Multicoincidence Measurements of Molecular-frame Photoelectron Angular Distributions For Core-Level Photoemission From Small Molecules

Kiyoshi Ueda
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
E-mail: ueda@tagen.tohoku.ac.jp

Abstract. Methodology of our molecular-frame photoelectron angular distribution (MFPAD) measurement including our projection method for the analysis of the data is described together with the results for C 1s photoemission from CO$_2$, focusing on the photoelectron satellite, aiming to illustrate current status of our MFPAD studies.

1. Introduction
Molecular core-level photoemission is one of the simplest reactions, yet it has been receiving continuous and remarkable attention as it provides a wealth of information about the target molecule. From a theoretical point of view, the most natural choice of the frame for the description of photoemission may be the molecular frame. One established experimental approach to the measurements of molecular frame photoelectron angular distributions (MFPADs) is to make angle-resolved photoelectron-photoion coincidence [1, 2]. A remarkable breakthrough of this coincidence technique has been brought by the use of position sensitive detectors [3]. To date, the MFPAD measurements have been carried out for core-level photoemission from many different molecules, such as, e.g., N$_2$ [2, 4], CO [5, 6], NO [7, 8], Ne$_2$ [9, 10], CO$_2$ [11, 12, 13], C$_2$H$_2$ [14], CF$_4$ [15], etc. In the present report, we first describe methodology of our MFPADs measurement. The experimental approach is similar to many other groups, often called cold-target recoil momentum spectroscopy or reaction microscope [16], while our projection method for the analysis of the data is unique. Then, we describe results for C 1s photoemission from CO$_2$, especially focusing on the photoelectron satellite, in order to illustrate current status of our MFPAD studies.

2. Methodology
2.1. Experiment
All the experiments described in this article have been performed on the c branch of the soft X-ray photochemistry beam line 27SU [17, 18, 19] at SPring-8. This beam line has a figure-8 undulator as a radiation source and provides linearly polarized light with the polarization axis in the horizontal or vertical direction [20, 21]. The photon beam was focused on a spot of size less than 0.2 mm in height and 0.5 mm in width at the intersection with the molecular beam. The present electron-ion multiple coincidence momentum imaging technique is based on recording the
time-of-flight (TOF) of both electrons and ions by multi-hit two-dimensional position sensitive detectors [11, 12, 22]. The electron and ion TOF spectrometers are placed face to face. Their axes are horizontal and perpendicular to both the photon beam and the molecular beam. Both the electron and ion spectrometers are equipped with a hexagonal multi-hit position-sensitive delay-line detectors (Roentdek). All fragment ions ejected in all directions of $4\pi$ sr are lead to the ion detector by the uniform elecric DC field, whereas the additional uniform magnetic field imposed by a set of Helmholtz coils outside the vacuum chamber helps the photoelectrons ejected in all directions of $4\pi$ sr to be guided to the electron detector. The TOFs of the electrons and ions were recorded with respect to the bunch marker of the synchrotron radiation source using multi-hit time-to-digital converters (TDCs). Knowledge of position and arrival time on the particle detectors, $(x, y, t)$, allows us to extract information about the linear momentum $(p_x, p_y, p_z)$ for each particle.

2.2. Projection method

Linearly polarized light may be fully characterized by a single vector, e.g. the electric vector $\vec{E}$, as shown in Fig. 1. Thus, for linear molecules, the MFPAADs will depend on three angles, $\theta$ and $\phi$, which give the direction of emission of the photoelectron in the molecular frame, and $\theta_n$, which is the polar angle describing the orientation of the molecular axis with respect to the direction of polarization. Note that for arbitrary molecular systems an additional azimuthal angle would have been employed to describe the orientation of the $E$ axis in the molecular frame. However, for linear systems, the value of such azimuthal angle becomes arbitrary and we will set it to zero by locating the $X$ axis in the plane defined by the $Z$ and $E$ axes as indicated in Fig. 1.

