The outer valence orbital momentum profiles of thiophene by electron momentum spectroscopy

S.F. Zhang, X.G. Ren, G.L. Su, C.G. Ning, H. Zhou, B. Li, F. Huang,
G.Q. Li, J.K. Deng *

Department of Physics, Tsinghua University, Beijing 100084, PR China

Received 24 September 2004; in final form 3 November 2004
Available online 25 November 2004

Abstract

We report here the first measurements of the complete valence shell binding energy spectra and the outer valence orbital momentum profiles of thiophene, 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. The summed experimental momentum profile of the HOMO $1a_2$ and NHOMO $3b_1$ is compared with the theoretical momentum distributions calculated using Hartree–Fock and density functional theory methods with various basis sets. The experimental measurement is well described by the calculations.
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Thiophene (C_4H_4S) is a five-membered aromatic heterocyclic molecule which is similar to furan and pyrrole. These three molecules play an important role in such industrial processes as the synthesis of biologically active compounds, and in the manufacture of pesticides and inorganic polymers [1]. Thiophene's oligomers and polymers can be used in material science as active layers in semiconductor-like devices [2], and furthermore, thiophene forms the basis for a series of heterocyclic compounds of importance in chemistry. Hence, thiophene has been widely studied not only by HeI and HeII photoelectron spectroscopy (PES) [3–5], X-ray PES [6,7], UV PES [8], synchrotron radiation [1,9], Penning ionization electron spectroscopy (PIES) [4,10], but also by the theoretical works [3,7,11]. Three doubly occupied π molecular orbitals (denoted π_1, π_2, π_3) are formed from four p-electrons donated by the carbon atoms together with the lone-pair from the heteroatom. The two least tightly bound of the π molecular orbitals namely π_2 ($3b_1$ in thiophene) and π_3 ($1a_2$ in thiophene) are delocalized and constitute the two outermost orbitals in thiophene [1].

Electron momentum spectroscopy (EMS), also known as binary (e, 2e) spectroscopy, has been demonstrated to be a unique chemical probe [12]. It can effectively image outer valence orbital electron densities and provide direct experimental information on the nature of electron transfer processes which are important in bonding and reactivity. The other two important five-membered aromatic heterocyclic molecules furan and pyrrole have been researched by EMS [13,14], but no EMS study of thiophene has been reported to our best knowledge. In this Letter, we report the complete binding energy spectra (5–37 eV) of thiophene and the summed momentum profile of its HOMO and NHOMO ($1a_2 + 3b_1$). The frontier orbitals are the most important for many chemical and physical properties [15]. The

---
* Corresponding author. Fax: +861062781604.
  E-mail address: djk-dmp@mail.tsinghua.edu.cn (J.K. Deng).

experimental momentum profile (XMP) is compared with the Hartree–Fock (HF) and density functional theory (DFT) calculations.

2. Theoretical background

In a binary (e, 2e) experiment using symmetric non-coplanar scattering geometry, the scattered and the ionized electrons are detected at the same kinetic energies and the same polar angles. Under the 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 [16]. In the PWIA, using symmetric non-coplanar geometry, the kinematic factors are effectively constant, then the EMS cross-section for randomly oriented gas-phase molecules could be given [16] by

$$\sigma_{\mathrm{EMS}} \propto \int \mathrm{d}\Omega \left| \langle \boldsymbol{p} \Psi_{\mathrm{f}}^{N-1} | \Psi_{\mathrm{i}}^{N} \rangle \right|^{2}, \tag{1}$$

where $\boldsymbol{p}$ is the momentum of the target electron state prior to electron ejection, and $|\Psi_{\mathrm{f}}^{N-1}\rangle$ and $|\Psi_{\mathrm{i}}^{N}\rangle$ are the total electronic wavefunctions for the final ion state and the target molecule ground (initial) state, respectively. The $\int \mathrm{d}\Omega$ 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 $|\Psi_{\mathrm{f}}^{N-1}\rangle$ and $|\Psi_{\mathrm{i}}^{N}\rangle$ are approximated as independent particle determinants of ground state target HF orbitals in which case Eq. (1) reduces to

$$\sigma_{\mathrm{EMS}} \propto S_{j}^{f} \int \mathrm{d}\Omega \left| \psi_{j}(p) \right|^{2}, \tag{2}$$

where $\psi_{j}(p)$ is the one-electron momentum space canonical HF orbital wavefunction for the jth electron, corresponding to the orbital from which the electron was ionized. The quantity S_{i}^{f} is the spectroscopic factor or pole strength and is the probability of the ionization event producing a $(\psi_{j})^{-1}$ one-hole configuration of the final ion state, $|\Psi_{\mathrm{f}}^{N-1}\rangle$. The estimated value of S_{i}^{f} can be obtained from a comparison of calculated and experimental cross-section. 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.

