Collision-energy-resolved metastable impact electron spectroscopy of thiophene and 2,2’-bithiophene: Stereodynamics in gas phase and adsorbed layer on Ag(110)

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Abstract. 2,2’-bithiophene in the gas phase was studied by ultraviolet photoelectron spectroscopy (UPS) and two-dimensional Penning ionization electron spectroscopy (2D-PIES) to obtain the information of stereodynamics in Penning ionization and anisotropic interaction around the ionization region. Thiophene and the 2,2’-bithiophene layer on a Ag(110) surface were investigated by two-dimensional metastable impact electron spectroscopy (2D-MIES). From the relative intensity in the UPS and PIES spectra and the collision energy dependence of partial ionization cross sections (CEDPICS) for 2,2’-bithiophene, ionization bands were assigned to π orbitals. A comparison with the CEDPICS for a gas molecule and the molecular layer on Ag(110) revealed that the attractive interaction between He⁺(2⁢S) and both thiophene and 2,2’-bithiophene was weak due to the formed molecular layer.

1. Introduction

Investigation of the surface state has become more important for a number of fields interested in nanoscience. Polythiophene and substituted polythiophenes are well-known conductive polymers, which are expected to be good organic electronic devices for molecular level technology [1, 2]. Molecular conductivity depends on the HOMO-LUMO energy gap, and this value is determined by factors such as the polymers substituents, the torsion angle, and the length of conjugation. Thiophene and 2,2’-bithiophene, the monomer and dimer of polythiophene, are the two most basic compounds which can be used to characterize the differences in materials based on factors such as conjugation length and torsion angle. Herein, we applied collision-energy-resolved metastable impact electron spectroscopy to both thiophene and 2,2’-bithiophene in a gas molecule or on a Ag(110) surface, and attempted to compare the anisotropic interaction between He⁺(2⁢S) and the thiophene with that between He⁺(2⁢S) and the 2,2’-bithiophene.

Electron spectroscopy using excited atoms as the ionization source is known as an effective method to analyze the surface state [3]. This is primarily because the approachable distance between the exited metastable atom and molecule is limited, and selective ionization occurs from the expanded molecular orbitals outside the molecule or the outermost molecular layer. This technique is referred to as Penning ionization electron spectroscopy (PIES) or metastable impact electron spectroscopy (MIES), and was developed by Čermák [4]. The Penning ionization (PI) process, found by Penning [5], is shown in the
equation below,

\[ M + A^* \rightarrow M^+ + A + e^- \]  \hspace{1cm} (1)

The PI process only occurs in the case of collision between an isolated molecule and a metastable atom. However, when a metastable atom collides with molecule on a metal surface, an electron is emitted by another ionization processes; resonance ionization and Auger neutralization [6]. Therefore, gas phase analysis is referred to as PIES, and surface analysis as MIES.

A coupled technique for selecting the velocity of \( A^* \) and analyzing the kinetic energy of the ejected electron has been developed [7] in which the two parameters can be measured simultaneously [8]. The two-dimensional PIES (2D-PIES) or 2D-MIES technique enables one to obtain the collision energy (translated from velocity) dependence of partial ionization cross sections (CEDPICS), thus providing valuable information on anisotropic interactions between metastable atoms and target molecules. This technique has been used to characterize a number of molecules in the gas phase [9]. Recently, we developed an experimental apparatus for surface measurements, and applied measurements to the organic molecular layer.

2. Experimental

The experimental setup for this investigation in the gas phase was previously reported [7, 8]. A metastable He beam was produced by a nozzle discharge source with a tantalum hollow cathode. \( \text{He}^*(2^1S) \) was quenched using a water-cooled He dc lamp, and pure \( \text{He}^*(2^3S) \) (19.820 eV) was used as the ionization source for PIES. For ultraviolet photoelectron spectroscopy (UPS), the He I resonance line (21.22 eV) was produced by discharging pure He gas. The emitted electron energy \( E_e \) was analyzed using a hemispherical energy analyzer. Calibration of the electron energy scale was made by reference to the lowest ionic state of \( \text{N}_2 \) mixed with the sample molecule. The background pressure in the chamber containing a collision cell was about \( 1.0 \times 10^{-4} \) Pa. \( \text{He}^* \) was pulsed using a rotating mechanical chopper disk, and time-resolved Penning ionization spectra \( I_e(E_e,t) \) were obtained as functions of the electron energy \( E_e \) and time-of-flight \( t \). Time-of-flight for \( \text{He}^*(2^3S) \) was converted to collision energy \( E_c \), and finally the CEDPICS \( \sigma(E_e,E_c) \) was obtained. The sample cell and sample line leading to the collision cell were heated to in order to vaporize the sample.

