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Selective bond breaking in adsorbates by core excitations

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Abstract

We survey recent experiments which show that, by excitation of specific core hole states in adsorbates on metal surfaces, selectivity can be obtained in the breaking of bonds. For processes leading to the desorption of ions, strong selectivity arises from neutralization by charge transfer during desorption, which is strongly affected by the coupling to the substrate. However, except for complex multiply excited core excitations ions constitute minority channels; for lower core excitations mostly neutrals are found to desorb. After development of efficient detectors for neutral molecules and fragments we have been able to show that even here selectivity can be found for certain primary excitations for certain bonds to break, even for such simple test systems as N_2 and CO on transition metal surfaces. An analysis of the decay electron spectra seemed to indicate that this may be connected with preferential decay of certain primary excitations into different final state channels. However, since more data have been accumulated and results for N_2 on Ru(001) can now be compared with N_2 on Ni(111), and those of N_2 with CO on Ru(001), it has become clear that even here the effect of the surface by preferential quenching of certain excitations through coupling to the substrate is the overriding factor. Thus the surface influence on selective bond breaking is corroborated for core excitations as well.

1. Introduction

Selective bond breaking is an important goal in chemistry. In molecular photochemistry it should be obtainable because one expects that electronically excited states have different repulsive strengths for different bonds. However, except for large molecules with considerable distances between functional groups it is not easily achieved. For valence excitations this is due to the distributed nature of the final states, as well as to redistribution by vibrational coupling between modes. But even for primary core excitations—for which the initial excitation can be very selectively deposited on a single atom—selectivity is often not obtained [1]. This is due to the fact that in most cases bond breaking is slow compared to core hole decay, so

that the main dissociative action stems from the repulsive potentials between the atoms in the *decay* states (for light atoms with predominating Auger decay: the two-hole or two-hole one-electron states) which again are quite distributed over the molecule; also usually many decay states contribute which evens out their action.

The topic of this report will be the interesting finding that this selectivity of core excitations can be enhanced for surface molecules. In this case there is not just the localized primary excitation and the fast core hole decay; in addition electronic coupling to the substrate can lead to selective transfer of charge and excitation energy. Vibrational coupling to the substrate is less important here because of the high effective mass of the substrate atoms. We will show for very simple test systems, N_2 and CO on close-packed transition metal surfaces, that selectivity results for desorbing particles, i.e. particles produced by bond breaking in the adsorbate complex.

Bond breaking at surfaces leads to desorption of ions as well as of neutrals. This field of electronically stimulated desorption, the surface analogue of molecular photochemistry, is often termed DIET (desorption induced by electronic transitions). The desorbing ions can easily be detected but usually constitute only minority channels; the majority neutrals are much more difficult to detect and therefore have been much less investigated. In the test systems mentioned, for which either molecule adsorbs in a linear way on the surface, two bonds can be broken, the adsorbate bond between the (C or N) end of the molecule and the substrate, and the inner bond of the molecule. An asymmetry between the yields of the respective products (O versus CO or N versus N_2 ; or the corresponding positive ions) then indicates selectivity. The way to deposit the primary core excitation on a particular atom is obvious for CO. For N_2 it can also be achieved because adsorption breaks the symmetry between the two N atoms, which introduces chemical shifts into the core excitation energies, so that the ‘inner’ and the ‘outer’ N atom—with respect to the surface—can be easily excited separately if sufficiently narrow radiation bandwidths are used. The latter have become available in third generation synchrotron light sources with sufficient intensities, which makes not only detection of neutrals, but also detailed measurements of decay electron spectra for selected primary excitations, possible.

The paper is organized in the following way. First we give a short summary of the main facts known about electronically stimulated desorption (DIET) in general [2]. An outline of the methods and apparatus used follows. Then we report data for the desorption of ions, together with some details on their properties. The main emphasis will be on the data for desorption of neutrals. Here we show that a preliminary explanation of the observed selectivity for N_2 on Ru(001) [3], which ascribed it to a predominance of different decay final states for the two N atoms, cannot be upheld in the light of more data. Instead we find that even here the surface plays the main role by selective excitation transfer for the different primary (and thus different secondary) excitations. A summary concludes the paper.

2. General properties of DIET signals from adsorbates on metal surfaces

This field has been actively investigated for almost 40 years, and the results have been summarized in proceedings [4] and special reports by various authors, including ourselves [2]. Therefore only a very brief summary of the main general facts found is needed here; for more detailed information we refer to these papers and the work cited therein.

The main characteristics of the observations for bond breaking in molecules adsorbed on surfaces is their very strong and selective modification compared to free molecules. Bond breaking here is usually observed by particles leaving the surface, although cases are known where the fragments formed all stay on the surface. On metal surfaces this modification consists in decreases of the fragmentation cross section, which can be represented by a quenching

probability, with which the primary cross section has to be multiplied, and which depends on the coupling to the surface. This coupling leads to charge and energy transfer from the localized excitation on the adsorbate to the substrate. Fast charge transfer (which recently has become measurable [5] and has been shown to lie in the range of below 1 fs to some fs, even for weak coupling) leads to the predominance of neutral desorbates; but also the total desorption cross sections are often strongly and selectively diminished. This selectivity is due to the competition between effects favouring delocalization of the primary excitation, with those favouring localization. For the same adsorbate, in most (though not all) cases stronger adsorption eases delocalization and increases quenching, which leads to differences between different adsorption states of the same molecule on the same or on different surfaces. Delocalization is also favoured for dense, ordered layers because of lateral delocalization in the layer, which can lead to distinct coverage effects; defect states, on the other hand, are preferentially desorbed. As to the action of different primary excitations, the strongest quenching is observed for simple single (single-hole, or single-hole–electron) excitations. The deeper the hole, and the more complex the excitation is, the less efficient is usually the quenching. This can be explained by the localization of excitations by correlation, for instance by Coulomb localization in two- (or more-) hole states [6]. Going from single-valence to multiple-valence, to single-core, to multiple-core excitations, the quenching factor decreases and the ratio between effective desorption cross section and primary excitation cross section goes from very small values to unity. The usually much steeper repulsive potentials in the Franck–Condon region for multiple-hole states strengthens this tendency for more efficient bond breaking. Stimulated desorption can therefore be used to investigate in more detail complex excitations with low primary cross sections, because they are strongly amplified relative to simple excitations by these effects.

In parallel, the predominance of neutral fragments decreases in the same sequence; for high multiple excitations essentially only ions, with negligible quenching, are found, and the thresholds for doubly or multiply charged ions are connected with triply or multiply excited states. Measurements of the photon energy (and polarization) dependences have made assignments of primary excitations possible, and those of detailed characteristics of the desorbing species (kinetic energy, internal excitation) have allowed conclusions about the potential energy curves for the excited and ground states of the adsorbates, and have corroborated the interplay of localization and delocalization of the excitations and charges.

