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Investigation of adenine, uracil, and ribose phosphate thin films prepared by electrospray in vacuum deposition using photoemission spectroscopy

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Abstract

Previous results showed significant ionization energy differences between thin films of the four ribonucleic acid (RNA) polynucleotides. The experiments reported here aim at the investigation of the origin of these differences. Since the ribose phosphate backbone is common to all RNA nucleotides, the nucleobases are the most likely candidate defining the ionization energy of RNA. Consequently, experiments were performed to investigate the electronic structure and ionization energies of thin films of two nucleobases (adenine and uracil, representative for purines and pyrimidines), and ribose phosphate. These experiments were performed using x-ray and ultraviolet photoemission spectroscopy (XPS, UPS) in conjunction with an electrospray based in vacuum multi-step deposition technique. The presented results clearly demonstrate a significant ionization energy difference between the two nucleobases, qualitatively matching the previous results on the homopolymers of adenosine and uridine (poly rA, poly rU). As expected, the ionization energy of the prepared ribose phosphate thin films was much larger than those of the nucleobases.

Keywords: Ultraviolet photoemission spectroscopy; X-ray photoemission spectroscopy; Electrospray deposition; Highly oriented pyrolytic graphite; Ribonucleic acid; Nucleobases; Ionization energy

1. Introduction

Recent investigations using photoemission spectroscopy (PES) on ribonucleic acid (RNA) homopolymer thin films revealed significant differences between their ionization energies, as well as their charge injection barriers to highly oriented pyrolytic graphite (HOPG), despite the general absence of significant interface dipoles at the interface. The ionization energies determined in these experiments were: 6.4 eV for poly guanosine (poly rG), 6.8 eV for poly adenosine (poly rA), 8.1 eV for poly cytidine (poly rC), and 8.5 eV for poly uridine (poly rU) [1]. The progression of these ionization energies (G<A<C<U) qualitatively agrees with the ionization energies of nucleobases, mononucleosides and mononucleotides as determined through gas phase PES and theoretical calculations [2–5]. This suggests that the nucleobases are responsible for the ionization energy differences found in RNA homopolymers. Hence, experiments were performed in which the nucleobases adenine and uracil, as well as ribose phosphate (for direct comparison) were deposited as thin films in vacuum on HOPG substrates, and their ionization energies and charge injection barriers relative to the HOPG Fermi level were determined. HOPG was used as substrate since it has only weak valence bands related emissions, and does not form interface dipoles with most organic materials. This allows the investigation of the electronic structure of the thin film deposits without much interference of substrate related emissions. The presented experiments were enabled by an electrospray based deposition technique, allowing the direct injection of molecular materials from solution into high vacuum. This enables the performance of multi-step thin film deposition with intermittent PES characterization without breaking the vacuum, hence interference of environmental contaminants is reduced to insignificant levels. The presented experiments clearly show that the nucleobases define the ionization energy and charge injection

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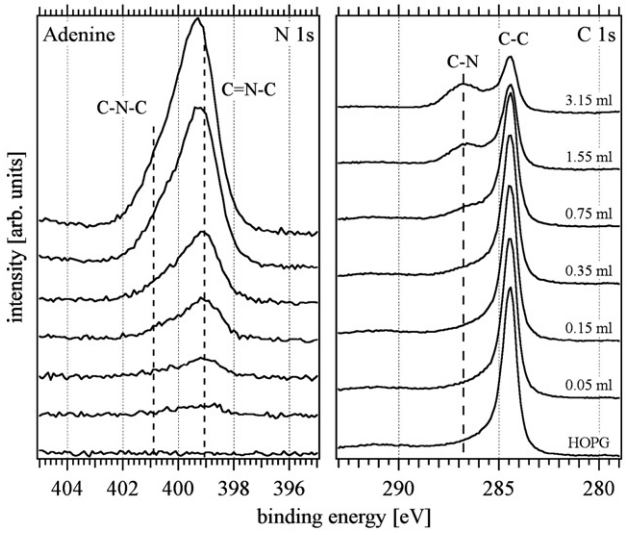

Fig. 1. XP-spectra of the N 1s (left) and C 1s (right) lines measured during the adenosine deposition sequence. Bottom spectra correspond to the freshly prepared HOPG surface before deposition.

barriers, and that the backbone does not contribute significantly to the charge transfer between nucleotides and other materials.

