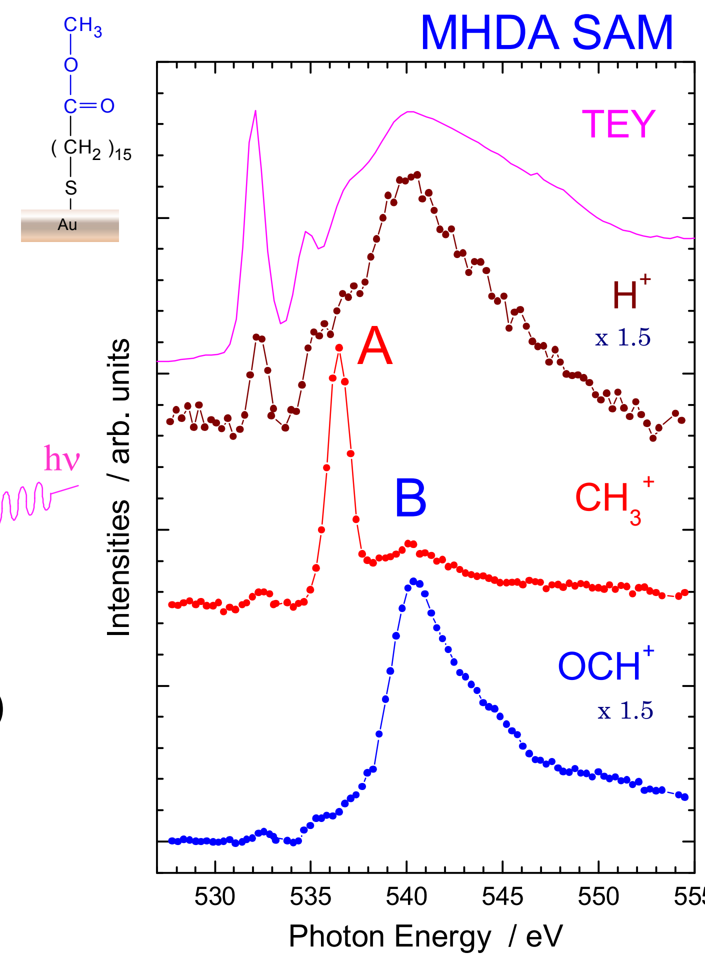
Ion Yield Spectra - C1s core level -



Ion Yield Spectra - O1s core level -







Typical result of
control of chemical bond scission

peak A : σ*(O-CH_3) ← O1s($COCH_3$)
peak B : σ*(C-OCH_3) ← O1s($COCH_3$)

Indirect Processes for Bond Dissociation

Such different dependence is due to the desorption mechanisms characterized as

- Direct Dissociation by core excitation
- Indirect Dissociation caused by
  - ･X-ray-induced electron stimulated desorption (XESD)
  - ･rapid energy redistribution in highly excited Auger states

