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Two dimensional band structure mapping of organic single crystals using the new generation electron energy analyzer ARTOF

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Abstract

We report on a novel type of photoemission detector, the Angle Resolved Time Of Flight electron energy analyzer (ARTOF), which enables electronic band structure determination under measurement conditions that are ideal for radiation-sensitive samples. This is facilitated through the combination of very high electron transmission and wide accessible angular range in one geometry. These properties make the ARTOF predestined to investigate specimens that strongly suffer from radiation damage during photoemission experiments under "standard" conditions, such as organic single crystals, as extremely low fluxes can be used while not compromising spectra accumulation times and signal-to-noise ratio. Even though organic single crystals are of increasing fundamental and applied scientific interest, knowledge of their electronic properties is still largely based on theoretical calculations due to major experimental challenges in measuring photoemission. In this work we show that the band structures of rubrene and tetracene single crystals can be obtained with unprecedented quality

using the ARTOF detector. The dispersion of the highest occupied band in rubrene is confirmed in accordance with an earlier report [1] and we disclose the absence of notable dispersion for the highest occupied energy level in the tetracene single crystal.

1. Introduction

Over the past decade conjugated organic molecules have received huge interest for the use in a variety of (opto-)electronic devices and are thus promising materials to complement and expand the applications based on conventional inorganic semiconductor electronics [2-5]. Already, organic semiconductors such as pentacene [6] and rubrene (5,6,11,12-tetraphenyltetracene) [7] have surpassed amorphous silicon in terms of charge carrier mobility in thin film transistors. Organic field-effect transistors based on tetracene and rubrene single crystals, for example, exhibit a hole mobility of over $2 \text{ cm}^2/\text{Vs}$ [8] and $15 \text{ cm}^2/\text{Vs}$ [7] at room temperature, respectively, which is close to or better than that of micro-crystalline Si-based transistors [9]. Other devices, e.g., light-emitting diode displays incorporating organics as well as organic solar cells are already commercially available.

Despite the encouraging achievements in device performance, the understanding of charge transport mechanisms in crystalline organic semiconductors is still incomprehensive. Theories developed in the past century for the understanding of charge transport in inorganic semiconductors seem to be insufficient to fully describe organic semiconductors, since for example electronic structure, carrier self-localization, morphology, the role of defects and doping can be fundamentally different in organic semiconductors [10, 11]. Currently, only the

ideal cases of band-like transport for delocalized charge carriers and small polaron transport for localized carriers are theoretically well understood [12-14].

The reported increase of hole mobility with decreasing temperature along the rubrene [010] crystal direction might be considered as a necessary indicator for band-like charge carrier transport [7, 9, 15-17]. This type of transport originates from an adequate overlap of the frontier π -orbitals of adjacent molecules resulting in orbital-derived electronic bands whose dispersion behavior correlates closely with the transport mechanism [18]. However, the contribution of this type of coherent transport versus that of an incoherent hopping transport to the effective charge carrier mobility is still under debate [13].

Understanding the electronic band structure is therefore a necessary prerequisite to unravel the charge transport mechanisms in organic semiconductors. Thus, single crystals are not only of fundamental but also of application relevant interest. Studying single crystals allows focusing on the intrinsic properties of organic materials, while extrinsic factors like impurities, defects, grain boundaries, and others, which influence the electrical properties, can be minimized. Angle-resolved ultraviolet photoelectron spectroscopy with synchrotron radiation excitation is established as the most powerful tool for probing the energy band structure of solids. However, the band structure measurement of (single crystalline) organic semiconductors is difficult due to their low conductivity on one hand and the low tolerance of conjugated organic compounds towards beam damage on the other hand [19]. Positive charging near the surface of the organic specimen due to the photoemission process causes electric fields that distort or even suppress a meaningful photoemission spectrum. Photoelectrons and their secondaries with a kinetic energy of several eV can break intramolecular bonds and result in chemical changes of the sample, e.g., *via* cross-linking and polymerization. Several strategies to avoid charging and beam damage have been developed

in the past years. Amongst them are the preparation of highly crystalline thin films [20-30], the cancelling of photo-holes by simultaneous irradiation with visible laser light [31-33], and last but not least simply the reduction of the synchrotron photon flux. The latter, however, bears the disadvantage of lower signal intensity and thereby decreasing signal-to-noise ratio at reasonable spectrum accumulation times. For instance, only in 2010 Machida et al. [1] succeeded in measuring a complete band structure of an organic single crystal, which has not been achieved before [32].

