Electronic Supporting Information

Quantitative Determination of a Model Organic/Insulator/Metal Interface Structure

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Experimental Methods

The XPS and XSW measurements were conducted at the end station of the I09 beamline at Diamond Light Source with a base pressure of ~4×10^{-10} mbar. A Cu(111) single crystal was cleaned by repeated sputtering and annealing cycles. The Co-P molecules (purchased from Frontier Scientific, purity 95%) were degassed thoroughly and evaporated from a home-built quartz crucible evaporator at a temperature of 600 K while the sample was kept at room temperature. The B 1s, C 1s and N 1s core levels were acquired using a photon energy of 641 eV, the Co 2p core-level spectra with a photon energy of 2400 eV. XP survey spectra, taken over a wide range of binding energies, showed no significant components other than the expected B, C, N, Co and Cu energy levels. The binding energy scale of the B 1s, C 1s, N 1s spectra were calibrated against the Cu 3p core level measured at the same photon energy and assumed to be at a binding energy of 75.14 eV.[1]

For the XSW measurements, the X-ray beam was defocused to approximately 400×400 µm^2 and stepped over the sample such that each XSW curve was acquired at a different sample position. To further avoid beam damage, the beam intensity was reduced to 20% by detuning the undulator. Possible beam damage was monitored by comparing the B 1s, C 1s and N 1s core-level spectra before and after each XSW measurement, whereby no changes were detected. The hemispherical electron analyzer, a VG Scienta EW4000 HAXPES with an acceptance angle of ±28°, was mounted at an angle of 90° with respect to the incident synchrotron light and with the center of its angular acceptance in the plane of the photon polarization. The XSW scans were obtained from the (111) Bragg reflection of Cu (E_{Bragg} ~ 2972 eV at 300 K and ~ 2981 eV at 50 K). The intensity of the crystal Bragg reflection was measured simultaneously to the absorption profiles, acquired from core-level photoemission yields, via a fluorescent screen mounted on the port of the incident X-ray beam by means of a CCD camera. Prior to each XSW measurement a reflectivity curve was acquired to determine the Bragg energy at a given position on the sample, and the subsequent XSW measurement was acquired across a window of ±5 eV around that energy. In total 17 unique sample spots were used for the measurements at 50 K, resulting in nine individual XSW spectra for Co 2p, three for C 1s, three for N 1s and two for B 1s. For the measurements at 300 K, in total 20 unique sample spots were used, resulting in eight individual spectra for Co 2p, eight for C 1s, two for N 1s and two for B 1s. The respective XP spectra were then averaged in order to improve the signal to noise ratio. The B 1s, C 1s and N 1s spectra were fitted with Voigt profiles (convolution of a Gaussian and a Lorentzian), while the Co 2p spectra were fitted with a convolution of an asymmetric Doniach-Šunjić lineshape and a Gaussian profile.

Integrated intensities of the core-level peaks were used to obtain the relative X-ray absorption. Non-dipolar corrections were applied according to Ref. [2]. An angle θ = 18°, as

defined in Ref.[2], was used for the XSW measurements using the (111) Bragg reflection. Analysis of the XSW profile yields two structural parameters, the coherent position (p^{111}) and the coherent fraction (f_{co}^{111}). The coherent position can be related to the average adsorption height, through $\bar{h} = (n + p^{111}) \cdot d_{111}$, with d_{111} = 2.087 Å (300 K) and d_{111} = 2.081 Å (50 K), respectively, being the layer spacing of Cu(111) and n an integer. The coherent fraction represents the level of order in the system, often equivalent to the fractional occupation of the adsorption site, and can vary within the range $0 \le f_{co}^{111} \le 1$. A detailed description of the XSW method can be found in literature.[3]

For our XPS and XSW measurements we utilized a low Co-P coverage of ~0.15-0.2 ML, comparable to the situation displayed in Fig. 1a of the manuscript. The molecular coverage was calculated with the cross-section corrected peak areas of the Co-P core levels and the Cu substrate. We neglect the attenuation of the Cu peak by the h-BN layer and the adsorbates, which lowers the measured signal from the substrate and renders the calculated value an upper limit.