The apparatus for 2D-MIES is shown in Figure 1. The He discharging source and mechanical chopper

![Figure 1. Experimental setup for MIES of a surface.](image-url)
for time-resolved measurements were the same as the setup for the gas phase. The electrons were detected by a dual microchannel plate (MCP) at the end of the flight tube through the retarding electrodes placed in the tube [10]. The electron energy spectra were not calibrated. Ag(110) was used as the metal substrate, and it was cleaned by annealing at 800 K and sputtered with Ar\textsuperscript{+} prior to experiments. Surface purity was confirmed by Auger electron spectroscopy. The background pressure in the collision chamber was about 3.0 \times 10^{-8} \text{ Pa}. The sample organic layer was evaporated on a Ag(110) surface after freeze-pump-thaw cycles, and the exposure was determined as a Langmuir unit.

3. Calculations
Quantum chemistry calculations using the Gaussian 03 package program [11] were performed in order to obtain electron density maps, ionization potentials and model potential energy curves. A standard 6-311++G** basis set was used for all calculations. The geometry of thiophene was selected from a microwave spectroscopic study [12], and 2,2’-bithiophene was selected from the optimized structure using density functional theory with the Becke’s three-parameter Lee-Yang-Parr functional (B3LYP) [13]. Ionization potentials were calculated by Outer Valence Green’s Function (OVGF) method [14]. In order to obtain information on the interaction between He\textsuperscript{*} and the target molecule, potential energy curves in various directions are needed. Since the calculation for highly exited states was difficult, instead of He\textsuperscript{*} a Li atom was introduced in interaction with thiophene or 2,2’-bithiophene because of the well-known similarity between He\textsuperscript{*}(2\textsuperscript{3}S) and Li(2\textsuperscript{2}S) [15]. This calculation was performed using B3LYP.
Figure 4. Interaction potential curves $V^*(R)$ for thiophene or 2,2'-bithiophene and Li along various directional approaches. For thiophene-Li, out-of-plane access to the center of the thiophene ring is shown by • and the S atom from the in-plane direction is indicated by ◦. For 2,2'-bithiophene, the center of C2-C2' single bond is indicated by ▲, the center of one thiophene ring from the out-of-plane direction is indicated by ▼, and the S atom from the in-plane direction is indicated by ▽.

4. Results and Discussion

4.1. gas phase analysis by 2D-PIES

Figure 2 shows UPS and PIES spectra for 2,2'-bithiophene in the gas phase. The electron energy scales for PIES are shifted to 1.40 (= 21.22 - 19.82) eV higher than that for UPS by the difference in the excitation energies. Figure 3 shows the log $\sigma$ vs. log $E_c$ plot of CEDPICS for 2,2'-bithiophene corresponding to each band in Figure 2. The electron density maps, simplified diagrams indicating component atomic orbitals and slope parameter $m$ was calculated by the least squares method and are also shown in the figure. Table 1 shows the observed and calculated ionization potential, orbital character and $m$ for 2,2'-bithiophene. Results for thiophene [16] are also shown in this table.

Nine clear bands are observed from the UPS and PIES spectra for 2,2'-bithiophene in Figure 2. The ionization potential calculated using the OVGF method shows that some ionization bands overlap in bands 2, 5, 6 and 7. Band 2 was assigned to the $\pi_4$ and $\pi_5$ orbitals, which is derived from the $\pi_2$ orbital of thiophene. The shape of spectrum from band 1 to 3 is very similar to that of biphenyl (C$_6$H$_5$-C$_6$H$_5$) [17]. When two degenerate 1e$_{1g}(\pi)$ orbitals in benzene are split by forming biphenyl, the $\pi_1$ and $\pi_6$ orbitals of biphenyl with a large band gap and $\pi_4$ and $\pi_5$ orbitals with a narrow band gap are formed. This suggests that 2,2'-bithiophene and biphenyl have similar electronic structures. The relative intensity of bands 5 and 6 in the PIES spectrum is larger than that in the UPS spectrum. This is because the $\pi_1$ and $\pi_2$ orbitals, which are expanded out of two thiophene rings, are involved in these two bands, and are advantageous for collision ionization between He$^*$ atoms. The relative intensity of band 2 in the PIES spectrum is also larger. On the other hand, that of bands 1 and 3 are not so large because $\pi_6$ (band 1) and $\pi_4$ (band 4) orbitals have more nodal planes than the other $\pi$ orbitals. Ionization probability by PI process depends on an overlap between 1s orbital of He$^*$ and each molecular orbital, and is lowered around nodal plane. The same trend is observed in the PIES spectra for biphenyl and other aromatic compounds [18]. In addition,
Figure 5. Coverage dependence of MIES spectra for thiophene on Ag(110) surface. The top shows PIES spectrum in the gas phase [16].

