Original Paper

Theoretical Study of Multi-atom Resonant Photoemission

H. Arai[*] and T. Fujikawa
Graduate School of Advanced Integration Science,
Chiba University, Yayoi-cho 1-33, Inage, Chiba 263-8522,Japan
[*]*arai@mat.chem.nagoya-u.ac.jp*

In order to study the photoelectron angular distribution near the Multi-Atom Resonant Photoemission (MARPE) threshold from linear molecules fixed in space, we have developed a theory based on nonrelativistic Keldysh Green's function approach. When the molecular axis is perpendicular to the X-ray polarization, we have to include the next order term in the structure factor in the order of R^{-4}. This term gives rise to asymmetry in the photoelectron angular distribution. We also show some calculated results for NO molecule which are compared with the recent experimental results. Overall features are well explained by the present calculations.

1. Introduction

Multi-atom resonant photoemission (MARPE) permits direct determination of near-neighbor atomic identities, because MARPE occurs when the photon energy is tuned to a core-level absorption edge of an atom neighboring an emitting atom [1, 2].

We have theoretically studied MARPE based on non-relativistic Keldysh Green's function theory. In this theoretical framework we have found that the local symmetry around the emitting atom plays a crucial role to observe MARPE signal: typically highly symmetric atomic arrangement around the emitter provides us no or weak MARPE signal, but lower symmetric arrangement gives rise to considerably strong one [3].

Recently, new experimental results are published. In Ref. [4] an investigation of a incident X-ray angle to a solid surface has been reported. In Ref. [5] photoelectron angular distributions have been measured from fixed-in-space simple molecules on the resonant energy by use of the coincidence technique. They found that the photoelectron angular distributions depend on the angle between the X-ray polarization and the molecular axis (parallel to z-axis).

To study angular dependence of MARPE effect, we develop a theory to describe the photoelectron angular

distribution in molecular frame. Then we demonstrate some calculated results for the N 1s photoemission from NO molecule near the O 1s threshold, which are compared with recent experimental results [5].

2. Theory

In previous study we have obtained a theoretical formula to discuss the photoemission intensity near the resonant threshold $I(\mathbf{p}, \omega)$ which measures the photoelectrons with linear momentum $\mathbf{p}$ excited by X-ray photons with energy ω [3],

$$
\begin{aligned}
I(\mathbf{p}, \omega) &= \left| \langle f_{\mathbf{p}}^- |\Delta| g_0 \rangle + i \langle f_{\mathbf{p}}^- |Z(\omega)| g_0 \rangle \right|^2 \\
&\times \delta[\varepsilon_p + E_0(N-1) - \omega - E_0(N)], \\
\Delta &\propto z
\end{aligned}
\tag{1}
$$

where the photoelectron wave function $f_{\mathbf{p}}^-$ approaches to the plane wave outside far from solid, however in solids it damps under the influence of the optical potential. The Dyson orbital g_0 is approximated by the core function ϕ_c from which a photoelectron is excited for the present discussion. The first term in eq. (1) describes the conventional photoemission processes in contrast to the second term which has the resonant contribution because it depends on ω. The nonlocal energy dependent

operator $Z(\omega)$, due to the radiation field screening, is given by use of the screened Coulomb interaction $W(\omega)$ [6-8].

$$i \langle f_{\mathbf{p}}^- | Z(\omega) | g_0 \rangle$$
$$\approx \sum_{sj} \frac{\langle f_{\mathbf{p}}^- g_j | W(\omega) | g_0 f_s \rangle}{\omega + \varepsilon_j - \varepsilon_s + i\eta} \langle f_s | \Delta | g_j \rangle . \tag{2}$$

The amplitude (2) describes the physical process initiated by the X-ray absorption process accompanying the virtual excitation from the hole state g_j to the particle state f_s which then deexcited to $f_s \to g_j$ and simultaneously real photoexcitation process $g_0 \to f_{\mathbf{p}}^-$ follows.

Here we derive some useful formulas to study the photoelectron angular distribution near resonant threshold from fixed molecules in space. The electron-photon interaction Δ is written by use of a rotation matrix $D_{m_p 0}^{(1)}$

$$\Delta = r \sum_{m_p} Y_{1m_p}(\hat{\mathbf{r}}) D_{m_p 0}^{(1)}(\hat{\mathbf{R}}) \tag{3}$$

where $\hat{\mathbf{R}}$ is Euler rotation to new z-axis, which yields a formula for the photoemission intensity in the molecular frame

$$I(\mathbf{p}, \omega) \propto \left| \sum_{m_p} \langle f_{\mathbf{p}}^- | r Y_{1m_p} | g_0 \rangle D_{m_p 0}^{(1)}(\hat{\mathbf{R}}) \right.$$
$$\left. + \sum_{m_p} \sum_{m'\alpha} A_{m_p}(\mathbf{R}_\alpha, \omega)_{m'} \langle f_{\mathbf{p}}^- | r Y_{1m'} | g_0 \rangle \right|^2 . \tag{4}$$

There $\mathbf{R}_\alpha$ is a position of a nearby resonant atom measured from the emitting atom.