Based on the strikingly different modulations of the individual N 1s components in XSW measurements as discussed below (Figs. S5, S7 and S8), we were able to differentiate in the XPS data between the nitrogen species of the h-BN layer and those assigned to nitrogen atoms in the Co-P. In accordance with our previous study,[4] two boron and nitrogen components were identified and assigned to the h-BN layer (B_0 = 190.4 eV and N_0 = 398.1 eV, respectively) and defective polymeric BN fragments (B_{def} = 191.0 eV and N_{def} = 398.5 eV), whereby the latter will be neglected in the discussion of this article.

Although the adsorption heights of h-BN and Co-P could be rationalized with intercalated Co-P molecules,[5] we can exclude this structure as intercalation requires substrate temperatures of ~ 470 K to initiate, and the Co 2p binding energy clearly indicates a decoupled molecule.

The STM experiments were performed in a custom-designed ultra-high vacuum (UHV) chamber housing a CreaTec STM operated at ~6 K. The base pressure during the experiment was $<2 \times 10^{-10}$ mbar. All STM images were recorded in constant-current mode using an electrochemically etched tungsten tip. The WSxM software was used to process the STM raw data.[6]

S1 – Coverage dependent adsorption site preference of Co-P on *h*-BN/Cu(111)

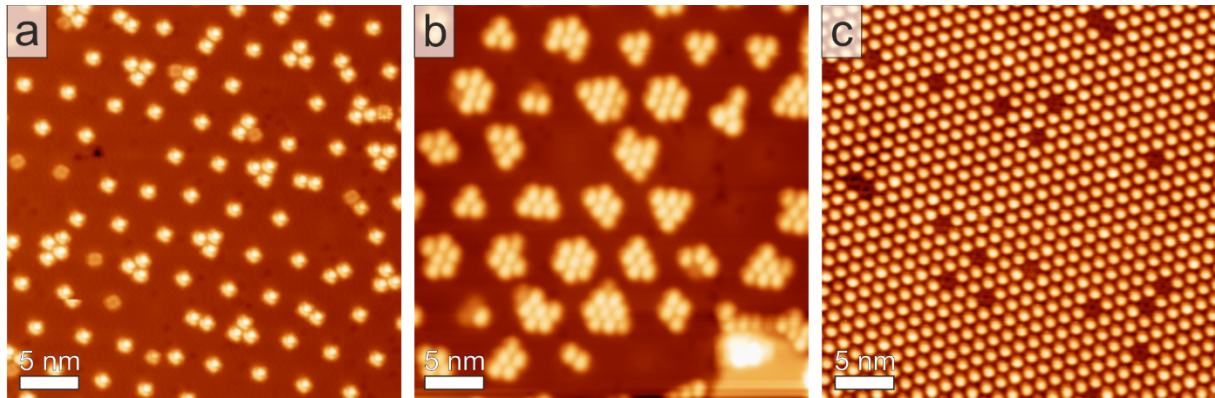**Figure S1** – STM images of adsorbed Co-P on *h*-BN/Cu(111) at a coverage of (a) ~0.15, (b) ~0.3, and (c) ~1 monolayer (ML) recorded at 6 K. A full monolayer is defined as the coverage of Co-P molecules, for which a densely packed layer is observed across the whole sample. Note that the dim molecules (imaged as "holes" in the layer) in (c) are free-base porphine (2H-P) that are present as residuals of the Co-P synthesis (purity 95%). Scan parameters: (a) U_b = 1.0 V, I_t = 41 pA, (b) U_b = 1.23 V, I_t = 120 pA, (c) U_b = 1.86 V, I_t = 4 pA.

