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Investigation of the highest occupied molecular orbital of cyclohexene by electron momentum spectroscopy [☆]

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Abstract

We report here the first measurements of the frontier highest occupied molecular orbital (HOMO) momentum profile and the complete valence shell binding energy spectra of cyclohexene by a binary $(e, 2e)$ spectrometer using the non-coplanar symmetric kinematics. The experimental orbital electron momentum distribution is well described by the theoretical calculations.

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1. Introduction

Electron momentum spectroscopy (EMS), also known as binary $(e, 2e)$ spectroscopy, has proven to be a powerful tool for investigating the electronic structures of atoms, molecules and solids [1–3] due to its unique ability to directly obtain the spherically averaged electron density distributions in momentum space for individual orbitals. By comparing experimental momentum distributions with theoretical calculations, EMS can provide very detailed information on the binding energies, orbital electron density distributions and give powerful proof for evaluating the quality of quantum chemical calculations as well as testing the effect of electron correlation in atoms and molecules. Furthermore, EMS also provide information relevant to issues of chemical reaction and molecular

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recognition [4,5], and the momentum space electron density distribution, which is sensitive to diffuse parts of the position wave function, could be considered as a criterion for molecular similarity and dissimilarity [5].

Cyclohexene (1,2,3,4-tetrahydrobenze), C_6H_{10}, is a chemical raw material and organic solvent widely used for pharmaceuticals industry and chemical reaction reagent [6–9]. Cyclohexene is also one of the fundamental structures in the stereochemistry of organic compounds. Its molecular geometry and conformational characteristics were extensively investigated using various experimental [10–12] and theoretical [10,12–14] methods. The equilibrium conformation of cyclohexene is a half-chair with C_2 point group symmetry [13]. In the reaction chemistry, the frontier orbital HOMO as well as the lowest unoccupied molecular orbital (LUMO) electron density distribution of the reactant molecules plays a determining role in directing reactivity [15,16]. In this Letter, we report the first complete valence shell binding energy spectra (4–34 eV) of C_6H_{10} and its HOMO electron momentum profile using EMS at an impact electron energy of 1200 eV plus binding energy with non-coplanar symmetric geometry. Our experimental momentum profile is compared with Hartree–Fock (HF) and density functional theory (DFT) calculations using various basis sets.

2. Experimental and theoretical background of EMS

The experiment technology of EMS and the associated reaction theory have developed rapidly since the pioneer research by Neudachin et al. [17], Camilloni et al. [18] and McCarthy and Weigold et al. [19]. The EMS experiment is based on kinematically complete $(e,2e)$ collision experiment, which is an electron impact single ionization process initiated by electrons of energy so high that the target structure is determined independently of the incident energy [3]. The azimuthal angle is scanned to obtain a profile of differential cross section versus recoil momentum for each energy resolved state of the residual ion.

Within some approximations, including the plane-wave impulse approximation (PWIA), and the binary encounter approximation in which the residual ion is a mere spectator and hence the collision operator depends only on the incident and recoil electrons, the EMS cross section for randomly oriented molecules can be given [1–3] by,

$$\sigma_{\text{EMS}} \propto \int d\Omega \left|\left\langle p\Psi_f^{N-1} \middle| \Psi_i^N \right\rangle\right|^2. \tag{1}$$

Where p is the momentum of the target electron prior to knockout. $|\Psi_f^{N-1}\rangle$ and $|\Psi_i^N\rangle$ are the total electronic wave functions for the $N-1$ electron final ion state and the N electron initial (neutral) state, respectively. The overlap of the ion and neutral wave functions in Eq. (1) is known as the Dyson orbital while the square of this quantity is referred to as an ion–neutral overlap distribution (OVD). Thus, the $(e,2e)$ cross section is essentially proportional to the spherical average of the square of the Dyson orbital in momentum space [3].

