Direct Observation of Distorted Wave Effects in Ethylene Using the (*e*,2*e*) Reaction

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We report here the direct measurements of electron momentum distributions for ethylene using the (*e*,2*e*) reaction at different impact energies from 400 to 2400 eV. The "turn up" effects in the (*e*,2*e*) cross sections of the $1b_{3g}$ orbital compared with the plane-wave impulse approximation calculations were observed at low and high momentum regions, and such discrepancies become smaller with the increase of the impact electron energies. It is suggested that the observed discrepancies are due to the distorted-wave effects in molecules, while appropriate theoretical calculations using distorted waves in molecules could not be achieved until now.

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Binary (*e*,2*e*) spectroscopy, or electron momentum spectroscopy (EMS), is now a well developed tool for the investigation of the electronic structure and electron correlation effects of atoms and molecules due to its unique ability to measure the orbital momentum distribution for binding energy selected electrons [1–3]. It is an electron impact ionization experiment in which kinematics all of the electrons are fully determined by coincident detection of two outgoing electrons. In (*e*,2*e*) reactions the interaction of the external electrons with the remainder of the system can be accounted by using several reaction approximations. One of these is the plane-wave impulse approximation (PWIA), in which the transfer of momentum to the residual ion is assumed to be due only to the momentum of the target electron at the instant of collision. Another approximation is the distorted-wave Born approximation or the distorted-wave impulse approximation (DWBA or DWIA), in which the motion of the external electrons is represented by elastic-scattering functions, calculated in a distorted potential, rather than by plane-wave functions.

The PWIA is adequate to describe the experimental results on atoms and molecules at the momentum (p) region of below 1.0 a.u. from the previous EMS measurements [1,2]. Some discrepancies between PWIA calculations and EMS measurements at the high momentum region have been observed and well understood by the distorted-wave effects [1,4]. Recently, some unexpected "turn up" in the (*e*,2*e*) cross sections have been observed at the low p region for the atom xenon 4d ionization process [5,6] and some particular molecular orbitals (π^*-like in character) [7,8]. The discrepancies for the atomic d orbital have been explained by the distorted-wave effects. However, the observed discrepancies in molecules have not been clarified, because the molecular DWIA theory could not be achieved due to the multicenter nature of molecule targets. Confirmation that the observed discrepancies are caused by distorted-wave effects would require a wide range of experimental impact energies, which is difficult in EMS experiments with previous spectrometers, or a molecular DWIA theory [8]. A solution to the experimental problem has been achieved via our recent development in the high performance of EMS spectrometer.

In this new EMS spectrometer a novel double toroidal analyzer equipped with a series of conical deceleration lenses are used for electron energy and angle analyzing, and electron position detection and data acquisition are realized by using a pair of wedge strip anode position sensitive detectors with a Universal Serial Bus multiparameter data-acquisition system [9]. The typical energy and time resolutions of 1.2 eV and 2 ns, and the θ and ϕ angle resolutions of $\pm 0.7^\circ$ and $\pm 1.9^\circ$, are achieved from the EMS measurements of argon and helium. The significant improvement in the coincidence count rate wins the ascendancy in the experimental periods. Typically, to obtain orbital electron density distributions with enough statistics, the experimental period of time with conventional EMS is about 2–3 weeks (day and night), however only 2–3 hours are needed by using this new spectrometer. Furthermore, the measurements within a wide range of impact energies (400–2400 eV) have been achieved by using this new EMS spectrometer, which has made it possible to convincingly investigate the molecular distorted-wave effects in detail.

In this Letter, the turn up effects of the $1b_{3g}$ orbital EMS cross sections occurring at low and high p region in ethylene (C_2H_4) were observed using the (*e*,2*e*) reaction at different impact energies of 400, 600, 800, 1000, 1200, 1600, 2000, and 2400 eV. The imagings of orbital electron density distributions in ethylene have been directly obtained. The $1b_{3g}$ orbital momentum distributions are provided as a function of impact energy. The theoretical calculations were carried out using PWIA, while the molecular DWIA theory could not be achieved due to the multicenter nature of molecule targets, which is also another motivation of the promotion of molecular distorted-wave theory by means of the impact energy dependence of the orbital momentum distributions, such as $1b_{3g}$ orbital in ethylene.