S2 – High resolution STM image of Co-P/*h*-BN/Cu(111) and STS data
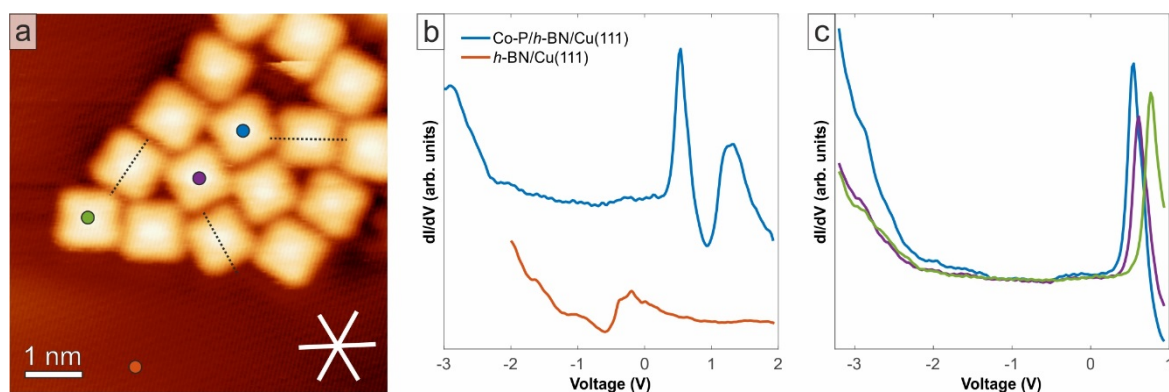

Figure S2 – (a) The high-resolution STM image of Co-P on *h*-BN/Cu(111) reveals a 4-fold symmetric appearance of the molecules, which are aligned with one of their molecular axes parallel to the principal directions of the underlying Cu(111) crystal. Scan parameters: U_b = -0.8 V, I_t = 100 pA (b) Scanning tunneling spectroscopy (STS) data recorded on the center of the Co-P molecule (marked blue) and the *h*-BN layer (orange). The sharp resonance at ~ 0.6 eV is assigned to Co-related electronic states. (c) The energy of this Co-related resonance shifts with the position of the Co-P molecule on the *h*-BN moiré.

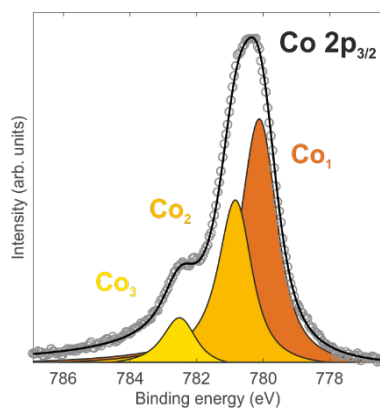## S3 – Additional XPS data of the Co 2p core level for high Co-P coverage

