

The effect of potassium on the adsorption of gold on the $\text{TiO}_2(110)\text{-}1 \times 1$ surface

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Received 21 April 2006, in final form 28 June 2006

Published 28 July 2006

Online at stacks.iop.org/Nano/17/4112

Abstract

Density functional theory (DFT) total-energy calculations have been used to investigate the effect of potassium on the adsorption geometry of gold on a $\text{TiO}_2(110)\text{-}1 \times 1$ surface. The gold prefers to sit between the two bridge oxygen atoms above the sixfold titanium atom. The addition of potassium significantly affects the bonding geometry of the gold. Potassium displaces gold from the bridge site and causes its migration to the top of the fivefold titanium atom. Our calculations suggest that potassium is bonded to the bridging oxygen atoms, and to the sixfold titanium atom as well as to gold. This excludes the formation of a K_2O -like compound at the surface.

1. Introduction

The rutile oxide surface has many applications of great technological impact, namely in catalysis, in the fabrication of gas-sensors, in electrochemical processes or in solar cell applications [1]. It is often used as a support material for small and disperse active metal nanoparticles. Sometimes, it is advantageous to use a bimetallic system instead of a single metal in order to improve the catalytic behaviour of these particles. Since alkali metals deposited on an oxide surface are known to act as promoters of catalytic reactions [1–4], the addition of potassium to a Au/TiO_2 system can modify its chemical reactivity and therefore enhance its catalytic performance. Basically, K reacts with a clean TiO_2 surface by transferring an electron charge to its surface and thus causing a change in the work function [5–8]. Some authors have claimed that this reaction leads to the formation of K_2O multilayers, which grow, extracting more oxygen atoms from the surface [9]. An alternative product of such a reaction can simply be a potassium titanate, known to have lower melting point than TiO_2 [10]. Such a compound can easily desorb from the surface, leaving it highly disrupted. The formation of a titanate has been invoked to explain the mechanism of enhanced selectivity of ethylene production during the hydrogenation of acetylene on a Pd/TiO_2 surface [11]. As

for the adsorption geometry of K on a clean $\text{TiO}_2(110)$, first-principles calculations as well as experimental findings indicate that it prefers the bridge site between the twofold oxygen atom [7, 8].

It was recently reported that gold dispersed on $\text{TiO}_2(110)$ can exhibit surprisingly high catalytic activity during the oxidation of carbon monoxide [12–14]. Generally, the performance of Au/TiO_2 catalysts is governed by the contact structure of the Au particles, their size and in some cases by the environment in which the catalyst is exposed [13]. Clusters comprising at minimum three Au atoms as well as particles not bigger than 5 nm have been mentioned to exhibit the highest catalytic activity [15–17]. The latter is probably connected to the metal–nonmetal transition as indicated by scanning tunnelling microscopy (STM) measurements [18]. In the published theoretical works on Au adsorption on a clean $\text{TiO}_2(110)$ surface, there is not yet a consensus as to its adsorption geometry. An early work pointed out that Au should occupy the on-top position of a fivefold coordinated Ti atom (Ti_{5c}) [19]. However, this study came out with a very large adsorption energy of 8.5 eV, which does not correspond to the accepted idea of weak interaction between gold particles and the TiO_2 support. Another paper by Yang *et al* [20], while suggesting the same on-top site as the best adsorption site, indicated smaller values of adsorption energies of 1.0–

1.5 eV. Lopez *et al* deduced from their DFT calculations [21] that Au should be located on top of a bridging oxygen atom. Their findings have been also supported by cluster calculations [22] which, however, disagree with Lopez's paper as to the values of the adsorption energies. Lopez indicated a value of 1.55 eV while the latter work found values closer to 1 eV. Recently, Wang and Hwang proposed that the most stable adsorption site for the Au atom on the stoichiometric TiO_2 surface is the fourfold hollow position over the fivefold coordinated Ti atoms, the bridging O atoms (O_{2c}) and the threefold coordinated in-plane O atoms (O_{3c}) [23]. Thus, in order to study the influence of K on a Au/interface, we aim first to determine the adsorption geometry of Au on a clean TiO_2 surface. To minimize Au–Au interaction, we will restrict our calculations to a low Au coverage by using one single Au atom per unit cell (3×1 supercell). Similar coverage will be used also for K in the co-adsorbed system. The optimal structures among all the investigated adsorption geometries will be used in the scanning tunnelling microscopy (STM) simulations.

