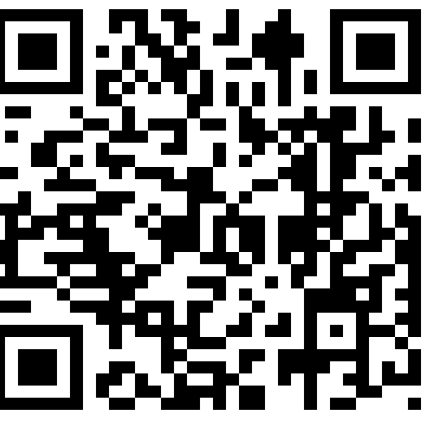


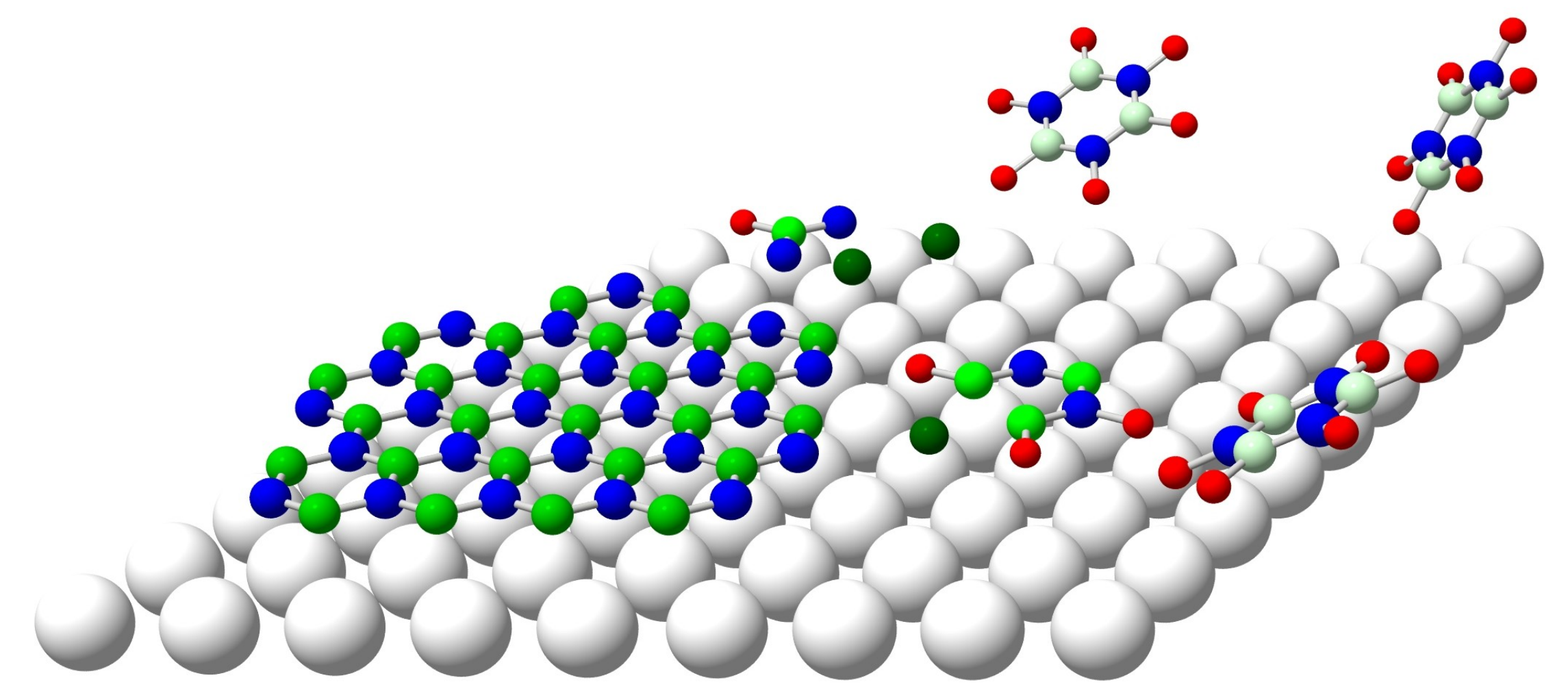