2. Experimental

The experiments were performed in an ultra high vacuum (UHV) system manufactured by SPECS GmbH (Berlin, Germany), which consists of a fast-entry load lock, two preparation chambers, and an analysis chamber equipped with XPS and UPS. This system operates at a base pressure of approximately 2×10^{-10} mbar. An in-house built electrospray injection (ESI) system was mounted to one of the preparation chambers through two differential pumping stages running at 0.1 mbar and 3×10^{-4} mbar (for more details on the experimental set-up see [6]). Solutions of adenine (Sigma, ≥99% purity), uracil (Sigma, ≥99% purity), and ribose phosphate (disodium dehydrate, Sigma, ≥99.8% purity) were prepared by adding each species to a 50/50 water/methanol mixture by volume so that a 1 mg/ml concentration was achieved. Deposition was carried out by injecting the solution through a 100 μm stainless steel capillary onto the 1 mm diameter ESI intake orifice at a rate of 4 ml/h. To reduce ambient contamination to negligible levels, nitrogen gas was flowed throughout deposition at a slight overpressure relative to atmosphere into the electrospray enclosure. During deposition, the pressure in the preparation chamber rose to approximately 10^{-5} mbar.

HOPG crystals (Mikromasch USA, "ZYA" quality) were cleaved in situ to attain a pristine, pure surface for deposition. Cleavage was achieved by fixing a metal foil to the top of the HOPG crystal with silver epoxy. The metal foil and the adhering top layer of substrate were then simultaneously removed via a manipulator arm in the UHV system, producing a clean graphite surface. Multi-step deposition series were performed for all three materials to determine their electronic structure and ionization energy. The sample surfaces were characterized by non-monochromatized x-ray and ultraviolet photoemission spectroscopy (XPS, UPS) after HOPG cleavage, and after each deposition step. XPS and UPS measurements were carried out using a dual SPECS XR 50 X-ray source (Mg Kα; $h\nu$=1253.6 eV) and a SPECS UVS 10/35 ultraviolet source (He I; $h\nu$=21.22 eV). During all measurements, the spectrometer was calibrated to yield the standard Cu $2p^{3/2}$ line at 932.66 eV and the Cu $3p^{3/2}$ line at 75.13 eV [7].

Igor Pro (Wavemetrics, Inc.) was used to analyze all photoemission spectra. Lines were fitted to the spectral onset and the intersect with the baseline determined to find cutoff positions.

3. Results and discussion

Figs. 1–3 show the C 1s, O 1s, N 1s, and P 2p XPS core level spectra series measured during the multi-step deposition sequences of adenine, uracil and ribose phosphate in vacuum

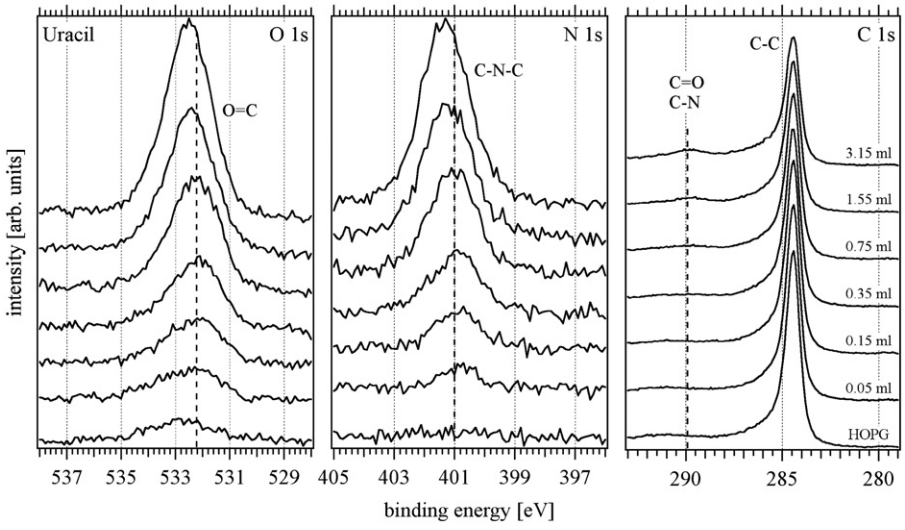

Fig. 2. XP-spectra of the O 1s (left), N 1s (center) and C 1s (right) lines measured during the uracil deposition sequence. Bottom spectra correspond to the freshly prepared HOPG surface before deposition.