Recent progress on electron momentum spectroscopy in application to the investigations on intramolecular interactions

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Abstract. The intramolecular interactions including the Jahn-Teller effect, the relativistic effect have been investigated by a newly developed multichannel (e, 2e) electron momentum spectrometer employing asymmetric non-coplanar kinematics with a high coincidence energy resolution of 0.5 eV.

1. Introduction

Binary (e, 2e) spectroscopy, also known as electron momentum spectroscopy (EMS), has been developed as a powerful tool for investigating the electronic structure of atoms and molecules since the pioneering works of McCarthy, Weigold and co-workers [1-3] some forty years ago. Basically two categories of information can be obtained by EMS: (i) binding energy spectra (BES) over a wide energy range usually covering the complete valence shell, and (ii) the angular distributions of (e, 2e) cross section for individual transitions giving rise to the peaks in BES. Within a series of approximations including the plane wave impulse approximation (PWIA) and the target Hartree-Fock (THFA) [3] or target Kohn-Sham approximation (TKSA) [4-6], this measured (e, 2e) cross section is proportional to the spherically averaged electron momentum distribution for a specific molecular orbital (MO). During the last decades EMS has been successfully applied to an increasingly wide variety of atomic, molecular and solid state targets [3, 7-9], not only providing stringent tests for quantum chemical calculations at Hartree-Fock (HF) [3], configuration interaction (CI) [10-12] and more recent Kohn-Sham density functional theory (DFT) [4-6] levels, but also providing the straightforward information for understanding chemical properties and reactivity through its unique ability of directly “imaging” the individual atomic and molecular orbitals, especially the chemical important valence (frontier) orbitals.

However, the further application of EMS is largely limited by the low coincidence count rate and the poor energy resolution (typically 1~2 eV). Most of the EMS applications are restricted to atoms and relatively small and stable molecules. For large and complex molecules or high order interactions, the conventional resolution is insufficient to resolve the closely spaced electronic states of valence orbitals. The key to improve the energy resolution is to ameliorate the sensitivity of the spectrometer. Over last two decades, great efforts have been made for the improvement of the sensitivity by introducing the simultaneous detection technique. One of the most important developments was the introduction of one-dimensional position-sensitive detectors (PSDs) for the parallel measurements over a wide range of energies for the two outgoing electrons by McCarthy, Weigold and co-workers.
[13-14]. In their work, position-sensitive detectors were employed for the parallel measurements on both energies and momenta (angles) over wide ranges. More recently, high efficiency EMS spectrometers for gas phase employing non-coplanar symmetric kinematics have been reported by Zheng et al. [15], Takahashi et al. [16] and Ren et al. [17]. And a spectrometer employing asymmetric non-coplanar kinematics has been reported by the authors [18]. The simultaneous detection in a large energy and momentum ranges by using two-dimensional position-sensitive detectors have provided with large advantages of not only the high sensitivity but also the better stability and reliability of the experimental data because of avoiding the influence resulted from the changes of electron current and gas pressure. An electron monochromator for incident beam has been brought into use in our instrument and a high coincidence energy resolution of 0.5 eV has been achieved. With the advantage of the good energy resolution, the EMS has been used to investigate the intramolecular interactions including the Jahn-Teller effect [19], the relativistic effect [20] as well as the hyperconjugative effect [21].

2. Theoretical background

EMS is based on \((e, 2e)\) collision experiment in which an electron from target atoms or molecules is cleanly knocked out by a high-energy incident electron and the residual ion acts as a spectator. Conservation of energy and momentum lead to

\[
\begin{align*}
\epsilon &= E_0 - E_1 - E_2 \quad (1) \\
p &= p_1 - p_2 - p_0 \quad (2)
\end{align*}
\]

where \(\epsilon\) and \(p\) are the binding energy and the momentum of the target electron, and \(E_i, p_i\ (i = 0, 1, 2)\) are the energies and the momenta of the incident and two outgoing electrons, respectively. Thus, by detecting the two outgoing electrons in coincidence, the binding energy and the momentum of the target electron can be determined.