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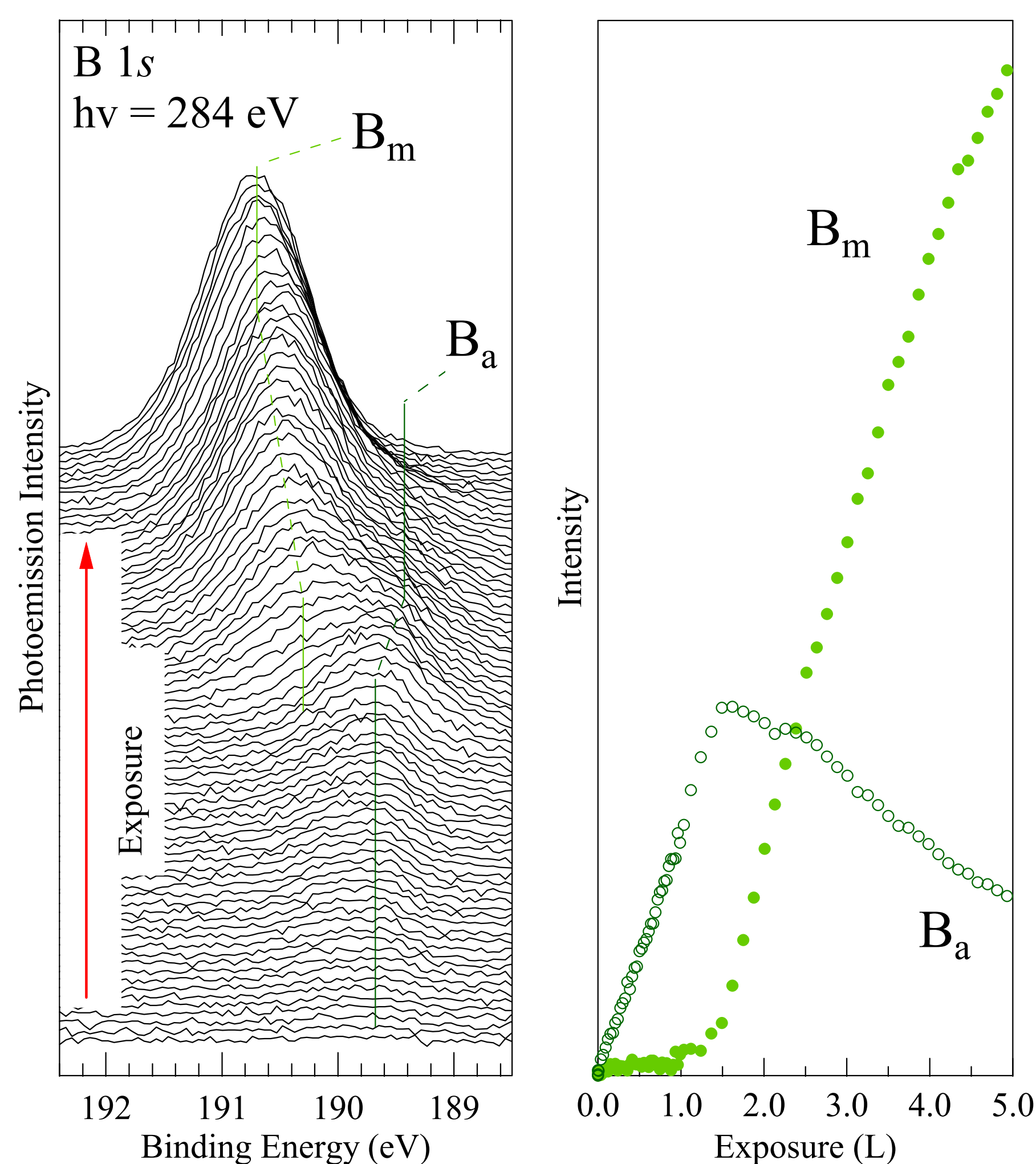
## INTRODUCTION