Figure S3 – XP spectrum of the Co $2p_{3/2}$ core level for a high Co-P coverage on *h*-BN/Cu(111) (~0.95 ML) acquired at 300 K. The ratio of Co_1 to Co_2 is ~ 3 : 2.
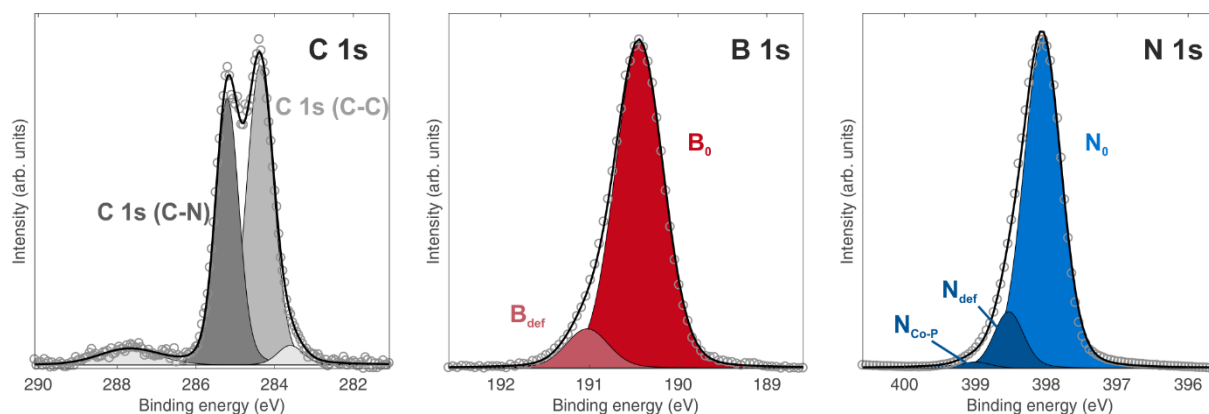
Figure S4 – XP spectra of the (a) C 1s, (b) B 1s and (c) N 1s core levels of a low-coverage (~0.15 ML) sample of Co-P on *h*-BN/Cu(111) recorded at 50 K. The fit parameters are summarized in Table S1.

Core level	E_b^0 (eV)	Γ (eV)	σ (eV)
C 1s (C-C)	284.4	0.12	0.63
C 1s (C-N)	285.2	0.12	0.54
B 1s (B$_0$)	190.4	0.08	0.50
B 1s (B$_{def}$)	191.0	0.08	0.46
N 1s (N$_0$)	398.1	0.11	0.48
N 1s (N$_{def}$)	398.5	0.11	0.37
N 1s (N$_{Co-P}$)	399.0	0.11	0.38
Co 2p (Co$_1$)	780.3	0.31	0.56
Co 2p (Co$_2$)	781.1	0.31	0.53
Co 2p (Co$_3$)	782.7	0.31	0.54

Table S1 – XPS fit parameters for the atomic species of Co-P/*h*-BN/Cu(111) comprising the peak position E_b^0, Lorentzian width Γ and Gaussian width σ obtained from the fits for the indicated components. Voigt line shapes are used for the curve-fitting of the C 1s, B 1s and N 1s core-level spectra, whereas a Doniach−Šunjić line shape was used to model the Co 2p$_{3/2}$ line
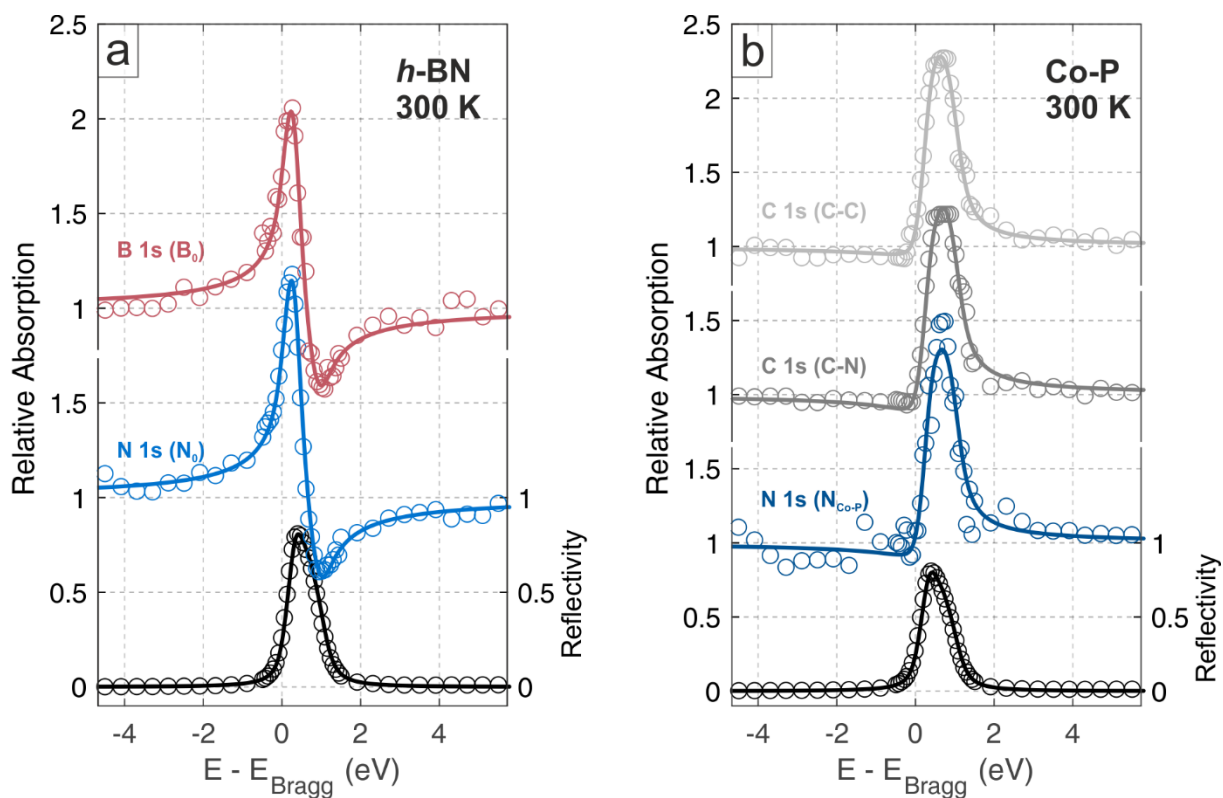
Figure S5 – XSW absorption profiles of the atomic species in (a) the *h*-BN layer, and (b) the Co-P molecules on *h*-BN/Cu(111) at the (111) Bragg reflection at 300 K and in the low coverage regime (~0.15 ML). Solid lines are fits to the data. Black data points are the reflectivity curve.

