Development of time-resolved electron momentum spectroscopy: toward real-time imaging of frontier electrons in molecular reactions

M. Yamazaki and M. Takahashi*

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

*Corresponding author: masahiko@tagen.tohoku.ac.jp (M. Takahashi)

ABSTRACT

This report will introduce a new experimental technique to readers, which we would like to propose towards advances in the field of molecular reaction dynamics. It is time-resolved electron momentum spectroscopy and aims to take in momentum space snapshots of the rapid change of molecular orbitals, which is the driving force behind any structural changes occurring in transient molecules. Following a description of the working principle of the technique, some preliminary result will be presented in order to illustrate the current performance of the apparatus.

Keywords: (e,2e) electron momentum spectroscopy; pump-probe technique; molecular reaction; frontier electron dynamics

1 Introduction

Through the last four decades of studies of binary (e,2e) spectroscopy or electron momentum spectroscopy (EMS), it has been demonstrated that the ionization reaction near the Bethe ridge is a sensitive probe for electronic structure and electron correlation in matter [1, 2]. This method involves coincident detection of the two outgoing electrons produced by electron impact ionization of a target atom or molecule. The ion recoil momentum q and the electron binding energy E_{bind} can be determined by coincident detection of the two outgoing electrons with the help of the laws of conservation of linear momentum and energy:

$$q = p_0 - p_1 - p_2 \qquad (1)$$

and

$$E_{bind} = E_0 - E_1 - E_2. \qquad (2)$$

Here the p_j's and E_j's (j = 0, 1, 2) are momenta and kinetic energies of the incident and two outgoing electrons, respectively. Under the high-energy Bethe ridge conditions [1-2], the collision kinematics can be described by the so-called electron Compton scattering [3],

analogous to X-ray Compton scattering, that most nearly corresponds to collision of two free electrons with the residual ion acting as a spectator. Then the momentum of the target electron before ionization p is equal in magnitude but opposite in sign to the ion recoil momentum q.

$$p = -q = p_1 + p_2 - p_0 \qquad (3)$$

Fig. 1 shows the symmetric noncoplanar geometry that has widely been used for EMS experiments. In this kinematic scheme, two outgoing electron having the equal energy ($E_1 = E_2$) and the equal scattering angle ($\theta_1 = \theta_2 = 45°$) with respect to the incident electron momentum vector are detected in coincidence. Then magnitude of the ion recoil momentum q or that of the target electron momentum p is expressed by

$$p = q = \sqrt{\left(p_0 - \sqrt{2}p_1\right)^2 + \left(\sqrt{2}p_1 \sin(\Delta\phi/2)\right)^2} \qquad (4)$$

where $\Delta\phi (= \phi_2 - \phi_1 + \pi)$ is the out-of-plane azimuthal angle difference between the two outgoing electrons. In this way, EMS cross section can be measured as a function of binding energy and target electron momentum. In other words, EMS enables one to look at electron orbitals in momentum space, providing unique and versatile information about electronic structure of matter.
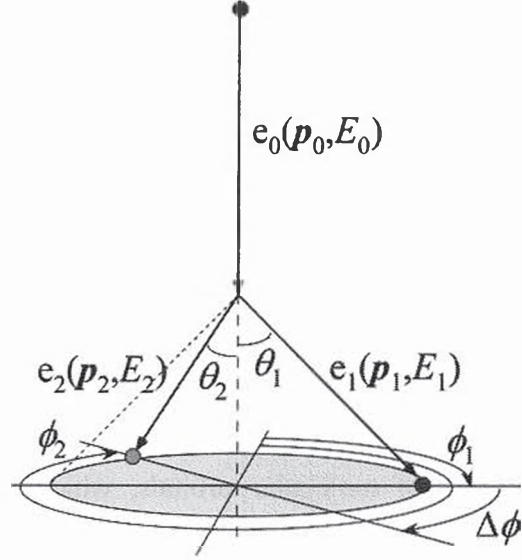

Fig. 1. Symmetric noncoplanar geometry for the binary (e,2e) reaction.

In spite of the remarkable feature, however, application of EMS has long been limited only to stable target atoms and molecules in their ground states. The reason for this may be due to an experimental difficulty that (e,2e) cross sections under the high-energy Bethe ridge conditions employed is extremely small compared to those at small momentum transfers or in the forward scattering directions of the electron projectile. Thus, in order to make EMS applicable to short-lived transient species, we have first developed a traditional, but extremely highly sensitive EMS spectrometer [4]. Based on this technical achievement, we have subsequently developed a time-resolved EMS (TR-EMS) apparatus [5] that employs an ultrashort-pulsed incident electron beam with a temporal width being in the order of a picosecond. This apparatus can be expected to be applied widely. One of the possible applications would be to take in momentum space snapshots of the rapid change of molecular orbitals, which is the driving force behind any chemical reactions. In the present paper, details and the working principle of the apparatus are given. Then, a preliminary result obtained by using the apparatus is presented in order to illustrate the current performance of the apparatus.

