
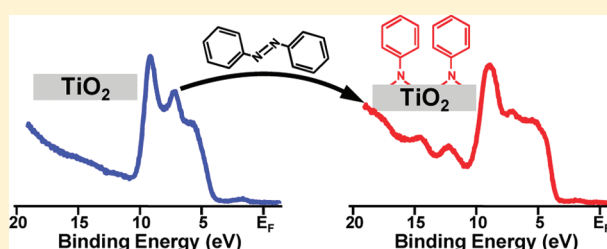


Photoemission Study of Azobenzene and Aniline Adsorbed on TiO₂ Anatase (101) and Rutile (110) Surfaces

Shao-Chun Li,[†] Yaroslav Losovyj,[‡] Vinod Kumar Paliwal,^{†,§} and Ulrike Diebold^{*,†,⊥}[†]Department of Physics and Engineering Physics, Tulane University, New Orleans, Louisiana 70118, United States[‡]Center for Advanced Microstructures and Devices, Louisiana State University, 6980 Jefferson Highway, Baton Rouge, Louisiana 70806, United States[§]Department of Physics, Dyal Singh College, Lodhi Road, New Delhi-110003, India[⊥]Institute of Applied Physics, Vienna University of Technology, Vienna, Austria Supporting Information

ABSTRACT: The electronic structure of azobenzene and aniline, adsorbed on two TiO₂ surfaces, anatase (101) and rutile (110), has been studied with ultraviolet synchrotron-based photoemission spectroscopy (UPS). At saturation coverage, azobenzene and aniline exhibit very similar molecular orbitals in UPS valence band spectra. Angle-resolved UPS exhibits anisotropy of the molecular states along the polar and azimuthal direction, as is expected for highly oriented superstructures. For a low coverage of azobenzene adsorbed on anatase, photon irradiation results in the conversion of the flat-lying molecule into two upright phenyl imide species. An irradiation-induced trans–cis isomer conversion is proposed to facilitate the azobenzene cleavage. These results confirm that the N=N double bond of azobenzene is cleaved by TiO₂ in the full-coverage regime and that the resulting intermediate is bonded to the substrate, in agreement with a previous scanning tunneling microscopy study and a proposed reaction scheme for azobenzene ↔ aniline conversion at TiO₂ surfaces [Li, S.-C.; Diebold, U. J. *Am. Chem. Soc.* **2010**, *132*, 64].



1. INTRODUCTION

TiO₂ has been widely studied due to its versatile applications in diverse fields, such as catalysis, photocatalysis, and solar energy conversion.^{1,2} It has attracted attention as a support for catalytically active gold nanoparticles, both in fundamental research and in technological applications. TiO₂-supported Au particles were first studied as catalysts for the low-temperature oxidation of CO.^{3,4} More recently, Au clusters on TiO₂ were also found to act as excellent catalysts for the chemoselective synthesis of nitroaromatics to anilines (hydrogenation) and anilines/nitroaromatics to aromatic azo compounds (dehydrogenation).^{5–7} Charge transfer from Au to TiO₂ was proposed to play an essential role in the reaction mechanism, and Au⁺ has been considered as the catalytically active site.^{5,6} It was also found that nitroaromatics preferentially adsorb on the TiO₂ support and the Au/TiO₂ interface via the nitro group, due to a cooperative effect between gold and TiO₂.⁷ A recent model study combining STM, LEED, and XPS, however, unveiled that the TiO₂ plays a more important role than merely acting as a support; both the rutile and the anatase phases of TiO₂ cleave the aromatic azo compound, azobenzene, in the absence of Au.⁸ At full coverage, STM, LEED, and XPS show the same signatures for both aniline and azobenzene overlayers on TiO₂.⁸ As shown in Scheme 1, azobenzene/aniline forms 1 × 2 superstructures on anatase (101) (two domains) and rutile (110) (one domain).⁸