Here we report on the measurements of complete band structures of rubrene and tetracene of unprecedented quality performed with the novel spectrometer ARTOF.

2. Experimental methodology

2.1. Electron spectrometer

Although the technique of photoemission is known for several decades, it is still under constant further development. The increasing understanding of the photoemission process itself allowed creating refined methods, ranging from core level photoemission measurements to, e.g., angle resolved photoemission (ARPES) or photoelectron diffraction (PED). This pushed the development of electron analyzers from measurements of the kinetic energy of photoelectrons and their angular distribution in one direction to multi-dimensional detection schemes. Further on, analyzer technology has evolved to provide better energy resolution, higher transmission, and faster acquisition times. Recent state-of-the-art systems are hemispherical analyzers with a 2-dimensional detector capable collecting spectra in angular mode. This allows measuring a selected cut of the Brillouin zone, while for the measurement of the full momentum plane next to the point of interest mechanical movement of the sample is required. In addition, the transmission of hemispherical analyzers is limited by slits, resulting in the countrate-vs-resolution problem. In many cases increasing the intensity of the

photon beam is beneficial; however, it cannot be applied for beam damage sensitive samples, like conjugated organic materials.

Here we report on a novel type of photoemission detector, which will help to overcome the fundamental problems mentioned above. Recently, in 2009, calculations for a new principle design were introduced [34] – the Angle Resolved Time Of Flight electron energy analyzer (ARTOF) - which allows for ‘mild’ measurement conditions in terms of very short spectrum acquisition times combined with a very low photon flux [34, 35]. This was achieved by

- 300 times higher electron transmission than hemispherical analyzers
- angle resolved measurements of a full 30° cone within one measurement
- data acquisition in the MHz range
- single bunch operation of the storage ring, i.e., low photon flux.

Therefore, the ARTOF design combines a number of features that make it predestined for investigating organic compounds. Even more so, the measurement of a full 30° cone facilitates an experiment without change of any geometrical parameter of the sample during measurement. This can be of paramount advantage (in particular but not only for small samples) because it is no longer necessary to rotate the sample; therefore changing the investigated sample area and the probed sample depth does not occur. Furthermore, the fixed geometry avoids parasitic effects on the measured band dispersion by a spatial variation of the incident photon energy and the correct orientation of a sample is no longer critical since the obtained energy dispersion can be rotated and shifted for correction after the measurement is finished. The continuous probing of the full band structure and the storage of the complete data set also makes it possible to check for any time dependent modifications of the sample.

Due to the basic principle of ARTOF – measurement of the flight time of an electron from a sample to the detector – it is limited to a pulsed photon source. On the other hand, the

benefits are capitalized by the combination of a time-of-flight tube with electron optics and a time- as well as a position-sensitive electron detector. Using electron optics theory it is possible to calculate trajectories of photo emitted electrons and from the measured transient time and position on the detector one can calculate its original energy and emission angle. Such design involves no slits and allows collecting most of the electrons emitted from the sample. Figure 1 shows the principal design of an ARTOF; details can be found elsewhere [34, 35].

Figure1: Electrons are emitted from the sample under different angles (multiple trajectories are shown in grey). This results in the different flight path and thus different flight times. By combining the drift tube with electron lenses and using a position sensitive detector in ARTOF instrument electron trajectories are well defined. Using electron optics calculation it is possible to obtain initial emission angle and energy of the electron from the time-of-arrival and position at the detector with a very high precision. The time of arrival is calculated as time difference between start pulse, when a photon bunch reaches the sample (t_0 in the figure) and the moment when electron hits MCP of the detector ($t_{arrival}$ in the figure).

