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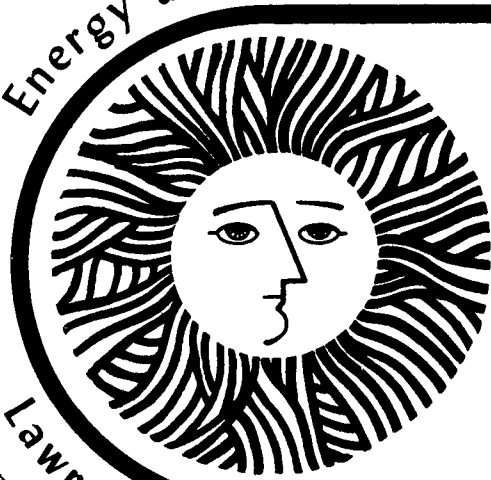
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ESCA In Environmental Chemistry

T. Novakov and S. -G. Chang

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ESCA IN ENVIRONMENTAL CHEMISTRY

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ABSTRACT

In this paper we describe the use of X-ray photoelectron spectroscopy (XPS or ESCA) for the chemical characterization of sulfur- and nitrogen-containing species of ambient pollution particulates. The strength and the limitations of this method are illustrated in research that led to a definitive chemical identification of nitrogen species tentatively assigned as amines and amides, based on ESCA results. In this case infrared spectroscopy has provided complementary information for the establishment of the molecular forms of these species.

Work performed under the auspices of the U. S.
Energy Research and Development Administration.

I. Introduction

Particulates (suspended particulate matter) play a major role in the overall air pollution problem. They are directly responsible for reduction of visibility and acidification of waters; and when deposited in the lungs, they may cause adverse health effects. These particulates can consist of solid or liquid substances. Sulfur, nitrogen, and carbon compounds are the major species from anthropogenic sources. In many circumstances these compounds may constitute about 80% of the dry mass of particulates resulting from fossil fuel combustion.

The speciation of atmospheric aerosol particles is an important task because many of their environmental effects will depend on their specific chemical and physical states. It is also important to determine the chemical compounds and species as they actually exist in aerosol form and not as they may appear in aqueous solutions. However, most analyses of pollution aerosol particles have employed wet chemical methods which reflect only the chemical composition in solution. Primarily on the basis of this type of measurement, different workers have concluded that the principal sulfur and nitrogen species are sulfate (SO_4^{--}), nitrate (NO_3^-), and ammonium (NH_4^+) ions, and suggested that the most likely combinations of these ions are ammonium nitrate, NH_4NO_3 , and ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$.⁽¹⁾ Nitric acid⁽²⁾ and sulfuric acid⁽³⁾ may also exist under certain circumstances. Wet chemical methods are of no use for insoluble aerosol species. Nondestructive physical methods, such as X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA), are therefore preferred for chemical characterization of collected particles. Application of this method has helped to uncover the presence of significant concentrations of reduced nitrogen species of the amino type ($-\text{NH}_2$) in ambient aerosol particles.⁽⁴⁾ These species could not be detected by wet

chemical methods. Furthermore, detailed ESCA studies⁽⁵⁻⁷⁾ of particulate samples, collected at various locations in California and elsewhere, have provided valuable information about the chemical states of carbon, nitrogen, and sulfur associated with aerosol particles. The results of these measurements show that on the average:

1. Nitrate (as nitrogen) is usually a relatively minor fraction of the total particulate nitrogen.
2. Ammonium, which may account for about one-half of the total particulate nitrogen, is not necessarily in the form of common salts such as ammonium nitrate or ammonium sulfate, but may also occur in a previously unrecognized form characterized by its relatively high volatility.
3. The above-mentioned nitrogen species of the amino type occur in concentrations similar to ammonium.
4. The principal chemical form of sulfur is sulfate, which we find exists primarily as sulfuric acid adsorbed on particles.
5. In addition to sulfate, sulfides are observed at some locations in concentrations comparable to, although always less than, sulfate.
6. Most of the particulate carbon appears in a neutral chemical state (i.e., nonoxygenated) compatible with both condensed hydrocarbons and primary combustion-generated carbonaceous material.

Recent ESCA results have also strongly suggested that the surface composition of particulates is similar to their bulk composition.^(7,8) Namely, the kinetic energies of the photoelectrons of interest to ESCA are relatively low (from about 200 to 1500 eV) as are the effective escape depths of electrons emitted. These escape depths are typically 15 to 40 Å for electron kinetic energies between 1000 and 2000 eV. This renders the ESCA method surface sensitive and thus very useful in surface chemical studies. However, because

of its surface sensitivity, objections could be raised that in the application of this method to particulate analysis, only the surface of the exposed particles will be analyzed and therefore the results will not be representative of the average composition of the particles. Alternatively, ESCA results, when compared with results obtained by means of a bulk analysis method such as wet chemistry or X-ray fluorescence (XRF), should provide information about which species are located on the sample surface. Studies of this kind were performed,⁽⁸⁾ and the results of ESCA sulfate analyses were compared with the results obtained by XRF and wet chemical methods. These results demonstrate a remarkable agreement between ESCA and bulk analytical methods. This may mean only that the surface and bulk compositions of ambient particulates, at least with respect to sulfate, are similar. We are unaware of any similar conclusion reached without the application of a surface-sensitive method such as ESCA.

In this chapter we will describe the use of photoelectron spectroscopy for chemical characterization of ambient and source-enriched particles, as well as some species produced by gas-particle reactions under laboratory conditions. Gas-particle reactions are important in atmospheric chemistry because most air pollution is caused by the combustion of fossil fuels that produce both the particulate and gaseous pollutants, with the former acting as catalyst and surface-active material. For example, surface and catalytic reactions of carbonaceous particles with SO_2 and NH_3 have been found to produce particulate sulfur⁽⁹⁾ and nitrogen⁽⁵⁾ species identical to those observed in the ambient air. Because of this, "synthetic" species produced under laboratory conditions were used for chemical characterization involving both ESCA and infrared spectroscopy, especially in cases where high concentrations of specific species were required.