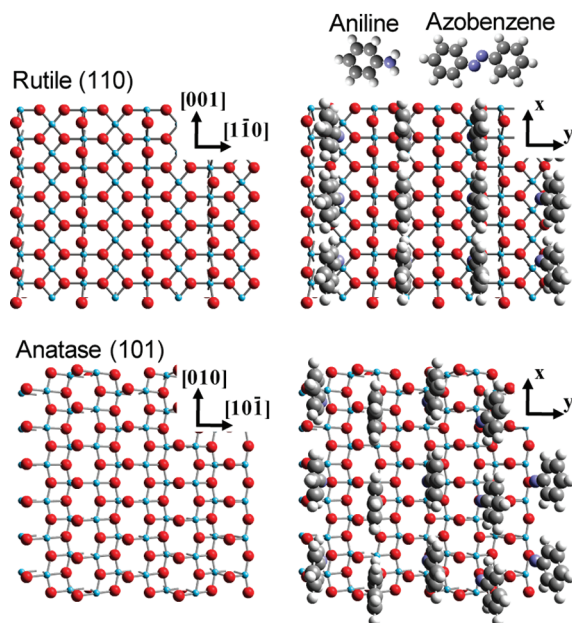
Aniline, C₆H₅NH₂, can be thought of as half an azobenzene molecule (C₆H₅N=NH₅C₆), with the N terminated by two extra hydrogen atoms (Scheme 1). From our previous STM study, it is clear that the N=N double bond of azobenzene is cleaved and that the resulting phenyl imide (C₆H₅N) is bonded to surface Ti_{5c} atoms.⁸ Although the STM and LEED results strongly suggest the same adsorption geometry of aniline and azobenzene, from these techniques alone, it is not possible to judge if both molecules form exactly the same species upon adsorption. In addition, the azobenzene cleavage mechanism needs to be clarified: at low coverages, isolated azobenzene adsorbs as an intact trans isomer molecule, as seen in STM,⁸ whereas the molecule is clearly dissociated at saturation coverage. We speculated that, as the coverage is increased, strengthened intermolecular interaction pushes the phenyl rings away from the substrate surface and thus facilitates the trans–cis isomerization, which enhances the coupling to the surface, resulting in a N=N bond cleavage.^{9,10} This hypothesis needs to be backed up with experimental data, from complementary techniques; in particular, we need information regarding the electronic structure of the adsorbed molecules.

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Scheme 1. Aniline and Azobenzene as Free Molecules and as Adsorbed on TiO₂ Rutile (110) (Top Panels) and Anatase (101) (Bottom Panels)^a



^a The clean surfaces are depicted on the left side. The *x* axes and *y* axes are defined according to *C*_{2v} symmetry. Red, oxygen; blue, Ti; gray, C; white, H; purple, N.

In this work, synchrotron-based photoemission was applied to study the evolution of the electronic structure upon incremental adsorption of azobenzene and aniline adsorption on TiO₂ anatase (101) and rutile (110) surfaces. Our UPS results suggest that the molecular orbitals formed upon azobenzene and aniline adsorption at full coverage are the same, supporting the proposed schemes of N=N double bond cleavage for azobenzene and the dissociation (or partial dissociation) of aniline adsorbed on the TiO₂ surfaces. For a submonolayer of azobenzene on anatase (101), photon irradiation is found to induce a structural change. We propose that photons induce a transition of flat-lying molecular azobenzene to perpendicularly adsorbed phenyl imide, potentially through photon-induced trans–cis isomerization.^{11,12}

2. EXPERIMENTAL METHODS

The UPS measurements were performed at the Center for Advanced Microstructures and Devices (CAMD) in Baton Rouge, LA, using the 3 m toroidal grating monochromator (3 m TGM) beamline. The UHV chamber is equipped with an electron energy analyzer with an angular acceptance of $\pm 1^\circ$ and a combined (including the monochromator) energy resolution of 150 meV or better.¹³ The base pressure of the UPS chamber is $\sim 5 \times 10^{-10}$ mbar.

All the photoemission spectra were taken with photon energies ranging from 40 to 50 eV. The emitted photoelectrons were collected with an analyzer moveable in-plane with the surface normal and the incident photon beam. The Fermi level position (*E*_F) was established from a copper piece in electrical contact with the sample. The valence band features are reported with respect to this Fermi level, and the emission angle is measured with respect to