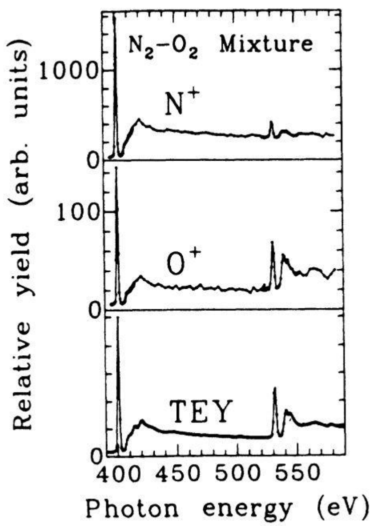
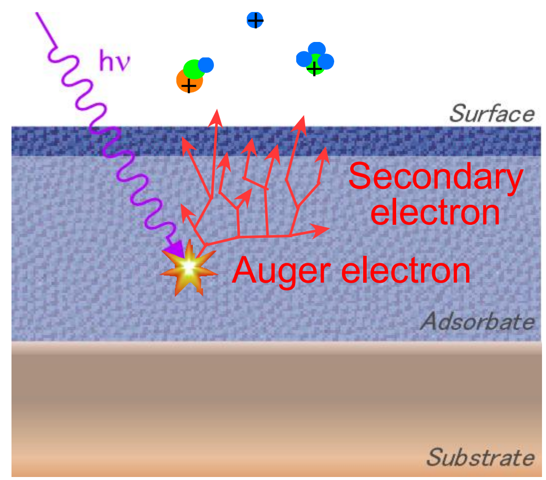
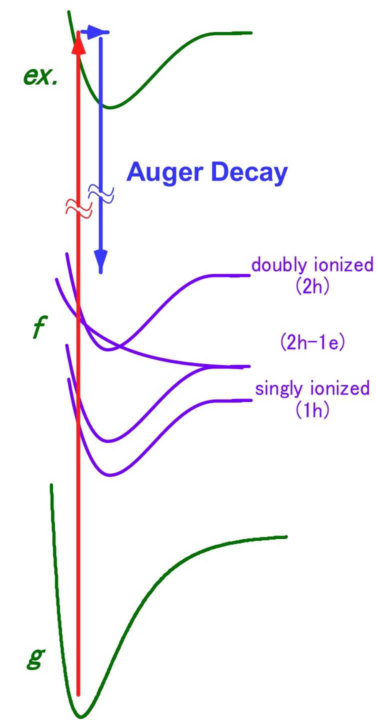


FIG. 3. Data reported by Parks *et al.* (Ref. 2) showing the N^+, O^+, and the total electron yield (TEY) from a condensed mixture of N^+ and O^+ near the N and O *K* levels.

C.C. Parks' Data referred by

D.E. Ramaker et al., Phys. Rev. B 38 (1988) 2099.





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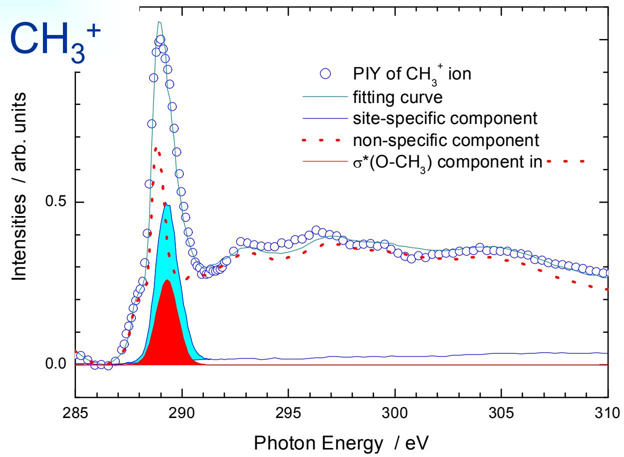
Quantitative Evaluation of Direct and Indirect Reactions

