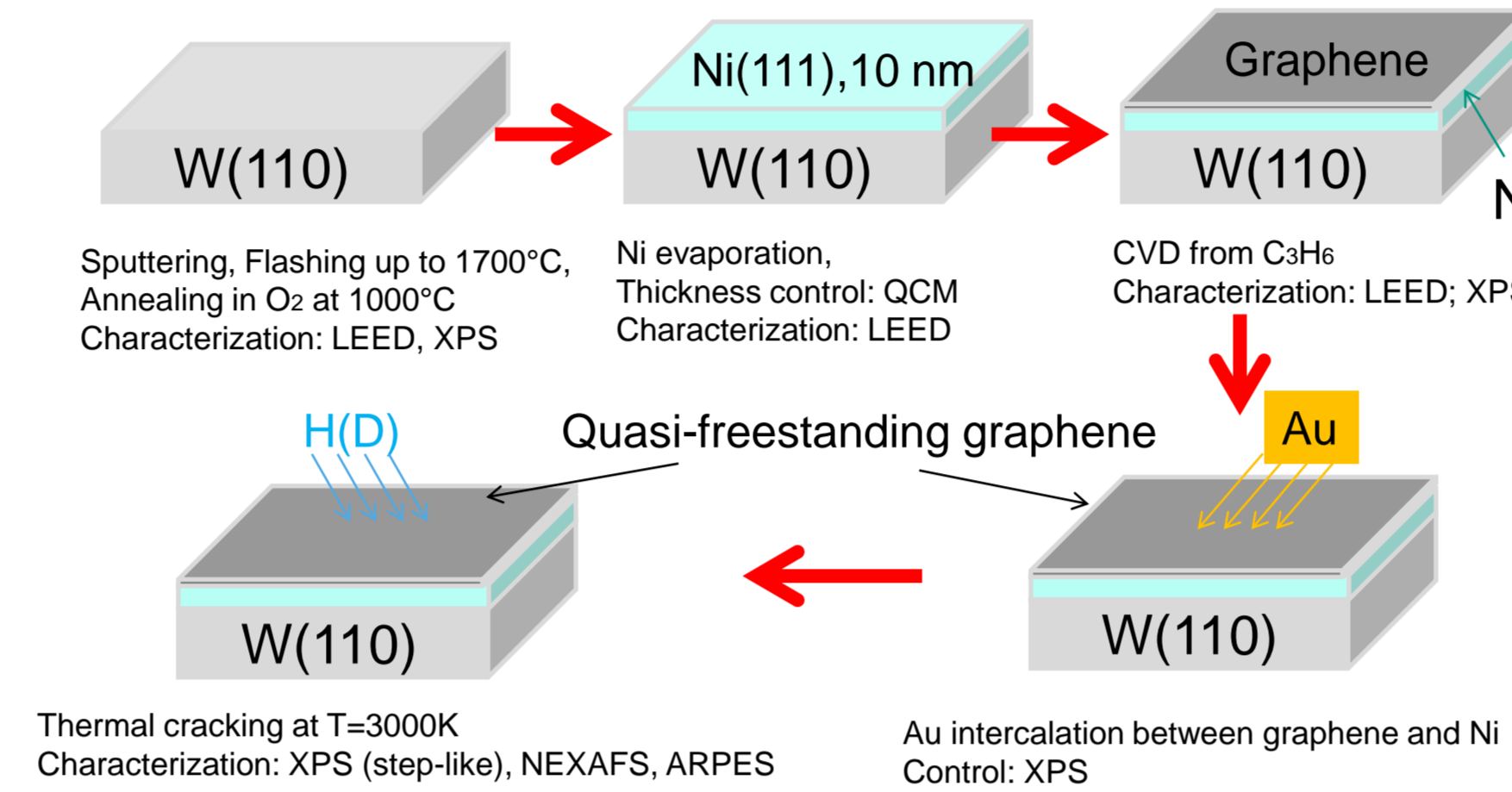


A. Nefedov, A. Paris, N. Verbitsky, Y. Wang, A. V. Fedorov, D. Haberer, M. Oehzelt, L. Petaccia, D. Usachov, D.V. Vyalikh, H. Sachdev, Ch. Wöll, M. Knupfer, B. Büchner, L. Calliari, L. V. Yashina, S. Irle, and A. Grüneis