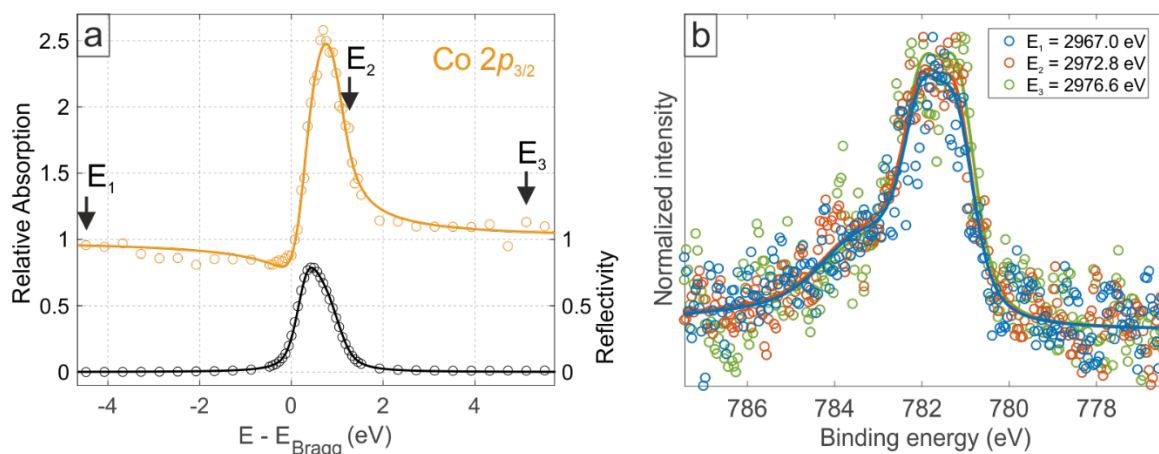# S6 – Comparison of the Co 2p line shape through the XSW condition

