Turn-up effects at low momentum for the highest occupied molecular orbital of oxygen at various impact energies by electron momentum spectroscopy

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The unexpected higher intensity at low momentum region in $(e, 2e)$ ionization cross sections, as called turn-up effect, was observed recently. This work systemically investigated this effect for the highest occupied molecular orbital of oxygen at various impact energies of 400, 600, 800, 1200, 1800, and 2400 eV by electron momentum spectroscopy. This turn-up became higher as the impact energy declined, which can be qualitatively predicted by the distorted wave explanation. However, it may be also due to some other dynamic interaction, such as the dynamic correlation. Since the oxygen molecule is the simplest multicenter system with such effects, this experimental result could be a test-bed for the accurate calculation of this effect in the molecular system.

I. INTRODUCTION

Electron momentum spectroscopy (EMS), also known as $(e, 2e)$ spectroscopy, is a powerful tool for investigating the electronic structure of matter. The basic principle of EMS is kinematically complete electron impact ionization, i.e., $(e, 2e)$ reaction. The differential cross section at sufficiently high energy is very sensitive to the energy-momentum density [1,2]. The observed momentum distributions (MD) can be directly compared with theoretical calculation under the assumptions of the Born, binary encounter, and plane wave impulse approximations (PWIA). This feature has made EMS have abilities to provide direct information for imaging of orbital electron densities and evaluating of basis sets and computational methods for quantum chemistry [3,4]. Recently, some unexpected discrepancies were observed between experimental and PWIA theoretical MDs at low momentum for atomic d orbitals and molecular π^* orbitals [5,6]. For atomic d orbital, the experimental MDs can be well-reproduced using the distorted wave impulse (DWIA) approximation instead of PWIA [7]. As an analogy, it is rational to ascribe this effect in the molecular system to the distorted wave effects, and this explanation can qualitatively predict the trend of turn-up as the impact energy varies. Unfortunately, the DW calculation for a molecule is too difficult due to the multicenter system now. Our motivation for this work is to systematically observe this effect in a simpler multi-center system, thus there are less difficulties for theoretical calculations. It is well-known that the highest occupied molecular orbital (HOMO) of oxygen is a typical π^* orbital, and it is also the simplest molecule with a π^* orbital. Moreover, the energy gap between HOMO and next HOMO is 4.4 eV, so the influence to the MD of HOMO from other orbitals can be totally ignored. The MD of HOMO was measured at various impact energies with our newly developed EMS spec-

trometer. These results could be an experimental test-bed for the further calculation in the molecular system.

II. METHODS

Our new EMS spectrometer has been described elsewhere [8], thus only a brief introduction is given here. With the double toroidal analyzer and the two-dimension position-sensitive detectors, the collection efficiency is about two orders of magnitude higher than that of our previous spectrometer [9,10], so the statistical accuracy and the reliability are improved significantly. The typical energy and time resolutions of 1.2 eV and 2 ns, and the θ and ϕ angle resolutions of ±0.7° and ±1.9° are achieved from the EMS measurements of argon and helium. The geometry arrangement of the spectrometer is symmetric noncoplanar. An incident electron of energy E_0 causes the ionization of the target system and the scattered and ionized electrons are detected in coincidence with the same kinetic energies and the same polar angles, i.e., $E_1 = E_2$, and $\theta_1 = \theta_2 = 45°$. In this kinematic arrangement, DWIA provides a good description of the collision. In the DWIA, the binary $(e, 2e)$ cross section for randomly oriented gas-phase targets is given by [1]

$$\sigma_{\text{EMS}} \propto \int d\Omega |\langle \chi^{(-)}(p_1)\chi^{(-)}(p_2)\Psi_f^{N-1}|\Psi_i^N\chi^{(+)}(p_0)\rangle|^2, \quad (1)$$

where Ψ_f^{N-1} and Ψ_i^N are the total electronic wave functions for the final ion state and the target molecule ground (initial) state, respectively. The 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 calculations 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 PWIA, the distorted waves are replaced by plane waves for the incoming and outgoing electrons and the $(e, 2e)$ cross section is simply given by [1]

