Stable single molecules for quantum optics and all-optical switches

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CHAPTER 4

Electron energy loss of terrylene deposited on Au (111): Vibrational and electronic spectroscopy

We have investigated the vibrational and electronic properties of terrylene by high-resolution electron energy-loss spectroscopy (HREELS), Fourier-transform infrared spectroscopy and low-temperature single molecule fluorescence spectroscopy. Terrylene thin films were sublimated in ultra-high vacuum on Au (111) surface in order to record the HREEL spectra. Polycrystalline *para*-dichlorobenzene was used as a matrix to isolate a single terrylene molecule at 1.5 K, and record its fluorescence spectrum. The infrared spectrum together with the vibrational components from the fluorescence spectrum were used for the assignment and identification of the active modes found in HREELS. Finally, we report a loss signal around 17,000 cm^{-1} (2.1 eV) for the first singlet electronic excited state in agreement with optical spectroscopy. Some of the vibrational degrees of freedom either IR- or Raman-active modes can be found in the HREEL spectra provided they fulfil the surface selection rules. Energy-loss spectroscopy could be used as a complementary technique to explore some other degrees of freedom which are not accessible by optical means.

4.1. Introduction

High- resolution energy-loss spectroscopy (HREELS) is a spectroscopic technique completely different to our optical techniques (SMS). On this technique, an electron beam is used as the excitation source instead of a stream of photons. It is a valuable method to characterize organic thin films because it is highly surface sensitive and induces little radiation damage[1]. From the spectral features in HREELS it is possible to learn about the orientation of molecules in organic thin films, such as Langmuir-Blodget films and polymer films. Loss signals bring information about molecular degrees of freedom that are excited at the surface or at the interface. Many studies are focused on the vibrational degrees of freedom of the selected molecule[2]. However, the electronic properties of organic semiconductor films[3,4] (molecular exciton band gap) have also been measured with HREELS, using an electron beam with moderately high energy (10 eV or higher) as excitation, and looking for energy losses in the range of 1 – 5 eV (8000 – 40000 cm^{-1}) where these transitions occur. These observations can be compared with optical spectroscopy in solution[5]. There have been also some reports of the observation of low-lying triplet states from organic semiconductor films, in particular naphthalene[6].

Organic semiconductors based on polyaromatic hydrocarbons (PAH's) have been used in the development of novel molecular electronic and photonic devices, such as organic light emitting diodes (OLED's), photovoltaic solar cells, optical switches and field-effect transistors[7-9]. The performance of these devices is determined by the complex combination of electronic and structural properties of the materials[10]. The electronic band gap of the semiconductor plays an important role in the electron and hole mobility[11] in organic field-effect transistors (OFET's). The interfacial and intermolecular interactions are strong driving forces that influence the final structure of the film, and therefore play a very important role in the properties of electronic devices such as the electroluminescence of some LED's[12-15].

The terrylene (Tr) molecule has a maximum absorption peak at the center of the visible spectra around 570 ± 10 nm, which corresponds to 2.1 ± 0.04 eV (band-gap on silicon, >1 eV). Terrylene has a large extinction coefficient, $\varepsilon \approx 10^5$ M^{-1}cm^{-1}, and a fluorescence quantum yield close to unity. It is very photostable when it is embedded in solid matrices[16] and polymers[17]. The undistorted terrylene molecule belongs to D_{2h} symmetry, and its planar structure, similar to that of perylene[18-20], makes it an interesting candidate for growing ordered films as well. Thanks to some of these optical, electronic and structural properties, Tr could find some applications as a red pigment or as a semiconductor medium for OFET's[11].

The other very important element in the design of semiconductor devices is the selection of a metallic substrate. Gold has been commonly used as contact material for source and drain electrodes in organic field effect transistors. It is one of the noble metals used as a substrate that presents moderate physisorption interactions with poly-aromatic molecules like terrylene. This is an important property to keep the vibrational and the electronic properties of the deposited molecule as unperturbed as possible[4]. Thus, as the main part of this work we present the characterization of ultra-high vacuum (UHV) deposited films of terrylene on Au (111) surface by means of surface sensitive techniques, mainly with HREELS.

As a very particular aim, we were interested in measuring the energy gap between the ground state and the lowest triplet excited state of terrylene ($S_0 \rightarrow T_1$), as has been done for naphthalene films using HREELS[6]. This information is crucial for the design of the optical experiment that may allow us to switch off the continuous fluorescence photon stream from a single terrylene molecule, by exciting the molecule into this triplet state[21]. In the case of Tr, the energy for the singlet excited state (S_1) is well known[22]. However, to our knowledge, the energy of the lowest triplet state (T_1) has never been measured. The main difficulty in this measurement stems from the weakness of the population yield of T_1 from the excited singlet state, and from the extremely weak yield of the radiative decay (phosphorescence) from the triplet state to the ground singlet state.