Such combined measurements were found to be very useful in establishing the actual chemical structure, while ESCA results by themselves cannot be used to establish this in most practical applications. The strength and the limitations of ESCA are illustrated in the research that led to a definitive chemical identification of nitrogen species tentatively assigned as amines and amides, based on ESCA results. In this case the infrared spectroscopy of synthetic species has provided the needed information for the establishment of their molecular form.

The ESCA analyses described in this chapter involve measurement of the chemical shift, determination of relative concentrations, measurements performed as a function of sample temperature, and determination of the volatility of species in vacuum. The fundamentals of ESCA have been described in great detail in a number of papers and monographs⁽¹⁰⁾; therefore only the essentials of the method relevant to the topics of this chapter⁽¹¹⁾ will be outlined here.

II. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a physical method well suited for chemical characterization of environmental pollutants such as airborne particulate matter. This method involves the analysis of the kinetic energies of photoelectrons expelled from a sample (usually solid) irradiated with monoenergetic soft X-rays. The kinetic energy of a photoelectron E_{kin} , emitted from an electron subshell i , is given by $E_{kin} = h\nu - E_i$, where $h\nu$ is the X-ray photon energy and E_i is the binding energy of an electron in that subshell. For a known X-ray energy, the determination of the photoelectron kinetic energies provides a direct measurement of the electron binding energies. The binding energies are characteristic of each element, which enables the identification of elements in the sample. The intensity of photoelectrons originating from

a subshell of an element is proportional to the concentration of atoms of that element in the active sample volume. The sample volume is determined by the electron escape depth and the physical size of the sample. This feature enables the method to be used for quantitative elemental analysis.

The strength of ESCA is in its ability to distinguish different chemical states rather than different elements. The electron binding energies are not absolutely constant but are modified by the valence electron distribution. The binding energy of an electron subshell in a given atom varies slightly when this atom is in different chemical environments. For example, the nitrogen 1s binding energy in a nitrate ion, NO_3^- , is greater than the nitrogen binding energy in an ammonium ion, NH_4^+ , by about 5 eV. These differences in electron binding energy are known as the chemical shift.

The origin of the chemical shift can be understood in terms of the shielding of the core electrons by the electrons in the valence shell. A change in the charge of the valence shell results in a change of the shielding, which affects the core electron binding energies. For example, if an atom is oxidized, it donates its valence electrons and thus becomes positively charged with respect to its neutral configuration. Some of the shielding contribution to the total potential is removed so that the binding energy of the core electron has increased. Conversely, the binding energies will show an opposite chemical shift for reduced species. The usefulness of ESCA for the analysis of samples of unknown chemical composition lies in the determination of the chemical shift and its interpretation. In practice, measurements of the chemical shifts are supplemented by the determination of relative photoelectron intensities, from which information about the apparent stoichiometry of species can be obtained.

III. Chemical Characterization of Particulate Sulfur and Nitrogen Species

ESCA analysis of ambient samples allows for a straightforward differentiation of different forms of atmospheric sulfate- and ammonium-containing species. The following distinctly different forms have been identified⁽⁷⁾:

1. Ammonium sulfate accounts for the entire ammonium and sulfate content of the sample.
2. Ammonium appears in concentrations above those expected for ammonium sulfate (and nitrate). The "excess" ammonium is volatile in vacuum.
3. Ammonium appears mostly in a volatile form independent of sulfate and nitrate.

In this section we will describe the measurements and results that have led to the above conclusions.

The capability of ESCA for straightforward differentiation of different forms of atmospheric sulfates is illustrated in Figure 1, where the nitrogen (1s) and sulfur (2p) spectral regions of two ambient samples are shown. (One was collected in West Covina, California, in the summer of 1973; and the other, in St. Louis, Missouri, in the summer of 1975.)^(12,13) The peak positions corresponding to NH_4^+ and SO_4^{--} are indicated. The solid vertical bar indicates the ammonium peak intensity expected under the assumption that the entire sulfate is in the form of ammonium sulfate. Obviously the observed ammonium content in the West Covina sample is insufficient to account for the sulfate by itself. This is in sharp contrast with the St. Louis sample, where the observed ammonium intensity closely agrees with that expected for ammonium sulfate.

The peak in Figure 1 denoted by $-\text{NH}_2$ corresponds to the particulate amine- or amide-type species that were first observed by means of photoelectron spectroscopy. Their chemical characterization and structural determination are discussed in the following section. In this section we will confine ourselves to the discussion of ammonium- and sulfate-containing species.

These results demonstrate that ammonium sulfate in the aerosols can easily be distinguished from other forms of sulfate such as that found in the West Covina samples. However, wet chemical analyses⁽¹⁴⁾ performed on West Covina samples collected simultaneously with the ESCA samples showed ammonium and nitrate concentrations substantially higher than those suggested by ESCA measurements. This apparent discrepancy between the two methods was subsequently explained by the volatility of some ammonium species in the ESCA spectrometer vacuum.^(5,6) These losses were not caused by the volatilization of ammonium sulfate since no volatile losses were observed in the St. Louis samples. Ammonium nitrate (negligible in these samples) and ammonium bisulfate compounds were found to be stable in vacuum for the periods of time usually required to complete the analysis. Therefore ammonium species other than these must be responsible for the apparent loss of ammonium in vacuum.

That the volatile ammonium is not necessarily associated with sulfate or nitrate ions is illustrated by the results represented in Figure 2. Here the changes in the nitrogen (1s) spectrum of a sample collected in a highway tunnel (Caldecott Tunnel, Oakland, California) are shown as a function of the sample vacuum exposure time.⁽⁷⁾ Obviously the ammonium peak intensity decreases with the vacuum exposure time. The intensity of the amino-type nitrogen species remains constant, however. The amount of nitrate in this sample was negligible compared with ammonium. The maximum ammonium peak expected under the assumption that the entire sulfate is ammonium sulfate is indicated by the solid vertical bar in Figure 2. It is obvious that the counterions for this ammonium are neither nitrate nor sulfate.

Figure 3 summarizes the findings about ammonium volatility in the three samples discussed above. The shaded bars at the far left of the figure indicate the expected ammonium intensity based on the assumption that all sulfate in the

sample is in the form of ammonium sulfate. It is evident from the figure that only the St. Louis sample contains ammonium sulfate, while the West Covina and the tunnel samples contain a different kind of ammonium which volatilizes in the spectrometer vacuum.

