

Atom-Selective Bond Breaking in a Chemisorbed Homonuclear Molecule Induced by Core Excitation: N₂/Ru(001)

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(Received 3 August 1999)

We observe photochemical selectivity for N 1s to π^* excitations of chemisorbed N₂. By narrow bandwidth synchrotron radiation we selectively excite one of the two atoms of the molecule. Photon stimulated desorption of neutral N atoms predominates for excitations of the N atom close to the surface, whereas excitation of the outer atom ejects predominantly N₂⁰ and small amounts of N⁺, demonstrating the predominant breaking of the inner or outer bond, respectively, of the N₂ adsorbate. Analysis on the basis of previously obtained decay electron spectra after atom-selective excitation can explain the mechanism of localized bond breaking.

PACS numbers: 79.20.La

It has long been the aim of photochemists to focus upon a specific atom in a specific chemical environment and use radiation to selectively cleave certain bonds. In order to separate element and bond specific effects, site selectivity obtained for identical atoms in only gradually different chemical environments is of particular interest. Perpendicularly adsorbed homonuclear diatomic molecules whose symmetry is broken by the bonding to the surface are perfect examples. To study effects resulting from this symmetry breaking, atom-selective probes are required. Particle and radiation emission stimulated by high resolution core electron excitation are very suitable because of the strongly localized nature of these electronic states. In previous experiments, such phenomena have been studied for N₂ chemisorbed on Ni(100), and on Ru(001). For both adsorption systems the molecules are weakly chemisorbed (bound by 0.5 eV for Ni [1] and 0.45 eV for Ru [2]), oriented perpendicularly to the surface [3,4] and organized in well ordered monolayers [$c(2 \times 2)$ for Ni, and $(\sqrt{3} \times \sqrt{3})R30^\circ$ for Ru]. For N₂/Ni(100), atom-selective N 1s x-ray photoelectron spectroscopy (XPS) which included also the extended ionization satellite region [5], x-ray absorption spectroscopy (XAS) [6], decay electron spectroscopy [6], and x-ray emission spectroscopy (XES) [7] have been performed, and their results have been compared with those of theoretical studies [7]. Based on the XES data, an allylic interaction of three π orbitals was proposed for the surface chemical bond [7]. All these atom-selective experiments became possible for N₂/Ni because the ionization and the π -resonant excitation energies are lower for the outer than for the inner atom by 1.3 and 0.4 eV [5,6], respectively, which in combination with narrow bandwidth synchrotron radiation from second and third generation storage rings made selective excitation of only one atom possible.

For N₂/Ru(001) very similar results have been obtained. In particular, a blueshift of 0.7 eV for the π -resonance energy of the inner atom with respect to the outer one has been found [8]. As for N₂/Ni [6], the different chemical

environments of the two atoms appear as different core hole decay channels after selective excitation [8]. The spectra resemble those of CO for C 1s and O 1s excitation, with metal-N*-N corresponding to metal-C-O* and metal-N-N* corresponding to metal-C*-O [8]. A similar correspondence was reported for the XPS satellite structure of N₂/Ni(100) [5].

Different core hole decay channels for the two atoms should induce different branching ratios of photon stimulated desorption (PSD) and dissociation reactions. A direct experimental access to the emitted reaction products is needed, therefore. In gas phase experiments, photochemistry by core excitations can easily be studied by monitoring the emitted photoions. For molecules on metal surfaces, the detection of the reaction products is more difficult because neutralization by electron transfer from the metal is very efficient and desorbing ions are rare, for valence [9] as well as for singly excited core hole states [10]. For N₂/Ru(001), neutral nitrogen molecules (N₂⁰) and atoms (N⁰) are the most likely desorption products for π -resonant N 1s excitation. By considerably increasing the sensitivity of a device that previously has been used for studies under low resolution conditions (bandwidth 1 eV) [11], we were able for the first time to measure photodesorption of these neutrals under high photon energy resolution conditions (150 meV bandwidth). Our data from $(\sqrt{3} \times \sqrt{3})R30^\circ$ -N₂ layers on Ru(001) (subsequently called $\sqrt{3}$ layers) indicate excitation site selectivity not only for the breaking of the substrate-adsorbate bond, but also for the intramolecular bond. We explain these findings using decay electron results from atom-selective decay electron spectra obtained previously [8].