We first report the vibrational spectroscopy of terrylene by HREELS. We use different complementary techniques to analyze and discuss the observations, including: Fourier transform infra-red (FTIR) absorption in a KBr pellet doped with Tr in a commercial spectrometer; quantum chemical calculations of terrylene vibrations by DFT B3LYP/6-31G(d,p) method from Deperasińska et al.[23] and the fluorescence spectrum from a single terrylene molecule, in *p*-DCB at 1.5 K[24]. The FTIR spectra showed almost one-to-one correspondence with the HREEL spectrum. However, some fluorescent active modes could also be observed in the HREEL spectrum. Finally, we studied the electronic properties of terrylene films by HREELS and compared to optical spectroscopy.

4.2. Experimental Part

All HREELS experiments were performed in a home-built UHV chamber at a base pressure of 3.0×10^{-10} mbar. A clean Au (111) surface was produced by repeated Ar^+ sputtering cycles and subsequent annealing at 650 °C. The cleanliness of the surface was determined by Auger electron spectroscopy (AES, from 80 - 560 eV) using a single-pass cylindrical mirror analyzer (CMA) with a coaxial electron gun at 2.7 kV (Varian CMSS-981). The presence of a reconstructed Au (111) surface was characterized by LEED with an incident beam energy E_0 = 45 eV. Terrylene powder (purchased from Chiron AS, Norway. Purity 99%) was directly inserted in the Knudsen cell that was separately pumped to 3×10^{-10} mbar. Then, it was baked for 24 hours at 373 K residual pressure of 3×10^{-8} mbar to be outgassed, dried and to eliminate possible carbon-containing compounds of lower molecular weight. The optimal sublimation parameters for terrylene in Au (111) were 469 ± 4 K ($196 \pm 4°C$) at a residual pressure of 8×10^{-10} mbar. Exposure times of $\approx$ 2 min led to a controlled deposition rate. After each exposure X-ray photoelectron spectroscopy (XPS) and HREELS were recorded one after the other. The α radiation from a Mg source (hv =1,253.6 eV) impinge the surface at -20° and the electrons are collected by the Leybold-Heraeus spectrometer under +20° relative to the surface normal. The HREELS experiments were performed with a home-built spectrometer in specular geometry, $\theta_{in} = \theta_{det}$ = can be 53º. The incident beam energy was set at E_0 = 5.0 eV for vibrational spectroscopy and 12 eV for electronic excitation. The

resolution of the spectrometer determined by measuring the FWHM of the elastic peak (loss at 0 meV) was 5 meV and 1.2 meV (40 and 10 cm^{-1}) respectively.

The complete fluorescence spectrum from a single terrylene has been measured using a poly-crystal of *para*-dichlorobenzene (*p*-DCB) as a host-matrix at 1.5 K.[CPC Submitted]. The Fourier-transform infrared spectrum was measured in a commercial FTIR-spectrometer. The sample was a very fine powder of Tr mixed with KBr as excipient, and then pressed to form a thin pellet.

4.3. Results and discussion

4.3.1. Vibrational spectroscopy of Terrylene

When an incident electron beam impacts the surface, the molecule has a probability to be excited to one of the vibrational levels of the ground state. As a result, the scattered electron transfers to the molecule some of its initial energy giving rise to the recorded energy-loss signal in the spectrum.

As a result of the excitation, an oscillating motion of the atoms of the deposited molecule induces a polarization of the gold electrons, creating a surface dipole. For molecular vibrations with atomic displacements perpendicular to the surface plane (out-of-plane modes), the electrostatic images enhance the dipole moment and the transition strength (left side of Scheme 4.1). For molecular vibrations with atomic displacements parallel to the surface (in-plane modes), the electrostatic images suppress the dipole moment (right side of Scheme 4.1). As a result, the intensities of the out-of plane vibrations are enhanced by the induced surface dipole while those of the in-plane vibrations are strongly suppressed as we will discuss along the paper.
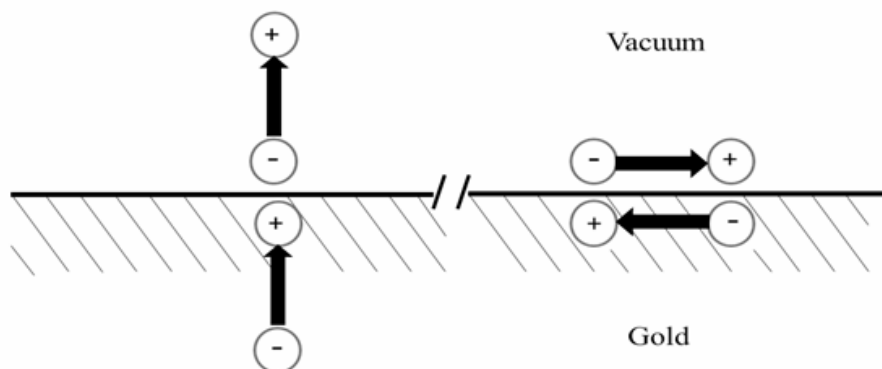
Scheme 4.1: *Shows the effect of electrostatic image charges in the metallic surface on the dipole moments of molecular vibrations. Left: out-of-plane dipole moments are strengthened by the image, enhancing the Coulomb interactions with impinging electrons. Right: for in-plane dipole moments, the image charges shields the field on impinging electrons and the Coulomb interaction with the mode is strongly suppressed.*