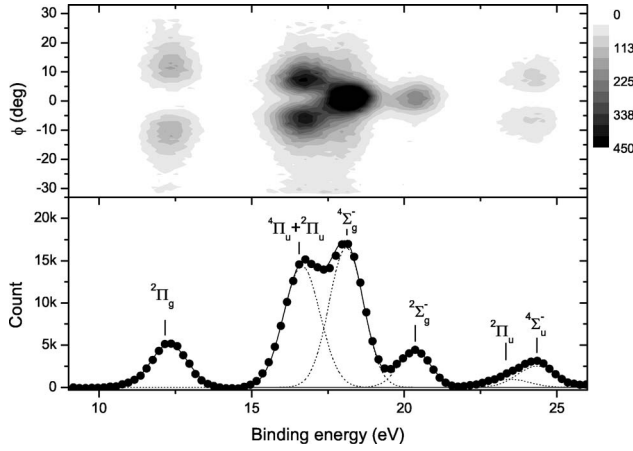*Corresponding author. Electronic address:
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FIG. 1. Angle resolved binding energy map (top) and summed over all ϕ angles (bottom) for O_2, obtained at an impact energy of 1200 eV. The dashed lines represent Gaussian fits to the individual peaks and the solid curve is the summed fit.

$$\sigma_{EMS} \propto \int d\Omega |\langle p\Psi_f^{N-1}|\Psi_i^N\rangle|^2. \quad (2)$$

The overlap of the ion and neutral wave functions in Eq. (2) is known as the Dyson orbital. The Dyson orbital can be directly calculated either by configuration interaction (CI) or by Green function (GF) methods, which are high demanding for computation power. The Dyson orbitals can be closely further approximated either with canonical HF orbitals (THFA), or with the Kohn-Sham orbitals of DFT (TKSA), then Eq. (2) is simplified as [11,12]

$$\sigma_{EMS} \propto S_i^f \int d\Omega |\psi_i(p)|^2, \quad (3)$$

where $\psi_i(p)$ is the momentum space canonical Hartree-Fock orbital or a momentum space Kohn-Sham orbital, and S_i^f is the pole strength. It should be noted that the correlation is included in the Kohn-Sham orbital through the exchange-correlation potential [13].

The electronic states of oxygen have been extensively studied by Rolke *et al.* [14,15] with EMS. The turn-up effect for HOMO $^2\Pi_g$ orbital at the low momentum region was observed at one impact energy of 1200 eV by them. Brion *et al.* suggested that it should be systematically investigated with a wide range of impact energies, thus the experiment was conducted at impact energies of 400, 600, 800, 1200, 1800, and 2400 eV. The oxygen gas with high purity of 99.99% was used.

III. RESULTS AND DISCUSSIONS

A typical experimental momentum-energy density map and the binding energy spectra for O_2 are shown in Fig. 1. It can be seen that the HOMO $^2\Pi_g$ is clearly resolved from other orbitals. The procedure of extracting experimental MDs from the density map can be found in our previous work [16]. KS and HF orbital MDs have been generated from DFT or HF calculations employing GAUSSIAN98 [17].
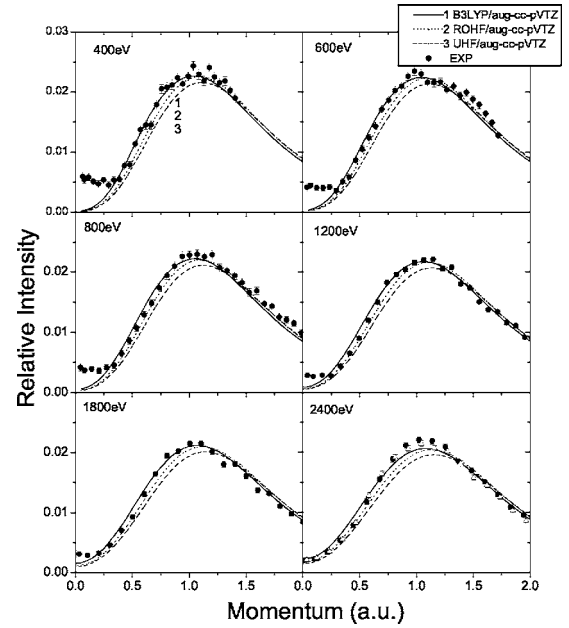