Figure S6 – (a) Normal incidence XSW Co 2p$_{3/2}$ absorption profile of Co-P on h-BN/Cu(111) in the low coverage regime (~0.15 ML) at the (111) Bragg reflection, acquired at 300 K and integrated over both the Co$_1$ and Co$_2$ species (see Fig. 1c in the manuscript). Solid line is the fit to the data. Black data points are the reflectivity curve. (b) Individual XP spectra at the photon energies E$_1$ = 2967.0 eV (blue), E$_2$ = 2972.8 eV (orange), and E$_3$ = 2976.6 eV (green) marked in (a) by black arrows. These overlaid spectra show that the line shape of the Co 2p does not vary through the standing wave condition.

		Low coverage, 50 K			Low coverage, 300 K		
	Core-level	f^{111}	p^{111}	Adsorption height $\bar{h}$ (Å)	f^{111}	p^{111}	Adsorption height $\bar{h}$ (Å)
	Co 2p (Co$_1$)	0.67 ± 0.04	0.98 ± 0.02	6.20 ± 0.04	0.60 ± 0.04	0.11 ± 0.02	6.49 ± 0.04
	Co 2p (Co$_1$)	0.68 ± 0.06	0.98 ± 0.03	6.20 ± 0.06	0.51 ± 0.06	0.06 ± 0.03	6.39 ± 0.04
Co-P	Co 2p (Co$_3$)	0.69 ± 0.09	0.98 ± 0.04	6.20 ± 0.08	0.58 ± 0.13	0.00 ± 0.07	6.26 ± 0.14
	Co 2p (Co$_1$ + Co$_2$)	0.67 ± 0.04	0.97 ± 0.02	6.18 ± 0.04	0.58 ± 0.04	0.09 ± 0.02	6.45 ± 0.04

Table S2 – Structural parameters of the XSW analysis of Co-P/h-BN/Cu(111) in the low coverage regime (~ 0.15 ML) at 50 K and at 300 K. The table summarizes the coherent fraction f^{111}, the coherent position p^{111} and the mean adsorption height $\bar{h}$ obtained from the analysis of the individual cobalt features Co$_1$ and Co$_2$, as well as the values determined from the analysis of the integrated peak area of both components in the XP spectra.

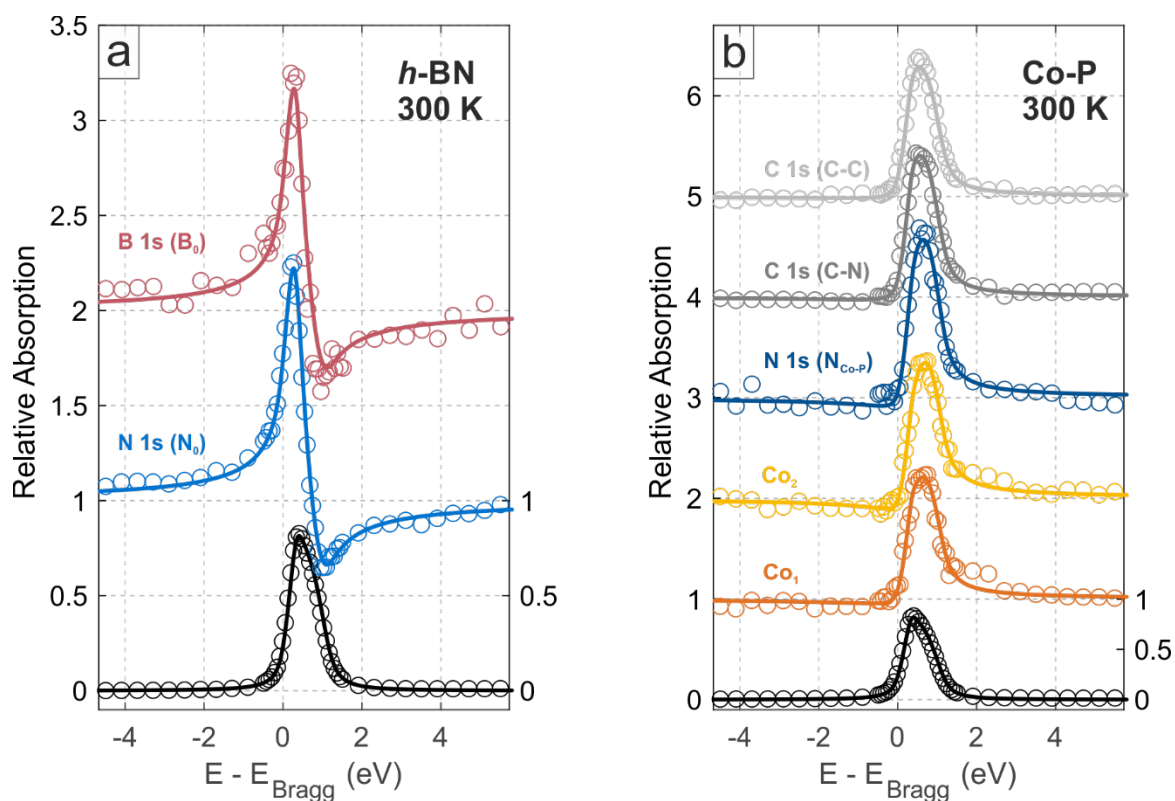## S7 – XSW absorption profiles – high coverage, 300 K