Motivation

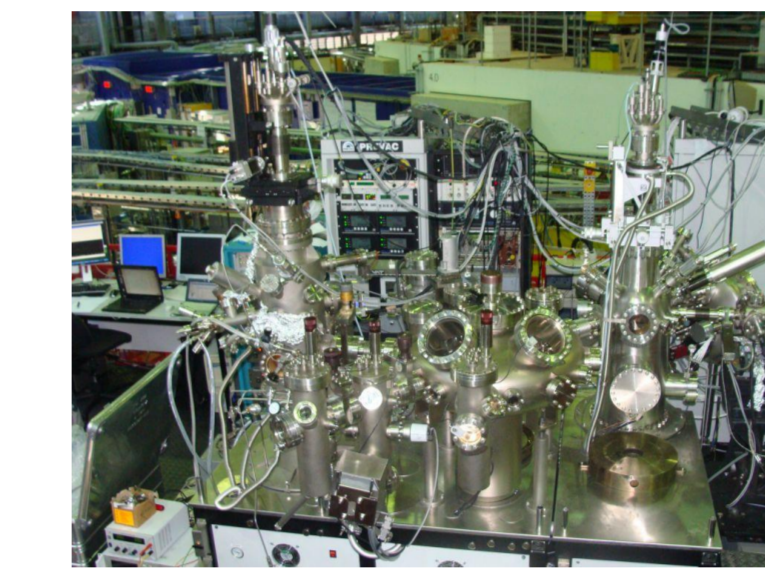
Kinetic isotope effects (KIEs), i.e. a different reaction constant for isotopes, are important phenomena in physical chemistry. They have been studied for a long time in their relation to the activation and rate of chemical reactions. A significant contribution to KIE are vibrational zero-point energy (ZPE) effects that upshift the energy of a chemical bond by half the phonon frequency of its constituents. Hence, KIEs are easy to observe in the hydrogen isotopes (deuterium and tritium) due to their large relative mass difference and were studied, even at the single-molecule level for hydrogen transfer in organic reactions including acid and base catalysis, enzyme reactions and catalytic decomposition. Most of these reactions were carried out with H and D in a molecular configuration and it was found that the reaction constant for the D compounds is lower than for the corresponding H compounds. These results are explained by the larger ZPE for H bonds, which results in a lower potential energy barrier to be overcome for H-bonds breaking as compared to D bonds. As a result, the bond-breaking reaction proceeds faster for the H compound than for the D compound. There have been very few reports on experiments carried out with one reactant being atomic H or D such as the H-D exchange reactions or reactions of H(D) with oxygen, where it was found that the oxygen-H(D) reaction proceeds equally fast for D and H. This was attributed to the absence of vibrational zero-point energy effects for the atomic species. Much less is known about the kinetics of these reactions in functional carbon materials based on hydrogenated graphene, such as novel 2D polymers. Here we present a novel inverse kinetic isotope effect involving the reaction of H/D radicals with the carbon atoms of epitaxial graphene. The advantages of graphene include a flat, well ordered large area surface with constant density of atoms. Therefore, the time-dependence of stoichiometry, which is necessary to describe the kinetics, can be precisely controlled and measured.