PMMA & MHDA SAM

PMMA

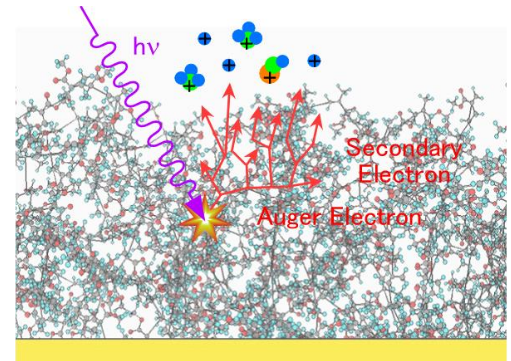
CH_3^+



at $\sigma^*(O\text{-}CH_3)$

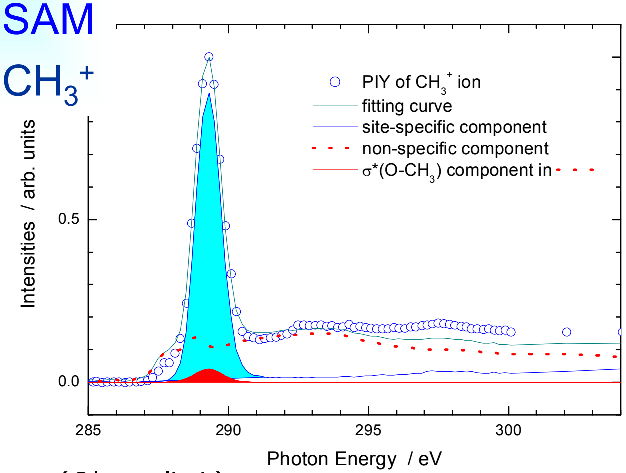
Direct
65 %

Indirect
35 %



SAM

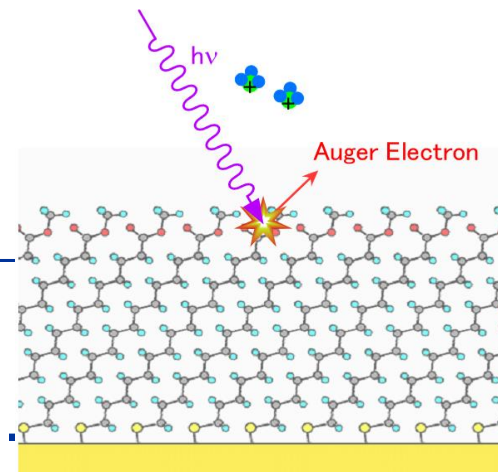
CH_3^+



(@lower limit)

Direct
90-95 %

Indirect
5-10 %



…ctive desorption)

…on induced by:

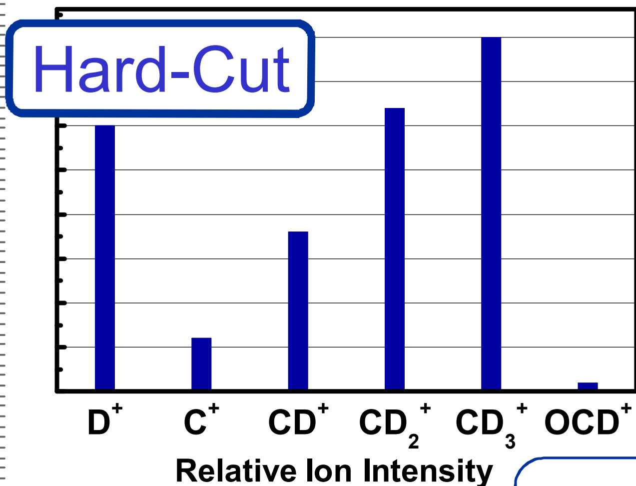
- electron stimulated desorption
- statistical energy redistribution in highly excited Auger states