2 Time-resolved electron momentum spectroscopy apparatus

Details of the TR-EMS apparatus have been described elsewhere [5], so a brief account of

it is given here (Fig. 2). The 800 nm output from a 5-kHz femtosecond laser is split into a pump path and an electron-generation path. 90% of the output is used to yield the pump laser pulse with an optical parametric amplifier, which is used to initiate chemical reaction of molecules in the target gas beam produced through either of a single tube gas nozzle and a multi-capillary beam source, after the 5-kHz repetition rate being halved by an optical chopper. On the other hand, 10% of the output is frequency tripled in a third-harmonic generator to produce electron pulses via the photoelectric effect. The photocathode is made of a silver film of forty-nm thickness, which is negatively biased to accelerate the electron pulses. The electron pulses are then used to induce EMS scattering. The time delay between the arrival of the pump laser pulse and the probe electron pulse is controlled with a computer-driven translation stage. The resulting EMS events are recorded by an EMS spectrometer for which an exceptionally large spherical analyzer (mean radius of 220 mm) is employed. Here, the two outgoing electrons in the symmetric noncoplanar geometry are dispersed by the spherical analyzer and detected by a large–area position sensitive detector. It should be noted that this apparatus produces two kinds of EMS datasets. One is data that are measured with pump laser and the other is reference data that are measured without pump laser. TR-EMS results can be obtained as difference spectra between these two datasets with an appropriate weight factor for the reference data.
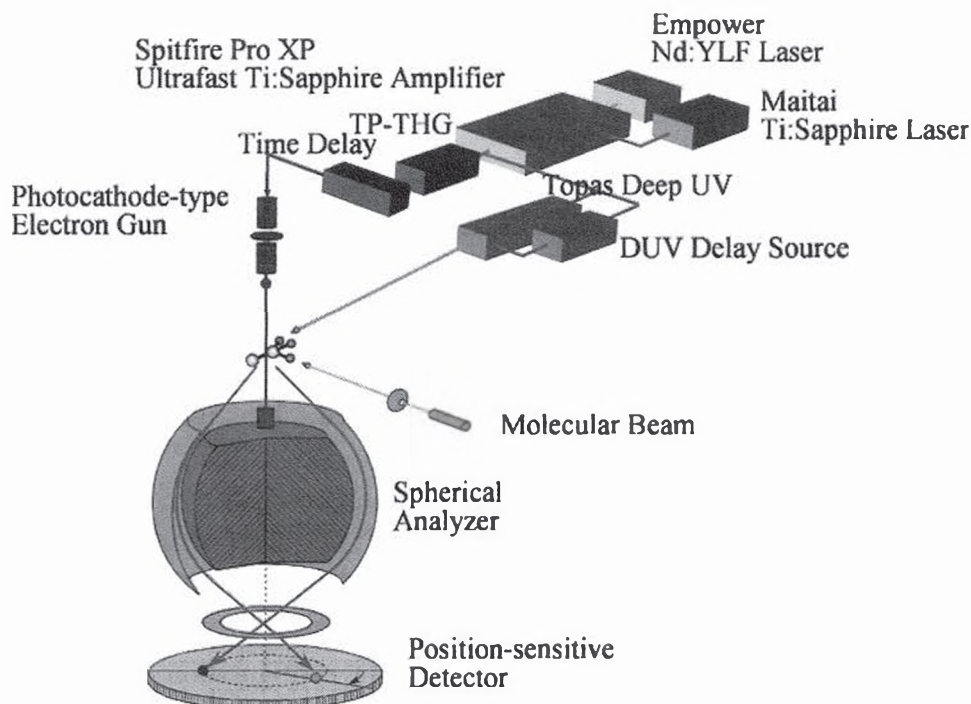

Fig. 2. Schematic of a time-resolved electron momentum spectroscopy apparatus.