3. Experimental techniques

3.1. Excitation sources and detectors

It is on this background that the following results have to be viewed. The main progress in the last 5 years has come about by advances in experimental techniques. The most important advance is the availability of third generation synchrotron radiation (SR) sources, which deliver high brightness light, so that high intensities at small bandwidths can be obtained. This makes inefficient excitation and detector schemes under high resolution possible (low cross section states; energy and angle distribution of decay electrons and ions; detection and further characterization of neutrals). The concomitant development of specialized detectors has been important as well.

Here, the detection of neutral particles is a necessity for surface systems (see above). For DIET by valence excitations with large cross sections, in particular under excitation with electrons or laser photons, large yields of reaction products are usual. State selective optical techniques such as laser induced fluorescence (LIF) or resonant multi-photon ionization

(REMPI) can successfully monitor desorbing molecules, fragments and single atoms [7]. Their potential to resolve electronic, rotational, vibrational and translational product energies allows maximum insight into the microscopic mechanisms of DIET. Although very successful in valence level photochemistry, these methods have not been applied to core excitation studies so far, for several reasons. The most important is that core excitation cross sections are much lower than those of valence excitations. The core excited state, on the other hand, can be very repulsive and create a rich variety of desorption/dissociation products. Most of these products will appear in many different quantum states, and state selective recording will be very time consuming, further hampered by a severe misfit between the duty cycles of storage rings (typically MHz) as excitation sources and high photon flux laser systems (kHz and less) as inevitable analytical tools for state selectivity.

We are optimistic that these obstacles will be overcome and that optical detection of neutrals with the potential of state resolution will be available soon; it will be the optimum choice for future studies of core induced photochemistry (together with coincidence detection schemes). In the meantime, however, alternative, less *specific*, but more *sensitive* approaches appear valuable, e.g. post-ionization by electron impact and mass filtering. Its sensitivity suffices for the use with third generation SR sources. Figure 1 shows a detector arrangement which is used in our laboratory. The light is 7° grazing with respect to the surface for maximum sensitivity. The polarization vector is either fully within the surface plane (A_{xy} polarization) or close to normal (7° off; A_z polarization). The neutral desorbates enter a highly sensitive quadrupole mass spectrometer (QMS) equipped with a liquid helium cooled copper cap around the ionizer. It provides perfect vacuum conditions inside (less than 10^{-14} mbar for all gases except He and Ne, which do not interfere with our measurements), which are necessary for recording the tiny PSD signals with good s/n ratio. It removes all particles (except H_2 , He and Ne) from the ionizer region by condensation and cryo-trapping onto its inner surfaces. H_2 is pumped by Ti getter films deposited onto the inner cold surface of the liquid helium cooled containment [8]. To further decrease the noise, we chop the flux of excitation photons, and process the QMS signal with a lock-in amplifier.

The most severe disadvantage of this method is the strong coupling of fragment and parent signals by cracking inside the ionizer. It can be mastered by careful calibration of the instrument with well known sources, and by operating the ionizer with different electron energies and fluxes which strongly affect the cracking behaviour. First results for CO/Ru(001) were reported in [9]. Since then, considerable progress has been made in sensitivity, which now allows us to detect even 'difficult' particles such as neutral hydrogen atoms [8], and makes measurements under high resolution conditions possible (see below). By pulsed operation of the ionizer and recording of the TOF distribution behind the mass filter, kinetic energies of fragments and molecules are now measurable and can be compared with kinetic energies of the respective ions [10].

Although electron and ion TOF techniques can also efficiently be employed for the determination of ionization edges [11], and for investigations of kinetic energy distributions of emitted ions [10, 12], most studies on electron and ion emission rely on standard, hemispherical electron energy analysers (for spectroscopy), partial electron yield detectors (PEYs; for photoabsorption measurements) and mass spectrometers (for PSD of charged products), respectively, which are well known and need not be discussed here in detail.

3.2. Investigated systems

Since its first observation for an isolated molecule [13] selective bond breaking by core excitation has attracted considerable interest. Gas phase and condensed layer studies revealed

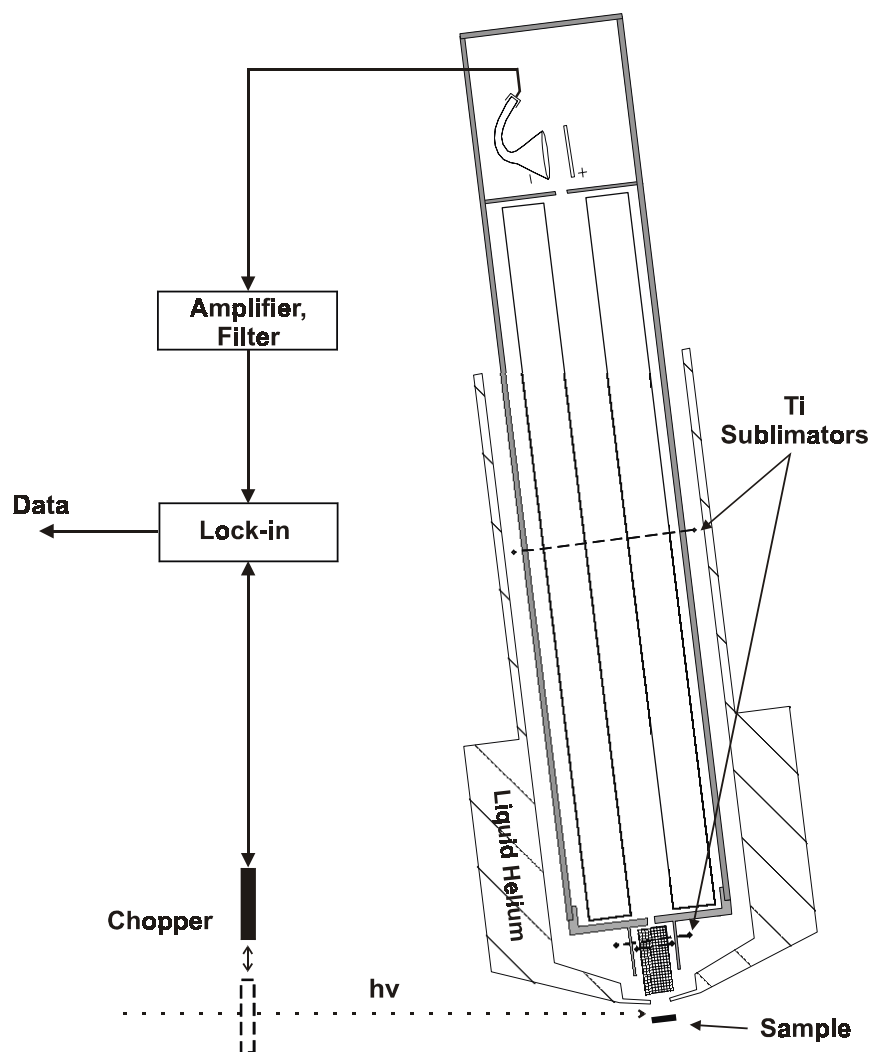


Figure 1. Detector for neutral particles (after [8]; see text for details).