In the case of linearly polarized light, the MFPAAD may be written as [23, 24]

$$I(\theta, \phi, \theta_n) = F_{00}(\theta) + F_{20}(\theta)P_2^0(\cos \theta_n) + F_{21}(\theta)P_2^1(\cos \theta_n) \cos \phi + F_{22}(\theta)P_2^2(\cos \theta_n) \cos 2\phi. \quad (1)$$

The $F_{JN}$ functions can be expanded in Legendre polynomials as

$$F_{JN}(\theta) = \sum_{J'} C_{J'JN} P_{J'}^N(\cos \theta), \quad (2)$$
where the $C_{J'JN}$ expansion coefficients may be written as

$$C_{J'JN} = \frac{1}{2\pi (1 + \delta_{N,0})} \left[ \frac{(2J' + 1)(2J + 1)(J' - N)! (J - N)!}{(J' + N)! (J + N)!} \right]^{\frac{1}{2}} H_{J'JN},$$

in terms of the $H_{J'JN}$ coefficients given by

$$H_{J'JN} = \frac{4\pi^2 E}{c} \sum_{l,m\mu} \sum_{l',m'\mu'} (-1)^{m+m'} \left[ \frac{(2I + 1)(2I' + 1)}{(2J + 1)(2J' + 1)} \right]^{\frac{1}{2}} I_{lm\mu} I_{l'm'\mu'}^*$$

$$\times \langle l'00|J'0\rangle \langle l',-m,m'|J'N\rangle$$

$$\times \langle 1100|0\rangle \langle 1,1,\mu,-\mu'|J,N\rangle,$$  \hspace{1cm} (4)

where $E$ is the photon energy, $c$ is the speed of light, and $\langle l, l', m, m'|J'N\rangle$ is a Clebsch-Gordan coefficient. In this way, all possible experimental information is encapsulated in the four $F_{JN}(\theta)$ functions.

There are a number of possible approaches for obtaining the $F_{JN}$ functions from angle resolved photoelectron-photoion coincidence measurements. See Refs. [23, 24] for pioneering work. In our case, we use projection methods [25, 26]. The projection methods rely on the fact that the expansions in Eq. (1) is in terms of orthogonal polynomials of $\theta_n$ and $\phi$. For simplicity, we assume here that the full $4\pi$ angular distributions of both photoelectron and ion recoil directions have been measured. The generalization to the case where the angles of the electron detections are limited is described in detail elsewhere [26, 27]. Then, the $F_{JN}(\theta)$ can be obtained as

$$F_{JN}(\theta) = \frac{(2J + 1)(J - N)!}{2\pi (1 + \delta_{N,0}) (J + N)!}$$

$$\times \int_0^\pi \sin \theta_n d\theta_n \int_0^{2\pi} d\phi I(\theta, \phi, \theta_n) P_{JN}^N(\cos \theta_n) \cos(N\phi).$$  \hspace{1cm} (5)

We can extract four one-dimensional $F_{JN}(\theta)$ functions from all the coincidence events using Eq. (5) and reconstruct MFPADs at each energy for any angle between the molecular axis and the $E$ vector using Eq. (1).

3. Results and discussion

3.1. C 1s MFPADs of CO$_2$

There are many different ways to present the experimental MFPADs and to compare them with the theoretical predictions. In Fig. 2, we present the MFPADs of C 1s photoemission from CO$_2$ at four photon energies, reconstructed from the four $F_{JN}(\theta)$ functions, by selecting the reaction geometry such that the electron is emitted in the plane defined by the molecular axis and the $E$ vector. Here, the angle $\theta_n$ between the $E$ vector and molecular axis is shown along the horizontal axis and the electron emission polar angle $\theta$ relative to the molecular axis is shown along the vertical axis. The shape resonance is located at 312 eV, where the electron emission is mostly at $\theta_n \sim 0^\circ$ ($\Sigma \rightarrow \Sigma$) and along the molecular axis ($\theta \sim 0^\circ$).

Figure 2 includes also photoelectron angular distributions calculated within a relaxed-core Hartree-Fock (RCHF) approximation using a molecular basis set obtained with Slater’s transition state approximation [11]. At first glance, the agreement between experiment and theory is very reasonable. However, a careful inspection reveals that, though calculated MFPADs are seen to always exhibit symmetry relative to the center because of the assumed $D_{\infty h}$ molecular symmetry, the measured MFPADs do not show this complete point symmetry at 312 eV.
Figure 2. Experimental and theoretical 2D plots of C 1s MFPADs of CO$_2$ at photon energies 303.8, 307, 312.2, 320.9, and 329.8 eV. The x axis denotes the angle $\theta_n$ between the $E$ vector and molecular axis, and the y axis the electron emission polar angle $\theta$ relative to the molecular axis. $\theta = 0^\circ$ and $180^\circ$ are the directions of O$^+$ and CO$^+$, respectively. The electron emission intensity is plotted on a color scale. These distributions have not been directly measured, but reconstructed from a parametrization of all available MFPADs for various molecular orientations. From [28]. See text for details.
In this MFPAD experiment, the molecular axis is defined by the two-body dissociation into O\(^+\) and CO\(^+\): \(\theta = 0^\circ\) corresponds to the direction of O\(^+\). Thus the observed asymmetry illustrates that the measured MFPADs are influenced by the by the detection of the asymmetric dissociation. If one could completely align the molecule in space and measure the angular distributions, one would not see such asymmetry. Thus the observed asymmetry indicates that the measured MFPADs cannot be interpreted without taking account of the subsequent Auger decay and fragmentation and in this sense the breakdown of the two-step model in which core-level photoemission and subsequent decay is considered to be independent and disentangled. Further detailed discussion is seen elsewhere [28].