The second term (resonant term) has the structure factor defined by

$$A_{m_p}(\mathbf{R}_\alpha, \omega)_{m'} = \frac{4\pi}{3} \rho^1(q, d)^2 G(L_d \, 1m_p | L_q)^2$$
$$\times y_{1m_p, 1m'}(\mathbf{R}_\alpha) D_{m_p 0}^{(1)}(\hat{\mathbf{R}}) \left(1 + \frac{\gamma}{\omega' + i\Gamma} \right) \tag{5}$$
$$\times \frac{1}{\omega' + i\Gamma}$$

This term is proportional to the factor of R_α^{-3}. $\rho^1(q, d)$ is a radial integral, $G(L_d \, 1m_p | L_q)$ Gaunt integral, ω' the photon energy measured from the resonant threshold, Γ the lifetime and γ the energy parameter due to the dynamical part of the screened Coulomb interaction $W(\omega)$ [3].

Let us consider a simple system, diatomic molecule whose molecular axis is perpendicular to the electric vector. We put $\hat{\mathbf{R}}_\alpha = (0\,0\,1)$ and it is sufficient to consider $m_p = \pm 1$. The photoelectron angular distribution in the direct photoemission process is controlled by $Y_{1\pm1}(\hat{\mathbf{r}})$ as seen from the first term in eq. (4). In the resonant term we obtain a contribution except for $m' = 0$ because the structure factor contains a factor of $Y_{2, m_p - m'}(\hat{\mathbf{R}}_\alpha)$ in $y_{1m_p, 1m'}(\mathbf{R}_\alpha)$. Therefore the photoelectron angular distribution in the resonant process is also controlled by $Y_{1\pm1}(\hat{\mathbf{r}})$. Both of them give the same angular pattern.

In simple molecules like NO and so on, bond distances are quite short in comparison with those in inorganic solids like MnO and so on. We should consider the next order term in the order of R_α^{-4}. Then the photoemission intensity is written by

$$I(\mathbf{p}, \omega) \propto \left| \sum_{m_p} \langle f_{\mathbf{p}}^- | r Y_{1m_p} | g_0 \rangle D_{m_p 0}^{(1)}(\hat{\mathbf{R}}) \right.$$
$$+ \sum_{m_p} \sum_{m'\alpha} A_{m_p}(\mathbf{R}_\alpha, \omega)_{m'} \langle f_{\mathbf{p}}^- | r Y_{1m'} | g_0 \rangle$$
$$\left. + \sum_{m_p} \sum_{m'\alpha} \bar{A}_{m_p}(\mathbf{R}_\alpha, \omega)_{m'} \langle f_{\mathbf{p}}^- | r^2 Y_{2m'} | g_0 \rangle \right|^2 , \tag{6}$$

where additional structure factor $\bar{A}_{m_p}$ is to be taken into account. This factor is obtained by replacing $y_{1m_p, 1m'}$ in the structure factor A_{m_p} by $y_{1m_p, 2m'}$, and is in the order of R_α^{-4}. The third term in eq. (6) provides the angular factor $Y_{2m'}(\hat{\mathbf{r}})$ in the photoexcitation operator instead of $Y_{1m}(\hat{\mathbf{r}})$ in the first and the second terms in eq. (6), which gives different photoelectron angular distribution in the arrangement where molecular axis is perpendicular to the electric vector.

In lower symmetric setup the second term also gives different angular distribution from the direct photoemission (the first term). These asymmetric angular distributions can provide us useful information on MARPE.