Atomic Position Dependence

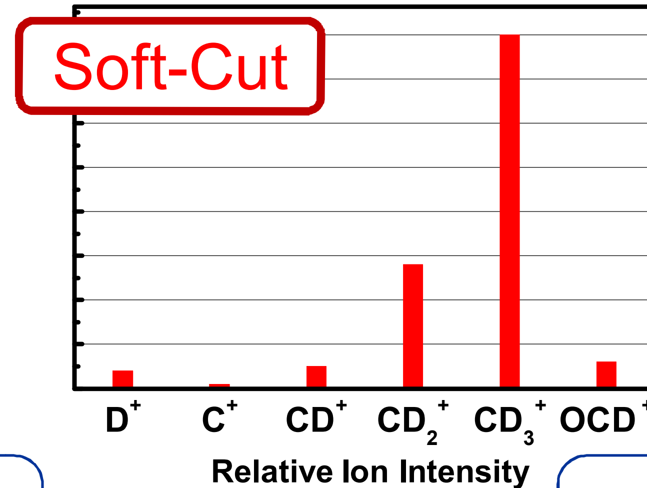
MHDA-d_3 SAM

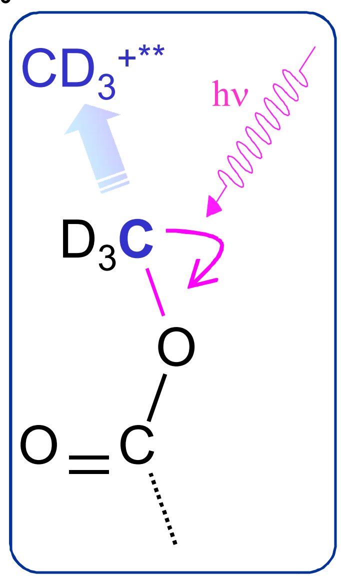
Fragmentation of desorbing CD_3^+ ion in the σ*(O-CD_3) ← C1s(OCD_3), O1s(OCD_3) excitations