We have applied this procedure routinely to analyze a number of ambient samples.⁽⁷⁾ Results of such measurements for six St. Louis samples are shown in Figure 4, where the ratio of the observed ammonium peak intensity to the peak intensity expected if the ammonium were in the form of ammonium sulfate is plotted as a function of the sample vacuum exposure time. It is evident that in addition to the cases of practically stoichiometric ammonium sulfate (samples 913 and 914), there are some in which the observed ammonium is found in excess of ammonium sulfate. The excess ammonium consists of volatile ammonium species which decrease until ammonium sulfate is the only ammonium species left (sample 917).

The anions corresponding to the volatile ammonium species cannot be identified with certainty at this time. One possibility is that these species are produced by the adsorption of ammonia on fine soot particles to form carboxyl and hydroxyl ammonium complexes which have volatility properties similar to those observed in ambient particulates.⁽⁵⁾ Another possibility is that these species could be due to ammonium halides which are also volatile in vacuum.

IV. Formation and Characterization of Particulate Amines

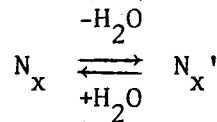
Until recently the presence of amines and/or amides in particulates was detectable only by means of ESCA. In the absence of a precise knowledge of their structure, we have in the past designated these species as N_x to indicate their unknown composition and the possibility that N_x consists of more than one species. Although the infrared spectroscopic technique has been used for the characterization of chemical species in ambient particulates,⁽¹⁵⁾ reduced nitrogen species have not been revealed by this method, because of their low

infrared absorption cross sections and the fact that many chemical species in ambient particulates contribute to the absorption in the same infrared regions as the reduced nitrogen species. The characteristic infrared absorption regions of the proposed reduced nitrogen species such as amides and amines are: NH stretching ($3500-3050\text{ cm}^{-1}$), >C=O absorption ($1850-1650\text{ cm}^{-1}$), NH deformation ($1650-1500\text{ cm}^{-1}$), and C-N stretching ($1250-900\text{ cm}^{-1}$ for aliphatic and $1350-1300\text{ cm}^{-1}$ for aromatic). The interference could arise from the presence of the following species: NH_4^+ (ν_3 and $\nu_2 + \nu_4$, $3500-3000\text{ cm}^{-1}$), H_2O (ν_2 , $1750-1550\text{ cm}^{-1}$), CO_3^{--} (ν_3 , near 1435 cm^{-1}), NH_4^+ (ν_4 , near 1400 cm^{-1}), NO_3^- (ν_3 , near 1360 cm^{-1}), and SiO_4^{--} , PO_4^{--} , and SO_4^{--} (ν_3 , $1200-1000\text{ cm}^{-1}$).

In order to determine the chemical structure of the species that were tentatively assigned to amines and amides, and in view of the difficulties when using i.r. spectroscopy with ambient samples, it appeared that a more straightforward way would be to study samples produced under laboratory conditions, which are free of the interfering species. It is possible to generate the N_x species in surface reactions of ammonia with fine soot or graphite particles. We have employed two methods for their synthesis: one involves surface reactions of ammonia with combustion-generated soot particles or graphite at elevated temperatures in the presence of gaseous oxygen; the other method also involves an ammonia surface reaction but with finely ground graphite powder at low temperatures in the absence of oxygen. These "synthetic" N_x species have properties identical to those observed in the ambient air particulates. To illustrate this we shall first describe the results obtained with ambient samples collected in two different regions of California, and then compare these results with those obtained with species synthesized by both high- and low-temperature ammonia-particulate carbon reactions.

Figure 5 shows the results of one such measurement⁽⁵⁾ for an ambient particulate sample, collected in Pomona, California, during a moderate smog episode (24 October 1972). The spectrum taken at a sample temperature of 25°C shows the presence of NO_3^- , NH_4^+ , and N_x . At 80°C the entire nitrate peak is lost, with a corresponding loss in the ammonium peak intensity. The shaded portion of the ammonium peak in the 25°C spectrum represents the ammonium fraction volatilized between 25 and 80°C. The peak areas of the nitrate and the volatilized ammonium are approximately the same, indicating that the nitrate in this sample is mainly in the form of ammonium nitrate. The ammonium fraction still present at 80°C but absent at 150°C is associated with an ammonium compound more stable than ammonium nitrate, such as ammonium sulfate. At 150°C the only nitrogen species remaining in the sample is N_x . At 250°C the appearance of another peak, labeled N_x' , is seen. The intensity of this peak continues to increase at 350°C. The total $\text{N}_x + \text{N}_x'$ peak area at 150, 250, and 350°C remains constant, however, indicating that a part of the N_x is transformed into N_x' as a consequence of heating.

N_x' species will remain in the sample even if its temperature is lowered to 25°C, provided that the sample has remained in vacuum. However, if the sample is taken out of vacuum and exposed to the humidity of the air, N_x' will be transformed into N_x . It was concluded that N_x' species are produced by dehydration of N_x :



Based on the described temperature behavior and on laboratory studies⁽⁵⁾ of reactions that produce species identical to those observed in ambient air particulates (see below), N_x was assigned to a mixture of amines and amides.

(N_x photoelectron peaks are broad indications of the presence of more than one single species.) Dehydration of the amide results in the formation of a nitrile, N_x' .

Synthetic N_x species whose ESCA spectra and temperature behavior are identical to the ambient particulate sample described above can be produced by surface reaction of ammonia with either graphite or combustion-produced soot particles.⁽⁵⁾ Results in Figure 6 show that N_x species produced by surface reactions of hot soot with NH_3 have the same kind of temperature dependence as the ambient samples. The spectrum taken at room temperature shows that most nitrogen species in this sample are of the N_x type. Heating the sample in vacuum to $150^\circ C$ does not influence the line shape or intensity. At $250^\circ C$, however, the formation of N_x' is evident. Further transformation of N_x to N_x' occurs at $350^\circ C$.

