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OPEN ACCESS

RECEIVED
23 January 2017

REVISED
2 March 2017

ACCEPTED FOR PUBLICATION
6 March 2017

PUBLISHED
11 April 2017

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PAPER

Designing the Rashba spin texture by adsorption of inorganic molecules

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Keywords: Rashba effect, spin–orbit coupling, molecular spintronics, density functional theory

Supplementary material for this article is available online

Abstract

Using the physisorption and chemisorption of inorganic molecules on $BiAg_2$/Ag(111) we demonstrate from first principles that the spin–orbit splitting and the spin direction of surface Rashba-split states can be manipulated selectively. Although NH_3 is physisorbed, it nevertheless leads to a slight enhancement of the outward buckling of the surface Bi that increases the magnitude of the Rashba splitting. On the other hand, the weakly chemisorbed BH_3 determines a strong inward relaxation of the surface Bi such that the occupied Rashba state shifts into Ag bulk states while a new unoccupied one is induced. Importantly, for the BH_3–$BiAg_2$/Ag(111) system the size of the out-of-plane spin polarization is significantly larger than the in-plane one at variance with the clean surface case.

Achieving control over the spin direction at surfaces offers the possibility to directly access a variety of physical properties in metallic [1], insulating [2] or semiconducting [3] systems and thereby opens new prospects in the field of spintronics. For instance, it provides the possibility to control the spin-direction in setups that utilize current induced spin-polarization or accumulation [4] or at interfaces to magnetic systems it can be exploited to exert spin–orbit torques in the magnetic layers [5]. Additionally, by tuning the magnitude of the out-of-plane spin polarization one can directly modify the strength of the Dzyaloshinskii–Moriya interaction in non-collinear magnetic systems [6].

In this respect, the spin–orbit coupling (SOC) plays a crucial role to manipulate the spin degree of freedom in spintronics [7]. In particular, the SOC is a crucial ingredient to describe the physical properties of the emerging classes of Rashba [8] and topological insulator (TI) [9] materials. More specifically, the Rashba–Bychkov [10–12] spin–orbit effect describes the spin-split electronic states of a spatial inversion asymmetric two-dimensional electron gas (2DEG) (for a recent review see, e.g., [13]). This effect opens the fascinating possibility to control the spin using only electric fields as initially suggested by Datta and Das for a spin field-effect transistor (FET) [14] and recently demonstrated for an all-electric spin FET device [15].

While the above mentioned applications focus on SOC effects in 2DEGs at interfaces, much attention also shifted to their manifestation in surface states. The first observation in this direction was made on the Au(111) surface [16], where a (spin) splitting of the surface state was observed that can be described in the Rashba model by the spin-splitting parameter k_{SO} [17] of $\approx$0.012 Å^{-1}. Subsequent studies using spin- and angle resolved photo emission spectroscopy (ARPES) measurements revealed large Rashba splittings at the low index surfaces of Bi [18], and Bi surface alloys [19, 20]. For instance, a $BiAg_2$/Ag(111) surface alloy exhibits a 'giant' spin splitting of $k_{SO} \geqslant 0.13$ Å^{-1}. Importantly, for this system it was demonstrated that a significant outward relaxation of the Bi atom is the key ingredient that leads to a larger Rashba splitting as compared to a Bi(111) surface [21]. Generally, it was emphasized that the driving force of this Rashba splitting is the asymmetry of the surface state wave function in the core region [17, 22].

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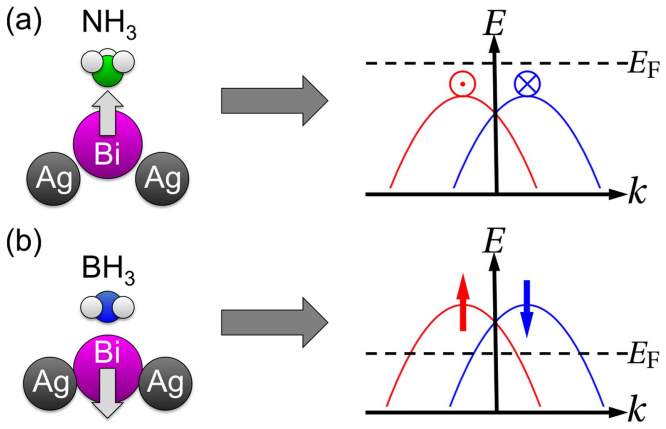

