Determination of Time Scales for Charge Transfer Screening in Physisorbed Molecules

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Using photoionization, photoabsorption, and deexcitation spectroscopies the dynamics of the N $1s$ core-hole states for N_2 physisorbed on graphite has been investigated. In the photoemission spectrum only the ionic $1s^{-1}$ state is observed. The Auger spectrum shows decay from both this ionic and a neutral $1s^{-1}1\pi_g$ intermediate state created by charge transfer from the substrate. The neutralization occurs with a characteristic time $\tau_{CT} = 9 \times 10^{-15}$ s. The coupling with the substrate is weak, preserving the gas phase triplet-singlet splitting of the neutral intermediate state.

The adsorption of molecules on solid surfaces is an important field of surface science. The electronic states of the molecules and the substrate may overlap substantially, causing strong hybridization and bonding—chemisorption. In other cases the overlap may be very small, resulting in almost free-molecular-like adsorbates—physisorption. Physisorbed molecules retain many of their properties from the gas phase. However, some unique dynamic effects related to the weak interaction in physisorbed overlayers have been demonstrated recently [1–3]. In this paper we will present novel results from this interesting area of weak-coupling physics.

The electronic structure of adsorbates is probed by a variety of spectroscopic techniques such as x-ray photoelectron spectroscopy (XPS), x-ray absorption spectroscopy (XAS), and Auger electron spectroscopy (AES). For the utilization of these and for the understanding of the relationship between them it is essential to have good knowledge about the dynamics of the ionization, excitation, and deexcitation processes. For chemisorption systems, the interpretation of XP spectra has been controversial. Starting from the weak-coupling limit, models have been developed which interpret the main and satellite lines as being due to screened and unscreened final states, respectively [4,5]. Alternatively they have been described as configuration interaction states starting out from a larger set of adsorbate-substrate hybride orbitals in the final state [6,7]. Important information about the core-hole dynamics has been obtained from investigations of the deexcitation spectra. In the case of strong adsorbate-substrate hybridization it has been concluded that the charge transfer screening is complete on the time scale of the core-hole decay [8–10].

In the present Letter we show that physisorbed molecules provide ideal systems for obtaining information on the core-hole dynamics. The coupling strength is such that it highlights the different characteristic time scales of the different spectroscopies. For N_2 on graphite no charge transfer screening occurs in the primary photoionization event. However, in the core-hole decay spectra, Auger processes starting from screened initial states are unambiguously identified. These states are observed to be exchange split due to the interaction with the open core. The characteristic time for the charge transfer screening is determined to be $\tau_{CT} = 9 \times 10^{-15}$ s. The present results provide important input for, e.g., calculations of the neutralization cross section in surface ion scattering.

The experiments were performed at the MAX Synchrotron Radiation Facility [11], using a photon energy resolution of 0.1 to 0.3 eV and an electron energy resolution of 0.3 eV. The sample, highly oriented pyrolytic graphite (HOPG), was cooled with a liquid-helium–flow cryostat to less than 25 K. One monolayer of nitrogen molecules was physisorbed in a phase with the molecular axes parallel to the surface [12].

Figure 1 compares XA and XP spectra for N_2 on graphite. The spectra are shown on a common energy scale referring to the photon energy for the XA spectrum and the binding energy relative to the Fermi level for the XP spectrum. It is immediately seen that the XAS peak appears at lower energy than the XPS peak. The XAS peak at 401.0 eV is due to the excitation of a $1s$ electron to the lowest unoccupied orbital, $1\pi_g$, in N_2. The fine structure corresponds to individual N_2 vibrational states. A fully screened XPS final state, neutralized by the transfer of an electron from the substrate to the $1\pi_g$ orbital, would have an energy corresponding to the x-ray absorption threshold [13]. Hence, the XPS final state at 403.9 eV is not the lowest possible core-hole state. It is a $1s^{-1}$ ionized state with no charge transfer screening from the substrate but screened by the image potential [14]. No peak is seen at the binding energy of the screened final state, and an upper limit of 1% of the main peak intensity can be given for this state.

