

The valence shell binding energy spectra and the HOMO momentum profile of butanone by electron momentum spectroscopy

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Abstract

We report here the first measurements of the complete valence shell binding energy spectra and the highest occupied molecular orbital (HOMO) momentum profile of butanone using the binary (e,2e) electron momentum spectrometer, at an impact energy of 1200 eV plus the binding energy and using symmetric non-coplanar kinematics. The experimental momentum profile of the highest occupied molecular orbital is compared with the theoretical momentum distributions calculated using Hartree–Fock and density functional theory methods with various basis sets. The experimental measurements are well described by density functional theory calculation.

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1. Introduction

Butanone, also known as methyl ethyl ketone, has a small autoprotolysis constant, relatively high permittivity and dipole moment as well as a pronounced differentiating effect, relative to many electrolytes; on account of these properties they are suitable as solvents for the determination of weak organic acids and bases, either individually or in mixtures [1]. A solution of perchloric acid in butanone [2,3] has been used as the titrant in the titration of weak organic bases in ketones, with visual or potentiometric end-point detection. Butanone is also a solvent of industrial interest for anthracene oxidation [4]. Therefore, the detailed molecular mechanism of the action of butanone is required, including a detailed knowledge of the molecular electron density, particularly the HOMO wavefunction, since the frontier orbitals are the most important for many chemical and physical properties [5–7]. Thus far, electron momentum

spectroscopy (EMS) is the only experimental technique, capable to image effectively the valence orbital electron density distributions. The EMS technique has been developed extensively for investigating, in momentum space, the valence electronic structures of atoms, molecules and condensed matters [8–13], coupled with high level quantum mechanical calculations, EMS is able to provide detailed quantitative information on the reactive parts of molecular electron densities. Cooper et al. [14] have assessed that the electron density topography can be much more effectively carried out in momentum space than in the more commonly used position space.

Butanone has been studied by HeI photoelectron spectroscopy (PES) [15–17], but, to our knowledge, no EMS study of butanone has been reported so far. In this Letter, we report the first measurements of the complete valence shell binding energy spectra and the electron momentum profiles of the HOMO of butanone. The experiment was performed at an impact energy of 1200 eV plus the binding energy and using symmetric non-coplanar kinematics. A sufficiently high impact energy (>1200 eV) and high momentum transfer were used to ensure the validity of the plane wave impulse

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approximation (PWIA). The measured momentum profile is compared with the Hartree–Fock (HF) and density-functional theory (DFT) calculations using different basis sets.

2. Theoretical background

Electron momentum spectroscopy, based on a binary ($e,2e$) ionization reaction, is an electron impact ionization process. Under the conditions of high impact energy and high momentum transfer, the target electron essentially undergoes a clean ‘knock-out’ collision and the plane wave impulse approximation (PWIA) provides a very good description of the collision. Considering the binary encounter approximation as well as the target Hartree–Fock approximation (THFA), the triple differential EMS cross-section for randomly oriented gas-phase target is [18]

$$\sigma_{\text{EMS}} \propto \int d\Omega |\psi_j(\mathbf{p})|^2, \quad (1)$$

where $\psi_j(\mathbf{p})$ is the one-electron momentum space canonical Hartree–Fock orbital wavefunction for the j th electron that corresponds to the orbital from which the electron is knocked out. The integral in Eq. (1) is known as the spherically averaged one-electron momentum distribution. To this extent, EMS has the ability to image the electron density of a selected orbital according to its binding energy.

The triple differential EMS cross-section has been re-interpreted [19] in the context of Kohn–Sham density functional theory and the Target Kohn–Sham Approximation (TKSA) supplies a result similar to Eq. (1), but with the canonical Hartree–Fock orbital replaced by a momentum space Kohn–Sham orbital $\psi_j^{\text{KS}}(\mathbf{p})$,

$$\sigma_{\text{EMS}} \propto \int d\Omega |\psi_j^{\text{KS}}(\mathbf{p})|^2. \quad (2)$$

It should be noted that accounting for electron correlation effects in the target ground state is included in the TKSA via the exchange–correlation potential. A more detailed description of the TKSA–DFT method could be found elsewhere [19].

In the present work, spherically averaged theoretical momentum profiles have been calculated using the PWIA. The HF and DFT calculations were carried out using the GAUSSIAN 98 program. The HF calculations of the momentum profiles were performed by using Eq. (1) with the basis sets of 6-31G and 6-311++G**. The B3LYP and B3PW91 functionals are used for the two DFT calculations, respectively. Two basis sets of 6-31G and 6-311++G** are used for the B3LYP calculations, and the aug-ccpVTZ basis set is used for the B3PW91 calculation. The geometry has been optimized for all the calculations.

