Development of time-resolved (e,2e) electron momentum spectroscopy: a tool for visualizing the motion of electrons during a chemical reaction

M Yamazaki, Y Kasai, K Oishi, H Nakazawa and M Takahashi
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
E-mail: masahiko@tagen.tohoku.ac.jp

Abstract. We report the instrumental design and technical details of an (e,2e) electron momentum spectroscopy (EMS) apparatus, which employs an ultrashort-pulsed incident electron beam with a repetition rate of 5 kHz and a pulse duration in the order of one picosecond. EMS data for the neutral Ar atom in the ground state measured by using the pulsed electron beam are presented to illustrate the potential abilities of the apparatus for ultrafast molecular dynamics. The results are discussed mainly in terms of signal intensity.

1. Introduction

Through many years of intensive studies, electron momentum spectroscopy (EMS), also known as binary (e,2e) spectroscopy, has been established as a means to look at molecular orbital patterns in momentum space [1-8]. Of particular note is its sensitivity to the behavior of the outer, loosely bound electrons that are of central importance in chemical properties such as bonding, reactivity, and molecular recognition. In spite of its long history of the technique, however, there has been yet no application to transient molecular species. This may be due to the difficulty of performing EMS study that is a kinematically-complete electron-impact ionization experiment at large momentum transfer and large energy loss where the (e,2e) reactions generally have quite small cross sections, in addition to the difficulty originating in the low intensity of ultrashort-pulsed incident electron beam [9] that is the primary requirement of conducting electron impact experiments on short-lived species.

Under these circumstances, we have first developed an EMS apparatus that has significantly improved the instrumental sensitivity by covering almost completely the available azimuthal angle range for the symmetric noncoplanar (e,2e) reaction [10]. This technical progress has subsequently been employed to develop a new EMS apparatus equipped with an ultrashort pulsed electron gun [11] or to develop time-resolved EMS (TREMS). In fact, although the data statistics leaves much to be desired, we have carried out for the first time TREMS experiments, while aiming to probe the three-body photodissociation dynamics of acetone S2 Rydberg state prepared by 195 nm pump laser [12].

In this paper, we report on the instrumental design and technical details of the TREMS apparatus. EMS data for the neutral Ar atom in the ground state measured by using an ultrashort pulsed electron beam are presented to illustrate the potential abilities of the apparatus for ultrafast molecular dynamics. Furthermore, expected outcome by additional use of the supersonic molecular beam technique is discussed to improve the currently available TREMS signal intensity.
2. EMS kinematics

EMS is a high-energy electron-impact ionization experiment at large momentum transfer and large energy loss, in which both the inelastically scattered and ejected electrons are detected in coincidence. The \((e,2e)\) reaction for the ionization of the target atom or molecule, M, can be described by

\[
\text{M} + e_0^- \rightarrow e_1^- + e_2^- + \text{M}^+ \quad (E_0, p_0) \quad (E_1, p_1) \quad (E_2, p_2) \quad (E_{\text{recoil}}, q).
\]  

Here the \(E_j\)'s and \(p_j\)'s \((j = 0, 1 \text{ and } 2)\) are the kinetic energies and momenta of the incident, inelastically-scattered and ejected electrons, respectively. Similarly, \(E_{\text{recoil}}\) and \(q\) represent the recoil energy and recoil momentum of the residual ion \(\text{M}^+\), respectively. If the thermal energy of \(\text{M}\) as well as \(E_{\text{recoil}}\) is negligibly small compared with any of \(E_j\)'s, one has the following conservation laws of energy and momentum:

\[
E_{\text{bind}} = E_0 - E_1 - E_2 \quad \text{and} \quad q = p_0 - p_1 - p_2.
\]  

Here \(E_{\text{bind}}\) is the electron binding energy (also called the ionization energy). Under the high-energy Bethe ridge conditions \([4, 6, 8]\), the collision kinematics most nearly corresponds to a collision of two free electrons while leaving the residual ion \(\text{M}^+\) to act as a spectator. The initial momentum of the target electron \(p\), before ionization, is then equal in magnitude and opposite in sign to \(q\):

\[
p = -q = p_1 + p_2 - p_0.
\]  

Thus, the EMS cross section can be measured as a function of \(E_{\text{bind}}\) and \(p\).