The core-hole states will mainly deexcite by Auger-type processes. The core ionized (XPS) state leaves two vacancies in the valence region. For the core excited (XAS) states the decay takes place in the presence of an additional valence electron. If this electron takes part in the Auger decay the process is referred to as a participator transition, and the final state is a similar one-hole state as created in valence-band photoemission. If, on the other hand, the additional electron is not directly involved
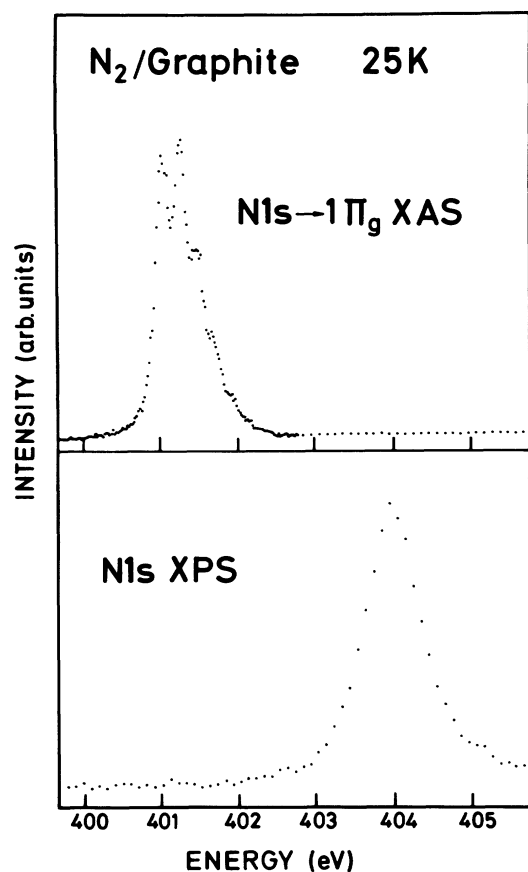
FIG. 1. The N $1s$ to $1\pi_g$ x-ray absorption and N $1s$ x-ray photoelectron spectra of one monolayer N_2 physisorbed on graphite. The energy scale is the difference between the initial and final states; photon energy for XAS and binding energy is relative to the Fermi level for XPS.

FIG. 2. N $1s$ hole decay spectra of N_2 [15]. 401.0-eV photon energy corresponds to excitation to the $1s^{-1}1\pi_g$ intermediate state, while 500-eV photon energy corresponds to the $1s^{-1}$ intermediate state. Generalized final-state configurations are given for the Auger and autoionization processes.

in the decay the process is denoted a spectator decay. These two processes will henceforth be denoted autoionization.

Figure 2 compares the decay spectra for four different situations: an autoionization spectrum of N_2 on graphite excited at the $1\pi_g$ resonance, the corresponding Auger spectrum after core ionization at higher photon energy, an Auger spectrum for N_2 which has been physisorbed with a double spacer layer of Ar between the N_2 and the substrate, and finally an Auger spectrum for N_2 in the gas phase [15].

The autoionization spectrum of N_2 on graphite, recorded at the $1\pi_g$ resonance (401.0 eV), is very similar to the gas phase autoionization spectrum [16,17]. The twin peaks at 390.3- and 391.3-eV kinetic energy correspond to the $1\pi_u^{-1}$ and $3\sigma_g^{-1}$ states, respectively, created by participator transitions. At lower kinetic energies we find mainly two-hole–one-particle final states formed by spectator transitions [18].

The shape of the gas phase KLL Auger spectrum [19], shown at the top of the figure, is completely different
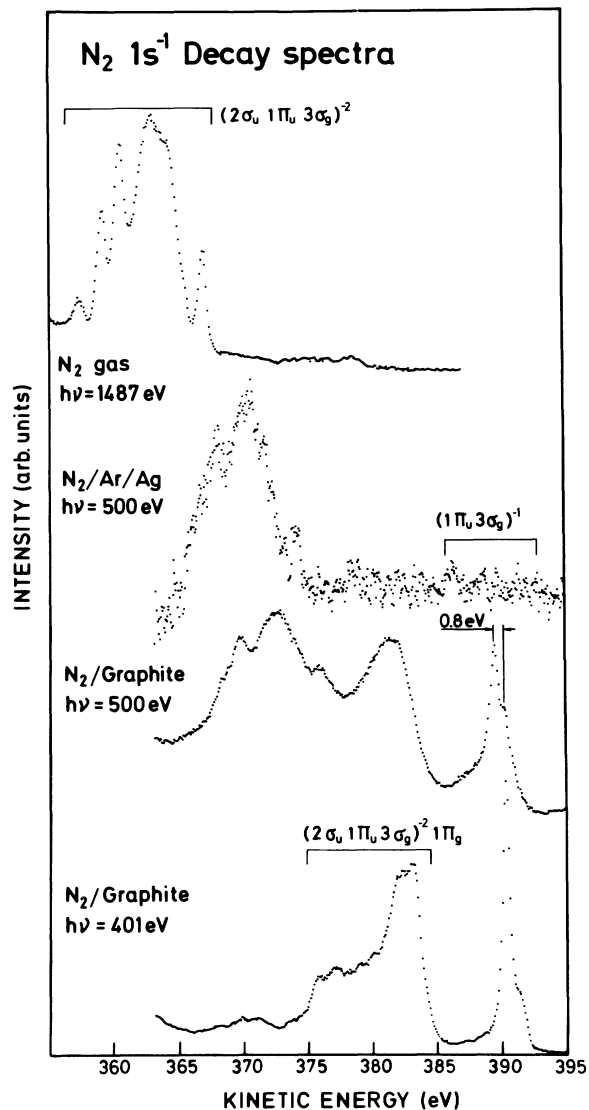
from the autoionization spectrum since the initial state of the core-hole decay is now a $1s^{-1}$ ionic state. The main intensity is found around 363-eV kinetic energy, approximately 20 eV lower than in the corresponding (spectator) transitions in the adsorbate autoionization spectrum. This decrease in kinetic energy is due to the different reference energies [15], the presence of the spectator electron, and the substrate screening for the adsorbed molecule [14].