Sample preparation and layout of the experiment

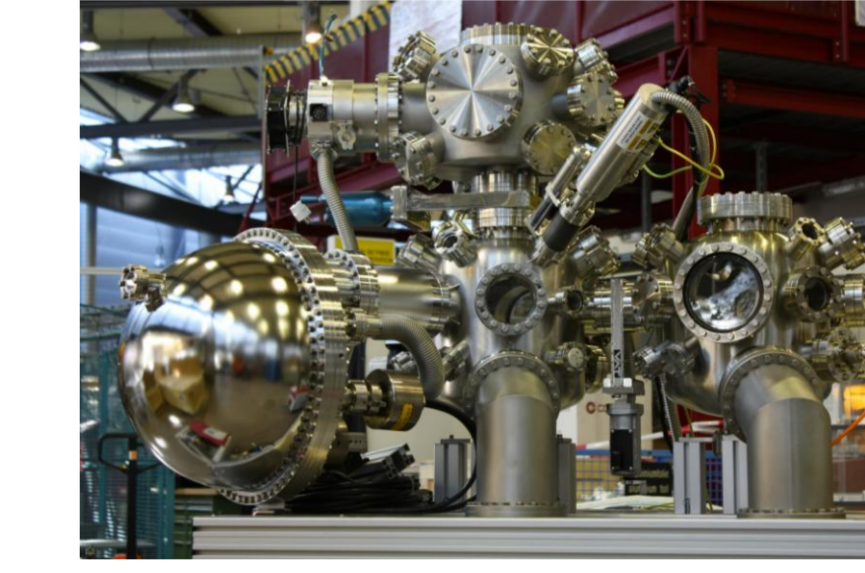


Experimental facilities: BESSY II and Elletra

Experimental stations @ BESSY II

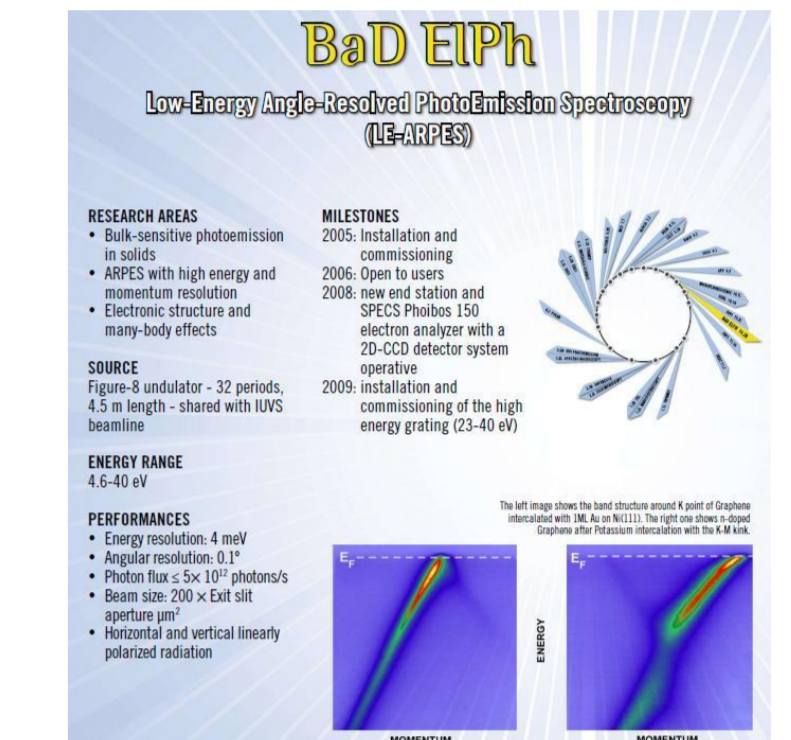


HESGM beamline



UE52 beamline

ARPES @ Elletra



H/D saturated graphene

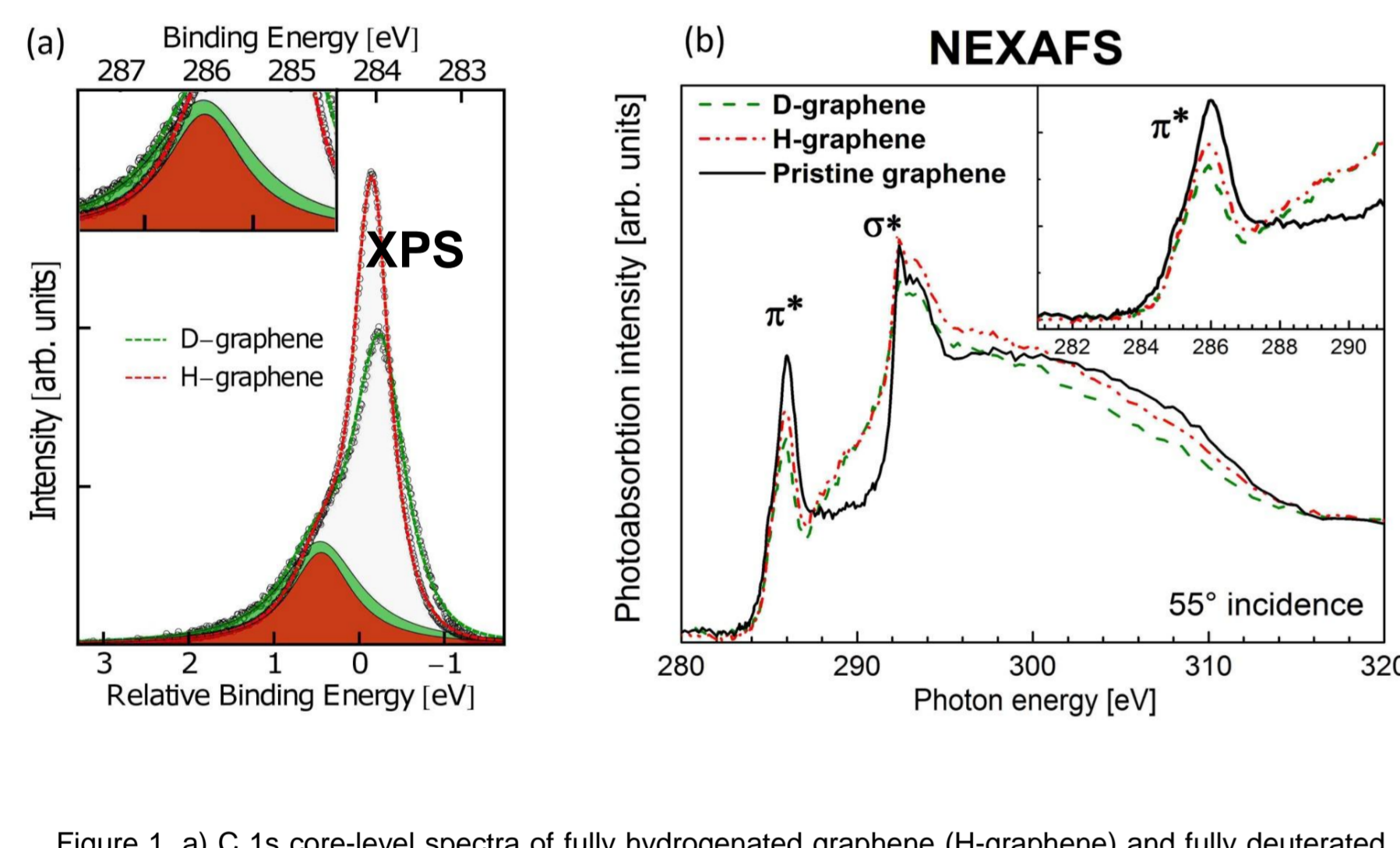


Figure 1. a) C 1s core-level spectra of fully hydrogenated graphene (H-graphene) and fully deuterated graphene (D-graphene). The H/C and D/C ratios are 25% and 35%, respectively. The red (green) line represents the fit to experimental data for H-graphene (D-graphene), while the red (green) area is the C₁ contribution from carbon atoms bonded to hydrogen (deuterium). Experimental spectra are normalized to the area under each curve. The inset depicts a magnification of the C₁ component. (b) Carbon K-edge NEXAFS spectra taken at 55° between the polarization vector and the surface normal, for pristine graphene, fully hydrogenated and fully deuterated graphene. Spectra are normalized to a common intensity for photon energies between 320 and 330 eV.