Figure 4.1 shows the HREEL (Fig.4.1a), the measured (Fig.4.1b) and the calculated (Fig.4.1c) infrared absorption, and the fluorescence (Fig.4.1d) spectra of Tr measured in the vibrational region from 0-3500 cm^{-1}. In the following, we discuss each of the modes appearing in the HREEL spectrum of a thin film of terrylene (Fig. 4.1a) in increasing frequency and compare to the other spectra. The HREEL spectra were always measured together with the XPS after each exposure time of 2 min.

The first loss signal on the wing of the elastic peak appears at 185 cm^{-1}. Although this region was not accessible to our IR spectrometer, the calculations predict a weakly out-of-plane bending mode, which is IR-active at 181 cm^{-1} and is in very good agreement with the HREEL peak. As expected, this IR-active mode is not observed in fluorescence.

The next loss signal comes at about 259 cm^{-1}. It appears broadened or split. Calculations predict an IR-active mode at 277 cm^{-1}, but also, a totally symmetric (Raman- and fluorescence-active) mode at 246 cm^{-1}. This Raman-mode corresponds to in-plane stretching of the whole molecule[23] along its long axis (strong peak in Fig.4.1d). We could not test whether the calculated IR-active mode appears in the IR spectrum, as our FTIR spectrograph cuts off at 300 cm^{-1}. Therefore, the loss peak at 259 cm^{-1} could arise from either of these modes, or from both.

The next component is a weak and broad (width 80 cm^{-1}) loss peak at 547 cm^{-1}. The corresponding region in the IR absorption spectrum shows multiple peaks at 492, 536 and 560 cm^{-1}. The fluorescence spectrum also shows modes in that region at 496, 542 and 588 cm^{-1}. Because of the low spectral resolution in HREELS (5 meV = 40 cm^{-1}) compared to that on IR absorption spectroscopy (1 cm^{-1}), it is difficult to propose any clear assignment of this broad peak.