2. Computational details

DFT calculations have been performed within the local density approximation [24] using ultra-soft Vanderbilt pseudopotentials [25] and planes waves with a cutoff energy of 30 Ryd. The Ti pseudopotential has a $3s^2 3p^6 4s^2 3d^1$ configuration including the 3s, 3p semicore states. The oxygen has been described by a $2s^2 2p^4$ electron configuration. K has been described by a $3s^2 3p^6 4s^1$ configuration with semicore states 3s and 3p. The Au pseudopotential was generated in a $6s^1 6p^{0.5} 5d^{9.5}$ configuration and includes semicore state 5d. The clean $\text{TiO}_2(110)$ surface was modelled using a (3×1) supercell having nine atomic layers with a vacuum region corresponding to 12 Å. Our calculations were carried out with the PWSCF code distributed with the quantum espresso package [26]. The results were assumed to be converged when the total energy difference with respect to the k-points were within 0.3 mRyd/atom. In our case, two k-points were found sufficient for the integration in the Brillouin zone. All the atoms have been allowed to relax until the Hellman–Feynman forces were found to be smaller than 1 mRyd au^{-1} . The following adsorption geometries were considered in our calculations (figure 1): bridging the two topmost oxygen atoms (Br_1), on top of a bridging oxygen atom (T_1), on top of a fivefold coordinated Ti atom (T_5), at the fourfold hollow site (H_1) over the fivefold coordinated Ti atom and the threefold oxygen atom, and at the fourfold hollow site (H_2) between the bridging oxygen, the threefold oxygen atom and the fivefold coordinated Ti atom. We first wanted to determine the equilibrium position of gold on a $\text{TiO}_2(110)$ surface before investigating the co-adsorption of both gold and potassium. One single Au atom was placed on one side of the slab at the above adsorption sites. This corresponds to a coverage of 0.167 ML in accordance to Onishi prescription [2]. We chose such low coverage in order to minimize the strong Au–Au interaction observed at higher coverage [23]. The same coverage was also used for potassium. Additional adsorption sites, i.e. Br_2 (figure 1) and T_2 , were taken into account in the case of co-adsorption. The T_2 site refers to the position on top of Au(K) in the co-adsorbed system. For the co-adsorption system, we first keep Au at its stable position determined from

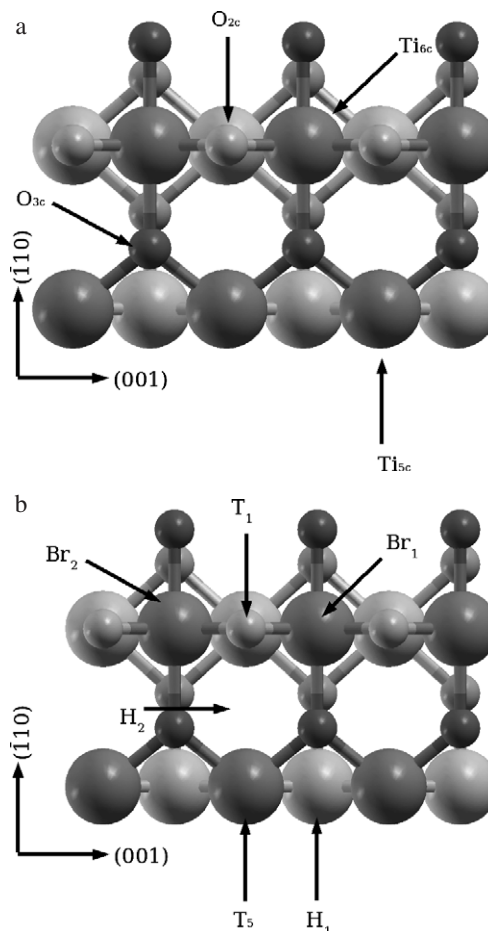


Figure 1. Top view showing the atoms of the uppermost layers of the $\text{TiO}_2(110)\text{-}1 \times 1$ surface (a). The big dark and grey balls represent Ti atoms of the first and second layer respectively. The small grey and dark balls denote bridging and in-plane oxygen atoms respectively. (b) Adsorption sites used in the calculations.

