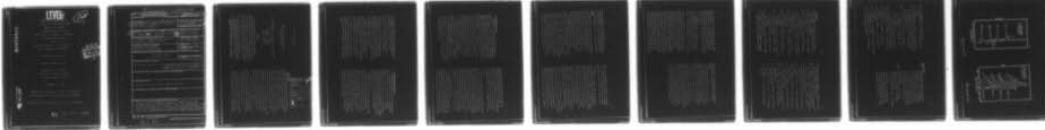


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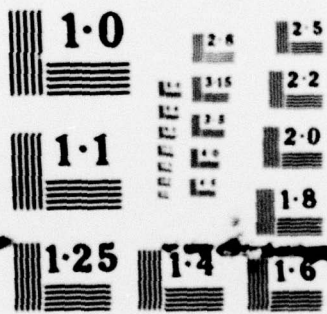
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Auger Spectra of Ammonia on Aluminum  
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by

Charles T. Campbell, J. W. Rogers, Jr.,  
R. L. Hance and J. M. White

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Auger Spectra of Ammonia on Aluminum  
and Oxidized Aluminum (a)

Charles T. Campbell (b) J. W. Rogers, Jr. (c) E. L. Hance (d)  
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Abstract

X-ray excited (KVV) Auger spectra are reported for submonolayer amounts of ammonia adsorbed at 128K on clean and oxidized polycrystalline aluminum. The spectra were deconvoluted using an instrument function derived from the measured losses associated with the  $M(1s)$  photoionization region. The resulting spectra are compared with gas phase and condensed  $NH_3$  spectra.

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1. Introduction

Auger electron spectroscopy (AES) is widely used as a method for the elemental analysis of surfaces but the potential of this method for chemical state identification has only recently begun to be appreciated (1). Experimentally, reports of the use of AES line shapes to identify surface chemical species are scattered throughout the literature and include carbon [2-7], oxygen [8,9] and nitrogen [10] spectra. There are also reports of AES applied to free molecules [1, 11-17] and thick molecular films [1, 18, 19]. The unique chemical information that is contained in Auger spectra of molecular species derives mainly from the very localized character of the core hole. In a core-valence-valence Auger transition, the initial core hole probes the local valence electron distribution and the measured relative intensity and line shape are therefore sensitive to changes in this distribution. In order to exploit the potential of this method, careful studies of simple molecular systems must be available. This has been done using small organic molecules in the gas phase and in thick molecular films (1).

Similar data is available for ammonia [10, 15-17]. From a surface science perspective, data for chemisorbed monolayer and submonolayer coverages is of considerable interest for at least two reasons: (1) to probe the intramolecular bonding changes that occur on passing from either

the gas phase or a molecular film to a chemisorbed phase and (2) to determine the coupling of electronic states of the substrate with those of the adsorbate. Unfortunately instrument broadening, high background levels and characteristic loss processes tend to distort the intrinsic Auger line shape and a suitable response function must be employed for deconvoluting the data [20-22]. In the case of molecular films and chemisorbed layers this function should remove from the measured spectrum contributions due to the finite resolution of the analyzer, the energy width of the excitation source and non-Auger features (characteristic losses).

As part of a thorough electron spectroscopic study of small molecules on aluminum [23], we report here the deconvoluted x-ray excited Auger spectra (XAES) of monolayer coverages of NH<sub>3</sub> on clean and oxidized Al. A response function derived from the M(1s) region of the x-ray photoelectron spectrum (XPS), rather than that from the traditional electron backscatter spectrum, was employed. The resulting spectra are compared with known gas phase [19] and molecular film [18] data. To our knowledge these are the first reported deconvoluted AES spectra of monolayer coverages of molecular species.

2. Experimental and Deconvolution

The experimental procedure has been described previously [24]. Residual oxygen levels on the clean polycrystalline Al substrate were reduced to less than 5% of an equivalent monolayer with evidence indicating that this oxygen is distributed throughout the surface thickness sampled in these experiments ( $\approx 30 \text{ \AA}$ ) making the actual impurity level on the surface  $< 1\%$ . A dynamically pumped and calibrated multichannel array detector was employed. Spectra were generated using Mg (K $\alpha$ ) x-ray excitation and were recorded digitally. The double-pass cylindrical mirror analyzer was operated at a constant pass energy of 100 eV.

As measured, XAES data is generally distorted by a large and rapidly varying secondary electron background and by characteristic losses suffered by Auger electrons as they leave the solid. We have handled these distortions using a method which has been successfully applied to LEIS [25]. It uses an analytical approximation suggested by Siekhaue [26] for secondary background removal and the van Cittert iterative deconvolution method [20,27] for removal of intrinsic energy losses and broadening due to finite analyzer resolution. Second-order polynomial least-squares smoothing [28] was applied uniformly to the deconvoluted data in an effort to reduce noise buildup [20,27].