Within a series of approximations including plane wave impulse approximation (PWIA), Born-Oppenheimer approximation and disregarding rotational functions, the triple differential cross-section of \((e, 2e)\) reaction in EMS \(\sigma_{EMS}\) turns out to be proportional to the squared form factor \(F^{{\phi}}_q(p)\), which is given by [3, 7, 22]

\[
F^{{\phi}}_q(p) = \int dQX'_q(Q)X_q(Q)\phi^{(f)}_q(Q)\phi_q(p, Q) 
\]

where \(X'_q(Q)\) and \(X_q(Q)\) are vibrational wavefunctions for initial and final states, \(\phi^{(f)}_q(Q)\) the overlap integral of the wavefunctions for the final ion and molecular residue left after the knockout of an electron from one-electron molecular orbital \(\phi_q(p, Q)\) in momentum space, and \(Q\) the set of coordinates determining the displacements from equilibrium of \(N\) atomic nuclei of the molecule. Equation (4) can further be reduced to [22]

\[
F^{{\phi}}_q(p) = g^{{\phi}}_q S^{(f)}_q(Q)\overline{Q} \phi_q(p, \overline{Q}) 
\]

where \(g^{{\phi}}_q = \int dQX'_q(Q)X_q(Q)\) is the Frank-Condon factor and \(\overline{Q}\) corresponds to some mean values of nuclear coordinates intermediate between the equilibrium coordinates of nuclei \(Q_0\) and \(Q'\) in the initial molecule and in the final molecular ion, respectively. Estimations made by Levin et al. [22] for light diatomic molecules showed that the value \(S^{(f)}_q(Q)\phi_q(p, Q)\) slowly varies in the range of \(Q\) values between \(Q_0\) and \(Q_0\), so the \(\overline{Q}\) value in the calculation for EMS studies is usually chosen as \(Q_0\) in the initial molecule. Moreover, since the vibrational states are not resolved by present electron momentum spectrometer, \(\sigma_{EMS}\) can be expressed as [3, 7, 22]

\[
\sigma_{EMS} \propto \int \left| S^{(f)}_q(Q_0) \right|^2 \int \left| \phi_q(p, Q_0) \right|^2 d\Omega_p, 
\]

The integral in the Equation (6) is known as the spherically averaged one-electron momentum distribution, or electron momentum profile. \(\left| S^{(f)}_q(Q_0) \right|^2\) represents the pole strength and \(\phi_q(p, Q_0)\) is
the one-electron canonical Hartree-Fock (HF) [3, 7] or Kohn-Sham wavefunction [4, 5] in momentum space for the $q$th orbital from which the electron is ionized.

**Figure 1.** Schematic diagram of high-resolution (e, 2e) spectrometer, showing electron gun 1, monochromator 2, accelerating lens 3, reaction region 4, Faraday cup 5, ejected electron analyzer system 6 and scattered electron analyzer system 7.

