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Distorted Wave Effects of the $1b_{3g}$ Orbital in Ethylene *

DENG Jing-Kang(邓景康)[1,2], LI Gui-Qin(李桂琴)[1,2], HUANG Jian-Dong(黄建东)[1], WANG Fang(王芳)[1],
NING Chuan-Gang(宁传刚)[1,2], LU Jie(卢杰)[1], HE Yao(何垚)[1], WANG Xiao-Dong(王晓东)[1],
ZHANG Yi-An(张亦安)[1], Gao Hong(高虹)[1], WANG Yan(王岩)[1], ZHENG Yan-You(郑延友)[1]
[1]*Department of Physics, Tsinghua University, Beijing 100084*
[2]*Key Laboratory for Quantum Information and Measurements, Ministry of Education*

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We study the unexpected distorted wave effects of the $1b_{3g}$ orbital in ethylene using a high resolution binary (e,2e) electron momentum spectrometer, at an impact energy of 800 eV plus the binding energy ($8-22$ eV) with symmetric non-coplanar kinematics. The experimental momentum profile of the $1b_{3g}$ orbital is obtained and compared with the data previously measured at an impact energy of 1200 eV plus the binding energy. Also, the experimental momentum profiles of the $1b_{3g}$ orbital are compared with the theoretical momentum distributions calculated by using Hartree–Fock and density functional theory methods. The experimental momentum profiles of the $1b_{3g}$ orbital of ethylene at different impact energies show that the cross section of the orbital below the momentum $p\sim 1$ a.u. is higher for lower impact energies.

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Electron momentum spectroscopy (EMS) is an effective technique for investigating the electronic structure of atoms, molecules, biomolecules and condensed matter. A detailed study of the kinematics of the income electron and two outgoing electrons in the binary (e,2e) scattering experiment allows additional information to be obtained from EMS. Not only can a binding energy spectrum be obtained in this manner, but also the triple-differential cross section for each peak in the binding energy spectrum can be determined. In particular, the EMS technique provides straight tests for quantum chemical calculations. The details of EMS experimental techniques and the associated theoretical analysis have been reviewed in detail elsewhere.[1-3] Under the conditions of high impact energy and high momentum transfer, the target electron essentially undergoes a clean "knock-out" collision and the distorted-wave impulse approximation (DWIA) provides a very good description of the collision.[1] In the DWIA, the binary (e,2e) cross section for randomly oriented gas-phase targets reads

$$\sigma_{\mathrm{EMS}} = (2\pi)^4 \left(\frac{p_1 p_2}{p_0}\right) \sigma_{\mathrm{Mott}} \cdot \left|\left\langle \chi^-(\boldsymbol{p}_1)\, \chi^-(\boldsymbol{p}_2)\, \psi_{\mathrm{f}}^{N-1} \right| \cdot \psi_{\mathrm{i}}^{N} \chi^+(\boldsymbol{p}_0) \rangle\right|^2, \tag{1}$$

where $\boldsymbol{p}_0$, $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ are the momenta for the incident and two outgoing electrons, respectively. ψ_{f}^{N-1} and ψ_i^N are the total electronic wavefunctions for the final ion state and target molecule ground (initial) state, respectively; $\chi^-(\boldsymbol{p}_1)$, $\chi^-(\boldsymbol{p}_2)$ and $\chi^+(\boldsymbol{p}_0)$ are the distorted waves for the two outgoing and one incoming electron, respectively; and σ_{Mott} is the Mott scattering cross section. The momentum of the orbital (ionized) electron, $\boldsymbol{p}$, is given by

$$\boldsymbol{p} = \boldsymbol{p}_0 - \boldsymbol{p}_1 - \boldsymbol{p}_2.$$

The momentum distribution can be well described by DWIA for atoms, but for molecules the calculation will be difficult due to the multi-centre potential problem. It is proven that, at reasonably high total energies, the distortion effects on the electron waves are apparently negligible and the plane-wave impulse approximation (PWIA) generally provides an adequate description of the binary (e,2e) cross sections. In the PWIA, the distorted waves are replaced by plane waves for the incoming and outgoing electrons and the cross section is given by[1]

$$\sigma_{\mathrm{EMS}} \propto S_{\mathrm{f}}^2 \int \mathrm{d}\Omega \left|\langle \boldsymbol{p}\psi_{\mathrm{f}}^{N-1} | \psi_{\mathrm{i}}^{N} \rangle\right|^2. \tag{2}$$