Figure 1. (a) The physisorbed NH_3 on $BiAg_2$/Ag(111) increases the outward relaxation of the surface Bi atoms that in turn determines an enhanced Rashba splitting of the occupied surface state. (b) On the other hand the weakly chemisorbed BH_3 molecule induces an inward relaxation of the Bi atoms such that the out-of-plane spin polarization for the BH_3–$BiAg_2$/Ag(111) system is significantly larger than its in-plane counterpart in contrast to the NH_3–$BiAg_2$/Ag(111) system. The spin directions for each band are indicated by red and blue arrows.

As regarding the issue how to tune spin–orbit effects for surface systems, several experimental and theoretical studies have proposed that the strength of the Rashba splitting can be tuned via adatom adsorption [23–27] or by a stoichiometry change of the surface alloy [28]. Furthermore, it was shown that a graphene layer on the Ir(111) surface protects the Rashba-split surface state from air [29] and keeps k_{SO} unaffected even when Au nanoclusters are deposited on the graphene layer [30], demonstrating that the 2DEG of the surface state can be isolated in a well-defined state. For adsorbed molecular systems such as C_{60}, iron octaethylporphyrin (FeOEP) and 3, 4, 9, 10-perylene-tetracarboxylic acid (PTCDA) the ARPES measurements performed in [31] indicated that they also did not alter the Rashba splitting of the $BiAg_2$/Ag(111) surface states due to a weak molecule–surface interaction. A recent study of PTCDA on $PbAg_2$/Ag(111), however, reports changes in the substrate bandstructure [32]. Also on a TI surface such as Bi_2Se_3(111), Rashba split interface states can be induced by organic molecules depending on the strength of the molecule–substrate interaction [33]. Furthermore, for the cobalt phthalocyanine (CoPc)/Bi_2Se_3 system a recent ARPES study demonstrated that the topological surface state is not present anymore in the first quintuple layer due to the molecule–surface hybridization, but nevertheless it is buried in the second quintuple layer [34].

While the above-mentioned studies were mainly focused on the size of the spin–orbit splitting, we show in this contribution that adsorbates can also be used to manipulate the spin-direction of the spin-texture in the 2DEG. In case of the Bychkov–Rashba effect, which is based on a uniform 2DEG in an electric field normal to the surface, the spins are oriented in the surface plane, perpendicular to the momentum direction. We demonstrate that the adsorption of inorganic molecules can be used to create in-plane surface potential gradients that induce a dominant out-of-plane spin polarization as illustrated in figure 1.

More specifically, the basic aims of this study are to tailor the magnitude of the (1) Rashba splitting and (2) out-of-plane spin polarization. The key mechanism is to modify the size of the Bi outward relaxation upon the molecular adsorption and to induce in-plane potential gradients. In practice, we achieved these goals for two exemplary inorganic molecular systems with an opposite electronic character. More precisely, the ammonia molecule (NH_3) has a pyramidal structure in which the electronic states are sp^3 hybridized and contains an electronegative N atom with a lone electron pair that usually plays an important role in the molecular bonding to a surface of choice [35]. On the other hand, the planar borane molecule (BH_3) is sp^2 hybridized containing an electropositive B atom with less electronic density as compared to N in NH_3 (i.e., an empty p_z orbital at B). On this basis, a considerable difference in the interaction between these two molecules and the $BiAg_2$/Ag(111) surface is to be expected.

Using the computational setup described in the supplementary material available online at stacks.iop.org/NJP/19/043017/mmedia, our *ab initio* calculations reveal that in the ground-state NH_3 adsorbs with the N at an fcc hollow site and BH_3 with its B atom in an hcp hollow site (see figure 2). Overall, the calculated adsorption energies [36] indicate that NH_3 is physisorbed ($E_{ads} = 0.23$ eV) while BH_3 is weakly chemisorbed ($E_{ads} = 0.50$ eV) on the $BiAg_2$/Ag(111) surface alloy.