**3. Instrument**

Figure 1 shows the schematic diagram of the high-resolution (e, 2e) spectrometer. It consists of an electron gun, a monochromator, an accelerating lens system, a Faraday cup, a hemispherical analyzer with a five-element retarding lens and a one-dimensional PSD for analyzing slow ejected electron, and a hemispherical analyzer with a six-element conical retarding lens and two-dimensional PSD for analyzing fast scattered electron. The asymmetric non-coplanar geometry near the Bethe ridge is employed. Electron beam generated from electron gun is retarded and monochromized by a monochromator. The monochromized electron beam is accelerated by a lens system to the desired energy ($E_0=2500$ eV + binding energy) and transferred to the reaction region where the electron beam impacts with the target injected by a nozzle of 0.5 mm inner diameter. A current of about 100 nA is typically collected by Faraday cup. The ejected electron ($E_b \approx 146$ eV) outgoing along polar angle $\theta_b = 76^\circ$ enters into the slow electron spherical analyzer and is detected by one-dimensional PSD. Taking the advantage of the energy dispersive property of the hemispherical analyzer, the ejected electron can be detected in an energy range of 6 eV ($146 \pm 3$ eV). The scattered electron ($E_a \approx 2354$ eV) outgoing along the conical surface with polar angle $\theta_a = 14^\circ$ enters into the fast electron spherical analyzer and is detected by two-dimensional PSD over a range of azimuthal angle of interest (relative azimuthal angle $\phi = -4^\circ \sim 36^\circ$). The analyzer maintains the azimuthal angle $\phi$ of the passing electrons and energy-disperses them along the radial dimension. Thus by using a pair of PSDs, it is possible to measure the energy and angular correlations for the two outgoing electrons in a wide range of both energy and relative azimuthal angle simultaneously. Three-dimensional EMS data (energy-momentum density), which is constituted by relative cross sections (coincidence counts) measured as a function of binding energy and electron momentum, can be collected at a fixed incident energy. With the help of the large cross section for the asymmetric kinematics and multi-channel technique, the sensitivity of the spectrometer is improved by a factor of hundreds compared to the conventional apparatus. Thus it is possible to employ a large sized monochromator (with mean radius of 200 mm) for incident electron beam and a high coincident energy resolution has been achieved. The electron gun, monochromator and two analyzers are located in three vacuum chambers fabricated from 304L stainless steel and differentially pumped using turbo molecular pumps to a background pressure of $1 \times 10^{-5}$ Pa. The ambient magnetic field is reduced to less than 5 mG by µ-metal shields and Helmholtz coils. The
electrostatic lenses and analyzers are fabricated from magnetic free 316L stainless steel or aluminum and apertures/slits from molybdenum. Each PSD is constituted by a pair of multi-channel plates and a Gear-type resistive anode. The signals output from the PSDs are processed and recorded by a multi-parameter coincident electronics and data acquisition system.

4. Jahn-Teller Effect
The Jahn-Teller (JT) effect means that a nonlinear molecule in an orbitally degenerate state distorts to a configuration of lower symmetry along suitable vibrational modes [23]. The JT splitting electronic states resulted from these distortions form conical intersections at the equilibrium geometry of the undistorted configuration, and therefore cause nonadiabatic transitions during nuclear vibrations of the molecule [24-27]. Cyclopropane, a simple molecule with high $D_{3h}$ symmetry in ground state, exhibits strong JT effect in the ionization of its highest occupied molecular orbital (HOMO) $3e'$, and has been an appropriate object to study the nature of JT effect in isolated molecule [26, 27].

Electronic structure of cyclopropane have been investigated extensively by means of photoelectron spectroscopy (PES). Basch et al. [28] reported the investigations on outer valence orbitals for some saturated three-membered rings including cyclopropane using PES combined with SCF calculations. The doublet bands at 10.53 and 11.30 eV were suggested to be assigned to the two JT splitting components of $3e'$ orbital. The difference for the asymmetry parameter $\beta$ associated with the two JT splitting bands of $(3e')^{1}$ state of cyclopropane was observed in the angular-resolved PES using dispersed polarized synchrotron radiation by Keller et al. [29]. On the other hand, Haselbach [30] and subsequent researchers [31] had investigated the JT distorted equilibrium geometries for radical cations of cyclopropane using different methods from semi-empirical MINDO/2 to high level ab initio calculations. Two energy minimized geometries of $C_{2v}$ symmetry, one is characterized by one shortened and two elongated C-C bonds (Ia$^+$) and another one by one elongated and two shortened C-C bonds (Ib$^+$), for the radical cations of cyclopropane were obtained. Haselbach evaluated the upper limit of the JT splitting energy by the energy differences of the highest two occupied molecular orbitals for the two neutral nonequilibrium systems using the geometries of radical cations. The potential energy surface for the ground state of radical cations of cyclopropane calculated by Venkatesan et al. [26] with the aid of an ab initio based quantum dynamical approach indicated that there were two geometries of $C_{2v}$ symmetry corresponding to a minimum and a saddle point. The dynamical simulations of PES for the $(3e')^{1}$ state of cyclopropane had also been carried out by means of nonadiabatic vibronic mixing of electronic states [26, 27].

