Molecular Switches

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Bistability Loss as a Key Feature in Azobenzene (Non-)Switching on Metal Surfaces**

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Stimulating a controlled conformational change of functional molecules adsorbed on solid surfaces is a key goal of molecular nanotechnology. Along this route molecular switches, that is, molecules that can be reversibly switched between metastable states in gas-phase or in solution, have been a primary target.[1]

Unfortunately, even at most unreactive close-packed noble-metal surfaces, such molecules generally do not show capabilities for light- or electron-induced switching. Molecular functionalization aiming to further decouple the photochromic moiety, both spatially and electronically, has been a standard strategy to regain the switching function, hypothesizing that excited-state quenching at the metal surface is a central reason for the loss of function upon adsorption. A prominent example is tetra-*tert*-butylazobenzene (TBA), which in contrast to its parent molecule azobenzene (Ab) can be successfully switched on a Au(111) surface.[2,3]

Notwithstanding, other unsuccessful attempts to switch both Ab and TBA at the closely related Ag(111) surface indicate that factors other than photochromic decoupling might also be important. Several explanations for why switching of TBA on other metal surfaces is not observed have been formulated,[4,5] but no unified picture specifying how surface interaction changes the stability and reactivity of metal-mounted azocompounds has yet been reached. Recalling that the existence of two metastable states is a fundamental prerequisite for switching, it is intriguing to realize that no previous studies have addressed the possibility that the absence of surface-mounted switching could as well simply stem from a change in ground-state stability.

On the basis of the well-understood Ab gas-phase isomerization mechanisms, we set out to investigate this point by studying the effect of coinage-metal surface adsorption on the ground-state barriers with dispersion-corrected density-functional theory (DFT) calculations.[6–9] Our results suggest that surface adsorption modifies the azobenzene ground-state stability in a way to, in fact, remove bistability and allow immediate thermal re-isomerization from the previously metastable state. Quite naturally, this idea requires a change in the design of molecular switches. In addition to a controlled decoupling of the photochromic moiety, functionalization needs to target a balanced stabilization of all structures involved in the isomerization to preserve the switching function upon surface mounting.

The vast number of mechanistic studies of Ab isomerization in gas-phase and in solution mainly focuses on two different mechanisms:[10–14] a dihedral rotation of one phenyl group around the central azo bridge and an initially planar inversion around one of the C–N=N bond angles, see Figure 1. Present consensus points towards a dominance of the rotational mechanism upon photoexcitation.[15,16] Nonetheless, in the ground state both mechanisms show significant barriers, 1.8 eV for rotation and 1.5 eV for inversion, as seen from the more stable *E*-Ab state. The rotational-barrier maximum also coincides with a state crossing with the first singlet excited state, explaining the conical-peak feature that is well reproduced by our DFT calculations.[12,14] Recomputing these barriers for Ab adsorbed on Ag(111) we find the inversion barrier almost unchanged. In contrast and as shown in Figure 1, the rotational barrier is drastically reduced by about 1 eV with respect to the *E*-Ab isomer and the conical-peak shape is gone. In addition, the metastable *Z*-Ab isomer changes its minimum energy geometry towards a higher dihedral angle and is destabilized by another 0.2 eV as compared to *E*-Ab, that is, while *Z*-Ab is 0.5 eV higher in

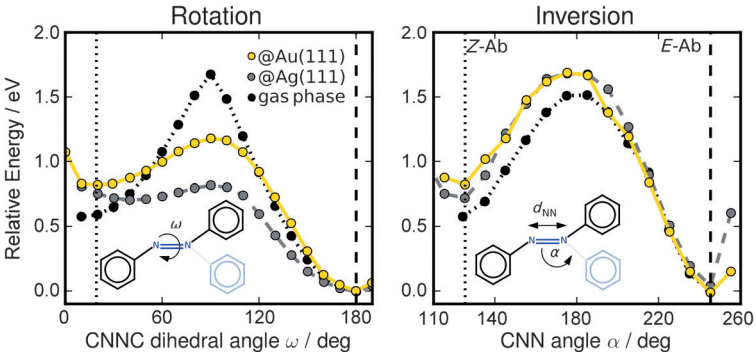

Figure 1. Minimum energy isomerization paths along the rotation (left) and inversion (right) coordinates. Shown are ground-state curves for the molecule in the gas phase (black), adsorbed on a Ag(111) surface (gray), and adsorbed on a Au(111) surface (yellow).

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energy in the gas-phase, it is 0.7 eV at the surface. These effects together leave the re-isomerization from *Z*-Ab back to the more stable *E*-Ab with a minimal zero-point energy corrected barrier of 50 meV, while simultaneously minimizing potential restrictions in the DFT description of the barrier region. Without even entering into the details of the light- or electron-driven excitation, this insignificant barrier alone would be enough to explain why Ab at Ag(111) will not switch—the fundamental bistability prerequisite to the switching function is simply lost. In particular, even if a very efficient photoexcitation mechanism to the *cis* state existed, the strongly vibrationally activated ground-state *Z*-Ab isomer resulting from the isomerization would still not be sufficiently stable to be observed.