2.2. Organic single crystals

Rubrene and tetracene single crystals were grown by physical vapor transport [36, 37] using sublimation under streaming N_2 (purity 99,9999%) at a flow rate of 20 sccm. The starting materials purchased from Sigma Aldrich were purified by gradient sublimation prior to crystal

growth. For rubrene (tetracene) the temperature gradient within the gas flow reactor was about $2.5^{\circ}\text{C}/\text{cm}$ ($1.9^{\circ}\text{C}/\text{cm}$) at a fixed sublimation temperature of 280°C (197°C). The obtained crystal sizes amount to $2\text{ mm} \times 4\text{ mm} \times 150\text{ }\mu\text{m}$ for rubrene and to $3\text{ mm} \times 5\text{ mm} \times 100\text{ }\mu\text{m}$ for tetracene. To prove the crystalline quality of the sublimation grown crystals, X-ray diffraction has been carried out with the momentum transfer oriented along the surface normal, i.e., along the (001) direction, on reference crystals of the same batch. The observed high-order diffraction peaks for rubrene (15th order) and tetracene (11th order) in combination with the low damping of the corresponding intensities indicate the long-range order of the crystals and thereby the single crystal character of the samples used for the ARTOF measurements. Figure 2 shows the bulk crystal structure of rubrene and tetracene together with the respective Brillouin zones.

Figure 2: Crystal structure of the rubrene and tetracene unit cells together with the respective Brillouin zones along the Γ -X and Γ -Y directions.

Conducting carbon tape was used to mount the crystals onto metallic sample holders and the edges of the crystals were subsequently decorated with silver paste for better electrical conduction to the sample holder. Prior to introducing the samples into UHV (ultrahigh vacuum) the crystals were cleaved with adhesive tape in air along their (ab)-gliding planes and immediately transferred into the UHV system. All photoemission experiments of the

rubrene single crystal were performed under UHV conditions (base pressure 1×10^{-9} mbar) at the 3m NIM beamline of the electron storage ring BESSY II of the Helmholtz Zentrum Berlin für Materialien und Energie GmbH (HZB). The photon energy was set to 30 eV, the illuminated rectangular sample area was 50 μm vertically by 400 μm horizontally. The tetracene band structure measurements were performed at the U125 beamline of the HZB applying a photon energy of 35 eV and a spot size of 100 μm vertically by 400 μm horizontally. All experiments were carried out at room temperature.

During the measurements the exit slit of the beamline was almost fully closed to reduce the photon flux by three orders of magnitude from typically 10^{10} to 10^7 photons per second for the rubrene measurements and $2 \cdot 10^8$ for tetracene. The rubrene single crystal was irradiated by a continuous wave laser at 405 nm and 14 mW (nominal laser power, defocused to 1.2 cm^2 to cover the whole single crystal surface area) to compensate for surface charging, which still occurred without laser (tetracene 473 nm, 80 mW nominal, defocused to 0.5 cm^2).

Using visible light from the beamline, the overlap of the synchrotron radiation spot and the laser light was regularly ensured during the experiments. Figure 3 represents the geometrical set-ups of our experiments.

Figure 3: Geometry of the experiment. Left hand side: set-up for the measurements of rubrene at the 3m NIM beamline. (note that the data have been recorded close to normal emission geometry in order to ensure the overlap between the laser light and the synchrotron radiation). Right hand side: set up at the U125SGM to investigate the tetracene single crystals and verify the rubrene data.

As described earlier [1, 19], the laser power was incrementally increased until the HOMO peak position and width remained constant upon further increase in laser power. This saturation was reached here at 14 mW (nominal laser power). However, due to geometrical restrictions of the experimental set-up the de-focused laser was fed through a window (transmittance of 85%) onto the sample at grazing incidence leading to an effective laser power density of 0.12 mW/mm^2 for rubrene and 1.60 mW/mm^2 in case of tetracene.

