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A High-Efficiency Electron Momentum Spectrometer for Direct Imaging of Orbital Electron Density *

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Direct three-dimensional images for orbital electron density are obtained by using our newly developed electron momentum spectrometer with simultaneous detection in energy and momentum, and the instruments resolutions of $\Delta\theta = \pm 0.7^\circ$, $\Delta\phi = \pm 1.9^\circ$, $\Delta E = 1.2\,eV$, and $\Delta T = 2.0\,ns$. The detection efficiency is about 100 times higher than conventional spectrometers. The design and performance of the apparatus are reported together with the experimental results on argon to show the extensive improvements in experimental resolutions, detection efficiency and versatility.

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In atoms, molecules, and solids, clouds of negative charge that determine the relative positions of the nuclei can be understood in terms of the motion of the electrons which form the clouds. A detailed knowledge of electron density distribution and electron motion is necessary to improve the understanding of molecular recognition and chemical reactivity. Usually one can describe a charge cloud as a density distribution in coordinate space, and can also equally well describe it as a velocity distribution, in momentum space, because a momentum space wavefunction is uniquely related to the corresponding position space wavefunction by Fourier transformation. The probability picture of electrons with certain energy–momentum combination can be measured by electron momentum spectroscopy (EMS).[1−4] EMS, also known as a binary $(e, 2e)$ spectroscopy, has been developed to be a powerful tool for the investigation of orbital electron density distributions and for the understanding and evaluation of electron wavefunctions in atoms and molecules. The experimental results of EMS provide the most direct experimental measurements of orbitals and bonding in matter,[4] which can contribute to understandings of the electronic structure, electron correlation effects and spectroscopic factor or pole strengths. Furthermore, it is noteworthy from a chemical standpoint that EMS provides very direct information on the binding energies, the behaviour (motion) of electrons and the electron density in the chemically reactive individual outer-valence orbitals and molecular recognition.[5]

However, most EMS studies have been limited to relatively small, stable molecules, while for large molecules and chemical interesting low density targets such as free radicals, ions and van der Waals molecules, conventional EMS instruments are ineffective because of the very low efficiency in detection. The limitation is caused by the fact that EMS is a coincidence counting experiment and that a very large proportion of the available signal is squandered due to finite ranges in the angular and energy detection. As a result of the limitation, many new types of experiments are unfeasible within a practical length of time with existing spectrometers, and their achievement will require major improvement in the detection efficiency of EMS. For the high performance EMS spectrometer to be achieved, a number of experimental challenges must be faced. These include: (i) the large region of detection simultaneously in energy and momentum of electrons, (ii) the low azimuthal angle ϕ resolution due to the fact that the toroidal analyser has focusing power only for the polar angle θ, (iii) the problem of the improvements of energy and angle (ϕ and θ) resolution following the loss of the coincidence count rate. Many types of EMS spectrometer have been made to date.[3,6−12] However, simultaneous high detection efficiency and high resolutions are eagerly needed in the development of the new EMS spectrometer.

Here we present a high detection efficiency and high resolution electron momentum spectrometer with simultaneous detection in energy and momentum. A novel double toroidal analyser (DTA) and a pair of two-dimensional position sensitive detectors with a new multi-parameter data-acquisition system based on universal serial bus[13] are used in our EMS spectrometer. The detailed electron optic simulation and experimental measurements indicate that the new DTA analyser has the performance of simultaneous

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detection in energy and azimuthal angle ϕ, which is crucial for the achievement of high efficiency or high count rate. Moreover, a high energy and angle ϕ and θ) resolutions can also be simultaneously achieved by using the novel DTA electrostatic analyser equipped with a conical deceleration lens system. In addition, good performances of detectors, data-acquisition systems and associated electronics are also helpful for the achievements of high efficiency and high resolutions. The three-dimensional image of orbital electron density distribution of atom argon is reported with the unprecedented system performance due to improvements in energy and angle resolution, detection sensitivity, coincidence counting rate, and experimental stability. The energy and temporal resolution approaches 1.2 eV and 2 ns, respectively. The θ and ϕ angle resolution is $\pm 0.7^\circ$ and $\pm 1.9^\circ$, respectively. The image of the electron density distributions can be directly obtained.

The scheme of the newly developed EMS spectrometer is shown in Fig. 1. The EMS experiment is based on kinematical complete $(e, 2e)$ collision single ionization process, where an incident electron "knocks out" an electron from the target and is scattered itself. The suitable experiment configuration, used in the majority of conventional EMS measurements, is the symmetric noncoplanar geometry. In this geometry, cross sections are measured for scattering at equal energies ($E_1 \approx E_2$), into equal polar angles ($\theta_1 = \theta_2 = 45^\circ$) and with varying the relative azimuthal angle ϕ.