Ultra-thin films grown on metal surfaces have attracted considerable attention because of their potential application in nanotechnology. In this context, the single layer of hexagonal boron nitride (*h*-BN) [1] is considered a promising candidate because of its appealing properties, such as the excellent thermal stability and, in particular, the large band gap which makes it an insulator isostructural to graphene, the new challenging material for future nanoelectronics. Among the several ways to synthesize a single layer of *h*-BN, the most common method used to obtain high quality films is by chemical vapor deposition (CVD) of a molecular precursor, e.g. benzene-like borazine ( $B_3N_3H_6$ ), at a metal surface. Although detailed studies have considerably improved the characterization of the morphology and electronic structure of the *h*-BN films, an exhaustive picture of the chemisorption properties of borazine on metallic substrates is still missing [2]. Here we report on the growth of a single *h*-BN layer through dissociation of  $B_3N_3H_6$  molecules on Ir(111), investigated by complementary experimental techniques: x-ray photoelectron spectroscopy (XPS), near-edge x-ray absorption fine structure (NEXAFS), temperature programmed desorption (TPD) and low energy electron diffraction (LEED).



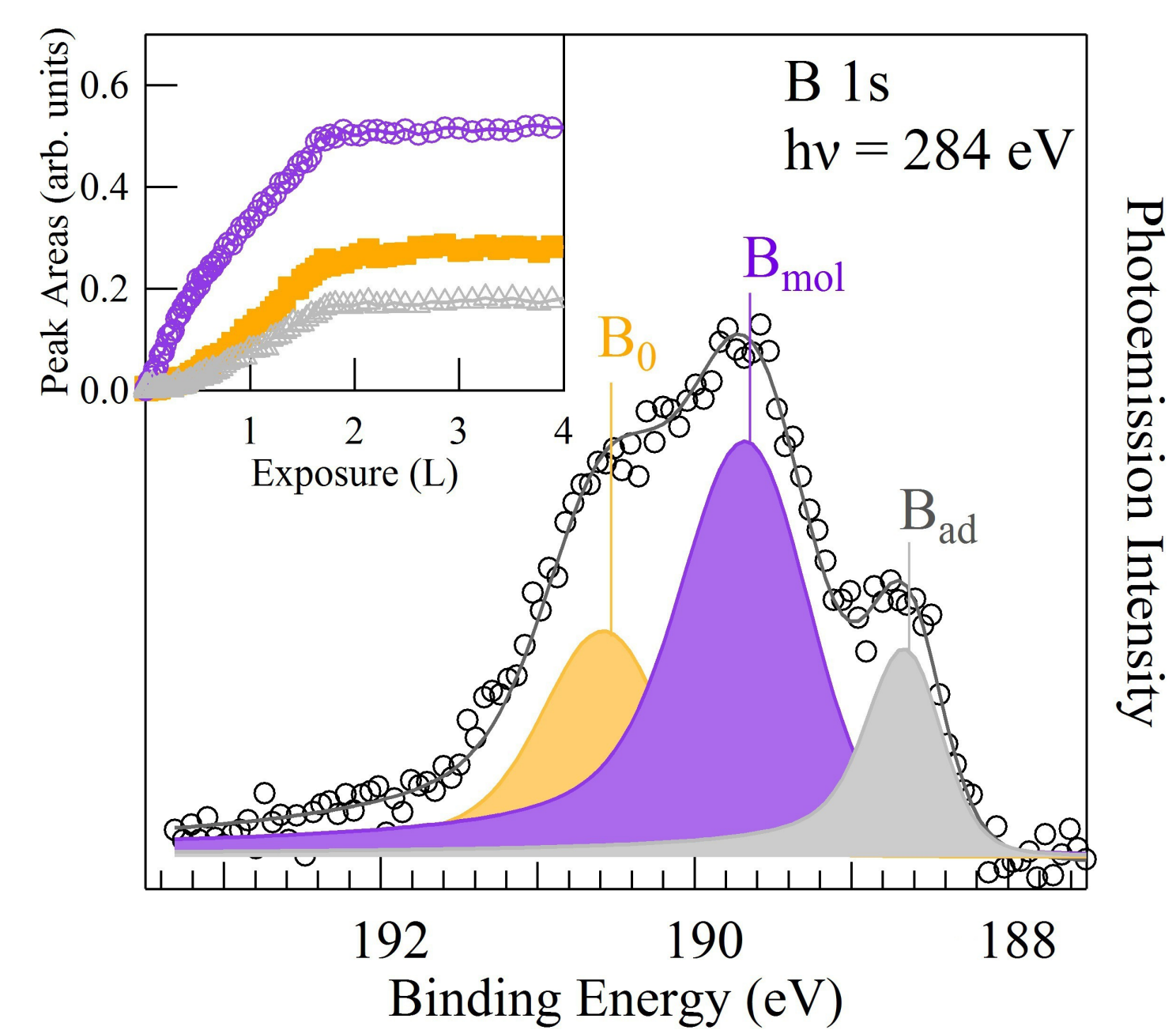
## LOW TEMPERATURE ADSORPTION

As a first experiment we monitored *in situ* the B 1s core level region during exposure of the Ir substrate to  $B_3N_3H_6$  at  $T = 170$  K (Figure 1). Up to  $\sim 1$  L the sequence of spectra displays only the  $B_a$  component at 189.7 eV, which is attributed to the borazine adsorbed molecularly on the surface. At higher exposures  $B_a$  diminishes in intensity and a new component emerges at 190.3 eV ( $B_m$ ). This new feature grows continuously with increasing exposures and moves towards high binding energies, indicating the formation of a condensed multilayer structure. By exploiting the polarization dependence of the NEXAFS  $\pi$  and  $\sigma$  resonances we determined the adsorption geometry of the molecule. We found that low temperature adsorption starts with the  $B_3N_3H_6$  molecules oriented parallel to the substrate and bound to it via  $\pi$  bonds. As the exposure increases, the subsequent surface crowding forces further molecules to anchor in a tilted configuration, forming the condensed multilayer structure on top of the first chemisorbed layer. The molecular saturation coverage is estimated to be 0.20 ML.

