

## Photoinduced Reconfiguration Cycle in a Molecular Adsorbate Layer Studied by Femtosecond Inner-Shell Photoelectron Spectroscopy

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A time-resolved study of core-level chemical shifts in a monolayer of aromatic molecules reveals complex photoinduced reaction dynamics. The combination of electron spectroscopy for chemical analysis and ultrashort pulse excitation in the extreme ultraviolet allows performing time-correlated 4*d*-core-level spectroscopy of iodine atoms that probe the local chemical environment in the adsorbate molecule. The selectivity of the method unveils metastable molecular configurations that appear about 50 ps after the excitation and are efficiently quenched back to the ground state.

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Function in molecular systems rarely occurs as single-step nonreversible transitions, but is usually the result of a complex sequence of electronic and structural reorganizations. Monitoring such processes requires capturing the whole evolution including all intermediate states on the relevant time scales, ranging from femtoseconds to nanoseconds. Of particular interest are surfaces functionalized with adsorbates for which the function can be controlled with light [1]. Both excitation mechanisms and reaction pathways differ between free and adsorbed molecules [2], and it is important to understand the differences such as absorption in the substrate and the quenching of adsorbate excitations [3]. Thus, adsorbates with dominant direct photoexcitation and weak substrate interaction are candidates to functionalize surfaces. In spite of the relevance of photoinduced surface reactions, our capabilities to study excitation, relaxation, and reaction pathways in real time are limited.

Probing molecular systems at a defined delay after an optical excitation with a second laser pulse constitutes the most eminent tool of femtochemistry. Also in surface photochemistry time-resolved spectroscopies provide information on the excitation mechanism and reaction pathway [2,3]. However, many methods lack selectivity to study large complex adsorbates. For example, in time-resolved photofragmentation or near-threshold photoelectron spectroscopy probe pulses in the UV to IR range are rarely selective for a certain bond or chemical species. In contrast, x rays are noninvasive and selective probes that interrogate core levels of specific elements. Electron spectroscopy for chemical analysis (ESCA) [4] detects chemical shifts, thereby delivering information about the element specific environment. The combination of ESCA with ultrashort pulse excitation in the soft-x-ray [extreme ultraviolet (EUV)] range thus provides a universal and highly

selective time-resolved probe in adsorbates. Ultrashort EUV light pulses are routinely produced by high harmonic generation (HHG), and a variety of ultrafast processes have been studied in atoms [5,6], molecules [7–9], and more complex systems such as surfaces [10–14] with a temporal resolution extending to the attosecond range [5] even on surfaces [13]. Time-resolved IR-pump–EUV-probe photoemission experiments using probe pulses in the 40 eV range revealed a transient electronic adsorbate state by probing the reversible IR induced valence electron change of adsorbed oxygen on a platinum surface [10]. However, time-resolved core-level spectroscopy of adsorbates were not yet reported.

Here we use ESCA to probe UV-induced electronic and structural dynamics in a self-assembled monolayer of iodo-phenylphenol on Si (100). Time-resolved core-level photoemission from the iodine marker atom reveals the direct photoexcitation of the molecular layer and a complex photoreaction proceeding via several intermediate states, finally reestablishing the initial state. We interpret the dynamics as metastable photoswitching to prefulvene-type isomers, and conclude that distinct light-driven processes occur in an adsorbate layer with almost 100% yield.

An overview of the experimental setup is shown in Fig. 1(a) together with the dominating excitation pathways [Fig. 1(b)] and characteristic photoemission spectra of iodo-phenylphenol on Si [Fig. 1(c)]. The spectra recorded for EUV-probe excitation preceding the UV-pump pulse (blue circles) and without UV-pump excitation (purple circles) coincide and UV-multiphoton photoemission background is negligible. The peaks at 46.0 and 44.3 eV exhibit a branching ratio of  $1.9 \pm 0.1$  (ratio of peak areas) and correspond to emission from the iodine 4*d*<sub>5/2</sub> and 4*d*<sub>3/2</sub> core states, respectively. Further details on photoelectron spectroscopy and sample preparation are provided as