Synthetic N_x' species will remain unaltered even when the temperature is lowered to room temperature if the sample remains in vacuum. However, if the sample is taken out of vacuum and exposed to moisture, N_x' will be transformed back to the original N_x compound. The behavior of the synthetic N_x species is thus identical with the behavior of ambient species, such as those found in the Pomona sample. We have tentatively concluded that the high-temperature ammonia-particulate carbon reaction results in the formation of a mixture of particulate amines and amides.

Concerning the mechanism of this reaction, we speculated previously⁽⁵⁾ that at elevated temperatures, ammonia will react by a nucleophilic substitution reaction with carboxyl groups associated with soot particle surfaces to produce an amide. This amide may become a nitrile by further dehydration. Alternatively, reaction with phenolic hydroxyl groups may yield an amine. Such reactions are to be expected because soot particles are composed not only of elemental carbon, but also of 1 to 3% hydrogen and 5 to 15% oxygen by weight. Oxygen associated

with soot particles is located in surface carbon-oxygen complexes, which typically are of carboxyl, phenolic hydroxyl, and quinone carbonyl type. Similar surface functional groups are easily formed when graphite is heated in an atmosphere of air and moisture.

Thus synthetic N_x species, produced in high-temperature surface reactions of soot or graphite with ammonia, are not well suited for infrared spectroscopic determination of the amide structure because of interference in the $>C=O$ region. Therefore, it would be advantageous to perform the infrared spectroscopic studies with samples that contain mostly particulate amines rather than a mixture of amines and amides. That such particulates exist in ambient air is suggested by the results shown in Figure 7 where the N (1s) ESCA spectra of a sample collected in Berkeley, California,⁽¹⁶⁾ are shown.

Figure 7a shows the ESCA spectrum of this sample, recorded while the sample was exposed to vacuum and X-ray bombardment for about 1.5 hours. The positions of the nitrate, ammonium, and amine peaks are indicated in the figure. The ammonium and nitrate peaks have a similar intensity, suggesting that these ions are present mostly as ammonium nitrate. Sulfate in the form of ammonium sulfate could also contribute to the ammonium peak. Figure 7b shows that a prolonged exposure of the sample to vacuum and X-ray bombardment has resulted in complete volatilization of ammonium and nitrate species. The only species that have remained in the sample are those that contain groups of the amino type. Heating of this sample to 350°C in vacuum resulted in a slight change in the line shape (Fig. 7c) in contrast to the ambient sample from Pomona whose temperature-dependent spectra are shown in Figure 5.

We have tentatively concluded that the Berkeley sample contains mostly amines, in contrast to the Pomona sample which contained a mixture of amines and amides.

In the laboratory we have successfully produced⁽¹⁷⁾ reduced nitrogen species which have ESCA spectra identical to those of the ambient samples just described and temperature behavior similar to those samples. The technique used involves extensive grinding of graphite powder in ammonia in the absence of oxygen at room temperature. An examination by ESCA of the nitrogen species produced by such a surface reaction shows that these species are similar to those observed in the Berkeley sample, consisting mainly of species tentatively assigned as amines (Fig. 8). Such synthetic samples were used for infrared studies.

The application of optical spectroscopy to study the structure of surface species on graphite is difficult because of its high absorption coefficient. The grinding technique employed enriches the concentration of surface nitrogen species. In order to help in assigning the vibrational frequencies, the samples were prepared by grinding graphite in both NH_3 and deuterated ammonia, ND_3 . After grinding, the carbon particles were thoroughly mixed with KBr powder, pressed into pellets, and used for Fourier transform infrared analysis.

Figures 9a and 9c show infrared spectra⁽¹⁷⁾ of the graphite particles after extensive grinding in an atmosphere of NH_3 and ND_3 , with expansions of these spectra in Figures 9b and 9d. These i.r. spectra suggest the occurrence of dissociative chemisorption of NH_3 on the carbon particle surface. Vibrational frequencies associated with the surface groups C-NH_2 , C=N-H , $\text{C}\equiv\text{N}$, and C-H are observed in Figures 9a and 9b. The isotope shifts shown in Figures 9c and 9d support these assignments. Surface CNH_2 groups give rise to two bands near 3400 cm^{-1} that are attributed to symmetric and antisymmetric N-H stretching modes. These two bands should shift to 2500 cm^{-1} for CND_2 . This shift is shown in Figures 9c and 9d. A NH_2 bending mode near 1580 cm^{-1} should shift to about 1200 cm^{-1} for the ND_2 group. However, a strong band due to the $k=0, E_{2g}$ phonon

mode of the graphite lattice⁽¹⁷⁾ and/or a vibrational mode of the aromatic structure of graphite⁽¹⁸⁾ also occurs at about 1580 cm^{-1} . Likewise, the C-N stretching mode vibrates at approximately 1200 cm^{-1} and appears in both the C-NH₂ and the C-ND₂ surface groups.

We have detected surface nitrogen groups indicating the dissociation of more than one bond in a molecule of ammonia. A band between 1600 and 1700 cm^{-1} could be assigned to immines (C=NH and C=N-C), a weak band at 2300 cm^{-1} to nitrile (C≡N), and one at 2180 cm^{-1} to isocyanide ($-\text{N}^+ \equiv \text{C}^-$).

The evidence of the dissociative chemisorption of ammonia on carbon particle surfaces is also supported by the appearance of the C-D stretching band at 2050 cm^{-1} . The assignment of the C-H stretching is ambiguous because the C-H stretching is near 2900 cm^{-1} where a vibrational band appears on both NH₃ and ND₃ samples. This band could be the overtone and/or combination bands resulting from the strong absorption band between 1300 and 1600 cm^{-1} . There is also a band, possibly of the same nature, at 2700 cm^{-1} in both samples.

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Figure 1. Nitrogen (1s) and sulfur (2p) regions in X-ray photoelectron spectra of two ambient samples. The peak positions corresponding to NH_4^+ , $-\text{NH}_2$ (N_X), and SO_4^{--} are indicated. The solid vertical bar represents the ammonium intensity expected under the assumption that the entire sulfate is in the form of ammonium sulfate. The difference in the relative ammonium content of the two samples is obvious. The sulfate and ammonium intensities in the St. Louis sample are compatible with ammonium sulfate. The ammonium content in the West Covina sample is insufficient to be compatible with ammonium sulfate. Both samples were exposed to the spectrometer vacuum for about one hour.