The reason for the strong preferential reduction of the rotational barrier lies in the formation of a strong chemisorption bond along this pathway. Whereas at both minimum energy structures and the inversion transition state (TS) the surface stabilization results, to more than 90%, just from dispersive interactions, the adsorption energy at the rotational TS comes to 40% from the semi-local DFT functional. Geometrically this covalent-bond contribution at the TS is indicated by a significant reduction of the vertical height (from 2.95 Å at *E*-Ab to 2.05 Å) and an elongation of the bond length of the central azo bridge (from 1.31 Å at *E*-Ab to 1.38 Å). In the orbital-projected density-of-states (DOS) shown in Figure 2, this different surface interaction at inversion and rotational TS can also nicely be discerned. At the inversion TS, the frontier orbitals exhibit only the same minimal broadening owing to the interaction with the metal bands, as had been found before for the two minimum-energy structures.[17] The small amount of charge transferred to the lowest-unoccupied molecular orbital (LUMO) shows that in all these cases the surface interaction can be understood in the classic Dewar–Chatt–Duncanson π-donor–π*-acceptor model for bonding between metals and conjugated organics.[18,19] Along the rotational path the frontier orbitals show instead a much stronger broadening and splitting. At the TS, the LUMO and highest-occupied molecular orbital (HOMO) are in fact almost degenerate and situated slightly below the Fermi level. The situation is thus highly reminiscent of a diradical state, known to be a highly active chemical intermediate for example in Diels–Alder reactions.[20] Visualizing the molecular frontier orbitals at the surface-adsorbed geometry, as shown in Figure 3, then immediately shows that both HOMO and LUMO orbitals have a nonbonding character and are perfectly arranged to interact with localized metal *d* states, as opposed to the orbitals found in the inversion barrier structure.

To paraphrase this, following rotation from the *E*-Ab isomer the azo bridge double bond is increasingly weakened and the two orbitals develop a nonbonding, diradical character. This reactive state is stabilized by efficiently accepting electron charge from the underlying metal. This stabilization is much stronger than the overall stabilization owing to dispersive interaction with the substrate. The latter increases only slightly from *Z*-Ab to *E*-Ab because of the increasingly parallel alignment of the two phenyl rings. Altogether this unbalanced way in which, particularly Ab, in the rotational TS

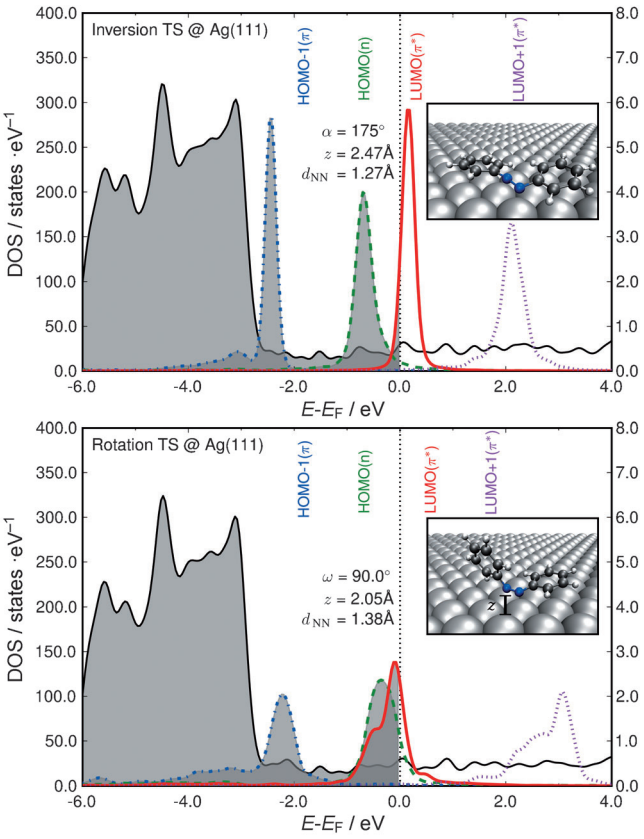

Figure 2. Density-of-states (DOS) for the TS along inversion (top) and rotation (bottom) isomerization of Ab on Ag(111) surface. Also shown is the DOS projected onto the molecular frontier orbitals, as well as the TS geometries, including important structural parameters.