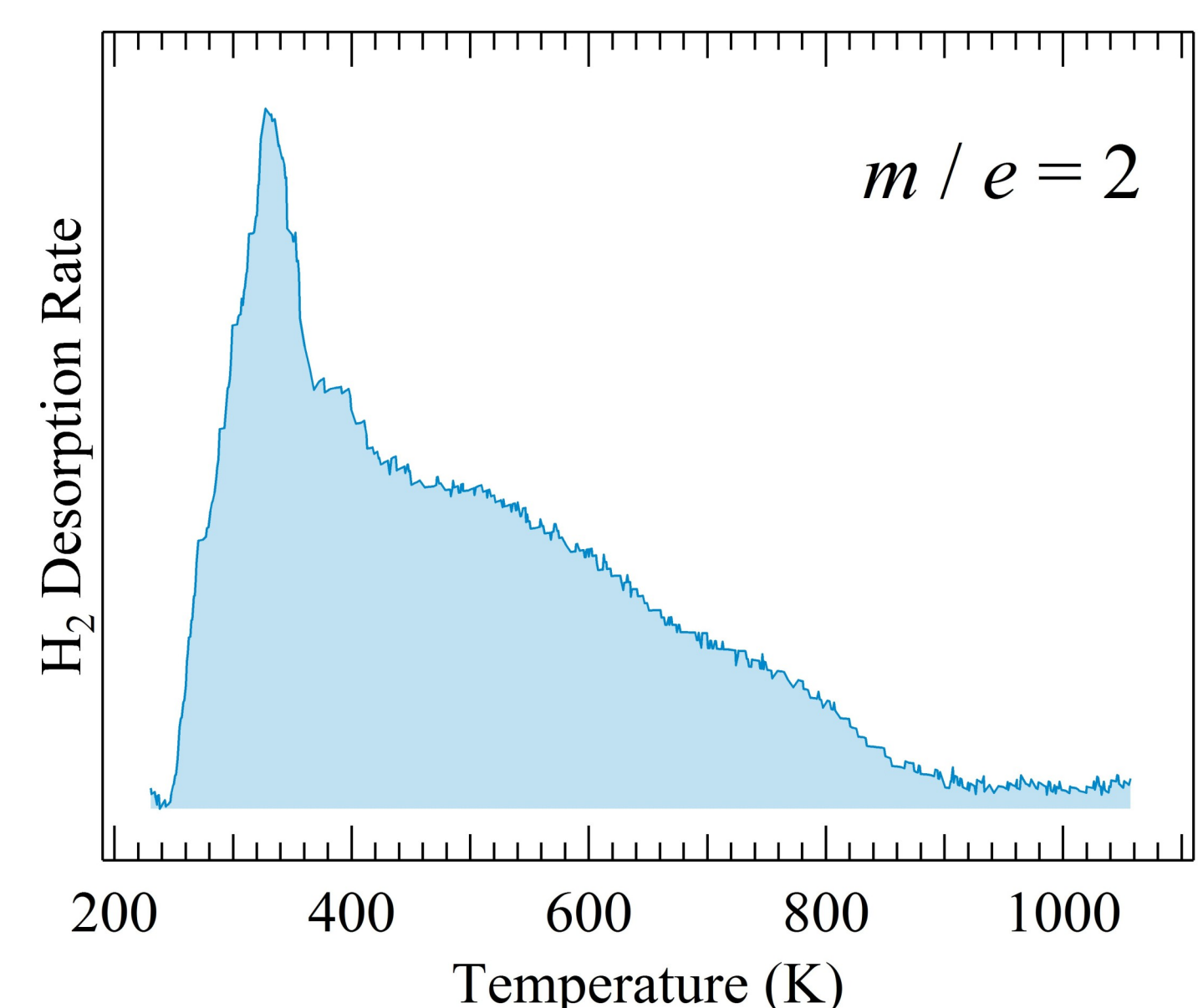


## *h*-BN GROWTH

As revealed by the multiple peak structure of the B 1s core level spectra, shown on the left,  $B_3N_3H_6$  deposition around room temperature ( $T = 330$  K) leads to the formation of atomic species and molecular fragments due to the brake-up of part of the BN ring.