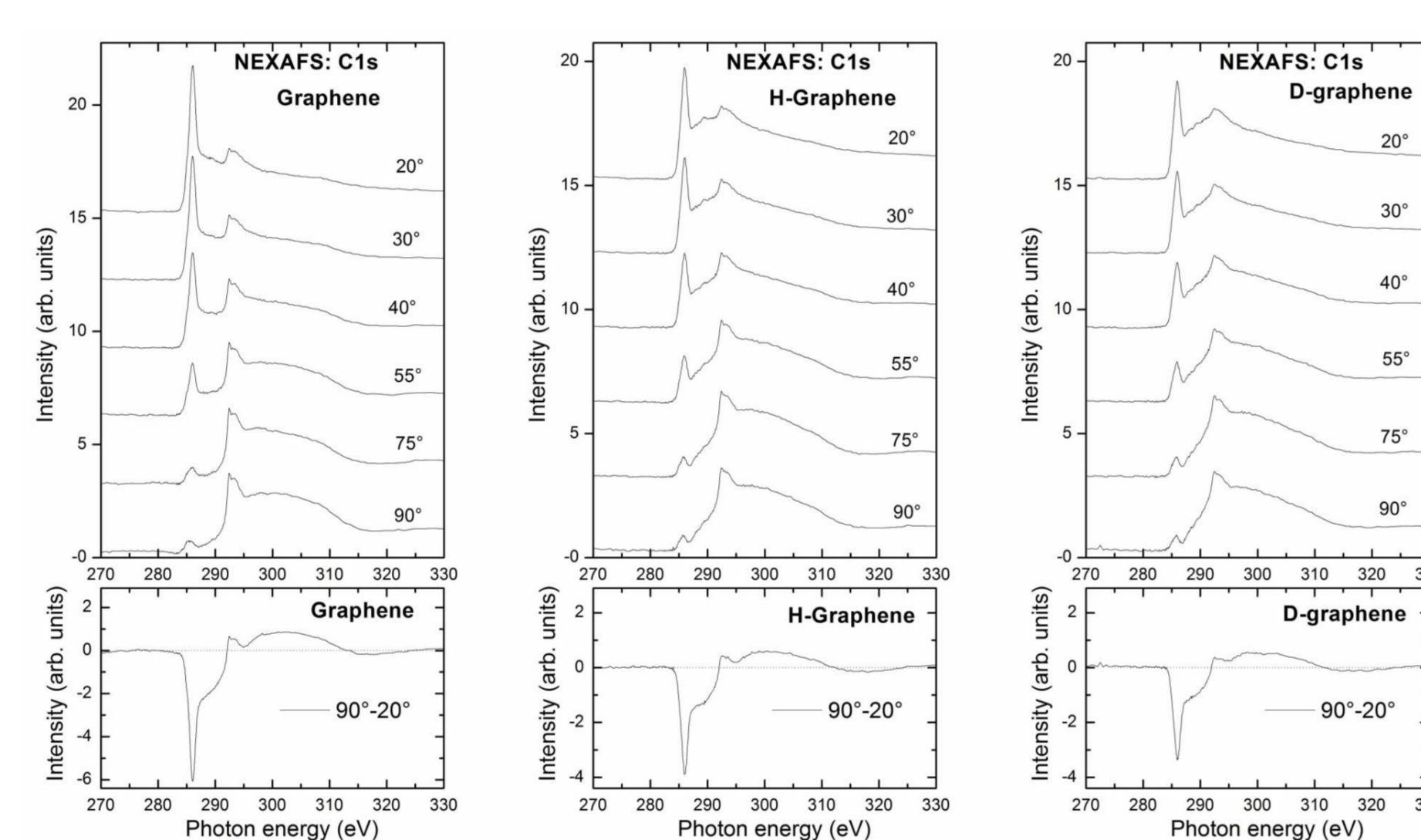


Figure 2: Upper panels: NEXAFS spectra of pristine, H- and D-graphene, taken at different angles between the surface normal and the photon polarization vector. Bottom panels: the difference between spectra taken at 90° and 20°.

