Photoemission dynamics in the molecular frame

A Yagishita¹, J Adachi¹ and M Yamazaki¹,²

¹ Photon Factory, Institute of Materials Structure Science, KEK
Tsukuba 305-0801, Japan
akira.yagishita@kek.jp

Abstract. Photoemission dynamics, based on the molecular frame photoelectron angular distribution, is reported. In the fast decay channel leading to Ne⁺ + Ne²⁺ of Ne₂ dimer, the molecular frame photoelectron measurements have been realized, and the core-hole localization observed. However, in the slow decay channel leading to Ne⁺ + Ne⁺, such measurements have not been applicable as expected. The molecular frame photoemission study has been extended to a non-axially symmetric H₂O molecule, and its experimental result has been well explained by a simple scattering model which is widely used in surface science.

1. Introduction
In an axial-recoil dissociation process the two fragments fly off exactly anti-parallel to one another. If the dissociation is initiated by the ejection of an electron like inner-shell photoionization, and that electron is detected in coincidence with the fragment ion pair, then the electron is tied to the direction of the molecular axis at the moment of dissociation. Assuming that this whole process takes place on a time scale that is short compared with a rotational period, such coincidence measurements can register molecular-frame photoelectron angular distributions [1, 2]. Namely, the angle-resolved photoelectron-photoion coincidence enables one to select the process with a well defined orientation of molecules from the photoionization of an ensemble of randomly oriented molecules in a gas phase.

By broadening the scope of feasible and meaningful experiments in this manner, one may hope in the longer term to develop a broader understanding of molecular photoionization dynamics. However, note that up to now, such experiments were performed exclusively on linear molecules, [3-8] and references therein, because the coincidence rate of all fragment ions from bent molecules decreases radically compared with that of ions from back-to-back fragmentation of linear molecules.

In this paper, two recent topics of photoemission dynamics in the molecular frame are reported; decay channel dependence of the photoelectron angular distribution in core-level photoionization of Ne₂ dimer [9] and 3D mapping of photoemission from a single oriented H₂O molecule [10]. In the first topic, it is demonstrated that the photoelectron-photoion coincidence measurement is a good internal clock of the molecule. In the second topic, it is discussed that the molecular-frame photoelectron angular distribution is tied to a molecular structure.

2. Experimental
Referring the idea of Eppink and Parker [11] and Lebech et al [12], we have successfully applied the multi-coincidence velocity-map imaging technique to obtain the molecular-frame photoelectron...
angular distribution (MF-PAD) [13]. The schematic of our experimental set-up is shown in figure 1. Linearly polarized soft x-rays from a planar undulator were monochromatized by a varied-space plane grating monochromator [14] and focused onto a supersonic molecular beam. Ions and electrons were guided by a uniform extraction electric field on opposite sides towards two area detectors with delay-line readout and detected in coincidence. The momenta of ions were determined from the flight times and the impact positions on the area detector. The projection of the electron momenta on a plane parallel to the electric field was determined from the positions. The polarization vector of the soft x-rays, being along the direction of the molecular beam, and the direction of the soft x-ray beam were in a plane parallel to the extraction electric field.

![Figure 1. Schematic of multi-coincidence velocity-map imaging spectrometer](image)

3. Results and discussion

3.1. Ne 1s photoemission from Ne2 dimer

If one specific atom having the core-hole can be distinguished from the measurement, the measured parameters are described by the localized core-hole state, and if not, they are described by the symmetry-adapted core-hole state. The core-orbital photoionization process of Ne2 dimer provides us an ideal showcase to resolve the elusive fundamental problem, because both removal of a 1s electron and successive Auger decay are essentially of atomic nature in the van der Waals molecules [15].

3.1.1. Ne 1s photoemission for Ne⁺–Ne₂⁺ decay channel. Figure 2 shows polar plots of Ne 1s photoemission relative to the dissociation axis of Ne⁺ + Ne₂⁺ breakup channels, which are produced via Auger decay and successive interatomic Coulombic decay (ICD) [15-20] as shown in figure 3. In the calculations, we employed the time-dependent density functional theory (TDDFT). The calculations were conducted using localized description of the core-hole state. The MF-PAD for the localized core-hole is shown by thin curve in figure 2, where the photoelectron is ejected from the right Ne atom. As can be seen in the figure, the MF-PAD for the Ne⁺ + Ne₂⁺ channel depends on the mutual angle between the polarization vector and dissociation axis. Surprisingly, broken inversion symmetry of the MF-PAD is seen clearly in the parallel geometry beyond the statistical errors of the data points, although the symmetry breaking is little recognized in the perpendicular geometry. The TDDFT calculations exhibit the lack of inversion symmetry as well, however, their patterns differ from the experimental ones in both the parallel and perpendicular geometries. The discrepancy is puzzling.

