Characterization of gas phase iron phthalocyanine with x-ray photoelectron and absorption spectroscopies

Ieva Bidermane [1,2], Roberta Totani[3], Cesare Grazioli[4,5], Monica de Simone[4], Marcello Coreno[6], Antti Kivimäki[6], John Åhlund[3], Luca Lozzi[3], Carla Puglia[*,1]

[1] *Department of Physics and Astronomy, Uppsala University, Box-516, 75120 Uppsala, Sweden*

[2] *Institut des Nanosciences de Paris, UPMC Univ. Paris 06, CNRS UMR 7588, F-75005, Paris, France*

[3] *Departement of Physical and Chemical Sciences, University of L'Aquila, Via Vetoio, I-67010 Coppito, L'Aquila, Italy*

[4] *CNR-IOM, Laboratorio TASC, ss. 14 km. 163.5, Basovizza, 34149 Trieste, Italy*

[5] *Departement of Chemical and Pharmaceutical Sciences, University of Trieste, Italy*

[6] *CNR-IMIP, Montelibretti, 00016 Rome, Italy; c/o Elettra-Sincrotrone Trieste, Basovizza, 34149 Trieste, Italy*

[*] *Corresponding author: e-mail carla.puglia@physics.uu.se,*

Abstract

Despite the numerous studies dedicated to phthalocyanine molecules adsorbed on surfaces, in monolayer or thin films, very few works have been focused on the characterization of vapors of these molecules. In this short article we present the C 1s, N 1s and Fe 2p photoemission results as well as N K-edge x-ray absorption data of iron phthalocyanine (FePc) in gas phase. A comparison with films of FePc shows a great similarity between these two systems, confirming the molecular

character of the thick films. The Fe 2p photoemission spectrum of the gas phase FePc, which has been shown for the first time, can be considered as a fingerprint of the Fe (II) ionic state of the central metal of the iron phthalocyanine. Both the XPS and XAS results show very similar structures observed for gas phase compared with thick film results.

1 Introduction.

Macro-cycle molecules like porphyrins and phthalocanines (Pcs) have attracted a huge number of research studies for their potential use as building blocks in functional materials [1]. The use of such molecules ranges from biomimetic catalysis [2–4], to solar cells [5] and to organic optical/electronic devices, just to mention a few. The magnetic properties of certain phthalocyanine molecules, such as iron phthalocyanine (FePc), studied in this work, are also of interest for molecular spintronics studies as prototypes of small molecular magnets [1]. Pc's are aromatic macro-cycles with a porphyrin-like structure in which the aza-bridge carbons are replaced by nitrogens, surrounded by four benzene rings (see Figure 1). A metal atom or two hydrogen atoms can occupy the center of the macro-cycle influencing the electronic, optical, and magnetic properties of the molecules and of the derived molecular materials. The possibility to design novel materials with desired and controlled characteristics demands a full understanding of the electronic structure of the molecules and of derived molecular materials. In our previous works we have studied the adsorption of FePc on surfaces both in monolayer and in multilayer coverage [6–8]. The characterization of FePc adlayers has been performed by means of photoelectron spectroscopy (PES). Our interest in these molecules and specifically in FePc is related to the capability of such macro-cycles to activate oxygen, an ability, which makes them useful in biomimetic catalysis [2,3]. The characterization of this process would be a fundamental step in the understanding of the catalytic activity of oxidase enzymes, a class of enzymes very important in nature as well as in industry. Since the activation of oxygen

seems to take place at the metal center of the molecules, causing a change of the metal ionic state, it would be particularly interesting to characterize the ionic state of the central metal atom under the activation reaction. Gas phase measurements of FePc are then very important in order to identify the modification in the electronic structure of the FePc, when film of such molecules would be exposed to, for example, high pressure of O_2. The effect can be most likely observed in the Fe 2p x-ray photoelectron spectroscopy (XPS) if the reaction takes place at the metallic center.