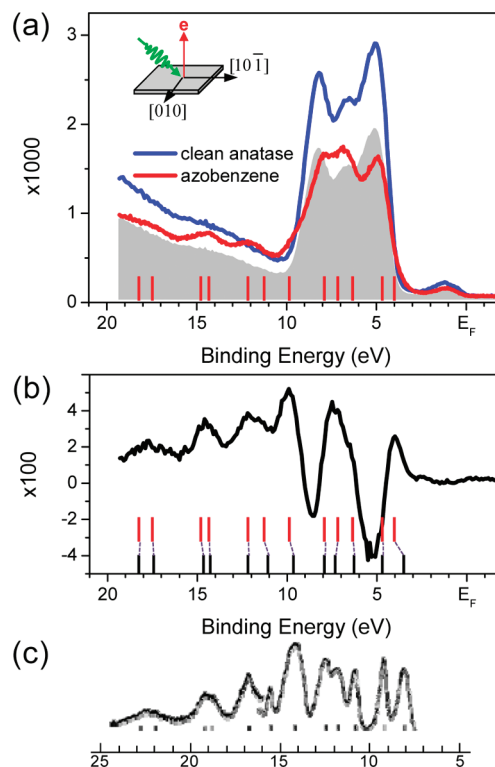


Figure 1. (a) Photoemission spectra ($h\nu = 50$ eV) of a clean TiO₂ anatase (101) surface (blue) and after adsorption of a saturation layer of azobenzene (red), normalized to the photon flux. The inset shows the experimental geometry: photon beam incident at an angle of 45° along the $[10\bar{1}]$ direction and collection of electrons emitted along the surface normal. (b) Difference spectrum obtained by subtracting the spectrum of clean anatase (rescaled to the gray curve in (a)) from the spectrum after azobenzene adsorption. (c) Photoemission spectrum of free aniline redrawn from ref 21. The molecular orbitals in the gas-phase spectrum are redrawn in (b) after shifting by 4.6 eV to account for the different reference levels. Small red lines in (b) show the shift of orbitals upon adsorption.

the surface normal. Photoemission measurements reported here were carried out at ambient temperature.¹³

A cut and polished natural mineral anatase was cleaned by Ar⁺ sputtering and annealing to 600 °C in UHV. Because of repeated cleaning cycles over a long period of time, this particular crystal showed a high degree of nonstoichiometry and the subsurface defects typical for reduced anatase (101).¹⁴ A commercial rutile TiO₂ (MTI Corp.) was cleaned with the same procedure as that for anatase. The rutile sample was slightly reduced before the UPS experiment. It was cut into two pieces that were mounted with their $[001]$ axis parallel and perpendicular to the incident beam, respectively. This makes it possible to take measurements of the same system in two orthogonal geometries. The surface cleanliness and structure of both crystals were checked by XPS, LEED, and STM in the laboratory, and no impurities were found from these techniques. LEED patterns measured on both samples display perfect 1×1 periodicity. The orientation of the rutile and anatase was characterized by both STM and LEED before the UPS experiment. The spectral intensity was normalized to the beam current.

Commercial azobenzene powder (Alfa Aesar, 98%) and aniline liquid (Alfa Aesar, 99+%) were each put into a glass vial and purified through cycles of pump–freeze–thaw. The purified

azobenzene powder exhibits orange crystallites, and the aniline liquid is light yellow. The purity of azobenzene and aniline was also checked with mass spectroscopy. Azobenzene or aniline gas was dosed through a leak valve from the vapor that forms above the substances at room temperature. The gas line was pumped by a turbo pump, and the base pressure inside the gasline was $\sim 10^{-10}$ mbar. During dosing, the pressure in the main chamber was controlled to less than 5.0×10^{-8} mbar. UPS measurements were resumed after the pressure was recovered. A full-coverage adsorption corresponds to 0.5 ML (monolayer) of phenyl imide, where 1 ML is defined as the one phenyl imide per TiO_2 unit cell, that is, $\sim 4.68 \times 10^{14}/\text{cm}^2$ for rutile (110) and $\sim 5.16 \times 10^{14}/\text{cm}^2$ for anatase (101).

3. RESULTS

Figure 1 shows photoelectron spectra (normal emission) of a clean anatase $\text{TiO}_2(101)$ surface (blue curve) and a surface with a full layer of azobenzene (red curve). A photon energy of 50 eV was selected, off the Ti resonance energies of 47 and 54 eV.¹⁵ Both spectra represent raw data, normalized by the photon flux only. In the spectrum of the clean surface, three valence band peaks (5.0, 6.7, and 8.0 eV) are discerned, consistent with the ones reported in the literature.^{15,16} The valence band is ca. 6.0 eV wide, and the valence band maximum is located at ca. 3.5 eV. The feature at higher binding energy, around 8.0 eV, is assigned to mainly O 2p–Ti 3d σ states, and the states at lower binding energy, ~ 5.0 eV, arise mainly from Ti 3d–O 2p π states, according to a previous report.^{15–19} The peak in between at ~ 6.7 eV is the so-called overlap peak, predominantly of O 2p character, mixed with Ti 3d t_{2g} orbitals, with a small component of Ti 4sp character.^{15–19} The Ti^{3+} defect state is located at ~ 1.1 eV below the Fermi level, which originates mainly from the subsurface defects, typically subsurface oxygen vacancies and Ti interstitials on a reduced anatase sample.^{14,20} The weak, broad feature at ~ 14.0 eV on the clean surface (blue curve in Figure 1a) is an artifact due to photoemission from the Ti 3s core levels, induced by second-order light from the toroidal grating monochromator; it is not considered any further.