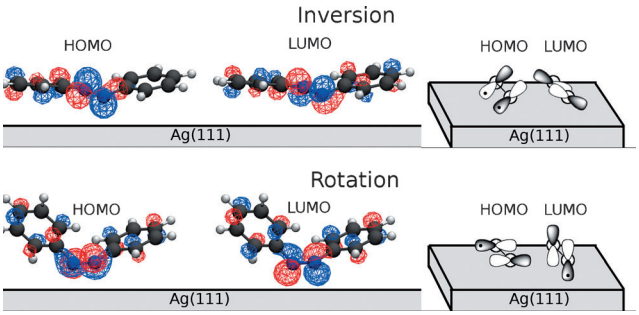

Figure 3. HOMO and LUMO orbital shape of Ab at Ag(111) for the inversion (top) and rotational (bottom) TS. Shown are both calculated isosurfaces (left) and schematic representations (right).

geometry interacts with the surface essentially eliminates the bistability feature of the molecule and impairs the switching function.

One way to regain a more balanced adsorption of all geometries is by reducing the electron availability and therewith the stabilization of the diradical state through charge transfer. On the substrate side, this is effectively achieved by a lowered Fermi energy level (higher work function), as for example, realized at the Au(111) surface. Indeed, this partly re-establishes the rotational barrier, as

shown in Figure 1. The resulting depth of 0.38 eV for the metastable *Z*-Ab basin is still much reduced compared to the gas-phase (1.02 eV) though. The experimentally observed electron-induced switching using an STM tip does, in fact, reveal the existence of a barrier on this surface.[21] In the case of photoinduced switching, vibronic coupling is very strong and energy on the order of eVs can be efficiently transferred from electronic to vibrational degrees of freedom. A reduced barrier of 0.38 eV might thus not be completely prohibitive to thermal back-reaction of a vibrationally hot *cis* isomer, and would then be one possible rationalization for the lacking photoswitching function of Ab at this surface. We stress, however, that only detailed knowledge of the excited-state dynamics can fully resolve the non-switching of Ab at a Au(111) surface.

Another route to achieve a more balanced binding of all involved geometries is by using molecular functionalization. However, this must follow different design strategies than those merely focused on a decoupling of the photochromic moiety, for example, in the present case the symmetric addition of *tert*-butyl groups in TBA. In fact, we calculate a *Z*-TBA basin at Ag(111) about as shallow as that of *Z*-Ab at Ag(111) and Au(111), that is, that the rotational TS bonding is barely affected by the functionalization.

In conclusion, we generalize that thermal isomerization of surface-adsorbed molecules, including double-bond twisting events, proceeds by way of barrier geometries that couple much stronger to the surface than the minimum energy or other transition-state structures. The ensuing lowering of the ground-state barriers might be sufficiently strong to eliminate the bistability prerequisite for switching, as illustrated here for azobenzene at Ag(111). Without doubt, molecular functionalization must centrally target a tuned interaction of the photochromic moiety with the underlying metal to prevent ultra-fast quenching of excited states important for the isomerization. However, as shown herein, a second target must also be to achieve a balanced surface interaction of all geometries involved in the isomerization process. For the present case of azobenzene-derivatives at noble-metal surfaces, this means to specifically aim at a selective destabilization of the diradical rotational transition state. As an intriguing and hitherto not pursued route this could be achieved by further reducing the substrate electron availability, for example, through electron-demanding coadsorbates that increase the work function.

Experimental Section

For our calculations we employ the pseudopotential plane wave code CASTEP 5.5.1[6] using standard library ultrasoft pseudopotentials.[22] Electronic exchange and correlation were treated with the semi-local PBE functional[7] and van der Waals interactions are accounted for using a semi-empirical dispersion correction scheme.[8,9] The detailed system setup, computational parameters and convergence behavior were described already in a previous publication.[17] In short, all calculations were performed with (6×4) and (6×5) frozen (111) four-layer surface slabs of Ag and Au with 350 eV or 450 eV plane wave cutoff for azobenzene and 3,3′,5,5′-tetra-*tert*-butylazobenzene (TBA), respectively. The vacuum was chosen to exceed 20 Å. All energy differences and adsorption energies were calculated at a $8\times4\times1$ Monkhorst–Pack grid[23] for azobenzene systems and a $6\times4\times1$ Monkhorst–Pack grid for TBA systems. Relative energies and adsorption energies are converged to ±20 meV. We note that the supercell approach used herein has been rigorously evaluated in previous work[17,24,25] and is known to accurately reproduce geometries, but overestimate absolute adsorption energies owing to the neglect of electronic screening in the dispersion correction.[24] For this reason, we have recalculated the minimum and transition-state energetics also with the screened dispersion correction approach recently introduced by Ruiz et al.,[26] without obtaining qualitative changes to the results reported in this work. We expect a similarly robust description of the covalent azo–metal interaction, considering the well-established accuracy of the employed PBE functional for nitrogen-based catalytic reactions at coinage metals.

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