Figure 6. Coverage dependence of MIES spectra for 2,2'-bithiophene on Ag(110) surface. The top shows PIES spectrum in the gas phase.

Figure 3 shows that the CEDPICS for bands 5 and 6 have a strong negative slope ($m = -0.54$ and $-0.48$). This is a typical feature for the $\pi$ orbital region in organic compounds including heterocyclic aromatic compounds [16, 19]. Table 1 shows the CEDPICS for thiophene, which also has a strong negative slope for each band corresponding to a $\pi$ orbital [16].

The slopes of CEDPICS are quite different for thiophene and 2,2'-bithiophene. The slope of CEDPICS for thiophene corresponding to $\pi$ bands is -0.26 for band 1, -0.40 for band 2 and -0.33 for band 4. In the case of 2,2'-bithiophene, CEDPICS corresponding to $\pi$ band 1, 2, 3, 5 and 6 are -0.48 $\sim$ -0.60. This suggests that the attractive interaction for the out-of-plane direction for 2,2'-bithiophene is stronger than that for thiophene, due to the two connecting thiophene rings and the longer conjugated chains. The CEDPICS for the $\pi$ bands ($m = -0.34 \sim -0.45$) of biphenyl [17] also show more negative slopes than those of benzene ($m = -0.32 \sim -0.40$) [19]. On the other hand, the CEDPICS corresponding to band 1 ($m = -0.50$ for 2,2'-bithiophene and -0.34 for biphenyl) are less negative than band 2 ($m = -0.58$ for 2,2'-bithiophene and -0.45 for biphenyl) and 3 ($m = -0.60$ for 2,2'-bithiophene and -0.42 for biphenyl). This results from the fact that $\pi_6$ orbital has three nodal planes, and does not disturb the out-of-plane region.

The model potential curves shown in Figure 4 show that the well depth of the interaction potential between Li and one thiophene ring of 2,2'-bithiophene from the out-of-plane direction is about 485 meV, six times deeper than that between Li and thiophene (about 76 meV). From this, theoretical evidence of strong attractive interaction between He* and 2,2'-bithiophene was obtained. The well depth of the interaction potential between Li and the center of the C-C single bond between two thiophene rings for 2,2'-bithiophene is about 400 meV, which has a low value and indicates an expanding $\pi$ orbital region at the molecular surface due to the connection of the two thiophene rings. Although the model potential shows a repulsive interaction between the Li and S atom from the in-plane-direction for both molecules, $n_S$ or $\sigma$ bands as well as $\pi$ bands have a strong negative slope ($m \leq 0$ for thiophene, $m \leq -0.30$ for 2,2'-bithiophene). This is thought to be because $\pi$ orbital expansion affects He* causing it to approach the $n_S$ or $\sigma$ orbitals.
4.2. surface analysis by 2D-MIES

Figure 5 and 6 show coverage dependence of MIES spectra for thiophene and 2,2'-bithiophene on Ag(110). The lower spectrum is that of a pure Ag(110) surface, and the upper set of spectra are measured during the sample exposure. The top spectrum is that of a gas sample PIES spectrum. Some of the bands observed in the PIES spectrum cannot be seen clearly in the MIES spectra. However, the $E_p$ from PIES spectrum was effectively determined and the IP could be calculated. Figures 7 and 8 show the CEDPICS and electron density maps corresponding to each band in figures 5 and 6. The exposure is 25 L for the thiophene layer and 23 L for the 2,2'-bithiophene layer because each band is sufficiently intense to analyze at these exposures.