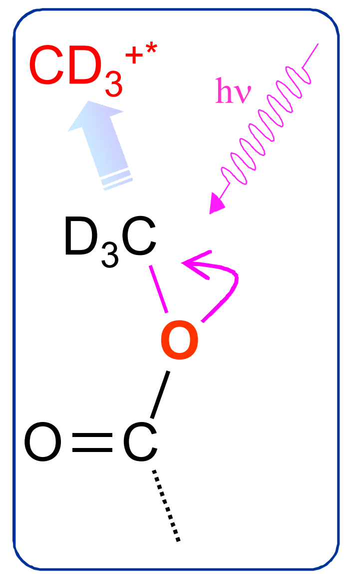
C_{1s} excitation



O_{1s} excitation

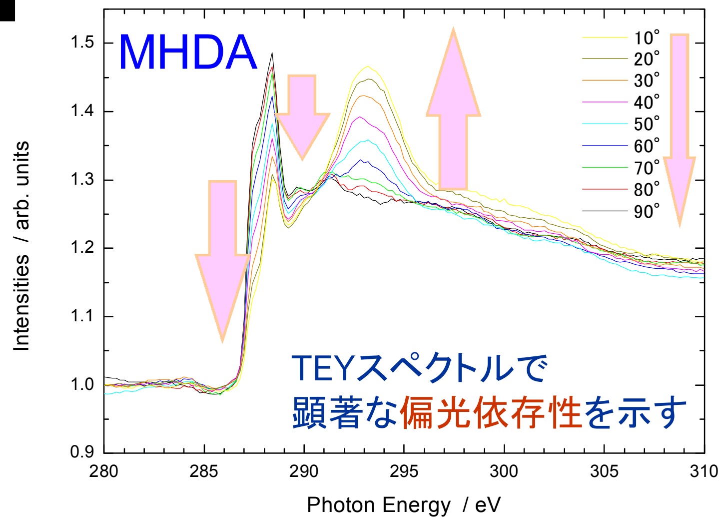


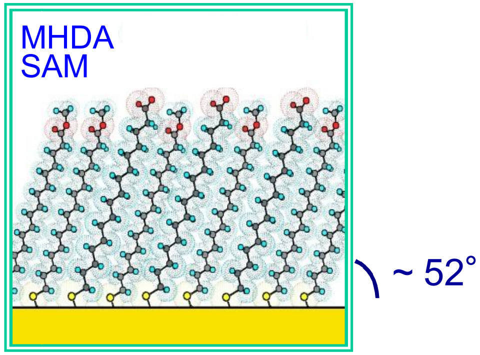


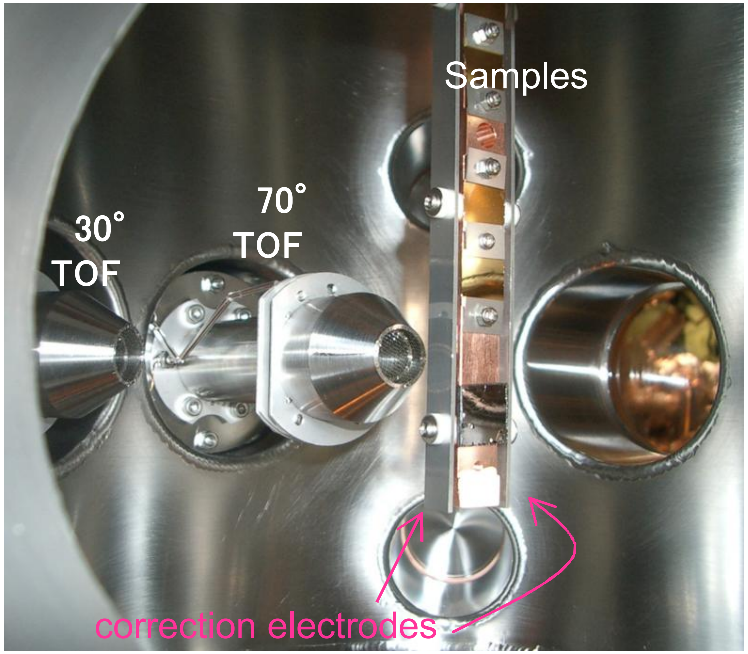


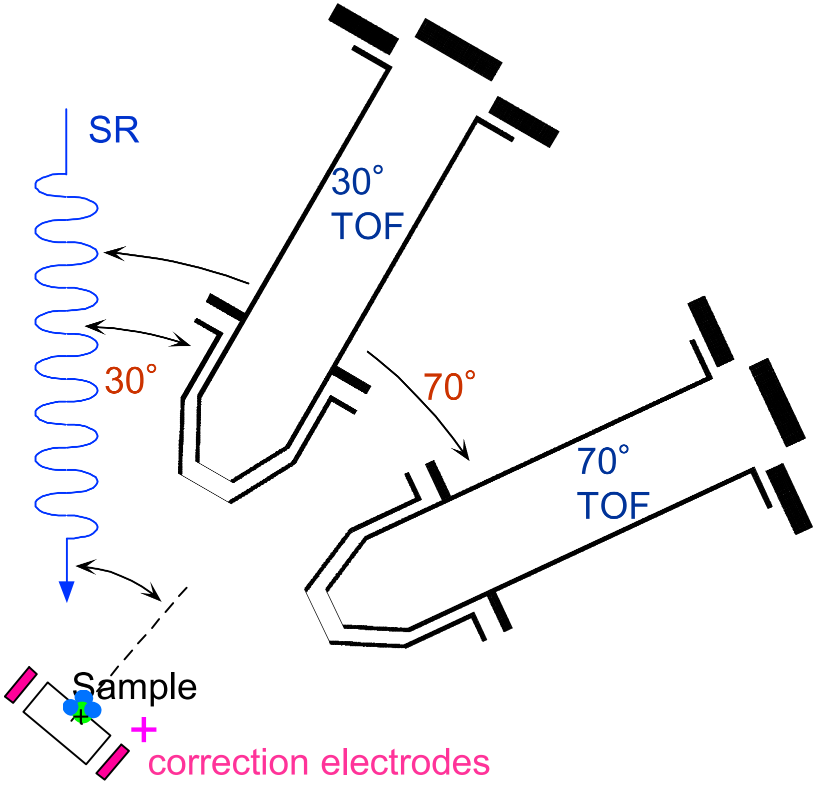
K. Tanaka et al.,
Rad. Phys. Chem., 75 (2006) 2076.