3. Experimental methods

The symmetric non-coplanar, energy dispersive, multichannel EMS spectrometer is used in this work and a detailed description of the spectrometer has been given elsewhere [20]. Briefly, two hemispherical electron energy analyzers, each having a five element cylindrical retarding lens system, are mounted on two independent horizontal concentric turntables inside a mu-metal shield in the vacuum system. In the present work, the polar angles of both analyzers are fixed at 45° . One turntable analyzer is kept in a fixed position, while the other can be rotated by a computer controlled stepping motor. Each electron energy analyzer can accept electrons in a range of kinetic energy from 596 to 604 eV simultaneously, but only those coincident electron pairs with summed energy in the range of 1200 ± 3.5 eV are recorded [20]. The binding energy resolution of the spectrometer was measured to be 1.2 eV FWHM. The experimental momentum resolution was estimated to be ~ 0.1 a.u. from the experiment of the argon 3p angular correlation. The sample of butanone (99.9% purity) was used without further purification.

4. Results and discussion

The point group symmetry of butanone is C_s . According to our theoretical calculation, the ground state electronic configuration can be written as

$$\begin{aligned} &(\text{core})^{10} (6a')^2 (7a')^2 (8a')^2 (9a')^2 (1a'')^2 (10a')^2 (11a')^2 (12a')^2 \\ &(2a'')^2 (13a')^2 (14a')^2 (3a'')^2 (15a')^2 (4a')^2 (16a')^2 \end{aligned}$$

In the ground state, the 40 electrons are arranged in 20 doubly occupied orbitals in the independent particle description. The valence electrons in butanone are distributed in 15 molecular orbitals. All the canonical molecular orbitals are either a' -type or a'' -type.

To obtain the experimental momentum profiles, 11 binding energy spectra over the energy range of 6–42 eV were collected at the out-of-plane azimuthal angles $\phi = 0^\circ, 1^\circ, 2^\circ, 3^\circ, 5^\circ, 7^\circ, 9^\circ, 11^\circ, 13^\circ, 15^\circ$ and 20° in a series of sequential repetitive scans. The valence shell binding energy spectra of butanone in the range of 6–42 eV for measurements at $\phi = 1^\circ$ and $\phi = 5^\circ$ at the impact energy of 1200 eV plus the binding energy are shown in Fig. 1. The spectra in Fig. 1 are fitted with a set of individual Gaussian peaks whose widths are combinations of the EMS instrumental energy resolution and the corresponding Franck–Condon widths derived from high resolution PES data [17]. The energy scale in Fig. 1 is calibrated with respect to the $(16a')^{-1}$ vertical ionization potential from PES data. The dashed lines indicate the fitted Gaussians for the individual peaks, while the solid line represents the sum.

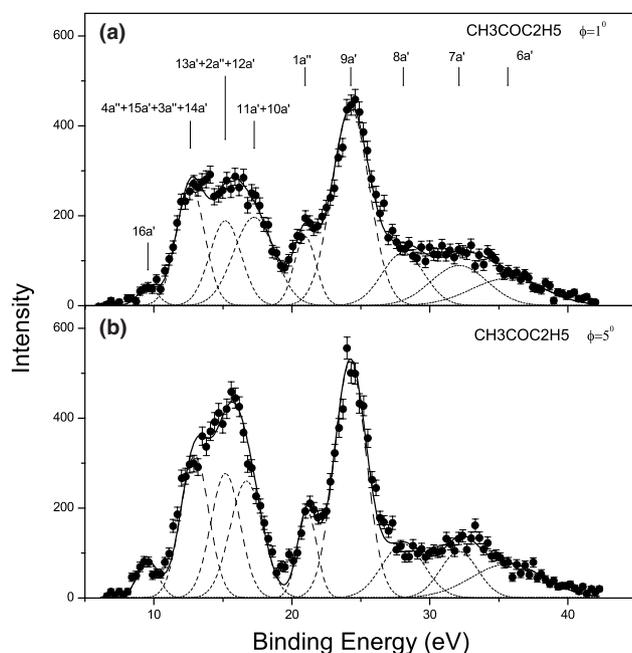


Fig. 1. EMS binding energy spectra of butanone at (a) $\phi = 1^\circ$ (b) $\phi = 5^\circ$. The dashed lines represent the Gaussian fit to the individual peaks and the solid curve is the summed fit.