Despite the high number of studies of molecular adlayers and films, only few studies of phthalocyanines in gas phase have been performed [9–13]. Gas phase experiments of such macro-cycle molecules are in fact quite challenging due to the high temperature needed to create a constant molecular vapor flux together with the requirement to keep the experiment set-up reliable and under control for several days. Here we present C 1s, N 1s and Fe 2p photoelectronspectra as well as N 1s x-ray absorption spectrum (XAS) of FePc in gas phase. The comparison with data of films of FePc on different substrates confirms the molecular-like character of thick films. The comparison of the Fe 2p photoemission spectra between gas phase and film samples is particularly informative. A similar line profile can be considered as a fingerprint of the ionic state (Fe II) of the central Fe atom in the molecule. This result is very important for further characterization of FePc overlayers or thin films used in a variety of technological applications.

2 Experimental.

The gas phase measurements were performed at the Gas Phase photoemission beamline at the Elettra Synchrotron in Trieste, Italy [14]. The iron phthalocyanine was purchased from Sigma-Aldrich in the form of crystalline blue powder with minimum purity of 90% and was thoroughly purified in vacuum following a precise procedure of evaporation [11], for which a home-built furnace with an effusive nozzle [15] was used.

The photoemission spectrum of Fe 2p was taken using a VG 150 mm hemispherical electron energy analyzer, equipped with six channel electron multipliers. The analyzer was mounted at the magic angle with respect to the E vector of the linearly polarized incident light [16]. The use of a pass energy of 20 eV and the monochromator slits of 50/100 μm at a photon energy of 815 eV led to an overall resolution of 720 meV. The binding energy scale of the spectrum was calibrated by performing a simultaneous measurement of the sample and of a calibration gas introduced into the experimental chamber. In case of Fe 2p, calibration with a F 1s line of SF_6 (Ip= 695.04 eV [17]) was used. The other photoelectron spectra (C 1s and N 1s) of gas phase FePc presented in this work were measured with a Scienta SES200 electron analyzer [18] mounted at the magic angle. A pass energy of 100 eV was used, resulting in an overall energy resolution of around 320 meV for both C 1s and N 1s PES. Gases used for calibration were CO_2 [19] and N_2 [20], respectively.

The XAS at the nitrogen K-edge was obtained by acquiring the Constant Final State (CFS) spectrum of the N KVV structure with the SES200 analyzer. For normalization purposes, the photon flux was measured with a calibrated Si photodiode. The photon energy scale was calibrated using the absorption line N 1s → $\pi^\star$ (v'=1) of N_2 at 401.10 eV [21] measured simultaneously with the absorption spectra. The resolution at the N 1s edge was approximately 150 meV.

The gas phase data presented in this paper have been compared to thermally evaporated thick films of FePc on Au(111) single crystal substrate. The molecular films have been investigated by X-ray photoelectron spectroscopy (XPS) using a monochromatized Al K_α source (1486.7 eV) and a hemispherical analyzer at the home laboratory at the University of L'Aquila, Italy. A clean Au(111) surface was obtained by cycles of Ar+ ion beam sputtering (900 eV) for 20 minutes, followed by annealing at ≈550 °C for 2 hours. The cleanness of the surface was checked by monitoring the intensities of the C 1s and O 1s core level peaks in the XPS spectra

and of the gold Fermi level. FePc, carefully degassed prior to deposition, were thermally evaporated on the substrate, kept at room temperature, from a heated quartz crucible in ultra-high vacuum conditions (base pressure $\approx 10^{-10}$mbar). The film thickness (about 10 nm) was checked using a quartz microbalance. For such a film thickness no signal from the Au 4f peaks was detected by XPS. The binding energy (BE) scale of the presented data were aligned to the gas phase peaks for a comparison of the profiles of the photoemission core lines. The resolution in the C 1s and N 1s and Fe 2p photoemission results was 300 meV. In this work we also include the XAS results of a thick film of FePc on Si(100) for comparison with the gas phase results, according to the experimental details reported by J. Åhlund et al.[6].

3 Results and Discussion

Figure 2 shows the C 1s photoelectron spectrum of gas phase FePc taken with a photon energy of 382 eV. The spectrum consists of two main features at 286.9 eV and 287.4 eV, which are related to the benzene-like (C(1), C(2) and C(3) in Figure 1) and the pyrrole-like carbons (C(4)). As already shown in previous works the intensity of peak at 287.4 eV also contains shake-up transitions of the benzene-type carbons [22]. The low intensity and broad feature observed at about 289.3 eV is mainly due to shake-up transitions from pyrrole-like carbons. The N 1s PE spectrum, taken with a photon energy of 495 eV, is shown in Figure 3. It consists of a quite broad feature at 404 eV due to the photoemission from the azabridge and central N atoms (N(1) and N(2), respectively, in Figure 1). Also in this spectrum, we can identify a broad feature at about 405.9 eV due to shake-up transitions. In Figure 4 we show the Fe 2p spectrum taken with a photon energy of 815 eV. The spectrum shows two components: Fe $2p_{1/2}$ at 726.8 eV and Fe $2p_{3/2}$ at 713.5 eV. The lines are quite asymmetric as already observed and reported in our previous work [6]. The asymmetry of the Fe $2p_{3/2}$ photoemission line can be ascribed to multiple transitions caused by the coupling of the core hole and the valence open

