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An investigation of the outer valance orbital electron density distribution of ethylene by electron momentum spectroscopy at 800 eV

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Abstract. Electron density distributions in momentum space of the outer valence orbitals of ethylene are measured by electron momentum spectroscopy (EMS) in a non-coplanar symmetric geometry. The impact energy was 800 eV plus binding energy (8–22 eV) and energy resolution of the EMS spectrometer was 0.95 eV. The measured experimental momentum distributions of the outer valence orbitals are compared with Hartree-Fock and Density Functional Theory (DFT) calculations. The shapes of the experimental momentum distributions are generally quite well described by both the Hartree-Fock and DFT calculations when large and diffuse basis sets are used, except for $1b_{3g}$ orbital. The experimental momentum profile of $1b_{3g}$ orbital clearly show remarkable "turn up" in the low momentum region comparing with theoretical calculation and experimental results at impact energy of 1200 eV.

PACS. 34.80.Gs Molecular excitation and ionization by electron impact

1 Introduction

Electron momentum spectroscopy (EMS), based on the binary $(e,2e)$ reaction, is now well established technique for the investigation of the valance electronic structure of atoms and molecules [1–6]. EMS can access the complete valance-shell binding energy range, though with lower resolution than that in most photoelectron spectroscopy (PES) studies, and the orbital electron density imaging information provided by EMS momentum profiles is unique. In particular, the electron momentum distribution information, obtained by the EMS technique, provides stringent tests for quantum chemical calculations at the Hartree-Fock (HF) level and also of correlated treatments such as Density Functional Theory (DFT).

The electronic structure of unsaturated doubly bonded hydrocarbon ethylene poses a challenging problem for quantum chemistry. Several EMS studies have been carried out for ethylene. The early EMS studies of ethylene by Dixon et al. [7], Coplan et al. [8], Tossell et al. [9] and Gorunganthu et al. [10], respectively. In these earlier measurements, the shapes of the experimental momentum profiles agreed qualitatively with results of modestly theory. The further studies of the complete valence shell were performed by Hollebone et al. [11] at impact energy 1200 eV and the energy resolution of the EMS spectrometer was 1.6 eV. From the results of Hollebone et al., the experimental momentum profiles can be described by HF and DFT calculations except $1b_{3g}$ orbital. There are an obvious discrepancy between the experimental results and the theoretical calculations for this orbital. The experimental cross-sections have a significant 'turn up' below the momentum $p \sim 1$ a.u.

In this paper, all outer valence orbital electron densities of ethylene are investigated. The experiments are carried out at impact energy 800 eV plus binding energy and the energy resolution FWHM is 0.95 eV. A higher resolution spectrometer is used in this work than earlier work. Theoretical momentum distributions are calculated by using the target Hartree-Fock approximation (THFA) and also with the target Kohn-Sham approximation (TKSA) [1–6]. The measured momentum profiles are compared with the HF and DFT calculations.

2 Theoretical background

In a binary $(e,2e)$ experiment, the scattered and the ionized electrons are detected at the same kinetic energies and the same polar angles in symmetric non-coplanar scattering geometry. The cross-section measurements are usually interpreted using the plane wave impulse approximation (PWIA). Considering the binary encounter approximation as well as the target Hartree-Fock approximation (THFA),

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the triple differential EMS cross-section for randomly oriented gas-phase targets is [1]

$$\sigma_{EMS} \propto \int d\Omega \left|\psi_j(p)\right|^2 \tag{1}$$

where $\psi_j(p)$ is the one-electron momentum space canonical Hartree-Fock orbital wavefunction for the jth electron that corresponds to the orbital from which the electron is ionized. The integral in equation (1) is known as the spherically averaged one-electron momentum distribution. To this extent, EMS has the ability to image the electron density in an individual orbital selected according to their binding energies.

The triple differential EMS cross-section has been reinterpreted [12] in the context of Kohn-Sham density functional theory and the Target Kohn-Sham Approximation (TKSA) supplies a result similar to equation (1) but with the canonical Hartree-Fock orbital replaced by a momentum space Kohn-Sham orbital $\psi_j^{ks}(p)$

$$\sigma_{EMS} \propto \int d\Omega \left|\psi_j^{ks}(p)\right|^2. \tag{2}$$

It should be noted that accounting for electron correlation effects in the target ground state is included in the TKSA via the exchange correlation potential. A more detailed description of the TKSA-DFT method could be found elsewhere [12].

