

COST STSM Reference Number: COST-STSM-CM0601-4862

STSM Applicant: Dr Sylwia Ptasinska, The Open University, Milton Keynes(UK) ,
s.ptasinska@open.ac.uk

Period: 05/07/2009 to 11/07/2009

Host: Prince Kevin, Sincrotrone Trieste S.C.p.A. di interesse nazionale, Trieste(IT),
prince@elettra.trieste.it

SCIENTIFIC REPORT

1. Purpose of the visit:

The initial aim of my STSM to the Elettra synchrotron was to study adsorption geometry of cytosine on Au (111) surface by using: XPS and NEXAFS techniques. However preliminary results obtained from proposed sample showed a strong contribution of water molecules in spectra. Therefore a chosen molecule to study during my STSM was one of DNA nucleotides, namely thymidine (dT). The molecular structure of thymidine ($C_{10}H_{14}N_2O_5$) is presented in Fig. 1. The structure of thymidine consists of the thymine base linked to a sugar molecule (deoxyribose) via a C-N glycosidic bond. In proposed studies, the changes of chemical states can be identified by measuring of valence and X-ray photoelectron (XPS) spectra of thymidine deposited onto Au (111) crystals. In addition NEXAFS allows a determination of the adsorption geometry and the empty state electronic structure of the adsorption complexes.

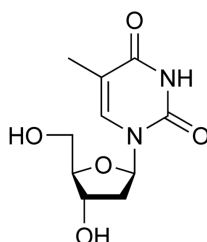


Fig. 1. Molecular structure of thymidine.

2. Description of the work carried out during the visit:

In the present studies the electronic structure and absorption geometry of dT molecules on a gold surface were investigated at different coverage, i.e. mono-, sub- and multi-layers. The obtained spectra for sub- and monolayers resemble each other, therefore in this report only spectra for multi- and monolayer are shown for comparison. An Au (111) single crystal was cleaned by Ar ion sputtering and annealing at 880 K and then dT was deposited onto the surface by evaporation of a sample which was placed in the oven heated in vacuum in order to be degassed. In the case of multilayer films, the thymidine powder was heated to 378 K and then dosed onto the crystal for about 1200 s. The thickness of formed films was estimated to be about 6 monolayers, but more detail estimation will be done. While in the case of a monolayer film of thymidine, first a few dT monolayers were deposited and then flashing to 350 K in order to desorb weakly bonded molecules.

Photoemission spectra were recorded with an angle of incidence of the synchrotron light of 30° with respect to the surface normal and an emission angle of 30° , using the multichannel electron analyzer. The total energy resolution of the analyzer and incident photons varied depending on photon energy and pass energy of analyzer. The

binding energy of photoelectron was calibrated by measuring the Fermi edge as well the known value for binding energy of inner electrons from gold (Au 4f). The O 1s XPS spectra were measured with the same analyzer but by using Al K α radiation from an X-ray tube. The NEXAFS spectra for thymidine monolayers were taken at the nitrogen and oxygen K-edges at normal (90°) and grazing (10°) incidence of the photon beam with respect to the surface.

3. Description of the main results obtained:

A. Valence band spectra of thymidine

The valence band spectra of thymidine on Au (111) from multi- and monolayers measured at photon energy of 120 eV are presented in Fig. 2. In both spectra the most dominant features observed are assigned to the gold d bands (2-8 eV binding energy) and sp bands below 8 eV. Therefore in order to analyse valence spectra from thymidine further processing of data has to be done, i.e. subtraction of Au spectrum before dT deposition. With a higher coverage, a peak with maximum at 9 eV shows a clearly visible increase of signal which can be assigned as vertical ionization energy (vIE). Previous studies using photoelectron spectroscopy techniques reported a value for vIE of 8.7 eV for thymidine.