The most intense loss peak in the HREEL spectrum around 800 cm^{-1} is observed at very low coverage. We can distinguish a weak shoulder at 690 cm^{-1}, a more intense shoulder at 760 cm^{-1} and the most intense component of all our spectra at resonant frequency of 815 cm^{-1}. The IR spectrum (Fig.4.1b) shows three strong modes at 696, 754 and 808 cm^{-1}. The calculations (Fig.4.1c) predict three modes around 800 cm^{-1}, two of them correspond to out-of-plane modes with frequencies at 765 and 829 cm^{-1} and one at 801 cm^{-1} for an in-plane mode. Figure 4.2 shows the atomic displacements for those three modes ordered by increasing frequency. The fluorescence spectrum shows only one weak peak at 786 cm^{-1}, possibly due to a combination of the long and short-axis deformation modes, corresponding to 544 + 243 cm^{-1} . No other active modes have ever been reported in this region from single molecule fluorescence spectra of terrylene in solid matrices[25-29].
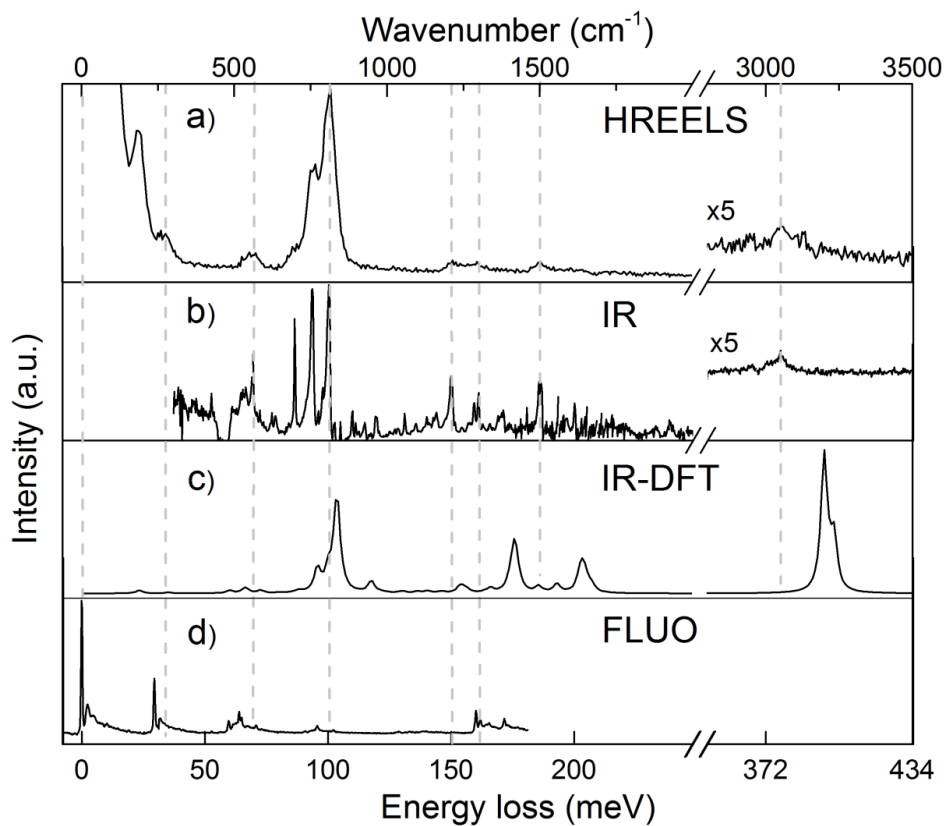
Figure 4.1: *a) specular HREELS of a terrylene film (14 min) on Au (111) recorded with energy beam $E_0 = 5.0$ eV with 5 meV resolution and 30 min acquisition time. b) FTIR of Terrylene in a KBr pellet. c) Calculated IR spectrum considering a FWHM $= 25$ cm^{-1}. d) Fluorescence spectrum from one single terrylene molecule at 1.5 K (the zero position corresponds to the zero-phonon line (ZPL) at 577.13 nm or 17327 cm^{-1}. The dotted lines are guides to follow the peak positions found in each spectrum.*
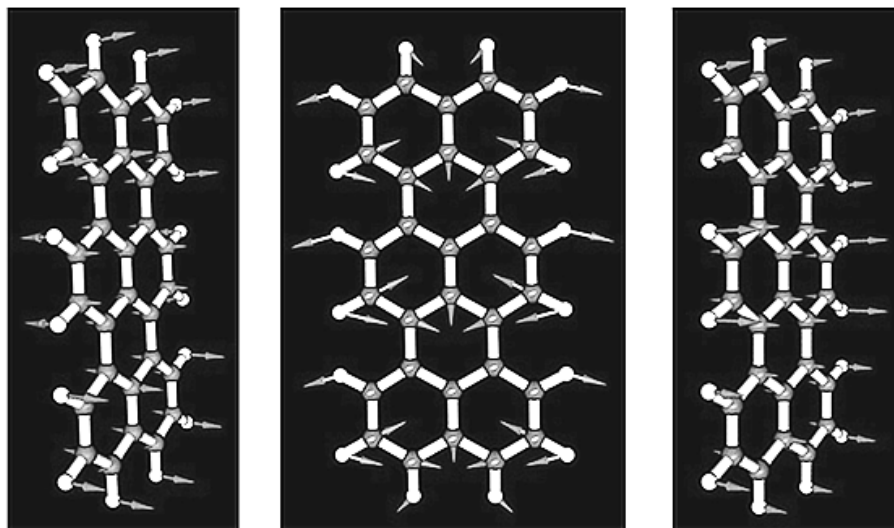
Figure 4.2: *Atomic displacements calculated for molecular vibrations of terrylene at 765 801 and 829 cm^{-1}, from left to right. Those modes might be the ones responsible for the strongest loss peak in EELS experiments. Drawings are made on the basis of calculation results published in [23], for which thank the authors of this work[23].*

The next HREELS signals at 1200 and 1280 cm^{-1} are weak but appear consistently even for very thin films. The corresponding FTIR spectrum presents maxima at 1208 and 1298 cm^{-1}. According to calculations these modes correspond to C-H in-plane wagging. Because the displacements are parallel to the metallic surface, their intensity should be strongly reduced by the electrostatic image effect (Scheme 4.1, right side). In fluorescence, another four in-plane modes appear at higher energies 1272, 1287, 1313 and 1357 cm^{-1}; but these are presumably Raman-active modes.