In the present work, spherically averaged theoretical momentum profiles have been calculated for the outer valence orbitals of ethylene using the PWIA. The Hartree-Fock and DFT calculations were carried out using the Gaussian 98 program. The Hartree-Fock calculations of the momentum profiles were performed by using equation (1) with the basis sets of STO-3G, 6-31G and 6-311++G**. The B3LYP functional [13–15] are used for the DFT calculations. Two basis sets of 6-31G and 6-311++G** are used for the B3LYP calculations.

3 Experimental methods

A symmetric non-coplanar, energy dispersive, multichannel EMS spectrometer is used in this work and a detailed description of the spectrometer is given elsewhere [16]. The gas-phase target molecules (~10^{-5} torr) are ionized by impact electron beam. Two outgoing electrons (scattered and ionized) are optically retarded, selected energetically by electrostatic analyzers and detected in coincidence by microchannel plate position sensitive detectors mounted on two independent horizontal concentric turntables. In the symmetric non-coplanar scattering geometry, the two outgoing electrons are selected to have equal polar angles ($\theta_1 = \theta_2 = 45°$) relative to the forward scattered electron beam. One analyzer turntable is kept in a fixed position while the other is rotated by a computer controlled stepping motor. The coincidence energy resolution of the spectrometer was measured to be 0.95 eV FWHM. The experimental momentum resolution is estimated to be ~0.1 a.u. from a consideration of the argon $3p$ angular correlation. The purification of ethylene sample was better than 99.0%, and no evidence of impurities was found in the binding energy spectra.

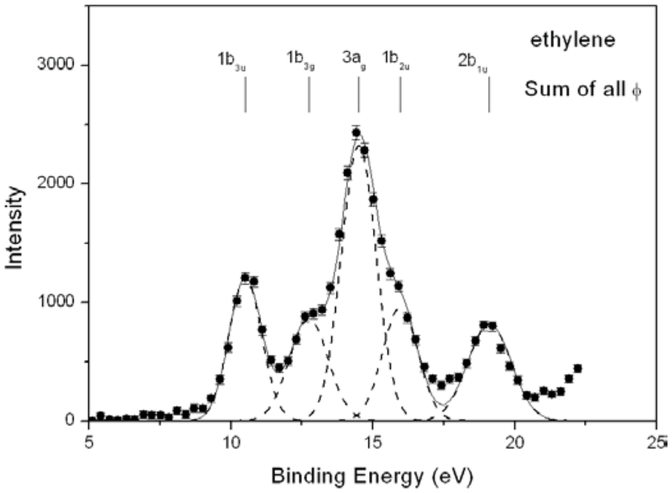

Fig. 1. EMS binding energy spectra of ethylene from 5 to 22 eV at summed over all seventeen ϕ angles, obtained at an impact energy of (800 eV + binding energy). The dashed lines represent Gaussian fits to the peaks and the solid curve is the summed fit.

4 Results and discussion

The point group symmetry of ethylene is D_{2h}. According to the molecular orbital theory, the ground state electronic configuration can be written as

$$core 2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 1b_{3g}^2 1b_{3u}^2.$$

To obtain the experimental momentum profiles, fourteen binding energy spectra over the energy range of 5–22 eV were collected at the out-of-plane azimuthal angles $\phi = -1°$, $0°$, $1°$, $2°$, $3°$, $4°$, $5°$, $7°$, $9°$, $11°$, $13°$, $16°$, $21°$ and $26°$ in a series of sequential repetitive scans. The valence shell binding energy spectrum of ethylene in the range of 5–22 eV for the summation over all the ϕ angles at the impact energy of 800 eV plus the binding energy is shown in Figure 1. The spectra in Figure 1 were fitted with a set of individual Gaussian peaks whose widths are in combination of the EMS instrumental energy resolution and the corresponding Franck-Condon widths derived from high resolution PES data [17]. The energy scale in Figure 1 was calibrated with respect to the $(1b_{3u})^{-1}$ vertical ionization potential from PES data. The dashed lines indicate the fitted Gaussians for individual peaks while the solid line represents the sum. The measured ionization potentials of this work and early published data [11,17,18] are compared in Table 1.