Figure 2. The variation in the observed ammonium peak intensity with vacuum exposure for a sample collected in a highway tunnel. The decrease in the peak intensity is caused by the volatilization of the ammonium species present in the sample. The solid vertical bar represents the ammonium intensity expected under the assumption that the sulfate in this sample is in the form of ammonium sulfate. The nitrate in this sample is also small compared with ammonium. The ammonium in this sample is considerably in excess of that expected for ammonium sulfate or ammonium nitrate.

Figure 3. Volatility properties of West Covina, St. Louis, and automotive ammonium aerosol. The shaded bars on the far left of the figure indicate the expected ammonium intensity if the entire sulfate were ammonium sulfate.

Figure 4. Volatility property of ammonium in six ambient St. Louis samples. The ratio of the observed ammonium peak to the one expected under the assumption that the entire sulfate in these samples is ammonium sulfate vs vacuum exposure time is shown. Note the cases of apparently stoichiometric ammonium sulfate (samples 913 and 914) and the cases where the volatile ammonium component is found in excess of that required for ammonium sulfate.

Figure 5. Nitrogen (1s) photoelectron spectrum of an ambient sample as measured at 25, 80, 150, 250, and 350°C.

Figure 6. Nitrogen (1s) spectrum of a soot sample exposed to NH_3 at elevated temperature as measured at 25, 150, 250, and 350°C.

Figure 7. Nitrogen (1s) regions in the ESCA spectrum of an ambient sample collected in Berkeley, California.

- a) Spectrum after the sample had been exposed to vacuum and X-ray bombardment for 1.5 hours.
- b) Spectrum of the same sample after it had been in vacuum for 48 hours.
- c) Spectrum of the same sample heated to 350°C.

Figure 8. Nitrogen (1s) spectrum of a sample produced by grinding graphite powder in an atmosphere of ammonia, measured at sample temperatures of 25°C and 350°C.

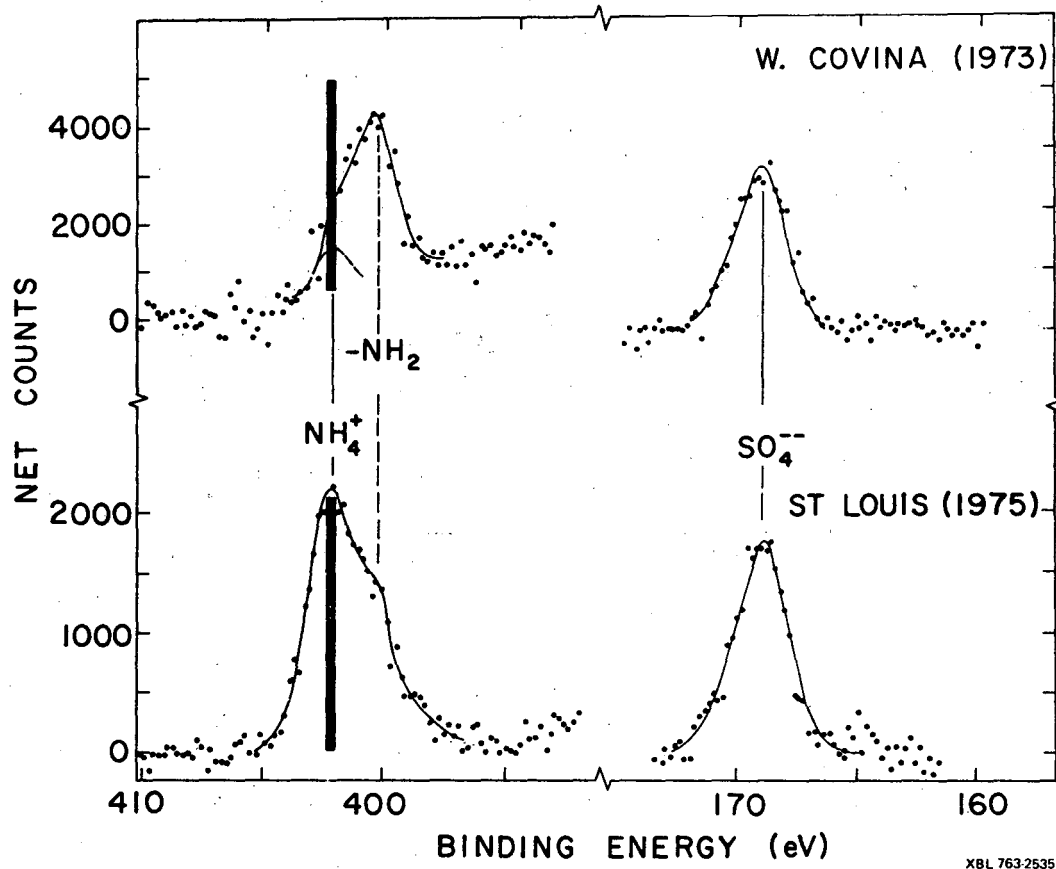
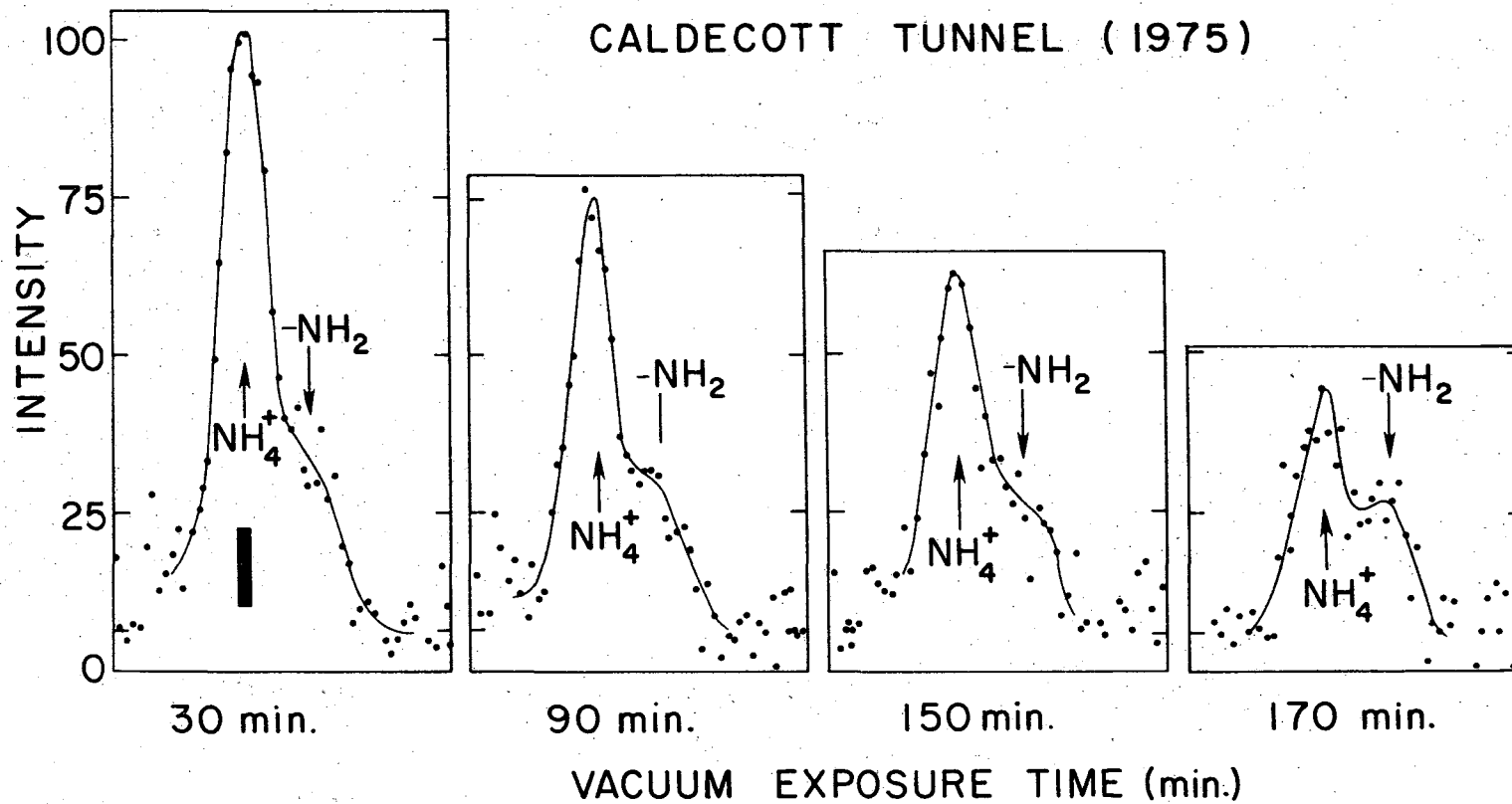


