Sensitive observations of orbital electron density image by electron momentum spectroscopy with different impact energies

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Abstract

Electron momentum spectroscopy studies of the ethylene highest occupied $1b_{3u}$ orbital are reported. The experiments were performed at impact energies of 400, 600, 800, 1000, 1200 and 1600 eV using a high resolution and high sensitivity (e, 2e) spectrometer. The orbital electron momentum distributions of $1b_{3u}$ are presented at a wide range of impact energies, which are used to examine the validity of plane wave impulse approximation and provide an experimental analysis of distorted wave effects in the higher momentum region of molecule with the variation of impact energy.
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Electron momentum spectroscopy (EMS), also known as binary (e, 2e) spectroscopy, has been developed to be a powerful tool for the investigations of orbital electron density distributions and the understanding or evaluation of electron wave functions in atoms and molecules [1–4]. The experimental results of EMS provide the most direct measurements of orbitals and bonding in matters, which can contribute to the understandings of electronic structure and electron correlation effects and pole strengths. Furthermore, it is noteworthy from a chemical standpoint that EMS provides very direct information on the binding energies, the behavior (motion) of electrons and the electron density in the chemically reactive individual outer valence orbitals and molecular recognition [5].

However, the potential of EMS has not been fully achieved as yet because of its experimental difficulties. Since 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. The measurements always suffer from large statistical uncertainty and poor energy resolution. As a result 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, resolution, stability and versatility of (e, 2e) experiment. Recently, a high resolution and high sensitivity (e, 2e) electron momentum spectrometer with simultaneous detection in energy and momentum at the symmetric non-coplanar geometry has been developed at Tsinghua University. In this (e, 2e) electron impact ionization experiment, a newly developed double toroidal analyzer (DTA) and a pair of wedge-strip-anode (WSA) position sensitive detectors (PSDs) with a USB multi-parameters data-acquisition system [6] are used. Moreover, a conical deceleration lens system is equipped to achieve higher energy resolution. The typical energy and coincidence time resolution of 1.2 eV and 2 ns, the θ and ϕ angle resolution of ±0.7° and ±1.9° are achieved from the EMS measurements of argon, helium and also ethylene in this Letter. Furthermore, the high quality data obtained at various electron impact energies using the newly developed spectrometer establish the versatility of EMS studies. Then, some challenging works in the (e, 2e) reaction

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could be investigated more accurately and comprehensively, such as the investigations of distorted wave effects [7,8], spectroscopic factors or pole strengths and the validities of some approximations in calculations, etc. [9,10].

The target molecule ethylene (C_2H_4) is the simplest doubly bonded hydrocarbon. Its electronic structure of unsaturated carbon–carbon bonds poses an important research aspect in quantum chemistry. In addition, ethylene is also an important reagent in drug synthesis and addition reactions in alkane systems. The comprehensive investigations of the highest occupied molecular orbital (HOMO) in ethylene are highly motivated by the desired understanding of C_2H_4 carbon–carbon double bond. Two EMS studies have been carried out for ethylene by Coplan et al. [11] and Brion and co-workers [12] using the impact energies of 400 and 1200 eV, respectively. Since EMS involves coincident detection of the two outgoing electrons produced by the (e, 2e) reaction with inherently small cross section, the previous experiments often suffer from the poor statistics. Moreover, the validities of plane wave impulse approximation (PWIA) can be further verified by the (e, 2e) measurements at different impact energies. And these measurements could be of great benefit to the understanding of distorted wave effects in molecules. Therefore, it would be worthwhile to reinvestigate the EMS studies of ethylene HOMO with experiments at higher statistical precision with different impact energies. The spectrometer performance can also be further demonstrated by the measurements of ethylene HOMO at a wide range of impact energies.

In the present Letter, we report the EMS measurements of ethylene at impact energies of 400, 600, 800, 1000, 1200 and 1600 eV, using a newly developed spectrometer that features high resolution and high sensitivity. The binding energy spectrum and orbital electron density contour image of complete valence shell for C_2H_4 have been presented. Furthermore, the orbital electron momentum distributions of ethylene HOMO obtained at the six different impact energies are compared in order to examine the validity of PWIA and provide the experimental analyzing of distorted wave effects in the higher momentum region as a function of impact energy.