EMS was also used by Tossell et al. [32] to explore JT effect for the $3e'$ orbital of cyclopropane. The experimental momentum profiles (XMPs) for the two JT splitting components showed indistinguishable intensity from one another, but both exhibited large density in zero-momentum region relative to the theoretical momentum profiles (TMPs) calculated based on the neutral molecular geometry of $D_{3h}$ symmetry. In terms of the picture produced by Haselbach [30], the TMPs calculated based on the two distorted $C_{2v}$ geometries could describe the intensity in zero-momentum region.

Therefore, Tossell et al. suggested that the large intensities observed in their experiment were attributed to the case that the electron momentum distributions for a molecular orbital vary in response to a change of molecular geometry which results in the mixing of a totally symmetric term into the wavefunction. Subsequently, Banjavčić et al. [33] reinvestigated the electron momentum distributions for the valence orbitals of cyclopropane by EMS with better energy and momentum resolutions (1.4 eV and 0.12 a.u. respectively). The XMPs for the two JT splitting components showed similar shape and intensity with no observed symmetric term. They concluded that the large intensity in zero-momentum region observed by Tossell et al. might be due to the lower momentum resolution (~ 0.28 a.u.). It is noted here that although the energy resolution of 1.4 eV in the experiment of Banjavčić et al. was better than that of Tossell et al., such resolution was not enough to resolve the JT splitting bands of $(3e')^{1}$ state with energy spacing of 0.78 eV. Thus the errors in the XMPs for the two JT splitting
components deduced by the deconvolution procedure rendered their conclusion suspect. JT effect for the 3$e'$ orbital of cyclopropane has been reinvestigated by using the high resolution EMS spectrometer with energy and momentum resolutions of 0.5 eV and 0.10 a.u. respectively [19].

Figure 2. (a) The solid circles and the open circles present the experimental momentum profiles for the two JT splitting components 1-JT and 2-JT of 3$e'$ orbitals of cyclopropane, the dash dot and the dashed lines present the theoretical momentum profiles calculated based on neutral equilibrium geometry of $D_{3h}$ symmetry and multiplied by the factor of 0.65 and 0.35 respectively, and the dotted and the solid lines denote the theoretical momentum profiles calculated based on the two distorted neutral nonequilibrium systems of $C_{2v}$ symmetry at B3LYP/aug-cc-pVTZ level. (b) The branching ratio of experimental momentum profiles for the JT splitting components 1-JT and 2-JT as a function of momentum.

In the binding energy spectra (BES) of cyclopropane, two slightly structures located at 10.47 eV and 11.25 eV corresponding to the two components of JT splitting (1-JT and 2-JT) have been observed. The XMPs and the experimental branching ratio as a function of momentum for the two JT splitting components 1-JT and 2-JT are presented respectively by solid and open circles in Figure 2. The error bars in this figure represent the overall error of the statistical and deconvolution uncertainties. The TMPs calculated using HF and B3LYP methods with the basis sets aug-cc-pVTZ are also plotted in Figure 2. Although the XMPs for the two components both display 'p-type' characters, they exhibit obvious differences both in intensity and in shape as shown in Figure 2(a). These differences are revealed more clearly in the branching ratio plotted in Figure 2(b). The branching ratio between the XMPs for 1-JT and 2-JT is generally equal to about 1.85 (being consistent with the previous theoretical calculations and PES measurements [26]) in momentum region $p > 0.5$ a.u., while it reduces to about 1.0 in zero-momentum region. By multiplying a factor of 0.65, the TMP for 3$e'$ orbital of cyclopropane neutral molecule (shown by dash dot line in Figure 2 (a)) is in fair agreement with the XMP for 1-JT. While the same TMP multiplied by a factor of 0.35 only reproduces the XMP for 2-JT in the high momentum region but obviously underestimates the intensity in the low momentum region as shown by dashed line in Figure 2 (a). Our experimental results are different from those of the previous EMS studies [32, 33]. The XMPs for 1-JT and 2-JT measured by Tossell et al. [32] were not distinguishable and both had large intensities in zero-momentum region. Banjavec et al. [33] also observed indistinguishable intensities between the XMPs for 1-JT and 2-JT but they declared no observation of the non-zero intensity near the origin. The good energy resolution and the parallel detection ability of the present apparatus insure more reliable deconvolution of BES and hence more reliable XMPs for the two JT splitting components.