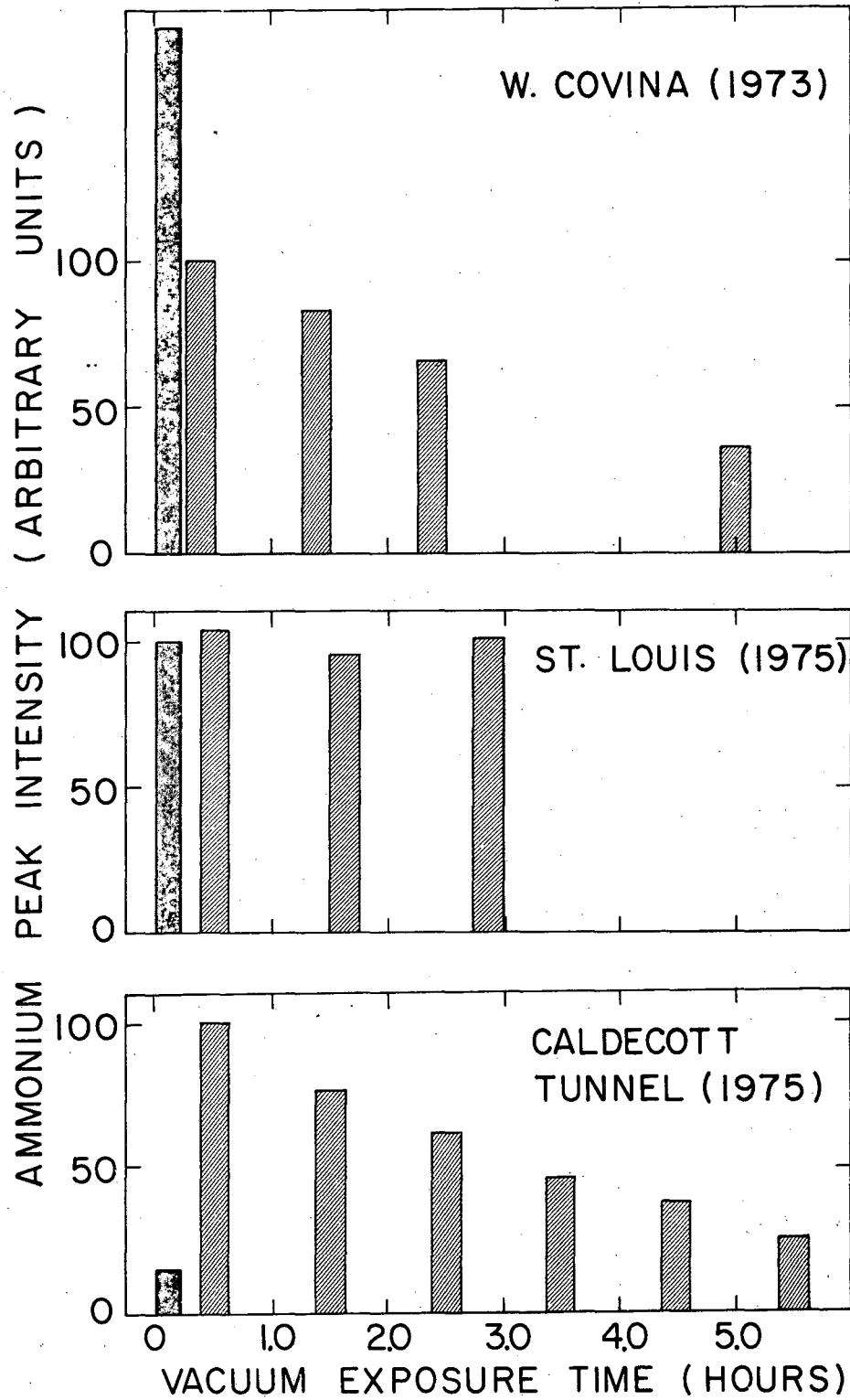
Figure 1



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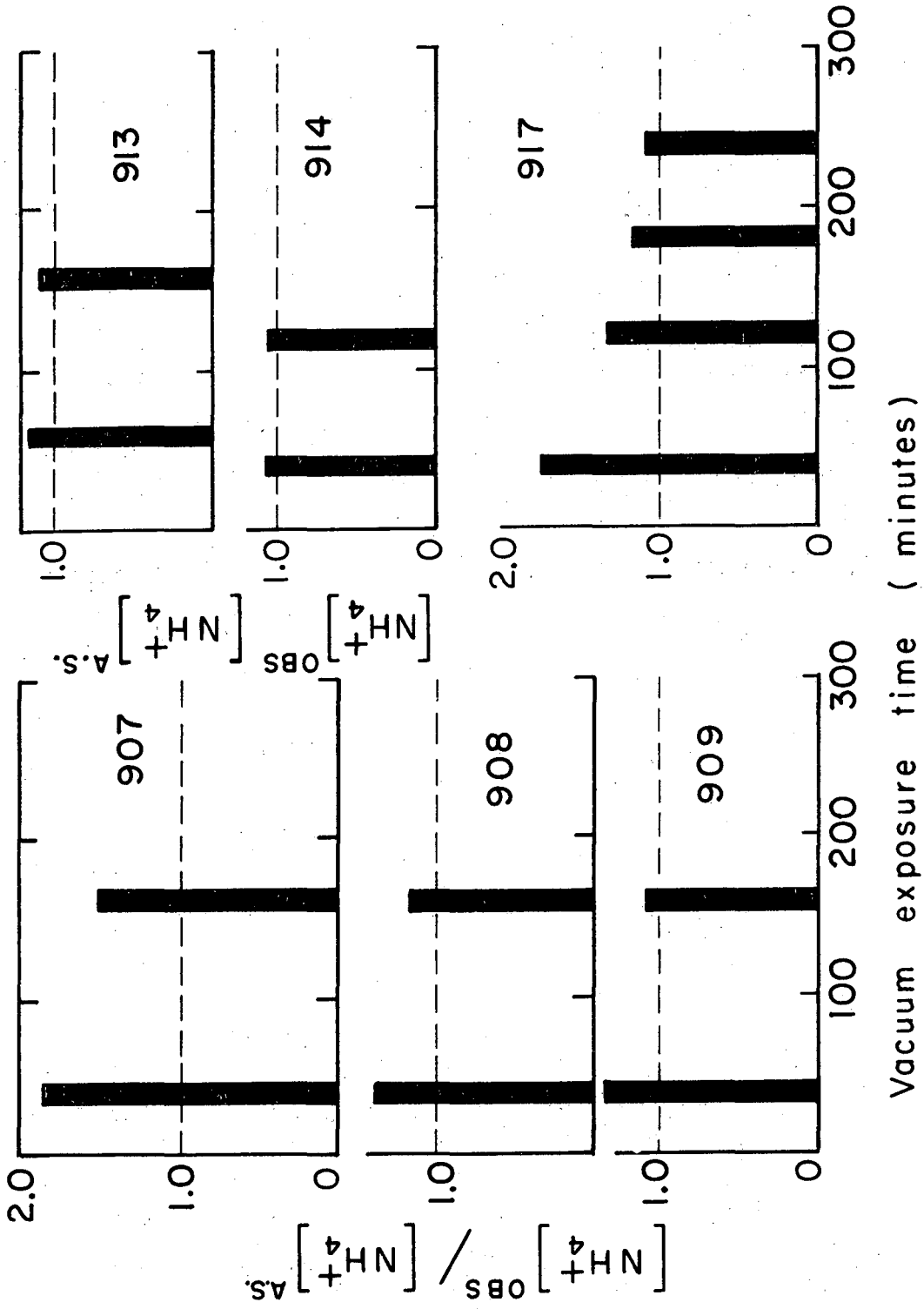