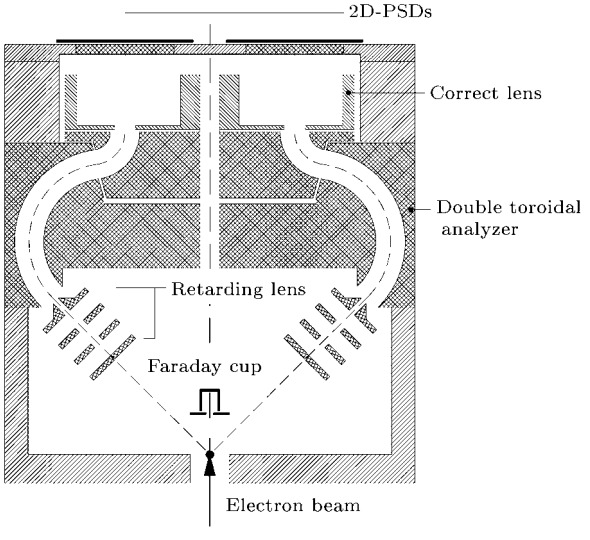

Fig. 1. The scale representation of the new EMS spectrometer which principally comprises an electron gun, an $(e, 2e)$ collision chamber, a molecular beam, an energy analyser system including the retarding lens, a pair of two-dimensional position sensitive detectors, and the corresponding electronics and a data-acquisition system.

Within the plane wave impulse and the target Hartree–Fock (HF) approximations, the EMS cross section (momentum distribution) is given by[1−3]

$$\sigma_{EMS} = \text{const} \times \int d\Omega |\Psi_i(\boldsymbol{p})|^2, \qquad (1)$$

where $\boldsymbol{p}$ is the momentum of the electron before ionization from the target, and $\Psi_i(\boldsymbol{p})$ is the momentum space-independent particle (orbital) wavefunction. The quantity $\int d\Omega$ gives the spherical average over the random orientations of the target molecules. In density functional theory (DFT), the target Kohn–Sham approximation[14] results in an expression similar to Eq. (1), while the electron correlation effect is accounted through the exchange-correlation potential. By using of these theories, EMS measurements have provided a powerful test of ab initio quantum chemical methods[1−4] and have been useful for the evaluation and design of very accurate wavefunctions.[1−3,15] With the significant improvement of count rate and the good performance of the energy and azimuthal angle resolution the image of electron density in atoms and molecules can be obtained directly and accurately within a proper experiment period. The application of EMS is extended to the fresh and comprehensive perspective of chemical interesting low density targets, the large biochemical molecules and cluster, the excited states of atoms and molecules, and chemical reaction or the other $(e, 2e)$ reaction with the low ionization cross section.

The energy and relative azimuthal angle (also momentum), in the form of the three-dimensional contour image of the argon orbital electron density distributions is shown in Fig. 2(a). Considering that the entire measurement period was only 3000 s, the remarkably high efficiency of the present spectrometer can be noticed. This contour image represents energy–momentum densities of argon valence electrons and contains a wealth of information of relative intensities, momentum distribution, symmetries of the various states involved, and satellite structure. From the intensity distribution along the abscissa axis, the binding energy spectrum is obtained as a function of angle, i.e. electron momentum. On the other hand, the orbital electron density distributions can be obtained along the vertical axis at a given binding energies region (represent individual orbital). A binding energy spectrum of argon has been obtained by summing up counts along the abscissa axis in the contour image, as shown in Fig. 2(b). This spectrum includes the $(3p)^{-1}$ and $(3s)^{-1}$ states, as well as the $(3s)^{-1}$ satellite states resulting from electron correlation effects. The negligibly small background contribution and good statistical precision confirm the accuracy of the spectrometer. The spectrum of both the $3p$ and $3s$ ionization states are well reproduced by the Gaussian curves with full width at half maximum (FWHM) of 1.2 eV.

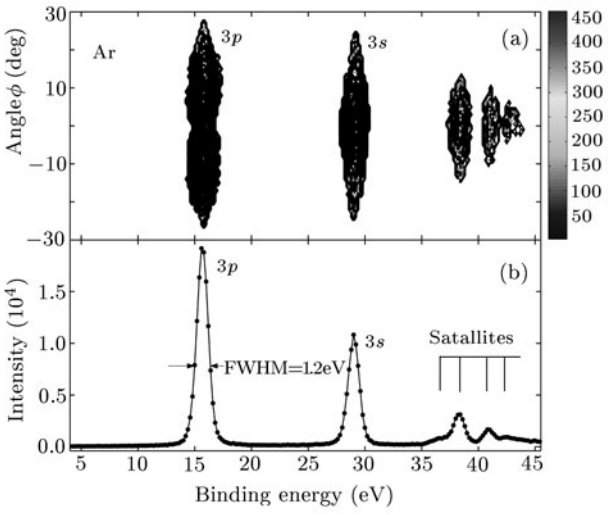

Fig. 2. Direct EMS images of argon obtained at the impact energy of 1000 eV with 100 eV pass energy in the analyser: (a) electron density contour images of argon $3p$, $3s$ and satellite states, (b) the binding energy spectrum of argon.

