

Investigation of the highest occupied molecular orbital of 1,3-cyclohexadiene by a (e, 2e) spectrometer

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Abstract

We report here the first measurements of the momentum profile of highest occupied molecular orbital and the complete valence shell binding energy spectra of 1,3-cyclohexadiene with impact energies of 600, 1200 and 2400 eV by a binary (e, 2e) spectrometer. The turn-up at low momentum could not be described by plane wave approximation calculations, but can be accounted for using the distorted wave effects. In addition, the distorted wave effects well predicted the experimental trends at lower and higher impact energy.

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1. Introduction

Electron momentum spectroscopy (EMS), based on a binary (e, 2e) ionization reaction, has been shown to be a powerful and informative experimental tool for study of the electronic structure of atoms, molecules, biomolecules and condensed matter [1–3]. The unique ability of EMS to measure electron momentum distributions of individual molecular orbitals has made it become an important experimental technique for study electronic structures. The frontier orbital HOMO is very important for many chemical and physical properties. In other studies of structure–reactivity relations and molecular similarity and dissimilarity, Cooper and Allan [4] suggested that it would be interesting and potentially fruitful if momentum space was calculated on a HOMO/LUMO (the lowest unoccupied molecular orbital) rather than a total density basis. Our experimental result and related theoretical investigation for 1,3-cyclohexadiene provided the details of its HOMO electron density distributions information in momentum space.

The ability to covalently attach small organic molecules to semiconductor surfaces has gained significant interest in recent years [5,6]. Several groups have begun to study these reactions in hopes that these or similar methods can be employed in the production of new hybrid technologies for device minimization [7]. Among these reaction types, cycloaddition-type reaction involving the Si dimers and unsaturated organics is the important type, and it has been extensively investigated for using as molecular devices. 1,3-Cyclohexadiene can react with the Si(1 0 0) surface via its two C=C bonds, and its HOMO mainly concentrate on the two C=C bonds. The electronic states of 1,3-cyclohexadiene have been investigated by He I PES and various theoretical methods [8,9]. As to our best knowledge, this work is the first time EMS study about 1,3-cyclohexadiene.

In this Letter, we report the complete valence shell binding energy spectra (5–32 eV) of 1,3-cyclohexadiene and its HOMO electron momentum profile using EMS at an impact electron energy of 600, 1200 and 2400 eV plus binding energy with a symmetric non-coplanar geometry. The experimental momentum profile is compared with Hartree–Fock (HF) and density functional theory (DFT) calculations using various basis sets. The

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discrepancy between experiment and theory is explained qualitatively with the distorted wave effects.

2. Methods

Recently, we have developed a new type EMS spectrometer with two orders higher efficiency than our previous one [10,11]. The basic principle of EMS is an impact ionization reaction, where the gas phase target molecules are ionized by a high energy electron beam [1–3]. The outgoing electrons (scattered and ionized) are angle and energy selected by a toroidal energy analyzer and then detected in coincidence. The experimental geometry is symmetric non-coplanar, i.e. the two outgoing electrons are selected to have equal polar angles ($\theta_1 = \theta_2 = 45^\circ$, angle between the outgoing electron direction and the incoming electron beam direction). The azimuthal angles (ϕ , angle between the outgoing electron direction in the plane normal to the beam direction, and $\phi = 0$ is the scattering plane) from -38° to 38° are simultaneously measured, so the detect efficiency is much higher. The typical measurement period is only several hours, while the previous one needs about a month. Moreover, all binding energy spectra (BES) at different angles were collected at same time, so the effects of instabilities of the electron beam and gas sample intensity were greatly reduced.

A profile of differential cross-section versus recoil momentum for each energy resolved state of the target molecules could be obtained from these BES at different ϕ angles. Under the binary encounter requirements of high impact energy and high momentum transfer, the initial momentum p of the knocked-out electron can be shown by

$$p = \left\{ (2p_1 \cos \theta_1 - p_0)^2 + [2p_1 \sin \theta_1 \sin(\phi/2)]^2 \right\}^{1/2}, \quad (1)$$

where p_1 , p_2 ($p_1 = p_2$) are the momentum of each of the two outgoing electron, and p_0 is the momentum of the incident electron.

