The valence shell binding energy spectra and frontier orbital momentum profiles of methylpropane (isobutane) by binary (e, 2e) spectroscopy

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Abstract

We report here the first measurements of the complete valence shell binding energy spectra and the frontier orbital momentum profiles of methylpropane, also known as isobutane ($CH_3CH(CH_3)CH_3$), using a high-resolution binary (e, 2e) electron momentum spectrometer, at an impact energy of 1200 eV plus the binding energy and using symmetric non-coplanar kinematics. Binding energy spectra of the complete valence shell have been obtained at a coincidence energy resolution of 0.95 eV FWHM. The experimental momentum profile of the HOMO ($6a_1$) and NHOMO ($5e$) frontier orbitals is also obtained and compared with the theoretical momentum distributions calculated using Hartree–Fock and density functional theory (DFT) methods with various basis sets. The experimental measurements are well described by the HF and DFT calculations. © 1999 Elsevier Science B.V. All rights reserved.

In the last two decades, 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 [1–7]. EMS can access the complete valence shell binding energy range, though with lower energy resolution than in most photoelectron spectroscopy (PES) studies. In particular, EMS measurements of the momentum profiles for individual orbitals in atoms and molecules have been shown to provide a sensitive method for the evaluation and design of extremely accurate SCF as well as highly correlated molecular wavefunctions and also DFT methods. The details of EMS experimental techniques and the associated theoretical analysis for atoms, molecules and condensed matter have been reviewed in detail elsewhere [1–7].

Study of the electronic structure of small saturated hydrocarbon molecules has received much interest. This is because not only these molecules are prototypes of larger hydrocarbons, but also they are important species for fuels where reforming of straight chain hydrocarbons into branched chain species is of importance. Saturated hydrocarbon molecules have been widely studied by PES [8–11], but until recently only the methane and ethane molecules had been studied by EMS [12–14], due mainly to the limited coincidence energy resolution of binary (e, 2e) spectrometers, which has been typically 1.2–1.5 eV FWHM at an impact energy of 1200 eV plus the binding energy. It has only recently become possible to investigate larger hydrocarbon molecules such as propane [15] and *n*-butane [16] and this has been achieved at Tsinghua University by obtaining an EMS energy resolution of 0.95 eV FWHM with a multichannel EMS spectrometer [17].

As part of a series study of saturated hydrocarbon molecules using the high energy resolution EMS spectrometer at Tsinghua University, we now report the first measurements of the complete valence shell binding energy spectra and the electron momentum profiles of the HOMO $(6a_1)$ and NHOMO $(5e)$ frontier orbitals of methylpropane $(CH_3CH(CH_3) CH_3)$, also known as isobutane. The experiment was performed at an impact energy of 1200 eV plus the binding energy and using symmetric non-coplanar kinematics [1]. The frontier orbitals are the most important for many chemical and physical properties [18]. A sufficiently high impact energy (> 1200 eV) and momentum transfer were used to ensure the validity of the plane wave impulse approximation (PWIA). The relatively large number of electrons in methylpropane renders accurate quantum chemical calculations quite difficult, thus the availability of good EMS experimental data is an important aid for developing satisfactory theoretical descriptions of both binding energies and the valence orbital electron densities in hydrocarbons.

Under conditions of high impact energy and high momentum transfer, the collision mechanism is very simple in that the ionized electron essentially undergoes a clean 'knock-out' collision. In this situation the plane wave impulse approximation (PWIA) provides a very good description of the collision [1]. In the PWIA, using symmetric non-coplanar geometry,

the kinematic factors are effectively constant [1] and the EMS cross-section for randomly oriented gas-phase molecules is then given [1] by:

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

where p is the momentum of the target electron state prior to electron ejection and $|\Psi_f^{N-1}\rangle$ and $|\Psi_i^N\rangle$ are the total electronic wavefunctions for the final ion state and the target molecule ground (initial) state, respectively. The $\int d\Omega$ represents the spherical average due to the randomly oriented gas-phase target. The overlap of the ion and neutral wavefunctions 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.

