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High-Resolution Measurements of the Nitrogen *K-LL* Auger Transitions of Chemisorbed Ammonia on a Molybdenum Surface

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Distinct "chemical effects" were observed among high-resolution, nonderivative, nitrogen *K-LL* Auger-electron distributions from chemisorbed NH_3 on molybdenum surfaces and gaseous NH_3, which depend on the electronic structures of the adsorbed species. A calculation in the semiempirical "equivalent-core approximation," based on photoelectron data, revealed the origins of the fine structure in the observed Auger spectra. It is concluded that NH_3 is chemisorbed as a $\mathrm{H}_{-\mathrm{Mo}}\text{--}\mathrm{N}_{-\mathrm{Mo}}\mathrm{H}_{x\leqslant 2}$ dissociative configuration at about room temperature and the surface nitride is formed at 450°C.

Many studies have been reported dealing with the configurations of adsorbed gases on surfaces and adsorbate binding energies. Techniques which have been used include photoelectron spectroscopy,[1] low-energy-electron spectroscopy,[2] ion-neutralization spectroscopy,[3] and field-emission spectroscopy.[4]

For the Auger process in molecules or adsorbates, an atom in different chemical environments results in different energy distributions of the Auger electrons, especially when valence states of the molecules are involved in the process ("chemical effects"). In earlier work done by Haas and Grant,[5] the chemical effect in a derivative form of the Auger spectra of several carbon compounds had been observed with relatively low energy resolution, although they failed to identify the peaks and structures of their spectra. Progress in experimental techniques as well as in the theoretical understanding of the Auger process enables us now, with the aid of a high-resolution electron spectrometer, to elucidate the origin of fine structure in the Auger spectra of adsorbed molecules on a solid surface.

In this paper, we report a chemical effect found in the nitrogen *K-LL* Auger spectra of gaseous and adsorbed ammonia on molybdenum surfaces at various temperatures. Figure 1 shows the high-resolution Auger spectra obtained. Special care was taken in order to obtain detailed structure in the spectra and, therefore, nonderivative spectra were measured with an energy resolution better than 200 meV. By comparing the fine structure in the spectrum shown in Fig. 1(d), with those of gaseous NH_3 ($\Delta E \leqslant 400$ meV) and molybdenum nitride, which were assigned by the equivalent-core approximation from a knowledge of the electronic structures of these two molecules, it is proposed that configurations of adsorbed ammonia on the surface are observed.

The Auger-electron-spectroscopy (AES) measurements were performed using a modified Simpson-Kuyatt high-resolution electron spectrometer[6] with a hemispherical 180° energy analyzer and with retarding electrostatic lenses. Auger electrons were produced with the use of a 1.3-keV electron beam. A polycrystalline molybdenum foil obtained from H. Cross Company, Ltd. was verified to be clean using AES after flashing the oxidized sample *in vacuo*. The minimum attainable pressure was 5×10^{-9} Torr. All the measurements were made in the presence of gaseous NH_3 *in situ* and data were accumulated in a multichannel analyzer in order to improve the

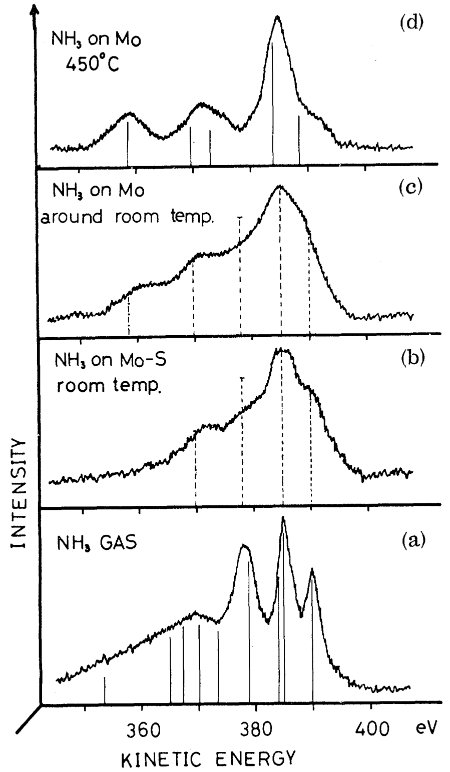


FIG. 1. High resolution, nonderivative nitrogen *K-LL* Auger spectra of (a) gaseous NH_3, (b) adsorbed NH_3 on a sulfur-segregated surface at room temperature, (c) on a clean surface at about room temperature, and (d) at 450°C. The vertical solid lines in (a) and (d) represent the energies calculated in the equivalent core approximation. The vertical broken lines in (b) and (c) represent observed energies and intensities for the peaks of gaseous NH_3. The dot-dashed line in (c) shows the observed value of Mo_2N which is at the lowest energy in (d).

signal-to-noise ratio. Background signals due to secondary electrons were subtracted from the signal by a data processor. In addition, the binding energies of molybdenum nitride and molybdenum oxide were also measured using a conventional x-ray photoelectron spectrometer in order to assign the observed Auger lines.