Alternatively, using the target Kohn–Sham approximation (TKSA) of DFT [17] and the associated (correlated) Kohn-Sham orbital (KSO) wave function $\psi_{j}^{\mathrm{KS}}(p)$ the cross-section becomes

$$\sigma_{\mathrm{EMS}} \propto S_{i}^{f} \int \mathrm{d}\Omega \left| \psi_{j}^{\mathrm{KS}}(p) \right|^{2}. \tag{3}$$

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 [17].

In present work, the calculations of thiophene have been carried out at the ab initio level, using the GAUSSIAN 98W program together with the HEMS program developed by UBC. The geometry of thiophene [18–20] 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 $\phi (\Delta\theta = \pm 0.6°$ and $\Delta\phi = \pm 1.2°)$ were included using the Gaussian-weighted planar grid (GW-PG) method [21].

3. Experimental

Details of the present EMS spectrometer have been described in earlier publication [22]. Briefly, incident electrons with an energy of 1200 eV plus binding energy are produced by an electron gun and ionize the target molecules. The two outgoing electrons emerging at $\theta = 45°$ are energy analyzed by two hemispherical electron energy analyzers and detected at 600 eV. By combining the energy analyzers with one-dimension position sensitive detectors, multi-channel EMS were carried out over a momentum range between 0.1 and 2.0 a.u. The energy resolution was determined to be 1.20 eV (FWHM) and the momentum resolution was estimated to be 0.1 a.u. by a measurement on the Ar 3p orbital. The sample of thiophene ($\geqslant 98.0\%$ purity) was used without further purification other than freeze–thaw cycles which used to remove dissolved air. No impurities were evident in the binding energy spectra.

4. Results and discussion

Like the furan and pyrrole, thiophene has C_{2v} symmetry. According to molecular orbital theory, the ground state electronic configuration can be written as [1,9]

$$(\text{core})^{18}\underbrace{(6a_1)^2(4b_2)^2(7a_1)^2}_{\text{innervalence}}$$

$$\underbrace{(8a_1)^2(5b_2)^2(9a_1)^2(6b_2)^2(10a_1)^2(7b_2)^2(2b_1)^2(11a_1)^2(3b_1)^2(1a_2)^2}_{\text{outervalence}}$$

The valence shell contains 13 molecular orbitals and can be divided into two sets of three inner-valence and 10 outer-valence orbitals.

In order to obtain the experimental momentum profiles, 11 binding energy spectra over the energy range of 5–37 eV were collected at the out-of-plane azimuth angles $\phi = 0°, 1°, 2°, 3°, 5°, 7°, 9°, 11°, 13°, 15°$ and $20°$ in a series of sequential repetitive scans. Fig. 1 shows the binding energy spectra of thiophene in the range 5–37 eV for measurements at $\phi = 0°$ and $\phi = 7°$ (incident energy of 1200 eV plus the binding energy). The spectra in Fig. 1 were fitted with a set of individual Gaussian peaks. The fitted Gaussians for individual peaks are indicated by dashed lines while their sums are represented by the solid lines. The widths of the peaks are combinations of the EMS instrumental energy resolution and the corresponding Franck–Condon widths derived from high resolution PES data [1], and the relative energy values of the peaks are given by the relative ionization energies determined by high resolution PES. The binding energy spectrum in Fig. 1a, ob-