Eq. (1) is greatly simplified by using the target Hartree–Fock approximation (THFA). Within the THFA, only final (ion) state correlation is allowed and the many-body wavefunctions $|\Psi_f^{N-1}\rangle$ and $|\Psi_f^N\rangle$ are approximated as independent particle determinants of ground state target Hartree–Fock orbitals in which case Eq. (1) reduces to

$$\sigma_{EMS} \propto \int d\Omega \, |\psi_j(p)|^2 , \qquad (2)$$

where $\psi_j(p)$ is the one-electron momentum space canonical Hartree–Fock orbital wavefunction for the *j*th electron, corresponding to the orbital from which the electron was ionized. The integral in Eq. (2) is known as the spherically averaged one-electron momentum distribution. To this extent EMS has the ability to image the electron density in individual 'orbitals' selected according to their binding energies.

Eq. (1) has recently been re-interpreted [19] in the context of Kohn–Sham density functional theory (DFT) and the target Kohn–Sham approximation (TKSA) gives a result similar to Eq. (2) but with the canonical Hartree–Fock orbital replaced by a momentum space Kohn–Sham orbital $\psi_j^{KS}(p)$:

$$\sigma_{EMS} \propto \int d\Omega \, |\psi_j^{KS}(p)|^2 . \qquad (3)$$

It should be noted that accounting of 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 may be found elsewhere [19].

THFA calculations of the momentum profiles were carried out using Eq. (2) and two basis sets: (1) 6-311G and (2) 6-311 + + G**. DFT calculations were carried out using the GAUSSIAN94 program with the B3LYP functionals [20–22]. The optimized geometry of methylpropane has been used for all the 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 ($\Delta\theta = \pm0.6°$ and $\Delta\phi = \pm1.2°$) were included using the Gaussian-weighted planar grid method [23].

Details of the electron momentum spectrometer constructed at Tsinghua University have been reported [17]. Therefore only a brief description is given in this Letter. 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 shielded vacuum system. In the present work, the polar angles of both analyzers are kept fixed at 45°. One analyzer turntable is kept in a fixed position while the other one is rotated by a computer-controlled stepping motor to vary the relative azimuth angle. Each energy analyzer has a position sensitive detector consisting of two micro-channel plates and a resistive anode in the energy dispersive exit plane. The energy range of each analyzer was set at 600 ± 4 eV with a pass energy of 50 eV. Electron impact ionization was carried out at an impact energy of 1200 eV plus the binding energy under the symmetric non-coplanar geometry. The energy resolution obtained in the coincidence experiment is a convolution of the two analyzer response functions and the energy distribution of the incident electron beam. It also depends on the deceleration ratio of the lens. This resolution, as well as the binding energy scale, was measured directly by using helium as a calibration gas. The coincidence energy resolution of the spectrometer was measured to be 0.95 eV FWHM. The experimental momentum resolution is estimated to be ~ 0.1 a.u. from a consideration of the argon 3p angular correlation. The sample of methylpropane from Matheson (99.9% purity) was used without further purification. No impurities were evident in the binding energy spectra.

The point group symmetry of methylpropane is C_{3v}. According to molecular orbital theory, the ground state electronic configuration can be written as

$$(core)^8 (3a_1)^2 (2e)^4 (4a_1)^2$$
$$\text{inner valence}$$

$$(5a_1)^2 (3e)^4 (4e)^4 (1a_2)^2 (5e)^4 (6a_1)^2$$
$$\text{outer valence}$$
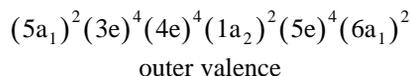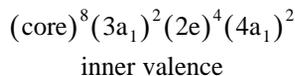
In the ground state, the thirty-four electrons are arranged in seventeen doubly-occupied orbitals in the independent particle description. The valence electrons in methylpropane are distributed in fourteen molecular orbitals and four of the orbitals are degenerate. All the canonical molecular orbitals are either a-type or e-type. The four e-type orbitals are each double degenerate. The assignment of the order of occupation for these valence orbitals, both by PES experiments and by molecular orbital calculations, has been discussed in detail in Refs. [8–11].