Generally, in view of a characteristic time scale of the order of $10^{-17}$-$10^{-16}$ sec. for the interaction time between the molecular target and an impinging electron with a kinematic energy of 2.5 keV, the electron momentum distribution relates to electron impact ionization event is vertical in nature. However, the previous theoretical studies [26, 34] have indicated that in a time dependent picture JT
effect corresponds to a femtosecond nonradiative decay in the case of cyclopropane, which is, to some extent, comparable to the interaction time of electron impact ionization. Meanwhile, the molecular orbital images show that the $3e'$ is C-C σ-bonding, respectively. Such bond character of $3e'$ orbital makes carbocycle deform easily when ionizing [31]. Therefore, the observed differences between the XMPs for 1-JT and 2-JT in present experiment could be ascribed to a change of molecular geometry at the instant of ionization.

The stringent theoretical description involves the calculation of the overlap integral in Equation (3) between neutral and ionic wavefunctions including electronic and vibrational functions. But this is beyond our ability. Therefore, similar to Tossell et al., we also resort to the picture presented by Haselbach [30]. Geometries of molecular ions are employed to calculate TMPs for neutral nonequilibrium systems to qualitatively explain the observations in XMPs for 1-JT and 2-JT.

The correlation diagram for HOMOs and next HOMOs of Ia and Ib and HOMO of the neutral equilibrium geometry of D$_{3h}$ symmetry (Ic) is shown in Figure 3. The ionizations from 6$b_2$ (Ia) and 6$a_1$ (Ib) orbitals correspond to the 1-JT component, and those from 5$a_1$ (Ia) and 5$b_2$ (Ib) orbitals correspond to the 2-JT component in BES. The TMPs for HOMOs and next HOMOs of Ia and Ib are calculated by B3LYP/aug-cc-pVTZ. The average of the TMPs for 6$b_2$ (Ia) and 6$a_1$ (Ib) orbitals, corresponding to 1-JT, and that for 5$a_1$ (Ia) and 5$b_2$ (Ib) orbitals, corresponding to 2-JT, are plotted in Figure 2 (a) by the dotted line and the solid line respectively. By comparison with XMPs, one can immediately find that the averaging TMP of 5$a_1$ (Ia) and 5$b_2$ (Ib) describe 2-JT in zero-momentum region better. The TMPs for individual orbitals of 6$b_2$, 5$a_1$ of Ia and 6$a_1$, 5$b_2$ of Ib (not convoluted with instrumental momentum resolution) are also drawn in Figure 4. It can be seen that only the TMP for 5$a_1$ orbital of Ia has the non-zero intensity at $p = 0$ a.u., revealing the origin of the high intensity of momentum profile for 2-JT in zero-momentum region. In this way, we phenomenologically explain the observed differences of XMPs for the two JT splitting components of cyclopropane: at the instant of ionization from doubly degenerate $3e'$ orbital, cyclopropane distorts from the equilibrium equilateral triangle geometry of D$_{3h}$ symmetry into two nonequilibrium isosceles triangle geometries of C$_{2v}$ symmetry. This distortion brings the symmetric term into the electronic wavefunction of 5$a_1$ orbital of Ia, which leads to the high intensity of the XMP for 2-JT in zero-momentum region.

5. Relativistic Effect
Relativistic effects in high-Z atoms and molecules containing high-Z atoms have been a subject with increasing interests [35-37]. Relativistic effects mainly include kinematical effects and spin-orbit coupling effects [36]. The former are caused by electrons moving with high velocity in the vicinity of a (heavy) nucleus and the latter result from the interactions between spin and orbital angular momentum. Relativistic effects not only influence the energies of the states, causing the energy levels to shift and split, but also influence the electronic wavefunction. It was believed in the earlier years that relativistic effects are negligible for valence electrons, since they are well shielded from the nucleus and their average speeds are far less than the speed of light. However, it was latterly realized that relativistic effects for valence electrons of high-Z atoms and molecules containing high-Z atoms may also be substantial [35, 37].