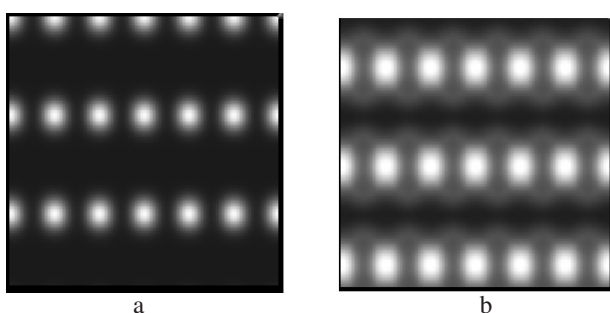
the previous calculations and place K at the remaining different adsorption sites. Then, an alternative scenario, in which Au is displaced by K from its equilibrium position and placed at other adsorption locations, was envisaged. The simulation of the STM images were done following the Tersoff–Hamann approximation, where the tunnelling current is proportional to the local density of states within a given bias voltage around the Fermi energy [27].

3. Results and discussion

First of all, we would like to compare our results of the surface relaxation of the clean system $\text{TiO}_2(110)\text{-}1 \times 1$ surface to the experimental findings as well as to the results of the previous theoretical calculations. In general, the theoretical calculations agree in the direction of the atomic displacements but disagree on their magnitude. Table 1 summarizes the results of some theoretical works [20, 23, 28] and experiments [29, 30]. Our results indicate that the bridging oxygen atoms moved inwards by 0.12 Å with respect to the unrelaxed slab. Previous results indicated a very small displacement of about $-0.02(-0.06)$ Å. The experiments suggest a downwards

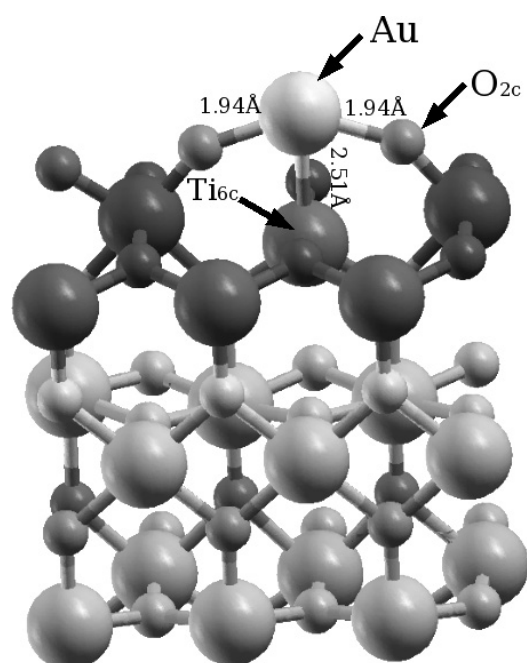
Table 1. Vertical atomic displacements in angstroms (\AA) of the clean $\text{TiO}_2(110)-1 \times 1$ surface with respect to the bulk terminated TiO_2 structure.

Atom	Exp. [28]	Exp. [29]	Theory [20]	Theory [23]	Theory [27]	Present calc.
O_{2c}	-0.27 ± 0.08	-0.10 ± 0.05	-0.06	-0.02	-0.02	-0.12
Ti_{6c}	0.12 ± 0.05	0.25 ± 0.03	0.13	0.19	0.23	0.08
Ti_{5c}	-0.16 ± 0.03	-0.19 ± 0.03	-0.15	-0.15	-0.11	-0.16
O_{3c}	0.05 ± 0.05	0.27 ± 0.08	0.13	0.18	0.18	0.12

**Figure 2.** Simulated constant-height STM images (± 1.7 eV, 3\AA): filled states (a) and empty states (b) for a clean $\text{TiO}_2(110)-1 \times 1$ surface. The height of the tip is chosen with reference to the plane passing through the topmost oxygen atoms.