In order to obtain the experimental momentum profiles, eleven binding energy spectra over the energy range of 8–32 eV were collected at the out-of-plane azimuth angles $\varphi = 0°$, 2°, 4°, 6°, 8°, 10°, 12°, 14°, 16°, 20° and 24° in a series of sequential repetitive scans. Fig. 1 shows the binding energy spectra of methylpropane in the range 8–32 eV for measurements at $\varphi = 0°$ and $\varphi = 6°$ (incident energy of 1200 eV plus the binding energy). The spectra in Fig. 1 were 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 [8]. The relative energy values are given by the relative ionization energies determined by high-resolution PES. The fitted Gaussians for individual peaks are indicated by dotted lines while their sum, i.e. the overall fitted spectra, are represented by the solid lines. The binding energy spectrum in Fig. 1a, obtained at the azimuthal angle $\varphi = 0°$, corresponds to a momentum $\bar{p} \approx 0.06$ a.u., and it is therefore dominated by 's-type' symmetric orbitals, which have a maximum cross-section at $p = 0$. Those orbitals having 'p-type' characteristics, i.e. antisymmetric and hence having a cross-section minimum at $\varphi = 0°$, are more prominent in Fig. 1b, which was taken at the
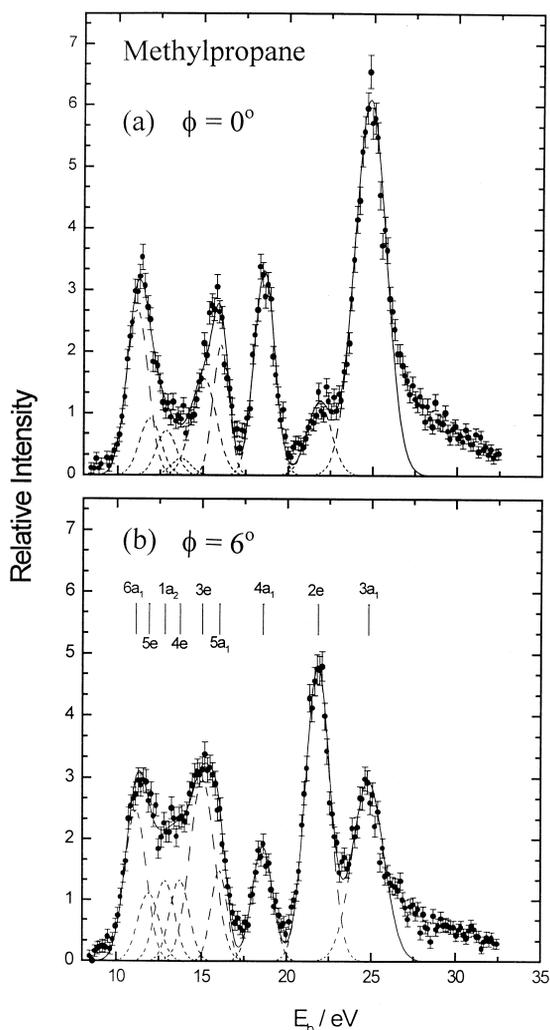
Fig. 1. Valence shell binding energy spectra of 1200 eV for methylpropane at (a) $\varphi = 0°$ and (b) $\varphi = 6°$. The dashed and solid lines represent individual and summed Gaussian fits, respectively.

azimuthal angle $\varphi = 6°$ ($\bar{p} \approx 0.49$ a.u.). The relative intensities in the $\varphi = 0°$ and $\varphi = 6°$ spectra reflect the different symmetries of the valence orbitals of methylpropane.

The PES spectra of the seven orbitals of the outer valence region have been reported by Kimura et al. [8] using a He I radiation source. In this latter work [8], the vertical ionization potentials of the $6a_1$, 5e, $1a_2$, 4e, 3e and $5a_1$ orbitals were determined to be 11.13, 11.7 (12.1), 12.85, 13.52 (13.9), 14.86 (15.3) and 15.95 eV, respectively. Since methylpropane is a non-linear molecule the PES spectra are complicated

by the Jahn–Teller effect. The energy splitting positions, due to the Jahn–Teller effect, of the degenerate 5e, 4e and 3e orbitals are indicated in the corresponding brackets (see above). These PES studies were extended by Potts et al. [11] using He II radiation source which also covered some of the inner valence region of methylpropane and structures at 18.37, 21.9 and 24.8 eV were assigned to the $4a_1$, 2e and $3a_1$ orbitals, respectively.