In the (e, 2e) electron impact ionization, an incident electron of energy E_0 causes the ionization of the target system. The EMS kinematics is completely determined by detecting the two outgoing electrons in coincidence, with energies E_1 and E_2, polar angles θ_1 and θ_2 and a relative azimuthal angle ϕ. The suitable experiment configuration, used in the majority of conventional EMS measurements, is the symmetric non-coplanar geometry in which cross sections are measured for scattering at equal energies ($E_1 \approx E_2$) with equal polar angles ($\theta_1 = \theta_2 = 45°$) and a varying relative azimuthal angle

ϕ. Under this experimental geometry, the magnitude of the precollision electron momentum $\vec{p}$ of the molecule is given by

$$p = \left[(2p_1 \cos \theta - p_0)^2 + \left(2p_1 \sin \theta \, \sin \left(\frac{\phi}{2} \right) \right)^2 \right]^{1/2}, \quad (1)$$

where p_0 is the momentum of the incident electron and p_1 is the momentum of the outgoing electrons.

Spherically averaged electron momentum distributions for individual (binding energy selected) orbitals are measured by EMS, which is the orbital imaging in the momentum representation [1–3]. Within the plane wave impulse and the target Hartree–Fock (HF)
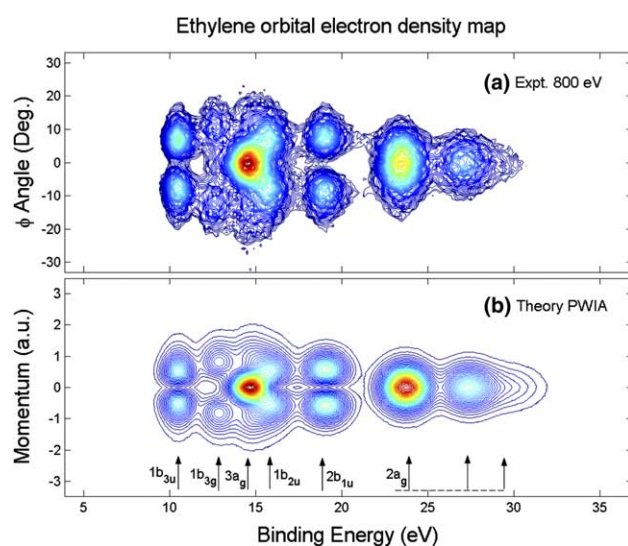

Fig. 1. The contour image of orbital electron densities for the ethylene: (a) experimental orbital electron density obtained at the impact energy of 800 eV with 100 eV passing energy in the analyzer; (b) theoretical calculation using DFT in PWIA level.
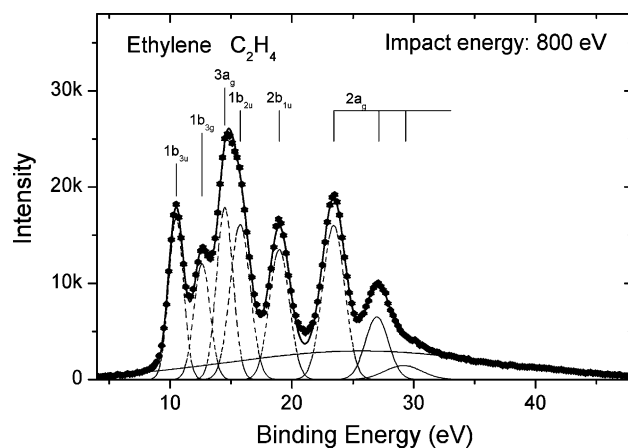

Fig. 2. Binding energy spectrum of ethylene obtained at impact electron energy of 800 eV, showing the $1b_{3u}$, $1b_{3g}$, $3a_g$, $1b_{2u}$, $2b_{1u}$ and $2a_g$ states, as well as the $2a_g$ satellite states. The dashed lines represent Gaussian fits to the peaks and the solid curve is the summed fit.

approximations, the EMS cross section (momentum distribution) is given by

$$\sigma_{EMS} \propto \int d\Omega |\Psi_i(\vec{p})|^2, \tag{2}$$

where $\vec{p}$ is the momentum of the electron before ionization from the target, and the momentum space-independent particle (orbital) wave function $\Psi_i(\vec{p})$ is the Fourier transform of the more familiar position space wave function $\Psi_i(\vec{r})$. 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 [13] results in an expression similar to Eq. (2), and the electron correlation effect is accounted through the exchange-correlation potential. By using of these theories, EMS measurements have be-

come a kind of experimental quantum chemistry and have been useful for the evaluation and design of accurate wave functions [1–4]. With the significant improvement of EMS coincidence count rate and the good performance of the energy and azimuthal angle resolution, the image of electron density in atom and molecules can be obtained directly and accurately within a proper experiment period.