interesting condensation effects [14]. Although elaborate experimental techniques including coincidence methods were employed even for surface systems [15], all experiments were restricted to detection of charged products. Creation of neutrals was only indirectly concluded, e.g. from asymmetries of the ion balance (e.g., see [16] for a study of core induced fragmentation of the H_2O molecule). While reliable for isolated molecules where ions dominate, this approach is ambiguous for condensates, and completely unsatisfactory for chemisorbates on metal surfaces. Because here ions are (often extreme) minority species, no clues on the majority channels can be based on their relative or absolute abundance. Direct detection of neutrals with set-ups such as ours is necessary.

In this overview we focus exclusively on data of chemisorbates on metals, and we choose the simplest existing systems for the investigation of selective bond breaking, namely perpendicularly chemisorbed diatomic molecules, to emphasize the principles. With narrow

bandwidth SR, we excite either the inner or the outer atom and monitor the dissociation/desorption products. Apart from charge, only three different scenarios exist: (i) the surface bond breaks and the intact molecules desorbs; (ii) the intramolecular bond dissociates and the outer atom desorbs; (iii) all bonds are broken and the two atoms are emitted. We study $N_2/Ru(001)$, $N_2/Ni(111)$ and $CO/Ru(001)$ prepared in $(\sqrt{3} \times \sqrt{3})$ layers where all chemisorption sites are equivalent on Ru(001) single-crystal substrates [17], and on (111) oriented single-crystalline Ni films epitaxially grown on the Ru(001) surface [18].

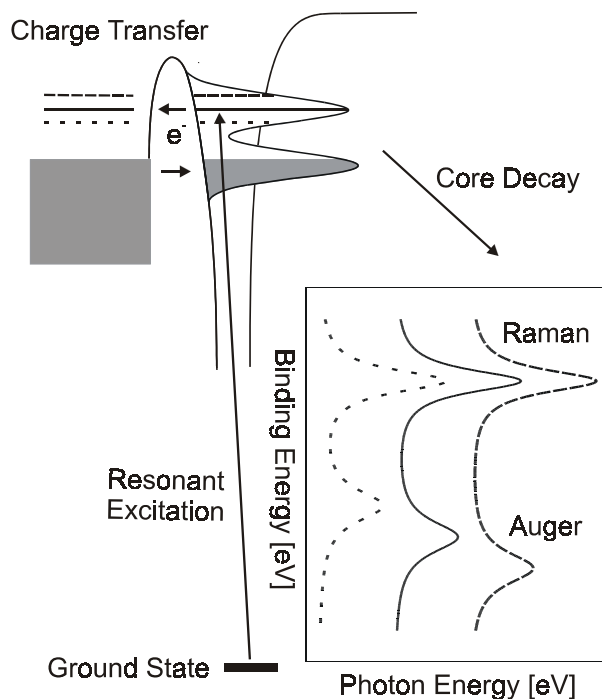


Figure 2. Determination of the lifetime of resonantly excited electrons by the resonant Auger Raman effect. The excited electron's lifetime before tunnelling into the metal (arrow to left) is obtained in units of the core hole lifetime from the ratio of the Raman fraction (at constant binding energy) and the Auger fraction of the decay electrons (at constant kinetic energy; see [5] for details). For the present case of chemisorbed molecules, subsequent charge transfer from the metal at the Fermi level (arrow to right) keeps the adsorbate neutral.

The nature of the chemisorptive bond is very similar for N_2 , CO , and NO on transition metal, and for CO on noble metal surfaces. The inner bond of the isolated molecules is strongly determined by the bonding 1π orbitals (the 2π orbital, empty except for NO , is strongly antibonding), while the upper σ orbitals are essentially nonbonding. The traditional model of the adsorbate bond of these molecules to transition and noble metals is the so-called Blyholder model [19], a frontier orbital model consisting mainly of σ donation and π backdonation; recently the three-centre bond model usually termed the allyl model [20] has been extended to these molecular adsorbates on the basis of x-ray emission spectroscopy (XES) results interpreted with ground state calculations [21–24]. The more sophisticated allyl model can explain more details, such as the distributions of the various hybrid orbitals over the molecule. However, in terms of the interactions important here both bonding models arrive at about the same conclusions, in that the π interaction ($d\pi-2\pi$ in the Blyholder model, or formation of

$1\tilde{\pi}$, $d\tilde{\pi}$, $2\tilde{\pi}^*$ hybrid orbitals in the allyl model) is bonding and the σ interaction (which leads to smaller changes of the unperturbed molecular levels; the lowest unoccupied state (6σ) far above the Fermi level has negligible influence on the surface bond) is antibonding for the adsorbate bond—the changes of the σ system brought about by chemisorption essentially *minimize* this repulsion.

Subtle balancing of these interactions explains why for a large variety of systems ranging from N_2 on transition metals [22] over CO on noble and transition metals [21, 23] to NO on transition metals [24] very similar UPS and XES data are found, and similar orbital schemes are derived. Due to more or less efficient compensation of attraction and repulsion, the chemisorption energies vary considerably (for our systems from 0.3 eV for $N_2/Ni(111)$ [25] and 0.45 eV for $N_2/Ru(001)$ [26] to 1.9 eV for $CO/Ru(001)$ [27]), although the electronic coupling is strong in *all* cases. This strong coupling is seen from the short lifetimes of resonantly excited electrons monitored by resonant Auger Raman measurements as visualized by figure 2. A core electron resonantly excited into the empty $2\tilde{\pi}^*$ orbital (using the allyl nomenclature here) can resonantly tunnel into the metal in less than a femtosecond, and will be replaced even faster by transfer of screening charge into the $d\tilde{\pi}$ orbital (we note that excess charge transfer into the $d\tilde{\pi}$ enhances the $2\tilde{\pi}^*$ admixture, turning it from non-bonding to antibonding; see above. This is particularly important for screening of multi-hole states as obtained by multiple ionization or Auger decay). The lifetimes of the resonance before electron tunnelling obtained from the ratio of resonant/non-resonant decay are nearly equivalent for $CO/Ru(001)$ (0.6 fs for [O 1s] $2\tilde{\pi}^*$ [5]) and for $N_2/Ru(001)$ (0.5 fs for [N 1s] $2\tilde{\pi}^*$ [23]), although the chemisorption energies are different by more than a factor of four.