Experimental and theoretical spherically averaged momentum profiles have been obtained for the outer valence orbitals of ethylene. Experimental momentum profiles

Table 1. Ionization energies (eV) for ethylene.

orbital	EMS[a]	PES[b]	XPS[c]	EMS[d]
$1b_{3u}$	10.51	10.68	10.51	10.51
$1b_{3g}$	12.75	12.80	12.85	12.8
$3a_g$	14.51	14.80	14. 66	14.7
$1b_{2u}$	15.97	16.00	15.87	15.9
$2b_{1u}$	19.11	19.10	19.23	19.1

[a] This work, [b] from reference [17], [c] from reference [18], [d] from reference [11].

are extracted from the sequentially obtained, angular-correlated, multichannel (binning mode) binding energy spectra, and therefore the relative normalizations for the different transitions are maintained. Various theoretical momentum profiles (TMPs) of the valence orbitals are obtained as described above. The finite experimental momentum resolution ($\Delta p \sim 0.1$ au) is also folded into the TMPs by using the GW-PG method [19]. The experimental and the theoretical momentum profiles have been placed on a common intensity scale by normalizing the experimental data for the HOMO ($1b_{3u}$) orbital to the B3LYP/6-311++G** TMP in Figure 2. The same normalization factor obtained in this procedure is then used for each individual orbital for all experimental and theoretical comparisons.

The theoretical and experimental momentum profiles of all the outer valence orbitals of ethylene are presented in Figures 2–6 using the above normalization. In the following discussion the comparisons between the theoretical calculations and the experimental data in this work (dot in Figs. 2–6) are provided. The experimental results of Hollebone et al. [11] (triangle) are also shown in Figures 2–6 for comparison.

The HOMO of ethylene is associated with the $1b_{3u}$ electrons peaked at 10.51 eV in Figure 1. The orbital has a p-type momentum shown in Figure 2. As can be seen, DFT and HF calculations with basis 6-311++G** model the XMP well in both intensity and shape. The other three calculations can not well describe the XMP, especially HF with STO-3G. The better quality of wavefunction is, the closer agreement with the experimental data gets. The experimental results at 800 eV are agreement with experimental results at 1200 eV.

The XMPs of the orbital $1b_{3g}$ located at 12.75 eV in Figure 1, which is interesting due to the fact that it is a π^* orbital, is shown in Figure 3 with the theoretical momentum profiles (TMPs). A 'p-type' momentum distribution is predicted by all of the calculations. As can be seen in Figure 3, in the momentum region from 1.0 to 2.0 a.u., DFT-B3LYP and HF methods with 6-311++G** and 6-31G basis sets well describe the experimental data in both intensity and shape, and model the experimental momentum profile very well. However, there is a significant discrepancy between experiment and theory in the low momentum region. The experiment data have a significant 'turn up' below $p \sim 1$ a.u. and all calculations underestimate the experimental intensity in the momentum range.

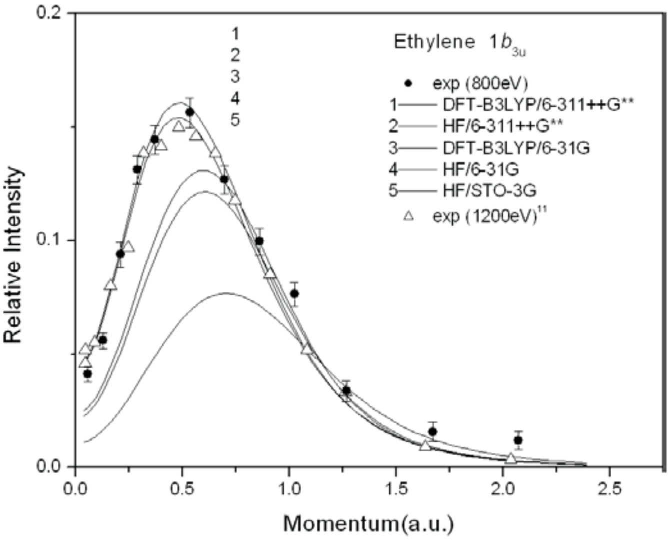

Fig. 2. The experimental momentum distribution in present work (dot) and from reference [11] (triangle) compared with theoretical calculations for the orbital $1b_{3u}$ of ethylene.