Equation (2) can be greatly simplified by using the target Hartree–Fock approximation (THFA). Within the THFA, only the final (ion) state correlation is allowed and the many-body wavefunctions ψ_{f}^{N-1} and ψ_{i}^{N} are approximated as independent particle determinants of the ground-state target Hartree–Fock (HF) orbitals in which Eq. (2) reduces to

$$\sigma_{\mathrm{EMS}} \propto S_j^{\mathrm{f}} \int \mathrm{d}\Omega \, |\psi_j(\boldsymbol{p})|^2, \tag{3}$$

where $\psi_j(\boldsymbol{p})$ is the one-electron momentum space canonical HF orbital wavefunction for the jth electron that corresponds to the orbital from which the electron is ionized, and S_j^f is the spectrum factor. The integral in Eq. (3) is known as the spherically averaged one-electron momentum distribution. To this extent, EMS has the ability to image the electron density in

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an individual orbital selected according to their binding energies.

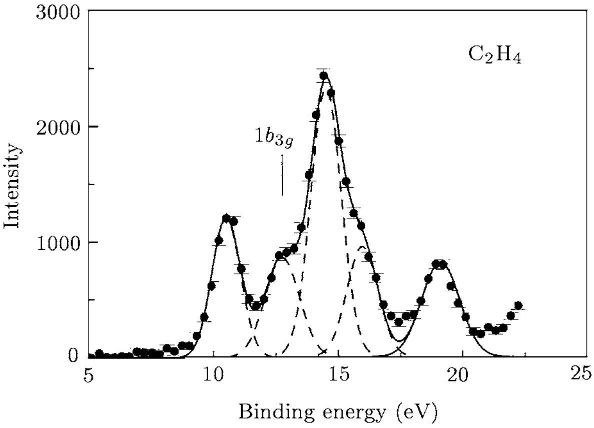

Fig. 1. Valence shell binding energy spectrum of ethylene for summation over all ϕ angles at an impact energy of 800 eV.

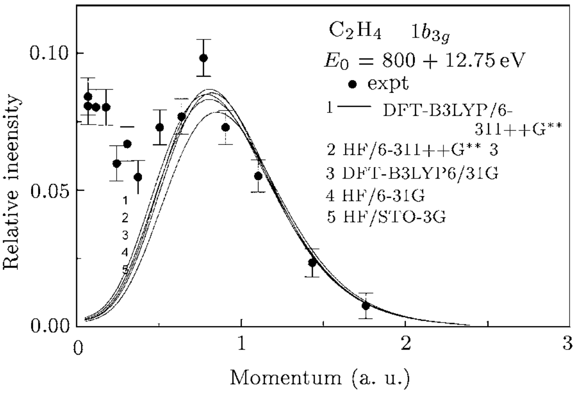

Fig. 2. Experimental momentum profiles of the $1b_{3g}$ orbital of ethylene at an impact energy of 800 eV, and the theoretical calculations.

Equation (2) has been re-interpreted[4] in the context of Kohn–Sham density functional theory (DFT). The target Kohn–Sham Approximation (TKSA) supplies a result similar to Eq.(3) but with the canonical HF orbital replaced by a momentum space Kohn–Sham orbital $\psi_j^{\mathrm{KS}}(\boldsymbol{p})$

$$\sigma_{\mathrm{EMS}} \propto \int \mathrm{d}\Omega \left|\psi_j^{\mathrm{KS}}(\boldsymbol{p})\right|^2. \tag{4}$$