tained at the azimuthal angle $\phi = 0°$, corresponds to a momentum $\bar{p} \approx 0.05$ 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 in position space and hence, having a cross-section minimum at $\phi = 0°$, are more prominent in Fig. 1b, which was taken at the azimuthal angle $\phi = 7°$ ($\bar{p} \approx 0.6$ a.u.). The relative intensities in the $\phi = 0°$ and $\phi = 7°$ spectra reflect the different symmetries of the valence orbitals of thiophene.
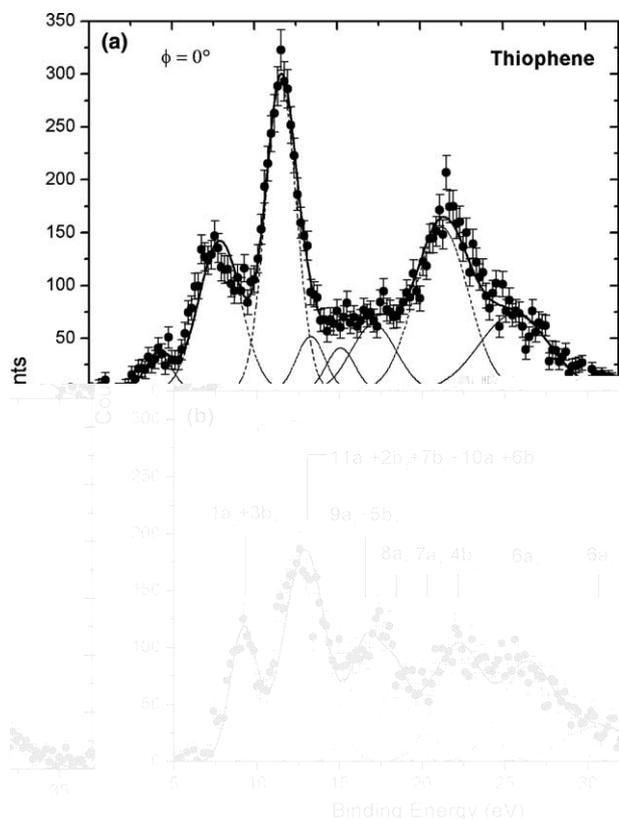
The average vertical ionization potentials (IPs) of the $1a_2 + 3b_1$, $11a_1 + 2b_1 + 7b_2 + 10a_1 + 6b_2$, $9a_1 + 5b_2$, and $8a_1$ outer orbitals are determined by the present EMS measurement to be 9.2, 12.9, 16.6 and 18.4 eV, respectively. The vertical IPs of the $7a_1$, $4b_2$ and $6a_1$ inner valence orbitals are determined to be 20.2, 22.2 and 26.3 eV. In addition, some rather weak satellite structures due to many-body correlation effects in the target or in the residual ion final states are also observed above 30.7 eV in the binding energy spectra. This satellite is likely due to ionization from $6a_1$ orbital [9]. The IPs of five orbitals $11a_1$, $2b_1$, $7b_2$, $10a_1$, $6b_2$ are very close and bands due to these orbitals have not been clearly resolved even in high-resolution PES [1,9]. The same is true of the next two orbitals $9a_1$ and $5b_2$. The differences in FWHM are due to the vibrational broadening of the lines.

The experimental momentum profiles are extracted by deconvolution of the same peak from the sequentially obtained binding energy spectra at different azimuthal angles [16]. In order to compare the experimental momentum distributions 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 work, the observed band areas in the outer valence between 5 and 20 eV at all measured ϕ have been summed up, and then normalized to the sum of the theoretical momentum profiles (TMPs) of the outer valence orbitals calculated using the DFT-B3LYP method and the aug-cc-pVTZ basis set.

The experimental sum of the first peak, as indicated in Fig. 1, corresponding to the HOMO $1a_2$ and NHO-MO $3b_1$ orbitals, has been determined since they are not well separated experimentally (the energy separation is only ∼0.65 eV). The summed XMP is compared, in Fig. 2, with the four summed TMPs calculated using HF (curves 1 and 2) with the 6-31G and 6-311++G** basis sets and DFT-B3LYP (curves 3 and 4) with the 6-311++G** and aug-cc-pVTZ 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

Fig. 1. Valence shell binding energy spectra of 1200 eV for thiophene at (a) $\phi = 0°$ and (b) $\phi = 7°$. The dashed and solid lines represent individual and summed Gaussian fits, respectively.
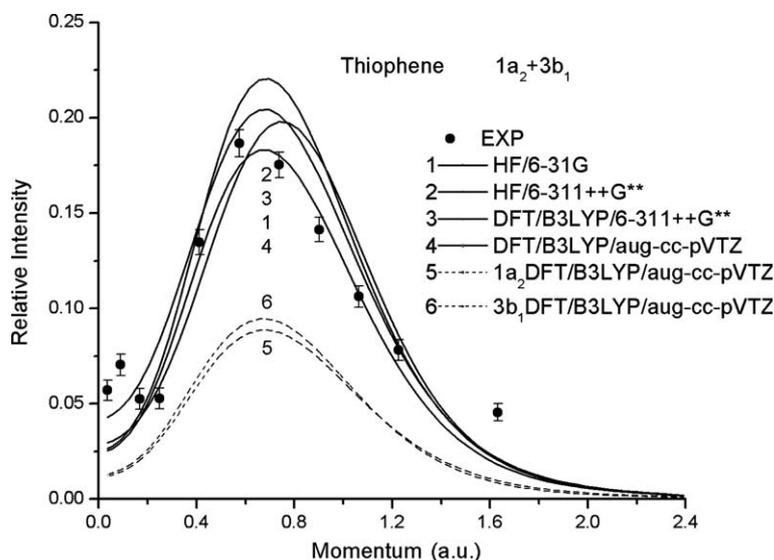
Fig. 2. Experimental and calculated momentum distributions for the HOMO and NHOMO summed orbitals ($1a_2 + 3b_1$) of thiophene. The TMPs are calculated by using Hartree–Fock (curves 1 and 2) with the 6-31G and 6-311++G** basis sets and DFT-B3LYP (curves 3 and 4) methods with the 6-311++G** and aug-cc-pVTZ basis sets. The individual theoretical momentum distributions of the HOMO and NHOMO, obtained using the DFT-B3LYP method with the aug-cc-pVTZ, are shown by dashed lines. All of TMPs are scaled by a factor of 0.90.