In weakly bound van der Waals dimers, both 1s photoemission and subsequent Auger decay with the lifetime of 2.4 fs take place at one site. On this basis, the decay process of core ionized Ne₂ can be described by a two-step model; in the first step the Auger decay occurs at the initial core-hole site leading to [Ne–Ne²⁺], and in the second step a charge separation into two sites takes place during successive decays, see figure 3. The ICD in the second step produces the Ne⁺ and Ne₂⁺ ion pair. Since the Ne⁺ fragment arises from the neutral atom of [Ne–Ne²⁺] system due to the ICD, one can presume
that the initial core-hole memory was carried by the resultant fragment Ne$^{2+}$ ion. Moreover, the lifetime of the order of 100 fs of the ICD for [Ne–Ne$^{2+}$] is much faster than the rotational period of about 100 ps. This is the reason why we have succeeded in measuring the MF-PAD for the Ne$^+$ + Ne$^{2+}$ decay channel, which shows non-inversion-symmetric patterns reflecting symmetry lowering of the core ionized [Ne–Ne$^+$] system.

3.1.2. Ne 1s photoemission for Ne$^+$–Ne$^+$ decay channel. Figure 4 shows polar plots of the Ne 1s photoemission relative to the dissociation axis Ne$^+$ + Ne$^+$ breakup channels which are produced via Auger decay and successive radiative decay as shown in figure 5. The TDDFT calculations were conducted using delocalized descriptions of the core-hole states. The MF-PAD for the delocalized core-hole state with $\sigma_g$ symmetry is shown by thin curve in figure 4, where the photoelectron is ejected coherently from both left and right Ne atoms, and those with $\sigma_u$ are also shown by thin curve. The superposition of the MF-PAD for $\sigma_g$ and $\sigma_u$ components is also shown with thin curve which is identical to the superposition of the MF-PAD for the localized core-holes on the left and right Ne atoms. The photoemission for the Ne$^+$ + Ne$^+$ channel depends only on the polarization vector. It is different from the calculated MF-PAD, but it is almost identical to the photoemission from randomly oriented dimers, although it is not shown here. This implies that the dissociation direction of two Ne$^+$ ions has no correlation with the dimer axis at the instant of the Ne 1s photoionization. Thus, the photoelectron angular distribution shown in figure 4 demonstrates an intriguing new phenomenon on the relaxation of the core-hole; the Ne$^+$ + Ne$^{2+}$ channel retains the memory of both the molecular orientation and the initial core-hole localization, while both are lost in the Ne$^+$ + Ne$^+$ channel.

The photoemission for the symmetric charge separation channel of Ne$^+$ + Ne$^+$ ought to be inversion symmetric, because the detection of such ions cannot distinguish the Ne atoms with their charge states. In fact, the experimental angular distribution is inversion symmetric. The present Ne 1s photoemission does not depend on the dimer axis at all, which results in a laboratory-frame photoelectron angular distribution (LF-PAD). In the two-step model, as shown in figure 5, a possible second step of fragmentation pathway to Ne$^+$ + Ne$^+$ from the Auger final [Ne + Ne$^{2+}$ (D: 2p$^2$)] state is a radiative decay, because the Auger final state is energetically lower than the triply ionized state and cannot give off its excess energy by electron emission. During a lifetime (~ns) of the radiative decay leading to the symmetric charge separation, the dicaticionic dimer can rotate many times with a period of ~100 ps. Therefore, the memory of the molecular axis at the instant of photoionization is perfectly lost in the Ne 1s photoemission. As a consequence, the observed coincident photoemission is not “MF-PAD” but “LF-PAD”. Actually, the observed PAD is well explained by the theoretical LF-PAD. That is, the
experimental $\beta$ values determined from the PAD are $1.72 \pm 0.02$ and $1.85 \pm 0.03$ for the parallel and perpendicular geometry, respectively, and the theoretical $\beta$ is 1.878, which is also in good agreement with the experimental $\beta$ values, $1.85 \pm 0.03$ determined from the LF-PAD. This good agreement certainly supports the idea that the coincident PAD for the Ne$^+ +$ Ne$^+$ channel is reduced to the LF-PAD.