The bearing of these considerations for our core-excited photodesorption experiments is the following. The core hole lifetimes (around 5 fs in our cases) are too short for important momentum transfer to the atoms, since the gradients of the potential energy of the core-excited states in the Franck–Condon region are rather small (apart from multiply excited states, see below). The electronic states governing dissociation/desorption are then the core hole decay states, which are a collection of (screened) two-valence-hole states; the screening states are always the $d\tilde{\pi}-2\tilde{\pi}^*$ states, which are repulsive for both the molecular and the adsorbate bond. Holes in the $1\tilde{\pi}$ states will be particularly destructive for the intramolecular bond, while σ holes combined with $2\tilde{\pi}^*$ electrons will mainly break the adsorbate-to-substrate bond.

4. Selected results on bond breaking

4.1. Core excitation induced desorption of ions

Ion desorption by selective core level excitation from chemisorbed CO on Ni [28], Ru [29, 30] and Cu [30] were among the first PSD experiments done with SR. These early examples revealed strong selectivity on excitation *type* and excitation *site*. For primary C1s excitation, i.e. allocation of the core hole to the atom close to the surface, only CO^+ ions and no fragments appeared, whereas for O1s excitation CO^+ , O^+ , C^+ and O^{2+} ions could be detected, although with very different shapes of the yield as functions of the photon energy, i.e. of the excitation *type*. The CO^+ signal was largest at the bound π resonance, whereas the fragment signals maximized at multi-hole, multi-electron states at higher energies. The reasons for these findings have been outlined in section 2. Ionic products dominate for the multi-electron states because they are (i) *highly dissociative*, favouring fast bond breaking and escape of the ions before charge transfer from the surface, (ii) *well localized* because of h–h/e–e interaction and (iii) because the cascading decay of their multiple primary holes supplies *enough positive charge* to sustain even rapid neutralization. This is best seen in figure 3, where we compare

the N^+ yields by N 1s excitation from (i) isolated molecules [31], and from N_2 chemisorbed on Ru [3, 32] and Ni [33]. The orientation of the electric field vector E with respect to the molecular axis is always as depicted in the lower right corner of figure 3 (A_{xy} polarization), for the chemisorbates by suitable orientation of the surface and for the gas phase data by alignment of the detector with respect to E .

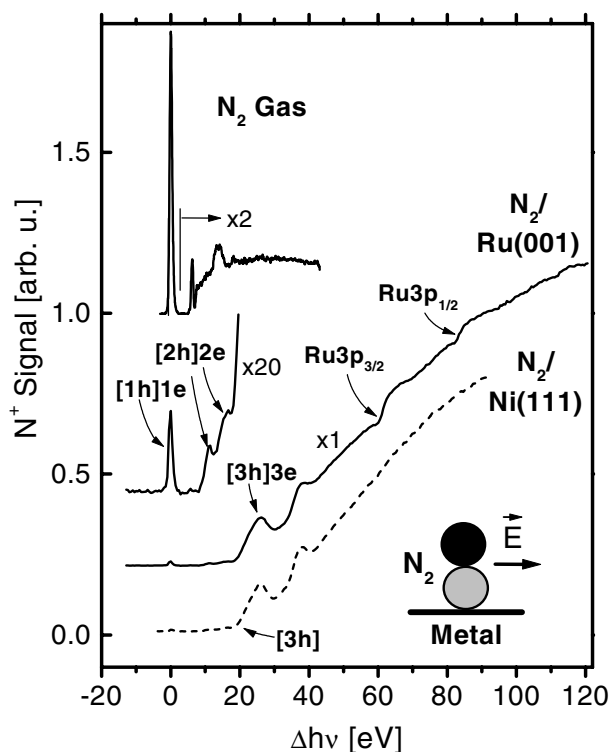


Figure 3. N^+ yield for N 1s excitation with A_{xy} light, from isolated molecules obtained in polarization resolved measurements (top; after [31]), and by N^+ PSD from $N_2/Ru(001)$ [3, 32] and $N_2/Ni(111)$ [33] (excitation geometry as indicated; photon energies with respect to the π resonance).

For isolated N_2 the N^+ yield follows closely the spectral shape of the photoabsorption [31, 34]. The π -resonance is the largest feature, followed by a smaller resonance at about 14 eV higher $h\nu$, which in high resolution studies has been assigned to overlapping [2h]2e states. Note that the σ resonance is not visible in this polarization. These states contain electrons in Rydberg orbitals (the assignments given in [34] are $[N 1s3\sigma_u]1\pi_g3\sigma$ and $[N 1s1\pi_u]1\pi_g3p\pi$ for maxima at 14 and 15 eV beyond the π resonance, respectively) and are (weakly) bound, as apparent from vibrational fine structure found in photoabsorption [34]. Narrow maxima in the range from 5.3 eV beyond the π resonance to the N 1s edge 9.1 eV above belong to [1h]1e Rydberg states with π symmetry [34].

For the N^+ yield from chemisorbed N_2 totally different results are obtained (figure 3). The π resonance and the [2h]2e states at 14 eV above are minor features which become visible only on an expanded scale, as shown; the [1h]1e Rydberg features have vanished. Instead another [2h]2e maximum appears 10 eV above the π resonance, which for isolated N_2 has been assigned by decay electron spectroscopy to a highly dissociative state with mainly

$[N\ 1s1\pi_u]1\pi_g^2$ character, that undergoes ultrafast dissociation (UFD) for the free molecule, i.e. dissociation during the lifetime of the core hole as pinpointed by the appearance of atomic decay lines ([35], see [32] for more details of PSD, and [36] for calculated term energies and oscillator strengths of these multi-electron states). All these maxima are small, however. The dominating features of the N^+ signal are broad peaks superimposed on an increasing background which sets in at 20 eV above the π resonance. Following previous results for PSD of chemisorbed CO [30], we have assigned the primary electronic states underlying these desorption phenomena to bound and continuum $[3h]ne$ states [32]. Their excitation cross section is very small, making their direct detection in XAS nearly impossible. Access is made possible by PSD, as seen from figure 3.

Comparing the N^+ spectra for Ni and Ru we clearly see that the obtained maxima are purely molecular features which do not depend on the substrate, either in shape or in energetic position. The only substrate induced features are structures at substrate core thresholds, such as the Ru 3p maxima in figure 3; for Ni(111) even clearer structures exist at the Ni 2p edges. Because these substrate induced features of the N^+ yield exhibit Fano-type line profiles (the Ni 2p edges beyond the energy range of figure 3 appear as dips and not as maxima) they are assumed to be due to interatomic core hole coupling [37], a process which in photoemission spectroscopy has been denoted MARPE (multi-atom resonant photoemission [38]). They cannot be explained fully by x-ray optical effects; their coupling mechanism is not understood at present.