The Auger spectrum of N_2 adsorbed on a surface with a spacer layer of Ar [Ag(110) was used in this experiment instead of graphite for practical reasons; this is of no consequence for the argument] is dominated by a

strong feature at 370 eV. This spectrum resembles the gas phase spectrum. It is only shifted by about 7 eV in the figure due to the different reference levels for the spectra [16] and to the polarization screening for the adsorbate [20].

Turning now to the N_2 on graphite Auger spectrum it is immediately clear that it contains spectral features typical for both autoionization and Auger transitions. At 390-eV kinetic energy a feature reminiscent of the $1\pi_u^{-1}$ and $3\sigma_g^{-1}$ single-hole final states is observed. Note, however, that this part of the spectrum is shifted down by 0.8 eV relative to the resonantly excited spectrum (401.0 eV). Around 373-eV kinetic energy, peaks are seen which have to be identified with free-molecular-like N_2 Auger transitions. The kinetic energy is 3 eV higher than for the corresponding transitions in $N_2/Ar/Ag(110)$, due to differences in work function and image potential screening [15,20]. We can thus identify two distinctly different parts in the spectrum: one due to transitions from a neutral $1s^{-1}1\pi_g$ state, and another one due to transitions from an ionic $1s^{-1}$ state. The latter part of the spectrum contains $(38 \pm 5)\%$ of the intensity. Since no neutral state was seen in the XP spectrum, the neutralization must occur after the primary ionization but on the time scale of the $1s$ hole lifetime. From the disappearance of the autoionization features when the N_2 molecules are separated from the substrate by the Ar layers it can be concluded that the electron comes from the graphite substrate and not from the surrounding molecules in the N_2 overlayer.

The charge transfer screening electron goes into the $1\pi_g$ orbital, which is the only unoccupied orbital of the ionic molecule below the Fermi level of the substrate. There is, however, a significant difference in the 390-eV region between the resonance spectrum and the spectrum excited at higher energies. The autoionization part of the spectrum can be decomposed into two parts, one weaker component identical to the resonance spectrum, and another dominating one shifted by 0.8 eV to lower energies. We attribute this to the exchange interaction in the $1s^{-1}1\pi_g$ configuration which leads to a splitting into singlet and triplet states. In the photoabsorption process only the singlet state is populated due to dipole selection rules. However, the triplet state has been identified at 0.83-eV lower energy by electron-energy-loss spectroscopy [21]. This agrees excellently with our observed splitting. The observation of the exchange splitting shows that the hybridization of the $1\pi_g$ orbital to the substrate is very weak $(\Delta \ll 0.8$ eV) as expected in the case of physisorption.

From the relative intensities of the neutral and ionic decay processes in the adsorbate Auger spectrum the neutralization rate can be determined. If we assume an exponential Auger decay of the core hole governed by the lifetime τ_Γ, and an exponential neutralization governed by the charge transfer time τ_{CT}, it is straightforward to

see that the probability for Auger decay from the neutralized state is given by the ratio $(1 + \tau_{CT}/\tau_\Gamma)^{-1}$. The lifetime τ_Γ of the core hole is 5.5×10^{-15} s $(\Gamma = 0.12$ eV) for free N_2 [22,23]. This yields a neutralization time $\tau_{CT} = 9 \times 10^{-15}$ s $(\pm 25\%)$. This can be compared to the similar charge transfer processes in ion neutralization spectroscopies, which yield typical neutralization times for ions incident on surfaces of the order of 10^{-15} s [24].

The neutralization time corresponds to an interaction width (Δ_{CT}) of 0.07 eV. In the Gunnarsson-Schönhammer model [4,8] the intensity ratio between the $1s^{-1}1\pi_g$ (screened) and $1s^{-1}$ (unscreened) states in the XP spectrum is determined by the hybridization width V and the energies of the screening level relative to the substrate levels in the initial and final states. Δ_{CT} has two contributions, one related to the hybridization width and another due to the adsorbate-substrate Auger process. This makes Δ_{CT} an upper limit to the hybridization width. Using $V = \Delta_{CT}$ yields a screened fraction of less than 0.001 in the XP spectrum [25], well below the experimental upper limit of 0.01.

In summary, we have shown that the neutralization of the $1s^{-1}$ core-hole states for N_2 on graphite occurs by charge transfer screening from the substrate on the time scale of the core-hole decay. This demonstrates the necessity of using a two-step model for the Auger process in these weakly coupled systems. The weak coupling of the screening level to the substrate makes the screened state invisible in the primary ionization spectra. Another manifestation of the weak coupling is that the orbital retains its molecular character and exchange split states are seen.

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