3. Results and discussion

3.1. Rubrene

Angle resolved photoemission data were collected with a conical acceptance angle of 30° resulting in a 3-dimensional set of data containing the kinetic energy of the photoelectrons as well as the full $k_{||}$ -band structure. While in the case of rubrene the band structure was clearly discernible in maps after 30 min. accumulation time, the data shown here were collected over 10 hours to provide for superior statistics. From these data ARUPS images in Γ -Y (and Γ -X) direction were extracted as shown in Fig. 4 (and Fig. 7 further below).

In Γ -Y direction one can clearly see an energy dispersion of the HOMO-derived band, while deeper lying bands do not exhibit an apparent dispersion. Due to geometrical restrictions of the set-up the sample normal formed an angle of about 24° to the azimuthal axis of the

analyzer. Therefore, the center of the Brillouin zone is located at an angle of -6° at which the HOMO center has a binding energy (E_B) of 1.2 eV as found for normal emission in the setup of Machida et al. [1]. Referring to the center of the Brillouin zone, with increasing (and decreasing) angles the HOMO-derived band emission intensity maximum clearly shifts towards higher E_B reaching a maximum binding E_B of 1.2 eV at -6° (and 12° respectively). This can be seen in detail by zooming into this energy region, as shown in Figure 5. The spectra give a dispersion width of 0.4 eV (for the peak intensity maximum) and are in full agreement with the experimental work of Machida et al. [1] and Ding et al. [38], and also with theoretical predictions by Li et al. [39] and da Silva et al. [40].

Figure 5: Zoom-in of the HOMO-band region of rubrene in Γ -Y direction. The x-axis was changed to $k_{||}$ by assuming the 18.2° period of the dispersion to correspond to the 0.72 nm unit cell size.

To facilitate easier comparability of our results with conventional ARUPS data, individual 2-dimensional spectra were extracted from the raw data in 1° steps (see Figure 6). Theory predicted a splitting of the HOMO-derived band at the Γ -point [39, 40] due to the presence of two inequivalent molecules in the unit cell (see Fig. 2). This should result in two peaks for the

emission feature centered at ca. 1.1 eV E_B in photoemission, which was previously observed experimentally only as a slight shoulder [1]; two peaks can clearly be discerned in the data presented here (compare highlighted spectra in Fig. 6). The Γ -X direction of the rubrene Brillouin zone, in contrast, does not show noticeable dispersion as can be seen in Fig. 7, in accordance with earlier work [1, 39, 40]. The visible slope of all peak onsets (about 50 meV between -14° and $+14^\circ$) is the result of a small misalignment of the sample during measurement.

Figure 6: Line scans of the valence band region, each line corresponds to an angle slice of 1° . The red lines mark 6° and -12° , which are the centers of the Brillouin zone. The blue line marks half the distance between Γ and Y at 3° .

Figure 7: 2D spectrum of rubrene in Γ -X direction

3.2. Tetracene

While the band structure of rubrene was thoroughly investigated previously [1, 38], and served here as prototypical example to demonstrate the capacity of the ARTOF, the band structure of tetracene single crystals has not been reported to date. Tetracene is often discussed in direct relation with rubrene since the latter can be seen as a tetraphenyl derivate of tetracene. Hole mobility values ranging from 0.15 to 2.4 cm^2/Vs [8, 41-44] have been reported for tetracene in its single crystalline form, which is about one order of magnitude lower than those for rubrene, which has drawn the attention of the community working on conjugated materials.

Band structure calculations for tetracene predict a significant width of the HOMO-derived band of about 160 meV to 625 meV at 0 K [45, 46] in the diagonal k-direction between Γ -X and Γ -Y, which is comparable to the calculated rubrene band widths [8, 43]. However, in organic single crystals a temperature dependence of the mobility has been observed, which corresponds to a reduction of the transfer integral due to interaction with lattice vibrations and

a loss of the band-like coherent transport. Ortmann et al. [10] have included the phonon interaction in their band structure calculations, which decreases the band widths significantly. Consequently, the width for the tetracene HOMO-derived band reduces from 464 meV for the undressed bare hole to 65 meV for the polaronic state at room temperature and with phonon interaction [10]. The question therefore remains what the effective bandwidth in tetracene is from an experimental point of view.

