Theoretical study of Photoelectron Angular Distributions for Dicationic Carbon Monoxide by the use of Full-Potential Multiple Scattering Theory

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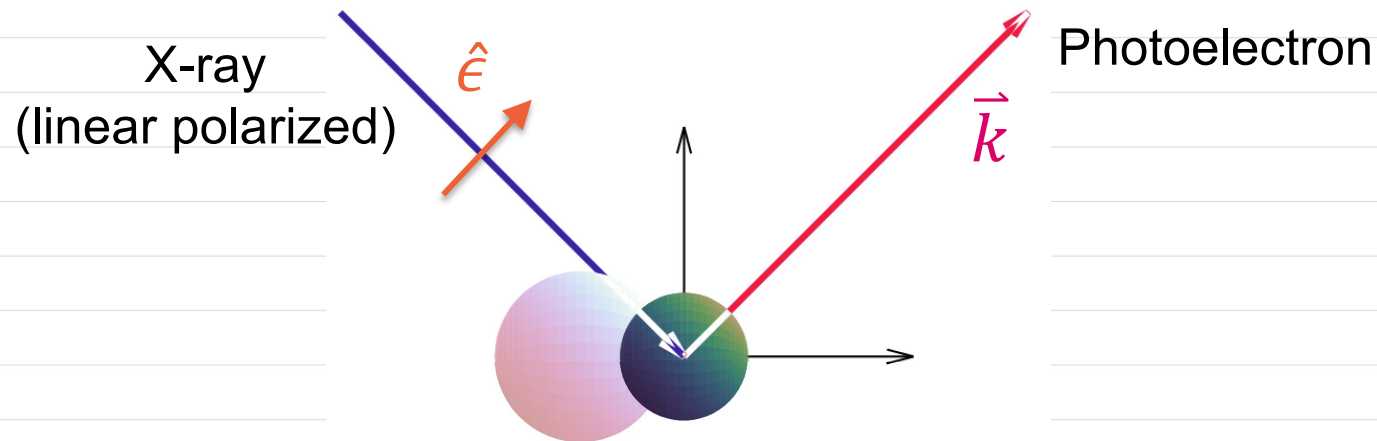6 Graduation school of Science and Engineering for Research, University of Toyama, Toyama, Japan

MFPADs & PA-MFPADs

- **MFPADs**

  = **M**olecular-**F**rame **P**hotoelectron **A**ngular **D**istributions

$$I(\mathbf{k}, \hat{\epsilon}) \propto \left| \langle \psi_f^{\vec{k}} | \hat{\epsilon} \cdot \mathbf{r} | \phi_i \rangle \right|^2 = \left| \frac{4\pi}{3} \sum_{m_p=-1}^{1} Y_{1m_p}^*(\hat{\epsilon}) \ \langle \psi_f^{\vec{k}} | r Y_{1m_p} | \phi_i \rangle \right|^2$$

X-ray
(linear polarized)

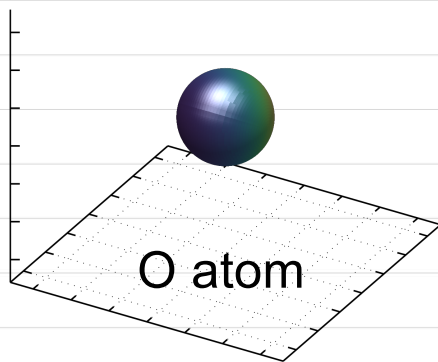$\hat{\epsilon}$

Photoelectron

$\vec{k}$

MFPADs & PA-MFPADs

- **MFPADs**

  Molecular-**F**rame **P**hotoelectron **A**ngular **D**istributions

- Distribution of Photoelectrons emitted from molecule (or atom) by linear-polarized X-ray

  ex.) **O 1s** MFPADs of Oxygen atom

O atom

MFPADs & PA-MFPADs

- **MFPADs**

  Molecular-**F**rame **P**hotoelectron **A**ngular **D**istributions

- Distribution of Photoelectrons emitted from molecule (or atom)

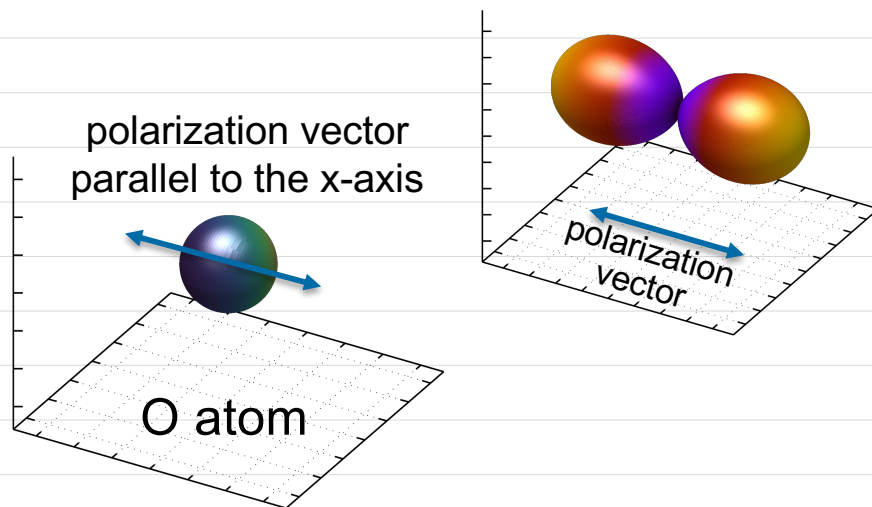 by linear-polarized X-ray

  ex.) **O 1s** MFPADs of Oxygen atom

polarization vector
parallel to the x-axis

O atom

polarization
vector

MFPADs from 1s orbital have p-orbital
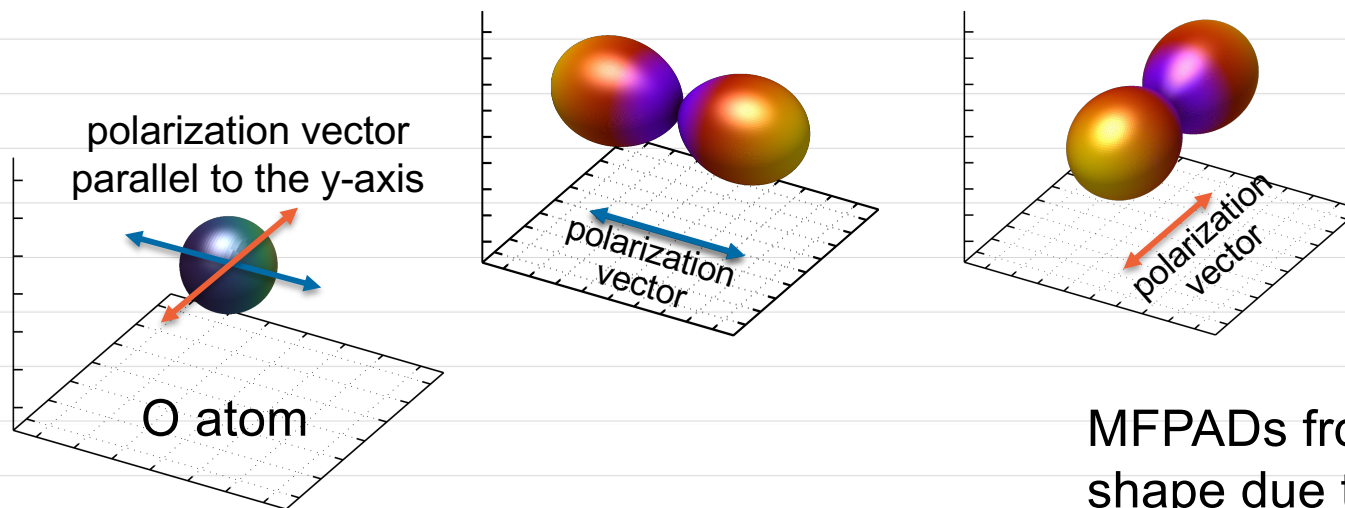shape due to the selection rule.