Figure 3 shows the experimental electron momentum profiles of argon $3p$ orbital with theoretical profiles by the HF and DFT. The experimental results are obtained by summing up intensities along the vertical axis in the contour image of Fig. 2(a) within the appropriate binding energy region of $3p$ states. The theoretical profiles were convoluted with the instrumental resolution ($\Delta\theta = \pm 0.7°$, $\Delta\phi = \pm 1.9$, $\Delta E = 1.2$ eV) according to the method reported in Ref. [16]. A significantly better statistical precision is evident in the electron momentum distributions in Fig. 3, as seen from the error bars. The comparison between the theoretical momentum profiles and the accurate experimental data indicates that the DFT calculations with the augmented correlation consistent polarized valence triple zeta (AUG-CC-PVTZ) basis set reproduce the experimental results better than other calculations. The experiment result is found to be in good agreement with the theory in the range of momentum smaller than ~ 1.7 a.u. for the argon $3p$ state. The discrepancies at higher momentum region are due to distortion effects,[1,17] where the plane wave impulse approximation (PWIA) regime is invalid. It is obvious that the new spectrometer is competent to carry out extensive investigation into distorted wave effect, for which most of the earlier EMS experiments are suffered from the low statistical precision.

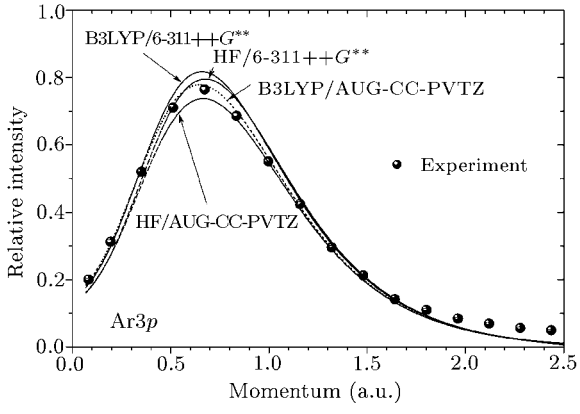

Fig. 3. Experimental and theoretical electron momentum profiles of argon $3p$ orbital. The broken and solid lines are the associated profiles by HF and DFT, respectively.

Furthermore, it would be interesting to compare some important performances with other EMS spectrometers. A brief comparison is described in Table 1. It can be seen from this comparison that high efficiency or count rate can be achieved with the simultaneous detection in both energy and momentum, which have been obtained by using the spectrometers with the spherical (90° sector)[11] and our double toroidal analysers. In comparison, the DTA performance has a better energy resolution than the spherical analyser. Although the energy resolution using the spherical analyser can be improved to 1.4 eV with the decelerating lens, its count rate will decrease about 4–5 times under this experimental condition.[11]

Table 1. Comparison of some different EMS spectrometers.

Year	Analyser	Performances		
		Energy resolution (eV)	Angle resolution (deg)	Count rate
1978[9]	Spherical analyser (90° sector)	1.4	Not mentioned	Low
2000[10]	Spherical analyser (90° sector)	2.2	$\Delta\theta = \pm 0.7$, $\Delta\phi = \pm 2.0$	Moderate
2002[11]	Spherical analyser (90° sector)	2.5	$\Delta\theta = \pm 0.75$, $\Delta\phi = \pm 2.2$	High
This work	Double toroidal analyser	1.2	$\Delta\theta = \pm 0.7$, $\Delta\phi = \pm 1.9$	High

Electron momentum spectroscopy now allows the direct and accurate image of electron density distribution in atoms and molecules with the high efficiency and high resolution spectrometer. The significant improvement in the coincidence count rate wins the ascendancy in the experimental periods. Typically, to obtain orbital electron density distributions with enough statistics for one sample, the experimental period of time with the conventional EMS is about 2–3 weeks (day and night), however only 2–3 h are needed by using the new spectrometer. The simultaneous achieved high resolutions in energy, momentum and coincidence rate allow us to extend the EMS studies to more complex systems. Moreover, the high quality data at the different incident electron impact energies 400 to 2400 eV can be obtained by the present

spectrometer, which establishes the versatility of EMS studies. With this spectrometer, many new and valuable experiments, such as the EMS studies in the large biochemical molecules, cluster, self-ionization and excitation state, the dilute target systems, and systematically investigating of distorted wave effects, are feasible within a practical length of time. Furthermore, the novel experimental technique in this new apparatus, especially the high performance DTA analyser, could also be utilized to the other correlated experiments, such as the double ionization, photon excitation and ionization.

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