**Figure 4.** Polar plot of the Ne 1$s$ LF-PAD from Ne$_2$ in coincidence with Ne$^+ +$ Ne$^+$ fragments at 10eV electron energy. The polarization vector (double headed arrow) and dissociation direction of the ion pair are indicated.

**Figure 5.** Calculated potential curves of Ne$_2$ dimer. Only the Auger final state, which can decay into the doubly ionized states via radiative decay, is drawn. The final state has the minimum at $R = 2.2$ Å.

3.2. O 1$s$ photoemission from a single oriented H$_2$O molecule

Figure 6 shows a vector correlation image of three particles, O$^+$, H$^+$, and H$^+$, produced by three-body break-up of H$_2$O$^{3+}$ following double Auger decay after O 1$s$ photoemission. The H$^+$ ion is emitted in a narrow angular range with respect to the O$^+$ ion and the momentum distributions of two H$^+$ ions are mirror symmetric to each other. It is also shown that the correlation angle between two H$^+$ momenta is slightly larger than the ground state bond angle ($\angle$HOH = 104.5$^\circ$) because of the Coulomb repulsive force. These results verify that the Coulomb explosion leading to three-body break-up of H$_2$O$^{3+}$ is immediate, maintaining the ground state shape of H$_2$O. Then, from the momentum vectors of the three fragment ions, the molecular orientation and intrinsic shape of H$_2$O in space at the instance of the O 1$s$ photoionization can be determined.

**Figure 6.** Momentum vector correlation among the three ions of O$^+$, H$^+$ and H$^+$ created in O 1$s$ photoionization of H$_2$O.

**Figure 7.** 3D angular distribution of O 1$s$ photoelectrons from fixed-in-space H$_2$O. Fitted curves to the experimental data were used.
By extending this approach to the quadruple coincidence of photoelectron–O–H–H, we have performed O 1s photoemission measurements from H2O molecules fixed in space. The key result is shown in figure 7, which depicts a 3D mapping of MF-PAD produced by incident light polarized along the molecular z-axis, at the photoelectron energy of 14 eV. The distance from the origin to the surface corresponds to the probability of finding the photoelectrons emitted into the direction of \((\theta, \phi)\), where \(\theta\) is the polar angle measured from the \(C_2\) axis, and \(\phi\) is the azimuthal angle from the x-axis. The orientation of the MF-PAD can occur only through the interference of partial waves between odd- and even- \(\ell\) [21–23]. This quantum interference effect results in the up-down asymmetry of the MF-PAD shown in figure 7, which is considerably deformed from the dipole shape of an atomic 1s \(\rightarrow kp\) transition. The photoionization dynamics seen in the MF-PAD is restricted by the symmetry of the photoelectron wavefunction as predicted by theories. Indeed, the \(a_1\) symmetry (twofold symmetry about the \(C_2\) axis) of the wavefunction created by the z-axis polarized photon is embodied in the 3-D MF-PAD.

Here, we apply a simple photoelectron diffraction model involving only a single scattering based on Huygens’ approach, to get an intuitive understanding of the MF-PAD. From Huygens’ point of view, the O atom acts as an emitter of primary waves which are subsequently scattered against the two H atoms. In constructing the total wavefield as a coherent sum of the primary and secondary contributions we neglect the multiple scattering of the electron waves. The scattering scheme of the electron wave is depicted in figure 8. The MF-PAD can be expressed by superposing the primary wave and two scattered waves [24, 25]. In the simulation of the MF-PAD we used the ground state geometry of H2O molecule, and introduced two parameters; the modulus and phase shift for the complex amplitude of e + H scattering. The fitting result of the simulation is shown in figure 9. As can be seen in the figure, the contribution of the two scattered waves from the H atoms, Young’s double-slit interference, is negligible, but the contribution of the primary and scattered waves shows a considerable interference effect between them; strong negative values on the O atom side and weak on the opposite side. Due to the interference, the strong orientation of the MF-PAD is well explained.

![Figure 8](image1.png)

**Figure 8.** Scattering scheme of the electron wave. The origin of the position is set at the O atom. The positions of the two H atoms are indicated by \(r_1\) and \(r_2\).