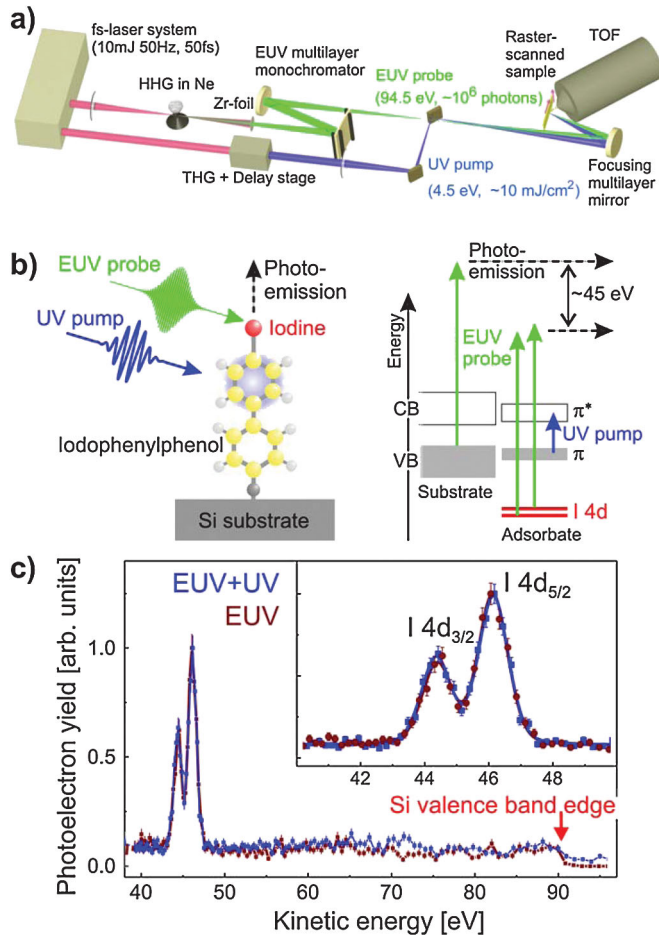


FIG. 1 (color). Experimental scheme. (a) Experimental setup for time-resolved ESCA. Part of the fundamental laser beam is focused into a neon gas target to generate EUV radiation by high-harmonic generation. A zirconium foil filters out the lower harmonics and the fundamental. The 63rd harmonic order at a wavelength of 13 nm (94.5 eV) is selected through a two-multilayer-mirror monochromator. UV pump pulses at 266 nm (4.5 eV) are generated via third harmonic generation (THG) using the rest of the fundamental beam. Both beams are refocused to about 25  $\mu\text{m}$  diameter (FWHM) spots on the sample. The energy of the emitted electrons is analyzed in a time-of-flight (TOF) spectrometer. (b) Excitation scheme for adsorbed iodo-phenylphenol on Si with excitation pathway (right). (c) Normalized photoelectron spectra of an iodo-phenylphenol monolayer on Si for EUV excitation only (purple circles) and for EUV excitation followed by UV-pump excitation at a delay of 3 ps (blue squares). The vertical error bars correspond to the statistical uncertainty.

supplemental material [15]. The iodine 4*d* photoemission yield before and after excitation by a sequence of UV pulses reveals an iodine desorption probability per UV pulse <5%. To avoid influences of this irreversible surface modification, the sample is raster scanned to a fresh sample spot after each UV laser pulse. Figure 2 displays iodine 4*d* core-level photoelectron spectra for different pump-probe delays reflecting the characteristic effects occurring after UV excitation. For negative delay, the pump-probe