A particularly important effect induced by both molecules on the $BiAg_2$/Ag(111) surface is the structural change upon molecular adsorption, namely how BH_3 and NH_3 modify the magnitude of the outward relaxation of the surface Bi atom, d_{Bi}. Despite of the weak interaction of NH_3 with this substrate, Bi is slightly pulled out of

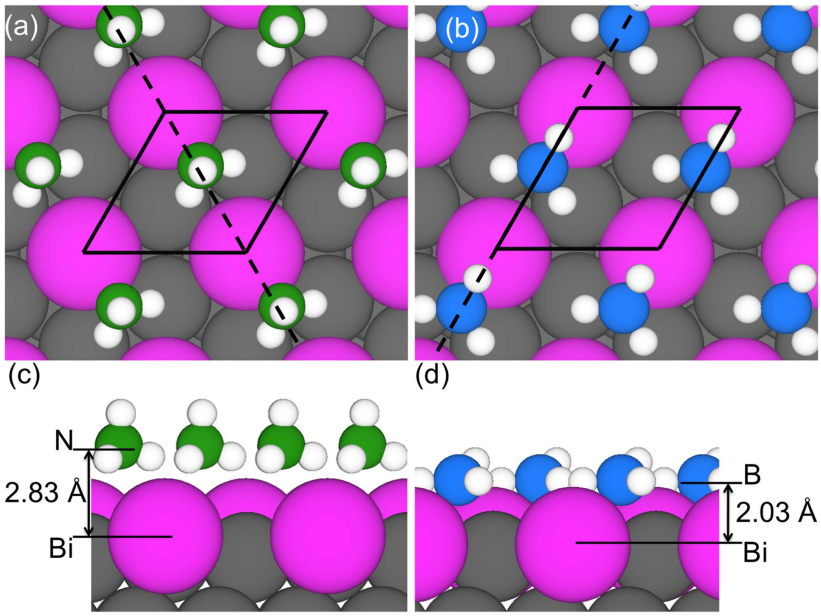

Figure 2. Top and side view of the ground-state geometry obtained for the physisorbed NH_3 (a), (c) in an fcc hollow site and the chemisorbed BH_3 (b), (d) in an hcp hollow adsorption configuration on $BiAg_2/Ag(111)$ with a $(\sqrt{3} \times \sqrt{3})R30°$ in-plane surface unit cell. The physisorption bonding mechanism of NH_3 on the surface alloy is suggested by the larger molecule–surface distance of 2.83 Å as compared to 2.03 Å obtained for the chemisorbed BH_3 on $BiAg_2/Ag(111)$. Color code: Bi (magenta), Ag (dark gray), N (green), B (blue) and H (light gray).

surface by about 10% leading to $d_{Bi}^{NH_3} = 0.67$ Å with respect to the clean surface buckling of 0.61 Å. Note that this behavior is similar to that observed for organic molecules adsorbed on a magnetic substrate that induces an outward relaxation of the surface atoms (i.e., skyhook effect) that further modifies the strength of their magnetic exchange interactions [37]. On the contrary, BH_3 adsorption leads to ~40% inward relaxation of the Bi resulting in $d_{Bi}^{BH_3} = 0.37$ Å. In the view of the correlation between the size of the Rashba splitting and the degree of the outward buckling of the Bi outlined in [21], these structural changes of the surface layer raise the expectation that the Rashba effect on the $BiAg_2/Ag(111)$ can indeed be selectively tuned by the adsorption of the two molecular species NH_3 and BH_3.