3.2. MFPADs for C 1s satellite of CO\(_2\)

The measurements of MFPADs has so far been performed exclusively on the intense photoelectron mainlines. Here, we describe the MFPAD measurement for the C 1s satellite of CO\(_2\). The appearance of satellites in photoelectron spectra is a signature of two-electron transitions accompanying a single photon ionization and thus provides us with the information about electron correlations in molecules.

The satellites can be classified phenomenologically into two groups [29, 30, 31, 32, 33]. The first group includes satellites whose excitation cross sections relative to the single-hole ionization cross section stay relatively constant (the “normal” satellites), while the second group includes those satellites whose relative excitation cross sections sharply decrease with increasing photon energy (the “conjugate” satellites). The different energy dependence for the normal and conjugate satellites stems from the fact that the final ionic states of the normal satellites have the same global quantum numbers as the mainline single-hole state, while those of conjugate satellites are different. For the K-shell photoionization of closed shell molecules with which we are concerned here, the angular momentum of the absorbed photon is carried away by the ejected electron both for the mainline and the normal satellites and is retained by the remaining ion for the conjugate satellites.

An alternative perspective is provided by a classification of correlation satellites based on the different lowest order diagrams of the many-body perturbation theory (MBPT) [34]. One of the two relevant contributions is termed “shake-up”, while the other is termed “internal inelastic scattering” [34]. The shake-up mechanism predominantly causes monopole excitation/ionization. Replacement of the two-electron integral for the shake-up (in MBPT) by
the overlap integral is known as the “shake-up model” [30, 31, 34]. In the internal inelastic scattering mechanism, on the other hand, multipole excitation becomes probable. Similarly to the shake-up mechanism, both normal and conjugate satellites may be excited by internal inelastic scattering. Thus, we have in total four different groups of correlation satellites, normal and conjugate satellites excited by shake-up and normal and conjugate satellites excited by internal inelastic scattering. Here, we aim to elucidate the mechanism of the satellite excitation based on the MFPAD measurement. We show that the observed satellite is an example of a conjugate satellite excited by internal inelastic scattering.

A left panel of Fig. 3 shows an electron spectrum recorded at a photon energy of 311.8 eV, i.e., ~14.2 eV above the C 1s threshold at 297.63 eV. Besides the mainline, we can see the satellite at a binding energy of ~11.5 eV relative to the mainline. A right panel of Fig. 3 depicts MFPADs of the unresolved satellite band. It is clear that the satellite photoemission is enhanced when the molecule is aligned along the E vector, revealing the predominance of the \( \Sigma_g \rightarrow \Sigma_u \) parallel transition, as in the case of the mainline at 311.8 eV (see Fig. 2). Thus, the global quantum number of the continuum state that consists of the ion and the photoelectron is \( \Sigma_u \). If it were a normal satellite, then the global quantum number of the ion state would be \( 2\Sigma_g^+ \) because the mainline (single-hole) state is \( 2\sigma_g^{-1} 2\Sigma_g^+ \). Then, the detected electron would be \( \sigma_u \), giving a node at \( \theta = 90^\circ \) in the MFPAD, as for the mainline (see Fig. 2). However, the MFPAD for the satellite clearly shows maximum intensity at \( \theta = 90^\circ \) (see Fig. 3). Thus the observed satellite is predominantly a conjugate satellite, as Schmidbauer et al. suggested for the S4 band [35]. The electron emission parallel to the molecular axis seen in Fig. 3 may reflect the contribution from the normal satellite S1.