H(D) kinetics: „in-situ“ XPS

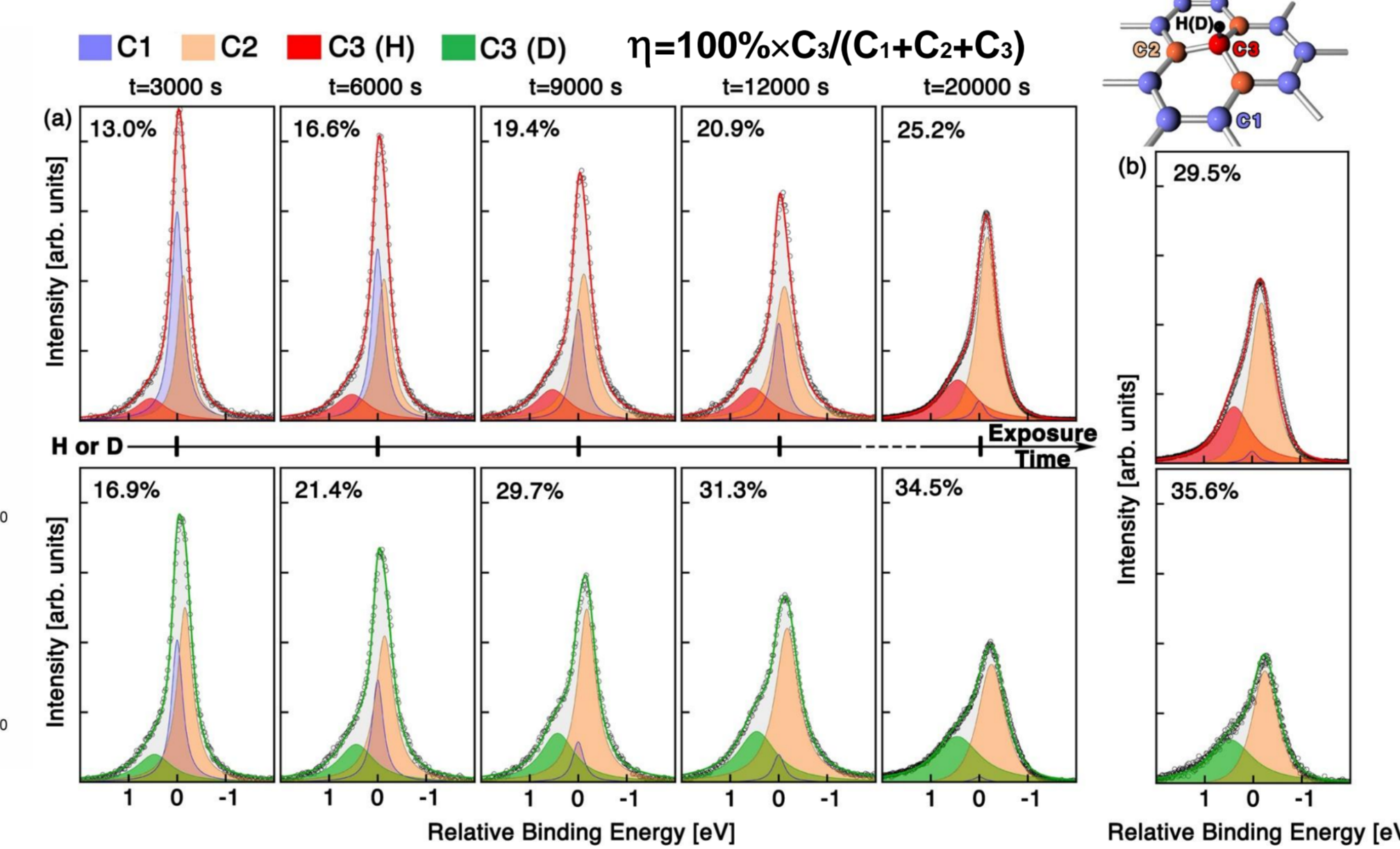
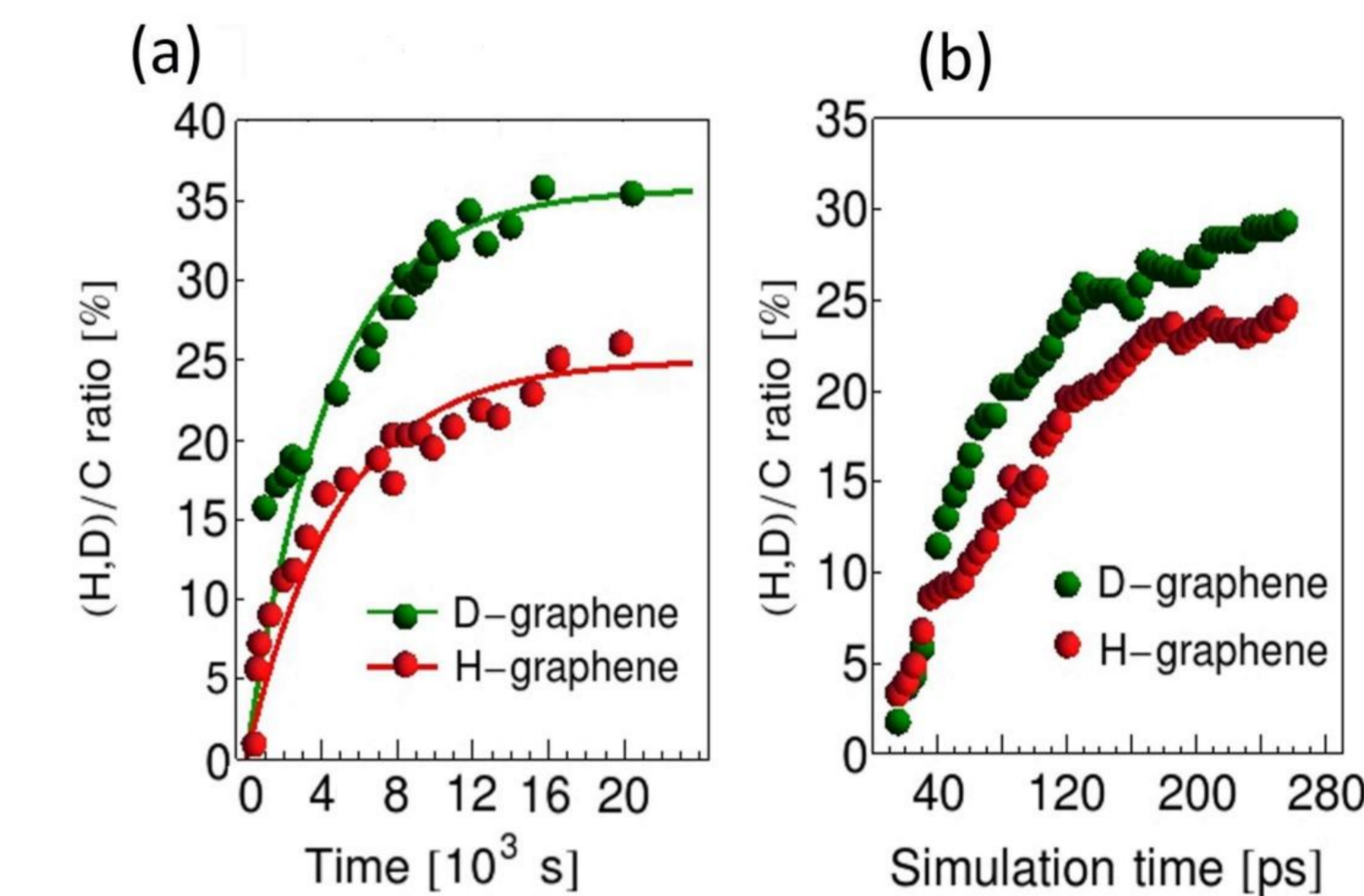


Figure 5. a) Time series of C 1s core-level spectra of graphene as a function of exposure to hydrogen (upper row) and to deuterium (lower row). The number denotes the atomic percentage of H/C and D/C atoms. All C 1s features are fitted with Doniach-Sunjić line shapes with components C₁ (blue) and C₂ (orange) representing unhydrogenated C atoms of graphene, while C₃ (red or green) is the contribution from carbon bonded to hydrogen or deuterium. C₁ has no neighboring C-H (C-D) bond and C₂ has a neighboring C-H (C-D) bond. (b) XPS spectra for fully hydrogenated graphene exposed to deuterium (upper plot) and fully deuterated graphene exposed to hydrogen (lower plot).