shell of the Fe atom [6, 23, 24].

Each figure contains insets with comparisons between photoemission results of gas phase and of FePc film on the Au(111) surface. We compare the C 1s, N 1s and Fe 2p spectra with the results of the film characterized by an Al K_α source (1486.7 eV) with similar experimental resolutions. The spectra of the film have been shifted to align with the gas phase spectral features for an easy comparison. The necessity for BE shifts originate from the different binding energy references used in the gas phase and surface measurements, i.e. vacuum level for gas phase and Fermi level for solid/metal samples. We observe that the line profiles in the gas phase and film spectra are very similar except for a slight broadening in the spectrum of the film, indicating the molecular like character of the films. The overall spectral broadening of the film (with respect to the gas-phase case) can be ascribed to intermolecular interactions leading to additional broadening of the film spectra. The similarity between the Fe $2p_{3/2}$ spectra of gas phase and film results is of particular interest. It allows us to identify the core line profile for the Fe^{+2} ion of the Fe(II)Pc molecules. Any change of the ionic state caused, for example, via molecule-surface or molecule-target gas interactions (in gas sensing or catalysis), would then be recognized as a change in the line profile as well as possible shift in BE positions.

In Figure 5 the N 1s x-ray absorption results are reported. The first $\pi^\star$ resonance is observed at around 398.5 eV. Other features are clearly seen at about 400.7 eV and 402.4 eV. At around 406 eV we can observe part of the intensity due to transitions to the state of σ character. The results obtained on thick film on Si(100) [6] are superimpossed (red line) on the gas phase spectrum (dotted line). The presented film spectrum is taken with a polarization vector of the incident light parallel to the sample surface. The intensity of the different spectral features of the FePc film on Si(100) is related to the geometrical arrangement of the molecules in the film. It has been shown by J.Åhlund et al. that FePc on Si(100) form ordered layers with

molecular planes almost perpendicular to sample surface [6]. We note great similarities of the two spectra at low photon energies, around the threshold region, with a little divergence at higher photon energy (406.8 eV). This indicates that the empty DOS in both cases is similar and represents the spectra of unperturbed FePc molecular spectrum. The slight differences in both spectra can be attributed to molecule-molecule interaction in the condensed phase, which can be different from the gas phase case. The indication for the quite important intermolecular interaction is evidences by the fact that the molecules choose to accomodate a staning up-right orientation, rather than flat-lying one.

4 Conclusion

We have presented a spectroscopic study of vapors of iron phthalocyanine. Even though many studies have been dedicated to the characterization of metal-free or metal-phthalocyanines during these last decades, very few works have dealt with gas phase experiments. In addition to C 1s and N 1s core photoemission lines, the main result is the Fe 2p PE spectrum since it can be considered as a fingerprint of the Fe(II) ionic state of the Fe central metal in Pcs. Applications of these molecules in catalysis or gas sensing can cause a change of the ionic state of the central metal atom, which will result in a different Fe 2p PE line profile. The present results can then be of fundamental importance for future studies of molecular over-layers of film under working conditions (e.g. characterizing catalytic processes studied under high-pressure of specific gases).