The next energy interval around 1500 cm^{-1} corresponds to the stretching of the carbon-carbon aromatic bonds. Only one band appears at 1495 cm^{-1} in the HREEL spectrum (Fig.4.1a). The calculations predict several modes within 1300 – 1600 cm^{-1}. Two of them with a significant IR activity are predicted, at 1402 and 1631 cm^{-1}; however a weak one at 1491 cm^{-1} matches the HREEL signal. The measured IR spectrum shows an intense mode at 1496 cm^{-1} in agreement with HREELS and calculations. The fluorescence spectrum does not extend to this frequency area because of the limitation of our spectrometer grating.

Finally, the HREELS shows a weak vibration at 3054 cm^{-1}, which can be attributed to a C-H stretching ν(C-H). This is in good agreement with the FTIR spectrum where this mode appears at 3065 cm^{-1}. However, the DFT calculation finds this mode at 3200 cm^{-1}. The clear frequency difference between calculation and experimental is due to an overestimation of the C-H mode energy, when this mode is used to normalize the whole spectrum, as required in DFT calculations.

All the modes are summarized in Table 4.1. On the whole we notice a fair agreement between the HREEL spectrum and the measured FTIR spectrum, both in position and relative intensity of the bands. It is likely that the HREELS peaks with the highest intensities correspond to out-of-plane modes enhanced by the electrostatic image effect discussed in Scheme 1. Nonetheless, some in-plane modes according to our assignment are visible in the HREEL spectrum and therefore are not completely suppressed by the electrostatic image effect. This may arise from a different excitation mechanism or from molecules that are not completely flat to the surface. Some of the differences in frequencies can arise from the different environments of the molecules, the gold surface in HREELS and the microcrystal environment in the IR KBr pellet measurement.

Table 4.1: *Frequencies (in cm^{-1}) of the main vibrational modes of terrylene found in HREELS on Au (111) surface, measured on terrylene in a KBr pellet by FTIR, calculated IR and fluorescence (or Raman), and from a single-molecule fluorescence spectrum[24], with maximum uncertainty ±5 cm^{-1}.*

Mode assignment	HREELS cm^{-1}	IR cm^{-1}	IR-DFT[23] cm^{-1}	Fluo-DFT[23] cm^{-1}	SMS[24] cm^{-1}
out-of-plane bending	185	-------	181	No active mode	No signal
long-axis stretching	259	-------	277	246	249
short-axis stretching	547	492 536 560	478 528 579	447 544 590	496 522 588
Out-of-plane C-H wagging	690 760 815	696 754 808	765 801 829	No active modes	Very weak 544+246
In-plane C-H bending	1200 1280	1208 1298	1232 1256	No active modes	No peaks
Aromatic C=C stretching	1495	1496 1612	1402 1491 1631	1307 1343 1391 1403	1272 1287 1313 1357
C–H stretching	3054	3065	3200	Not reported	------

In gas phase, fluorescent- (or Raman-) active modes are IR-inactive because of the central symmetry of the molecule[23], therefore "no active mode" is written in the table in case. Dotted lines means not measured due to experimental limitations. "No peaks" corresponds to a part in the spectrum were no components were observed.

4.3.2. HR-EEL spectrum at increasing exposition times

Figure 4.3 shows HREELS spectra for increasing exposure times 14, 30, 70 and 100 min. These spectra display clear changes. The most striking feature in these spectra is the relative intensity decrease of the modes around 800 cm^{-1}, which we assigned to out-of-plane C-H wagging. The decrease in intensity could arise from a different structure of the molecules at larger thickness or from a decrease of the interaction with the surface.

A second feature is the appearance of two new modes for larger thicknesses, at 400 cm^{-1} and around 1090 cm^{-1}. The first one becomes visible after 30 min and stays unchanged at longer exposure times. The second one is in the aromatic stretching area and it could appear because of a change in orientation of the terrylene molecules when the film becomes thicker.

Finally, we observe a shift of the C-H stretch from 3054 cm^{-1} to 2920 cm^{-1}. It is not possible to ensure that these peaks correspond to the same molecular vibration because of the big frequency mismatch. But in case they are the same, the direct change of the electrostatic interaction with the gold surface as the film becomes ticker could explain the frequency shift. As an alternative reason, a different C-H stretch mode could be excited at high thickness because of a different molecular orientation.