It should be noted that the electron correlation effects on the target ground state is included in the TKSA via the exchange correlation potential. A more detailed description of the TKSA-DFT method can be found elsewhere.[4] In the PWIA, the results of the momentum spectrum, using the HF and DFT methods, are in agreement with the experimental results. However, unexpected effects in the binary (e,2e) cross sections at low momenta have recently been observed in EMS experiments with some molecules.[5,6] There is an obvious discrepancy between the experimental results and the theoretical calculations for orbital π^* (pseudo-π) of several molecules. The experimental cross sections have a significant turn up below the momentum $p{\sim}1$ a.u. One of the explanations for this phenomenon is due to distorted wave effects.[6] The reason why the distortion effect could arise at low momentum region, i.e. larger r, has been discussed in Ref. [6]. However, the calculation of distorted wave effects could not be applied to molecules at present. Further investigation for this explanation, i.e. the "turn up" of the experimental data caused by the distortion effect, can be carried out in an experimental manner. If the incident energy decreases, as we know, the interaction between the target and incoming electrons and the interaction between the target and the outgoing electrons increase, thus the distorted wave effects are enhanced. Inversely, the distorted wave effects decrease with the increasing impact energy. In this letter, we have investigated experimentally the distorted wave effects for the ethylene $1b_{3g}$ orbital at the impact energy of 800 eV plus the binding energy, which is different from the impact energy of 1200 eV used by other previous experiments.

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

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

In the experiment, electron impact ionization was carried out at an impact energy of 800 eV plus the binding energy (8 − 22 eV) under a symmetric noncoplanar geometry. Details of the spectrometer constructed at Tsinghua University have been reported previously[7] and only a brief description is given in this letter. Two hemispherical electron energy analysers, each having a five-element cylindrical retarding lens system, were mounted inside a μ-metal shielded vacuum system. The polar angles of both the analysers were fixed at 45°. One analyser turntable was fixed while the other was rotated to vary the relative azimuth angle. Each energy analyser had a position sensitive detector consisting of microchannel plates and a resistive anode in their energy disperse exit plane. The energy range of each analyser was set at $600 \pm 4\,\mathrm{eV}$ with a pass energy of 50 eV. The base pressure of the main vacuum chamber was about 4×10^{-5} Pa. The gaseous sample was introduced into the collision chamber located at the centre of the main chamber under the control of a variable leak valve. Under normal operation conditions, the ambient pressure was in the range lower than 10^{-3} Pa while the pressure in the collision region was estimated to be two orders of magnitude higher. The energy resolution of the spectroscopy, 0.95 eV in the full width at half maximum (FWHM), was measured directly by using helium as a calibration gas. The experimental momentum resolution is estimated to be better than 0.1 a.u. in consideration of the argon $3p$ angular correlation. The purification of the sample of ethylene was better than 99.9%, and no evidence of impurities was found in the binding energy spectra.

To obtain the experimental momentum profiles, fourteen binding energy spectra over the energy range of 8 − 22 eV were collected at the out-of-plane azimuthal angles $\phi = -1^\circ$, 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 8 − 22 eV for the summation over all the ϕ angles at the impact energy of 800 eV plus the binding energy is shown in Fig. 1. The spectra in Fig. 1 were fitted with a set of individual Gaussian peaks whose widths are a combination of the EMS instrumental energy resolution and the corresponding Franck–Condon widths derived from high-resolution PES data.[5] The dashed lines indicate the fitted Gaussians for individual peaks while the solid line represents the sum. The band located at 12.75 eV corresponds to the ionization of the $1b_{3g}$ orbital. For comparison, the valence shell binding energy spectrum of ethylene from 5 eV to 35 eV obtained in the (e,2e) reaction for summation over all the ϕ angles at the impact energy of 1200 eV plus the binding energy can be seen in Fig. 2(a) of Ref. [5], which was obtained by using a spectrometer with an energy resolution of 1.6 eV in FWHM. The use of a high-resolution spectrometer is favourable to recognize the experimental momentum profiles of the $1b_{3g}$ orbital specifically.