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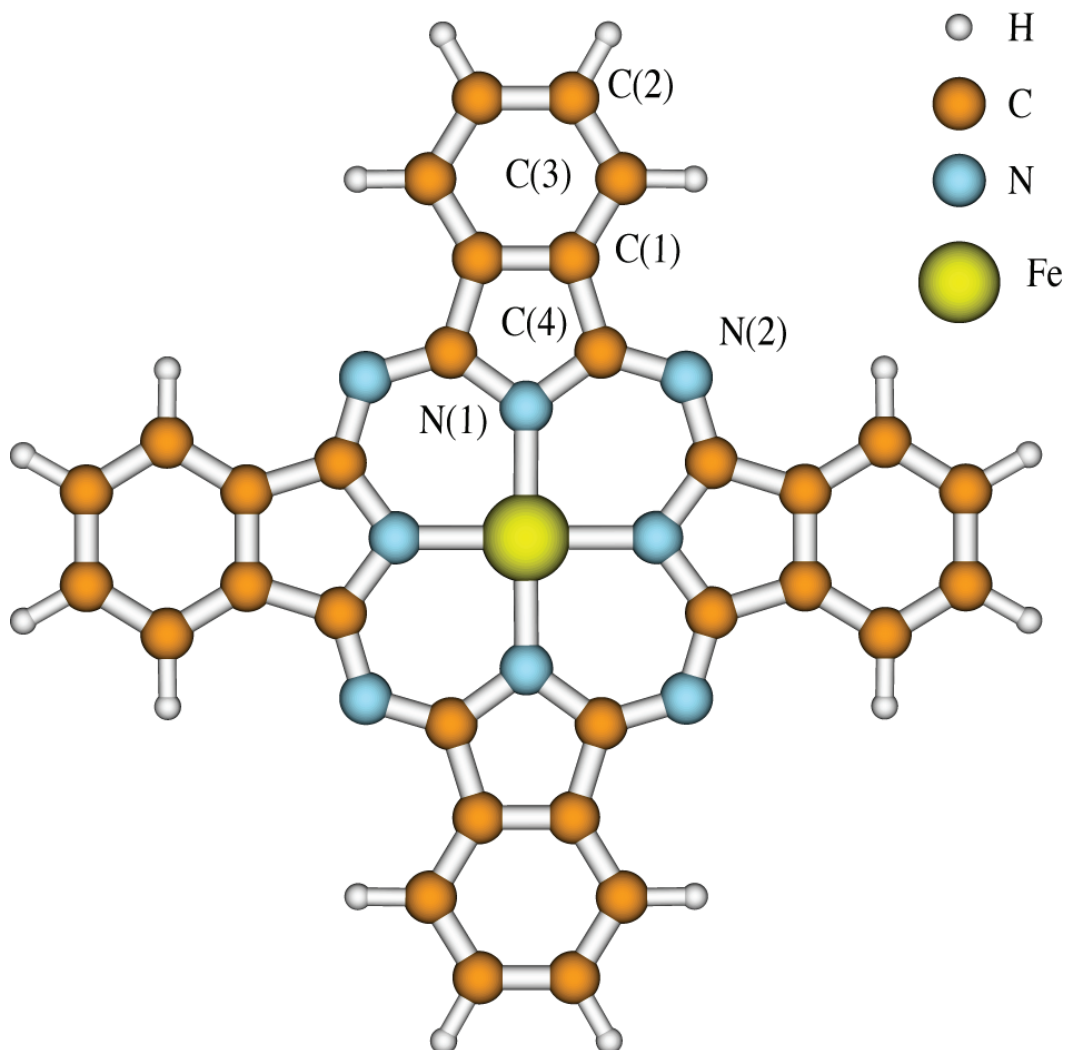