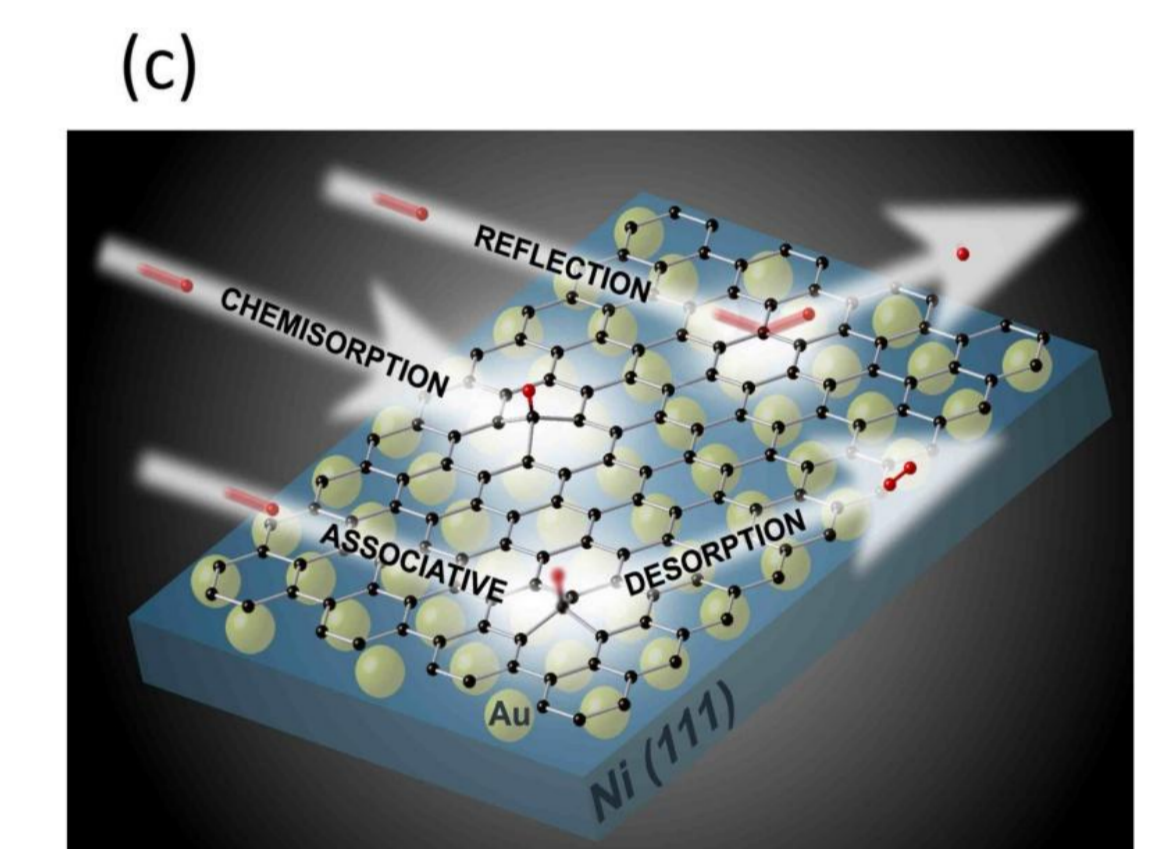
Reaction kinetics



$$\frac{d\eta}{dt} = I \cdot P_{\text{ads}}(1-\eta) - I \cdot P_{\text{des}} \cdot \eta$$

$$\eta[\%] = 100 \cdot P_{\text{ads}} / (P_{\text{ads}} + P_{\text{des}}) \times (1 - \exp[-I(P_{\text{ads}} + P_{\text{des}})t])$$

Figure 6. a) H/C and D/C ratios determined by XPS (points) along with the best fit for the chemisorption curve using a phenomenological kinetic model. b) H/C and D/C ratios determined by QMMD simulation according to scheme presented in Figure 7. c) Sketch of the H/D reflection, chemisorption and associative desorption processes on the graphene surface that were found to be relevant in the QMMD simulations and included in the phenomenological model.



Probability	P _{ads}	P _{H2} (P _{D2})	P _{refl}
hydrogenation	0.036	0.108	0.856
deuteration	0.058	0.104	0.838

Table 1: Probabilities of chemisorption (P_{ads}), reflection (P_{refl}) and associative desorption P_{H2} (P_{D2}) for an incoming H or D atom, as derived by the fit to the experimental data in Figure 6(a).

Angle dependence

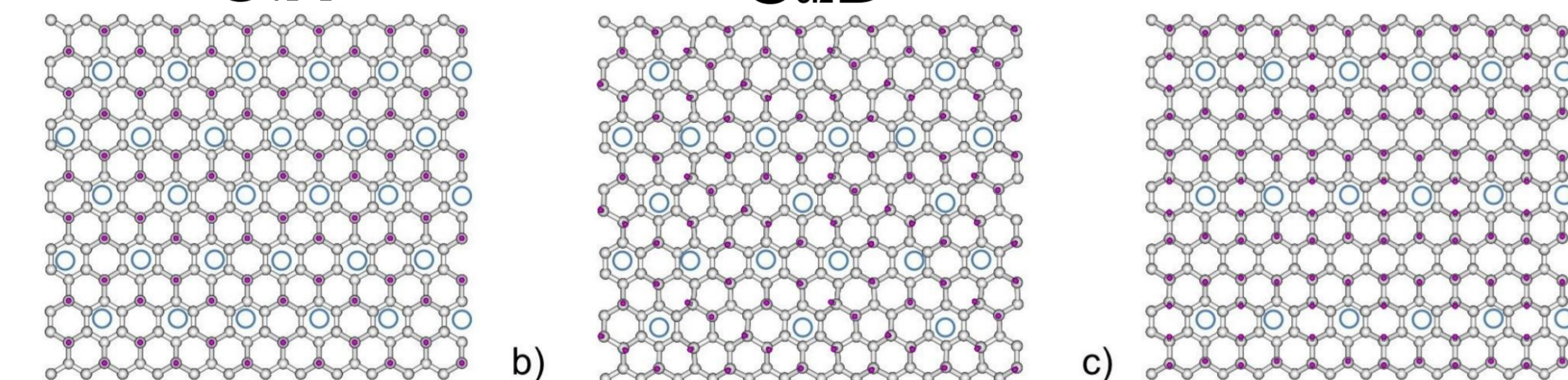


Figure 4: (a) Final configuration of hydrogenated graphene. A C-H structure with aromatic rings is achieved. (b) and (c) Possible final configuration for deuterated graphene. The two geometries correspond to final structures C_{3.2}D and C_{2.7}D, respectively.