Under the plane wave impulse approximation (PWIA), the EMS binary (e, 2e) differential cross-section for randomly oriented gas-phase molecules is given by [3,12]

$$\sigma_{\text{EMS}} \propto S_j^f \int d\Omega |\psi_j(p)|^2, \quad (2)$$

where $\psi_j(p)$ is the independent-particle momentum space wavefunction for the j th electron that was ionized. S_j^f is called spectroscopic factor or pole strength. The integral in Eq. (2) is known as the spherically averaged one-electron momentum distribution. Therefore, EMS has the ability to image the electron density distribution in individual orbital selected according to their binding energies.

In EMS, the individual orbitals are selected by the binding (or ionization) energy. With the double toroidal energy analyzer used in the present work, BES are collected at different azimuthal angles ϕ at same time. Distributions as a function of angles ϕ are obtained by deconvolution of these BES using Gaussian functions located at each ionization energy. The widths of the Gaussian functions can be determined from a consideration of published PES vibronic manifolds and the instrumental energy resolution. For each ionization process, the set of areas of fitted peaks is plotted as a function of momentum which is calculated from ϕ using Eq. (1). To compare the experimental momentum distributions with the relative cross-sections calculated as a function of momentum using Eq. (2) above, the effects of the finite spectrometer acceptance angles in both θ and ϕ ($\Delta\theta \approx \pm 0.7^\circ$ and $\Delta\phi \approx \pm 1.9^\circ$) should be included. This was achieved with the Gaussian method [13] in this work.

The sample of 1,3-cyclohexadiene measured in this work was >97% purity, and several freeze–pump–thaw cycles were performed before using. No impurities were observed in the binding energy spectra.

3. Result and discussion

1,3-cyclohexadiene has C_2 point group symmetry and its electronic configuration in the ground state can be written as

$$(\text{core})^{12} (4a)^2 (5a)^2 (4b)^2 (5b)^2 (6a)^2 (7a)^2 (6b)^2 (7b)^2 (8a)^2 \\ (8b)^2 (9b)^2 (9a)^2 (10b)^2 (10a)^2 (11b)^2 (11a)^2.$$

In the ground state, the 44 electrons are arranged in 22 double-occupied orbitals in the independent particle description. All the molecular orbitals are either A or B symmetry. The binding energy for each valence orbital is obtained from He I PES data [8]. In the PES work, the vertical ionization potential of the 11a HOMO was 8.25 eV, and the 11b, 10a, 10b, 9a, 9b, 8b, 8a, 7b, 6b and 7a orbitals were determined to be 10.7, 11.3, 11.8, 12.7, 13.5, 14.0, 14.0, 14.9, 16.4 and 16.4 eV, respectively.

In the present EMS work, seven structures can be identified in the binding energy spectra of Fig. 1. The vertical ionization potential of HOMO 11a is determined to be 8.25 eV. Since the small energy separation among these orbitals, the averaged ionization potentials for 11b + 10a + 10b + 9a, 9b + 8b + 8a + 7b, 6b + 7a and 4b + 5b + 6a were determined as 11.1, 13.7, 16.4 and 19.2 eV, respectively. And 5a and 4a was given to be 23.1 and 25.5 eV, respectively. It should be noted that the average ionization energy in this work is pre-determined by PES, then is little shifted to have a best fitting of the summed energy spectra. The very broad structure