In our EMS experiment a symmetric noncoplanar kinematic is used. An incident electron of energy E_0 causes the ionization of the target system and the scattered and ionized electrons are subsequently detected in coincidence at the same kinetic energies and the same polar angles, i.e., $E_1 \approx E_2$, and $\theta_1 = \theta_2 = 45°$. In this kinematic arrangement the ionized electron essentially undergoes a clean "knockout" collision, and the DWIA can provide a description of the collision [1,5]. In the DWIA, the $(e,2e)$ cross section for randomly oriented targets is given by

$$\sigma_{(e,2e)} = 2\pi^4 \frac{p_1 p_2}{p_0} \sigma_{\mathrm{Mott}} \int d\Omega |\langle \chi^{(-)}(p_1)\chi^{(-)}(p_2)\psi_f^{N-1}|\psi_i^N \chi^{(+)}(p_0)\rangle|^2, \tag{1}$$

where σ_{Mott} is the Mott scattering cross section. $|\psi_f^{N-1}\rangle$ and $|\psi_i^N\rangle$ are the total electronic wave functions for the final ion state and the target molecule ground (initial) state, respectively. p_0, p_1 and p_2 are momenta for the incident and the two outgoing electrons, respectively. $\chi^{(-)}(p_1)$, $\chi^{(-)}(p_2)$, and $\chi^{(+)}(p_0)$ are distorted waves for the two outgoing and incoming electrons, respectively. Distorted-wave effects allow for the influence (distortion) of the incoming and outgoing electron waves by the target and the ion, which can be investigated using Eq. (1) if the wave function of the target and ion are known with high accuracy.

Within the PWIA the distorted waves are replaced by plane waves for the incoming and outgoing electrons and the $(e,2e)$ cross section is given by

$$\sigma_{(e,2e)} = 2\pi^4 \frac{p_1 p_2}{p_0} \sigma_{\mathrm{Mott}} \int d\Omega |\langle p\psi_f^{N-1}|\psi_i^N\rangle|^2, \tag{2}$$

where p is the orbital (ionized) electron. Since the kinematic factors preceding the integral in Eq. (2) are essentially constant [1,2], accurate electronic structure information for the target and ion can be obtained by using the $(e,2e)$ spectroscopy.

The typical ethylene (C_2H_4) orbital electron density distribution was directly observed, as shown in Fig. 1(a), at an impact electron energy of 1000 eV with 100 eV passing energy in the analyzer. This three-dimensional image represents dependences on energy momentum for densities of ethylene valence electrons and contains the information on relative intensities, momentum distribution, symmetries of the states involved, and satellite structures. The orbital symmetry and its binding energy spectrum can be directly and accurately obtained with this image. From the intensity distribution along the binding energy axis the binding energy spectrum is obtained at a different angle ϕ, i.e., electron momentum. On the other hand, the orbital electron density distributions can be obtained along the ϕ angle axis at a given binding energy region (representing an individual orbital). Figure 2 shows the binding energy spectra for an individual azimuthal angle of (a) $\phi = -11°$ and (b) the sum of all angles, which are directly obtained from the three-dimensional image. The spectra include 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. The spectra of the highest occupied

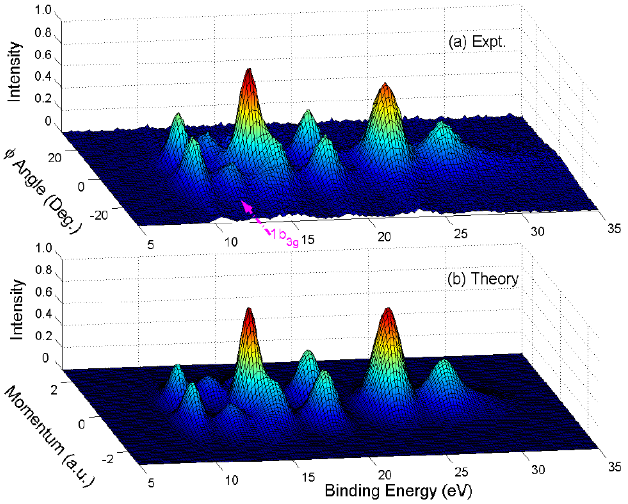

FIG. 1 (color online). The orbital electron density distributions for the ethylene. (a) Experimental orbital electron density obtained at the impact energy of 1000 eV and (b) theoretical calculation using DFT in PWIA.