The spectrum of a full layer of azobenzene on this surface is shown as the red curve in Figure 1a. The shape of the valence band changes upon adsorption, and several additional peaks appear at higher binding energies. These are easily identified as stemming from the molecular orbitals of the adsorbate.

For an analysis of these orbitals, the difference spectrum is plotted in Figure 1b. It was obtained by, first, rescaling the spectrum of the clean surface (plotted as the gray shadow in Figure 1a) and then subtracting it from the spectrum of the full-layer azobenzene (red curve). Generally, adsorbates might induce a binding energy shift of the valence band and thus introduce dip-and-peak artifacts in difference spectra. We have carefully checked for such a possibility. From the difference spectra, it is apparent that the HOMO is located at the valence band maximum, with a peak at ~ 4.0 eV below the Fermi level, which is also confirmed in the spectra of azobenzene on rutile surfaces (see below). Figure 1c shows a gas-phase spectrum of free aniline for comparison, taken from the literature.²¹ Comparison with the orbitals of the free molecule orbitals is useful to identify the adsorbed species, as well as the degree of hybridization with the substrate.

Figure 2 shows photoemission spectra of a saturation coverage of azobenzene (red curve) and aniline (black curve) adsorbed on

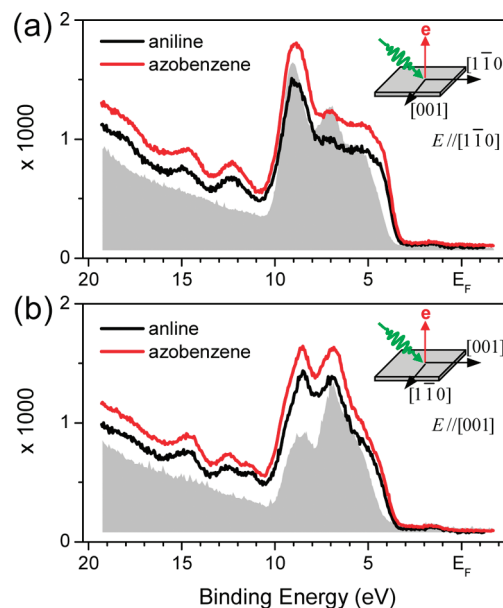


Figure 2. Photoemission spectra ($h\nu = 44$ eV) of a full layer of aniline (black) and azobenzene (red) adsorbed on a rutile $\text{TiO}_2(110)$ surface. The inset shows the experimental geometry: electric field along $[1\bar{1}0]$ in (a) and along $[001]$ in (b), respectively, an incidence angle of 45° , and normal emission. The gray areas show the rescaled spectra of corresponding clean surfaces.

the rutile $\text{TiO}_2(110)$ surface, respectively. The experimental geometry is illustrated in the inset. The spectra are taken with the polarization of incoming light along two azimuths, $E//[1\bar{1}0]$ and $E//[001]$. For comparison, the corresponding clean TiO_2 spectra are also plotted as the gray shadow. The spectra after azobenzene and aniline adsorption are remarkably similar. Adsorption of both species induces changes in the TiO_2 valence band, as is the case for azobenzene on anatase (Figure 1). The additional peaks in the energy region from 10.5 to 19 eV stem from the adsorbates. Combining this result with our previous STM/LEED study,⁸ one can conclude that the same, or very similar intermediates, formed upon azobenzene and aniline adsorbed on rutile TiO_2 .

Figure 3a shows the evolution of the photoemission spectra with photon beam exposure, after dosing a submonolayer of azobenzene (~ 0.2 – 0.3 ML) on anatase (101). This is the coverage regime where we expect intact azobenzene molecules according to STM results.⁸ All the spectra shown in Figure 3 were collected in a single sweep; each sweep takes about 3–5 min. The spectra are plotted in chronological order from the bottom up. The bottom curve was taken on a fresh spot that was never exposed to the synchrotron beam. The difference spectra (azobenzene/anatase minus clean anatase, after properly rescaling the clean spectrum) are plotted in Figure 3b. The first (difference) spectrum shows only a peak located at ~ 7.0 eV in the valence band region and a shoulder at ~ 5.0 eV, which is overlapped with the original valence band peak. During repeated scans, the photoemission spectra change gradually, and the (difference) spectrum obtained in the 11th sweep (top) closely resembles the one for a full coverage of azobenzene (compare Figure 3a, top, with Figure 1a,b). Except for a slightly lower intensity, the peaks in the difference spectra look very similar; the molecular orbitals of the submonolayer coverage after prolonged exposure to the photon beam have the same binding energies as