FIG. 2. Measured and calculated spherically averaged momentum distribution for HOMO orbital of O_2 at impact energy of 400, 600, 800, 1200, 1800, and 2400 eV. The open triangle legend represents the experimental data of an additional run at E_0=2400 eV. The calculated distributions have been convoluted with the experimental momentum resolution.

The ground state of O_2 is an open shell system, so the restricted open shell Hartree-Fock (ROHF) and unrestricted Hartree-Fock (UHF) methods have been used. The DFT calculations have been performed using the hybrid Becke-Perdew-3-parameters-Lee-Yang-Parr (B3LYP) functional (see GAUSSIAN98 manual [17] and references therein). Figure 2 illustrates the experimental MDs for HOMO $^2\Pi_g$ and compared calculations with ROHF, UHF, and DFT methods using standard Dunning's correlation consistent polarized valence basis sets of triple zeta quality augmented by diffusive functions (aug-cc-pVTZ) [18]. The turn-up at the low momentum region remarkably decreases as the impact energies increased from 400 to 2400 eV. The slight difference among these calculated MDs at different impact energies is due to that the momentum resolution is dependent on the impact energy. It can be seen that ROHF, UHF, and DFT theoretical methods generally well reproduce the experimental distribution except in the $p < 0.25$ a.u. region. Nevertheless, DFT and ROHF give some better description than UHF, which is in agreement with the conclusion of Rolke *et al.* [15]. Moreover, DFT appears to give the best depiction to the experimental MDs encompassing all the impact energies. It should be noted that all these theoretical calculations fail to reproduce the experimental turn-up at $p < 0.25$ a.u. at lower impact energy. According to Brion *et al.*, this turn-up was ascribed to the distorted wave effects [3]. The explanation is quite straightforward: the momentum $\boldsymbol{p}$ is related to the gradient of the position space wave function, and for a d-like orbital, the gradient at a given direction is close to zero in the near nuclear region, thus there are distorted wave effects at low momentum [6]. However, since the $\boldsymbol{p}$ is a vector which

has three components, the radial component of p close to zero does not imply that p is close to zero. Actually, the angular momentum L for an atom is a good quantum number, and $L=r\times p$, so the nearer to the nuclear region, the bigger the momentum. Moreover, the momentum operator is a localized operator which cannot directly generate the intensity distributions. Therefore, although the DW explanation can give some qualitatively correct prediction, it is not perfect and also not rigorous before the quantitative agreement between experiment and DW theory for a molecular system. It is interesting to note that Knippenberg *et al.* also observed a turn-up at the low momentum region for the HOMO orbital of norbornene (C_7H_{10}) [19]. However, their turn-up is the intrinsic property of the orbital, which can be well-described by PWIA calculation, not a dynamical process. Their results provided a good example of the high sensitivity of EMS for the low momentum cross section, and the validity of computational methods which is at the same level to that used in this work. Thus it is totally impossible that the unexpected turn-ups for HOMO of O_2, which were systematically investigated at various impact energies in this work, are due to an experimental artifact. The effects may also be possible due to some other dynamic interaction, such as the dynamic correlation [20]. It is well-known that the correlation usually manifests more remarkably at the lower energy and larger r (lower momentum) region. The accurate theoretical calculations for the unexpected turn-up effects at low momentum are expected to further disclose the nature behind this phenomenon.

In summary, the turn-up effects for the HOMO orbital of oxygen, which is the simplest molecule with a π^* orbital, were investigated with EMS at various impact energies. These results can be the test-bed for further theoretical calculations.

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