MFPADs & PA-MFPADs

- **MFPADs**

  Molecular-**F**rame **P**hotoelectron **A**ngular **D**istributions

- Distribution of Photoelectrons emitted from molecule (or atom) by linear-polarized X-ray

  ex.) **O 1s** MFPADs of Oxygen atom

polarization vector parallel to the y-axis

polarization vector

O atom

polarization vector

MFPADs from 1s orbital have p-orbital shape due to the selection rule.
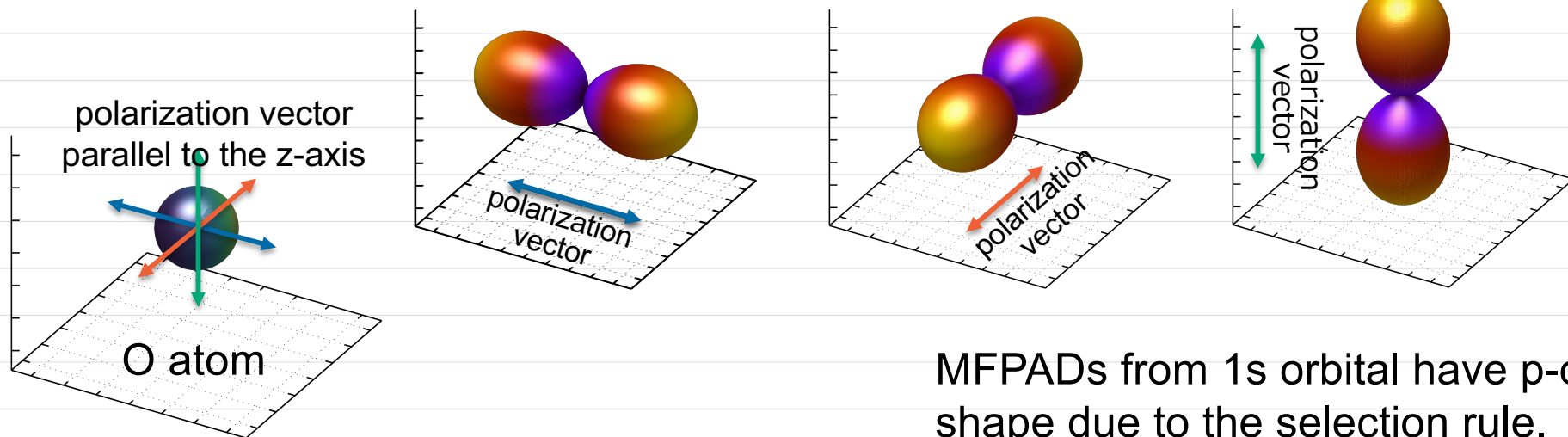
MFPADs & PA-MFPADs

- **MFPADs**

  Molecular-**F**rame **P**hotoelectron **A**ngular **D**istributions

- Distribution of Photoelectrons emitted from molecule (or atom)
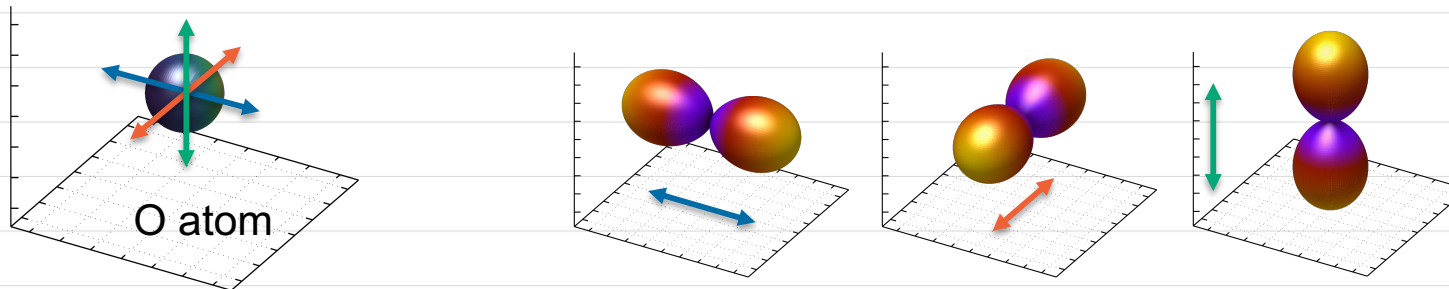 by linear-polarized X-ray

  ex.) **O 1s** MFPADs of Oxygen atom

polarization vector
parallel to the z-axis

O atom

polarization
vector

polarization
vector

polarization
vector

MFPADs from 1s orbital have p-orbital
shape due to the selection rule.

MFPADs & PA-MFPADs

O 1s MFPADs of Oxygen atom

O atom

O 1s MFPADs of CO molecule

Scattering
by carbon atom

CO molecule

polarization
vector

polarization
vector

polarization
vector
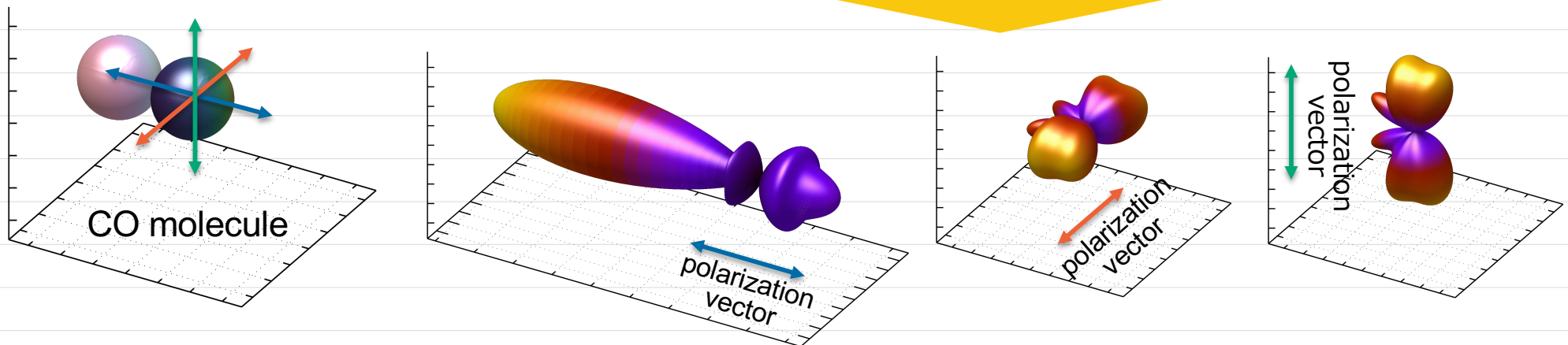
The MFPADs reflect molecular structure.

MFPADs & PA-MFPADs

- **PA-MFPADs**

  = **P**olarization-**A**veraged **-**

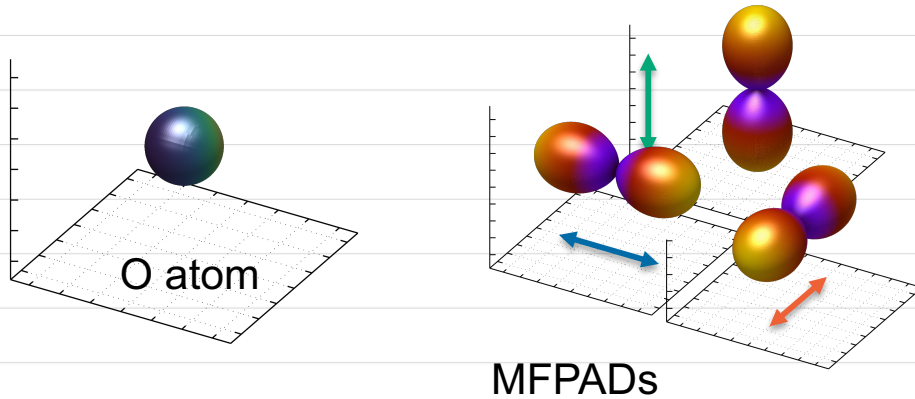 **M**olecular-**F**rame **P**hotoelectron **A**ngular **D**istributions