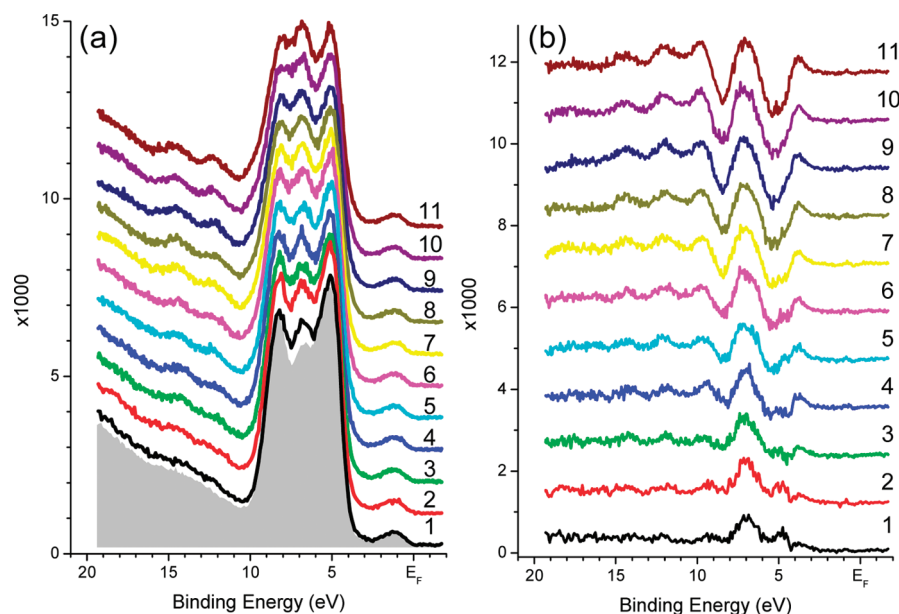


Figure 3. Effect of photon irradiation on a submonolayer (0.2–0.3 ML) of azobenzene adsorbed on anatase (101). Photon energy of 50 eV, incidence angle of 45°, normal emission. (a) A series of successive single-sweep photoemission spectra numbered and plotted in chronological order from bottom to top. The gray area in (a) is the rescaled spectrum of the clean anatase (101) surface. (b) Difference obtained by subtracting the rescaled spectrum of the clean anatase surface from the respective spectra displayed in (a).

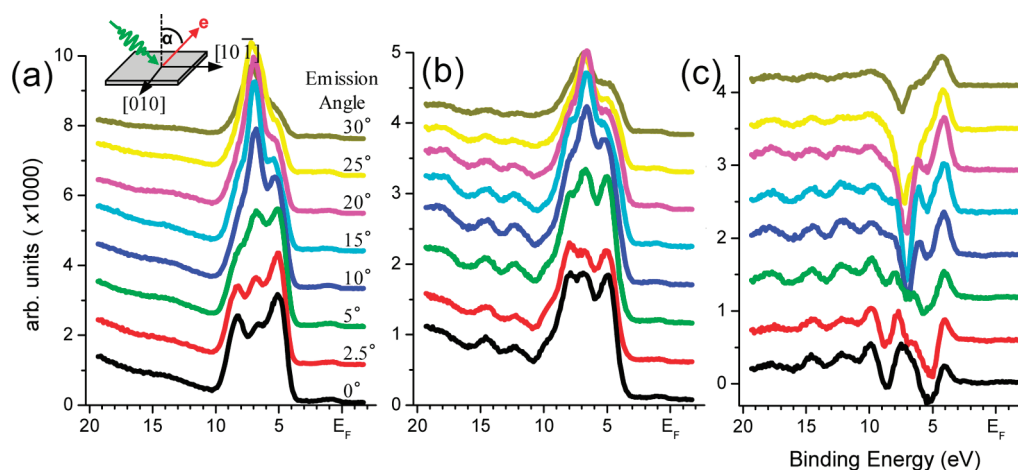


Figure 4. Angle-resolved photoemission of (a) the clean anatase (101) and (b) after adsorption of a full layer of azobenzene. (c) Difference spectra obtained by subtracting the rescaled clean anatase spectra from the azobenzene spectra. The emission angles range from 0° to 30°. Photon energy of 50 eV, incidence angle of 45°, electric field vector parallel to $[10\bar{1}]$, and detector in plane subtended by the surface normal and photon beam.

for a saturation coverage of azobenzene. Also, the valleys in the difference spectra, indicative of attenuation and/or rehybridization of the TiO_2 valence band, are similar. It needs to be emphasized that such a photon exposure-dependent change was only observed for the low-coverage case, not for a saturation coverage of azobenzene, where we expect an already-cleaved entity to reside on the TiO_2 surface.