All data were taken at the BW3 beam line of HASYLAB at DESY in Hamburg. The Ru(001) substrate was cleaned by Ar⁺ sputtering, heating in oxygen, and annealing, and the cleanliness was checked by XPS. The $\sqrt{3}$ N₂ layers were prepared by dosing N₂ through a microcapillary doser onto the Ru crystal while slowly cooling it to 80 K. This procedure results in a minimum amount of coadsorbed

nonperpendicularly bound N_2 , which exists in defects of the $\sqrt{3}$ layer [2]. After dosing, small residues of this nonperpendicular species were removed by heating under thermal desorption control and its absence was checked by polarization resolved partial electron yield (PY) measurements.

The light was 7° grazing with respect to the surface, with the polarization vector either fully within the surface plane (A_{xy} polarization) or 7° off normal (A_z ; here used only for PY measurements). The neutral particles were detected with a highly sensitive quadrupole mass spectrometer (QMS) fitted with a liquid helium cooled copper cap over the ionizer. The residual gas in the ionizer region was efficiently removed by condensation and cryo trapping onto the cap's inner surfaces [11], and by getter films evaporated from two Ti sources inside the cap. To enhance the signal/background ratio, the light was chopped and the QMS signal processed by a lock-in amplifier. N_2^0 and N^0 signals were recorded. The N_2^0 signal was used to properly subtract its contribution to the N^0 species due to cracking by electron impact inside the ionizer. The cracking pattern was obtained by careful calibration runs under identical operation conditions of the ionizer. We also measured the yield of decay electrons with a standard partial electron detector at grazing exit angle for maximum surface sensitivity, in parallel with either the ion or the atom yield. Desorbing ions were detected by a separate QMS. The system base pressure was 2×10^{-11} mbar.

An overview of the spectral shapes of PSD and PY signals obtained with excitation by A_{xy} light (photon energy bandwidth: 400 meV) is given in Fig. 1. The photon energy calibration has been taken from Ref. [8], where careful comparisons with *in situ* measured multilayer spectra had been done. In the PY, and in the PSD signals of neutrals, the π resonance ($[N\ 1s]2\pi$; we use the $C_{\infty v}$ notation for the molecular orbitals to account for the broken symmetry, see Ref. [7]) is the dominant feature. In the N^+ signal it is very weak and structures at higher excitation energies prevail. The maxima around 410 and 415 eV which also appear in the N atom signal but are absent in the N_2^0 trace can be assigned to $[2h]2e$ excitations known from decay electron spectroscopy [12] and XAS data [13,14] obtained for the isolated molecule (because of the limited space, details will be discussed elsewhere [10]). In the multiple shake-off regime far beyond the N $1s$ threshold (not shown in Fig. 1) the ion yield increases even more strongly, in good agreement with previous PSD results on chemisorbed CO [15], indicating that PSD of N^+ is a minority channel at the π resonance. N^0 and N_2^0 are clearly the dominant PSD products. Comparing the spectral shapes of these signals with that of the PY, differences become obvious. Apart from the enhancement of the atom signal for the mentioned multi-electron excitation states compared with N_2^0 -PSD and the PY, we find clear changes of the $[N\ 1s]2\pi$ maxima, in shape and peak position. We also observe a step to the left of the π resonance and an

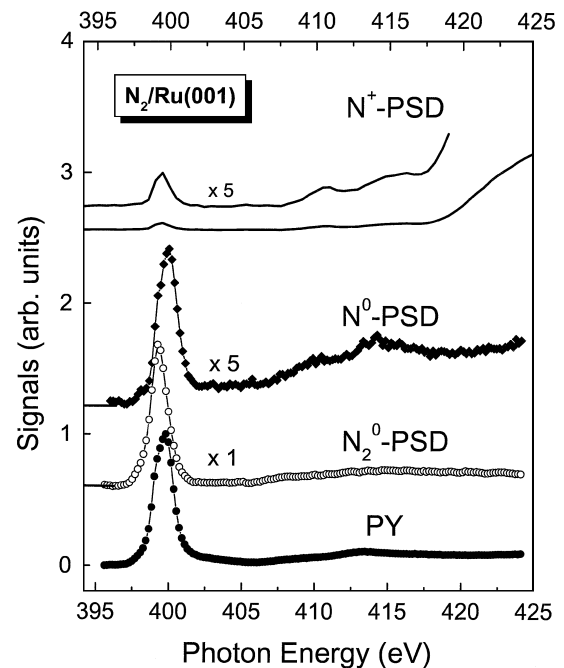


FIG. 1. Partial electron yield (PY), and N_2^0 , N^0 , and N^+ PSD from $(\sqrt{3} \times \sqrt{3})R30^\circ$ - N_2 on Ru(001) for N $1s$ excitation with A_{xy} light (see text). For N^0 and N_2^0 the prethreshold values are indicated.