displacement by $0.27(0.10) \text{\AA}$. Our results come closer to the later experimental findings. The oxygen relaxation by 0.27\AA was obtained from x-ray diffraction measurements. The discrepancy may arise from the method used in the determination of the nuclear positions of the atoms. X-ray diffraction probes the distribution of electron density but not the nuclear atomic positions. Moreover, the sixfold coordinated Ti atoms (Ti_{6c}) move upwards by 0.08\AA . The experiments indicated $0.12(0.25) \text{\AA}$, while the other theoretical works give 0.13 , 0.19 , and 0.23\AA . The best agreement between theory and experiments is found for the downward relaxation of the Ti_{5c} atom. As for the O_{3c} atoms, there is discrepancy among the experimental results. Our calculated value agrees with that of [20]. It is likely that the differences found between theory and experiments are due to the difficulty in finding the global absolute minimum energy of such a flat surface. Furthermore, we simulated constant-height STM images (figure 2) at a bias voltage of 1.7 eV in order to see if we could reproduce the main experimental results. The filled state image shows bright spots corresponding to the position of the bridging oxygen atoms in agreement with the experiment [31]. The contrast was reversed in the empty states images, in which the Ti rows appeared as bright protrusions. This is consistent with the fact electrons are tunnelling to empty states located at the Ti cations rather than to the bridging oxygen atoms occupying the topmost level on the surface.

The results for the geometry optimization of gold (0.167 ML) on a $\text{TiO}_2(110)-1 \times 1$ suggest that the structure with Au located at the bridging position has the lowest total energy (table 2, figure 3). Our results differ from those of previously published papers, which indicated the preference of Au for a fivefold coordinated Ti atom [19, 20], the on-top site of the bridging oxygen [21, 22] or the fourfold hollow site over the fivefold coordinated Ti and the in-plane and bridging

**Figure 3.** View of the bonding geometry of Au at the bridge site on the $\text{TiO}_2(110)-1 \times 1$ surface.**Table 2.** Total energy calculations for Au adsorbed at different sites.

Configurations	Total energy related to the configuration with the minimum energy (mRyd)
Br_1	—
H_2	10
T_1	20
H_1	50
T_5	60

oxygen [23]. The disagreement between our results and the above ones is probably connected to the theoretical approaches used in the calculations. It is known that relaxation is very important for the rutile surface. The use of an unrelaxed slab [19] may significantly affect the results. The adoption of a cluster approach [22], of another functional like GGA-RPBE [21] or GGA-B3LYP [22], as well as the use of a different coverage [20–22] in the calculations may also explain the differences between the theoretical findings. Owing to the slight difference in the total energies calculated for the H_2 and the bridge sites, the discrepancy in the structure with the lowest total energy between our results and those of [23] may not be a major problem, since gold may be jumping forth and back between them. The interatomic distances between gold and the bridging oxygen was found to be 1.94\AA , reflecting

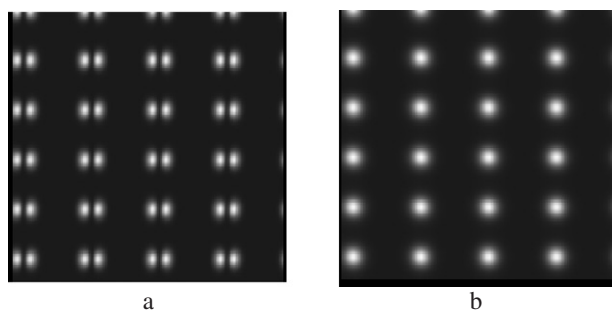


Figure 4. Simulated constant-height STM images (± 1.7 eV, 3 Å): filled states (a) and empty states (b) for Au adsorbed on a bridge site at a $\text{TiO}_2(110)-1 \times 1$ surface. The height of the tip is chosen with reference to the plane passing through the Au atoms.

Table 3. Total energy calculations for the K–Au/ $\text{TiO}_2(110)$ system.

Configurations	Total energy related to the configuration with the minimum energy (mRyd)
K/Br ₁ –Au/H ₂	—
K/Br ₁ –Au/T ₅	4
K/Br ₁ –Au/H ₁	18.34
K/Br ₁ –Au/Br ₂	104.46
K/Br ₁ –Au/T ₁	108.55
K/Br ₁ –Au/T ₂	131.92
Au/Br ₁ –K/H ₂	90.14
Au/Br ₁ –K/Br ₂	104.46
Au/Br ₁ –K/T ₅	119.95
Au/Br ₁ –K/T ₁	124.03
Au/Br ₁ –K/H ₁	161.01
Au/Br ₁ –K/T ₂	221.02