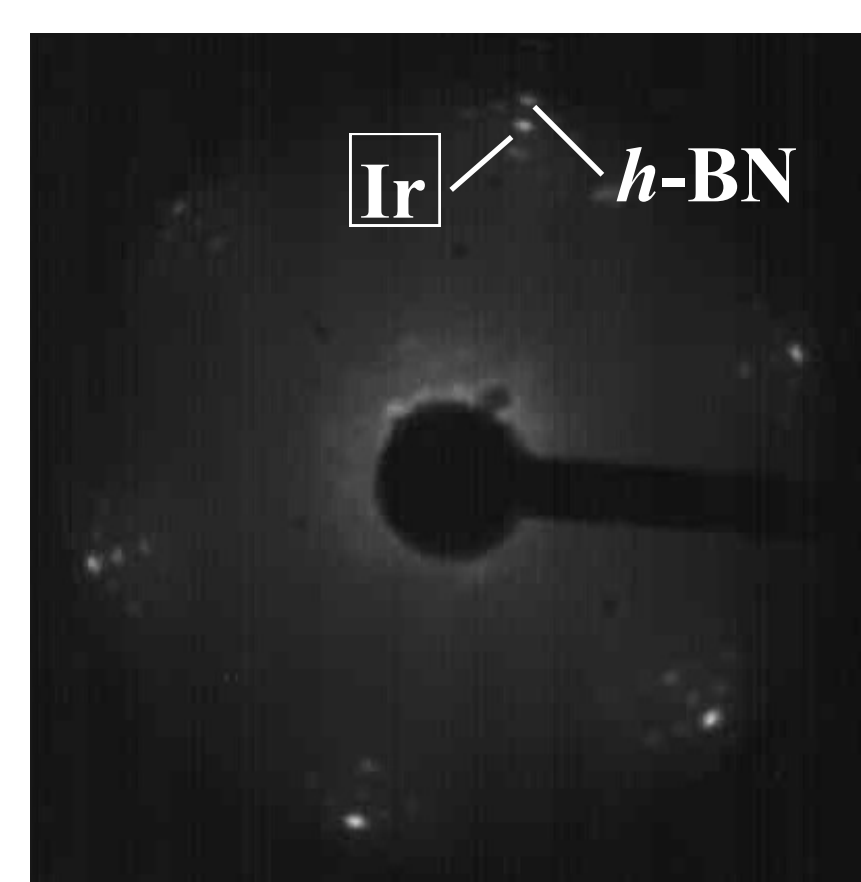
The dissociation process is further confirmed by the  $H_2$  thermal desorption spectrum (right figure), which indicates that the dehydrogenation starts already at 250 K and goes on over a broad temperature range up to 900 K, with a maximum desorption rate at about 330 K.



## REFERENCES

- [1] Corso, M.; Auwärter, W.; Muntwiler, M.; Tamai, A.; Greber, T.; Osterwalder, J.; Science, **2004**, 303, 217–220.
- [2] Simonson, R.; Paffett, M.; Jones, M.; Koel, B.; Surf. Sci., **1991**, 254, 29 – 44.

## A SINGLE *h*-BN LAYER



LEED image of the Ir(111) surface after CVD of  $B_3N_3H_6$  at 1070 K shows the principal substrate spots surrounded by a hexagonal network of diffraction spots due to the formation of the *h*-BN layer. The line profile analysis of the diffraction pattern reveals a superstructure with a periodicity of  $(13 \times 13)$  BN units ( $a = 0.250$  nm) on top of  $(12 \times 12)$  Ir unit cells ( $a = 0.272$  nm). A long-range ordered layer is obtained for  $B_3N_3H_6$  deposition above 1000 K. NEXAFS spectrum at the N K-edge shows a marked angular dependence which allows to distinguish between  $\pi$  ( $A'$ ,  $A''$ ) and  $\sigma$  ( $B$ ,  $C$ ) resonances. The complete absence of  $\pi$  components at normal incidence indicates that the *h*-BN lattice is lying flat on the substrate. The N 1s and B 1s core level photoemission spectra display similar double peak structures reflecting the variation of the interaction of

the *h*-BN layer to the substrate: the low BE main components ( $N_0$  and  $B_0$ ) are related to the layer region weakly bounded to the Ir atoms, while the high BE components ( $N_1$  and  $B_1$ ) represent the region strongly interacting with the substrate. This interaction leads to measurable changes also in the Ir  $4f_{7/2}$  spectra: besides the bulk ( $Ir_b$ ) and surface ( $Ir_s$ ) peaks characteristic of the pristine Ir(111), an adsorbate-induced component grows ( $Ir_i$ ).