## 3. Calculated Results and discussion

In this section we show the calculated N 1s photoelectron angular distributions from a fixed-in-space NO molecule near the MARPE threshold: We expect that N 1s photoemission can show the resonant behavior near the O 1s $\to \pi^*$ excitation. We calculate the photoelectron angular distributions for the following geometry
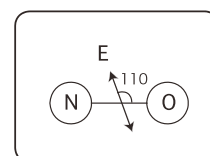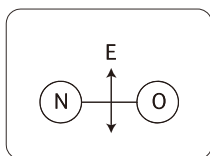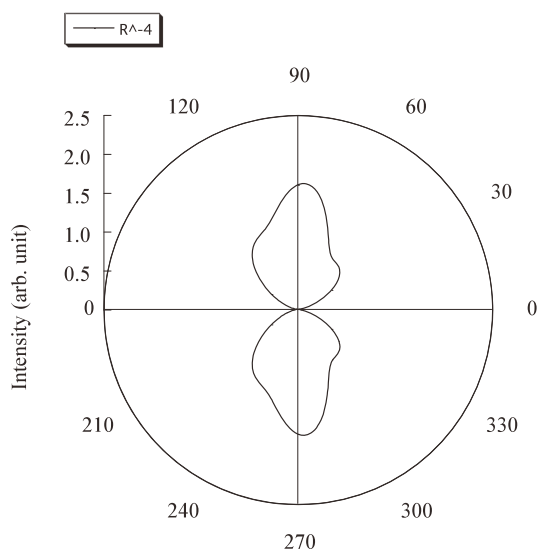
(a) 121.7 eV (on res.)
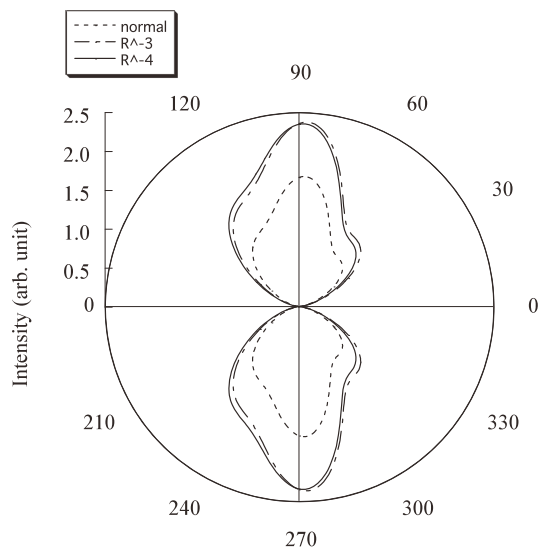
(a) 121.7 eV (on res.)
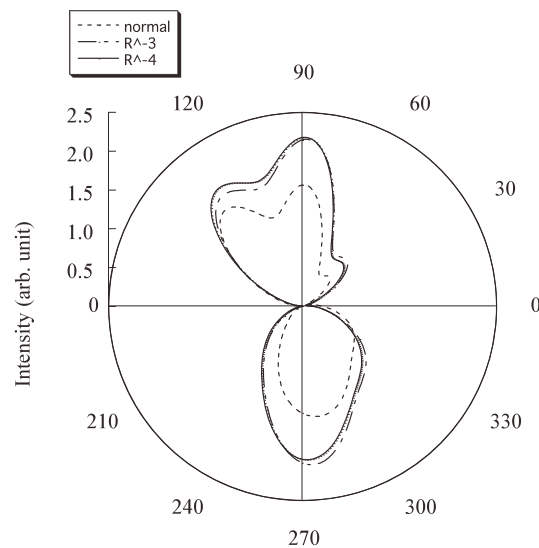
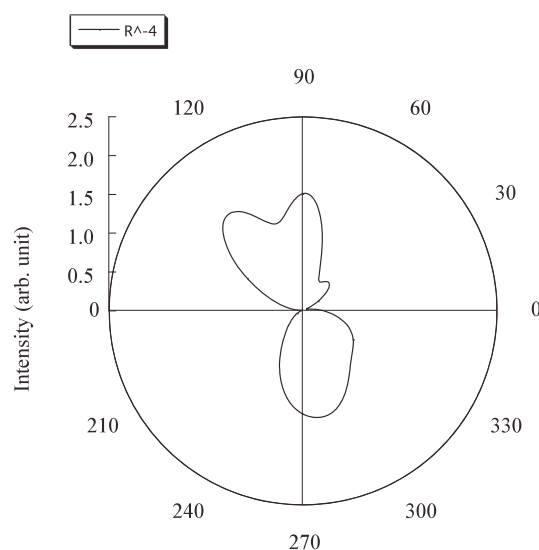(b) 124.7 eV (off res.)

(b) 124.7 eV (off res.)

Figure 1: Calculated θ plots of the N 1s photoelectron angular distribution in the zx-plane. The X-ray polarization is perpendicular to the molecular axis: NO molecule is on the z-axis ($\theta = 0°$) and X-ray polarization is parallel to x-axis ($\theta = 90°$). Dashed line shows the normal photoemission, dash-dotted line resonant photoemission up to the first (R^{-3}) order as described by eq. (4), solid line up to the second (R^{-4}) order as described by eq. (6).

setup: N atom is on the origin and O atom is on the z axis ($\theta = 0°$), and X-ray linear polarization is in the x-axis ($\theta = 90°$). We assume that the energy parameter $\gamma = -1$

Figure 2:As same as those in Fig.1, except the X-ray polarization relative to the molecular axis. The angle between them is 110 degree.

eV as used in the previous paper [3].