![Figure 1](image1.png)  

**Figure 1.** Symmetric noncoplanar geometry for the study of the binary \((e,2e)\) reaction.

Figure 1 shows the symmetric noncoplanar geometry that has been widely used for EMS experiments. In this kinematic scheme, two outgoing electrons having equal energies \((E_1 = E_2)\) and equal scattering polar angles \((\theta_1 = \theta_2 = 45^\circ)\) are detected in coincidence. The magnitude of the ion recoil momentum \(q\) or that of the target electron momentum \(p\) is given by

\[
|q| = |p| = \sqrt{\left(p_0 - \sqrt{2} p_1\right)^2 + \left(\sqrt{2} p_1 \sin(\Delta\phi/2)\right)^2}.
\]  

Here, \(\Delta\phi\) is the out-of-plane azimuthal angle difference between the two outgoing electrons.

3. Apparatus

Details of the TREMS apparatus have been described elsewhere \([11]\), so a brief account of it is given here. Its major components are illustrated in fig. 2. It involves a large scattering chamber which
houses an electron gun chamber and a beam catcher chamber, in addition to a target beam source and an EMS spectrometer. A continuous flow of sample gas is injected from either of a single tube gas nozzle and a multi-capillary beam source [13, 14]. 5-kHz output from a femtosecond laser is split into a pump path and an electron-generation path. The pump laser (189–2600 nm) proceeds, after its repetition rate is halved (2.5 kHz) by using an optical chopper, into a vacuum chamber where it interacts with atoms or molecules in the target gas beam. On the other hand, the electron-generation laser (267 nm) is directed toward a back-illuminated photocathode (40-nm Ag film) to produce an electron packet via the photoelectric effect. The resulting electron packet is then accelerated and is used as a pulsed incident electron beam by crossing it with the target beam to probe with EMS transient species involved. The EMS spectrometer employed is exceptionally large and is almost doubled in size (mean radius of 220 mm) compared to our traditional EMS spectrometer [10], in which the two outgoing electrons in the symmetric noncoplanar geometry are dispersed by a spherical analyzer and detected by a large-area position sensitive detector (PSD). Note that space charge effects broaden temporal width as well as kinetic energy distribution of the pulsed electron beam as it propagates. Hence, the path length from the photocathode to the ionization point has been designed to be as short as possible (10 mm). This helps not only to maintain the temporal width of the pulsed electron beam within one picosecond but also to keep its kinetic energy distribution less than 5 eV.

Figure 2. Schematic of a time-resolved electron momentum spectroscopy apparatus. Abbreviations are: OPA for optical parametric amplifier, THG for third harmonic generator, BS for beam splitter, L for lens, EG for electron gun, BC for beam catcher.

The synchronization of the pump laser (120 fs) and probe electron (~1 ps) pulses is made with a method for finding time-zero that we have developed [11]. Here, a transient high density electron cloud is created on a Ag wire, located at the ionization point, by intense pump laser irradiation. Time-
zero, the time when both pulses simultaneously intersect in the molecular beam, can be determined by investigating how amount of change in kinetic energy distribution of elastically scattered electrons, produced by collision of the probe electron pulse with the Ag wire, is brought about due to the transient electron cloud or space charge effects.

It may be worthwhile to note that the TREMS apparatus has been designed in such a way that a supersonic target beam source chamber can be attached, shown by broken lines in fig. 2. In this configuration, the supersonic target beam can be used instead of a multi-capillary beam source. The expected outcome by the use of the supersonic beam is discussed in Sec. 4.2.

4. Results and discussion

4.1. EMS data for Ar

In general, TREMS requires the measurement of two kinds of EMS datasets. One is data that are measured using the pump excitation laser as a function of delay time between the pump laser and probe electron pulses. The other is reference data that are measured without the pump laser, that is, traditional EMS data. TREMS results are then obtained as difference spectra between the two EMS datasets with an appropriate weight factor for the reference data. In other words, the quality of TREMS results is governed primarily by the qualities of the two EMS datasets. As such, traditional EMS experiments using the ultrashort pulsed electron gun offer the opportunity to assess the potential of the present apparatus for performing experiments on ultrafast molecular dynamics. Thus, we have conducted a traditional EMS experiment on Ar at an incident electron energy of 1.2 keV by using the 5-kHz pulsed electron beam but without the 2.5 kHz pump pulse laser. The EMS data were obtained by accumulating for 8 days runtime with the incident electron beam intensity of 38 pA.