### 3. Results and Discussion.

Loss spectra for ammonia-covered Al and oxidized Al are shown in Fig. 1. Further proof of the identity of the adsorbed species described here can be found in ref. 36, which reports complementary UPS and XPS data. A backscatter spectrum for 397 eV electrons interacting with an ammonia-saturated aluminum surface (128 K) is shown in Fig. 1(a). At this temperature, a multilayer cannot be formed [29] and the spectrum clearly shows bulk (15.0, 31.5 and 41.5 eV) and surface (9.75 eV) Al plasmons [30,31]. This spectrum is identical to that obtained for clean Al.

Figure 1(b) shows a spectrum under similar conditions except the Al surface was provided by exposure to 260 L of  $O_2$  at room temperature to produce a 4-7 Å film of oxide [31]. The peaks at 7.2 eV and in the region between 15 and 22 eV can be explained in terms of an Al/ $Al_2O_3$  interface plasmon [32] and surface and bulk plasmons in  $Al_2O_3$  [33]. Both (a) and (b) illustrate that the presence of submonolayer coverages does not alter the loss features of the substrate.

The spectra of Fig. 1(c) and (d) show losses that occur behind the x-ray excited N(K<sub>1s</sub>) core ionization. Figure 1(c) is for a submonolayer coverage comparable to (a) while (d) is for a multilayer of  $NH_3$  condensed on Al at 106K. The no-loss peaks are the N(K<sub>1s</sub>) photoelectron transitions for  $NH_3$  (ads) (BE = 400.4 eV). To its right in (c) are the N(K<sub>1s</sub>) transitions for dissociated  $NH_3$  (BE = 396 eV) and the Mg K<sub>α,β</sub> satellite of the no-loss peak (BE = 391 eV).

In spectrum (d) there is no evidence for the dissociated ammonia feature while the x-ray satellite is clear. The only structure in the loss region of (d) is a broad featureless minimum near 22 eV. No substrate loss structure or losses characteristic of ammonia (6.5, 9 and 11 eV) are present [34]. It is interesting that (b) and (d) have similar line shapes that appear to be characteristic of molecular crystals such as methanol [19].

The search for an appropriate instrument response function with which to deconvolute the XPS data prompted the investigation of the loss region associated with the N(K<sub>1s</sub>) transition. Curve (c), after smoothing with a 9-point quadratic algorithm [28], was used because the losses experienced by a photoelectron escaping from a molecule adsorbed on top of the surface are more likely to be similar to those experienced by an Auger electron escaping under identical conditions, than to the losses experienced by a backscattered electron which is strongly coupled to substrate-related loss processes. This is particularly true in the present case due to the high intensity of plasmon losses in Al. One disadvantage of using the N(K<sub>1s</sub>) transition is that the electron kinetic energy is much larger than for the Auger electron of interest.

The deconvoluted results for a 37 L exposure of  $NH_3$  on clean and oxidized Al at 128 K are shown in Fig. 2 [29]. Also plotted for comparison, are the spectra for gas phase [17] and solid  $NH_3$  [18]. The labels at the top of the figure refer to the two-hole final state of the Auger process. The spectra of the gas, solid and  $NH_3$  (ads) on clean Al (curves a, b and d)

have been aligned with the provided spectrum (curve c) by shifting each spectrum to higher KE (by the amount indicated in the figure caption) so as to match the  $3s^2$  peak positions. The kinetic energies are referenced to the Fermi level of Al:  $E_F(NiS)$  - 400.4 eV.

Theoretically, there are eleven possible transitions for  $NH_3$  (gas) but several involve triplet final states and have low intensity [35]. Six well resolved bands appear in the gas phase spectrum (a). The orbitals involved in the transitions near 373 and 380 eV are valence orbitals with N-H and nitrogen lone-pair character respectively. Since UPS results [36] indicate that the nitrogen lone-pair ( $3a_1$ ) participates in the surface bond, the  $3a_1^2$  and  $3a_1 1e$  transitions should be most affected in (b) and (c).

The solid  $NH_3$  spectrum (d) exhibits five bands and a shoulder at ~385 eV. The  $3a_1 1e$  and  $3a_1^2$  peaks are not resolved. Larkins, et al. [18] attribute this to hydrogen bonding in the molecular crystal. They find transitions involving the  $3a_1$  orbital are significantly broadened compared to the gas phase, from 2.2 to 7.0 eV in the case of the  $3a_1^2$  transition. Jamison [38] has recently shown that hole-hole interactions in doubly ionized lone pair orbitals cause significant static relaxation effects. Condensed molecules which form hydrogen bonds involving lone-pair orbitals exhibit large changes in the intensity of the transition derived from the doubly ionized lone pair orbital as compared to the gas phase [19].