The PES spectrum of the outer valence shell has been reported by Kimura et al. [17]. In this work, the vertical ionization potential of the $16a'$ is determined to be 9.56 eV, the averaged vertical ionization potentials of the $(4a'' + 15a' + 3a'' + 14a')$, $(13a' + 2a'' + 12a')$ and $(11a' + 10a')$ are determined to be 12.65, 15.18 and 17.26 eV, respectively. While $1a''$, $9a'$, $8a'$, $7a'$ and $6a'$ orbitals are determined to be 20.96, 24.26, 28.07, 32.12 and 35.66 eV, respectively.

In the EMS binding energy spectra of Fig. 1, however, only some of the orbitals could be clearly resolved. The ionization peak for the HOMO, $16a'$, at 9.56 eV is well resolved. But the other outer valences are overlapped seriously, which were not resolved in the high resolution PES of Kimura et al. [17]. The orbitals $1a''$ and $9a'$ are well resolved in our spectra, but the peaks of $8a'$, $7a'$ and $6a'$ orbitals are broad.

Experimental momentum profiles shown in Fig. 2 are extracted from the sequentially obtained, angular-correlated binding energy spectra, and therefore the relative normalizations for the different transitions are maintained. For the HOMO, various theoretical momentum profiles (TMPs) are obtained as described in Section 2. The finite experimental momentum resolution ($\Delta p \sim 0.1$ a.u.) is also folded into the TMPs by using the Gaussian-weighted planar grid method [21]. The experimental and the theoretical momentum profiles have been placed on a common intensity scale by normalizing the experimental data for the HOMO orbital to the B3PW91/aug-ccpVTZ TMP. The experimental and the theoretical momentum profiles show

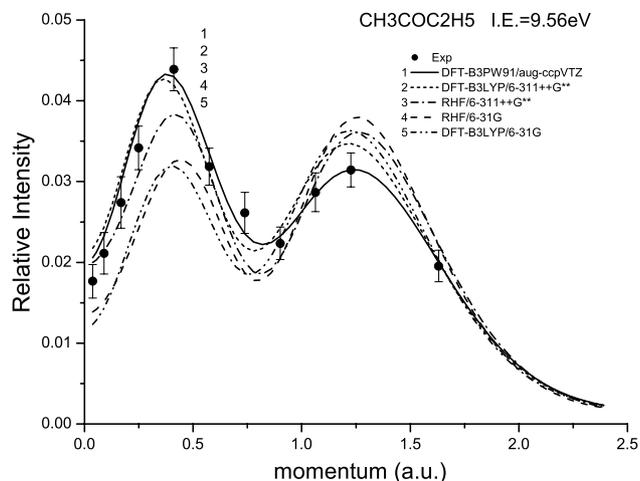


Fig. 2. The experimental and calculated momentum distributions for the HOMO of butanone.

the expected 'p-p type' distribution. There are some differences in five theoretical momentum profiles, the intensity of the first peak is higher than the second peak for calculations using high basis sets 6-311++G** and aug-ccpVTZ, agreeable to our experimental results. On the contrary, for the basis set 6-31G, the intensity of the second peak is higher than the first one in the momentum profile. It can be concluded from comparing the theoretical calculations with experimental results in Fig. 2 that TMPs calculated using DFT and HF with 6-31G cannot provide good description of the experimental momentum profile and the shapes of the intensity distributions are significantly in difference. Even the HF and DFT calculations at the 6-311++G** level still significantly overestimate the experimental results at momenta above ~ 1.0 a.u. This means that the density distributions of the HOMO cannot be described correctly by theoretical calculation either HF or DFT with basis sets 6-311++G** and 6-31G. It can be seen from Fig. 2 that the B3PW91 calculation provides very good quantitative agreement with the EMS measurement. A better fit to the XMP by B3PW91 calculation with aug-ccpVTZ indicates that electron correlation effects are very important for the HOMO of butanone, dynamic electron correlated effects must be included for quantitative modeling of HOMO electron densities in butanone.

5. Summary

In summary, the valence shell binding spectra and the HOMO momentum profile of butanone were measured firstly by using the binary (e,2e) electron momentum spectrometer. The experimental momentum profile is compared with the theoretical momentum

distributions. The experimental profile is well described by B3PW91 with aug-ccpVTZ calculation and electron correlated effects are included in theoretical calculation for quantitative modeling of HOMO electron densities in butanone.

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