- MFPADs averaged over all the polarization directions

$$
\begin{aligned}
I^{\mathrm{ave}}(\mathbf{k}) &\equiv \frac{1}{4\pi} \int d\hat{\epsilon}\, I(\mathbf{k}, \hat{\epsilon}) \\
&\propto \frac{1}{4\pi} \left(\frac{4\pi}{3}\right)^2 \sum_{m_p, m_p'} \left(\int d\hat{\epsilon}\, Y_{1m_p}^*(\hat{\epsilon})\, Y_{1m_p'}(\hat{\epsilon}) \right) \langle \psi_f^{\vec{k}} | r Y_{1m_p} | \phi_i \rangle \langle \phi_i | r Y_{1m_p'}^*(\hat{\mathbf{r}}) | \psi_f^{\vec{k}} \rangle \\
&= \frac{1}{3} \left\{ \left| \langle \psi_f^{\vec{k}} | z | \phi_i \rangle \right|^2 + \left| \langle \psi_f^{\vec{k}} | x | \phi_i \rangle \right|^2 + \left| \langle \psi_f^{\vec{k}} | y | \phi_i \rangle \right|^2 \right\}
\end{aligned}
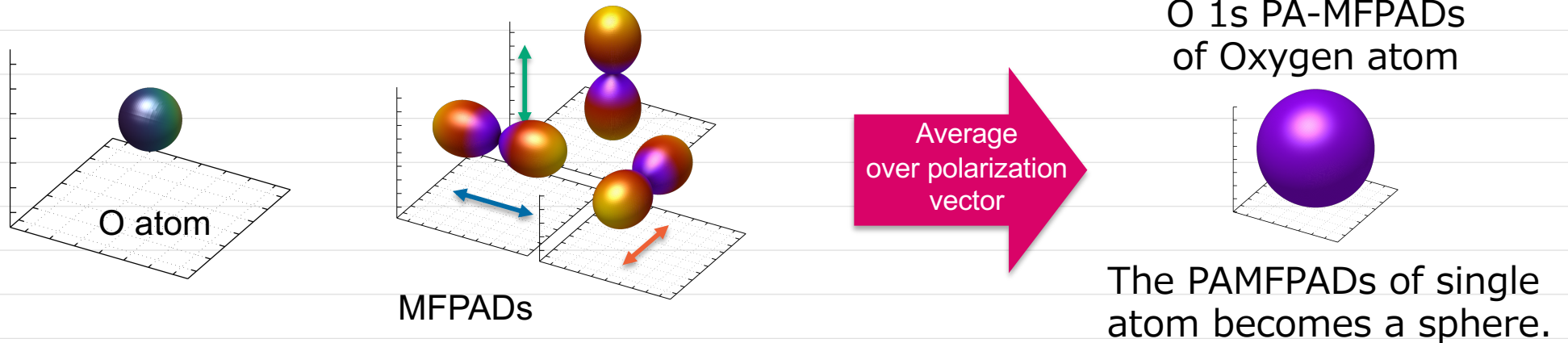$$

PA-MFPADs=(Average of MFPADs with x/y/z polarization)

$$I^{\mathrm{ave}}(\mathbf{k}) \equiv \frac{1}{4\pi} \int d\hat{\epsilon}\; I(\mathbf{k}, \hat{\epsilon}) \;\propto\; \frac{1}{3}\left\{ \left|\langle\psi_{\mathrm{f}}^{\vec{k}}|z|\phi_{\mathrm{i}}\rangle\right|^2 + \left|\langle\psi_{\mathrm{f}}^{\vec{k}}|x|\phi_{\mathrm{i}}\rangle\right|^2 + \left|\langle\psi_{\mathrm{f}}^{\vec{k}}|y|\phi_{\mathrm{i}}\rangle\right|^2 \right\}$$

O atom

MFPADs

MFPADs & PA-MFPADs

$$I^{\mathrm{ave}}(\mathbf{k}) \equiv \frac{1}{4\pi} \int d\hat{\epsilon}\, I(\mathbf{k}, \hat{\epsilon}) \; \propto \; \frac{1}{3}\left\{ \left|\langle \psi_{\mathrm{f}}^{\vec{k}}|z|\phi_{\mathrm{i}}\rangle\right|^2 + \left|\langle \psi_{\mathrm{f}}^{\vec{k}}|x|\phi_{\mathrm{i}}\rangle\right|^2 + \left|\langle \psi_{\mathrm{f}}^{\vec{k}}|y|\phi_{\mathrm{i}}\rangle\right|^2 \right\}$$

O 1s PA-MFPADs
of Oxygen atom

O atom

MFPADs

Average
over polarization
vector

The PAMFPADs of single
atom becomes a sphere.
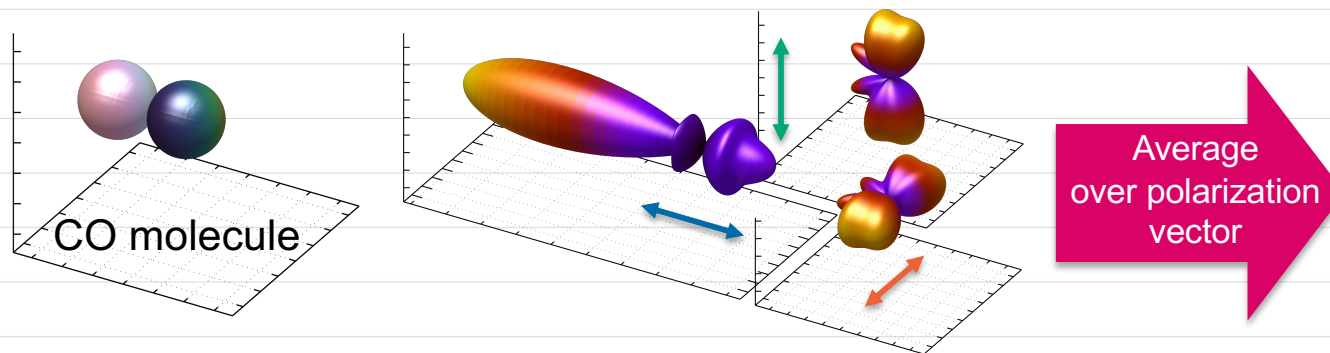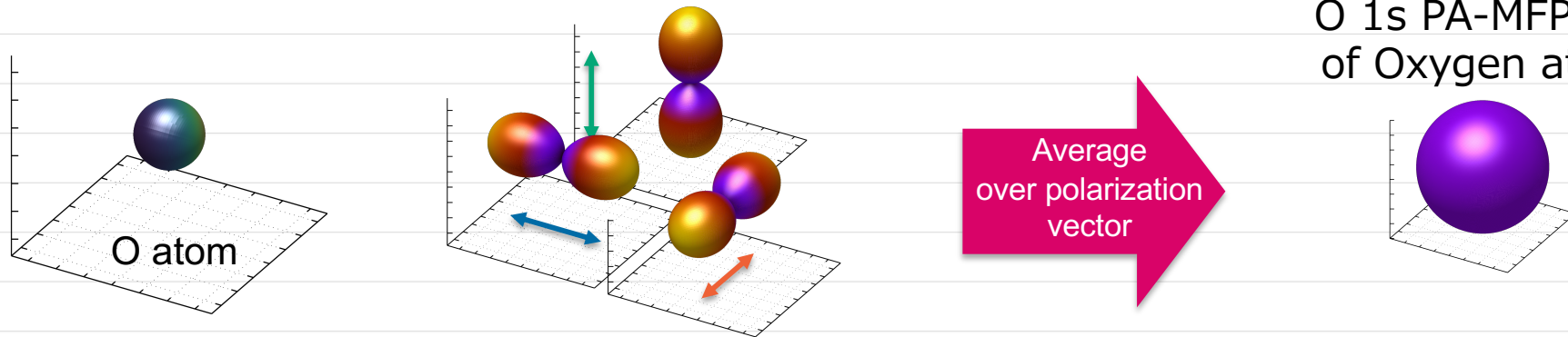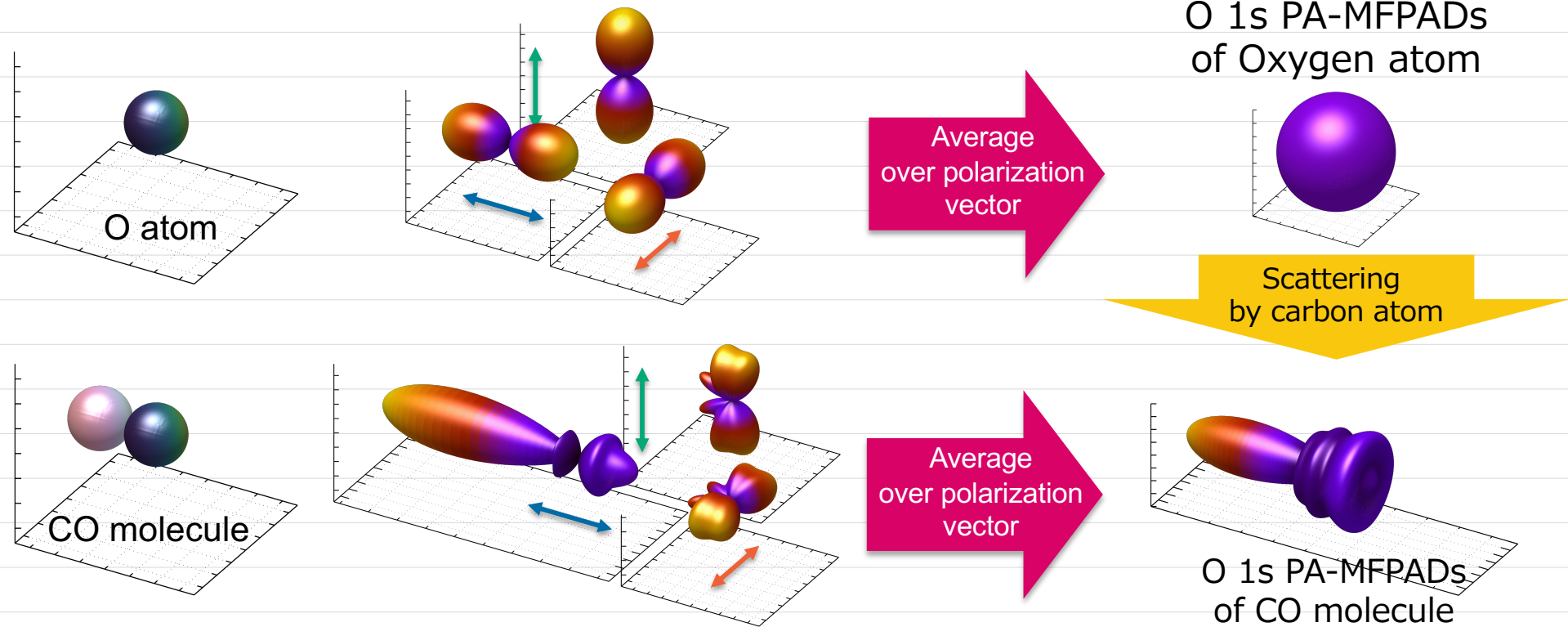
MFPADs & PA-MFPADs