Before continuing this survey with DIET of neutrals, we summarize what insights can be obtained by monitoring ions from electronically stimulated reactions of chemisorbates. Ions show strong selectivity on excitation site and excitation type. Kinetic energy distributions of ions can easily be measured by analysers based on TOF or electrostatic particle deflection, and their evaluation can help to discriminate primary electronic states, and to clarify microscopic details of the bond breaking process. Particularly highly dissociative multi-hole/multi-electron states tend to be strong in the ion signals. This is a consequence of the different steps involved in the DIET process. The cross section for desorption of ionic species can be written as

$$\sigma_{des,i} = \sum_j \sigma_{pr,j} P_{esc,i,j}$$

with the desorption cross section $\sigma_{des,i}$ for the product species i , the primary excitation cross section $\sigma_{pr,j}$ for the electronic state j and the escape probability $P_{esc,i,j}$, which represents the probability that an excitation event of state j leads to a desorption event in channel i . For branching into ionic channels, $P_{esc,i,j}$ can be written as the product of two probabilities, namely $P_{dis,i,j}$, which denotes the probability that the relevant bond is broken, and $1 - P_{neu,i,j}$, standing for the probability that the product particle is not neutralized. From the above considerations it is clear that $P_{dis,i,j}$ as well as $1 - P_{neu,i,j}$ approach unity for highly dissociative and highly charged primary states.

This shows that PSD can be a versatile tool for the spectroscopic investigation of these states, particularly if their excitation cross sections are too small for standard techniques. The strong selectivity on site and state would, however, be of practical relevance only if competing channels with appreciable cross sections leading to neutral products were absent, as found for isolated molecules. Determining integral selectivity requires the analysis of the balance of *all* reaction channels. If those of highest product abundance are neglected, no reliable clues about overall selectivity can be obtained. Even extreme selectivity is of negligible practical importance if it exists only in sub-percent channels.

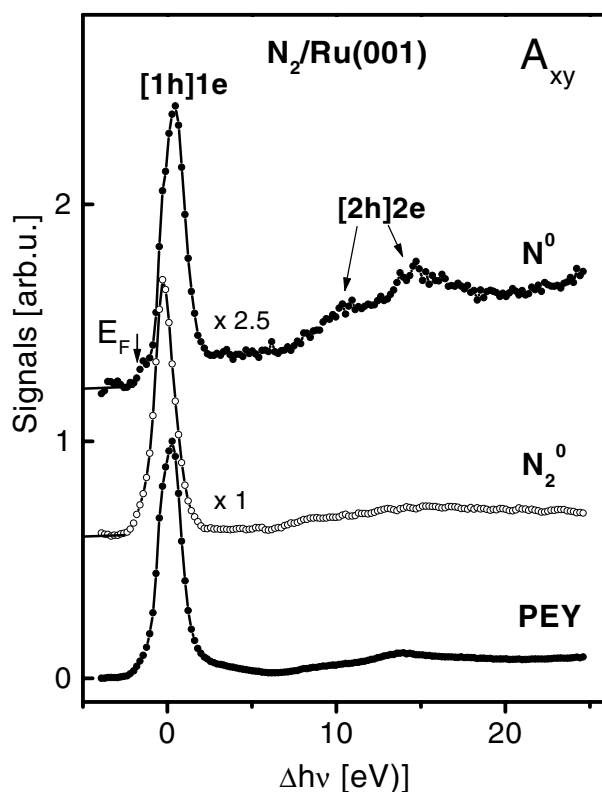


Figure 4. PSD yield of neutral N_2 and N from $N_2/Ru(001)$. E_F denotes the position of the Fermi edge. Photon energies with respect to the π resonance $[N\ 1s]2\pi^*$. The $[2h]2e$ states at 10 eV, 14 and 15 eV above $[N\ 1s]2\pi^*$ are well known from spectroscopy of isolated molecules (see text).

4.2. Core excitation induced desorption of neutrals

4.2.1. Low spectral resolution experiments. Any reaction products missing in figure 3 must be neutrals (multiply charged ions are negligible, see [32]). Figure 4 displays the yields of neutral N_2 and N from $N_2/Ru(001)$ obtained with the apparatus of figure 1 by excitation with a photon energy bandwidth of about 0.5 eV. The x-ray absorption spectrum (XAS) measured with a partial electron yield (PEY) is also depicted in figure 4. Comparing figures 3 and 4, we find the spectral shapes of the neutrals desorbing from the chemisorbate much more closely related to the N^+ yield from the isolated molecule than to the N^+ yield from adsorbed N_2 . The π -resonance dominates in neutral DIET, as it does in XAS. When detecting neutrals we do not monitor minority channels, firstly because the sensitivity of our detector for neutrals is much smaller than that for ions (we can detect single ions, but need at least 10^9 desorbing neutrals per second for the s/n ratio of figure 3), and secondly because the spectral shapes of the neutral yields now mimic the XAS behaviour of the main $[1h]1e$ channel and not of low cross section multi-electron states. There are, however, indications that the escape probability particularly for N atoms is smaller than unity for π -resonant excitation of N_2/Ru . One point is that the N atom yield is smaller than the N_2 yield by a factor of 2.5, and the other that the $[2h]2e$ states known from figure 3 are enhanced with respect to XAS in the N , but not in the N_2 yield from $N_2/Ru(001)$ (figure 4). For $N_2/Ni(111)$ the yield ratios are different. Here, the N and

N_2 signal amplitudes are practically identical at the $[N\ 1s]2\pi^*$ resonance (compare figures 5 and 7 below), and the escape probability is not enhanced for the $[2h]2e$ states. We will come back to this observation below.