For the conjugate satellite excited by shake-up (within the shake model), the dipole excitation of the core electron to an unoccupied molecular orbital (bound-bound dipole integral) is accompanied by the monopole ionization of the valence electron (bound-free overlap integral). If the observed C 1s (2\( \sigma_g \)) satellite is caused by this conjugate shake-up term, the 2\( \sigma_g \) electron is promoted to the LUMO 2\( \pi_u^* \) via dipole excitation (since this transition moment is by far larger than any other), and one valence electron is shaken off via the monopole transition. In this case, the photoexcitation is a \( \Sigma_g \rightarrow \Pi_u \) perpendicular transition. However, as already noted, the satellite excitation is enhanced by the \( \Sigma_g \rightarrow \Sigma_u \) parallel transition. Thus the observed conjugate satellite is not excited by shake-up.

Let us now examine whether the observed satellite is consistent with the prediction for internal inelastic scattering. In this scenario, the photoelectron interacts with the valence electron and exchanges momentum. A plausible assignment of the satellite state is \( 2\sigma_g^{-1} 1\pi_g^{-1} 2\pi_u^* \). Adding a \( \sigma_g \) photoelectron to this ion, it is possible to construct a \( \Sigma_u \) continuum state. The observed MFPAD shown in Fig. 3 agrees with the \( \sigma_g \) symmetry. Also, internal inelastic scattering between the photoelectron and the valence electron in a \( \pi_g \) HOMO with O 2\( \pi \) lone-pair character is expected to be enhanced when the initial photoelectron current ejected from the central C is towards the O atom, i.e., for the \( \Sigma_g \rightarrow \Sigma_u \) parallel transition. Thus, all of our observations, i.e., that the satellite emission intensity is highest for a parallel transition and that the satellite MFPAD is peaked perpendicular to the molecular axis, strongly support classification as a conjugate satellite excited by internal inelastic scattering, with the assignment of the remaining ion \( 2\sigma_g^{-1} 1\pi_g^{-1} 2\pi_u^* \). Further detailed discussion is seen elsewhere [36].

Acknowledgments
The work has been carried out in fruitful collaborations with X.-J. Liu, G. Prümper, H. Fukuzawa, T. Teranishi, M. Takahashi, N. Saito, Y. Morishita, H. Yoshida, I. Koyano, A. De F anis, A. Cassimi, A. Czasch, L. Schmidt, R. Dörner, R.R. Lucchese, R. Montuoro, A.N. Grum-Grzhimalo, K. Wang, B. Zimmermann, and V. Mckoy, with the approval of JASRI, and supported by JSPS.
References