profiles for the HOMO $1a_2$ (curve 5) and NHOMO $3b_1$ (curve 6), obtained by using the DFT-B3LYP method with the aug-cc-pVTZ basis set, are also shown in Fig. 2 under the summed momentum distributions. In order to make the TMPs and XMP agree with each other, it is necessary to multiply the TMPs by a factor of 0.90. Thus, the pole strengths S_i^f of the $1a_2^{-1}$ and $3b_1^{-1}$ states are determined to be 0.90. These are in good agreement with the theoretical pole strength of 0.92 by Von Niessen [3]. Some discrepancies between the TMPs and XMP in the low momentum region can be attributed to the error limits of the data.

5. Summary

In summary, we report the first measurements of the outer valence $1a_2 + 3b_1$ momentum profile of thiophene and the complete valence shell binding spectra. The summed experimental momentum profile of the $1a_2 + 3b_1$ orbital is also compared with the theoretical momentum distributions calculated using HF and DFT methods with various basis sets. The experimental measurement is well described by the HF and DFT calculations. In particular, the pole strengths of the HOMO and NHOMO have been obtained and are in good agreement with the theoretical calculation.

References

[1] D.M.P. Holland, L. Karlsson, W. von Niessen, J. Electron Spectrosc. Relat. Phenom. 113 (2001) 221.
[2] A.J. Heeger, in: W.R. Salaneck, I. Lundström, B. Rånby (Eds.), Conjugated Polymers, Oxford University Press, New York, 1993.
[3] W. Von Niessen, J. Electron Spectrosc. Relat. Phenom. 27 (1989) 129.
[4] T. Munakata, K. Kuchitsu, J. Electron Spectrosc. Relat. Phenom. 20 (1980) 235.
[5] P.J. Derrick, L. Åsbrink, O. Edqvist, et al., Int. J. Mass Spectrom. Ion Phys. 6 (1971) 177.
[6] S.A. Chambers, T.D. Tomas, J. Chem. Phys. 67 (1977) 2596.
[7] A. Giertz, M. Bässler, O. Björneholm, et al., J. Chem. Phys. 117 (2002) 7587.
[8] M.H. Palmer, I.C. Walker, M.F. Guest, Chem. Phys. 241 (1999) 275.
[9] A.D.O. Bawagan, B.J. Olsson, K.H. Tan, et al., Chem. Phys. 164 (1992) 283.
[10] N. Kishimoto, H. Yamakado, K. Ohno, J. Phys. Chem. 100 (1996) 8204.
[11] W. Von Niessen, W.P. Kraemer, L.S. Cederbaum, J. Electron Spectrosc. Relat. Phenom. 8 (1976) 179.
[12] C.E. Brion, G. Cooper, Y. Zheng, et al., Chem. Phys. 270 (2001) 13, and references therein.
[13] M. Takahashi, K. Otsuka, Y. Udagawa, Chem. Phys. 227 (1998) 375.
[14] M. Takahashi, R. Ogino, Y. Udagawa, Chem. Phys. Lett. 288 (1998) 821.
[15] K. Fukui, T. Yonezawa, H.J. Shingu, J. Chem. Phys. 20 (1952) 722.
[16] I.E. McCarthy, E. Weigold, Rep. Prog. Phys. 91 (1991) 789, and references therein.

[17] P. Duffy, D.P. Chong, M.E. Casida, D.R. Salahub, Phys. Rev. A 50 (1994) 4704.

[18] G. Herzberg, Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, New York, 1966.

[19] Józef S. Kwiatkowski, J. Leszczyński, I. Teca, J. Mol. Struct. 436–437 (1997) 451.

[20] I.V. Kochikov, Yu.I. Tarasov, V.P. Spiridonov, et al., J. Mol. Struct. 567–568 (2001) 29.

[21] P. Duffy, M.E. Casida, C.E. Brion, D.P. Chong, Chem. Phys. 159 (1992) 347.

[22] J.K. Deng, G.Q. Li, Y. He, et al., J. Chem. Phys. 114 (2001) 882.