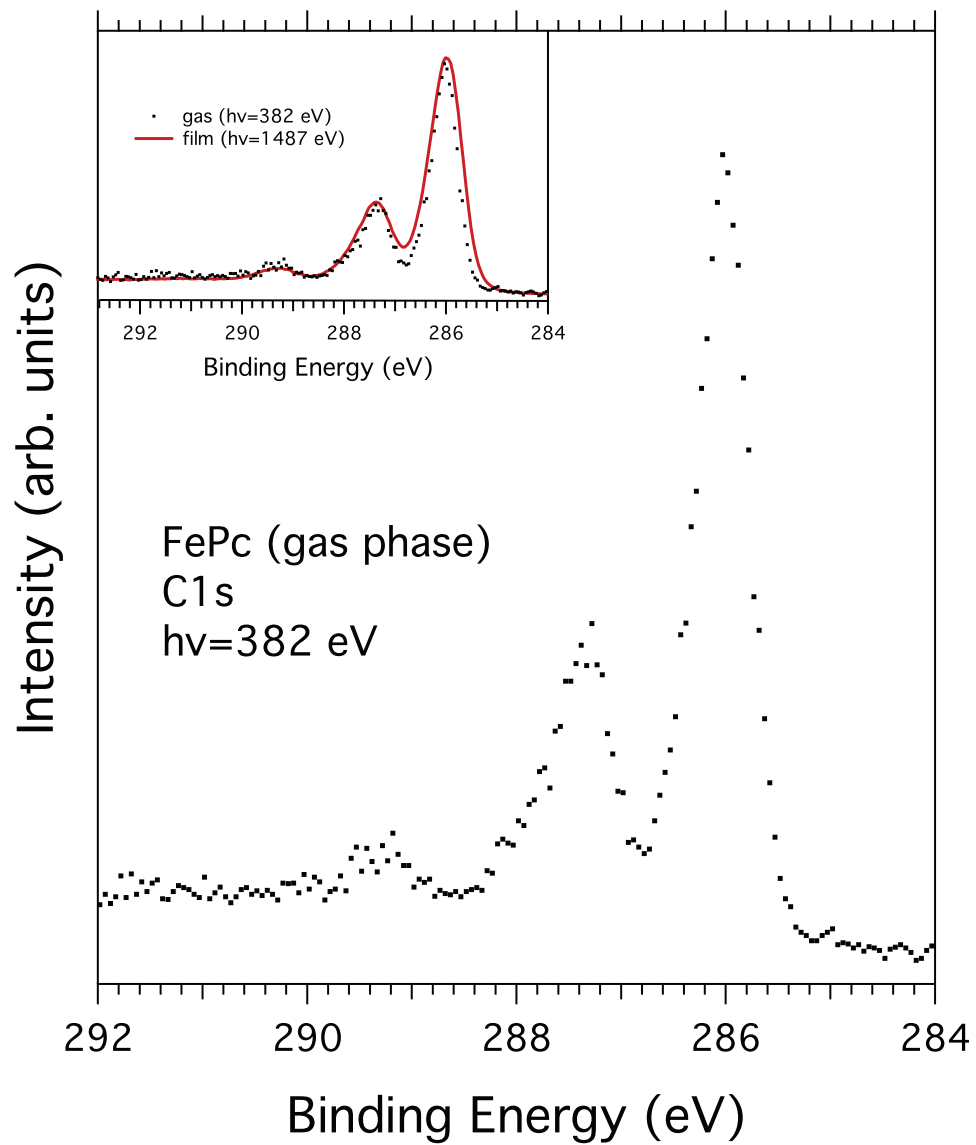Fig. 1. Molecular structure of a Iron phthalocyanine (FePc)