Angle-resolved photoemission spectra of a full-layer of azobenzene on anatase (101) are shown in Figure 4a,b; the corresponding difference spectra are displayed in Figure 4c. The intensities of the orbitals in the region from 10.5 to 19.0 eV exhibit a clear angular dependence. For example, the peak at ~ 18.0 eV binding energy is maximized at ca. 15–20°, and the peak at 12.0 eV at ca. 15°. Note that, for higher emission angles

(30°), the peaks attributed to the molecular orbitals show a marked decrease in intensity, while their binding energy is only weakly dependent on the emission angle. In contrast, the orbitals that are overlapped with the valence band, ranging from 3.5 to 10.5 eV, vary in both intensities and binding energies (see also the difference spectra Figure 4c), indicative of hybridization with the TiO_2 valence band.

Figure 5 shows angle-resolved photoemission of a saturation coverage of azobenzene on rutile (110) for the two principal polarization directions. For reference, the corresponding clean surface spectra are plotted in gray. The spectral features exhibit a clear azimuthal dependence. For example, in the region from 10 to 13 eV, two peaks are resolved for $E//[001]$, while there is only one peak for $E//[1\bar{1}0]$. The intensity of the peaks also

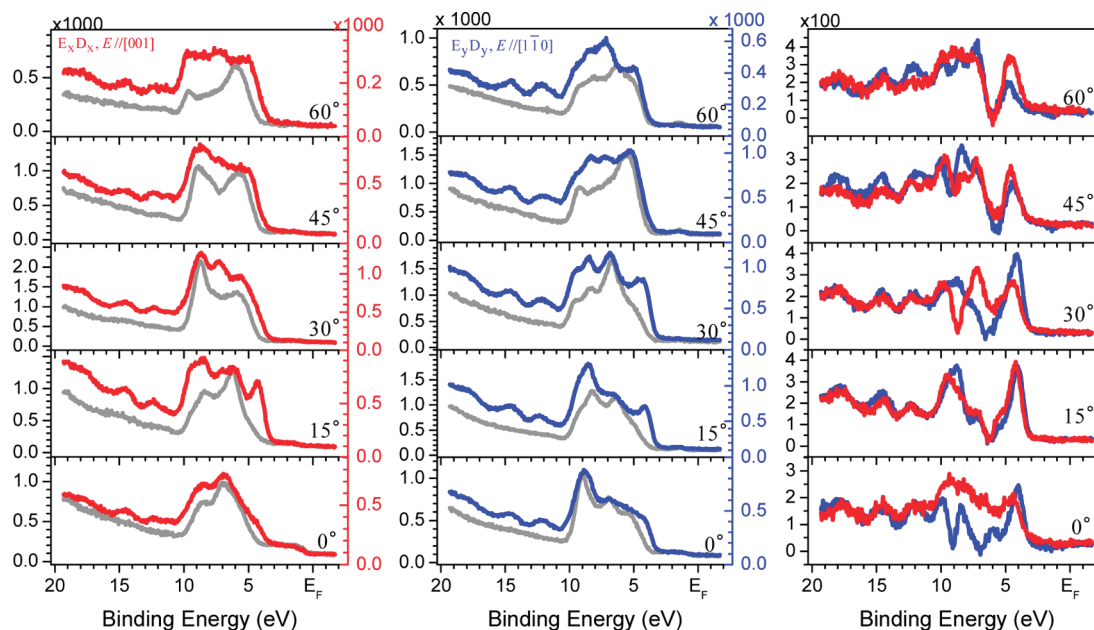


Figure 5. Angle-resolved photoemission of a full-layer azobenzene adsorbed on the rutile $\text{TiO}_2(110)$ surface. Left and middle panels: spectra normalized to photon flux. $E//[001]$ (red) and $E//[1\bar{1}0]$ (blue). The corresponding spectra of the clean surface are shown in gray. Right panel: difference spectra. Photon energy of 44 eV, incidence angle of 45° , and detector (D) parallel to the electric field (E).