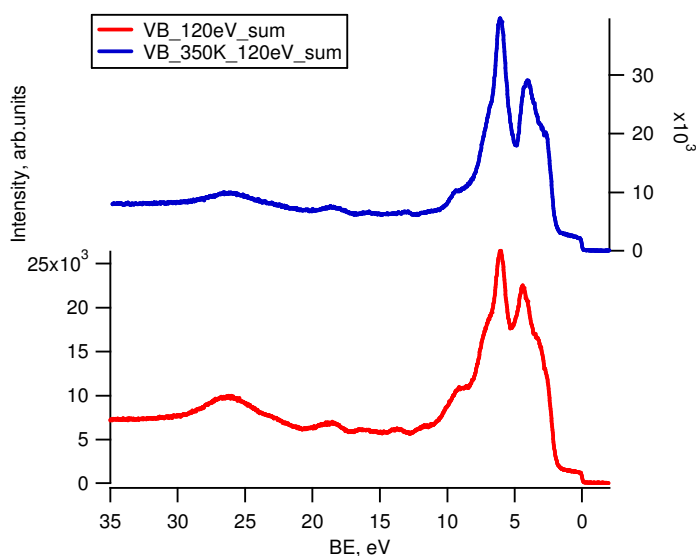


Fig.2. Valence band spectra of thymidine on Au(111) for multilayer (red line) and monolayer (blue curve) films.

Previous gas phase studies on UV photoelectron spectroscopy of nucleosides of DNA and RNA have shown the existence of a large number of valence orbitals in those molecules (*J. Phys. Chem.*, 1981, 85, 3851 and *J. Electron Spectrosc. Relat. Phenom.* 1996, 82, 61). A clear assignment of the lowest-energy photoelectron band to a specific molecular orbital seems to be unlikely. However, earlier studies of free nucleobases indicate that in all of the cases the first photoelectron band can be assigned to the removal of the electron from the highest occupied p orbital (p₁), which has a vertical ionization energy that is at least 0.5 eV less than that of the

second highest occupied orbital. This observation suggests that the highest occupied orbital in each of the nucleosides also gives rise to a resolved band. Molecular calculations were performed by Yu et al (*J. Phys. Chem.*, 1981, 85, 3851) to interpret the photoelectron spectra they obtained from volatile nucleosides. Those calculations predict that, for these nucleosides, some of the highest occupied molecular orbitals are localized on the bases, some on the sugar, and some distributed over both moieties.

B. Core level XPS spectra.

High resolution XPS spectra of C 1s, N 1s and O 1s for mono- and multilayer of thymidine films are presented in Fig. 3-5. A comparison of spectra obtained for different coverage has shown shifts of peak positions towards lower binding energies (BE) of all elements of dT monolayer films. These shifts indicate the interaction of atoms with the Au surface. In addition, the C 1s spectrum for multilayer films is much less resolved than those for monolayer films, most likely due to molecular interaction of neighbouring molecules in the film.

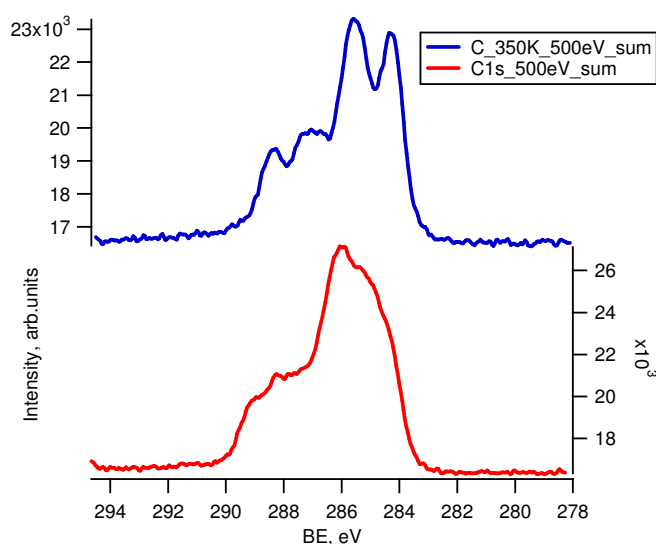


Fig.3. C1s spectra of thymidine on Au(111) for multilayer (red line) and monolayer (blue curve) films.

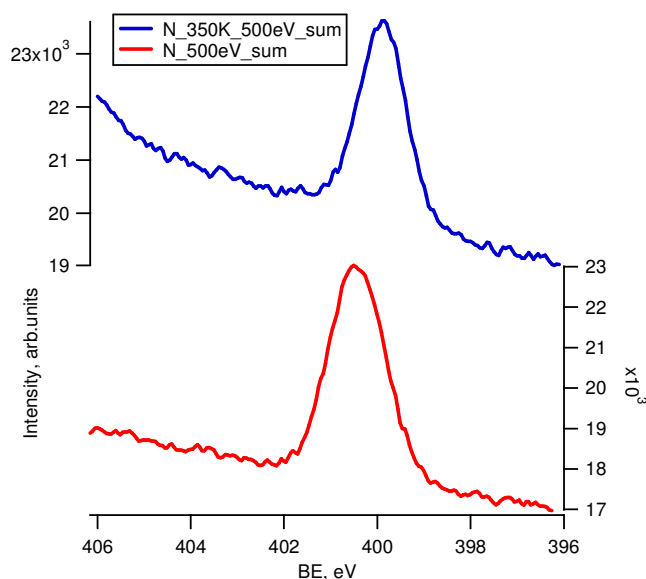


Fig.4. N1s spectra of thymidine on Au(111) for multilayer (red line) and monolayer (blue curve) films.