Experimental Setup for Polarization-dependent PSID









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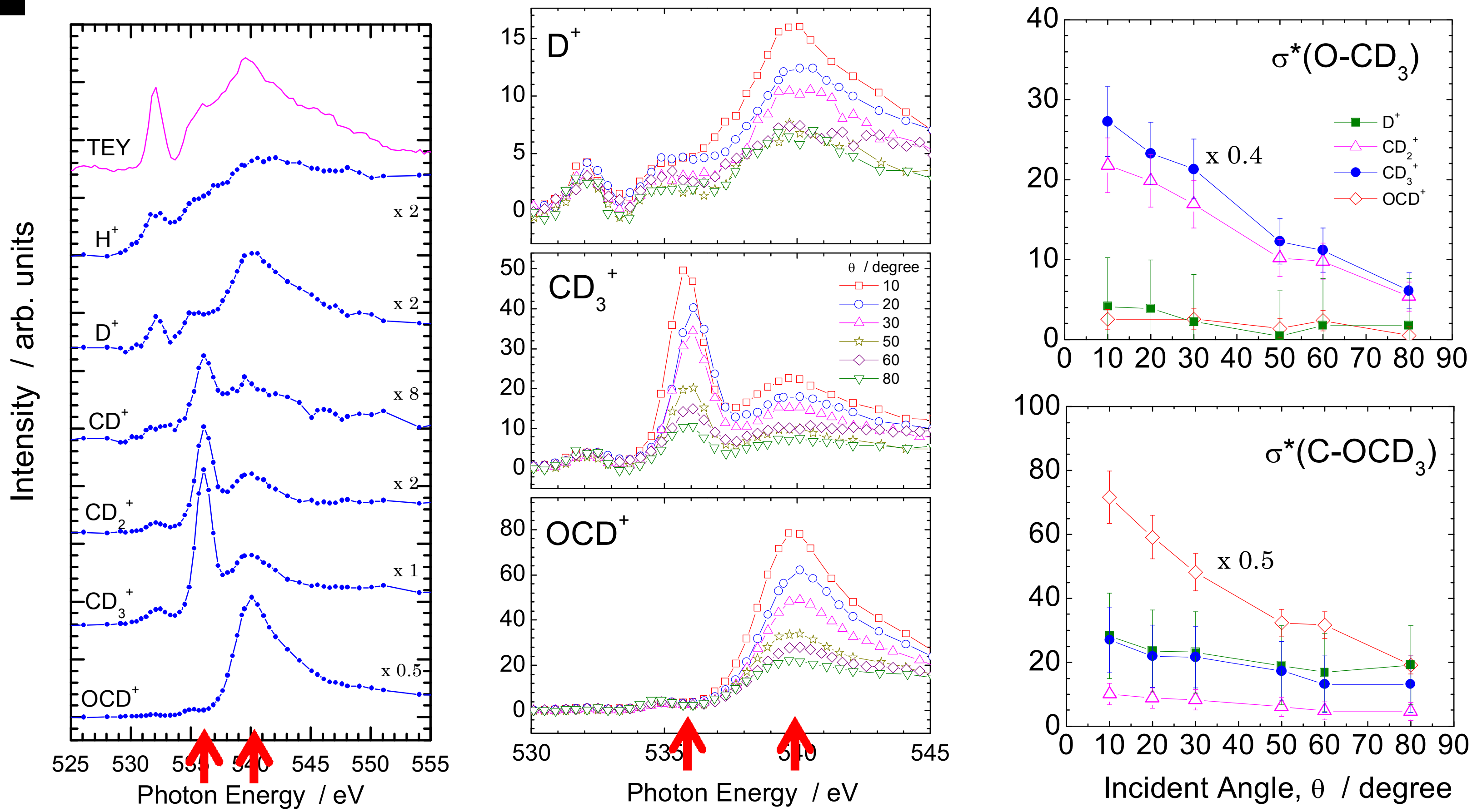
Polarization Dependence of PSID - O K-edge