Fig. 2 C1s photoemission spectrum of FePc gas phase. In the inset a comparison with C1s photoemission spectrum of a film of FePc on Au(111)
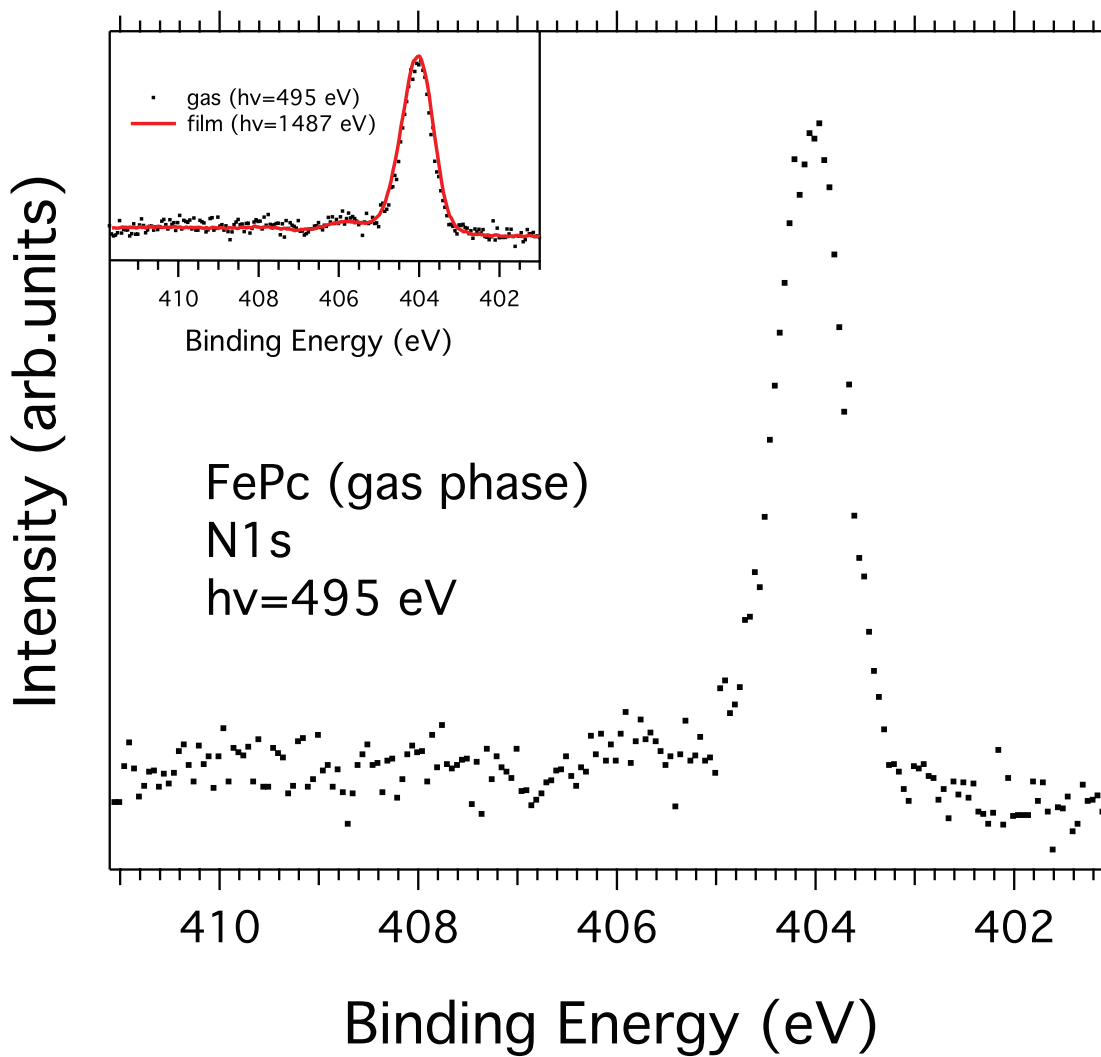
Fig. 3 N1s photoemission spectrum of FePc gas phase. In the inset a comparison with N1s photoemission spectrum of a film of FePc on Au(111)
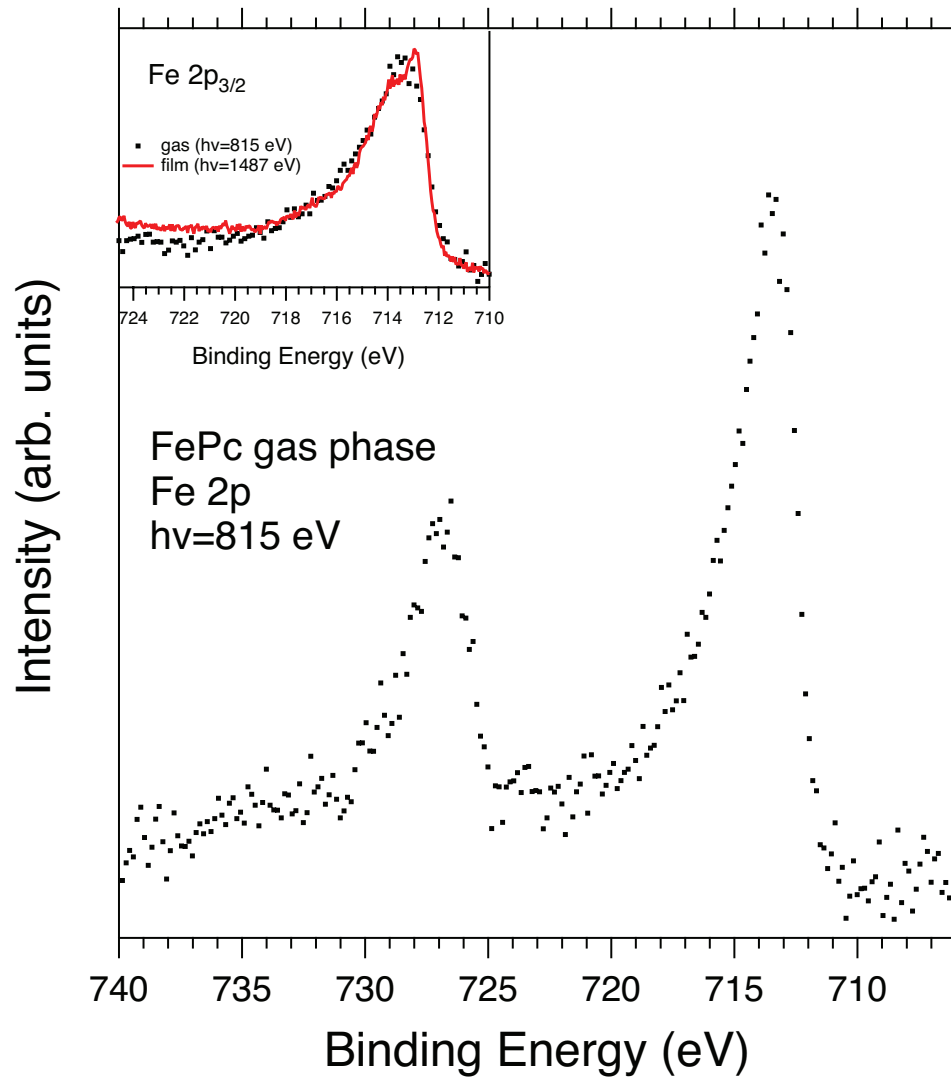