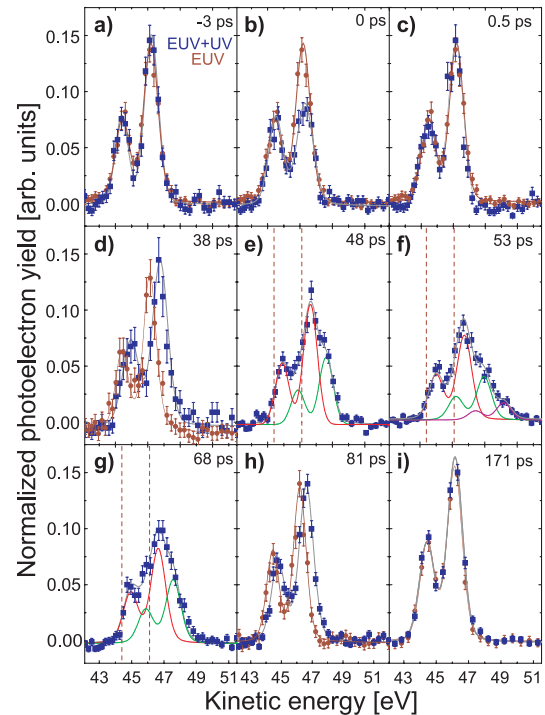


FIG. 2 (color). Iodine 4*d* core-level spectra for various pump-probe delays. Positive delay corresponds to UV-pump excitation (266 nm, 50 fs, 10  $\text{mJ cm}^{-2}$ , peak intensity of about  $3 \times 10^{11} \text{ W cm}^{-2}$ ) followed by EUV-probe excitation (94.5 eV, estimated pulse duration 7–15 fs, and flux  $10^5$  photons per pulse). EUV reference spectra are shown in (a)–(d), (h), (i) for comparison (purple line and filled circles). Vertical dashed lines in (e)–(g) indicate the positions of the 4*d* peaks observed in the reference spectra. After background subtraction the spectra are normalized to the total peak area, except for the pump-probe spectrum shown in (b) for which the  $4d_{3/2}$  peak area is set equal to the  $4d_{3/2}$  peak area of the normalized EUV reference. The continuous lines are best fits obtained with a single doublet of pseudo-Voigt lines (a)–(d), (h), (i) and multiple doublets (e)–(g). Two and three different local environments for the iodine atom are obvious for (e), (f), respectively. The corresponding fit components are shown as solid lines in red, green, and purple.

photoemission spectrum and the EUV reference spectrum are identical [Fig. 2(a)]. A pronounced drop of the  $4d_{5/2}$  emission is observed around zero delay [Fig. 2(b)] whereas the peak positions are unchanged. The different normalization used in Fig. 2(b) reflects the observation that indeed the  $4d_{3/2}$  emission is unaffected by the UV excitation. Already 0.5 ps after the pump excitation the effect in the branching ratio vanishes and the spectrum is identical to the reference spectrum again [Fig. 2(c)]. In the adjacent time window of about 40 ps a transient shift of the iodine doublet to lower binding energy occurs [Fig. 2(d)]. The shift is almost linear with time and reaches about 0.6 eV relative to the 4*d* binding energy without UV excitation. No significant change in the spin-orbit splitting, branching ratio, and the linewidth of both peaks is observed, and the spectra are well fitted by a single doublet of pseudo-Voigt lines.

For a delay of 40–70 ps a transient change of the iodine  $4d$  line shape is observed [Figs. 2(e)–2(g)]. The high-energy slope of the doublet is smeared out and shifted to higher kinetic energy. Accordingly, some of the iodine atoms experience an additional core-level shift whereas some of them reside in an unchanged local environment. The overall spectral shape, i.e., the minimum between  $d_{3/2}$  and  $d_{5/2}$  peak, can only be described by several contributions with distinct energetic shifts corresponding to iodine in distinguishable environments. This is confirmed by a second independent data analysis, i.e., a deconvolution of the spectra with the reference spectra, that yields separated peaks in the distribution of chemical shifts at the same characteristic shifts as the fitting procedure. The spectrum for 48 ps delay [Fig. 2(e)] is composed of two distinct fractions of iodine atoms characterized by a chemical shift relative to the unperturbed system of 0.6 and 1.5 eV. For a slightly larger delay [Fig. 2(f)], even a third fraction ( $\sim 15\%$ ) appears characterized by a chemical shift of 3 eV. The coexistence of these three components persists only in a short time window, and for a delay  $>60$  ps the third component disappears again [Fig. 2(g)]. For an even larger delay the spectrum is well fitted with a single Voigt doublet [Fig. 2(h)]. The chemical shift of this doublet decreases until pump-probe spectrum and reference spectrum overlap again for a delay of 170 ps [Fig. 2(i)]. Note that all iodine atoms exhibit the same  $4d$  core-level binding energy as prior to the pump excitation indicating negligible photodesorption of the iodine. This agrees well with the UV-pump induced iodine desorption yield of  $<5\%$  per pulse. Figures 3(a) and 3(b) summarize the chemical shifts observed in the pump-probe experiment.