the sum of their respective atomic radii. Moreover, there is strong bonding between Au and the Ti atom (Ti_{6c}) directly beneath it. Their bonding distances amounts to 2.51 Å. This Ti atom and the remaining two Ti_{6c} atoms relax respectively by -0.38 and 0.18 Å with respect to their positions mentioned in table 1. The two bridging oxygen atoms attached to Au move upwards by 0.5 Å related to their atomic coordinates displayed in table 1. We found that Au adsorption induces a shortening of the bonds between the Ti_{6c} atoms and the bridging oxygens (1.82 Å at the clean TiO_2 compared to 1.75 Å upon deposition of gold). In general, the influence of gold is limited to the bridging oxygens and the sixfold coordinated Ti atoms. The atomic coordinates of the O_{3c} atoms and the Ti_{5c} atoms are not affected. The preference of gold for the bridging position is a common behaviour of all group IA, IB elements with the TiO_2 surface. It is known that alkali metals such as Li, Na or K, which have one valence ‘s’ electron, like to occupy the bridge site between the two topmost oxygen atoms [1]. On the other hand, monovalent noble metals such Cu and Ag also prefer the bridge site [22]. Thus, the preference for this adsorption position is linked to their similar valence electronic structure. The main difference between Au and the alkali metals consists in the strong reaction between the latter with the TiO_2 surface leading to their oxidation, whereas Au, like other noble metals (Cu, Ag), at small coverage forms covalent bonds with the same surface. Upon the deposition of Au on a $\text{TiO}_2(110)$ surface, the electron charge density should be redistributed at the surface and this should be reflected

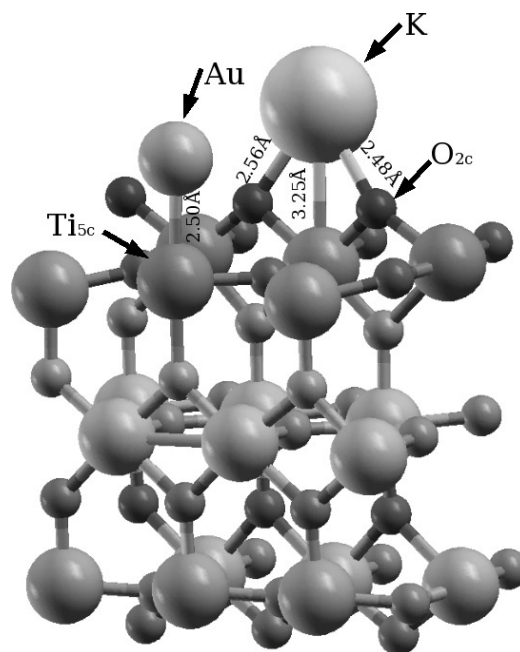


Figure 5. View of the final bonding geometry of both Au and K at the $\text{TiO}_2(110)-1 \times 1$ surface upon relaxation. Au was previously placed at the H_2 site. After relaxation, it moves to the T_5 position.

in the STM images. In the simulated STM empty states image (figure 4) gold appears as white spots. In contrast, we can see in the filled states map two bright protrusions corresponding to the two covalent interactions between gold and the bridging oxygen atoms. Table 3 displays the total energy calculated for the K–Au/ $\text{TiO}_2(110)$ system. It appears that the deposition of potassium at the Au/ $\text{TiO}_2(110)$ surface leads to the displacement of Au by K from the bridging position. By putting respectively K and Au at the bridge and the H_2 site, we obtained a configuration with the minimum energy upon atomic relaxation. However, because of the repulsive interaction between gold and potassium, Au moves from the H_2 position to the nearby T_5 position (figure 5). Placing Au directly at the T_5 site gives almost the same total energy (there is actually a small energy difference of 4 mRyd). The bond length between Au and this fivefold coordinated Ti was found to be 2.50 Å. This is similar to the calculated Au–Ti bond length for the K-free surface. Potassium is tilted from the surface normal and forms asymmetric bonds with the two bridging oxygen atoms (2.56 Å, 2.48 Å). Furthermore, K interacts with both Ti and Au atoms. This suggests that the presence of a K_2O -like compound on the surface is unlikely. Gold is ‘embedded’ in a titanate-like structure. Such modification of the gold adsorption geometry should influence the performance and selectivity of the catalyst. The potassium effect depends most likely on the coverage. Metallization of the surface occurring at higher K doses may thus have a negative effect instead of a positive one. Theoretical STM images of the co-adsorbed system (figure 6) indicate that both empty and filled states are dominated by gold electronic states in agreement with the projected density of states (PDOS) onto atomic ‘s’ states of both K and Au (figure 7). This is very interesting. For example, one