Figure S7 – XSW absorption profiles of the atomic species in (a) the *h*-BN layer, and (b) the Co-P molecules on *h*-BN/Cu(111) at the (111) Bragg reflection at 300 K and in the high coverage regime (~0.95 ML). Solid lines are fits to the data. Black data points are the reflectivity curve.

		High coverage, 200 K			High coverage, 300 K		
	Core-level	f^{111}	p^{111}	Adsorption height $\bar{h}$ (Å)	f^{111}	p^{111}	Adsorption height $\bar{h}$ (Å)
Co-P	C 1s (C-C)	0.30 ± 0.02	0.16 ± 0.02	6.59 ± 0.04	0.24 ± 0.02	0.18 ± 0.02	6.64 ± 0.04
	C 1s (C-N)	0.32 ± 0.03	0.16 ± 0.02	6.59 ± 0.04	0.31 ± 0.02	0.19 ± 0.02	6.66 ± 0.04
	N 1s (N_{Co-P})	0.37 ± 0.06	0.13 ± 0.04	6.53 ± 0.08	0.47 ± 0.05	0.16 ± 0.03	6.60 ± 0.06
	Co 2p (Co_1)	0.33 ± 0.06	0.09 ± 0.04	6.45 ± 0.08	0.27 ± 0.04	0.12 ± 0.03	6.51 ± 0.06
	Co 2p (Co_2)	0.40 ± 0.08	0.07 ± 0.05	6.41 ± 0.10	0.40 ± 0.03	0.11 ± 0.02	6.49 ± 0.04
	Co 2p (Co_3)	0.34 ± 0.14	0.02 ± 0.13	6.30 ± 0.26	0.39 ± 0.10	0.03 ± 0.06	6.32 ± 0.12
	Co 2p ($Co_1 + Co_2$)	0.33 ± 0.03	0.07 ± 0.02	6.41 ± 0.04	0.31 ± 0.04	0.12 ± 0.03	6.51 ± 0.06
h-BN	B 1s (B_0)	0.53 ± 0.04	0.60 ± 0.02	3.34 ± 0.04	0.58 ± 0.06	0.61 ± 0.03	3.36 ± 0.06
	N 1s (N_0)	0.62 ± 0.02	0.60 ± 0.01	3.34 ± 0.02	0.61 ± 0.02	0.60 ± 0.01	3.34 ± 0.03

Table S3 – Comparison of the structural parameters of the XSW analysis of Co-P/*h*-BN/Cu(111) at 200 K and at 300 K. The table summarizes the coherent fraction f^{111}, the coherent position p^{111} and the mean adsorption height $\bar{h}$ for all atomic species in the Co-P molecule and the *h*-BN layer.