The typical orbital electron density map of ethylene was directly obtained, as shown in Fig. 1a, at impact electron energy of 800 eV with 100 eV passing energy in the analyzer. The theoretical result was obtained using DFT method in PWIA level and shown in Fig. 1b. The contour image represents energy–momentum densities of ethylene valence electrons and contains the information on relative intensities, momentum distribution,
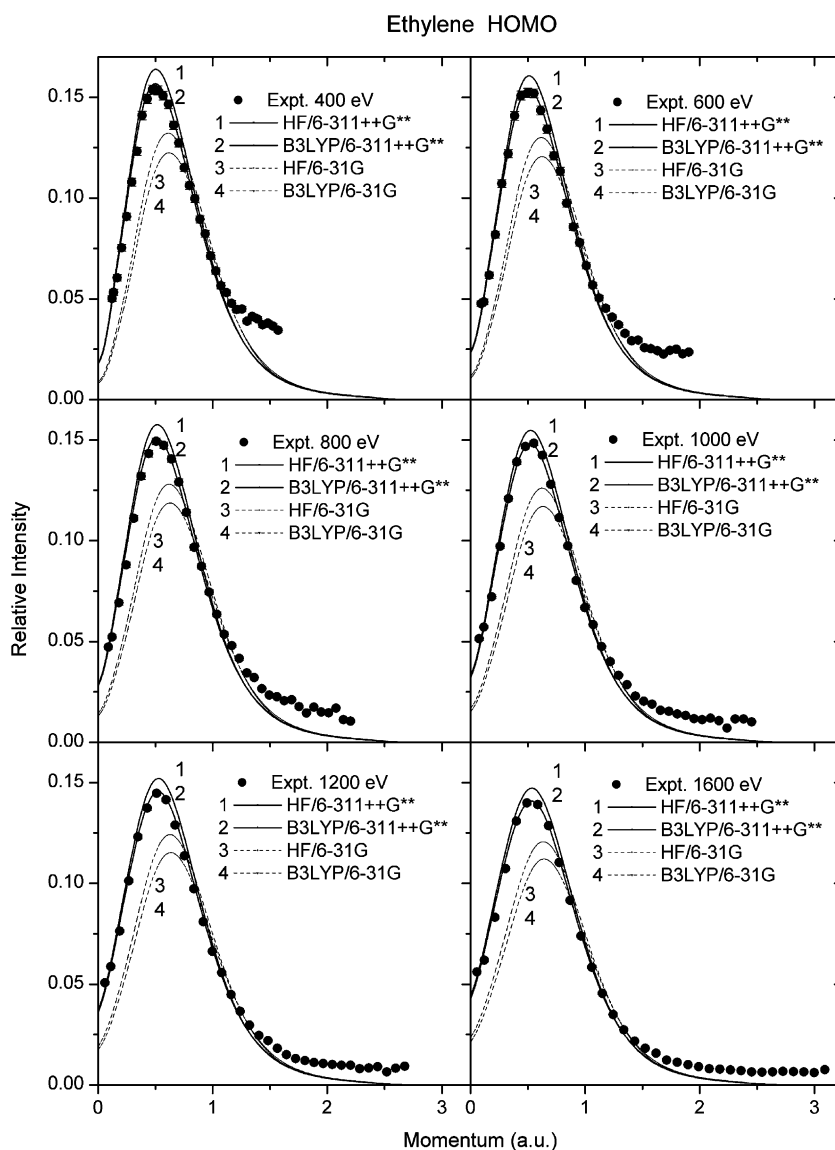

Fig. 3. The experimental orbital electron momentum profiles for the $1b_{3u}$ HOMO orbital of ethylene at different impact energies of 400, 600, 800, 1000, 1200 and 1600 eV compared with the theoretical calculations using DFT and HF methods in PWIA.

symmetries of the states involved, and satellite structures. The orbital symmetry and binding energy spectrum can be directly and accurately obtained from this experimental image. A binding energy spectrum of ethylene has been obtained by summing up intensities along the binding energy axis in the experimental electron density contour image, as shown in Fig. 2. This spectrum includes the $1b_{3u}$, $1b_{3g}$, $3a_g$, $1b_{2u}$, $2b_{1u}$ and $2a_g$ states, as well as the $2a_g$ satellite states resulting from electron correlation effects. The good statistical precision confirms the accuracy of the data by using the spectrometer.

From the qualitative comparison between the experimental orbital electron density image (Fig. 1a) and the theoretical calculation (Fig. 1b), we can observe that the experimental orbital electron density can be reasonably described by the theoretical calculation. In order to more cautiously compare the theoretical calculation with experimental results, we measured the orbital electron density of ethylene at different impact electron energies of 400, 600, 800, 1000, 1200 and 1600 eV. The HOMO orbital electron density distributions were obtained along the ϕ angle axis at a given binding energies region (represent individual orbital). The experimental electron momentum distributions and the theoretical calculations of $1b_{3u}$ HOMO orbital at these impact electron energies are shown in Fig. 3. The theoretical orbital electron momentum distributions are calculated by DFT and HF methods with 6-311++G** and 6-31G basis sets in PWIA level. For comparing with the experimental electron momentum distributions, these theoretical profiles were convoluted with the instrumental resolution ($\Delta\theta = \pm 0.7°$, $\Delta\phi = \pm 1.9°$, and $\Delta E = 1.2$ eV) according to the method in Ref. [14].