The  $d_{5/2}/d_{3/2}$  branching ratio around zero delay is shown in Fig. 3(c), showing a strong reduction of the branching ratio. The temporal width of about  $250 \pm 80$  fs (FWHM) is obtained from fitted Gaussians and gives an upper limit for the cross correlation of EUV pump and UV probe pulse. The branching ratio depends on the electronic configuration and can significantly deviate from the ratio determined from the degeneracy of the involved states [16,17]. In an oriented ensemble an electronic alignment, i.e., a nonequilibrium population of the magnetic sublevels of the spin-orbit split core-level states, influences the branching ratio. Theoretical treatment of x-ray absorption shows that the alignment of core levels is linearly related to an alignment of the valence orbitals [16]. The absorption of a photon in the preferentially oriented iodo-phenylphenol induces an electronic alignment, and thus also affects the spin-orbit split core levels and the observed branching ratio. Structural influences on the branching ratio are excluded since (i) no chemical shift is observed parallel to the branching ratio drop, (ii) the dominating structural dynamics occurs on the 50 ps time scale, and (iii) the known effects of structural reorientation on the branching ratio are rather small [18]. Thus we attribute the branching ratio drop to an UV-pump induced alignment of the adsorbate valence electrons proving direct UV photoexcitation

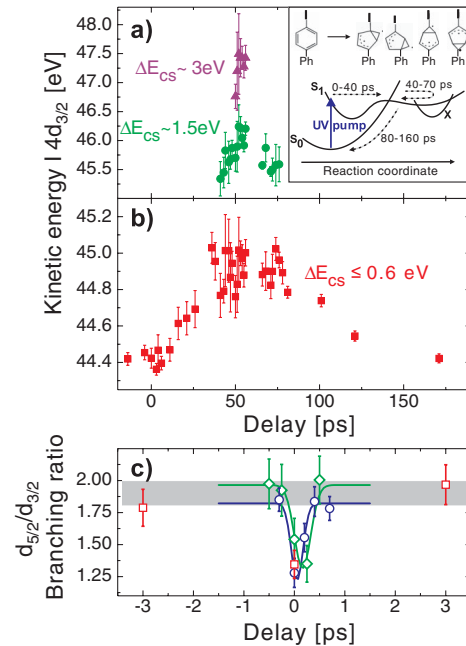


FIG. 3 (color). Pump-probe effect of core-level chemical shift and branching ratio. (a),(b) Center of the iodine  $4d_{3/2}$  lines after fitting the spectra as a function of the pump-probe delay for the contribution with the energetic shifts up to 0.6 eV [(b), red squares], those with about 1.5 eV [(a), green circles], and 3 eV chemical shift [(a), purple triangles]. The error bars represent the  $2\sigma$  confidence interval of the fit. The inset in (a) shows possible intermediate state configurations and a schematic of the potential energy surface. (c) Iodine  $4d_{5/2}$  to  $4d_{3/2}$  branching ratio variation for the pump-probe delay between  $-3$  and  $3$  ps for three different measurements on two different samples. The solid lines represent fitted Gaussians corresponding to two data sets to allow the determination of the width and position of the observed branching ratio drop.

of the adsorbate. For iodobenzene in the gas phase direct  $\pi$ - $\pi^*$  excitation in the phenyl ring and excitation of a repulsive  $n$ - $\sigma^*$  state of the carbon-iodine bond are known [19–21]. Because of the negligible dissociation we favor a direct  $\pi$ - $\pi^*$  excitation of the phenyl ring [Fig. 1(b)].