enhanced intensity to its right for the N^0 signal. The step has previously been observed in Ref. [8] and explained as a Fermi-level step [16]. Although photoabsorption and PSD of atomically adsorbed nitrogen could be an alternative interpretation [5], we believe it to be a molecular feature, because great care was taken to avoid accumulation of N atoms from photon induced dissociation of N_2 molecules on the surface (dissociative adsorption can be excluded for our dosing conditions), and because no atomic decay lines were found in Ref. [8]. The enhanced intensity to the right of the π resonance must be due to transitions into metal (i.e., bond) derived states because molecular levels are lacking in this energy range.

We now switch to the high resolution mode (photon bandwidth 150 meV) and analyze the shapes of the π -resonant peaks more closely (Fig. 2). The individual traces are obviously composed of two components, energetically separated by 0.7 eV, in varying mixtures. To arrive at a quantitative analysis, we use the spectral shapes of the two components that have been obtained in Ref. [8] from a careful decomposition of the XAS signal. These two components which have been derived from decay electron results under narrow band excitation are shown underneath the PY trace in Fig. 2. After an adjustment of their relative amplitudes by not more than 5% accounting for different weighting factors of the individual decay electron channels due to different angular acceptances of the PY detectors in the two experiments, we arrived at a perfect fit of our PY trace (Fig. 2; all data obtained in our experiments are

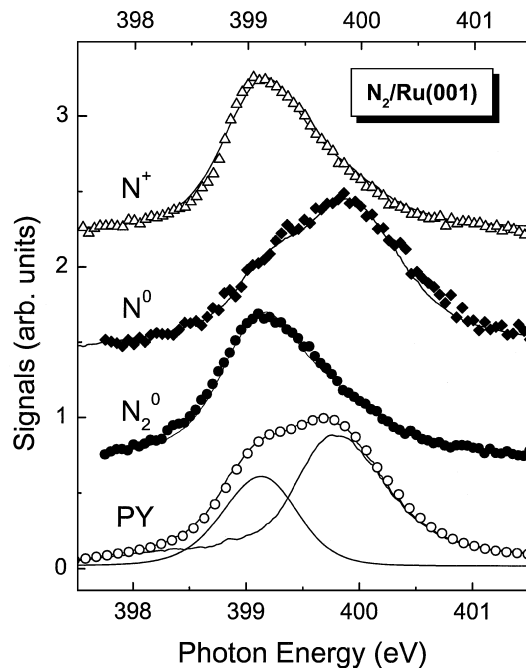


FIG. 2. PY and PSD of N^+ , N^0 , and N_2^0 from $N_2/Ru(001)$ obtained under high photon energy resolution conditions (bandwidth 150 meV, A_{xy} light). Varying contributions from $N 1s$ excitations of the outer (low energy) and the inner (high energy) N atoms are obtained for the different signals. PY and PSD signals measured in our study are displayed as scatter symbols. Fitted curves obtained by linear combinations of the inner/outer components of the PY signal are indicated as straight lines. The decomposition of the PY signal into the two components (see bottom curves) was taken from Ref. [8].

displayed as scatter symbols, and the fitted curves based on the decomposition of Ref. [8] as straight lines). The contribution with the higher excitation energy belongs to the inner N atom as for $N_2/Ni(100)$ [6,8]. The different areas of the two components reflect the excitation site-dependent densities of available final states. We now fit our PSD data by linear combinations of these two components and obtain best results for main contributions of $78 \pm 2\%$ outer component for N^+ -PSD, $77 \pm 3\%$ outer component for N_2^0 -PSD, and $65 \pm 4\%$ inner component for N^0 -PSD (to account for the increasing N^0 signal due to transitions into metal derived states, a small background signal linearly increasing with photon energy has been added here). We arrive at these numbers by taking the experimentally obtained ratio of the two components. If we normalize their amplitudes, i.e., divide by their different excitation cross sections in order to obtain results on a “per photon” scale, our numbers change to 84%, 83%, and 56%. In summary, we find that photodesorption of atomic ions and neutral molecules is mainly due to excitations of the outer N atom, whereas fragmentation into neutrals is enhanced if the inner N atom is π resonantly excited.