![Figure 9](image2.png)

**Figure 9.** The experimental data on x-z plane in figure 7 and fitting result. The dipole shape is the primary wave contribution, the dotted curve is the interference between the primary and scattered waves, and tiny two loops along the z-axis are the double-slit interference. Solid lines are positive and dotted line negative.

4. **Summary**
We have demonstrated two new directions on photoemission dynamics in the molecular frame, based on the multi-coincidence velocity-map imaging measurement. One direction is the time scale discussion of core-hole decay owing to the high sensitivity of MF-PAD to the molecular symmetry. The other direction is the extension of MF-PAD to the non-axially symmetric molecule. The present
results enable one to compare the full 3D MF-PAD from a single oriented molecule with photoelectron diffraction patterns from the relevant adsorbed molecules on surface. It is quite interesting, because it might make the interaction between molecule and surface clear. Even more importantly, the successful application of the simple scattering model to the MF-PAD suggests that a new field of ultrafast molecular structure determination due to MF-PAD measurements will be opened, if possible to control its orientation in space, using a future x-ray laser.

Acknowledgements

The experiments have been performed under the approval of the Photon Factory Program Advisory Committee (Project No. 2005G099, 2005G108, 2007G056 and 2007G550). The present work was supported by a Grant-in-Aid for Scientific Research (B) 19340114. M. Y. is grateful for the support of the Japan Society for the Promotion of Science.

References

[1] Golovin A V, Cherepkov N A and Kuznetsov V V 1992 Z. Phys. D 24 371
[2] Shigemasa E, Adachi J, Oura M and Yagishita A 1995 Phys. Rev. Lett. 74 259
[3] Geßner O, Hikosaka Y, Zimmermann B, Hempelmann A, Lucchese R R, Eland J H D, Guyon P-M and Becker U 2002 Phys. Rev. Lett. 88 193002
[4] Yagishita A, Hosaka K and Adachi J 2005 J. Electron Spectrosc. Relat. Phenom. 142 295
[5] Weber T et al. 2004 Nature 431 437
[6] Rolles D et al. 2005 Nature 437 711
[7] Lebech M, Houyer J C, Dowek D and Lucchese R R 2006 Phys. Rev. Lett. 96 073001
[8] Adachi J, Hosaka K, Teramoto T, Yamazaki M, Watanabe N, Takahashi M and Yagishita A 2007 J. Phys. B: At. Mol. Opt. Phys. 40 F285
[9] Yamazaki M, Adachi J, Kimura Y, Yagishita A, Stener M, Decleva P, Kosugi N, Iwayama H, Nagaya K and Yao M 2008 Phys. Rev. Lett. 101 043004
[10] Yamazaki M, Adachi J, Teramoto T, Yagishita A, Stener M and Decleva P 2009 J. Phys. B: At. Mol. Opt. Phys. 42 051001
[11] Eppink A T J B and Parker D H 1997 Rev. Sci. Instrum. 68 3477
[12] Lebech M, Houyer J C and Dowek D 2002 Rev. Sci. Intrum. 73 1866
[13] Hosaka K, Adachi J, Golovin A V, Takahashi M, Watanabe N and Yagishita A 2006 Japan. J. Appl. Phys. 45 1841
[14] Watanabe M, Toyoshima A, Azuma Y, Hayashi T, Yan Y and Yagishita A 1997 Proc. SPIE Int. Soc. Opt. Eng. 3150 58
[15] Santra R and Cederbaum L S 2003 Phys. Rev. Lett. 90 153401
[16] Cederbaum L S, Zobeley J and Tarantelli F 1997 Phys. Rev. Lett. 79 4778
[17] Jahnke T et al 2004 Phys. Rev. Lett. 93 163401
[18] Öhrwall G et al 2004 Phys. Rev. Lett. 93 173401
[19] Morishita Y et al 2006 Phys. Rev. Lett. 96 243402
[20] Jahnke T et al 2007 Phys. Rev. Lett. 99 153401
[21] Chandra N 1987 J. Phys. B 20 3417
[22] Reid K L and Powis I 1994 J. Chem. Phys. 100 1066
[23] Kuznetsov V V, Cherepkov N A, Fecher G H, Schönhense G 2002 J. Chem. Phys. 117 7180
[24] Fadley C S 1993 Surf. Sci. Rep. 19 231
[25] Woodruff D P and Bradshaw A M 1994 Rep. Prog. Phys. 57 1029