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## Progress Highlight

# First-principles measurements of charge mobility in organic semiconductors: Valence hole–vibration coupling in organic ultrathin films

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## ABSTRACT

Although a great deal of research has been conducted on the electrical properties of organic devices, numerous crucial problems still remain. Of these, the study of charge mobility in organic semiconductor systems has been one of the most important subjects that has remained a puzzle for many years. It is essential to quantitatively understand conduction charge–molecular vibration coupling as well as the intermolecular interaction to discuss mobility. This article describes recent successes with direct measurements of valence hole–vibration coupling in ultrathin films of organic semiconductors with ultraviolet photoelectron spectroscopy (UPS), which can be used to experimentally study charge mobility based on energy and momentum conservation rules. The method may thus be categorized as a first-principles study of charge mobility. The detection of hole–vibration coupling of the highest occupied molecular orbital (HOMO) state in a thin film by UPS is essential to comprehending hole-hopping transport and polaron-related transport in organic semiconductors. We also need to experimentally determine energy-band dispersion or energy-level splitting in a molecular multilayer to obtain information on intermolecular interactions. Since the information on these is concealed behind the finite bandwidth of the HOMO in UPS spectra, we need to obtain high-resolution UPS measurements on organic thin films. Only careful measurements can attain the high-resolution spectra and provide these key parameters in hole-transport dynamics. A key method in achieving such high-resolution UPS measurements is also described.

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## 1. Introduction

Most of the over 82 million registered materials are organic [1], and many of them form solids by weak intermolecular interaction. Organic semiconductors are promising materials for electronic functions created by weak intermolecular interaction coupled with individual molecular characteristics, and have been increasingly studied to enable the electronic functions for device applications to be comprehensively understood. A key figure-of-merit of organic semiconductor devices is their charge-carrier mobility ( $\mu$ ), especially in a thin film. As the electrical conductivity ( $\sigma$ ) is given by  $\sigma = nq\mu$ , where  $n$  is the carrier concentration and  $q$  is the charge of the carrier concerned, one must understand the physical origin of  $\mu$ , viz., the coherent-band or incoherent-hopping conduction. Although many electrical measurements have been conducted to investigate charge mobility, most of the work has been directed to obtain  $\mu$  phenomenologically from  $I$ – $V$  measurements. Coherent conduction is dominated by band dispersion [2,3] if the mean free path of the carrier is much larger than the intermolecular distance, and thereby experimental measurements of dispersion relations are required. Hopping conduction is specified by two physical parameters, the transfer integral ( $t$ ) and the charge reorganization energy ( $\lambda$ ). The  $t$  is the measure of intermolecular interaction, and  $\lambda$  is related to charge-vibration coupling [4,5]. While some direct experimental determinations have been reported on organic semiconductor thin films, direct experimental studies of vibration coupling in organic semiconductor film were not done until 2002 [3,6]. Ultraviolet photoelectron spectra (UPS) experimentally involve information on the coupling between the conduction hole and molecular vibration. UPS measurements can thus offer key information that is necessary to unravel the fundamental mechanism in the carrier-transport properties of organic devices.

The origin of the UPS bandwidth for organic solids was discussed extensively until the end of the 70s [7–9]. After the work done by Salaneck et al., in 1980 [9], the UPS bandwidth of the highest occupied molecular orbital (HOMO) state in organic films was considered to have been mainly dominated by the dependence of relaxation (polarization) energy [8] on the site/depth, since it yielded a broadened UPS feature with a full-width-at-half maximum (FWHM) of  $> \sim 0.4$  eV. As a result, it was considered that intermolecular energy-band dispersion could not be measured, since the dispersion width may be smaller than the spectral bandwidth due to the dependence of relaxation (polarization) energy [10–15] on the site/depth. Unfortunately, the measurement of hole–vibration coupling in organic thin films has also been believed to be impossible, although the possibility of molecular vibration contributing to the width of the highest occupied molecular orbital (HOMO) band in UPS has been suggested by taking into consideration the excellent one-to-one correspondence of the valence-band features to those in gas-phase [7], and evidence was found for a tetracene film in an early work on UPS [16]. Therefore, gas-phase UPS spectra, where hole–vibration coupling is resolved for HOMO, have been used in theoretical studies of hole-hopping mobility ( $\mu_{th}$ ) [4,5,17–19]. There is a serious problem in

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