From these data, it is hard to understand the origin of the observed spectral changes. But in general, it is likely that the molecules are almost lying flat on the surface at low coverage, but they could rearrange in three-dimensional aggregates at higher coverage. For a better understanding, it will be necessary to probe the structure of the deposited films as a function of thickness, and in particular to determine the orientation of the molecules.
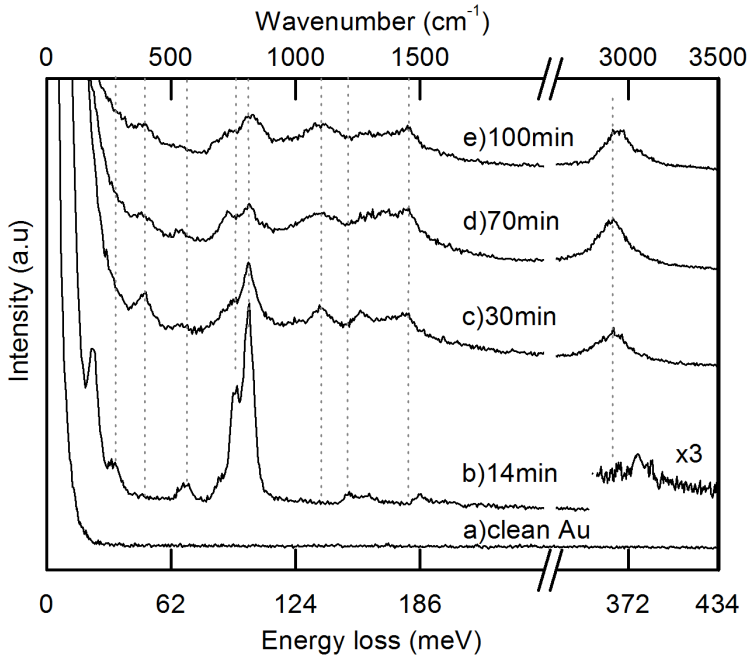
Figure 4.3: *Specular HREELS spectra for increasing terrylene film thickness on top of Au (111). The first spectrum is the base line obtained from a clean Au (111) surface before deposition. The dotted lines are guides to help to follow the peak evolution. The beam energy was $E_0 = 5.0$ eV; and an integration time 30 min.*

4.3.3. EELS probing of electronic excitations of terrylene

Figure 4.4 shows the HREEL spectrum of terrylene thick films for the complete spectral-loss between 0 and 22, 000 cm^{-1}. Intense peaks are clear in the vibrational region between 0 - 4000 cm^{-1} (as discussed in previous sections). Then, it is also possible to distinguish a clear and broad signal in the high-energy loss region between 16,000 and 20,000 cm^{-1} (2.0 and 2.5 eV) which is centered at 18,147 cm^{-1} (2.25 eV). Looking in more detail into this broad feature is it possible to see a maximum loss signal around 2.1 eV. This is in good agreement with the optical spectroscopy (Chapter 3 of this thesis)

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and therefore be assigned to the singlet-to-singlet electronic transition. Even further, the other component at 18, 550 cm^{-1} (2.3 eV) agrees with the expected vibro-electronic transition found in the optical spectrum. Next, we look for the spin-forbidden singlet-to-triplet electronic transition of terrylene. This transition has been predicted by quantum chemical calculations to lie at about 8,000±800 cm^{-1} (1±0.1 eV). However, as can be seen in Fig 4.4, no clear signal appears around this interval in the energy loss spectra. It is possible to see a weak feature at 1.8 eV that cannot be assigned to any of the know terrylene electronic states.
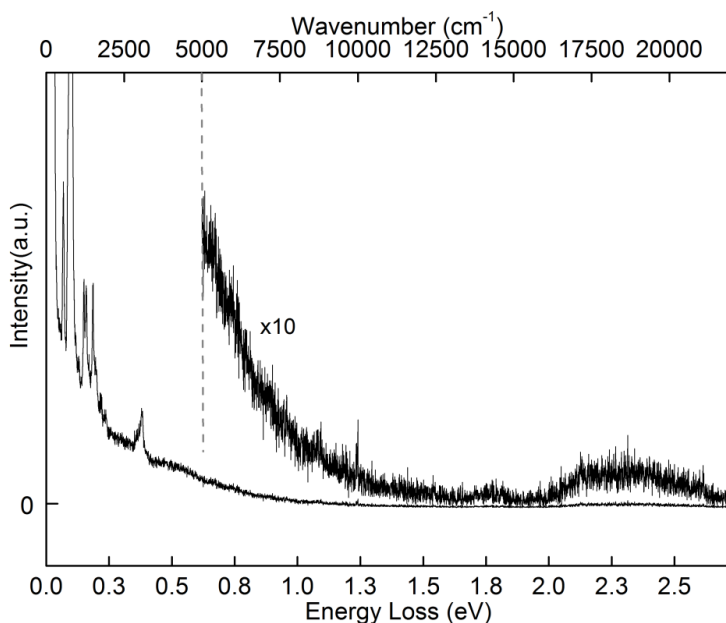
Figure 4.4: *EELS probing of electronic excitations of terrylene. The sample is a thick film (2 hours exposure) of terrylene on Au (111). It was probed with a 12 eV electron beam in specular geometry.*