The band intensity of thiophene is proportional to the exposure, and the relative intensity of each band is similar to that of the PIES spectrum. This indicates that the outermost molecular orientation is independent of layer thickness and is advantageous in that it ionizes from the $\pi$ orbital. On the other hand, the intensity of bands 4 and 5 for 2,2'-bithiophene are slightly stronger than those of bands 6 and 7 at lower coverage ($\sim$ 22.5 L). However, the four bands have equal intensity at 46.8 L. Bands 4 and 5 are thought to primarily correspond to the $n_S$ and $\pi$ orbital and bands 6 and 7 mainly corresponded to the $\sigma$ orbital, therefore, the band intensity reflects the out-of-plane orbital for bands 4 and 5, and the in-plane orbitals for bands 6 and 7. This spectral change suggests that the in-plane orbital was advantageous in that it ionizes by increasing exposure and molecular inclining from a flat-lying orientation on the substrate. As the layer gets thicker, more spectral change will be observed because interaction between outermost layer and substrate gets weaker and molecular layer forms amorphous or crystal structure. Research on a thiophene and 2,2'-bithiophene monolayer on Ag(111) deposited by NEXAFS [20], suggested that the thiophene ring of both molecules is parallel to the substrate. Furthermore, MIES for thiophene and 2,2'-bithiophene at a lower exposure have the same features.

The negative slope of CEDPICS corresponding to the $\pi$ orbitals for the thiophene layer on Ag(110)
Table 1. Band assignments, observed and calculated ionization potential (IP) and obtained slope parameter \( (m) \) for 2,2’-bithiophene and thiophene.

\[
\begin{array}{cccccc}
\text{a) 2,2’-bithiophene} & \text{IP / eV} & \text{orbital} & \text{m} & \text{gas layer} \\
\hline
\text{band} & \text{obs.} & \text{calc.} & \text{character} & \text{gas} & \text{layer} \\
1 & 7.89 & 7.72(0.89)^{a} & 20b(\pi_{5}) & -0.50 & -0.22 \\
2 & 9.21 & 8.95(0.89) & 22a(\pi_{5}) & -0.58 & -0.19 \\
 & 9.06(0.89) & 19b(\pi_{4}) \\
3 & 9.71 & 9.54(0.88) & 21a(\pi_{3}) & -0.60 & -0.36 \\
4 & 11.53 & 11.60(0.89) & 20a(nS_{2}) & -0.37 & -0.18 \\
5 & 11.91 & 12.01(0.89) & 18b(nS_{1}) & -0.54 & -0.24 \\
 & 12.38(0.83) & 17b(\pi_{2}) & 19a \\
 & 12.57(0.88) \\
6 & 13.05 & 13.11(0.85) & 16b(\pi_{1}) & -0.48 & -0.12 \\
 & 13.28(0.85) & 18a \\
7 & 13.57 & 13.56(0.89) & 17a & -0.44 & -0.21 \\
 & 13.84(0.88) & 16a \\
 & 13.89(0.88) & 15b \\
8 & 15.21 & 15.64(0.86) & 13b & -0.39 & 0.02 \\
9 & 16.41 & 17.12(0.86) & 14a & -0.32 & -0.08 \\
\end{array}
\]

\[
\begin{array}{cccccc}
\text{b) thiophene} & \text{IP / eV}^{b} & \text{orbital} & \text{m} & \text{gas} & \text{layer} \\
\hline
\text{band} & \text{obs.} & \text{calc.} & \text{character} & \text{gas} & \text{layer} \\
1 & 8.96 & 8.77 & 1a_{2}(\pi_{3}) & -0.26 & -0.17 \\
2 & 9.58 & 8.98 & 2b_{1}(\pi_{2}) & -0.40 & -0.32 \\
3 & 12.04 & 12.01 & 6a_{1}(nS) & -0.15 & 0.09 \\
4 & 12.49 & 12.48 & 1b_{1}(\pi_{1}) & -0.33 & -0.26 \\
5 & 13.15 & 13.29 & 4b_{2} & -0.04 & -0.03 \\
6 & 13.71 & 13.44 & 5a_{1} & -0.05 & -0.09 \\
7 & 14.26 & 14.52 & 3b_{2} & -0.13 & -0.11 \\
8 & 16.52 & 16.88 & 4a_{1} & -0.19 & 0.01 \\
9 & 17.62 & 18.06 & 3a_{1} & -0.08 & -0.10 \\
\end{array}
\]

\[^{a}\text{Pole strength is shown in parenthesis.}\]
\[^{b}\text{Reference [16].}\]