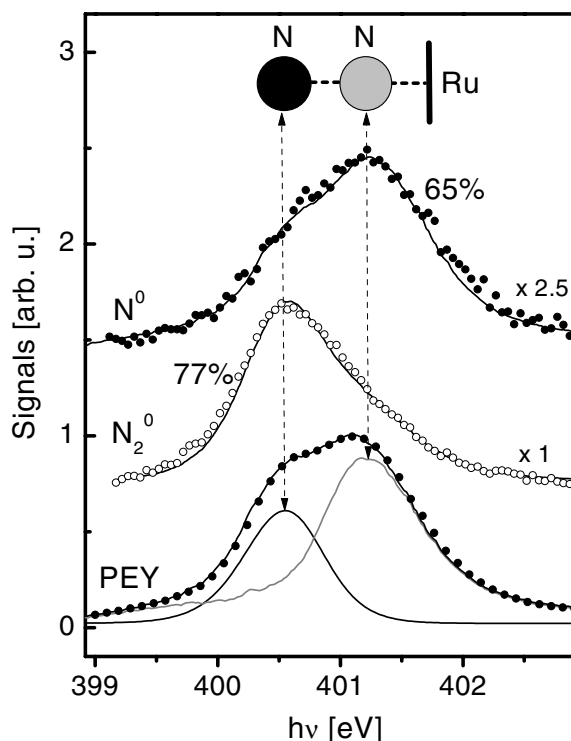


Figure 5. Photoabsorption (measured by partial electron yield, PEY), and photodesorption (PSD) of neutral N_2 and N , for π -resonant excitation of $N_2/Ru(001)$ with narrow band excitation conditions (after [3]). The scatter symbols denote the experimental data, the full lines are linear combinations of the curves of selective photoabsorption by the outer (lower photon energy) and the inner (higher photon energy) N atoms, with the weight factors given as percentages. The decomposition of the integral PEY curve into the contributions of the individual atoms is derived from decay electron spectra under atom selective excitation (figure 6; see [3] for details).

4.2.2. High spectral resolution experiments. First we consider $N_2/Ru(001)$. In figure 4 the peak shapes of the π resonance are different in XAS, and in PSD of N and N_2 . Details are resolved in high resolution measurements with 0.15 eV photon bandwidth, which are depicted in figure 5. All curves are composed of two components with varying weights. These components are due to selective excitation of the inner or the outer N atom as shown in figure 5. For the inner atom, the π resonant excitation energy is larger by 0.7 eV than for the outer atom. The assignments of inner/outer atom are based on the ordering of the XPS binding energies determined by photoelectron diffraction (see [3] and references therein), and on decay spectra of chemisorbed N_2 and CO utilizing the $Z + 1$ approximation. Comparing $C\ 1s$, $O\ 1s$ and $N\ 1s$ decay spectra [23] with the $N\ 1s$ data taken at the energy positions of the two XAS maxima (figures 5 and 6), we find close correlation between those from the $C\ 1s$ and the lower photon energy $N\ 1s$, and between those of the $O\ 1s$ and higher energy $N\ 1s$ excitation. With the $Z + 1$ analogy depicted in figure 6, we arrive at the above assignment in agreement with

the photoelectron diffraction data. Nearly identical spectroscopic results have been obtained before for $N_2/Ni(100)$ [39]. By analysing the amplitudes of the individual contributions to the decay spectra as a function of $h\nu$, we decompose the XAS curve into the contributions of excitations of the inner and outer atom (figures 5 and 6).

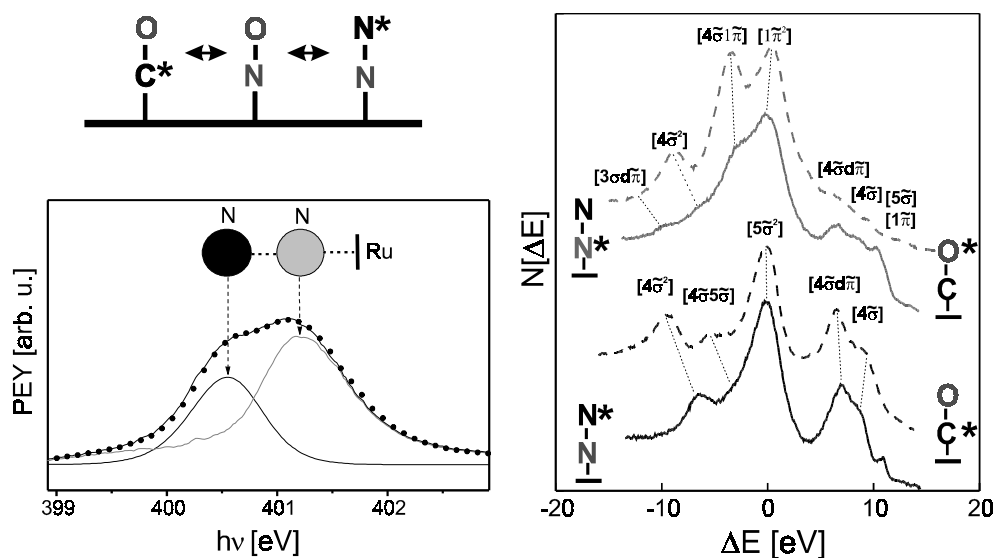


Figure 6. Top, left: $Z+1$ analogy for core excited N_2 and CO. Right: comparison of decay spectra of CO/Ru(001) for C 1s and O 1s excitation, and of N_2 /Ru(001) for excitation of the inner/outer N atoms at the energy positions indicated in the XAS spectrum at bottom, left (the N_2 and CO decay spectra, taken from [23], are aligned at the main peaks).

We can now carry this decomposition over to the desorption data. Fitting the PSD curves by linear combinations of these two components reveals selectivity in the excitation site. For excitation of the *outer* atom, desorption of the *intact* molecule is pronounced (to 77%), whereas excitation of the *inner* N preferentially *breaks* the molecular bond (to 65%). We cannot tell as yet whether the substrate bond breaks as well for the latter, i.e. whether one N atoms stays at the surface or whether both are desorbed (to discriminate between these alternatives would require precise determination of residual N, which is difficult because of the very small fraction of the adsorbed nitrogen which is desorbed under high resolution conditions. We expect, however, that breaking the strong molecular bond will break the weak adsorbate bond as well with high probability). In any case, the selectivity is clearly opposite to that naively expected for local bond breaking at the site of excitation.

In a previous publication [3] we have shown that it appeared possible to trace this reaction selectivity back to excitation-site-dependent differences in the evolution of the electronic states. We assumed the following.

- (i) No major contribution of the primary core excited state itself to the dissociation dynamics because the π resonance is a bound state, which contributes only a few vibrational quanta to the kinetic energy of the fragments that is necessary to overcome the dissociation barrier.
- (ii) Instead, the highly excited valence states reached after core decay were considered to be the sources for acceleration of the nuclei. Although unambiguous pinpointing of correlations between bond breaking and electronic decay would require coincidence techniques, which are available for ions and electrons, but not yet for neutrals and electrons, we assumed

that correlating the main channels in desorption and the main channels in electron decay was justified because neutrals are majority species.

- (iii) We furthermore neglected selectivity imposed by the surface apart from the asymmetry induced in hole decay by adsorption, as compared with the isolated molecule (see above).