It can be seen from the comparison of the experimental HOMO momentum profiles and theoretical calculations that the experimental data can be well described by the PWIA theoretical calculations in the lower momentum region at wide range of impact energies. The theoretical calculations using DFT-B3LYP method with 6-311++G** basis set can provide an excellent description of the experimental measurements, which indicates that inclusion of dynamic electron correlation effects method with the saturated diffuse and polarization basis set calculation is essential for description of ethylene HOMO in the chemically important larger r (lower p) region. Moreover, some discrepancies at higher momentum (smaller r) region are dissimilarly observed at different impact energies, which are mainly due to distorted wave effects [1] since the PWIA regime is not valid at higher momentum region. The occurrence of distortion effects at higher momenta can readily be understood because this region of electron momentum profile involves significant penetration by the incoming electron into the smaller r region near to the nucleus [7]. In order to provide the convictive investigation of distorted wave effect at higher momentum region, the

intensity differences between experimental data and theoretical calculation were obtained at different impact energies, as shown in Fig. 4, where the intensity differences are defined to be the sum of the differences between the experimental momentum distributions and the PWIA theoretical calculations using B3LYP/6-311++G** within the momentum range from 1.0 to 1.6 a.u. It can be seen from the figure that the distorted wave effects at higher momentum region become smaller with the increase of impact energies, which is consistent with the theoretical anticipation in atomic targets by Brion et al. [7] and McCarthy and co-workers [15]. Unfortunately, the theoretical calculations using distorted wave approximations in molecules cannot be achieved due to the multi-center nature of molecular targets until now. The accuracy and validity of investigating the distorted wave effects in atoms and molecules using this newly developed spectrometer could be further demonstrated by the analytic results of intensity differences at wide range of impact energies, as shown in Fig. 4.

In summary the orbital electron density distributions for the ethylene $1b_{3u}$ HOMO at different impact energies of 400, 600, 800, 1000, 1200 and 1600 eV were measured by using a newly developed (e, 2e) electron momentum spectrometer with the non-coplanar symmetric kinematics, and the orbital electron density contour image and binding energy spectrum of C_2H_4 have been provided. Comparing the experimental HOMO electron momentum distributions with the theoretical calculations at different impact energies, we can observe that the PWIA method is valid in the lower momentum region (below ~ 1.0 a.u.) at a wide range of impact energies from 400 to 1600 eV. In addition, the good agreements between experimental data and theoretical calculations, using DFT-B3LYP method with 6-311++G** basis set indi-
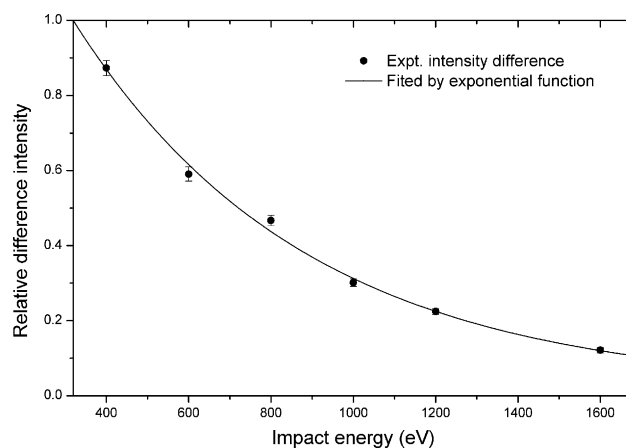

Fig. 4. The intensity differences of the HOMO orbital electron momentum distributions as a function of impact energy, which is defined to be the sum of the differences between experimental data and PWIA theoretical calculation using B3LYP/6-311++G** basis set within the momentum range from 1.0 to 1.6 a.u.

cate that the calculation including the dynamic electron correlation effects with the saturated diffuse and polarization basis set, is essential for accurate description of the ethylene HOMO in the chemically important larger r (lower p) region. The significant 'turn up' effects of EMS cross sections in $1b_{3u}$ HOMO of ethylene target are observed at the higher momentum region compared with the PWIA theory, which are mainly due to the distorted wave effects. And the observed distorted wave effects become smaller with the increase of the impact energies. Such variation of distorted wave effects as a function of impact energy could provide a further demonstration for the accuracy and validity of investigating the distorted effects in atoms and molecules using this newly developed (e, 2e) spectrometer.

Acknowledgments

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