Figure 3 shows the $\Delta \phi$-angle integrated binding energy spectrum of Ar as well as the momentum dependence of the EMS cross sections or the momentum profiles of the Ar 3p and 3s orbitals. In the binding energy spectrum, the main bands due to ionization from the 3p and 3s orbitals and the satellites are clearly resolved. The overall energy resolution is found to be 5.6 eV.

![Figure 3](image)

Figure 3. (a) $\Delta \phi$-angle integrated binding energy spectrum of Ar and comparison of momentum profiles for the (b) 3p and (c) 3s orbitals between experiment and theory.

It can be seen that each momentum profile exhibits its own characteristic shape; the 3p momentum profile has a maximum at around $p = 0.6$ a.u. and its intensity falls off with the decrease in $p$, while the 3s one has a maximum at the momentum origin. Also included in figs. 3(b) and (c) are associated theoretical momentum profiles calculated by using the distorted-wave Born approximation (DWBA) theory [15], which are normalized at the maximum values. Various momentum resolution values have been tested, by folding those into the DWBA calculations according to the procedure of Migdall et al.
[16], so that the resulting theoretical momentum profiles reproduce the experimental well. As a result, the instrumental momentum resolution of the present apparatus has been found to be 0.5 a.u. at $\Delta \phi = 0^\circ$. This value is poor when compared to 0.2 a.u. achieved with our traditional EMS apparatus [10]. The most probable reason for this may be that in the pulsed electron gun any electrostatic/magnetic lens and a second collimating aperture are not employed. Since space charge effects can act not only in the direction parallel to the beam axis but also in the perpendicular plane, the telefocus beam property may have been lowered.

4.2. Discussion
The results in fig. 3 clearly demonstrates that (e,2e) experiments using an ultrashort pulsed electron beam have been realized, opening up possibilities of EMS studies on short-lived transient species. Indeed, as mentioned above, we have carried out for the first time TREMS experiments, while aiming to probe the three-body photodissociation dynamics of acetone $S_2$ Rydberg state prepared by 195 nm pump laser [12]. There is, however, ample room for improvements mainly in signal intensity, as can be seen by turning one’s eyes upon the statistics of the results in fig. 3. Generally speaking, (e,2e) coincidence count rate in EMS experiments is proportional to the number of targets in the ionization volume. In continuous target beam sources, however, the beam intensity is usually limited by the size and capacity of the associated vacuum pumps. The same is true with our TREMS apparatus. Introduction of a pulsed target beam source, operating at the same 5 kHz as the laser system, or a higher-intensity target beam source is therefore one of our next priority. For this purpose, simulations to access the target beam quality such as the target number density at the ionization point have been extensively made by using the DS2V program [17].

Figure 4. Calculated target number densities.

An example of the simulations is presented in fig. 4. Fig. 4(a) displays a flow property of the currently-used single-tube gas nozzle of 1 mm i.d. with its tip being located 3 mm apart from the ionization point. On the other hand, fig. 4(b) shows a flow property of the supersonic beam from an aperture of 0.5 mm i.d. through a skimmer having an inside diameter of 0.3 mm. The target number densities at around the ionization point are plotted in fig. 4(c) as a function of the distance from the ionization point in the direction perpendicular to the beam axis. Here, the filled squares represent the target number densities generated by the single tube gas nozzle with the stagnation pressure of $1\times10^2$ Pa, while the filled circles and the open triangles show those by the supersonic beam with the pressure of $1\times10^2$ Pa and $1\times10^5$ Pa respectively. Note that the stagnation pressure of $1\times10^2$ Pa for the single
tube gas nozzle and that of $1 \times 10^5$ Pa for the supersonic beam is the upper limit for keeping the ambient pressure in the scattering chamber, where the PSD is settled, lower than $1 \times 10^{-4}$ Pa.

It is evident from the fig. 4 that the beam divergence is much better for the supersonic beam than the single tube gas flow, as expected. Also evident is that the supersonic beam with $1 \times 10^5$ Pa provides 5 times larger target number densities than the single tube gas nozzle with $1 \times 10^2$ Pa. This strongly suggests that provided a pulsed nozzle (a 7 μs pulse with 5 kHz repetition rate [18]) is employed, the target number density and hence the TREMS signal is increased by a factor of 140 compared to the present experimental conditions. For this purpose, such a high-intensity target beam source has been constructed and installed to the TREMS apparatus.

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