To investigate this issue in more detail, we focus now on the electronic structure of the hybrid molecule–surface systems as revealed by the calculated band structures obtained by taking into account the SOC. We first note that our theoretical band structure obtained for the clean $BiAg_2/Ag(111)$ surface (cs) is in good agreement with previous experimental and first-principles investigations [20, 21] (see figure 3(a)). In figures 3(b) and (c) the band structures obtained for NH_3 and BH_3 on $BiAg_2/Ag(111)$ are presented, respectively. In case of NH_3 (see figure 3(b)), the Rashba splitting of the occupied surface state is indeed increased from the clean surface value of $k_{SO}^{cs,occ} = 0.09$ Å^{-1} to $k_{SO}^{NH_3,occ} = 0.10$ Å^{-1} by about ≈10% as expected due to the enhanced outward relaxation of the Bi upon molecular adsorption. Remarkably, this increase of the Rashba spin splitting is as large as the whole spin–orbit splitting of the Au(111) surface state [16]. Overall, this behavior is a direct consequence of the fact that the increased outward buckling of the Bi added more p_z and $p_{(x,y)}$ character to the occupied surface state, which has in case of the clean surface mainly (s, p_z) character[2]. This makes this surface state more asymmetric that is the key ingredient to obtain a sizeable Rashba splitting [17, 22]. Additionally, the Rashba splitting of the first unoccupied surface state is $k_{SO}^{NH_3,unocc} = 0.09$ Å^{-1} being by 0.01 Å^{-1} larger than that for the clean surface.

It is important to note that this outcome of our *ab initio* study is in contrast to the experimental results obtained for a physisorbed π-conjugated organic molecule such as CuPc on $PbAg_2/Ag(111)$ [32] or C_{60} on $Bi_2Se_3(111)$ [33], which indicated that the Rashba spin-split surface electronic states were not modified by the molecular adsorption. Qualitatively, we assign this strikingly different behavior to the specific nature of the molecular electronic states that mediates the molecule–surface interaction: while for CuPc and C_{60} the dispersion interaction is related to delocalized π molecular electronic states, the NH_3 interacts with the $BiAg_2/Ag(111)$ surface mainly via the lone pair localized at the nitrogen atom. Overall, this difference leads to a surface structural change in the case of the inorganic NH_3 molecule while this effect is not present for the organic ones.

[2] For the clean surface the orbital contribution at $\bar{\Gamma}$ is s: 47.6%, p_x: 7.7%, p_y: 7.7% and p_z: 20.2% while for the NH3–surface system it amounts to s: 41.1%, p_x: 9.3%, p_y: 9.3% and p_z: 20.9%.

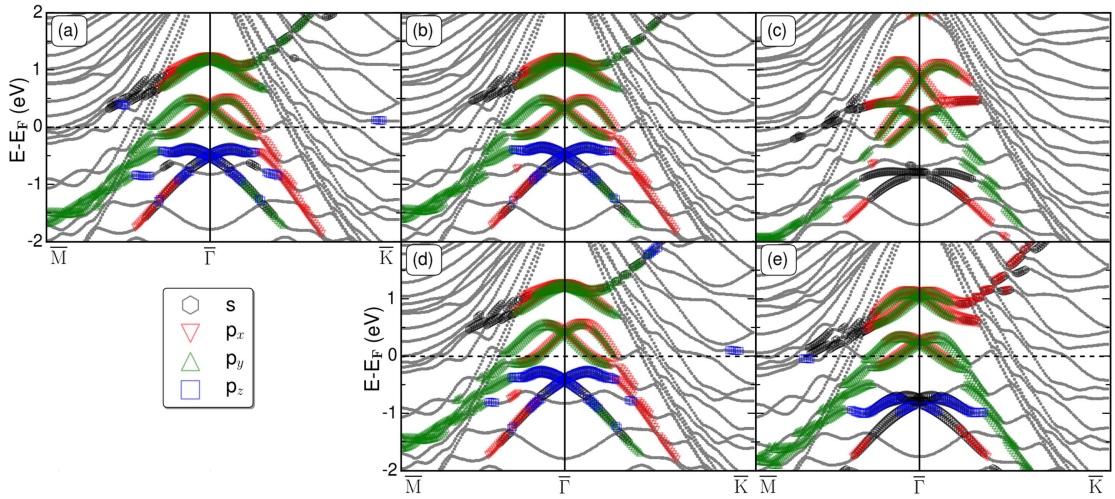

Figure 3. Comparison of the band structures obtained with SOC for (a) clean $BiAg_2/Ag(111)$, (b) NH_3–$BiAg_2/Ag(111)$, (c) BH_3–$BiAg_2/Ag(111)$, (d) the NH_3-induced clean surface geometry and (e) the BH_3-induced clean surface geometry. The orbital character of the electronic states for a contribution larger than 8% for the surface layer atoms is indicated as follows: *s* (black), p_x (red), p_y (green) and p_z (blue).