By using the target Hartree–Fock approximation (THFA) [3] or the target Kohn–Sham approximation (TKSA) [20], in which the Dyson orbital is approximated with the neutral state canonical HF or KS orbital, the EMS cross section can be further simplified by

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

Where $|\psi_j(p)\rangle$ is the one-electron momentum space canonical HF or KS orbital wave function in the neutral initial state for the jth electron that was ionized. The integral in Eq. (2) is known as the spherically averaged one-electron momentum distribution (MD). Therefore EMS has the ability to image the electron density distribution in individual orbital selected according to their binding energies.

In the present Letter the EMS experiment was carried out using an energy dispersive multichannel electron momentum spectrometer, for which the details of construction and operation have been reported earlier [21]. The coincidence energy resolution of the spectrometer was measured to be 1.2 eV FWHM from the experiment on the argon 3p ionization.

The experimental momentum profiles (XMPs) were obtained by fitting the experimental binding energy spectra (BES) at each azimuthal angle and then converting the angular dependence of the area under each band into the momentum distribution [3]. The theoretical momentum profiles are obtained using the HF and DFT methods. The effects of the finite spectrometer acceptance angles in both θ and ϕ ($\Delta\theta = 0.6^\circ$ and $\Delta\phi = 1.2^\circ$) were also folded into the calculations. The cyclohexene sample ($> 99.0\%$ chemically purity) was used without further purification. No impurities were observed in the binding energy spectra.

3. Results and discussions

Cyclohexene (C_6H_{10}) has the C_2 point group symmetry according to the molecular orbital theory [13]. Its ground state electronic configuration can be written as,

$$(\mathrm{Core})^{12}\underbrace{(1a)^2(2a)^2(1b)^2(3a)^2(2b)^2}_{\text{inner valence}}$$

$$\underbrace{(3b)^2(4a)^2(4b)^2(5a)^2(6a)^2(7a)^2(5b)^2(6b)^2(8a)^2(9a)^2(7b)^2(8b)^2}_{\text{outer valence}}$$

In the ground state, the 46 electrons are arranged in 23 double-occupied orbitals in the independent particle description. All the molecular orbitals are either a-type or b-type. There is no degeneracy in these orbitals. The assignment of the order of occupation for these valence orbitals, both from the PES experiments and the molecular orbital calculations, has been discussed in Refs. [22,23].

The calculations of cyclohexene momentum profiles were carried out at the ab initio level, using the GAUSSIAN 98W together with the HEMS program developed by UBC. The instrumental angular (momentum) resolution was incorporated in the calculations using the UBC RESFOLD program based on the Gaussian weighted planar grid (GWPG) method [24].

To obtain the experimental momentum profiles, 12 binding energy spectra over the energy range of 4–34 eV were collected at the out-of-plane azimuthal angles ϕ, 0°, 1°, 2°, 3°, 4°, 6°, 8°, 10°, 12°, 14°, 16° and 21° in a series of sequential repetitive scans. The valence shell binding energy spectra (BES) of cyclohexene for measurements at the azimuthal angle $\phi = 1^\circ$ and $\phi = 12^\circ$ are shown in Fig. 1. Due to the energy resolution limitation of EMS spectrometer, only seven Gaussian peaks are fitted to the binding energy spectra for the 17 valence orbitals, as shown by dashed curves in Fig. 1, the solid curve represents the sum of these Gaussian peaks. The positions and widths of the Gaussian peaks are determined using the ionization potentials and Frank–Condon widths (folded with the present instrumental energy resolution of 1.2 eV) estimated from the high-resolution PES [22,23]. Small adjustments have been applied to compensate the asymmetries of the shapes of the Frank–Condon profiles.

The PES spectra of the outer valence orbital region have been reported by Bieri et al. [22] using He I radiation source. In the PES work, the vertical ionization potential of the 8b HOMO was 8.94 eV, and the 7b, 9a, 8a, 6b, 5b, 7a, 6a, 5a, 4b and 4a orbitals were determined to be 10.7, 11.3, 11.7, 12.8, (13.5), 13.2, 13.8, (14.5), 15.2 and 16.3 eV, respectively. These PES studies were extended by Streets and Potts et al. [23], which included some of the inner valence region of C_6H_{10}.