The C 1s spectrum of low-coverage thymidine (Fig. 3) can be assigned to different carbon species by comparison with previous results obtained for thymine. The following species are involved: hydrocarbons (C-C, C-H), carbon bound to nitrogen (C-N, N-C-N), amide carbon (N-C=O) and urea carbon [N-C(=O)-N] with characteristic binding energies of approximately 285, 286-287, 288 and 289 eV, respectively. Here, in the case of nucleotides, with addition of deoxyribose sugar, new contributions are expected to be observed at binding energy of around 286.5 eV, which can be attributed to the carbon atom attached to oxygen forming C-O-C and the C-OH bonds in the sugar unit (cyclic ether and alcohol, respectively) and from a C-N glycosidic bond. In monolayer films, the strongest shifts are observed for low BE peak of C 1s, which come from carbon atoms which are thymine ring members. Thus we can conclude that the thymine moiety strongly interacts with Au surface while the sugar moiety not so significantly. The N 1s core-level peak in Fig. 4 has a binding energy between 402 and 399 eV. Since the sugar does not contain nitrogen, no significant changes in comparison to thymine spectra are expected. A comparison of the N 1s spectra for a low and high coverage has shown a lowering of binding energy for monolayer film of thymidine.

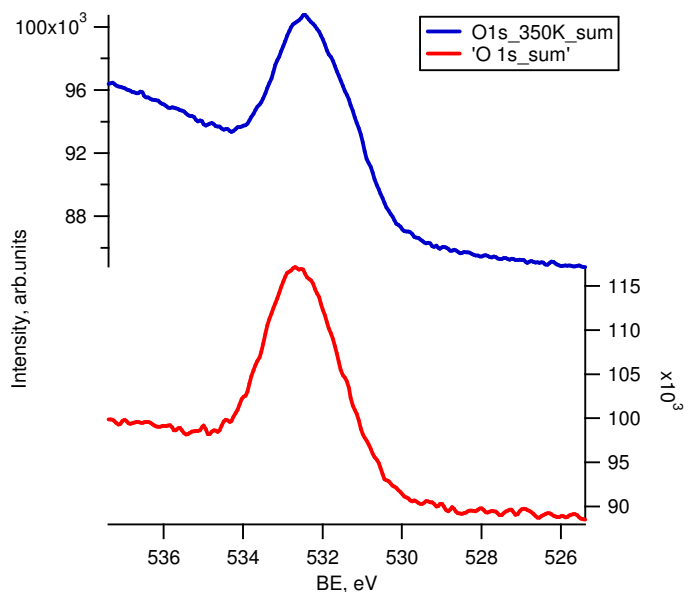


Fig.5. O1s spectra of thymidine on Au(111) for multilayer (red line) and monolayer (blue curve) films.

In the case of the O 1s spectra for thymine, a single peak located at a binding energy between 531-532 eV is assigned to the C=O bond. The effect of adding sugar to a nucleobase increases the width of the O 1s peak. The broadening of the O 1s peak can be due to overlapping of two peaks interpreted as C-OH and C=O bonds which results in one observed peak in spectrum for multilayer films (Fig. 5). The lower BE peak can be attributed to carboxyl groups whereas that for the higher BE peak to alcohol. The situation changes for the low coverage of Au crystal where a shoulder at the low BE peak appears. This shift can reflect the interaction of oxygen atoms of thymine with the gold substrate.

C. NEXAFS spectra of thymidine monolayer.

The NEXAFS spectra of multilayer films of thymidine are not presented here as they showed a random orientation of molecules. The nitrogen and oxygen K-edge spectra at normal and grazing incidence are shown in Fig. 6 and 7, respectively.