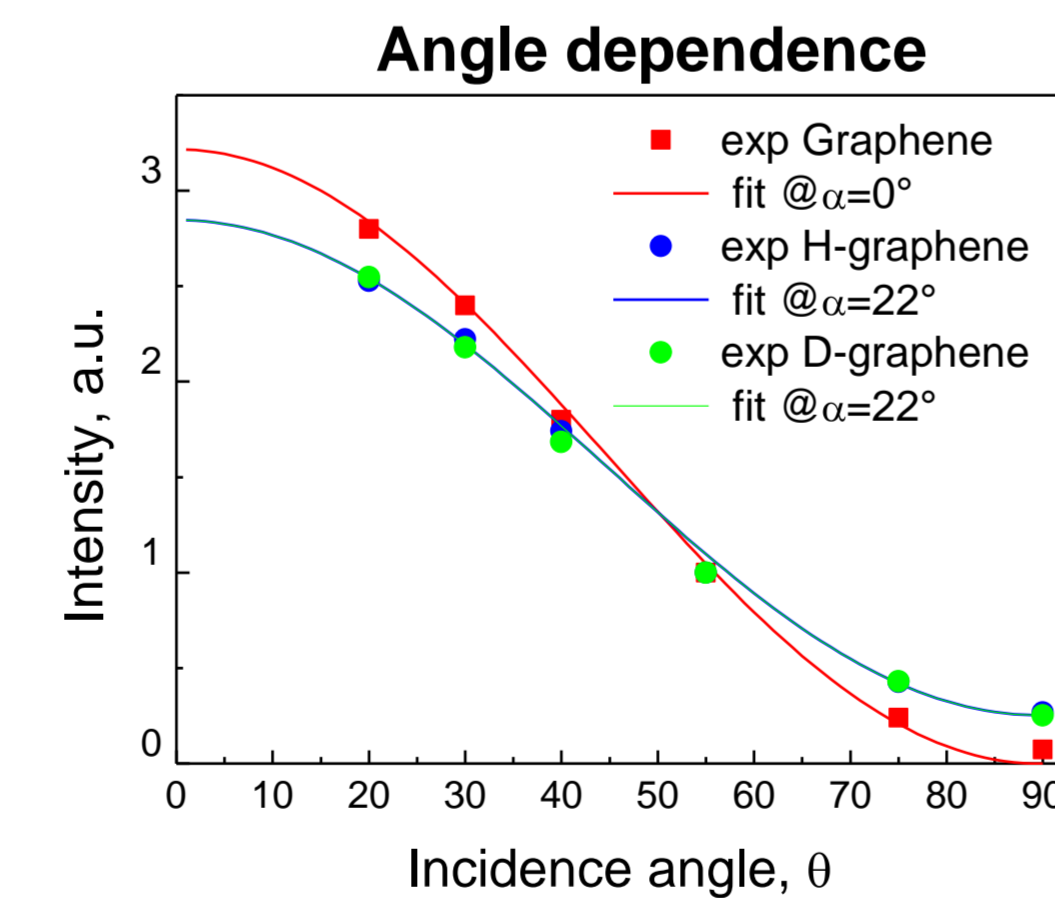


Figure 3: Angle dependence of pi*-resonance intensity of pristine, H- and D-graphene.

Summary

- We have observed a strong kinetic isotope effect (KIE) for the hydrogenation/deuteration reaction on quasi-free-standing monolayer graphene leading to substantially higher saturation coverage of D as compared to H.
- The unique geometry of the experiment and the relatively low flux of H/D atoms allowed us to study the surface chemistry of graphene during hydrogenation/deuteration monitoring the whole reaction in situ and in real time by photoemission spectroscopy.
- The experimental results for hydrogenation/deuteration are well described using a phenomenological kinetic model with terms for chemisorption, associative desorption and reflection of H/D atoms.
- The observed significant difference in the reaction involving H and D with graphene is relevant for isotope specific chemical reactivity in functional carbon materials and is important for the intensive research regarding atomic control of chemical reactivity at the nanoscale.
- The deuterium-doped graphene develops a band-gap similar to that observed for hydrogen [Haberer et al, Nano Letters 6, (2010), 3360] and consequently that the electronic isotope effect is weak.