3   Sample result

A show-case experiment has been conducted by using the TR-EMS apparatus but without pump laser. Here, the target molecule of choice is the deuterated acetone molecule in its ground state. The incident electron energy was about twelve hundreds electron volt and its beam intensity was 50 pA. Diameter of the target gas beam was 2 mm. The energy resolution in binding energy spectra was 5 eV, which was almost the same as the energy spread in the incident electron beam due to space charge effects. The experimental results were obtained through accumulation of data for 14 days runtime. Fig. 3 shows a $\Delta\phi$-angle integrated binding energy spectrum of the deuterated acetone molecule thus obtained without pump laser. Note that ionization bands from the valence molecular orbitals are significantly overlapped to the adjacent bands due to the poor energy resolution of 5 eV employed. Nevertheless, it is possible to check the quality of the experimental data by making a comparison with theory.
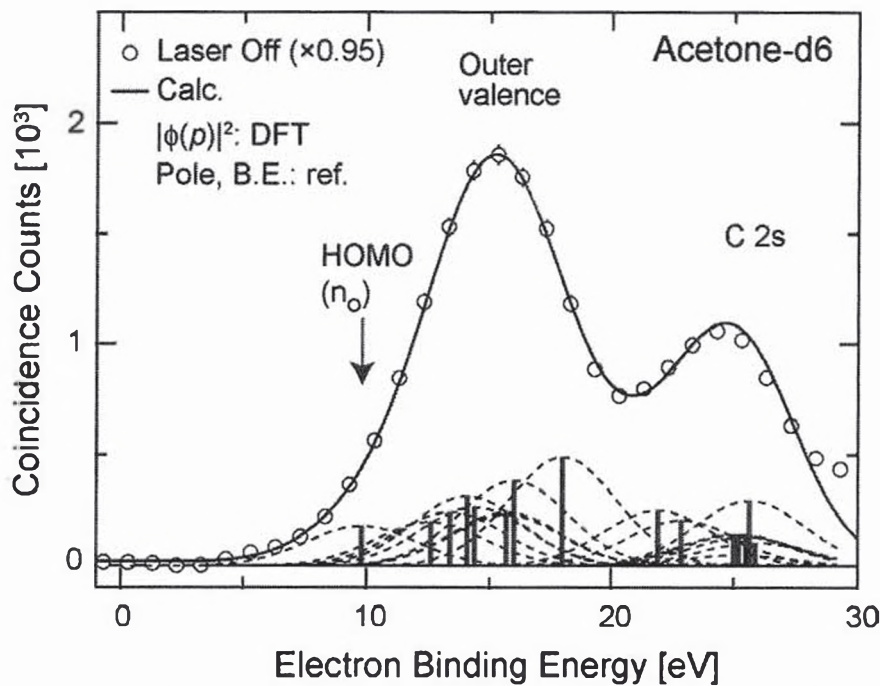

Fig. 3. $\Delta\phi$-angle integrated binding energy spectrum for the deuterated acetone molecule, obtained by using an ultrashort-pulsed incident electron beam.

The scattering theory most used in EMS is the plane wave impulse approximation (PWIA). Within the PWIA, EMS cross section for a gaseous molecule is proportional to the product of two physical quantities. One is a quantity called pole strength or spectroscopic factor, which represents a probability for finding one-hole electron configuration in the final ion state. The other quantity is the spherically-averaged electron momentum density distribution of the ionized orbital. Here, the spherically averaging is due to the random orientation of gaseous targets. According to the PWIA, an associated binding energy spectrum can be created by calculating the integrated value of the spherically-averaged electron momentum distribution over the covered momentum range for each bound molecular orbital with their own binding energies, and by summing up those after being convoluted with the instrumental energy

resolution of 5 eV. The resulting theoretical spectrum is also presented in Fig. 3. Here, the relevant wave functions for molecular orbitals were obtained with density functional theory at the equilibrium molecular geometry and the experimental pole strength distribution in the literature [6] was employed.

It can be seen from Fig. 3 that there is a good agreement between experiment and theory. This observation confirms that successful EMS measurements by using an ultrashort pulsed incident electron beam have been achieved, opening the door for detailed future studies of the change of molecular orbitals that are the driving force behind any molecular reactions. In fact, a preliminary but the first TR-EMS result has successfully been obtained recently, for the photo-induced three body dissociation process of acetone at 195 nm [7].

Acknowledgements

References

[1] E. Weigold and I.E. McCarthy, *Electron Momentum Spectroscopy* (Kluwer Academic /Plenum Publishers, New York, 1999).

[2] M. Takahashi, Bull. Chem. Soc. Jpn. **82**, 751 (2009).

[3] R.A. Bonham and H.F. Wellenstein, in: B. Williams (Ed.), *Compton Scattering* (McGraw-Hill, New York, 1977).

[4] M. Yamazaki, H. Satoh, M. Ueda, D. B. Jones, Y. Asano, N. Watanabe, A. Czasch, O. Jagutzki, and M. Takahashi, Meas. Sci. Technol. **22**, 075602 (2011).

[5] M. Yamazaki, Y. Kasai, K. Oishi, H. Nakazawa, and M. Takahashi, Rev. Sci. Instrum. **84**, 063105 (2013).

[6] Y. Zheng, J. J. Neville, C. E. Brion, Y. Wang, and E. R. Davidson, Chem. Phys. **188**, 109 (1994).

[7] M. Yamazaki, Y. Kasai, K. Oishi, H. Nakazawa, and M. Takahashi, 2013 XXVIII ICPEAC Abstracts of Contributed Papers.