On this basis we concluded that the selectivity seen in the data of figure 5 can be explained by the different post-decay states which prevail for π -resonant excitation of the inner and the outer N atom, respectively. Figure 6 shows that for excitation of the inner atom (N_i or C) mainly states with single or double holes in the all-bonding 1π state result, whereas for excitation of the outer atom (N_a or O) mainly holes in the σ states are formed, which contribute much less to the intramolecular bond. Considering the electronic nature of the N_2^- (and CO^-) surface bond outlined in section 3.2, and allowing for the overall antibonding action of additional screening electrons in the $2\tilde{\pi}^*$ orbital, an explanation of the selectivity seen in figure 5 on the basis of decay data appeared very plausible. However, this simple picture has been shaken by subsequent measurements which showed that, while assumptions (i) and (ii) above are likely to be warranted, (iii) is not.

Now we consider $N_2/Ni(111)$. Figure 7 displays high resolution PSD data from $N_2/Ni(111)$, corresponding to those from $N_2/Ru(001)$ of figure 5. The spectral shapes of the XA spectra are very similar for nitrogen on the two substrates, apart from the slightly larger splitting of 0.86 eV of the two components belonging to the outer/inner N atoms, compared to 0.7 eV for $N_2/Ru(001)$. However, the strong excitation site-dependent selectivity seen in N_2 and N PSD for the Ru substrate has now nearly vanished. While a trend in the same direction is still noticeable, the differences are by far less pronounced: the N_2 yield is still somewhat increased for excitation of the outer atom, and the N signal is larger for excitation of the inner, but the strong asymmetry obtained for N_2/Ru is reduced to a few per cent. Following our preliminary interpretation of the Ru results, one would have to assume a reduced selective branching into the various *post-decay* states for this system, to explain these surprising differences.

Such an effect was, however, disproved by further measurements. Decay spectra from $N_2/Ru(001)$ and $N_2/Ni(111)$ measured at an emission angle of 45° (where decay electrons for *all* probable symmetries of final states can be detected [40]) are *nearly identical* for the two substrates (figure 8). Small differences are only seen for final states including $[d\tilde{\pi}]$ holes, i.e. holes in that orbital which is most sensitive to variations of the metal density of states, but not in the final states with $[1\tilde{\pi}]$ and $[1\tilde{\pi}^2]$ contributions, which we considered as the main sources of dissociation.

Comparing the Ni and Ru results we have to conclude that although the dissociative nature of the post-decay states *may* influence the branching behaviour seen in the PSD experiment, *additional* processes must exist which influence it to a comparable or even predominant extent. Two mechanisms appear likely to perturb the simple molecular picture sketched above. First, we have to consider that the electronic decay may not stop at the first step after core hole decay, but may proceed in further cascades, particularly for double-hole states with higher binding energy. The large line widths commonly obtained in decay spectra from chemisorbates on metals, which indicate short lifetimes of the post-hole states, provide strong evidence for the existence of multi-step decay. Second, we have to take into account that the strong quenching of electronic states by the metal substrate can magnify small differences in branching ratios. This second effect is well known from the MGR model [41] and best demonstrated by the enhancement of the isotope effect on desorption cross sections by low escape probabilities P_{esc} [42]. It simply means that for absent quenching all channels i targeting a distinct product j may succeed, even if some channels are better suited than the rest because of more rapid progression on the reaction co-ordinate (either because of lower mass as in the case

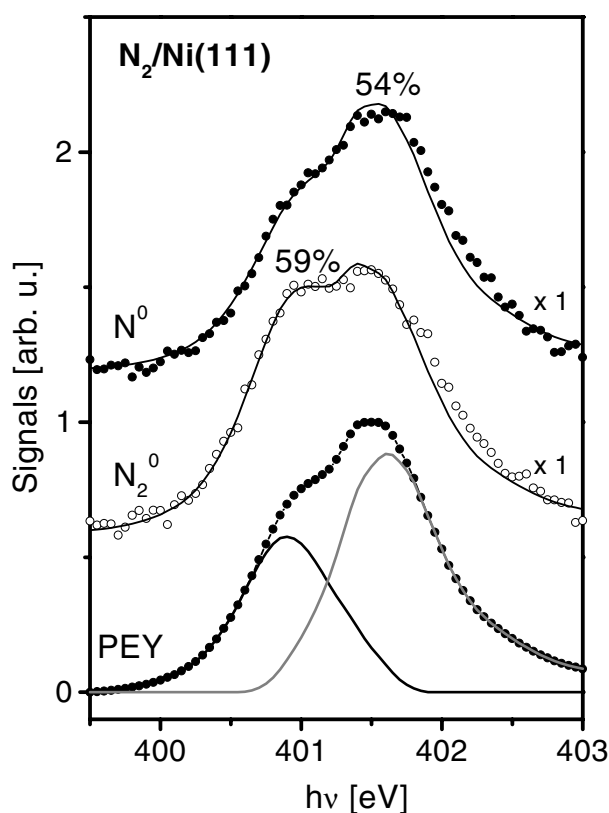


Figure 7. Photoabsorption (PEY), neutral N_2 and N PSD for π -resonant excitation of $N_2/Ni(111)$ under high spectral resolution conditions [33]. Symbols, lines, and decompositions are as in figure 5.

of the isotope effect, or because of steeper potential curves, faster acceleration of the nuclei and higher product energies). However, if dissipation processes—such as substrate-induced quenching—exist, then the better suited channels are favoured.

We believe that such an influence of the surface involved governs the different selectivity seen for Ni and Ru to a large extent. We base this interpretation particularly on the fragment results. For N_2/Ni the relative amplitude of the N^0 signal is larger than for N_2/Ru , and enhanced dissociation by the highly dissociative $[2h]2e$ states compared to π -resonant excitation—which is seen for Ru in figure 4—is absent. The escape probability from Ni must be closer to unity, therefore, and the selective enhancement of strong channels must be reduced. As soon as absolute numbers for $P_{esc,i,j}$ are available from future experiments, a quantitative modelling of this surface effect will become possible.