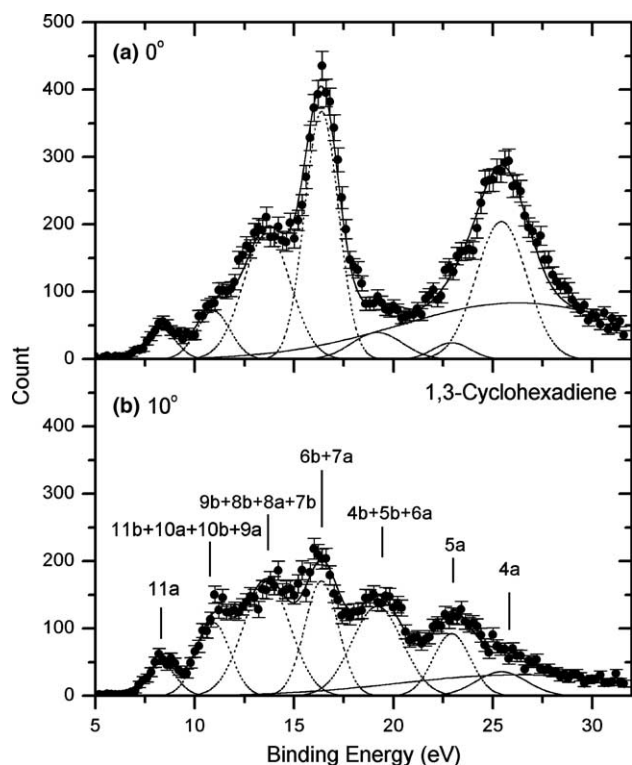


Fig. 1. Binding energy spectra of 1,3-cyclohexadiene at: (a) $\phi = 0^\circ$ and (b) $\phi = 10^\circ$ with 1200 eV impact energy plus binding energy. The dashed and solid lines represent individual and summed Gaussian fits, respectively.

with a peak at 26 eV in Fig. 1 is due to the residual backgrounds and close spaced satellite lines at high energy region. For two dimensions detectors, the background

could not be clear subtracted due to the marginal image distortion and the coincidental time spectrum structures. The differences in FWHMs of these peaks are due to the vibrational broadening of the lines.

To obtain the experimental momentum profiles, these BES were grouped under ϕ angles with a step 1° . The BES of 1,3-cyclohexadiene measured at the azimuthal angle $\phi = 0^\circ$ and $\phi = 10^\circ$ are shown in Fig. 1. The BES were fitted with a series of individual Gaussian peaks whose widths are combinations of the EMS instrumental energy resolution (FWHM = 1.1, 1.3, 1.5 eV at impact energy of 600, 1200 and 2400 eV, respectively) and the corresponding Franck–Condon widths derived from high-resolution PES data. The dotted lines fitted to Gaussian curves indicate the individual peaks, while the solid lines represent their sum fitted spectra.

The experimental momentum profiles were extracted by deconvolution of the same peak from the BES at different azimuthal angles. As Fig. 2 shows, the experimental momentum distributions of 1,3-cyclohexadiene HOMO 11a with the impact energy of 600, 1200 and 2400 eV are compared with various theoretical momentum profiles, which have incorporated the experimental instrumental angular resolutions. The slight difference between theoretical distributions at 600, 1200 and 2400 eV is due to that the experimental momentum resolution will become better at lower impact energy. The calculations were implemented in GAUSSIAN program. It can be seen that HF (curve 3 with 6-311++G** basis set, and curve 4 with 6-31G*) and DFT (B3LYP method, curve 1 with 6-311++G* basis set, and curve 2 with 6-31G*)

