

Ion Desorption by Resonant Core Excitation of Biphenyl Monolayers

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1 Introduction

Soft X-rays can be used to selectively excite core-electrons of specific atoms in molecules; therefore, it has great potential for site-selective chemical bond breaking, also known as the “molecular scalpel” [1]. While such selective bond breaking has not been clearly identified in gas phase experiments, it has been reported in ion desorption from molecules adsorbed on surfaces. Our previous studies have suggested the key role of interaction between the excitation site and substrate for achieving site-selective bond breaking [2].

In this study, we investigated the ion desorption dynamics from self-assembled monolayers (SAMs) of biphenyl molecules adsorbed on gold substrates. A biphenyl molecule is composed of two phenyl rings and its molecular conductance is dramatically varied depending on the torsional angle between two rings. Therefore, we focused on the core-excitation dynamics of biphenyl SAMs with different torsional angles and degrees of π -conjugation [3, 4].

2 Experiment

We employed SAMs of two biphenyl molecules with torsional angles. The torsion was achieved by the addition of two methyl groups to the upper phenyl ring (Fig. 1). The molecules have a methyl ester groups (-COOCH₃) as the tail group. The SAM samples were prepared by immersion of Au substrates into 1 mM solution of the precursor molecules.

To examine the core-excitation dynamics, we performed time-of-flight mass spectrometry (TOF-MS) of ions desorbed from core-excited SAMs. The experiment was carried out at Photon Factory (PF) BL-2B in the hybrid operation mode. We used a mechanical pulse selector synchronized to the master clock of the storage ring operation to utilize only the single-bunch component of radiation [5]. The measurements were performed at room temperature under ultrahigh vacuum conditions of approximately 2×10^{-6} Pa. The X-ray incidence angle was set to 20°, and the ions were measured in the normal emission geometry.

The samples were evaluated by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. The measurements were conducted at BL-13 of HiSOR. The

spectra were obtained at the C and O K-edges by the total electron yield (TEY) method measuring the sample drain current.

3 Results and Discussion

The obtained NEXAFS spectra of the SAM samples exhibited noticeable polarization dependence in the intensity of C 1s $\rightarrow \pi^*$ (C = C, C = O) transition peaks, which suggested nearly upright orientation of the molecules on the Au surface.

In the TOF spectra obtained in the C K-edge region, clear peaks corresponding to CH_n⁺ (n = 0-3) ions were observed at C 1s $\rightarrow \sigma^*$ (O - CH₃) transitions [2]. The spectra for non-substituted biphenyl SAM exhibited sufficient fragmentation, as shown in Fig. 1. Notably, the relative yields of C₂H_m⁺ (m = 2-5) ions are significantly increased in the TOF spectrum for SAM with the larger torsional angle. Furthermore, the spectrum suggested reduced degree of fragmentation of the CH_n⁺ ions. From the interrelationship between ion desorption and the energy relaxation process involving charge transfer, it can be inferred that charge transfer between the molecule with a larger torsional angle and the substrate is suppressed in these observations. Therefore, this suppression of charge transfer can be attributed to the diminished π -conjugation caused by the larger torsional angle.

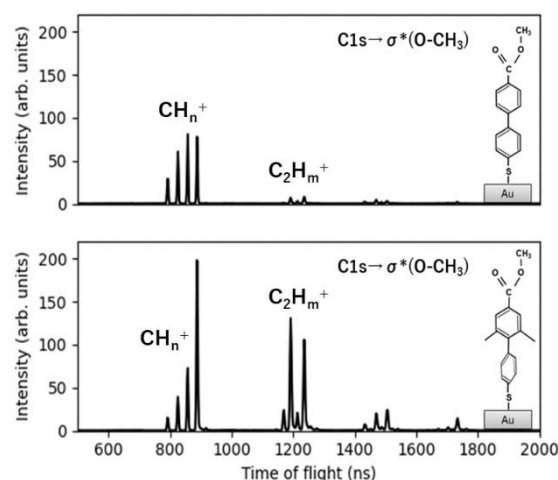


Fig. 1: Ion TOF mass spectra measured for core-excited biphenyl SAMs.

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References

- [1] W. Eberhardt *et al.*, *Phys. Rev. Lett.* **50**, 1038 (1983).
- [2] S. Wada *et al.*, *Phys. Condens. Matter.* **18**, 1 (2006).
- [3] A. Masillamani *et al.*, *Chem. Eur. J.* **18**, 10335 (2012).
- [4] L. Venkataraman *et al.*, *Nature* **442**, 904 (2006).
- [5] J. Adachi *et al.*, *J. Phys.: Conf. Ser.* **1412**, 152092 (2020).

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