MHDA-d_3 SAM

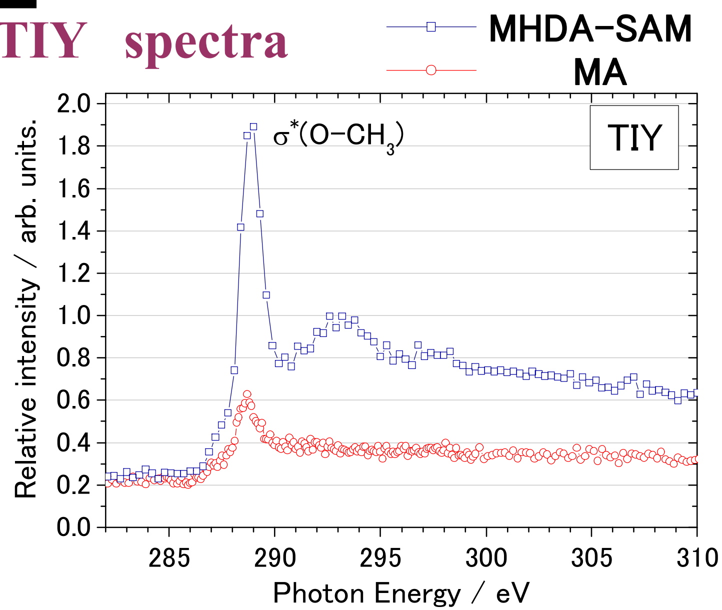


- In the $\sigma^*(O\text{-}CD_3)$ excitation, CD_2^+ and CD_3^+ ions indicate intense polarization dependence and almost same trends, while D^+ and OCD^+ are almost independent.
- In the $\sigma^*(C\text{-}OCD_3)$ excitation, OCD^+ ion is most dependent one on the polarization.
- This variation means that polarization dependence sensitively reflects difference of desorption process and ions produced by direct chemical bond scission indicate higher dependence.

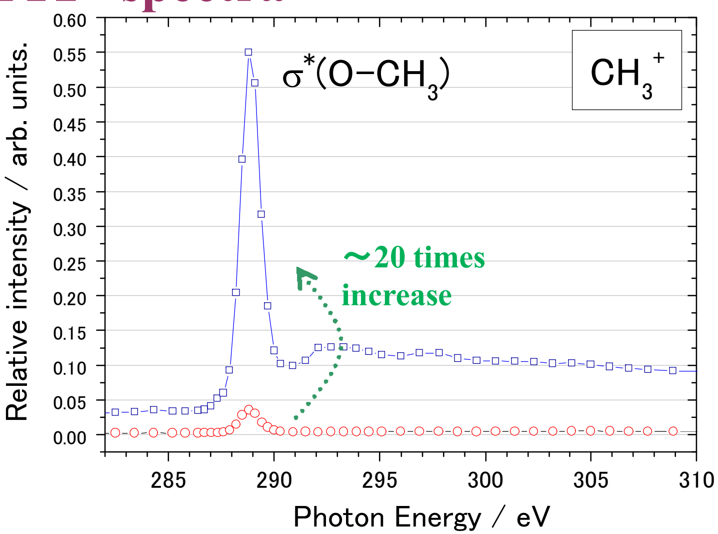
Cain Length Dependence of PSID - C K-edge