Next we consider $CO/Ru(001)$. CO chemisorbed in a $(\sqrt{3} \times \sqrt{3})$ layer on $Ru(001)$ is our last example; it provides a second argument against the simple decay channel picture proposed in [3]. As mentioned above, chemisorbed CO was one of the first systems for which core induced bond breaking was investigated with synchrotron radiation [28]. For C 1s excitation of $CO/Ru(001)$, no fragment ions in the desorption signal were found [29,30]. Figure 9 compares PSD of neutrals at the C 1s and O 1s π resonances [43]. At the $[O\ 1s]2\pi$ resonance O atoms and CO molecules desorb at a ratio of about 1:2 (the factor of 0.7 at the O trace includes

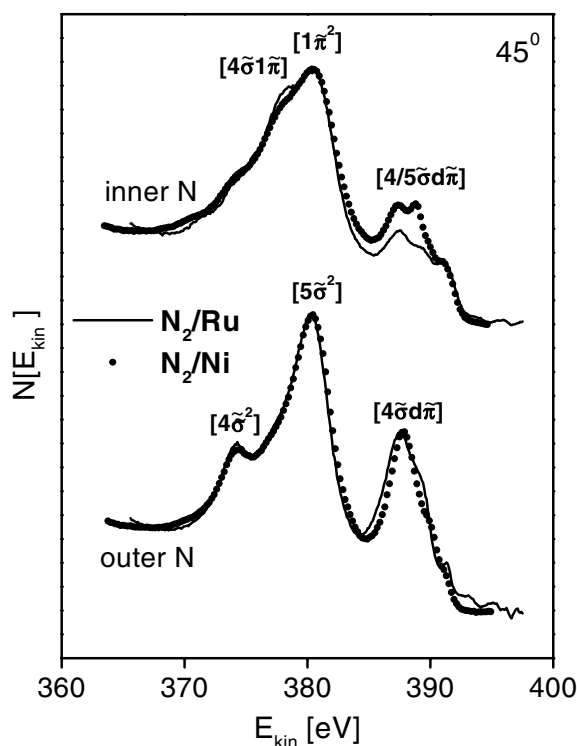


Figure 8. N 1s decay spectra for $N_2/Ru(001)$ (full line) and $N_2/Ni(111)$ (dots; aligned at the main maximum) for core excitation of the inner (top) and the outer N atom (bottom), recorded at 45° with respect to the surface normal [33].

different detector sensitivities due to different product velocities [10]; for C 1s excitation no such kinetic energy data are available as yet. We also note that O 1s data obtained with an earlier, less refined version of our detector [9] were in full agreement with the most recent results, apart from their inferior signal/noise ratio). At the $[C\ 1s]2\pi$ resonance, fragment and molecule yields are practically identical. This result is surprising for two reasons.

- (i) It differs qualitatively from that obtained for ions, where at the O 1s edge the O^+ fragment ions prevail in desorption, and at the C 1s edge the molecular ions.
- (ii) It is also unexpected on the basis of the nitrogen results and the molecular decay picture of [3]. For N_2/Ru and N_2/Ni the fragment signal was largest for excitation of the inner atom, although strongly modulated by surface effects. Here the relative contribution of the fragment signal also maximizes for excitation of the inner atom as well, but this is *against* the expectation derived from the equivalent core picture. Figure 6 clearly shows that the decay spectra of excitations at the C are correlated to those for the *outer* N atom, and of those for the O of CO to those of the *inner* N atom. We again encounter a situation where assumptions based on molecular properties are *not* corroborated by experiment, and strong modifications by surface effects are obvious, which here not only change the amplitude of selective enhancement of distinct channels, but invert their ratios. The fragmentation efficiency of the $[C\ 1s]2\pi$ resonance clearly violates the $Z + 1$ analogy (the validity of which, however, is weakened here by the fact that only the electronic properties of the molecules were considered, and not their changes by the surface bond).

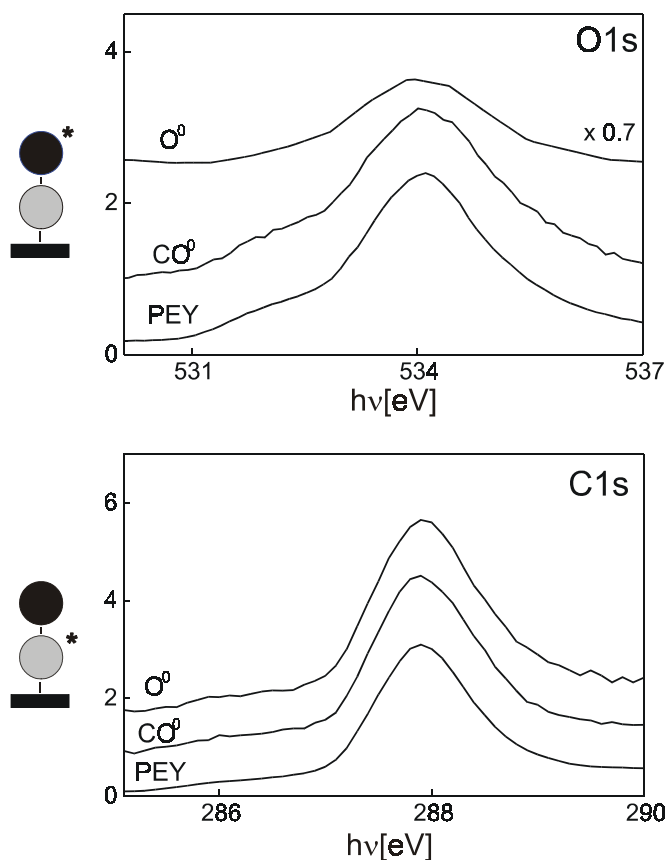


Figure 9. O⁰ and CO⁰ PSD from CO/Ru(001) for O 1s (top) and C 1s (bottom) excitation (from [43]; the factor of 0.7 takes differences in kinetic energies into account [10]; for C 1s excitation no kinetic energy data are available).

5. Conclusions and summary

Although the present data do not suffice to fully explain the physical reasons for the striking differences of the N₂ and CO results, we can clearly state the existence of strong surface effects in selective bond breaking by core excitations of adsorbed molecules. We can safely exclude that the branching ratio of bond breaking at the π resonance, i.e. induced via core states which by themselves are not dissociative, is governed *exclusively* by the first step of the electronic evolution after core decay—in this respect we have to revise our initial explanation. The strong additional influence of the surface became clear from the nitrogen results on two surfaces, where the *more strongly* bound adsorbate (N₂/Ru(001)) exhibited *larger* selectivity. For CO the agreement of fragmentation data and assumptions based on decay spectroscopy alone is even worse. Modification of the branching by further, hitherto unrevealed steps in the decay cascade are likely. We expect those to show up in the shake-off electrons at the very low energy end of the electron spectrum, which is best accessed by TOF methods. Strong surface effects are expected for these states as well. We believe that our results convincingly demonstrate the importance of the investigation of neutral desorption products.

Summarizing our findings, we want to close with a recipe. For optimum selectivity in bond breaking by core (and certainly also by valence) excitations we have to search for

- stimulated reactions with channels leading to distinct products that are proceeding faster than others,
- dissipation processes which favour the fast channels, e.g. quenching due to geometrical vicinity of the (metal) surface, and
- limited dissipation in order to get sufficiently high yield.

Obviously the two last points contradict each other, so compromises have to be struck, and it might be difficult to simultaneously fulfil all criteria for a particular system.

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