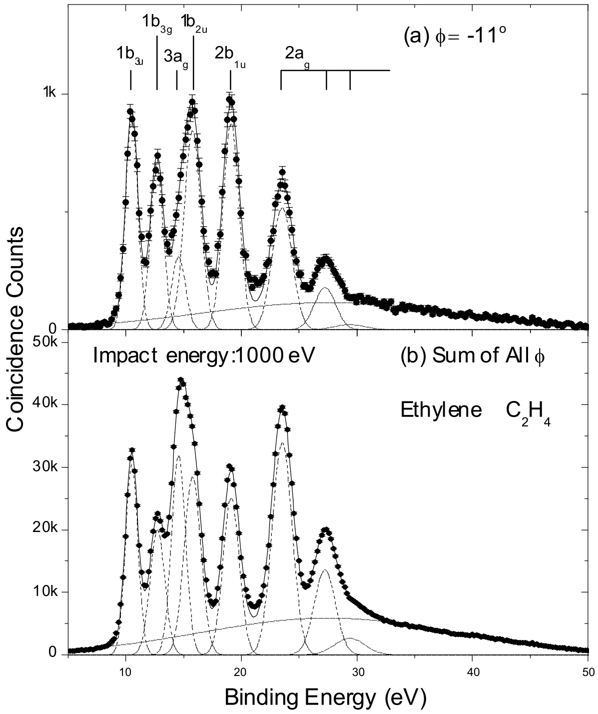

FIG. 2. Binding energy spectra of ethylene at (a) $\phi = -11°$ and (b) summed over all ϕ angles, obtained at impact electron energy of 1000 eV. The dashed lines represent Gaussian fits to the peaks and the solid curve is the summed fit.

molecular orbital $1b_{3u}$ ionization states are well reproduced by the Gaussian curves with FWHM about 1.2 eV.

The theoretical image of the ethylene orbital electron density distribution is obtained using density functional theory (DFT-B3LYP) method in PWIA, as shown in Fig. 1(b). Comparing the experimental ethylene orbital electron density image [Fig. 1(a)] with the theoretical calculation [Fig. 1(b)] we can observe somewhat of a turn up effect at the low p region of the $1b_{3g}$ orbital in the experimental image. In order to give a convincing experimental proof of this effect we measured orbital electron density images of ethylene at different impact electron energies of 400, 600, 800, 1000, 1200, 1600, 2000, and 2400 eV. Convincing investigations of the turn up caused by distorted-wave effects at the low p region would require a wide range of impact energies in experiments as suggested by Brion and co-workers [8]; it is difficult in conventional EMS experiments. The experimental electron momentum distributions and the theoretical calculations of the $1b_{3g}$ orbital at these impact electron energies are shown in Fig. 3. The theoretical momentum distributions were calculated within target Hartree-Fock and Kohn-Sham approximations using the HEMS program developed at UBC [7], the position space molecular orbitals were calculated by using the GAUSSIAN 98W suite program [10] with a molecular geometry in Ref. [11]. For comparing with the experimental measurements, 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. [12]. The significant turn up effects of the $(e,2e)$ cross sections compared with the PWIA theoretical results at high and low p regions have been observed, and such turn up effects become smaller with the increase of the impact electron energies in the $(e,2e)$ reaction, which could be subjected to some particular effects that current theoretical treatments have not given full consideration, such as the distorted-wave effects.

The occurrence of distortion effects of the $1b_{3g}$ orbital in ethylene at high p region can readily be understood since this region of the electron momentum profile involves significant penetration by the incoming electron into the smaller r region, near the nucleus. This is confirmed by both experiments and calculations [4] in that such distortion effects at the high p region become smaller with the increase of the impact energies for atomic targets. Such effects can also dramatically increase $(e,2e)$ cross sections at the low p region in the particular case of atomic Xe $4d$, Cd $3d$, and Zn $3d$ orbitals [5,6,13,14]. It was amazing to see that the turn up effects occurred at the low p region since such regions of the electron density are normally considered to be located at larger r, i.e., far from the nuclei. The further comparison between the experimental electron momentum profiles for Xe $4d$, Zn $3d$, and Cd $4d$ orbitals and the theoretical calculations using DWIA and DWBA strongly suggest that these turn up effects of $(e,2e)$ cross sections in the low p region are due to the distorted-wave effects [5,6]. Furthermore, the DWIA calculations in Cr $3d$, Zn $3d$, Mo $3d$, Cd $4d$ orbitals at different impact energies [5] indicate that the magnitude of the turn up caused by distortion of the electron waves should decrease with the increase of the impact energies. A rational model has suggested that these low p distorted-wave effects arise from the gerade (even) nature of d ($l = 2$) atomic orbitals [5].