Figure 8: 2D spectrum of the k_{vertical} -integrated slices of the tetracene 3D data set. A conventional waterfall plot of the HOMO region can be found on the right side in steps of 1° .

Figs. 8 and 9 show cuts through the measured Brillouin zone cone in which the slices of perpendicular k -directions were integrated (similar to Figs. 4 and 7 for rubrene). On the right side of the 2D-cuts the detailed waterfall plot of the topmost valence region can be found in steps of 1° . The spectra were recorded in normal emission since the experimental setup was slightly different for the tetracene measurements. Contrary to the case of rubrene, the direction of Γ -X and Γ -Y could not be identified because no significant $k_{\parallel}$ -dependence of the HOMO-derived emission feature (maximum intensity at $E_B = 1.10$ eV) or HOMO-1 – derived feature (maximum intensity at $E_B = 2.60$ eV) can be observed in the 3D data set. The projected 2D spectra therefore also do not show any $k_{\parallel}$ -dependence. This is an unexpected

finding because pentacene has a similar triclinic single crystal structure and shows significant dispersion in thin films that show bulk-like structure as shown by, e.g, Ohtomo et al. [26], and the width of the HOMO-derived band was predicted theoretically to be similar to that of tetracene [45, 47].

Figure 9: 2D spectrum of the $k_{\text{horizontal}}$ -integrated slices of the tetracene 3D data set. A conventional waterfall plot of the HOMO region can be found on the right side in steps of 1° .

Furthermore, the tetracene HOMO peak width of 0.7 eV is larger than the rubrene HOMO width and less structure is visible. The tetracene HOMO is asymmetric with a high binding energy (BE) side tail and a considerably steep low BE onset. A peak width of 0.35 eV is necessary to fit the steep HOMO onset, which is the same value for the two components of the rubrene HOMO. However, if further components of the same width are introduced to fit the whole tetracene HOMO, a minimum of three peaks is necessary to reproduce the spectrum. This points towards a pronounced electron-vibron coupling in the photoemission process, which results in vibronic replica at high BE of the vibrational ground state transition, in analogy to reports for the spectral shape of the HOMO of pentacene [48, 49]. Alternatively, the width as well as the relative peak distance is comparable to UPS data found in literature for tetracene *thin films* on Si(111), Ag(111), Cu(110), or GaSe passivated Si(111) [50-53].

Hence, the larger peak width might be due surface structural defects after cleavage that would not be visible in XRD spectra. We exclude beam damage and charging because of the steep low BE onset and the lack of time dependent changes if we compare data acquired at different times. The lack of band dispersion in the tetracene spectra can thus be either a result of the temperature dependence of the orbital overlap or a result of surface disorder, which will be the subject of future studies.

Summary

In the last years the band structure of rubrene layers and single crystals evoked significant interest due to their implications for organic electronic devices and were studied by several groups. These investigations were taken as references to examine the possibilities of a novel type of photoemission detector, the ARTOF. While conventional studies on organic single crystals suffer from the sensitiveness of the specimen, the ARTOF with its very high transmission and angular acceptance allows for very fast measurements under extremely mild conditions. Together with the fact that there is no change in experimental geometry throughout the whole experiment, the ARTOF seems to be the most appropriate detector for these kinds of investigations. Providing an extraordinary quality of data within a comparably short time of data acquisition at low photon flux, it opens a door to experiments which were difficult to perform in the past.

We reproduced and even improved the rubrene single crystal band structure data to verify the performance of the ARTOF. Our experiments on tetracene single crystals revealed the absence of a recognizable band structure at room temperature and therefore motivate further investigation into temperature dependent measurements of oligoacene single crystals.

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