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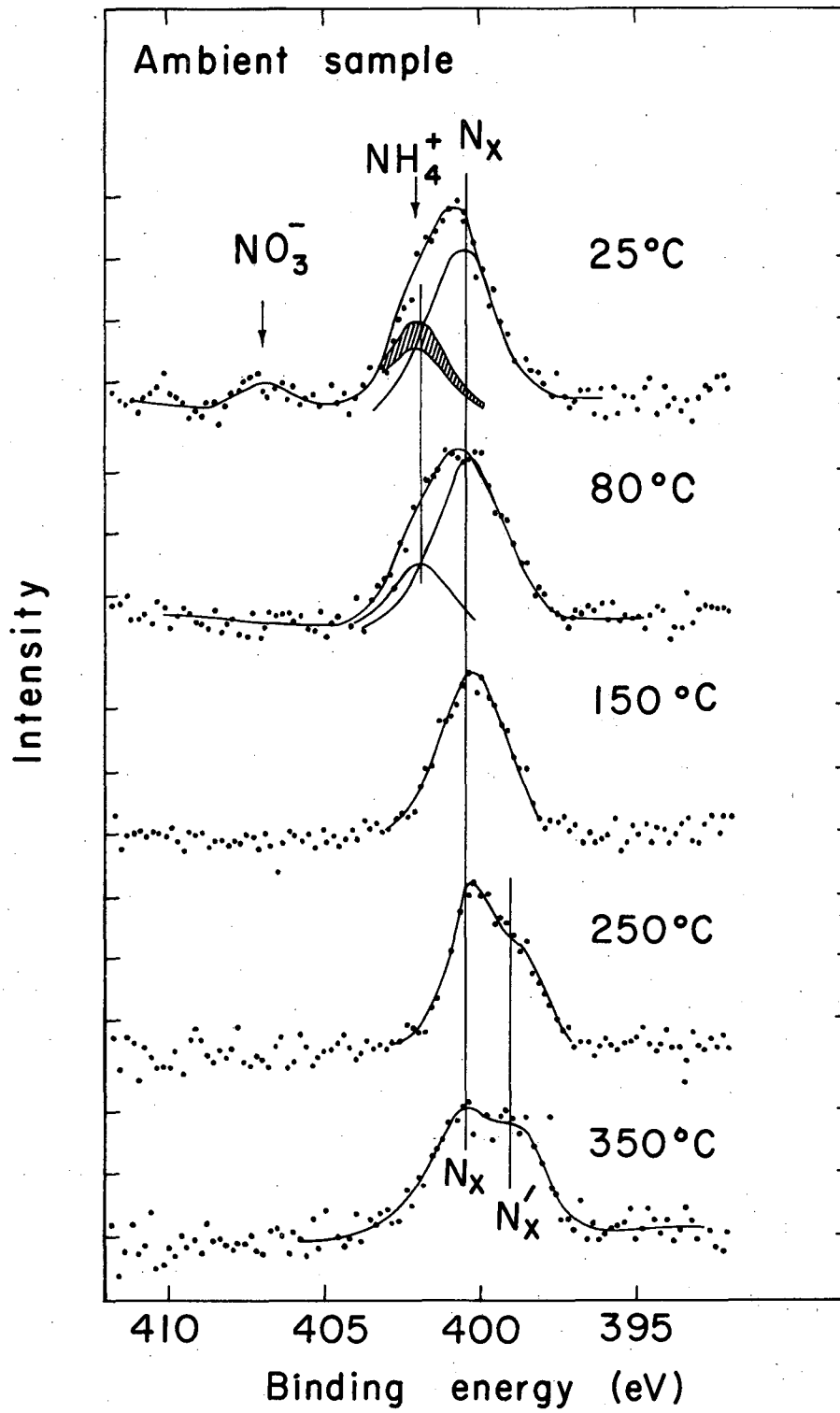
XBL 763-2536