was observed at bands 1 \( (m = -0.17) \), 2 \( (m = -0.32) \) and 4 \( (m = -0.26) \). These three slopes are less negative than those in the gas phase \((-0.26, -0.40\) and \(-0.33, \) see Table 1\), but remain negative compared to other \( n_{S} \) or \( \sigma \) bands \( (m = 0.09 \sim -0.11) \). The same trend was observed for CEDPCIS corresponding to most \( \pi \) orbitals for the 2,2’-bithiophene layer. Therefore, 2D-MIES to the molecular layer was demonstrated to behave similar to 2D-PIES for gas molecules. On the other hand, these results show an attractive interaction between either thiophene or 2,2’-bithiophene and He\(^{+}\). The out-of-plane interaction is weak when these molecules form molecular layer from the gas phase. This may be due to limiting molecular orientation and rotation. In the gas 2D-PIES study for benzene, increasing slope value \( m \) was observed by
using supersonic molecular beam comparing to effusive molecular beam [21]. This is because supersonic beam is composed of oriented molecules and probability that the molecular plane of benzene is parallel to the He$^*$ beam is decreased. Similar stereodynamic effect can be suggested to the thiophene or 2,2’-bithiophene thin layer of which most thiophene rings are parallel to the surface. For the clarification, more investigation into the mechanism of CEDPICS for the molecular layer should be carried out.

5. Summary
Using UPS, 2D-PIES and 2D-MIES, the gas or molecular layer of thiophene and 2,2′-bithiophene were investigated to study stereodynamics and anisotropic interaction for these molecules. A number of bands in the spectrum for thiophene and 2,2’-bithiophene were assigned to the $\pi$ orbital based on the UPS and PIES spectra and the negative slope of the CEDPICS. The slope of CEDPICS corresponding to $\pi$ band for 2,2′-bithiophene in the gas phase was more negative than that for thiophene in the gas phase. This was attributed to the connection between the two thiophene rings and the longer conjugated chain. The difference in the CEDPICS between the gas for thiophene or 2,2′-bithiophene and the molecular layer on the Ag(110) surface was observed. Results suggested that the molecular orientation caused the interaction between 2,2′-bithiophene and He$^*$ to be weak.

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References
[1] Roncali J 1997 Chem. Rev. 97 173
[2] Reddinger J L and Reynolds J R 1999 Adv. Polym. Sci. 145 57
[3] Kubota H, Munakata T, Hirooka T, Kondow T, Kuchitsu K, Ohno K and Harada Y 1984 Chem. Phys. 87 399
[4] Čermák V 1966 J. Chem. Phys. 44 3781
[5] Penning F M 1927 Naturwissenschaften 15 818
[6] Hagstrum H D 1979 Phys. Rev. Lett. 43 1050
[7] Mitsuke K, Takami T and Ohno K 1989 J. Chem. Phys 91 1618
[8] Ohno K, Yamakado H, Ogawa T and Yamata T 1996 J. Chem. Phys. 105 7536
[9] Kishimoto N and Ohno K 2007 Int. Rev. Phys. Chem. 26 938
[10] Yamakita Y, Tanaka H, Maruyama R, Yamakado H, Misaizu F and Ohno K 2000 Rev. Sci. Instrum. 71 3042
[11] Frisch M J et al. GAUSSIAN 03 Gaussian Inc. Pittsburg, PA, 2003
[12] Nygaard L, Nielsen T, et al. 1969 J. Mol. Structure 3 491
[13] Becke A D 1993 J. Chem. Phys. 7 5648
[14] Ortiz J V 1996 J. Chem. Phys. 104 7599
[15] Niehaus A, 1981 Adv. Chem. Phys. 45 399
[16] Kishimoto N, Yamakado H and Ohno K 1996 J. Phys. Chem. 100 8204
[17] Kishimoto N, Hagiwara Y, Ohno K, Knippenberg S, François J P and Deleuze M 2005 J. Phys. Chem. A 109 10535
[18] Ohno K, Mutoh H, and Harada Y, 1983 J. Am. Chem. Soc. 105 4555
[19] Takami T and Ohno K 1992 J. Chem. Phys. 95 6523
[20] Väterlein P, Schmelzer Z, Taborski J, Viczian F, Bäßler M, Fink R, Umbach E and Wurth W 2000 Surf. Sci. 452 20
[21] Horio T, Maruyama R, Kishimoto N, and Ohno K, 2004 Chem. Phys. Lett. 383 73