Figure 1(a) shows the nitrogen *K-LL* Auger transitions for gaseous NH_3 at a pressure of 10^{-3} Torr (P_{NH_3}). In order to assign each peak, the energies of the Auger transitions ($E_{K\text{-}LL}$) associated with NH_3 were calculated semiempirically, using

$$E_{K\text{-}LL}(Z)=E_K(Z)-E_L(Z)-E_L(Z+1), \qquad (1)$$

where $E_A(Z)$ is the binding energy of some level A of an atom of atomic number Z. An Auger process can be considered as a combination of the simple processes,[7]

$$Z \rightarrow Z(\overline{K})^+ + e^-, \qquad (2a)$$

$$Z \rightarrow Z(\overline{L})^+ + e^-, \qquad (2b)$$

$$Z(\overline{L})^+ \rightarrow Z(\overline{L}\overline{L})^{2+} + e^-, \qquad (2c)$$

where $Z(\overline{A})^+$ denotes the hole states in the A shell of an atom of atomic number Z. Accordingly, the energy to be used for the ejection of the electron in Reaction (2c) is exactly $E_K(Z)-E_L(Z)$. In this last process, the binding energies of the remaining electrons to be ejected from the L shell $[E_L(Z)^+]$ can be approximately substituted by $E_L(Z+1)$ (in the equivalent-core approximation). In this study, the equivalent-core approximation,[8] which has been successfully used to evaluate binding energies in photoelectron spectroscopy, was extended to the two-hole state in the Auger process. In fact, calculations to this approximation predict the observed Auger spectra for carbon, oxygen, and nitrogen compounds.[9] Empirical binding energies for the molecular orbitals of gaseous NH_3 determined by a photoelectron-spectroscopy technique[10] were used for the calculation, i.e., 405.6 eV for $1a_1$, 27.5 eV for $2a_1$, 15.8 eV for $1e$, and 10.9 eV for $3a_1$. The molecular orbitals of H_2O using the binding energies (18.4 eV for the O-H σ bond, 12.6 eV for the lone electron pair in oxygen, and 32.2 eV for the oxygen $2s$ orbitals) were chosen for the evaluation of $E_L(Z+1)$ in Eq. (1) because the effective potential exerted on an electron in a valence orbital of H_2O and on an electron in a corresponding orbital of NH_3^+ may be almost identical. Possible NH_3 Auger emission lines and their assignments (final hole states) are listed in Table I where the Auger energies are referred to vacuum level.

As shown by vertical lines in Fig. 1(a), the calculated and observed energy positions are displaced to higher energies by 7.6 eV in order to fit the highest peak to those in the other spectra of adsorbed ammonia under various conditions which will be discussed later. Since the work function of the sample after NH_3 adsorption is approximately 3.9 eV,[11] the remainder of the 7.6-eV shift is probably due to a relaxation effect caused by adsorption. No data on the relaxation effect for the Auger transition due to adsorption with which to compare our shift are available at present. Apparently, calculations with this approximation predict the observed relative peak positions fairly well as is demonstrated in Fig.

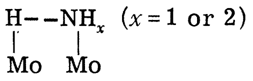
TABLE I. Observed energies of the *K-LL* Auger transitions of nitrogen for gaseous NH_3 and adsorbed NH_3 at 450°C, and the Auger energies for NH_3 and Mo_2N calculated in the equivalent-core approximation.

NH_3 (Gas)			
OBSERVED	(+7.6 eV)	ASSIGNMENT (FINAL STATE)	CALCULATED
382.2 eV	(389.8 eV)	$(3a_1)(3a_1)$	382.1 eV
377.4	(385.0)	$(1e)(3a_1)$	377.2
		$(3a_1)(1e)$	376.3
369.6	(377.2)	$(1e)(1e)$	371.4
		$(2s)(3a_1)$	365.5
		$(3a_1)(2s)$	362.5
361.6	(369.2)	$(2s)(1e)$	359.7
		$(1e)(2s)$	357.6
---		$(2s)(2s)$	345.9
NH_3 at 450°C			
OBSERVED		ASSIGNMENT	CALCULATED FROM Mo_2N
392.0 eV		$(KL_{2,3}N_{4,5})$	(388.5 eV)
385.0		$KL_{2,3}L_{2,3}$	384.0
375.0		$KL_1L_{2,3}$	373.0
372.0		$KL_{2,3}L_1$	369.5
358.9		KL_1L_1	358.5

1(a). Consequently, the 398.8-eV (1), 385.0-eV (2), and 377.2-eV (3) peaks in Fig. 1(a) are associated with the final states having two holes in $(3a_1, 3a_1)$, $(3a_1, 1e)$, and $(1e, 1e)$, respectively. Here, $3a_1$ and $1e$ correspond to the molecular orbitals for the lone pair electrons and valence electrons of the N-H σ bond of NH_3, respectively. A group of vertical lines centering around 369.2 eV is due to the $2s$ nitrogen state combined with the $3a_1$ or $1e$ state.