In the case of BH_3 (see figure 3(c)) the occupied $BiAg_2/Ag(111)$ surface state is pushed into the projected Ag bulk states (see figures 2 and 3 in the supplementary material) upon molecular adsorption due to the significant inward relaxation of the Bi atom by ~40%. Hence, this observation implies that the chemisorbed BH_3 allows to selectively move the occupied surface state away from the Fermi energy E_F. The Rashba splitting of the unoccupied surface state is preserved upon BH_3 adsorption with a spin splitting comparable with that of the clean surface. Remarkably, the weakly chemisorbed BH_3 on $BiAg_2/Ag(111)$ induces a Rashba-like (linear in k) spin-splitting of an unoccupied surface state at $\approx$1 eV above the Fermi energy that was 3rd order spin split in the case of the clean $BiAg_2/Ag(111)$ surface. Note that this new Rashba-like surface state is characterized by $k_{SO}^{BH_3,unocc2} = 0.09$ Å^{-1} being similar to the occupied Rashba split state of the clean surface[3].

Again, as in the case of the physisorbed NH_3, the impact of the weakly chemisorbed BH_3 on the Rashba-split surface states of the $BiAg_2/Ag(111)$ substrate is qualitatively different with respect to behavior evidenced in [32, 33] for organic molecules. In particular, the inorganic BH_3 molecule leads to an inward relaxation of the surface Bi atoms in constrast to the outward relaxation of the Pb ones for PTCDA on $PbAg_2/Ag(111)$ [32]. Moreover, even if it is weakly chemisorbed, BH_3 induces a new unoccupied Rashba spin-split surface state on $BiAg_2/Ag(111)$ similarly to the strongly chemisorbed sulphurated H_2Pc organic molecule on $Bi_2Se_3(111)$ [33]. Generally, these results of our first-principles study clearly illustrate the versatility of the inorganic molecules to chemically functionalize the electronic structure of a hybrid molecule–surface Rashba system.

To gain a further insight into the origin of the differences between the electronic structure of the clean $BiAg_2/Ag(111)$ surface alloy and those of the hybrid molecule–surface systems we firstly investigated the electronic structure related to the molecule–surface hybridization (the hybridization effect) or the Pauli repulsion-induced charge rearrangement at the molecule–surface interface (the Pauli repulsion effect). Then, we analyzed these results with respect to the effect of the molecular-induced structural changes via the rehybridization of the surface atoms states (the geometrical effect) on the calculated band structure obtained for the geometries of the hybrid systems with the molecules removed (see figures 3(d) and (e)).

For the NH_3-induced geometry, figure 3(d) clearly indicates that the calculated band structure is very similar to that of the hybrid molecule–surface system shown in figure 3(b). This observation suggests that the corresponding changes in the band structure are mainly a geometrical effect. More specifically, the splitting of the occupied surface state amounts to $k_{SO}^{NH_3\text{-induced,occ}} = 0.10$ Å^{-1} as in the case of the NH_3–surface system. Moreover, the Rashba splitting of the unoccupied state is reduced to $k_{SO}^{NH_3\text{-induced,unocc}} = 0.08$ Å^{-1}, which coincides with the value obtained for the clean surface. This observation leads to the conclusion that for the physisorbed NH_3 on the $BiAg_2/Ag(111)$ surface the increased Rashba splitting of its unoccupied surface state is related to an interfacial charge rearrangement due to the Pauli repulsion effect as indicated by the charge density difference plot shown in figure 4(a).

[3] We also note in passing that in general the dispersion of the Rashba split surface states is slightly anisotropic in the *k*-space but a detailed analysis of this feature of the calculated band structures for both molecule–surface systems is beyond the scope of this study.