$$I^{\text{ave}}(\mathbf{k}) \equiv \frac{1}{4\pi} \int d\hat{\epsilon}\ I(\mathbf{k}, \hat{\epsilon})\ \propto \frac{1}{3}\left\{ \left| \langle \psi_{\text{f}}^{\vec{k}} | z | \phi_{\text{i}} \rangle \right|^2 + \left| \langle \psi_{\text{f}}^{\vec{k}} | x | \phi_{\text{i}} \rangle \right|^2 + \left| \langle \psi_{\text{f}}^{\vec{k}} | y | \phi_{\text{i}} \rangle \right|^2 \right\}$$

O 1s PA-MFPADs
of Oxygen atom

O atom

Average
over polarization
vector

CO molecule

Average
over polarization
vector

MFPADs & PA-MFPADs

$$I^{\mathrm{ave}}(\mathbf{k}) \equiv \frac{1}{4\pi} \int d\hat{\epsilon}\, I(\mathbf{k}, \hat{\epsilon}) \;\propto\; \frac{1}{3}\left\{ \left|\langle \psi_{\mathrm{f}}^{\vec{k}} | z | \phi_{\mathrm{i}} \rangle\right|^2 + \left|\langle \psi_{\mathrm{f}}^{\vec{k}} | x | \phi_{\mathrm{i}} \rangle\right|^2 + \left|\langle \psi_{\mathrm{f}}^{\vec{k}} | y | \phi_{\mathrm{i}} \rangle\right|^2 \right\}$$