We now try to explain our results on the basis of the surface bond model for chemisorbed N_2 derived from

XES [7], and of the decay electron spectra of Ref. [8]. In Ref. [7] it was shown by atom-specific experimental and theoretical results that the chemisorptive bond of nitrogen can be described by an allylic configuration comprising the two N as well as the nearest metal atom, resulting in a system of three π orbitals. The π orbital with the largest electron binding energy is bonding with respect to all three atoms. It is mainly derived from the $1\pi_u$ molecular orbital (MO) of the isolated N_2 , with small, but significant, contributions from metal d states. The second π orbital is essentially nonbonding with mainly metal character. The highest π orbital is antibonding for the adsorbate and the intramolecular bond. It is derived from the π^* (2π ; isolated N_2 : $1\pi_g$) MO of the molecule, with contributions from metal d and p states. For $N_2/Ni(100)$ it was found to be unoccupied and is expected to be here as well; it plays a role as screening orbital upon core hole creation. The σ orbitals are polarized in a way that minimizes repulsion with metal sp states [7]. To explain the observed atom-selective PSD branching, we analyze the consequences of distinct core hole decay final states for the surface bond. We neglect ultrafast processes, i.e., bond breaking during the lifetime of the core hole, because the potential curves for this core excited state are neither strongly repulsive nor strongly attractive in the Franck-Condon region, for the intramolecular [17] as well as for the adsorbate bond.

In Ref. [8] it has been shown that very different core hole decay states are obtained for primary excitations of the outer and the inner N atom. Inner N $1s$ holes mainly decay into final states with $[1\pi^2]$ and $[1\pi 4\sigma]$ double holes, whereas $[5\sigma^2]$, $[4\sigma^2]$, and a manifold with main contributions of $[4\sigma 2\pi]$ configurations dominate for outer excitations. We further note that we have to consider full relaxation of the final states after core decay on the time scale of PSD, i.e., $2h2e$ states, with the topmost π orbital as screening orbital. The 1π orbital is strongly bonding with respect to the molecular bond, and a double hole efficiently dissociates the nitrogen molecule, in particular, if the additional charge transfer into the energetically highest, overall antibonding π orbital is taken into account. This explains the large fragment signal for selective excitation of the inner N atom, whereas most decay states of outer excitations leave the intramolecular bond intact (we neglect the tiny N^+ signal, which clearly is a minority species that cannot easily be traced back to the majority channels of the decay spectrum and is likely to be related to Auger satellite channels). The intramolecular bond is weakened less by 4σ and 5σ holes, which predominate in the decay states following outer excitations, than by 1π holes which prevail for inner excitations. For the substrate-adsorbate bond these σ orbitals are mainly repulsive and their ionization should not weaken the bond at all. The strength of the metal-adsorbate bond is, however, decreased by transfer of screening charge into the antibonding π orbital, and probably also by an increase of the 1π -binding energy due

to the positive charge in the σ states. Such a binding energy shift of the all-bonding π orbital would deplete its coupling with metal states and weaken the adsorbate bond. Although the occupation of the antibonding π^* orbital by screening electrons is likely to be similar for double 1π holes on the one hand and double σ holes on the other, we find much less fragmentation events because the intramolecular bond is weakened more strongly for the 1π double hole than for the 4σ and 5σ double holes. [We note that our analysis is not complete because, e.g., all final states containing holes in inner valence levels (3σ) have not been included because of lacking decay electron data. The existence of these minority channels easily explains why the decompositions of our PSD-spectra are not "pure," but show only strong enhancements according to the main decay channels that dominate for the individual species.]

In summary, we have shown that PSD of neutral particles in combination with narrow band excitation allows us to obtain an atom-selective view on photoinduced bond breaking in adsorbed molecules. Compared with PSD of ions, majority channels are monitored. We find very different PSD branching ratios for π -resonant excitations of the inner and outer N atoms of perpendicularly adsorbed N_2 , which can be well understood by considering the prevailing decay states after atom-selective excitation. Because neutral particles dominate by far in PSD from adsorbates on metal surfaces, our findings are important for all applications in spectroscopy or technology where electronically stimulated bond breaking is encountered. We stress that the usual observations of PSD ions would not give any of these insights.

We thank the staff of HASYLAB, in particular, T. Möller, C. Nowak, and A. Kolmakov, for help during the experiments. Valuable and stimulating discussions with W. Wurth are gratefully acknowledged. This study was supported by the Deutsche Forschungsgemeinschaft (SFB 338 C10). S. Frigo acknowledges support of the U.S. Department of Energy, Basic Energy Sciences, Office of Energy Research, under Contract No. W-31-109-ENG-38.

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