In the present EMS work, the vertical ionization potential of frontier HOMO 8b is determined to be 9.05 eV. The averaged vertical ionization potentials of the $(7b + 9a + 8a)$, $(6b + 5b + 7a + 6a + 5a + 4b)$ and $(4a + 3b)$ are determined to be 11.35, 13.33 and 15.89 eV, respectively. Some spectroscopic strengths above 27.5 eV in the binding energy spectra are observed which may due to correlation effects in the target or in the final state of residual ion.

The experimental momentum profiles (XMPs) were extracted by deconvolution of the same peak from the sequentially obtained binding energy spectra at different azimuthal angles [1–3]. The measurement of the cyclohexene HOMO 8b experimental momentum profile is shown in Fig. 2 together with the theoretical momentum

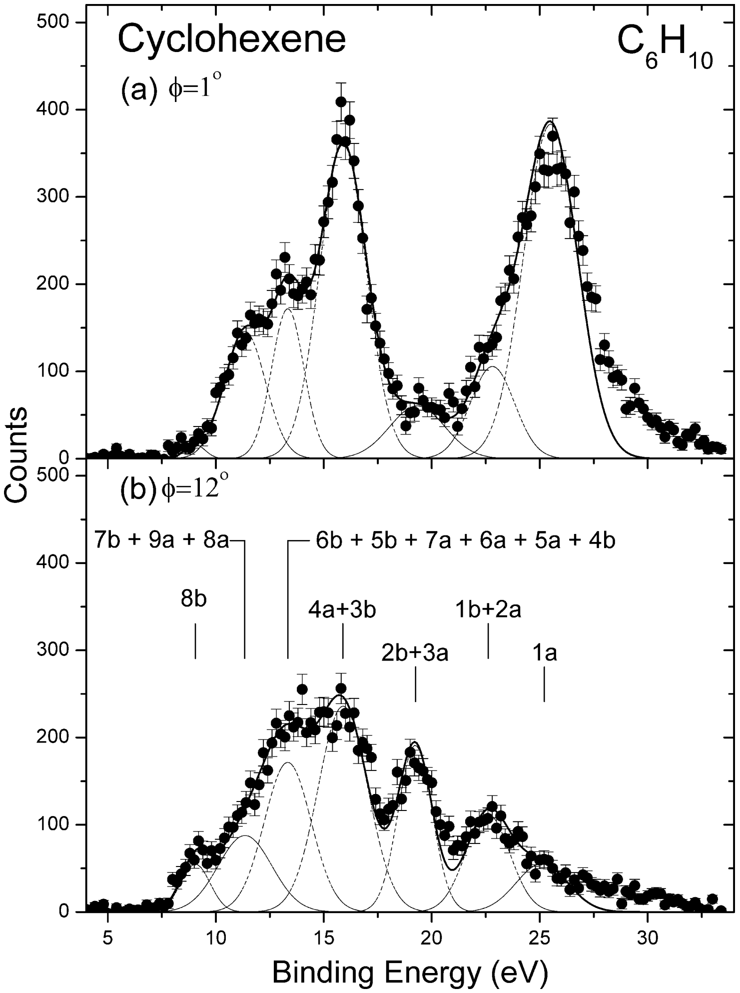

Fig. 1. Binding energy spectra of cyclohexene at $\phi = 1°$ (a) and $\phi = 12°$ (b). The dashed and solid lines represent individual and summed Gaussian fits, respectively.