O atom

O 1s PA-MFPADs of Oxygen atom

Average over polarization vector

Scattering by carbon atom

CO molecule

Average over polarization vector

O 1s PA-MFPADs of CO molecule

Only the scattering effect by surrounding atoms is extracted.
= PA-MFPADs
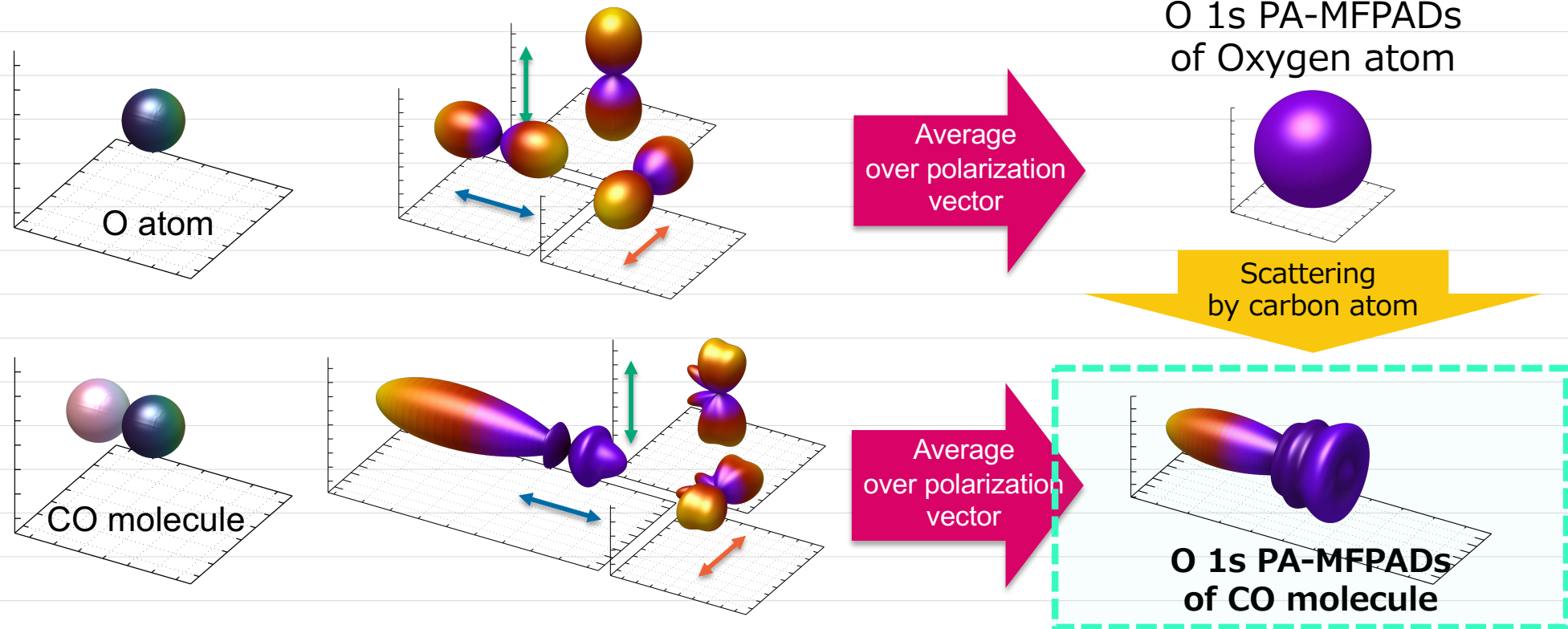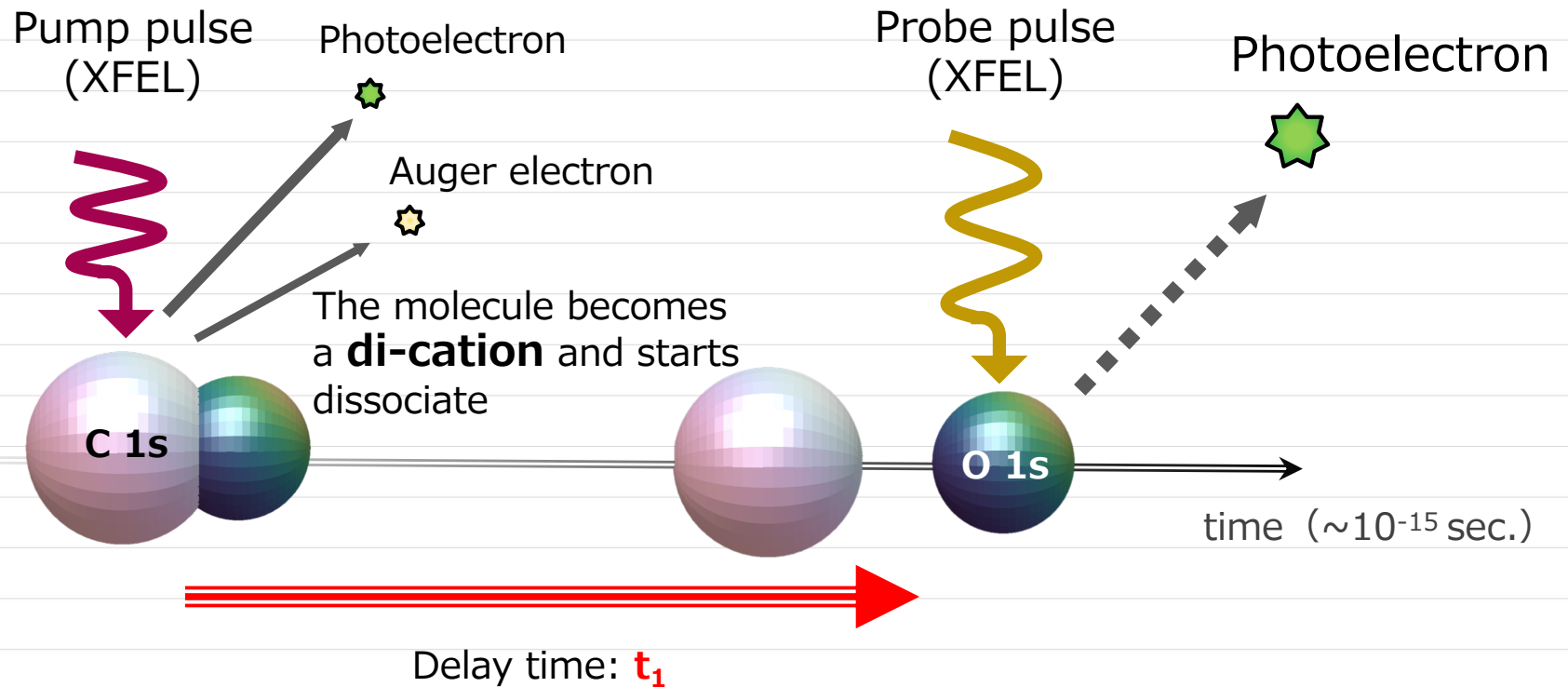
Introduction
MFPADs & PA-MFPADs

$$I^{\text{ave}}(\mathbf{k}) \equiv \frac{1}{4\pi} \int d\hat{\epsilon}\, I(\mathbf{k}, \hat{\epsilon}) \;\propto\; \frac{1}{3}\left\{ \left|\langle \psi_f^{\vec{k}} | z | \phi_i \rangle\right|^2 + \left|\langle \psi_f^{\vec{k}} | x | \phi_i \rangle\right|^2 + \left|\langle \psi_f^{\vec{k}} | y | \phi_i \rangle\right|^2 \right\}$$

O atom

CO molecule

Average over polarization vector

O 1s PA-MFPADs of Oxygen atom

Scattering by carbon atom

Average over polarization vector

O 1s PA-MFPADs of CO molecule

Only the scattering effect by surrounding atoms is extracted. = PA-MFPADs

・ **PA-MFPADs measurement
with 2-color XFEL** @European XFEL in 2 years (Prof. Ueda, Tohoku Univ.)

Pump pulse (XFEL)

Photoelectron

Auger electron

The molecule becomes a **di-cation** and starts dissociate

C 1s

Probe pulse (XFEL)

Photoelectron

O 1s

time $(\sim 10^{-15}$ sec.$)$

Delay time: t_1

Prediction for experiment

Theory & Calculations

1. Multiple Scattering Theory

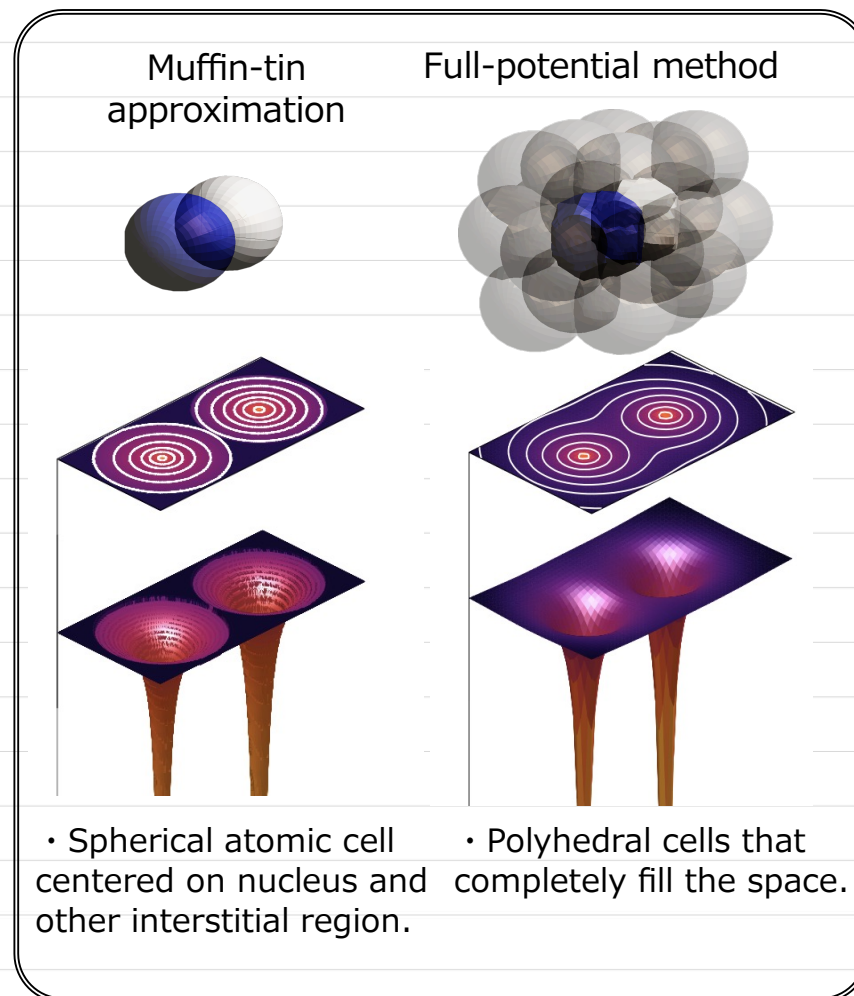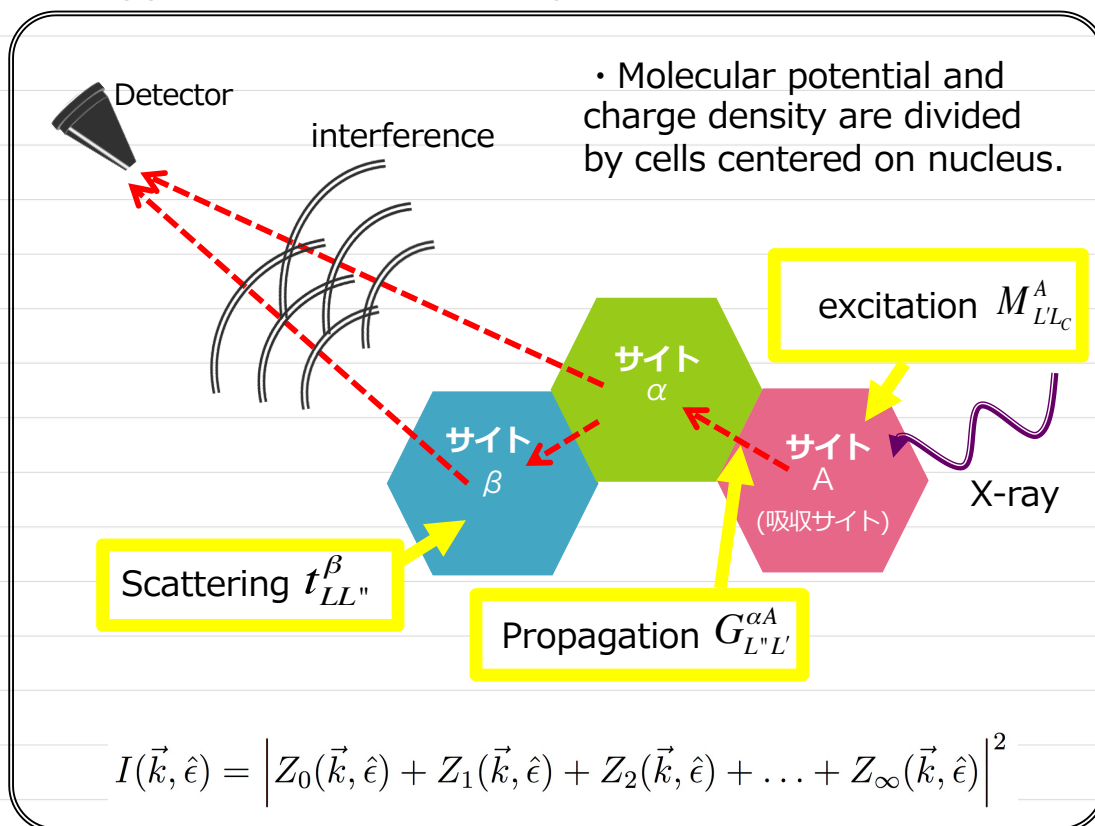   Muffin-tin approximation & Full-potential method