The theoretical calculations of the momentum profiles were carried out, based on Eqs. (3) and (4) by the HF and DFT methods with the basis set of 6-311++G** and 6-31G and HF/STO-3G. The keyword of the DFT calculation is B3LYP. The optimized geometry of ethylene has been used for all calculations. In order to compare the calculated cross sections with the experimental electron momentum profiles, the effects of the finite spectrometer acceptance angles in both θ and ϕ ($\Delta\theta = \pm 0.6^\circ$ and $\Delta\phi = \pm 1.2^\circ$) were included by using the Gaussian-weighted planar grid method.[8]

The experimental momentum profiles (XMPs) of ethylene have been extracted by deconvolution of the sequentially obtained angular-correlated binding energy spectra. The XMPs of the orbital $1b_{3g}$, which is interesting due to the fact that it is a π^* orbital, are shown in Fig. 2 with the theoretical momentum profiles (TMPs) calculated by using the DFT-B3LYP (curves 1 and 3) and HF (curves 2 and 4) methods with the 6-311++G** and 6-31G basis sets, respectively. Curve 5 is the result calculated by HF/STO-3G. A "p-type" momentum distribution with a node at zero momentum is predicted by all of the calculations, due to the symmetry of this predominantly C–H bonding orbital. As can be seen from Fig. 2, in the momentum region from 1.0 to 2.0 a.u., the better the quality of the wavefunction, the closer the agreement with the obtained experimental data. Curves 1 − 4 describe the experimental data well, 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 experimental data have a significant "turn up" below the momentum $p \sim 1$ a.u. and all calculations underestimate the experimental intensity in the momentum range. A similar "turn-up" phenomenon 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.[5] For comparison, the momentum profile of the orbital $1b_{3g}$ in ethylene at the incident energy of 1200 eV plus the binding energy can be seen in Fig. 5 of Ref. [5]. The inadequacies in the peak fitting and deconvolution procedure are excluded by comparing the theoretical and experimental results of the summation over all the outer valences, as discussed in Ref. [5]. The impossibility of a symmetry breaking due to the vibrational coupling is also discussed in the literature.[5] The discrepancy between the experimental results and the theoretical calculations could be considered due to the distorted wave effects. Unfortunately, the distorted wave effects could not be calculated for molecules until now, although the possibility of applying distorted wave calculations to molecules using static exchange potentials has been discussed recently.[9,10] However, the results of DWIA calculations for atoms Cr $3d$ and Mo $4d$ at 1200 eV supported the possibility that the "turn up" of intensity at low momentum for orbital π^* of the molecules is caused by the distortion effect.[6] According to the molecular collision theory, the lower the energy of the incident electron, the stronger the interaction of the electron and the target, and then the greater the magnitude of the distorted wave effect. The experimental data in Fig. 2 of this letter and Fig. 5 of Ref. [5] show that the cross section at the low momentum region is higher at an impact energy of 800 eV than that at 1200 eV. The distorted phenomenon is more evident with the intensity of the interaction, that is, with the decrease of the incident energy. The comparison of the experimental momentum profiles in this letter with those published previously[5] support the theoretical predictions.

References

[1] McCarthy I E and Weigold E 1991 *Rep. Prog. Phys.* **91** 789, and references therein

[2] Brion C E 1993 *Phys. Elec. At. Coll. Proc. XVIII ICPEAC* (AIP press) p 350, and references therein

[3] Zheng Y et al 1995 *Science* **270** 786

[4] Duffy P et al 1994 *Phys. Rev.* A **50** 4704

[5] Hollebone B P, Neville J J et al 1995 *Chem. Phys.* **196** 13

[6] Brion C E and Zheng Y et al 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** L223

[7] Deng J K, Li G Q et al 2001 *J. Chem. Phys.* **114** 882
Deng J K, Li G Q et al 2000 *Chin. Phys. Lett.* **17** 795

[8] Duffy P et al 1992 *Chem. Phys.* **159** 347

[9] Mazevet S, McCarthy I E et al *J. Phys. B: At. Mol. Opt. Phys.* **29** L901

[10] McCarthy I E and Rossi A 1994 *Phys. Rev.* A **49** 4645