profiles (TMPs) calculated using the HF and DFT-B3LYP methods with various basis sets. The experimental instrumental angular resolutions have been incorporated in these calculations. In order to compare the experimental momentum distribution with the theoretical ones, we need one normalization factor common for all bands. Usually, this normalization factor is determined by normalizing the experimental and theoretical momentum distributions of the outermost valence ionization to the common intensity scale, since the outermost valence ionizations are expected to exhibit pole strength close to unity. In this Letter we use the HOMO orbital to determine this normalization factor. The theoretical momentum distribution used for normalization is calculated by DFT-B3LYP method employing AUG-CC-PVTZ basis set. In Fig. 2 the experimental momentum profile is compared with the theoretical results. The small basis sets Hartree–Fock calculations (6-31G, 4-31G and STO-3G, curves 5, 6 and 7, respectively) give poor intensity in the low momentum region (below 1.0 a.u.) and shift the position of the maximum a little to high-momentum end compared with the experimental HOMO orbital electron momentum profile. The HF and DFT calculations with 6-311++G** basis set (curves 1 and 2) provide the correct position of the maximum. However, the calculations overestimate the observed intensity in the low momentum region. Using the

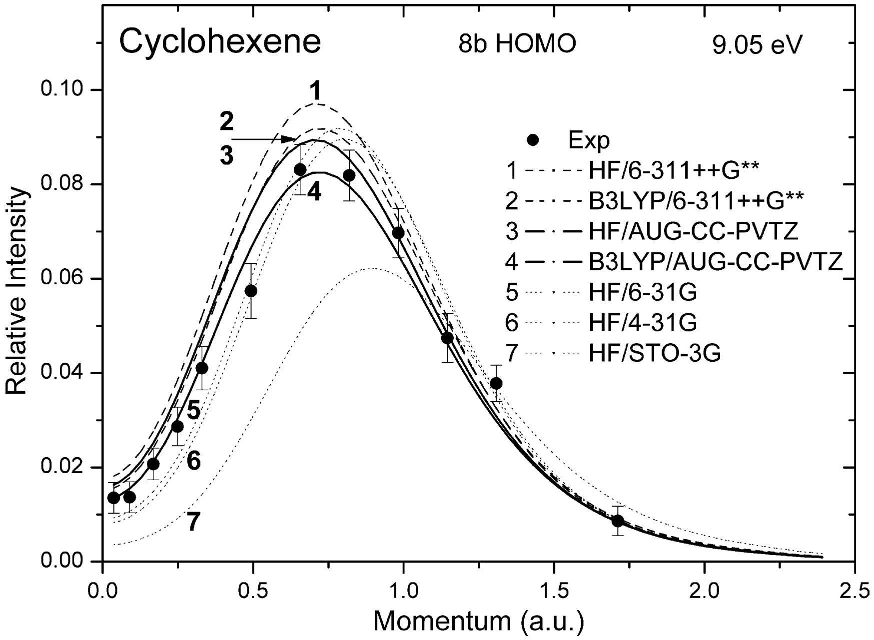

Fig. 2. Experimental and theoretical momentum distributions for the frontier 8b HOMO of cyclohexene. The theoretical momentum profiles are calculated using Hartree–Fock (curves 1, 3, 5–7) and DFT-B3LYP (curves 2 and 4) methods with the AUG-CC-PVTZ, 6-311++G**, 6-31G, 4-31G and STO-3G basis sets.

AUG-CC-PVTZ basis set better descriptions of C_6H_{10} HOMO electron momentum distribution in the proper intensity and the correct position of maximum can be achieved with the HF and DFT-B3LYP calculations (curves 3 and 4). The good performance of the AUG-CC-PVTZ basis set indicates that the calculations using the saturated diffuse and Dunning's correlation consistent polarization basis set can provide a good prediction of the chemical important frontier orbital of cyclohexene. All the calculations show that the momentum profile of C_6H_{10} HOMO has a p-type character, which is the case as shown in our EMS experiment.

4. Conclusion

In summary, the first measurements of the complete valence shell binding energy spectra and momentum profile for C_6H_{10} HOMO are reported. The experimental momentum profile of the HOMO orbital is also compared with the theoretical momentum distributions calculated using the HF and DFT methods with various basis sets. The experimental measurement is well described by the HF and DFT calculations with the saturation basis sets. Our experimental results and the theoretical investigations for cyclohexene provided the details of the HOMO electron density distribution information in momentum space.

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