2. Dependence of PA-MFPADs on electronic structure

3. Dependence of PA-MFPADs on bondlength

1. Multiple Scattering Theory
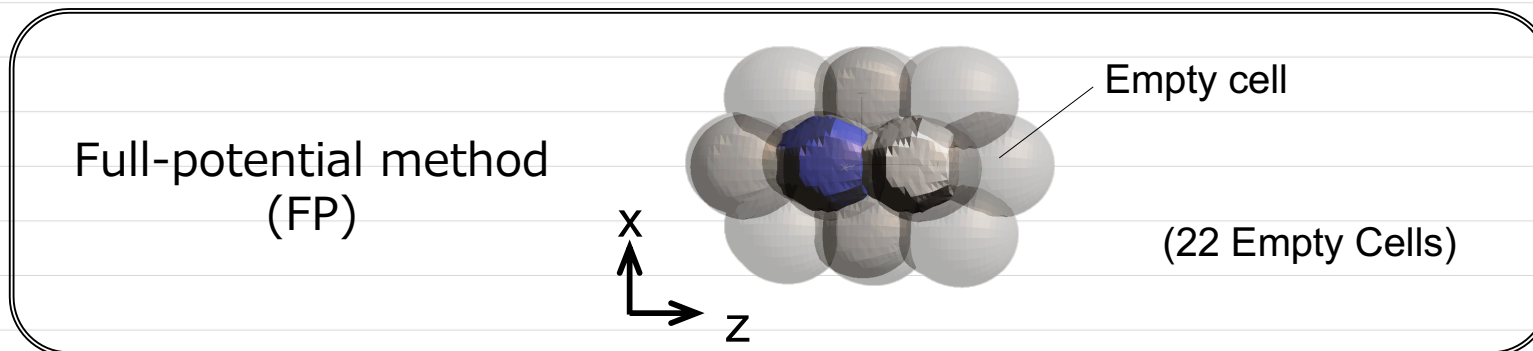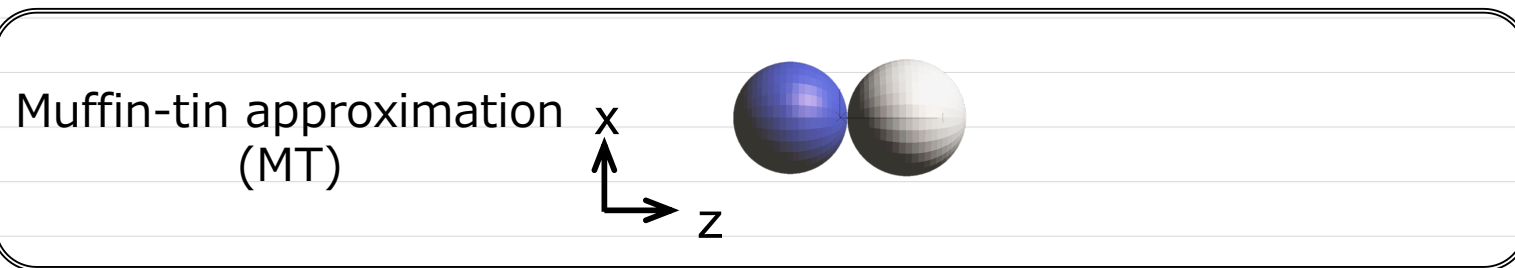## Muffin-tin approximation & Full-potential method

- PA-MFPADs calculations based on multiple-scattering theory with muffin-tin approximation and full-potential method.

Detector

interference

・Molecular potential and charge density are divided by cells centered on nucleus.

excitation $M_{L'L_C}^{A}$

サイト α

サイト β

サイト A (吸収サイト)

X-ray

Scattering $t_{LL''}^{\beta}$

Propagation $G_{L''L'}^{\alpha A}$

$$I(\vec{k}, \hat{\epsilon}) = \left| Z_0(\vec{k}, \hat{\epsilon}) + Z_1(\vec{k}, \hat{\epsilon}) + Z_2(\vec{k}, \hat{\epsilon}) + \ldots + Z_\infty(\vec{k}, \hat{\epsilon}) \right|^2$$

Muffin-tin approximation

Full-potential method

・Spherical atomic cell centered on nucleus and other interstitial region.

・Polyhedral cells that completely fill the space.

- Computational condition
  - Calculation code: **FPMS, MsSpec**

Muffin-tin approximation
(MT)

x
z

Full-potential method
(FP)

Empty cell

(22 Empty Cells)

x
z

C-O bondlength: 1.1283 Å
Kinetic energy of photoelectron : 100 eV
Optical potential : Real part of Hedin-Lundqvist potential