[1] A.V. Golovin, N.A. Cherepkov, and V. Kuznetsov, Z. Phys. D 24, 371 (1992).
[2] E. Shigemasa, J. Adachi, M. Oura, and A. Yagishita, Phys. Rev. Lett. 74, 359 (1995).
[3] K. Ueda, J. Electr. Spectrosc. Relat. Phenom. 141, 73 (2004); and papers in this special issue.
[4] M. Schöfler et al., Science 320, 892 (2008).
[5] F. Heiser, O. Gessner, J. Viehhaus, K. Wieliczek, R. Hentges, U. Becker, Phys. Rev. Lett. 79, 2435 (1997).
[6] A. Landers et al., Phys. Rev. Lett. 87, 13002 (2001).
[7] W.B. Li R. Montuoro, J. C. Houver, L. Journel, A. Haouas, M. Simon, R.R. Lucchese, and D. Dowek, Phys. Rev. A 75, 052718 (2007).
[8] H. Fukuzawa et al., J. Phys. B: At. Mol. Opt. Phys. 41, 045102 (2008).
[9] K. Kreidt et al., J. Phys. B: At. Mol. Opt. Phys. 41, 101002 (2008).
[10] M. Yamazaki, J. Adachi, Y. Kimura, A. Yagishita, M. Stener, P. Decleva, N. Kosugi, H. Iwayama, K. Nagaya, and M. Yao, Phys. Rev. Lett. 101, 043004 (2008).
[11] N. Saito, et al., J. Phys. B: At. Mol. Opt. Phys. 36, L25 (2003).
[12] N. Saito, K. Ueda, A. De Fanis, K. Kubozuka, M. Machida, I. Koyano, R. Dörner, A. Czasch, L. Schmidt, A. Cassimi, K. Wang, B. Zimmermann, and V. McKoy, J. Phys. B: At. Mol. Opt. Phys. 38, L277 (2005).
[13] T. Teramoto, J. Adachi, K. Hosaka, M. Yamazaki, K. Yamanouchi, N.A. Cherepkov, M. Stener, P. Decleva, and A. Yagishita, J. Phys. B: At. Mol. Opt. Phys. 40, F241 (2007).
[14] J. Adachi, K. Hosaka, T. Teramoto et al., J. Phys. B: At. Mol. Opt. Phys. 40, F285 (2007).
[15] H. Fukuzawa, X.-J. Liu, T. Teranishi, K. Sakai, G. Prümper, K. Ueda, Y. Morishita, N. Saito, M. Stener and P. Decleva, Chem. Phys. Lett. 451, 845 (2008).
[16] J. Ullrich, R. Moshammer, A. Dorn, R. Dörner, L. Ph. H. Schmidt, and H. Schmidt-Böcking, Rep. Prog. Phys. 66, 1463 (2003).
[17] H. Ohashi, E. Ishiguro, Y. Tameneri, H. Kishimoto, M. Tanaka, M. Irie, T. Tanaka, T. Ishikawa, Nucl. Instrum. Methods A 467-468, 529 (2001).
[18] H. Ohashi, et al., Nucl. Instrum. Methods A 467-468, 533 (2001).
[19] K. Ueda, J. Phys. B: At. Mol. Opt. Phys. 36, R1 (2003).
[20] T. Tanaka and H. Kitamura, Nucl. Instrum. Methods A 364, 368 (1995).
[21] T. Tanaka and H. Kitamura, J. Synchrotron Radiation 3, 47 (1996).
[22] K. Ueda and J.H.D. Eland J. Phys. B: At. Mol. Opt. Phys. 38, S839 (Einstein Special issue) (2005).
[23] R.R. Lucchese, A. Lafosse, J.C. Brenot, P.M. Guyon, J.C. Houver, M. Lebech, G. Raseev and D. Dowek. Phys. Rev. A 65, 020702 (2002).
[24] D. Dowek In: Many-Particle Quantum Dynamics in Atomic and Molecular Fragmentation, J. Ullrich, V.P. Shevelko (eds.) (Springer, Berlin-Heidelberg 2003) p. 261-282.
[25] R.R. Lucchese, R. Montuoro, A.N. Grum-Grzhimailo, X.-J. Liu, G. Prümper, Y. Morishita, N. Saito, K. Ueda, J. Electron Spectrosc. Relat. Phenom. 155, 95 (2007).
[26] X.-J. Liu, R.R. Lucchese, A.N. Grum-Grzhimailo, Y. Morishita, N. Saito, G. Prümper, and K. Ueda, J. Phys. B: At. Mol. Opt. Phys. 40, 485 (2007).
[27] G. Prümper, D. Rolles, H. Fukuzawa, X.-J. Liu, Z. Pesic, I. Dumitriiu, R.R. Lucchese, K. Ueda and N. Berrah J. Phys. B: At. Mol. Opt. Phys. 41 (in press).
[28] X.-J. Liu, H. Fukuzawa, T. Teranishi, A. De Fanis, M. Takahashi, H. Yoshida, A. Cassimi, A. Czasch, L. Schmidt, R. Dörner, I. Koyano, N. Saito, and K. Ueda, Phys. Rev. Lett. 101, 109901 (2008).
[29] U. Becker and D.A. Schirley, Phys. Scrip. T31, 56 (1990).
[30] L. Ungier and T.D. Thomas, Phys. Rev. Lett. 53, 435 (1984).
[31] J. Schirmer, M. Braunstein, and V. McKoy, Phys. Rev. A 44, 5762 (1991).
[32] K. Ueda, M. Hoshino, T. Tanaka, M. Kitajima, H. Tanaka, A. De Fanis, Y. Tameneri, M. Ehara, F. Oyagi, K. Kuramoto, and H. Nakatsuiji. Phys. Rev. Lett. 94, 243004 (2005).
[33] M. Ehara, H. Nakatsuiji, M. Matsumoto, T. Hatamoto, X.-J. Liu, T. Lischke, G. Prümper, T. Tanaka, C. Makochekanwa, M. Hoshino, H. Tanaka, J. R. Harries, Y. Tameneri, and K. Ueda, J. Chem. Phys. 124, 124311 (2006).
[34] V. Schmidt, Rep. Prog. Phys. 55, 1483 (1992).
[35] M. Schmidbauer, A.L.D. Kilcoyne, H.M. Köppe, J. Feldhaus, and A.M. Bradshaw, Phys. Rev. A 52, 2095 (1995).
[36] X.-J. Liu, H. Fukuzawa, T. Teranishi, A. De Fanis, M. Takahashi, H. Yoshida, A. Cassimi, A. Czasch, L. Schmidt, R. Dörner, K. Wang, B. Zimmermann, V. McKoy, I. Koyano, N. Saito, and K. Ueda, Phys. Rev. Lett. 101, 023001 (2008).