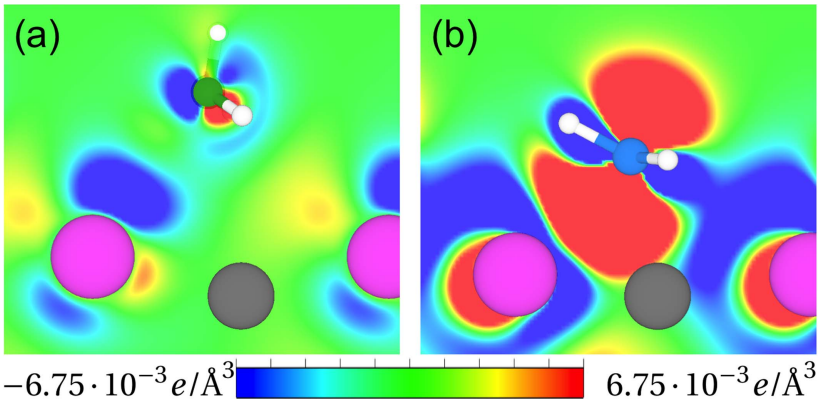

Figure 4. Charge density difference plot for (a) NH_3 and (b) BH_3 adsorbed on the $BiAg_2/Ag(111)$ surface in a plane normal to the substrate as indicated in figure 2 by dashed lines. Note that the weak charge rearrangement at the NH_3–surface interface due to the Pauli repulsion is a fingerprint for a physisorption bonding mechanism. In contrast, the BH_3–surface system exhibits a significant charge rearrangement typical for chemisorption that especially involves a charge gain in the p_z atomic-like state of boron.

In case of the BH_3-induced geometry, the band structure displayed in figure 3(e) indicates that the occupied Rashba split surface state is also moved into the projected Ag bulk states as already noticed for the molecule–surface system. Surprisingly, this observation implies that for the chemisorbed BH_3 on $BiAg_2/Ag(111)$ this shift of the occupied Rashba split surface state is predominantly a geometrical effect related to the significant inward relaxation of the Bi atoms. Besides this, as in the case of the NH_3-induced surface geometry, the unoccupied Rashba split surface state also shows a reduced splitting of the size of $k_{SO}^{BH_3\text{-induced,unocc}} = 0.08$ Å^{-1} similarly to the clean surface value while $k_{SO}^{BH_3\text{-induced,unocc2}} = 0.04$ Å^{-1} is significantly smaller. Overall, as illustrated in figure 4(b), this behavior is essentially related to a hybridization effect due to the mixing of the molecule and surface electronic states.

As already discussed in literature [20, 38], the clean $BiAg_2/Ag(111)$ surface is described by an anisotropic 2DEG characterized by an asymmetric out-of-plane potential as well as an in-plane structural inversion asymmetry (SIA) leading to a strong enhancement of the Rashba effect compared to that measured for Au(111) [16]. In particular, in contrast to the Rashba model that favors an in-plane spin polarization of the surface states, an asymmetric in-plane surface potential gradient due to SIA determines also a sizeable out-of-plane spin polarization P_z [20]. In contrast to the small out-of-plane polarization P_z of the clean surface (see figures 5(a) and (b)), our first-principles calculations indicate that both physisorbed NH_3 and chemisorbed BH_3 molecules considered in our study can specifically enhance the asymmetry of the in-plane surface potential and therefore they can tune the magnitude of P_z of the corresponding hybrid molecule–surface systems. More specifically, in the case of NH_3/BH_3 on $BiAg_2/Ag(111)$ this effect is illustrated for the surface Bi and Ag atoms in figures 5(c) and (d)/(e) and (f), respectively. Interestingly, a quantitative analysis of the out-of-plane spin polarization along the $\overline{\Gamma M}$ and $\overline{\Gamma K}$ directions for the occupied states of the BH_3–$BiAg_2/Ag(111)$ system revealed that $P_z^{BH_3} \leqslant 70\%$ (see figure 5(f)) while the in-plane one $P_{xy}^{BH_3} \leqslant 50\%$ (see figure 5(e))[4]. When compared with $P_z^{BiAg_2/Ag(111)} \leqslant 10\%$ of the clean surface [20], our *ab initio* results suggest that indeed a weakly chemisorbed molecule can be employed to change the dominant in-plane spin polarization of the clean surface to out-of-plane for the hybrid system. Note that in the case of the physisorbed NH_3 molecule on $BiAg_2/Ag(111)$, $P_z^{NH_3} \leqslant 20\%$ (see figure 5(d)) and $P_{xy}^{NH_3} \leqslant 65\%$ (see figure 5(c)) for the occupied states.