Figure 1 shows the calculated results at two different photon energies; (a) photoelectron kinetic energy 121.7 eV (on O 1s → π^* resonance) and (b) 124.7 eV (off-resonance) [5]. As expected the off-resonance (normal) photoemission shows the maximum intensity paral-

lel to the X-ray polarization, but scattering effects give a deviation from simple $\sin^2\theta$ distribution. Even for small difference of excitation energy (3eV), the resonant behavior vanishes as obtained in Fig. 1(b). In Fig. 1(a), as discussed in the previous section, the dash-dotted line calculated by eq. (4) should be similar to that predicted by non-resonant theory. However we can expect the resonant enhancement of the photoelectron intensity. If we measure the photoelectron intensity as a function of photon energy at fixed direction, we can observe the MARPE feature on the resonant energy. The solid line is given by eq. (6) which has electric quadrupole transition operator Y_{2m}. Each relative resonant contribution, for example, $R^{-3}/(\text{normal})$ and $R^{-4}/(\text{normal})$, are 141.7% and 149.6% at $\theta = 120\deg$, and 141.7% and 128.8% at $\theta = 30\deg$.

Figure 2 shows the same ones as those in Fig. 1 except the X-ray polarization; 110º tilted from the molecular axis. We can see the different angular distribution caused by the resonant effect even in the pattern of R^{-3} order because the resonant term in eq. (4) produces a different angular part other than the non-resonant term in this molecular orientation. Of course the angular distribution up to the R^{-4} order also gives more deviated pattern.

These calculated results can be compared with the experimental ones [5]. Overall features are quite similar; but Yamazaki *et al.* found that the intensity enhanced by the resonant effect has a peak along the electric vector. In the case where the X-ray polarization is perpendicular to the molecular axis, we also find the same behavior, as shown in Fig. 1(a). The difference between the on- and off-resonant angular pattern is only modified from the second (R^{-4}) order resonant effect. In the case where the X-ray polarization is tilted from the molecular axis, our results does not explain the detailed observed behavior, however overall feature is well explained. To obtain better agreement, we should use more sophisticated optical potential beyond muffin-tin approximation. In this case the modification from the resonant effects should be observed with much stronger intensity than that in the perpendicular case because the first (R^{-3}) order resonant term plays an important role.

4. Concluding Remarks

In this work we have developed the angular dependent MARPE theory in order to study the effects of molecular orientation. We also explicitly demonstrate the calculated results near the MARPE threshold excited from a NO molecule fixed-in-space. This molecule is in low symmetry, which can give rise to MARPE.

We should note that MARPE effect is typically measured when we monitor the photoemission intensity as a function of photon energy at fixed measurement direction which is dominated by the first order term in the order of R^{-3}. On the other hand photoemission angular distribution provides information from the higher order terms. As demonstrated here, the photoelectron angular distribution near resonant threshold has rich information on the structure factors. For the system with short interatomic distance R as considered here, the next order term in R^{-4} plays some important role in MARPE analyses.

References

[1] A. W. Kay, E. Arenholz, B. S. Mun, F. J. Garcia de Abajo, C. S. Fadley, R. Denecke, Z. Hussain and M. A. Van Hove, *Science* **281**, 679 (1998).

[2] A. W. Kay, F. J. Garcia de Abajo, S. H. Yang, E. Arenholz, B. S. Mun, N. Mannella, Z. Hussain, M. A. Van Hove and C. S. Fadley, *Phys. Rev. B* **63**, 115119 (2001).

[3] H. Arai and T. Fujikawa, *Phys. Rev. B* **72**, 075102 (2005).

[4] N. Mannelle, S. H. Yang, B. S. Mun, F. J. Garcia de Abajo, A. W. Kay, B. C. Sell, M. Watanabe, H. Ohldaq, E. Arenholz, A. T. Young, Z. Hussain, M. A. Van Hove and C. S. Fadley, *Phys. Rev. B* **74**, 165106 (2006)

[5] M. Yamazaki, J. Adachi, T. Teramoto and A. Yagishita, *J. Phys. B* **40**, F207 (2007)

[6] T. Fujikawa and H. Arai, *Recent Res. Devel. Physics* **4**, 657 (2003).

[7] T. Fujikawa and H. Arai, *Chem Phys. Lett.* **368**, 147 (2003).

[8] T. Fujikawa and H. Arai, *J. Elect. Spect. Relat. Phenom.* **149**, 61 (2005).