The nitrogen *K-LL* Auger spectrum resulting from adsorbed NH_3 on a clean molybdenum surface ($P_{NH_3} = 1\times10^{-7}$ Torr) at 450°C exhibits a distinctly different feature, as is shown in Fig. 1(d). At this temperature and NH_3 pressure, the formation of molybdenum nitride on the surface has been suggested from the analyses of conventional Auger peak intensities,[12] for which the amount of surface nitrogen was observed to rise rapidly at the beginning of ammonia adsorption, and then followed by a gradual increase. Matsushita and Hansen[13] have reported in their flash desorption experiment that only molecular nitrogen is desorbed when NH_3 is admitted at 500°C. In fact, the spectrum in Fig. 1(d) is very similar in shape to the oxygen and carbon *K-LL* spectra of molybdenum oxide and carbide,[9] being not far from the *K-LL* spectrum[14] for atomic nitrogen calculated on the basis of an ionic model and an *LS* coupling scheme in which the nitrogen is negatively ionized to the neon structure. Therefore, the energies for the Auger transitions associated with Mo_2N were also evaluated semiempirically using the equivalent-core approximation. In this case, $E_L(Z)$ was determined from the energy band structures of Mo_2N, whereas $E_L(Z+1)$ was estimated from the energy band structures of MoO_3. In the present experiment, these energies were measured by x-ray photoelectron spectroscopy, i.e., K level: 396.5 eV, L_1: 17 eV, $L_{2,3}$: 6.0 eV for nitrogen, $N_{4,5}$: 2.0 eV for Mo in Mo_2N, L_1: 21 eV, $L_{2,3}$: 6.5 eV for oxygen in MoO_3. The absolute values calculated also agree reasonably well with the observed spectra, both referring to the Fermi level [see Fig. 1(d) and Table I]. The peaks at about 358.9, 373, and 385.0 eV are assigned to KL_1L_1, $KL_1L_{2,3}$, and $KL_{2,3}L_{2,3}$ of the nitrogen atom in the nitride, respectively. The 392.0-eV peak can be attributed to the cross transition from the L level of nitrogen to the $N_{4,5}$ level of molybdenum.

Figure 1(b) shows the spectrum of NH_3 adsorbed on molybdenum sulfide ($P_{NH_3} = 1\times10^{-7}$ Torr). The vertical broken lines shown in the figure represent the position and intensity of each peak in the spectrum of gaseous NH_3. This spectrum is very similar to that of gaseous NH_3 except for two points. One is the broadening of each peak which can be attributed to the interaction between an adsorbed species and the surface. Another prominent feature is that the intensity of 379-eV peak associated with the K-$(1e)(1e)$ transition decreased from the amount shown by the broken line. Since the $1e$ electronic state corresponds to the N-H σ-type bonding orbital, the decrease of this peak indicates that the N-H bond is strongly affected by chemisorption onto the surface. Therefore, a dissociative configuration like



$$\underset{\mathrm{Mo}}{\underset{|}{\mathrm{H}}}\text{--}\underset{\mathrm{Mo}}{\underset{|}{\mathrm{NH}_x}}\quad (x=1\text{ or }2)$$

seems more likely, although how many hydrogens per adsorbate are left remains to be determined. The K-$(1e)(1e)$ transition may change drastically with the dissociation of the N-H bond, because this transition includes a pair of electrons in the $1e$ state. This structure is consistent with the one proposed by Kemball based on the results of mass spectroscopic experiments.[15]

Figure 1(c) shows the spectrum of NH_3 adsorbed on a clean molybdenum surface at about room temperature. This spectrum appears to be an admixture of the spectra of the NH_3 gas [Fig. 1(a)] and the nitride [Fig. 1(d)], that is, an appreciable shoulder at 390 eV corresponding to the K-$(3a_1)(3a_1)$ transition and the 358-eV peak characteristic of the nitride appear in the spectra. As in the case of Fig. 1(b), the intensity of the 378-eV peak is less than the corresponding one in the gaseous spectrum. As the temperature of the molybdenum is raised, the 358-eV peak characteristic of the molybdenum nitride increased, while the 378-eV (N-H σ) and 390-eV peaks (nitrogen lone pair) decreased, accordingly. The general features approach those of the nitride K-LL spectrum. This temperature dependence indicates further dissociation of the remaining N-H bond of the adsorbate, reducing to the nitride structure.

It should be noted that the 358-eV peak due to the nitride does not appear in the spectrum of Fig. 1(b). It is reasonable to assume that, on the surface of the molybdenum sulfide, the heat of formation for the sulfide is so large (about 80 kcal) that nitride formation is prohibited on the surface during adsorption. Such a phenomenon can be easily distinguished in these spectra.

This shows that high-resolution AES is a very sensitive tool for the study of the molecular structure and valence electronic states of surface species. In addition, the equivalent-core approximation can explain the energies for the Auger processes studied here, being accurate enough to identify the origins of each peak, which is necessary for the study of the structure of surface species. High-resolution AES should be emphasized as a useful tool for studying the electronic and molecular structure of surface species as well as a tool for conventional elemental analysis.

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