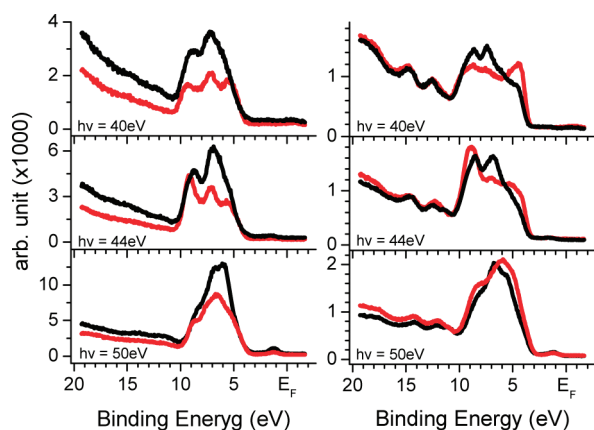


Figure 6. Normal emission spectra taken with three different photon energies (40, 44, and 50 eV) of the clean rutile (110) surface (left panel) and of the surface with a saturation coverage of azobenzene (right panel). Black and red are for $E//[001]$ and $E//[1\bar{1}0]$, respectively.

shows a polar angle dependence; for example, for both azimuths, the peak at 14.5 eV has the highest intensity at a polar angle of $\sim 15^\circ$.

Figure 6 shows normal emission spectra obtained with various photon energies, again for the two azimuthal orientations ($E//[001]$ and $E//[1\bar{1}0]$). Note the strong increase in the intensity of the HOMO level at a photon energy of 40 eV, where emission from Ti-derived levels is suppressed by resonant photoemission effects.¹⁷

4. DISCUSSION

All UPS results point toward the fact that azobenzene is cleaved on both TiO_2 polymorphs and that the resulting phenyl imide species exhibit some preferred orientations at full coverage

(0.5 ML) with clearly dispersive features in the range of 3.5–10.5 eV, in agreement with our previous STM study.⁸ In particular, the UPS spectra after dosing aniline and azobenzene (Figure 2) are virtually identical. Moreover, the difference spectrum for a full layer of azobenzene on anatase is remarkably similar to the gas-phase spectrum of aniline (Figure 1c) from the literature.²¹ We could not find a reference spectrum for azobenzene, but a comparison of the calculated molecular orbitals (Figure S1, Supporting Information) of both species suggests a significant difference in the number, intensity, and spacing of UPS peaks, should the azobenzene stay intact upon adsorption. To account for the difference in reference level (Fermi level and vacuum level for UPS and gas-phase spectra, respectively), the gas-phase spectrum in Figure 1c is shifted by 4.6 eV with respect to the surface one. Whereas the peaks at higher binding energy show small energy shifts, indicating a weak interaction with the substrate, the HOMO peak position shows a significant change toward higher binding energy. As expected, the peaks that overlap with the valence band are affected more strongly, and the suppressions located at ~ 5.0 and ~ 8.5 eV indicate a significant redistribution of spectral weight within the substrate valence band.

The situation at low azobenzene coverage is quite different from the full-coverage case. The UPS spectrum for a fractional monolayer (0.2–0.3 ML) of azobenzene on anatase (Figure 3, bottom curve) shows only a trace of the characteristic molecular orbitals at 10.5–18 eV binding energy. Photon irradiation causes a drastic change in the spectral shape, and, after prolonged exposure (curves 11 in Figure 3), the UPS spectrum and the difference spectrum closely resemble the saturated aniline/dissociated azobenzene spectra, except for a somewhat smaller intensity of the peaks and valleys that correspond to the molecular orbitals and rehybridized substrate states, respectively. Our previous STM study showed that azobenzene is adsorbed molecularly as a flat-lying trans isomer.⁸ The initial azobenzene

configuration, characterized by the first scan (curve 1 in Figure 3), might indeed correspond to the flat-lying and intact molecule. The difference spectrum for the first scan resembles the case of benzene adsorbed on a Ni(110) surface.²² For the flat-lying benzene/Ni(110), normal emission shows only two peaks at ~ 8.0 and ~ 10.9 eV,²² due to symmetry selection rules. Similarly, a flat-lying azobenzene trans isomer could contribute fewer molecular peaks for normal emission. As the azobenzene is being cleaved, the resulting N binds to substrate Ti sites and the phenyl ring flips to a more upright position. At the same time, more peaks start to appear in the spectrum as the sweep is repeated. Because the anatase surface does not have mirror symmetry perpendicular to the [010] direction, it is difficult to determine which selection rules are at work. We can probe experimentally whether photoemission in our geometry is sensitive to phenyl rings that lie flat: in angle-resolved photoemission for the full-coverage case (Figure 4), the orbitals disappear for higher polar angles, which, in the case of an approximately upright phenyl imide species, mimics the situation for a flat azobenzene molecule and normal emission.