Electronic isotope effect

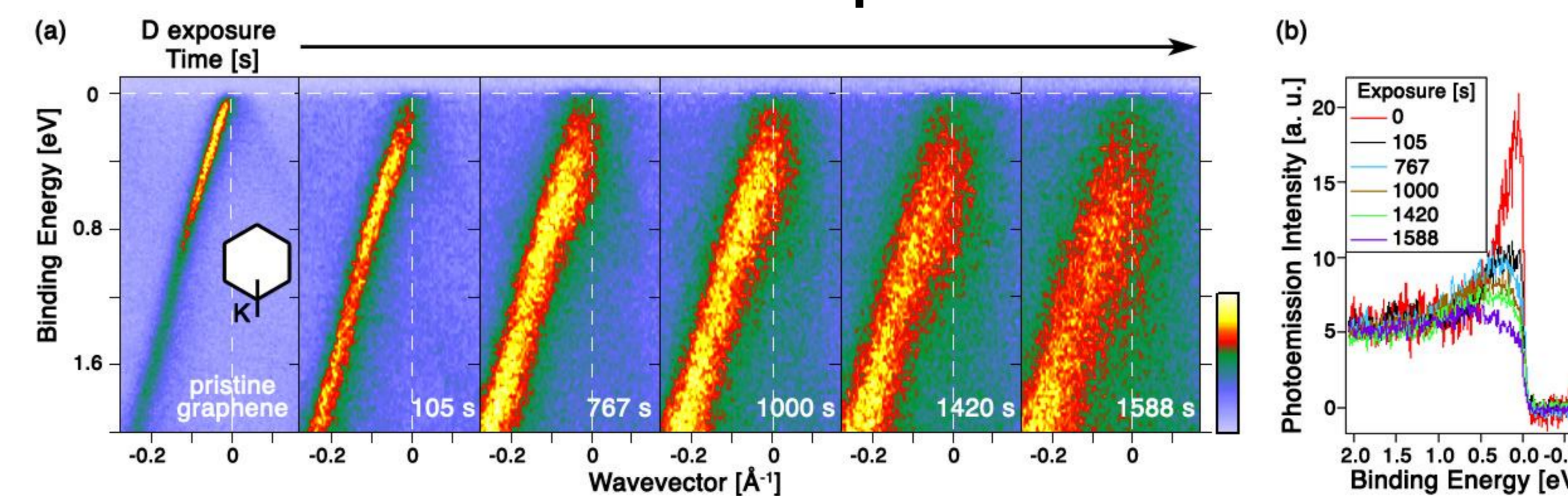


Figure 8: (a) ARPES spectra close to the K point for increasing D chemisorption. The direction of measurement is indicated in the 2D Brillouin zone and the time of exposure is denoted in each spectrum. (b) Electron energy dispersion curves at the K point for this chemisorption series. A common intensity scale for all D doping levels is used.

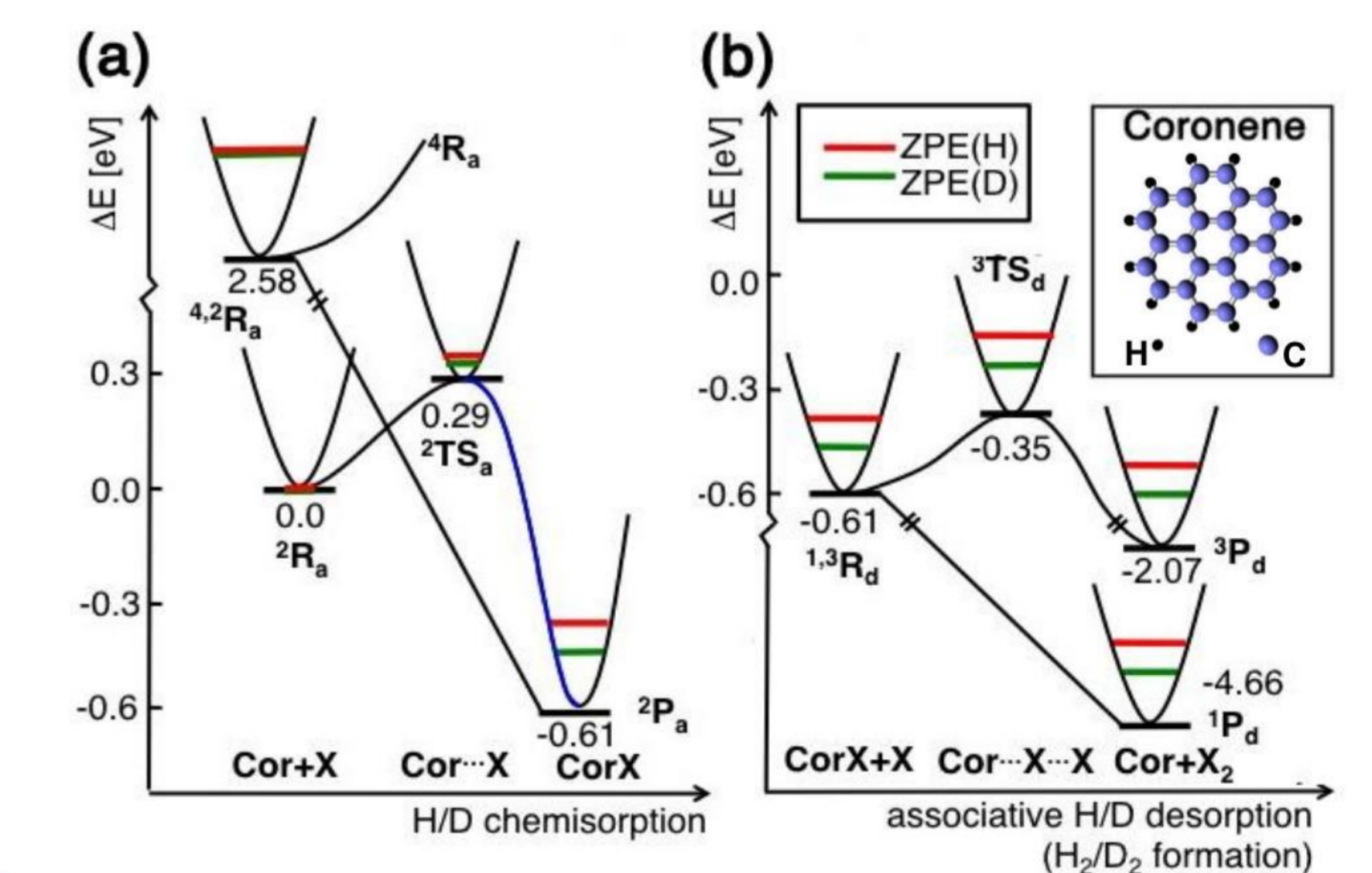


Figure 7: (a) Potential energy curves and barriers for the different stages of hydrogen (red lines) and deuterium (green lines) chemisorption on coronene. Note the differences of C-H and C-D bonds due to ZPE effects after chemisorption. Cor+X is the initial state with a free H or D atom, Cor--X is the transition state, while CorX is the final stage with an adsorbed H or D on coronene. (b) Energy potential curves of H and D for the stages of an associative desorption process (the inset shows a sketch of the coronene molecule). Cor+X is the initial state with one free and one adsorbed H or D atom, Cor--X--X is the transition state, while Cor+X₂ is the final stage with the molecule leaving coronene.