1. Multiple Scattering Theory

Muffin-tin approximation & Full-potential method

Calculation results : O1s PA-MFPADs of CO molecule

Muffin-tin approximation

（計算結果　省略）

Full-potential method

（計算結果　省略）

（計算結果　省略）

C–O bondlength : 1.1283 Å

Kinetic energy of photoelectron : **100 eV**
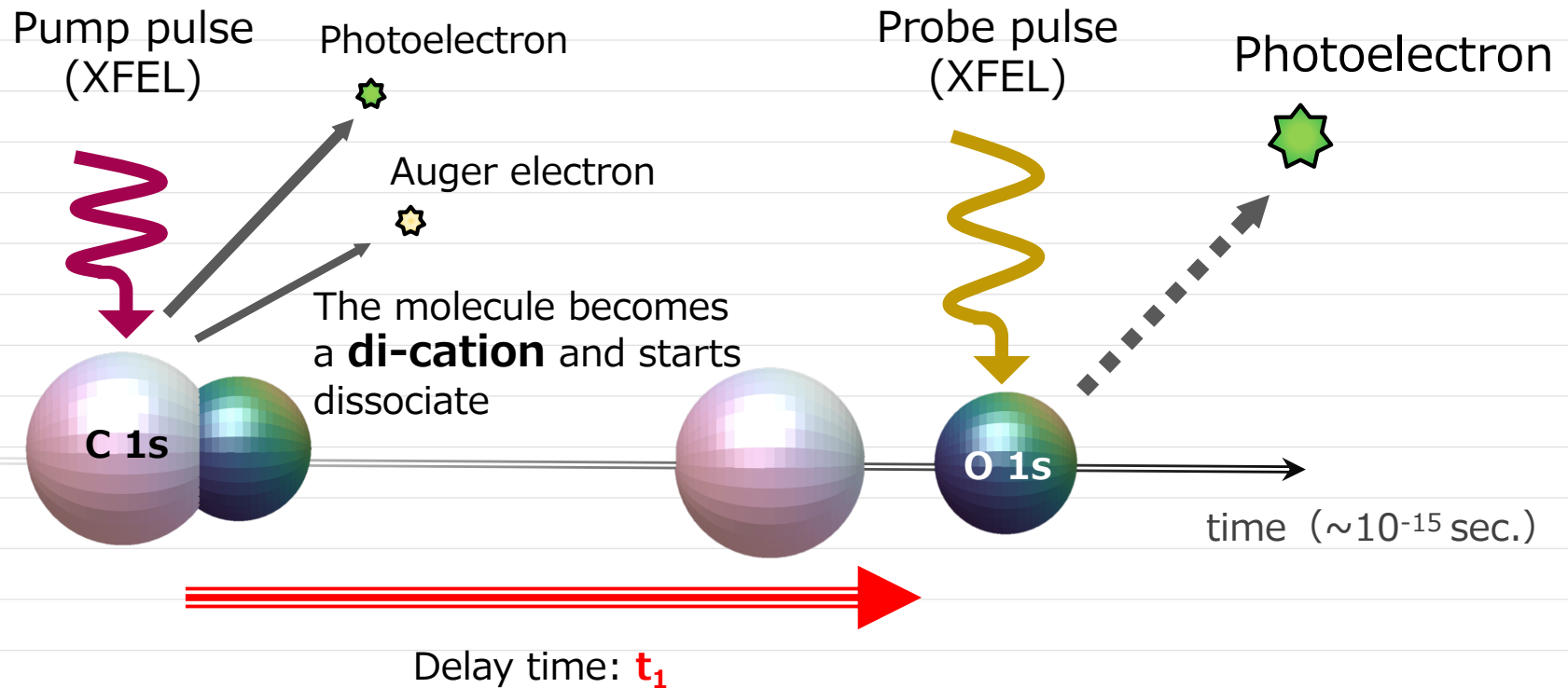
Optical potential : Real part of Hedin-Lundqvist potential

**The Muffin-tin approximation doesn't work well
for the PA-MFPADs calculation even in high-energy region (~100eV)**

2. Dependence on electronic structure

- **The PA-MFPADs calculated with Muffin-tin approximation and Full-potential method clearly differ from each other.**

  – Detailed structure of molecular potential is not negligible.

  – Charge density and molecular potential are constructed by just superimposing the potentials of each atoms (non–SCF way).

  ↓

- **Charge density and molecular potential should be calculated in SCF with keeping electron-holes.**

  – These calculation were performed with RASPT2 method by using a quantum chemistry package "MOLCAS".

・ **Pump-Probe measurement
with 2-color XFEL** @European XFEL in 2 years (Prof. Ueda, Tohoku Univ.)

Pump pulse
(XFEL)

Photoelectron

Probe pulse
(XFEL)

Photoelectron

Auger electron

The molecule becomes
a **di-cation** and starts
dissociate

C 1s

O 1s

time（~10^{-15} sec.）

Delay time: t_1
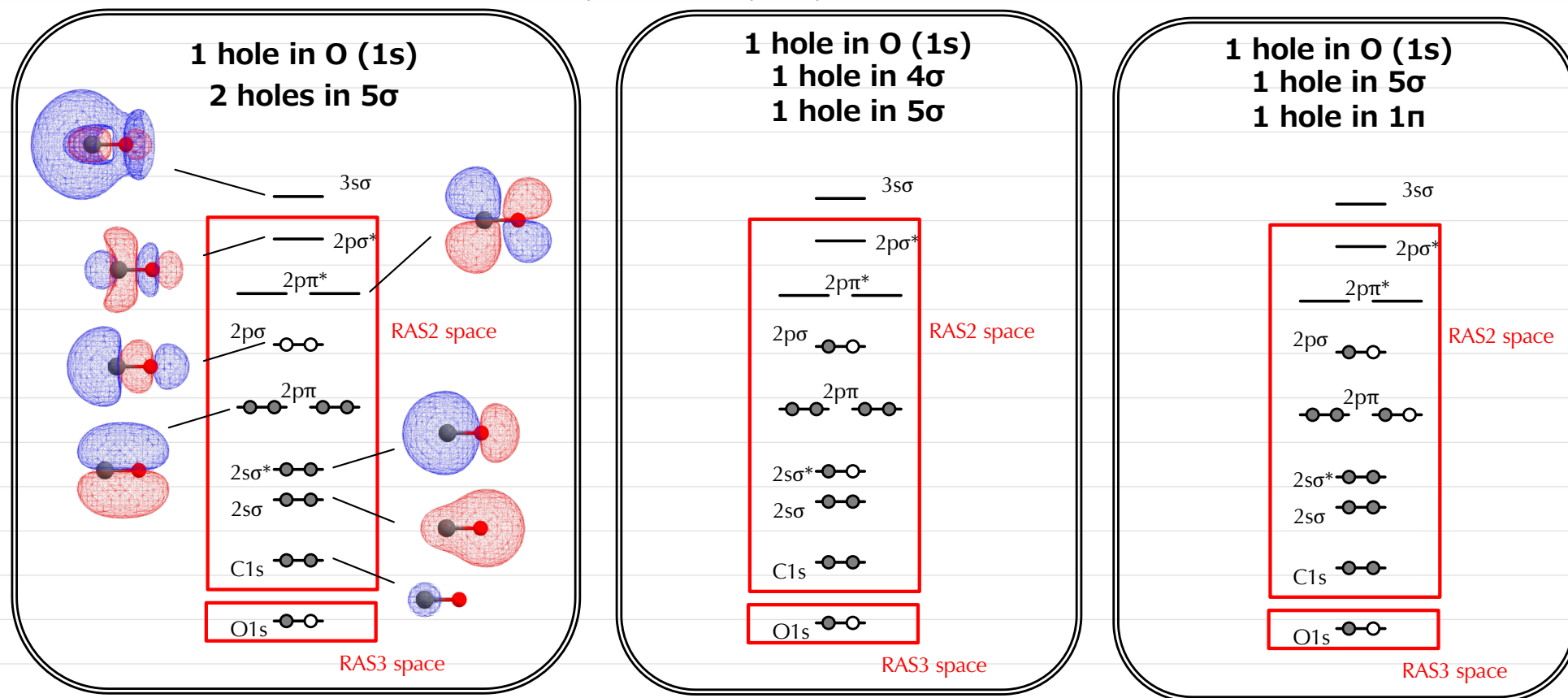
Charge-density distribution