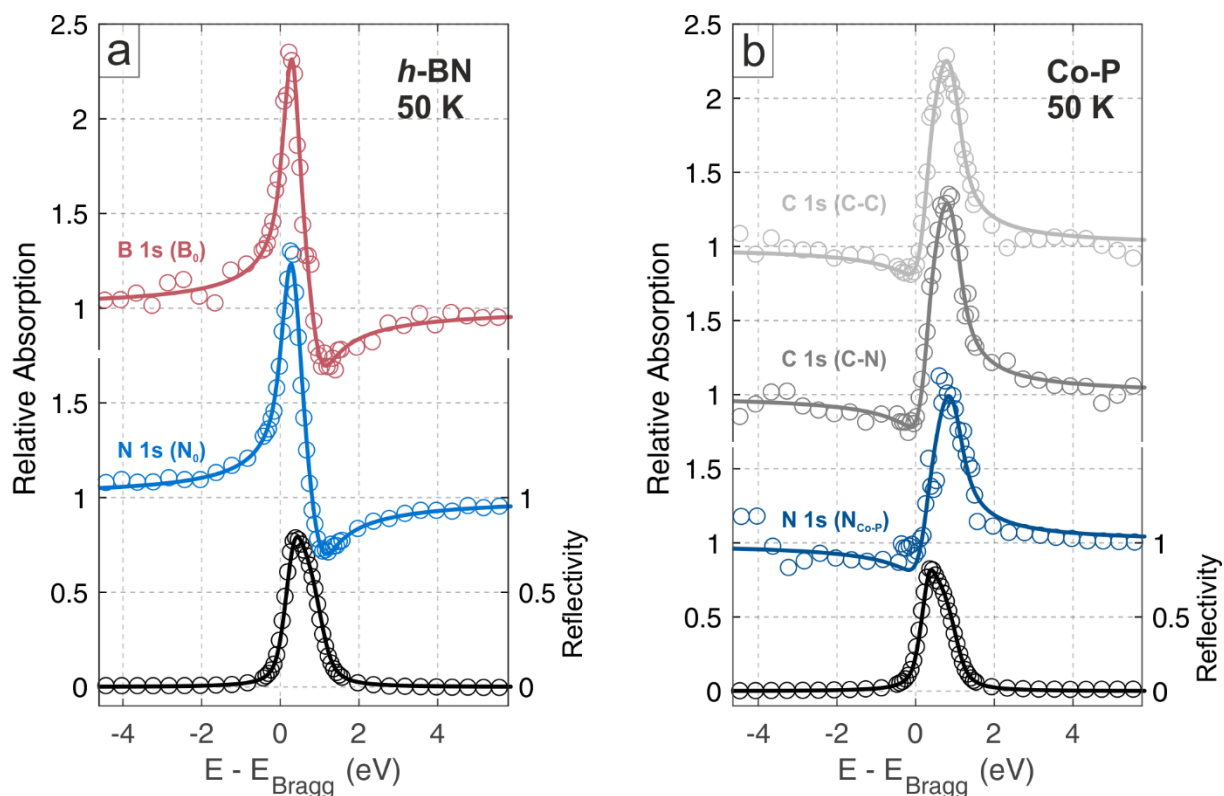# S8 – Additional XSW absorption profiles – low coverage, 50 K

Figure S8 – XSW absorption profiles of the atomic species in (a) the *h*-BN layer, and (b) the Co-P molecules on *h*-BN/Cu(111) at the (111) Bragg reflection at 50 K and in the low coverage regime (~0.15 ML). Solid lines are fits to the data. Black data points represent the reflectivity curve.

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