It is well known that trans isomer azobenzene transforms into the cis isomer upon exposure to UV light.^{23–25} This reduces the π interaction of azobenzene with the substrate. The more intimate contact between the N=N double bond and the substrate in the cis isomer could then result in a more effective splitting of the molecule. In ref 8, we argued that, for saturation coverage, the N=N double bond cleavage by TiO₂ also occurs via a trans–cis isomer conversion. Although we cannot rule out other possible causes for the observed photon-induced dissociation in the synchrotron beam (photoinduced secondary electrons or excitation of the TiO₂ substrate come to mind), it is conceivable that the same mechanism is at work for molecularly adsorbed *trans*-azobenzene on TiO₂. It is interesting to speculate whether photon irradiation could also assist in the synthesis of nitroaromatics on Au/TiO₂-based catalysts at low temperature.

Lastly, we would like to address whether adsorption of aniline and azobenzene results in exactly the same intermediate, as suggested by the virtually identical spectra in Figure 2. In particular, for aniline, the question arises whether one or both H atoms are split off from the N when the molecule adsorbs on TiO₂. One also has to consider that some degree of hydroxylation of the TiO₂ surface is unavoidable, even for single crystals under UHV conditions: on slightly defective TiO₂ surfaces, hydroxyls usually form upon water dissociation at surface oxygen vacancies.^{26–29} It is thus possible that the cleaved azobenzene (phenol imide) picks up a surface H and forms a partially hydrogenated imide. One way to check for this is the analysis of UPS spectra taken under various geometrical configurations, where peaks are suppressed due to selection rules.³⁰ For example, an upright, fully dissociated aniline species on rutile (110) should have a C_{2v} symmetry, and the symmetry of the molecular orbitals can be assigned as a₁, a₂, b₁, and b₂. Thus, for different polarizations of the exciting photon beam (E-field and detector D parallel (x) and perpendicular (y) to the molecular axis, that is, parallel to [001] and [110] for rutile (110), respectively (see Scheme 1), some peaks should be suppressed. For example, the HOMO of aniline is b₁. In principle, the b₁ state is observable along one azimuth ($E_x D_x$) and not for the other one ($E_y D_y$). However, the experimental result is not in agreement with this expectation; see Figure 5. Note that the HOMO is observed for both $E//[1\bar{1}0]$ (D_y) and $E//[001]$ (D_x), while the intensity exhibits a rather different emission angle dependence. Thus, it

appears that the C_{2v} symmetry is not preserved on the surface, either because the molecules are partially hydrogenated or possibly because they are tilted from the upright position.

5. SUMMARY

Synchrotron-based valence band photoemission has been applied to investigate the evolution of the electronic structure upon azobenzene/aniline adsorption on TiO₂ surfaces, anatase (101) and rutile (110). At saturation coverage of half a monolayer, the UPS spectra of azobenzene and aniline are virtually identical, consistent with formation of a phenyl imide species. Our results are inconclusive as to whether the N end of the phenyl imide species loses one or both H atoms; the symmetry of the adsorbate is reduced from the C_{2v} configuration, which could result from either an incomplete dissociation of the N and/or a tilt or rotation of the phenyl imide species. The data are, however, consistent with the proposed model⁸ that a coverage-dependent trans–cis isomerization is instrumental in N=N bond cleavage: the initial UPS spectrum from a submonolayer coverage of azobenzene changes upon prolonged exposure to the photons, resulting in the same product as is observed for full coverage of azobenzene and aniline. Moreover, angle-dependent measurements show consistence with an initially flat-lying azobenzene molecule, while the dissociated phenyl imide species is in an (approximately) upright position. In conclusion, the present UPS result together with our previous STM, XPS, and LEED study⁸ conclusively shows that TiO₂ is instrumental in the N=N bond cleavage and that this mechanism has to be taken into account for Au/TiO₂ catalysis of nitroaromatics. As a final note, the observed photon-induced effects could also be useful in the heterogeneous catalysis of nitroaromatics.

■ ASSOCIATED CONTENT

S Supporting Information. Calculated molecular orbitals for aniline and azobenzene with the free program GAMESS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: diebold@iap.tuwien.ac.at.

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■ NOTE ADDED IN PROOF

It has come to our attention that a recent theoretical study [Prates Ramalho, J. P.; Illas, F. *Chem. Phys. Lett.* **2011**, *501*, 379–384] reports that adsorption of azobenzene on rutile (110) weakens the N=N double bond while a dissociation was not observed.