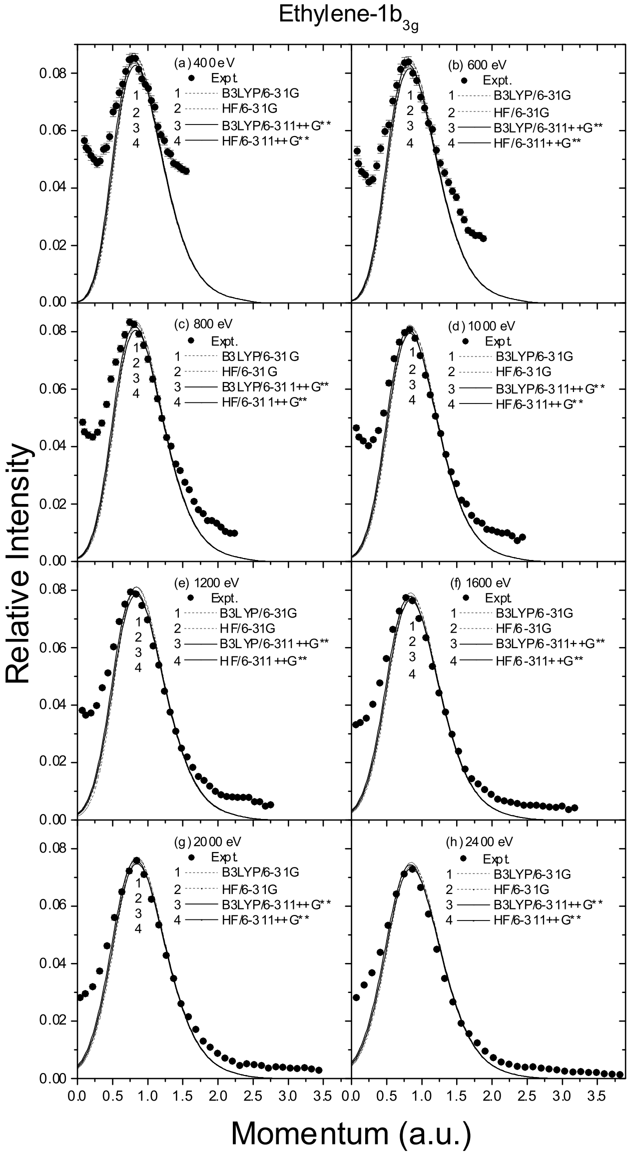

FIG. 3. The experimental orbital electron momentum distributions (dots) for the $1b_{3g}$ of ethylene at impact energies of (a) 400, (b) 600, (c) 800, (d) 1000, (e) 1200, (f) 1600, (g) 2000, and (h) 2400 eV compared with the theoretical calculations using DFT and Hartree-Fock methods in PWIA.

In our present $(e,2e)$ experiment for ethylene, the turn up effects of $1b_{3g}$ orbital have been observed at a wide range of experimental impact energies from 400 to 2400 eV as

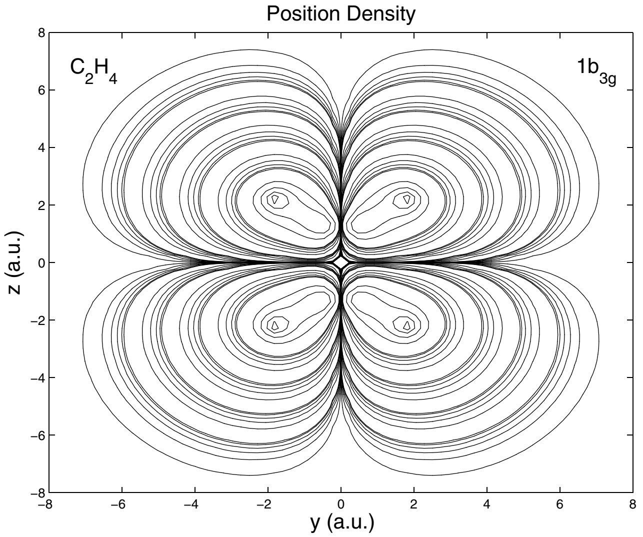

FIG. 4. Orbital wave function plot for ethylene $1b_{3g}$ in coordinate space.

shown in Fig. 3. The observed turn up effects of the $1b_{3g}$ orbital become smaller with the increase of the impact energies; such a phenomenon is consistent with the theoretical anticipations using distorted-wave theory in the nd atomic orbitals [5]. Considering the orbital wave function plot of $1b_{3g}$, as shown in Fig. 4, we can find that the $1b_{3g}$ orbital is d-like or π^*-like in character. Such particular molecular orbitals are similar to d-type atomic or π^* molecular orbitals with regard to symmetry. Therefore the observed turn up effects at the low p region of the ethylene $1b_{3g}$ orbital momentum distributions due to the distorted-wave effect could be confirmed. Unfortunately, the theoretical calculations using DWIA and DWBA in molecules cannot be achieved due to the multicenter nature of molecular targets until now.

In conclusion, the electron momentum profiles for the ethylene $1b_{3g}$ orbital at different impact energies of 400, 600, 800, 1000, 1200, 1600, 2000, and 2400 eV were measured by using our newly developed $(e,2e)$ EMS spectrometer. Typical three-dimensional images of electron density distributions for ethylene and binding energy spectra are obtained. The impact energy dependence of momentum profiles of the $1b_{3g}$ orbital are reported at a wide range of impact energy for the first time; significant turn up effects of EMS cross sections compared with the PWIA calculations in $1b_{3g}$ orbital are observed. With further consideration of the $1b_{3g}$ orbital symmetry it has been confirmed that such turn up at the low momentum region of EMS are due to distorted-wave effects. The developments of apropos theoretical calculations are expected for d-like or π^*-like orbitals in molecules.

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