The average vertical ionization potentials of the $6a_1$, 5e, $1a_2$, 4e, 3e and $5a_1$ outer orbitals are determined by the present EMS measurement to be 11.13, 11.9, 12.85, 13.71, 15.03 and 16.03 eV, respectively. The three peaks corresponding to the removal of an electron from the $4a_1$, 2e and $3a_1$ inner valence orbitals at 18.58, 21.83 and 24.83 eV binding energy, respectively, are clearly separated. The differences in FWHM are due to the vibrational broadening of the lines. The measured EMS binding energies are consistent with the PES values [10,11] for the outer and inner valence orbitals as shown in Fig. 1. In addition, some rather weak structure due mainly to correlation effects in the target or in the residual ion final states is also observed above 26 eV.

Experimental momentum distributions have been extracted by deconvolution of the sequentially ob-
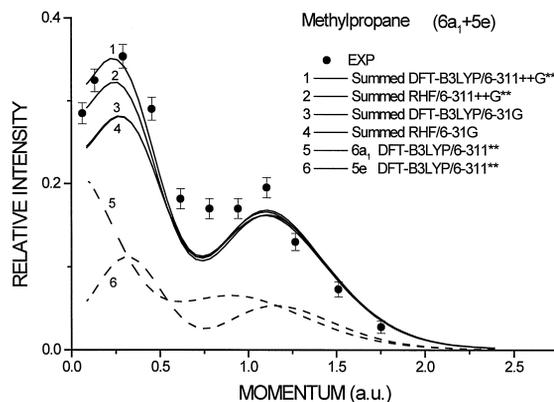
Fig. 2. Experimental and calculated spherically averaged momentum distributions for the HOMO and NHOMO summed orbitals $(6a_1 + 5e)$ of methylpropane. The TMPs are calculated using Hartree–Fock and DFT-B3LYP methods with the 6-31G and $6\text{-}311 + +G^{**}$ basis sets. The individual theoretical momentum distributions of the HOMO and NHOMO of methylpropane, obtained using the DFT-B3LYP method with the 6-311** basis sets, are shown by dashed lines.

tained angular-correlated binding energy spectra, and therefore the relative normalization for the different transitions are maintained. The experimental sum of the first two peaks, as indicated in Fig. 1, corresponding to the $6a_1$ HOMO and 5e NHOMO orbitals, respectively, has been determined since they are not well separated experimentally (the energy separation is only ~ 0.77 eV). The summed experimental momentum distribution is compared, in Fig. 2, with the four summed theoretical momentum profiles calculated using Hartree–Fock (curves 2 and 4) and DFT-B3LYP (curves 1 and 3) with the 6-31G and $6\text{-}311++G^{**}$ basis sets. The angular resolution has been incorporated in the calculations using the UBC RESFOLD program based on the GW-PG method [23]. The individual theoretical momentum profiles for the HOMO (curve 5) and NHOMO (curve 6), obtained by using the DFT-B3LYP method with the $6\text{-}311^{**}$ basis set, are also shown in Fig. 2 under the summed momentum distributions. It can be seen that both summed TMPs calculated using DFT and HF with the $6\text{-}311++G^{**}$ provide quite good agreement with the shape of the XMP. The best fit is provided by the DFT-B3LYP calculation with the $6\text{-}311++G^{**}$. Details of the XMPs and TMPs for the complete valence region will be published later [24].

In summary, we report the first measurements of the complete valence shell binding spectra and the momentum profiles for the sum of the HOMO and NHOMO orbitals of methylpropane by EMS, as well as associated calculations. The binding energies are in excellent agreement with photoelectron spectroscopy data. The experimental momentum profiles of the two frontier orbitals are well described by Hartree–Fock $6\text{-}311++G^{**}$ calculation. The density functional theory (DFT) calculations using B3LYP functionals with the $6\text{-}311++G^{**}$ basis set also give a good agreement with the experiment. The full details of the experimental results and the associated theoretical analysis for methylpropane will be described later [24].

Acknowledgements

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