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Fig. 4: Fe 2p photoemission spectrum of FePc gas phase. In the inset a comparison with Fe $2p_{3/2}$ photoemission spectrum of a film of FePc on Au(111)
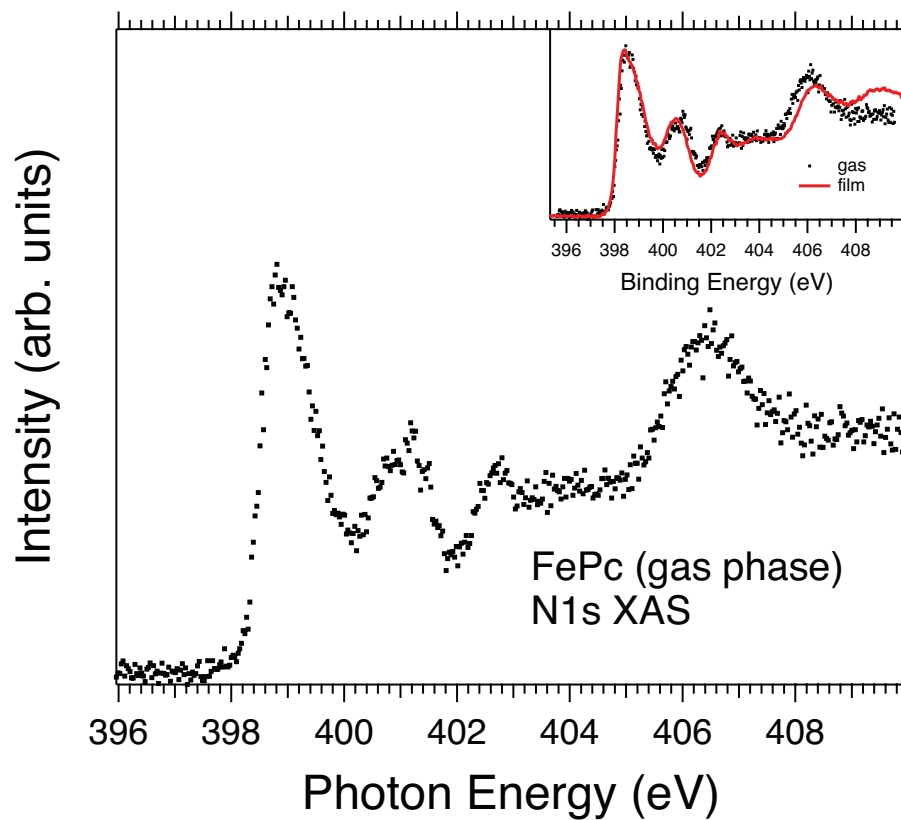
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Fig. 5: N1s X-ray absorption spectrum of FePc gas phase. In the inset a comparison with N1s XAS photoemission spectrum of a film of FePc on Si(100)[ref. john]