Larkins et al. [18] suggest that the satellite, whose KE is slightly higher than the  $3a_1 1e/3a_1^2$  bands, can be assigned to excitation of the  $N(1s)$  [ $1s_1$ ] electron to an unfilled Rydberg state of the same symmetry, followed by a normal Auger process.

Unfortunately our results in Fig. 2 do not reflect the natural linewidths of the Auger lines, one desired result of deconvolution. This is because: 1) smoothing was necessary in the instrument response and the XAES spectra and 2) the  $N(1s)$  lines contain broadening due to the width of the excitation source which is not present in AES lines. The deconvolution here served mainly to remove the broad loss tail associated with electrons emitted from the  $NH_3$ (a) as shown in Fig. 1(c).

Spectra (b) and (c) show the deconvoluted  $N(KVV)$  transition for submonolayer coverages of  $NH_3$  adsorbed on clean and oxidized Al. Curve (c) from Fig. 1, after additional smoothing, was used as the instrument response function in the deconvolution. In their raw form both spectra are broadened and show no pronounced features except the satellite associated with the  $3a_1 1e$  and  $1e^2$  transitions. The similarities between the spectral features of (b) and (c) with those of solid and gaseous  $NH_3$  not only positively "fingerprint" the adsorbed species as molecular  $NH_3$ , but also justify the use of this response function for the deconvolution rather than that obtained by the electron backscattering method. To our knowledge, this is the first reported deconvolution of the Auger spectrum of a submonolayer coverage of an adsorbed

spectra. Spectrum (b), as compared to the others, shows a significant loss of intensity in the  $3s_{1/2}^2$  region, a differential shift of the  $3s_{1/2}$  transition, and significant intensity in the satellite region. This amount is only weakly chemisorbed; thus, we ascribe most of these intensity shifts to final state relaxation effects due to the presence of the Al substrate.

The similarity between (c) and the spectrum of solid  $NH_3$  (d) suggests that  $NH_3$  is in a similar environment in the hydrogen bonded molecular crystal and on the oxidized surface. This is not surprising in view of the ionic nature of the oxidized Al surface and observed photoemission results [36]. Hydrogen bonding in the molecular crystal involves sharing of a covalently bonded, electropositive hydrogen atom with the lone-pair of a neighboring nitrogen atom. Oxidation of Al creates Lewis acid sites ( $Al^{3+}$ ) in the surface region which, due to their small size and electropositive properties, should form a good substitute for a covalently bonded hydrogen in hydrogen bond formation. Comparing both (c) and (b) to (d), it is apparent that adsorption on the oxidized surface resembles solid  $NH_3$  more than  $NH_3$  adsorbed on clean Al. Both XPS and UPS data [36] indicate that more  $NH_3$  is adsorbed on oxidized than clean Al surfaces. A greater concentration of  $NH_3$  could tend to enhance the spectral features of (c) compared to (b). Oxidation of Al increases the surface area [37]; thus it cannot be determined from the present data whether the increased amount of  $NH_3$  adsorbed on oxidized as compared to

clean Al, is due to a stronger interaction of  $Al_2O_3$  with  $NH_3$ , or merely an increase in surface area following oxidation.

Further evidence supporting the conclusion that  $NH_3$  bonded to oxidized Al is in an environment similar to that in a condensed  $NH_3$  layer comes from the relative shifts in energy necessary for alignment of (b) and (d) with (c). Ammonia in a condensed multilayer is poorly screened by the substrate Fermi sea. As a result, the kinetic energies of all  $N(KVV)$  transitions are lower relative to those of a screened  $NH_3$  molecule. The  $N(KVV)$  transitions shown in (b), for  $NH_3$  bound to the clean metal are relaxed  $\sim 4.7$  eV compared with solid  $NH_3$ . Likewise, localization of electron density from the Al Fermi sea into ionic Al-O bonds following oxidation, should render this surface less effective in screening holes created on adsorbed  $NH_3$  molecules compared to clean Al. This is experimentally verified by comparison of (c) and (d) which are almost equivalently screened. In the totally unscreened case of gaseous  $NH_3$  (a), the shift of all transitions is enormous ( $\sim 10$  eV) as expected.