To summarize, in this theoretical study we demonstrated that for the $BiAg_2/Ag(111)$ surface alloy the fingerprint features of its Rashba spin-split surface states can be specifically modified via *physisorbed* as well as *chemisorbed* inorganic molecules. More precisely, the physisorbed NH_3 on $BiAg_2/Ag(111)$ induces an increase of the outward buckling of the surface Bi atoms that in turn strengthens the Rashba splitting of the occupied surface state (i.e., it is a geometrical effect) while the Rashba splitting of the unoccupied one is enlarged due to the molecular-induced weak interfacial charge reordering (i.e., it is a Pauli repulsion effect). On the other hand, the weakly chemisorbed BH_3 leads to an inward relaxation of the Bi atoms such that the occupied Rashba spin-split surface state is shifted in the projected Ag bulk states. Interestingly, the interaction of BH_3 with $BiAg_2/Ag(111)$ also determines an additional spin splitting of an unoccupied surface state that for the clean surface was not Rashba spin split by SOC.

[4] For the BH_3-induced geometry the calculated band structure indicates that $P_z^{BH_3\text{-induced}} \leq 50\%$ while the in-plane component $P_{xy}^{BH_3\text{-induced}} \leq 78\%$.

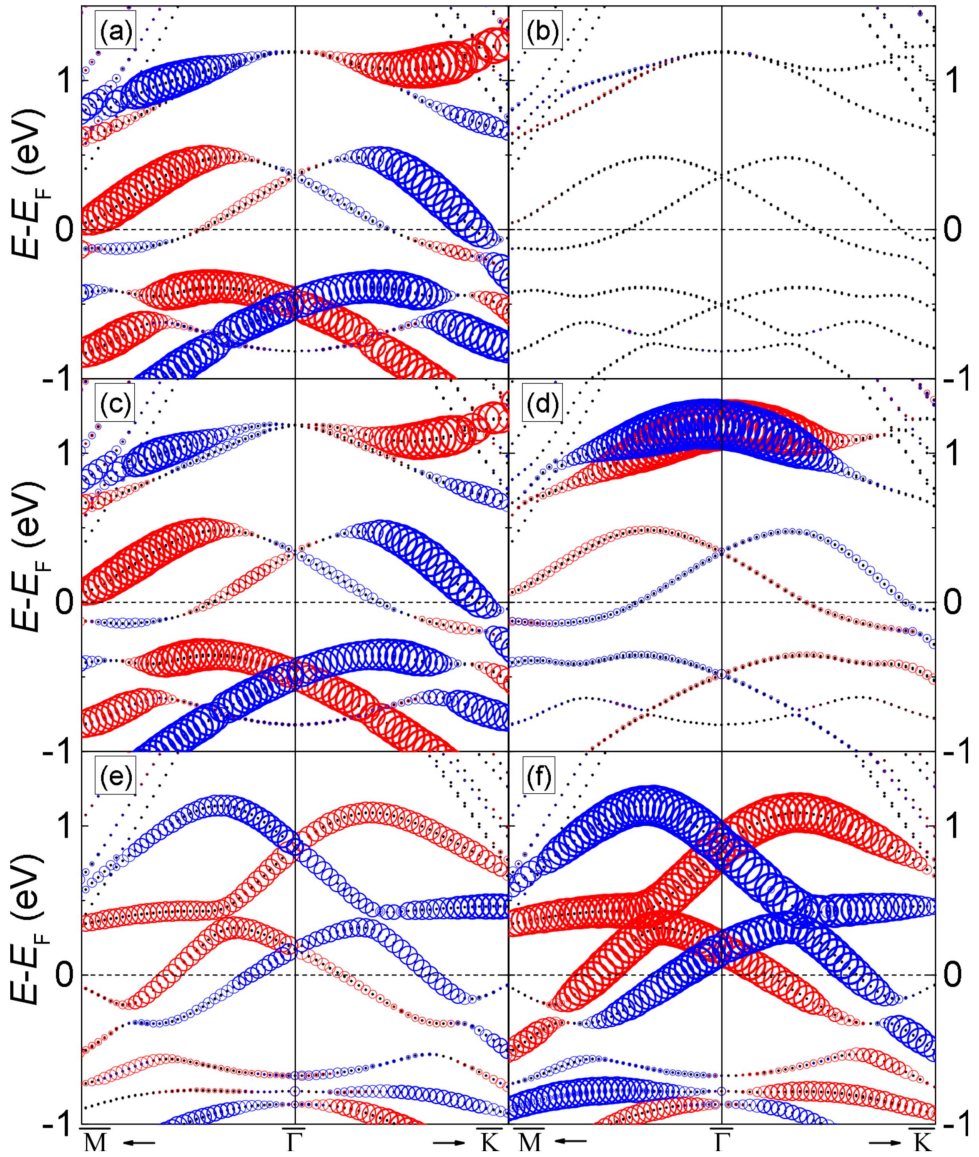

Figure 5. (a) The in-plane P_{xy} and (b) out-of-plane P_z spin polarization as defined in [21] for the clean $BiAg_2$/Ag(111) surface modeled by a symmetric slab. (c) The in-plane P_{xy} and (d) out-of-plane P_z spin polarization for the NH_3–$BiAg_2$/Ag(111) hybrid system. (e) The in-plane P_{xy} and (f) out-of-plane P_z spin polarization for the BH_3–$BiAg_2$/Ag(111) hybrid system. Note that the out-of-plane P_z for BH_3–$BiAg_2$/Ag(111) is significantly larger than the in-plane P_{xy} one or as compared to the clean surface case. The large out-of-plane spin polarization of the second unoccupied surface state of the NH_3–$BiAg_2$/Ag(111) system close to $\overline{\Gamma}$ will not be considered here as in terms of transport experiments it is too far away from the Fermi energy. Red (blue) represents a positive (negative) spin magnetization larger than 2% and the size of the symbols is proportional to the magnitude of the calculated spin polarization.