The UV-pump pulse initiates complex dynamics in the substrate-adsorbate system resulting in significant iodine core-level shifts of up to 3 eV. For an emitter embedded in an adsorbate layer, both local bonding and electrostatic effects in the adsorbate layer [22,23] affect the photoelectron energy. We exclude surface photovoltage effects [11] at the Si-adsorbate interface, the formation of a lateral homogeneous double layer within the adsorbate layer, and a transient charging of the adsorbate layer, as these effects would affect the kinetic energy of electrons emitted from the Si valence band maximum which is not observed [Fig. 1(c)]. We conclude that the observed core-level shift is caused either by a transient change of the iodine bonding or by a charge redistribution in the adsorbate layer.

The core-level shift for various iodine bonds is known only for equilibrium configurations and provides no help to identify transient chemical species far from equilibrium.

The photochemistry of benzene derivatives and halogen aryls provides guidelines for possible reaction pathways such as radiative decay and internal conversion [24], inter-system crossing [25], valence isomerization to prefulvene [26,27], ring opening [25], and fragmentation and dissociation reactions. We rule out mechanisms that have low probabilities to reestablish the initial state, i.e., dissociation, fragmentation, and ring opening. In addition, a purely photophysical reaction, such as internal conversion, inter-system crossing, or radiative relaxation, cannot account for the formation of a metastable state and the observation of bifurcation to other states. Thus, valence isomerization to prefulvene remains the most plausible reaction pathway. A detailed analysis of the  $S_0 \rightarrow S_1$  decay of benzene reported a reaction pathway via prefulvene which then can bifurcate to  $S_0$  benzene or benzvalene [27]. Thus, we identify the metastable intermediate state characterized by 0.6 eV core-level shift as a prefulvene-type configuration of the adsorbed iodo-phenylphenol that forms about 50 ps after photoexcitation. The two additional states are attributed to additional prefulvene-type isomers, triplet states, or benzvalene derivatives that are temporarily populated. Possible structures of prefulvene-type intermediates and a simplified schematic of the potential energy surface and typical time constants are shown as the inset in Fig. 3(a). The formation of these metastable states requires substantial geometric reorganization and is accompanied by charge redistribution in the complex explaining the large transient chemical shifts and the long time involved with intermediate state formation. The prefulvene-type configuration characterized by a chemical shift of 0.6 eV persists for almost 30 ps and only then relaxes. This behavior suggests that some reorganization of the molecule is required before the relaxation channel to the ground state opens. Thus, the dynamics can be imagined as metastable photoswitching of an adsorbate. This together with the observation that all iodine atoms participate in this “switching” process shows that very distinct light-driven processes can occur in an adsorbate layer with almost 100% selectivity. This is in striking contrast to photochemical reactions of small adsorbed molecules typified by an indirect excitation via hot surface electrons and fast relaxation and associated quenching of surface reactions [3]. Thus, proper design of the adsorbate therefore should allow bistable ultrafast photoswitching—an issue of significant interest for future applications.

The potential of the here-demonstrated time-resolved ESCA of surface dynamics goes well beyond the presently investigated system. With techniques based on high-harmonic generation or free electron lasers, ultrashort widely tunable EUV pulses are available and allow probing core levels of a large variety of even heavy elements. The method is thus applicable to study many light-driven processes occurring at surfaces and for sufficiently high EUV energy provides time-resolved multielement signatures that will provide valuable information even about

complex adsorbate and surface dynamics. Time-resolved core-level spectroscopy is still in its infancy, and we envisage that with an increasing database this method will also evolve “fingerprinting” capabilities for particular nonequilibrium chemical bonding environments. This will greatly facilitate the interpretation of observed chemical transients, and thus broad applications of the here-demonstrated time-resolved ESCA in surface chemistry and physics are anticipated.

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