EMS has been used to explore relativistic effects on the electronic wavefunctions for atoms [38-42] since the earlier works of Cook et al. [38, 39]. Although the energy resolution of their spectrometer (~1.6 eV) was not sufficient to resolve the 5p_{3/2} and 5p_{1/2} doublet of xenon (with an energy spacing of ~1.3 eV), Cook et al. tried to obtained the electron momentum distributions and the branching ratios for 5p_{3/2} and 5p_{1/2} by a certain deconvolution procedure and their results showed clear and direct manifestations of relativistic effects on one-electron wavefunctions. Later on, the similar results had been achieved for 6p_{3/2} and 6p_{1/2} doublet of lead by Frost et al. [40]. Relativistic effects on the (e, 2e) triple differential cross sections for the K-shell ionizations for silver and gold were reported by Bonfert et al. [41], and more recently relativistic effects on electron momentum distributions for inner shell 4d orbital of xenon were reported by Ren et al. [42]. EMS has been used for the first time to explore relativistic effects on the electronic wavefunctions for molecule by employing the high resolution (e, 2e) spectrometer with energy and momentum resolution of about 0.5 eV (FWHM) and 0.10 a.u. respectively [20]. The previous experimental studies [43-45] indicate that the spin-orbit splitting energy is about 0.73 eV for the highest occupied molecular orbital (HOMO) 5e of CF3I and can be partially resolved by the spectrometer.

The first two bands at 10.47 eV and 11.15 eV in the observed BES are the spin-orbit doublet 5e_{3/2} and 5e_{1/2} for the ionization from iodine lone-pair orbital of 5e. Figure 5(a) shows the individual XMPs for the spin-orbit splitting components 5e_{3/2} and 5e_{1/2}. It is clearly shown in the figure that the XMPs...
for the two components exhibit different intensities, being greater for 5e_{3/2} than for 5e_{1/2} in the
momentum region p < 1.0 a.u. and smaller in the momentum region p > 1.0 a.u.. The TMPs calculated
using non-relativistic HF method with the basis sets CRENBL(I)/6-311G*(C, F) can not describe the
individual XMPs at all. The branching ratio of the two individual XMPs plotted as a function of the
momentum is also shown in Figure 5(b). Non-relativistic theory predicts that the branching ratio is
independent on the momentum and simply equals to the relative statistical weights, namely 1:1. But
the observed branching ratio in Fig. 5(b) obviously deviates from the value of 1.

The similar phenomena had been observed in the previous studies on relativistic effects for high-Z
atoms [36, 39]. According to the theoretical studies [36], the radial density distribution for the spin-
orbit component with small quantum number j of total angular momentum expands much more than
that with large j in momentum space due to relativistic effects. As a result, the intensity of momentum
distribution for large j component in low momentum region is greater than that for small j component
and the case is inverted in high momentum region. According to this picture, the observed differences
between the XMPs for 5e_{3/2} and 5e_{1/2} in the present experiment should be ascribed to relativistic effects.

6. Summary
A multichannel (e, 2e) electron momentum spectrometer employing asymmetric noncoplanar
kinematics with a high coincidence energy resolution of 0.5 eV has been used to investigate the
intramolecular interactions including the Jahn-Teller effect [19], the relativistic effect [20]. The energy
resolution is just efficient to resolve the JT and spin-orbit splitting components. The individual
electron momentum distributions for the outer valence orbitals including the two Jahn-Teller splitting
components for the highest occupied molecular orbital 3e' of cyclopropane have been obtained.
Compared with the results of high level quantum chemistry calculations, the observed differences
between the experimental momentum profiles for the two Jahn-Teller splitting components have been
phenomenologically explained, showing the influences caused by the change of molecular geometry at
the instant of ionization from doubly degenerate 3e' orbital on the electron momentum distributions.
The individual electron momentum distributions for the two spin-orbit splitting components 5e_{3/2}
and 5e_{1/2} of iodine lone-pair orbital of CF$_3$I have been obtained, together with their branching ratio as a
function of momentum. The experimental results show the obvious relativistic effects on the
wavefunctions for 5e_{3/2} and 5e_{1/2} orbitals.

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