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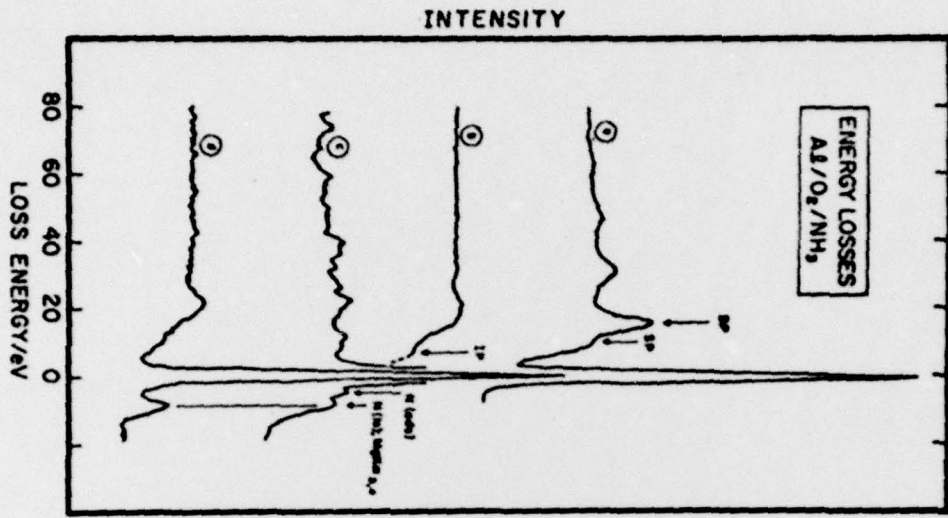
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#### Figure Captions

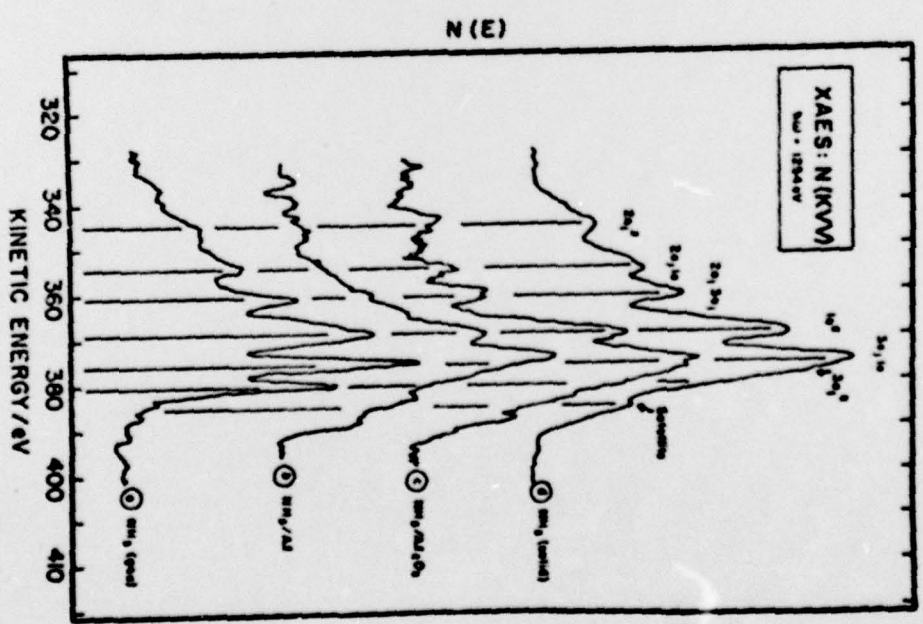
Figure 1. Electron energy loss spectra of  $\text{NH}_3$  on clean and oxidized Al. a) electron backscatter spectrum of 397 eV electron on the Al surface saturated with  $\text{NH}_3$  at 128 K. b) Same as (a) except the surface was preoxidized with 260 L  $\text{O}_2$ . c) Losses behind the  $\text{N}(1s)$  peak for the same conditions as (a). d) Losses behind  $\text{N}(1s)$  for a multilayer of  $\text{NH}_3$  condensed on Al at 106K.  $\text{IP}$  = bulk plasmon,  $\text{SP}$  = surface plasmon,  $\text{IP}$  = interface plasmon.

Figure 2. XAES of the  $\text{N}(KVV)$  region, for adsorbed, condensed and gas phase  $\text{NH}_3$ . The spectra were arbitrarily shifted by an amount  $\Delta E$  to align the  $1s^2$  transitions with those of curve (c). a)  $\text{NH}_3$  gas (177),  $\Delta E = -9.1$  eV. b) Saturation  $\text{NH}_3$  coverage on clean Al at 128 K,  $\Delta E = -4.0$  eV. c) Saturation  $\text{NH}_3$  coverage on oxidized (260 L  $\text{O}_2$ ) Al at 128 K,  $\Delta E = 0.0$  (reference). d) Condensed multilayer  $\text{NH}_3$ , [18],  $\Delta E = +0.7$  eV.



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Fig. 1  
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Fig. 2  
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