Finally, a striking outcome of our first-principles study is that both molecule–$BiAg_2$/Ag(111) systems induce a *tunable* out-of-plane spin-polarization P_z normal to the surface. In this regard it is important to note that for the BH_3–$BiAg_2$/Ag(111) system the magnitude of the out-of-plane spin polarization P_z is *larger* than the in-plane one. To conclude, our *ab initio* results are the first and necessary step to unveil how physisorbed as well as chemisorbed inorganic molecule–surface systems can be designed to rationally modify specific properties such as the orientation of the spin polarization for a fine control of the spin transport in spintronics devices.

Acknowledgments

SB, NA and VC gratefully acknowledge financial support from the Volkswagen-Stiftung through the 'Optically Controlled Spin Logic' project and by the Deutsche Forschungsgemeinschaft (DFG) through the Collaborative Research Center SFB 1238 (Project C01). The authors gratefully acknowledge the Gauss Centre for Supercomputing (GCS) for providing computing time through the John von Neumann Institute for Computing (NIC) on the GCS share of the supercomputer JUQUEEN [39] at Jülich Supercomputing Centre (JSC). GCS is

the alliance of the three national supercomputing centres HLRS (Universität Stuttgart), JSC (Forschungszentrum Jülich), and LRZ (Bayerische Akademie der Wissenschaften), funded by the German Federal Ministry of Education and Research (BMBF) and the German State Ministries for Research of Baden-Württemberg (MWK), Bayern (StMWFK) and Nordrhein-Westfalen (MIWF). The authors gratefully acknowledge the computing time granted by the JARA-HPC Vergabegremium and VSR commission on the supercomputer JUROPA/JURECA [40] at Forschungszentrum Jülich.

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