electronic state

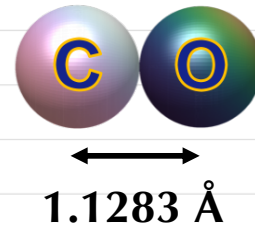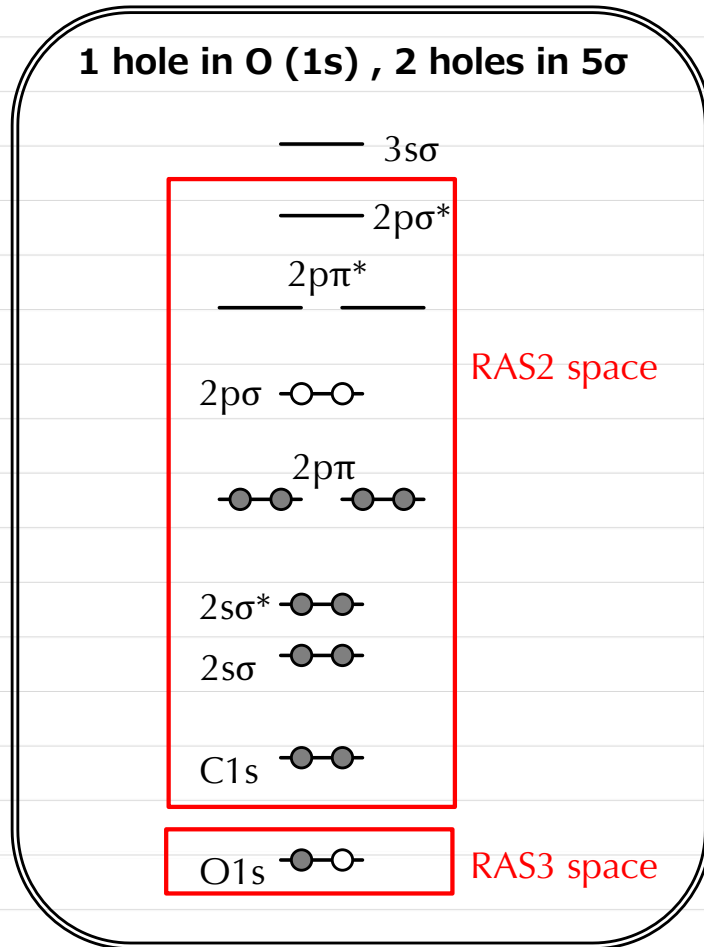|	1 hole in O (1s) 2 holes in 5σ	1 hole in O (1s) 1 hole in 4σ 1 hole in 5σ	1 hole in O (1s) 1 hole in 5σ 1 hole in 1π
Basis set			
6-31G* (small)			
		（計算結果　省略）	
ANO-RCC-VQZP (large)			

Dependence of basis-set

1 hole in O (1s) , 2 holes in 5σ

3sσ

2pσ*

2pπ*

RAS2 space

2pσ

2pπ

2sσ*

2sσ

C1s

O1s   RAS3 space

1.1283 Å

（計算結果　省略）

Dependence of Basis-set

1 hole in O (1s)
2 holes in 5σ

1.1283 Å

（計算結果　省略）

（計算結果　省略）

6-31G*

ANO-RCC-VQZP
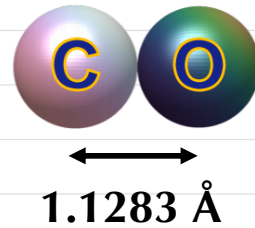
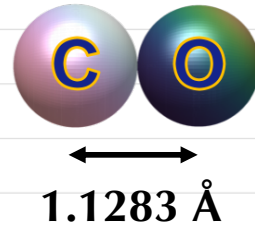**The shapes of PA-MFPADs does not depend much on the basis set.**

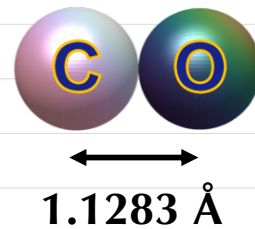# 2. Dependence on electronic structure

Dependence on electronic state

C O

1.1283 Å

（計算結果　省略）

(Basis set : ANO-RCC-VQZP (large))

Dependence on electronic state

（計算結果　省略）

C O

1.1283 Å

$1\sigma^{-1} 5\sigma^{-2}$
$1\sigma^{-1} 4\sigma^{-1} 5\sigma^{-1}$
$1\sigma^{-1} 5\sigma^{-1} 1\pi^{-1}$

(Basis set : ANO-RCC-VQZP)

The shapes of PA-MFPADs depend on the electronic structure.

3. Dependence on bondlength

CO dication O1s PA-MFPADs

C-O bondlength : **1.1283 Å ~ 2.0283 Å (0.1 Å step, 10 snapshots)**
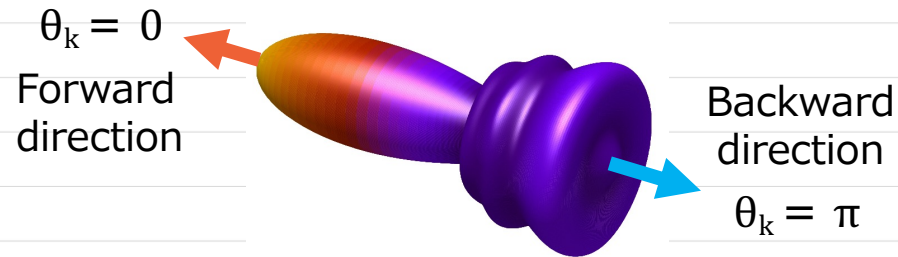
Kinetic energy of photoelectron: 100 eV

Optical potential：Real part of Hedin-Lundqvst potential

1 hole in O (1s) , 2 holes in 5σ, Basis set : 6-31G*

（計算結果　省略）

The PA-MFPADs are sensitive to molecular structure change.

3. Dependence on bondlength

$\theta_k = 0$

Forward direction

Backward direction

$\theta_k = \pi$

（計算結果　省略）

$\theta_k = 0$

$\theta_k = \pi$

The forward/backward intensities oscillate as a function of bondlength _R_.

3. Dependence on bondlength

・Comparison with single-/double- scattering calculation with MT approximation.

MT & Single-scattering	MT & Double-scattering	FP & Matrix-inversion

PA-MFPADs intensity

$\theta_k = 0$

（計算結果　省略）

$\theta_k = \pi$

C-O bond length **R (a.u.)**

PA-MFPADs intensity

$\theta_k = 0$

（計算結果　省略）

$\theta_k = \pi$

R (a.u.)

PA-MFPADs intensity

$\theta_k = 0$

（計算結果　省略）$\theta_k = \pi$

R (a.u.)

$$I(\theta_k = 0) \propto \underbrace{1 + \frac{2|fC(0)|\cos(\phi^{C0})}{R} + \frac{|f^C(0)|^2 + 2|f^O(\pi)||fC(\pi)|\cos(\phi^{O\pi}+\phi^{C\pi}+2kR)}{R^2}}_{\text{Single-scattering}} + \frac{2|f^O(\pi)||fC(\pi)|^2\cos(\phi^{O\pi}+2kR)}{R^3} + \frac{|fO(\pi)|^2|fC(\pi)|^2}{R^4}$$

Double-scattering

$$I(\theta_k = \pi) \propto \underbrace{1 - \frac{2|fC(\pi)|\cos(\phi^{C\pi}+2kR)}{R} + \frac{|f^C(\pi)|^2 - 2|f^O(0)||fC(\pi)|\cos(\phi^{00^+}\phi^{C\pi}+2kR)}{R^2}}_{\text{Single-scattering}} + \frac{2|f^O(0)||fC(\pi)|^2\cos(\phi^{00)}}{R^3} + \frac{|fO(0)|2|fC(\pi)|^2}{R^4}$$

Double-scattering

$\cos(2kR)$ **: oscillation term**

Double- and higher scattering – Oscillation of forward-scattering intensity
Single- and higher scattering – Oscillation of backward-scattering intensity
They have frequency 2kR same as EXAFS → Useful for experiment analysis

Summary and Perspectives

- For PA-MFPADs simulation, muffin-tin approximation doesn't work well even in high-energy region (K.E. of photoelectron ~100eV).

- PA-MFPADs reflect the difference in electronic states.

  → PA-MFPADs simulation should be performed by full-potential method with molecular potential and charge density calculated in SCF with keeping electron-holes.

- PA-MFPADs is sensitive to molecular structure change.

- Forward-/backward- intensities of PA-MFPADs of CO molecule oscillate as a function of C-O bondlength R.

- The frequency of the oscillations is $2kR$ and it come from interference terms.

- For the analysis of experimental results, we will consider the width of nuclear wave-packets and thermal broadening.

Thank you for your attention !