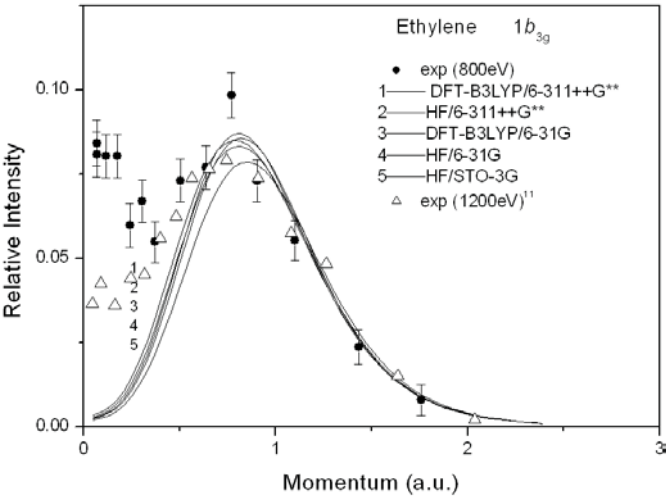

Fig. 3. The experimental momentum distribution in present work (dot) and from reference [11] (triangle) compared with theoretical calculations for the orbital $1b_{3g}$ of ethylene.

A similar 'turn-up' phonominon in the experimental momentum profiles of the $1b_{3g}$ orbital of ethylene in the low momentum region was also observed at the impact energy of 1200 eV (triangle in Fig. 3). The "turn up" phenomena of the $1b_{3g}$ orbital is more evident at impact energy 800 eV than 1200 eV, a strong 'sp-type' is demonstrated. The discrepancy between the experimental results and the theoretical calculations could be considered the distorted wave effects. Unfortunately, the distorted wave effects can not be calculated for molecules till now. A possible clue for understanding the observations here may be found on the Cr $3d$ ionization process [20], which is know as the only case where distorted wave effects in the low momentum region have been verified by theoretical calculations. And Brion et al. [20] proposed an interpretive model that such unexpected "turn up" is due to the high angular momentum

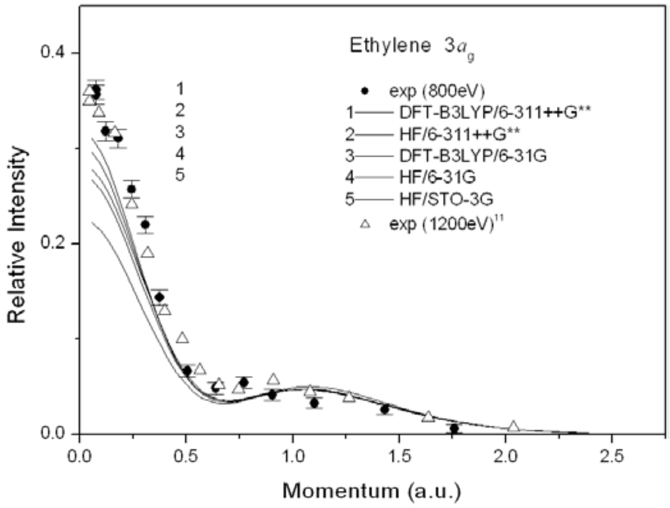

Fig. 4. The experimental momentum distribution in present work (dot) and from reference [11] (triangle) compared with theoretical calculations for the orbital $3a_g$ of ethylene.

effects and the even-parity nature of an atomic d orbital. Furthermore, they suggested that similar effects may occur for atomic d- or π^*-like molecular orbitals in diatomic and small polyatomic molecules that exhibit gerade type symmetry [21]. Clearly, the $1b_{3g}$ orbital of ethylene is of gerade type and the discrepancy of the low momentum region could be explained using the interpretive model of Brion et al. [20].

Furthermore, the interaction of the electron and the target is strong with the decrease of incident electron energy, and the distorted wave effect of low momentum region expects notable. Comparing the cross-section at 800 eV impact energy with that at 1200 eV, see Figure 3, the results support the theoretical prediction.

Experimental and theoretical momentum profiles for $3a_g$ orbital, peaked at 14.51 eV in Figure 1, are shown in Figure 4. Both experimental and theoretical momentum profiles show 's-type' distributions. The theoretical calculations are nevertheless quite well model the XMP over the entire momentum range. However, experimental momentum profiles are agreement well between impact energy 800 eV and 1200 eV.