4.4. Conclusions

HREELS is a surface-sensitive technique which provides information about modes inaccessible by optical means. The selection rules and excitation mechanisms of HREELS are thus complementary to optical spectroscopy. We have succeeded in electronically exciting terrylene to the first excited-singlet state using the HREELS electron beam, but the spin-forbidden transition towards the lowest triplet state remains unknown. The strongest terrylene vibration modes in HREELS appearing around 800 cm^{-1} have never been reported before from fluorescence spectroscopy. The HREEL spectrum agrees fairly well with the IR absorption. With support from calculations, we assign the two strongest modes to C-H out-of-plane wagging (Fig. 4.2). To progress in the assignment of the other HREELS modes, delicate structural studies in the sub-monolayer regime are the natural next steps of this work.

More broadly, we have shown that terrylene is a suitable molecule for controlled deposition in an UHV system. We were able to produce organic films on Au (111) which were stable for many hours of exposure to the electron beam and to X-rays. Terrylene shows a good compatibility and weak interactions with gold which may prove interesting for future organic electronics devices.

4.5. Acknowledgments

Reference List

1. Ibach, H.; Balden, M.; Bruchmann, D.; Lehwald, S. Electron-Energy Loss Spectroscopy - Recent Advances in Technology and Application. *Surface Science* **1992,** *269*, 94-102.

2. Tautz, F. Structure and bonding of large aromatic molecules on noble metal surfaces: The example of PTCDA. *Progress in Surface Science* **2007,** *82* (9-12), 479-520.

3. Nakamura, T.; Iwasawa, K.; Kera, S.; Azuma, Y.; Okudaira, K. K.; Ueno, N. Low-energy molecular exciton in indium/perylene-3,4,9, 10-tetracarboxylic dianhydride system observed by electronic energy loss spectroscopy. *Applied Surface Science* **2003,** *212*, 515-519.

4. Shklover, V.; Tautz, F. S.; Scholz, R.; Sloboshanin, S.; Sokolowski, M.; Schaefer, J. A.; Umbach, E. Differences in vibronic and electronic excitations of PTCDA on Ag(111) and Ag(110). *Surface Science* **2000,** *454*, 60-66.

5. Bulovic, V.; Burrows, P. E.; Forrest, S. R.; Cronin, J. A.; Thompson, M. E. Study of localized and extended excitons in 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) .1. Spectroscopic properties of thin films and solutions. *Chemical Physics* **1996,** *210* (1-2), 1-12.

6. Swiderek, P.; Michaud, M.; Hohlneicher, G.; Sanche, L. Electron-Energy Loss Spectroscopy of Solid Naphthalene and Acenaphthene - Search for the Low-Lying Triplet-States. *Chemical Physics Letters* **1990,** *175* (6), 667-673.

7. Haas, U.; Thalacker, C.; Adams, J.; Fuhrmann, J.; Riethmuller, S.; Beginn, U.; Ziener, U.; Moller, M.; Dobrawa, R.; Wurthner, F. Fabrication and fluorescence properties of perylene bisimide dye aggregates bound to gold surfaces and nanopatterns. *Journal of Materials Chemistry* **2003,** *13* (4), 767-772.

8. Winder, C.; Matt, G.; Hummelen, J. C.; Janssen, R. A. J.; Sariciftci, N. S.; Brabec, C. J. Sensitization of low bandgap polymer bulk heterojunction solar cells. *Thin Solid Films* **2002,** *403*, 373-379.

9. Kudo, K.; Iizuka, M.; Kuniyoshi, S.; Tanaka, K. Device characteristics of lateral and vertical type organic field effect transistors. *Thin Solid Films* **2001,** *393* (1ГÇô2), 362-367.

10.   Wood, S.; Kim, J. S.; James, D. T.; Tsoi, W. C.; Murphy, C. E.; Kim, J. S. Understanding the relationship between molecular order and charge transport properties in conjugated polymer based organic blend photovoltaic devices. *Journal of Chemical Physics* **2013,** *139* (6).