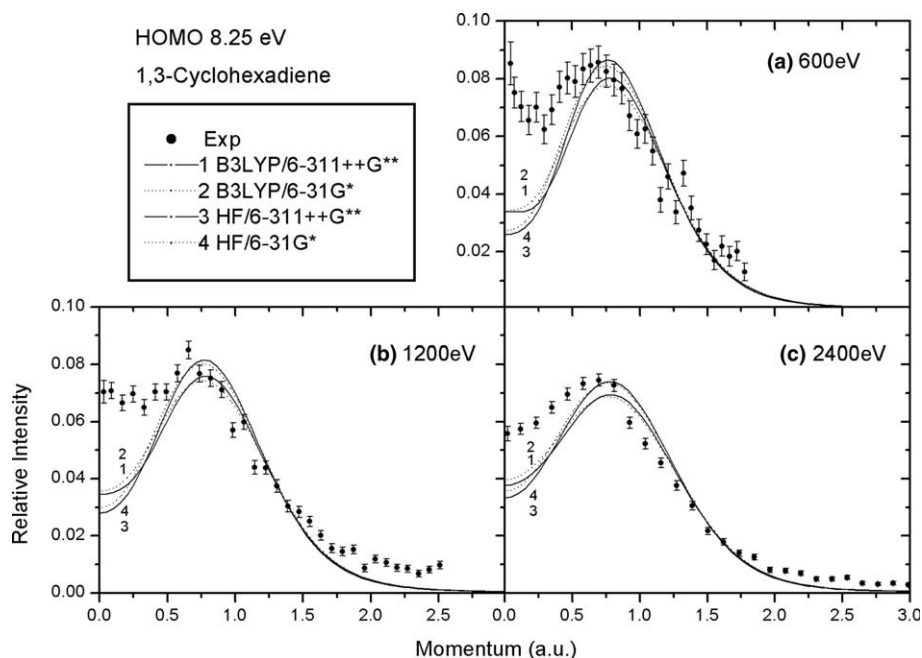


Fig. 2. Experimental and calculated momentum distributions for HOMO 11a orbital of 1,3-cyclohexadiene with: (a) 600 eV, (b) 1200 eV and (c) 2400 eV impact energy. The theoretical momentum profiles are calculated using HF (curves 3 with 6-311++G** basis set, and curves 4 with 6-31G*) and DFT (B3LYP method, curve 1 with 6-311++G* basis set, and curve 2 with 6-31G*).

(B3LYP method, curve 1 with 6-311++G** basis set, and curve 2 with 6-31G*) well describe the experimental result in region of $0.5 \text{ a.u.} < p < 1.5 \text{ a.u.}$ in Fig. 2b. However, in the regions of momentum lower than 0.5 a.u. and higher than 1.5 a.u. there is discernable discrepancy between experiments and calculations. It is not likely due to the leakage of intensity from neighboring orbitals because there is a 2.5-eV energy gap to the next orbital. Moreover, the next four orbitals are all p-type, which could only lower the turn-up if there was leakage. A possible explanation for this is the distorted wave effects. Generally, higher momentum transfer is contributed from the electron in nearer nucleus region, and lower momentum from further nucleus region, so the distortion will become more evident at higher momentum. Nevertheless, the smaller momentum transfer might also come from the nearer nucleus region in some d-like orbitals, such as π^* orbital [14–18], because the momentum is related to the gradient of the position space wavefunction: low momentum is corresponding to the low gradient of the position space wavefunction. For d-like orbitals, the gradient of wavefunctions is very low in the region near the nucleus [16]. So nucleus would distort the projectile electron more remarkably for lower momentum transfers on d-like orbitals, and PWIA is no longer applicable. The theoretical calculation shows that part of the 1,3-cyclohexadiene HOMO has d-like symmetry, which is mainly contributed from the two C=C bonds as Fig. 3 shows. To confirm this explanation, the experiment was carried out again at 600 and 2400 eV. It is expected that the discrepancy will become more evident at 600 eV than that of 1200 eV because the nucleus will distort the electron waves greater at lower impact energy, while less observable at 2400 eV. Consequently, as Fig. 2 shows, the distorted wave effect explanation predicts well the experimental trends. The quantitative calculation for distorted wave effects in molecular orbital is still a challenge for theorists by far due to the multi-center system.

4. Conclusion

4. Conclusion

In summary, we reported the first measurements of the complete valence shell binding energy spectra and momentum profile for 1,3-cyclohexadiene HOMO orbital by EMS. The experiment was conducted at impact energies of 600, 1200 and 2400 eV. The turn-ups at low momentum are not described by plane wave approximation calculations, but can be accounted for using the distorted wave effects. The distorted wave effects well predicted the experimental trends at lower and higher impact energies.

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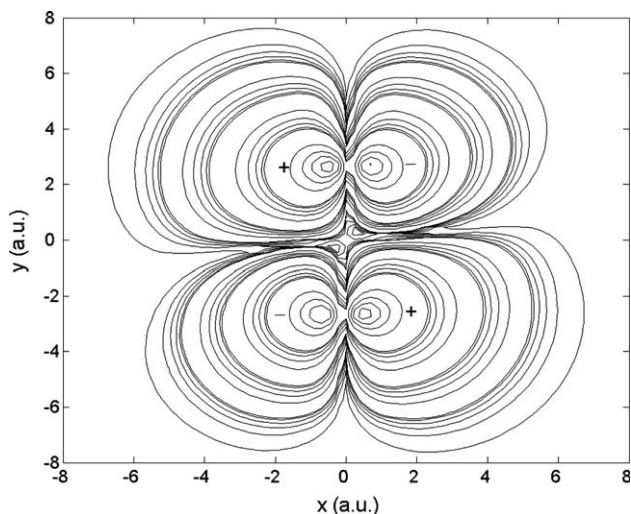


Fig. 3. Electron density map in position space of HOMO orbital of 1,3-cyclohexadiene calculated at DFT-B3LYP/6-31G level. The two C=C bonds are in the $x = 0$ plane in approximation.