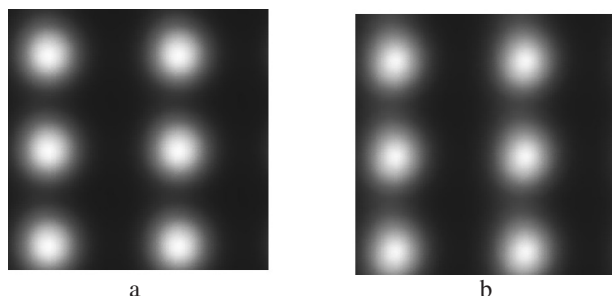


Figure 6. Simulated constant-height STM images (± 1.7 eV, 3 \AA): filled states (a) and empty states (b) for K–Au/TiO₂(110) system. The height of the tip is chosen with reference to the plane passing through the K atoms.

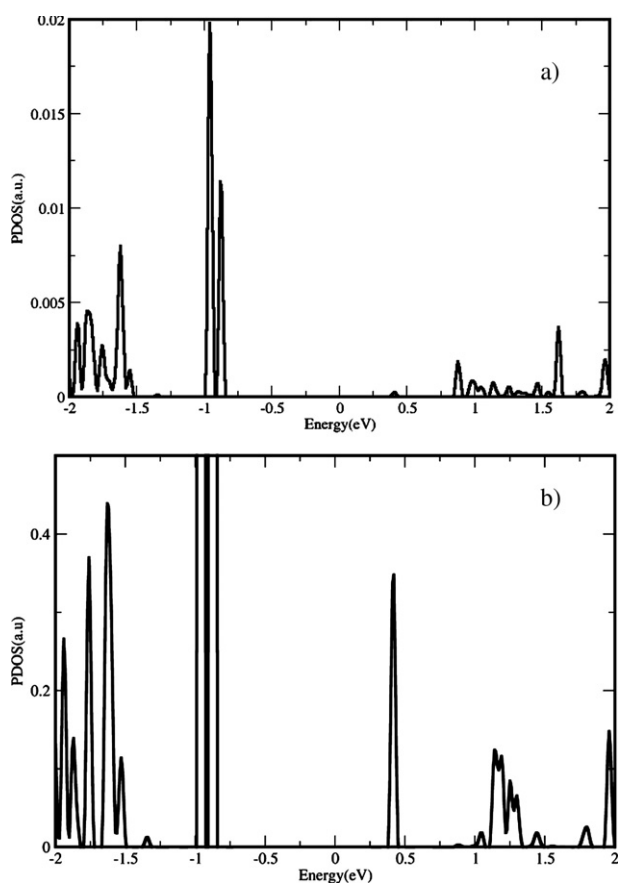


Figure 7. Projected density of states onto atomic 's' states of potassium (a) and gold (b). All values are relative to the Fermi energy, which is set to zero.

would expect tunnelling into empty states to be dominated by electronic states located at the K atom because of geometrical reasons (K lies 0.55 \AA higher than gold) and because of the charge transfer occurring from K to the substrate. Gold-related white spots appear bigger in size and are not spherical. Moreover, they are not located exactly on top of the Au atom, suggesting the bonding between Au and K is most likely polarized and that gold attracted the electrons more to itself than K did, because of its higher electronegativity.

4. Conclusion

Density functional theory calculations have been used to study the co-adsorption of gold and potassium on the TiO₂(110) surface. Gold prefers the bridge site between the two topmost oxygen atoms with which it forms covalent bonds. Au also interacts strongly with the sixfold coordinated Ti atom located beneath it. The addition of K to the Au/TiO₂(110) system leads to the displacement of Au from the bridge site. Consequently Au diffuses away on top of a fivefold coordinated Ti atom. The K reaction with the TiO₂(110) surface suggests the formation of a titanate-like structure on the surface.

Acknowledgments

This work was supported by the Grant agency of the Academy of Sciences of the Czech Republic (Grant No. IAA1010413), the Institutional Research Plan No. AVOZ10100521 and the KONTAKT Programme 9/2004 of the Ministry of Education, Youth and Sports (Bilateral co-operation between the Czech Republic and the Hungarian Republic).

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