11.   Karl, N. Charge carrier transport in organic semiconductors. *Synthetic Metals* **2003,** *133*, 649-657.

12.   Toda, Y.; Yanagi, H. Electroluminescence of epitaxial perylene films. *Applied Physics Letters* **1996,** *69* (16), 2315-2317.

13.   Kazmaier, P. M.; Hoffmann, R. A Theoretical-Study of Crystallochromy - Quantum Interference Effects in the Spectra of Perylene Pigments. *Journal of the American Chemical Society* **1994,** *116* (21), 9684-9691.

14.   Komolov, S.; Aliaev, Y. Influence of the substrate properties on the electronic structure of organic film-inorganic substrate interfaces. *Technical Physics* **2007,** *52* (9), 1163-1168.

15.   Barlow, S. M.; Raval, R. Complex organic molecules at metal surfaces: bonding, organisation and chirality. *Surface Science Reports* **2003,** *50* (6-8), 201-341.

16.   Kosciesza, R.; Luzina, E.; Wiacek, D.; Dresner, J.; Kozankiewicz, B. Photo-stability of single terrylene molecules in 2,3-dimethylnaphthalene crystals. *Molecular Physics* **2009,** *107* (18), 1889-1895.

17.   Wirtz, A. C.; Dokter, M.; Hofmann, C.; Groenen, E. J. J. Spincoated polyethylene films for single-molecule optics. *Chemical Physics Letters* **2006,** *417* (4-6), 383-388.

18.   Unwin, P. J.; Jones, T. S. Vibrational properties of ordered perylene thin films on GaAs(100) and InAs(111)A. *Surface Science* **2003,** *532*, 1011-1016.

19.   Gao, L.; Sun, J.; Cheng, Z.; Deng, Z.; Lin, X.; Du, S., X; Gao, H. Structural evolution at the initial growth stage of perylene on Au(111). *Surface Science* **2007,** *601* (15), 3179-3185.

20.   Lee, S. K.; Zu, Y. B.; Herrmann, A.; Geerts, Y.; Mullen, K.; Bard, A. J. Electrochemistry, spectroscopy and electrogenerated chemiluminescence of perylene, terrylene, and quaterrylene diimides in aprotic solution. *Journal of the American Chemical Society* **1999,** *121* (14), 3513-3520.

21.   Orrit, M. Nano-optics - Quantum light switch. *Nature Physics* **2007,** *3* (11), 755-756.

22.   Orrit, M.; Bernard, J.; Zumbusch, A.; Personov, R. I. Stark-Effect on Single Molecules in A Polymer Matrix. *Chemical Physics Letters* **1992,** *196* (6), 595-600.

23.   Deperasinska, I.; Zehnacker, A.; Lahmani, F.; Borowicz, P.; Sepiol, J. Fluorescence studies of terrylene in a supersonic jet: Indication of a dark electronic state below the allowed transition. *Journal of Physical Chemistry A* **2007,** *111* (20), 4252-4258.

24.   Navarro, P.; Tian, Y.; van Stee, M.; Orrit, M. Stable Single-Molecule Lines of Terrylene in Polycrystalline para-Dichlorobenzene at 1.5 K. *Chemphyschem : a European journal of chemical physics and physical chemistry* **2014,** *15* (14), 3032-3039.

25.   Tchenio, P.; Myers, A. B.; Moerner, W. E. Vibrational Analysis of the Dispersed Fluorescence from Single Molecules of Terrylene in Polyethylene. *Chemical Physics Letters* **1993,** *213* (3-4), 325-332.

26.   Kummer, S.; Basche, T.; Brauchle, C. Terrylene in P-Terphenyl - A Novel Single-Crystalline System for Single-Molecule Spectroscopy at Low-Temperatures. *Chemical Physics Letters* **1994,** *229* (3), 309-316.

27.   Kozankiewicz, B.; Bernard, J.; Orrit, M. Single-Molecule Lines and Spectral Hole-Burning of Terrylene in Different Matrices. *Journal of Chemical Physics* **1994,** *101* (11), 9377-9383.

28.   Palewska, K.; Lipinski, J.; Sworakowski, J.; Sepiol, J.; Gygax, H.; Meister, E. C.; Wild, U. P. Total Luminescence Spectroscopy of Terrylene in Low-Temperature Shpolskii Matrices. *Journal of Physical Chemistry* **1995,** *99* (46), 16835-16841.

29.   Deperasinska, I.; Kozankiewicz, B.; Biktchantaev, I.; Sepiol, J. Anomalous fluorescence of terrylene in neon matrix. *Journal of Physical Chemistry A* **2001,** *105* (5), 810-814.