The orbital $1b_{2u}$ is located at 15.97 eV in Figure 1, The orbital has a 'p-type' distributions shown in Figure 5, and all theoretical calculations model the XMP well. The experimental momentum profiles are also agreement well between impact energy 800 eV and 1200 eV.

Experimental and theoretical momentum profiles for orbital $2b_{1u}$, located at 19.11 eV, are shown in Figure 6. The orbital $2b_{1u}$ also shows a 'p-type' momentum distribution, and experimental results at two different impact energies are consistent. The calculated momentum profiles from HF and DFT give a similar shape with the XMP, but higher in intensity than the XMP. This discrepancy has been discussed in reference [11].

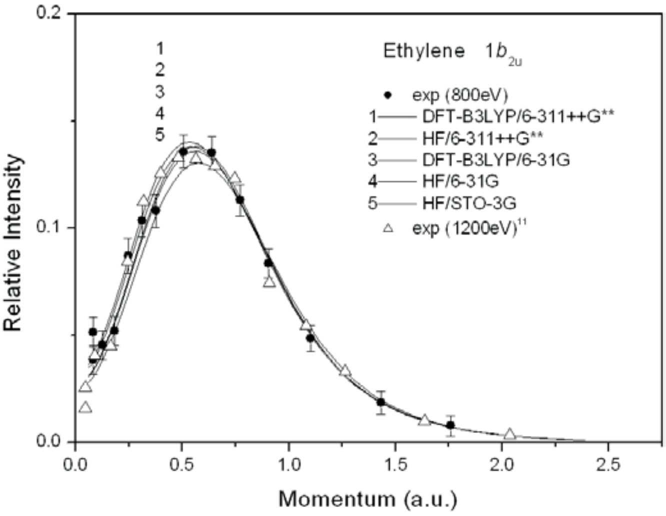

Fig. 5. The experimental momentum distribution in present work (dot) and from reference [11] (triangle) compared with theoretical calculations for the orbital $1b_{2u}$ of ethylene.

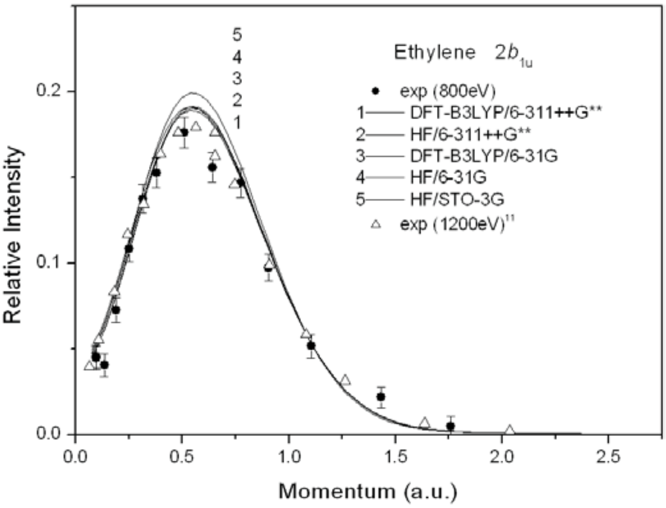

Fig. 6. The experimental momentum distribution in present work (dot) and from reference [11] (triangle) compared with theoretical calculations for the orbital $2b_{1u}$ of ethylene.

5 Summary

In summary, the detailed experimental and theoretical investigations of all outer valence orbital electron densities of ethylene by electron momentum spectroscopy at impact energy 800 eV are reported. The experimental momentum distributions are compared with the associated calculations and experimental results at impact energy 1200 eV. The binding energies are in excellent agreement with previously published PES data. The experimental momentum profiles are described by Hartree-Fock 6-311++G**, 6-31G and STO-3G calculations and Density Functional Theory calculations using B3LYP function. A strong discrepancy between theoretical calculations and experimental data is observed for the momentum distributions of the $1b_{3g}$ orbital in the low momentum region due possible to distorted wave effects. From the discussion of outer valence orbitals $1b_{3u}$, $1b_{3g}$, $3a_g$, $1b_{2u}$ and $2b_{1u}$, we can see that the experimental momentum profiles of these orbitals except orbital $1b_{3g}$ are agreement well at impact energies 800 eV and 1200 eV, and can be modelled well by theoretical calculation, i.e. the PWIA model the XMP well at impact energy both 800 eV and 1200 eV. However, for orbital $1b_{3g}$, the experimental momentum profile can not be described by the PWIA.

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