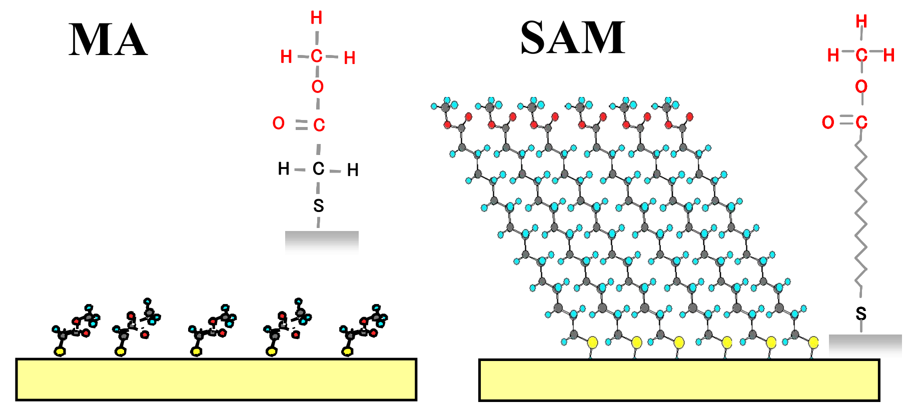
MA & MHDA SAMs

TIY spectra

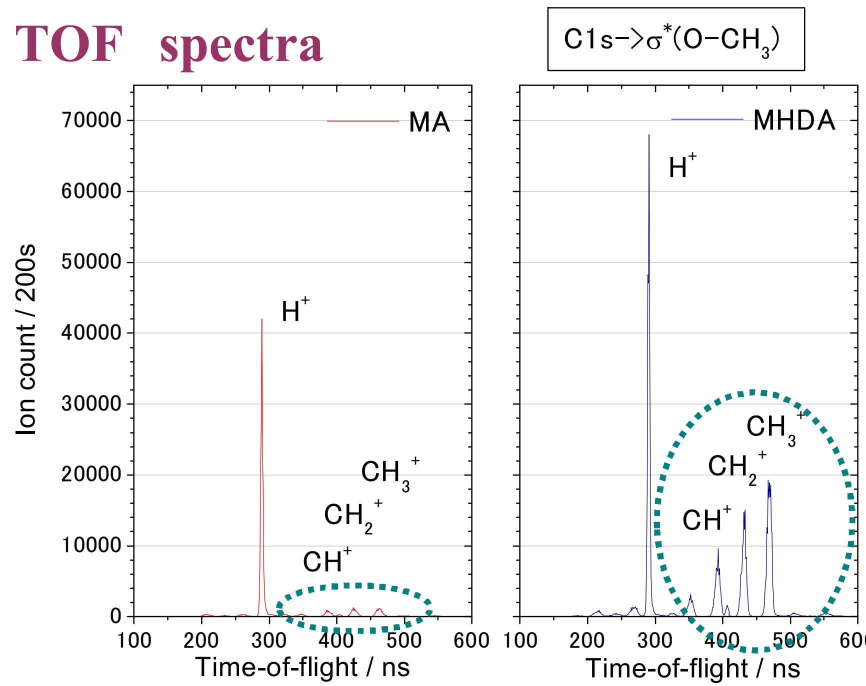


PIY spectra



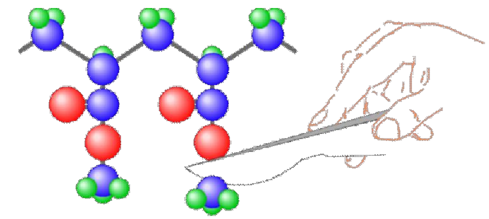


TOF spectra



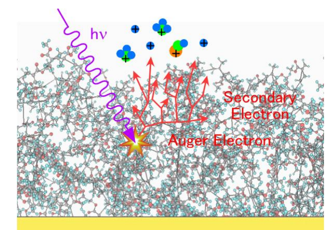
Summary

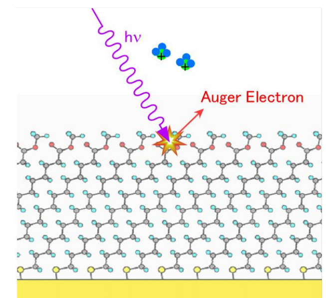
内殻励起特有の選択的イオン脱離反応

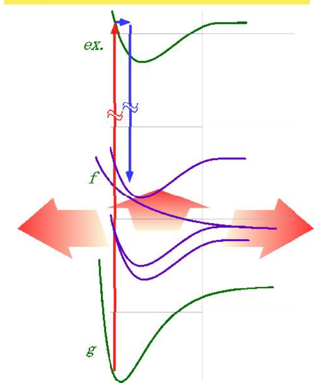


- イオン脱離では内殻励起による直接解離と、間接的な解離反応が共存・競争している
- これらを定量的に評価することに成功
- 中性脱離は間接過程が主成分
- 間接過程にはXESD（X線誘起電子刺激脱離）の他に、サーマルな反応（Auger崩壊後の内部エネルギーの統計的な非局在化による反応）も存在
- XESDのプロセスを始めて観測

→ 分子環境を変えることで反応プロセスの違いが明確に







- 和田,田中，放射光, 18 (2005) 148.
- S. Wada et al., J. Phys.: Condens. Matter, 18 (2006) S1629.
- K. Tanaka et al., J. Electron Spectrosc. Relat. Phenom., 119 (2001) 255.