The nitrogen resides in the thymine ring, thus the N K-edge spectra can be used to get more inside concerning adsorption geometry of thymidine. The N K-edge spectra can be divided into two regions. Peaks due to transition to π^* orbitals are located around 400 eV and peaks due to transition to σ^* orbitals are located above 405 eV. More detail description of observed peak for thymine molecules is given in previously reported studies (*Surf. Sci.* 2003,532–535, 261). The polarization-dependent N K-edge spectra in Fig. 6 show that the π^* region is completely suppressed at normal incidence. Since the electric field vector of the incident photon beam is parallel to the surface at normal incidence this means that thymine ring structure has flat-lying geometry on gold surface.

Similarly the assignment of observed features in the O K-edge spectra can be given here. Peaks located near 532 eV can be attributed to π^* orbitals of carbonyl groups (C=O bonds) and peaks above 535 eV to σ^* orbitals of oxygen species in nucleobase

and sugar moieties. The NEXAFS spectra for the oxygen K-edge also show anisotropic features (Fig. 7).

From these results we can conclude that the thymine ring in dT molecule adsorbed on Au (111) crystal is parallel to the surface, while the plane of sugar ring is slightly tilted to the surface.

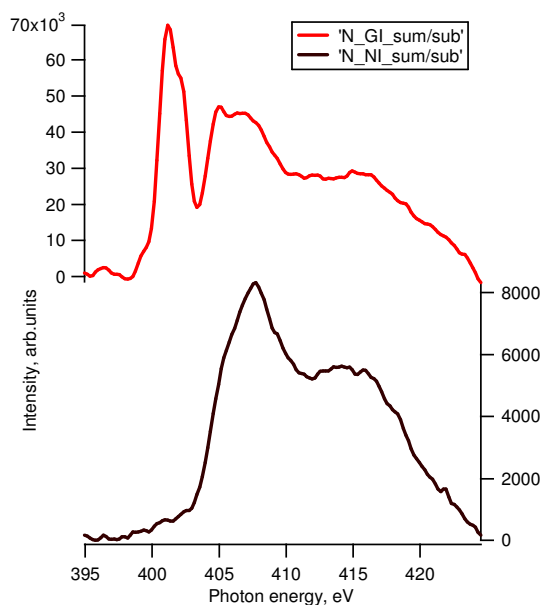


Fig.6. N K-edge NEXAFS spectra at normal (NI) and grazing (GI) incidence for monolayer films of thymidine on Au(111).

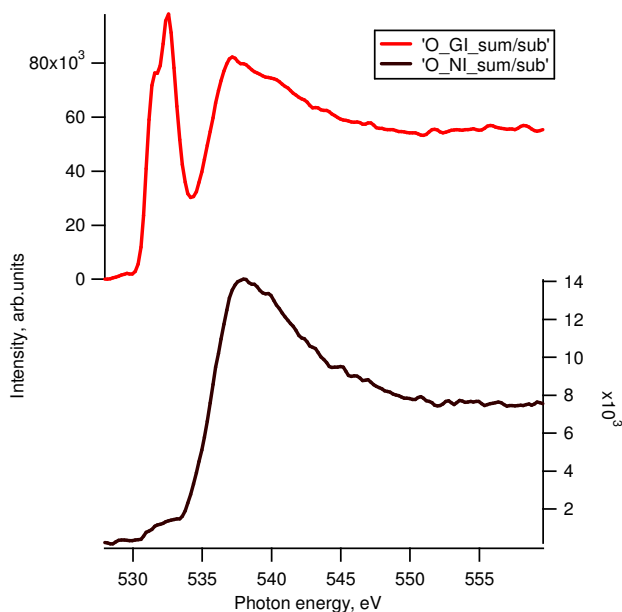


Fig.7. O K-edge NEXAFS spectra at normal (NI) and grazing (GI) incidence for monolayer films of thymidine on Au(111).

4. Future collaboration with host institution:

The further collaboration between the applicant and the host institution is planned. Presently a new project is in preparation concerning studies on XPS and NEXAFS of DNA nucleobase-fullerene complexes.

5. Projected publications/articles resulting from the STSM:

Presented results in this report are going to be published after more detailed analysis of all experimental data. In addition those results are going to be compared with those obtained for thymidine molecules adsorbed onto Cu (110) surfaces.

In addition the applicant is going to perform the DFT calculations with DMol3 package in order to better understand the geometry adsorption of thymidine.

6. Confirmation by the host institute of the successful execution of the mission:
(attached to the email)