Figure 3



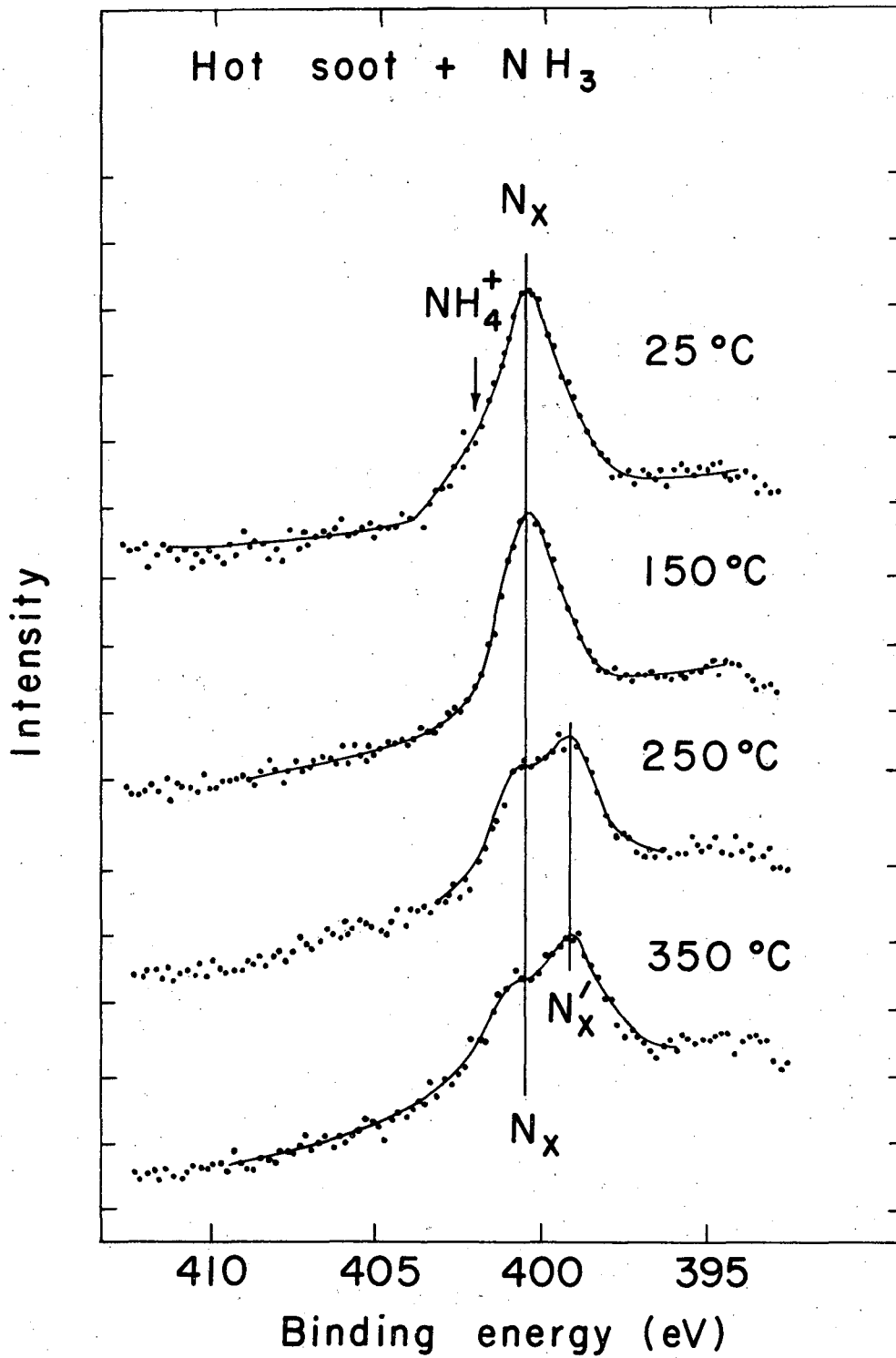
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Figure 4



XBL746-3532

Figure 5



XBL746-3531

Figure 6

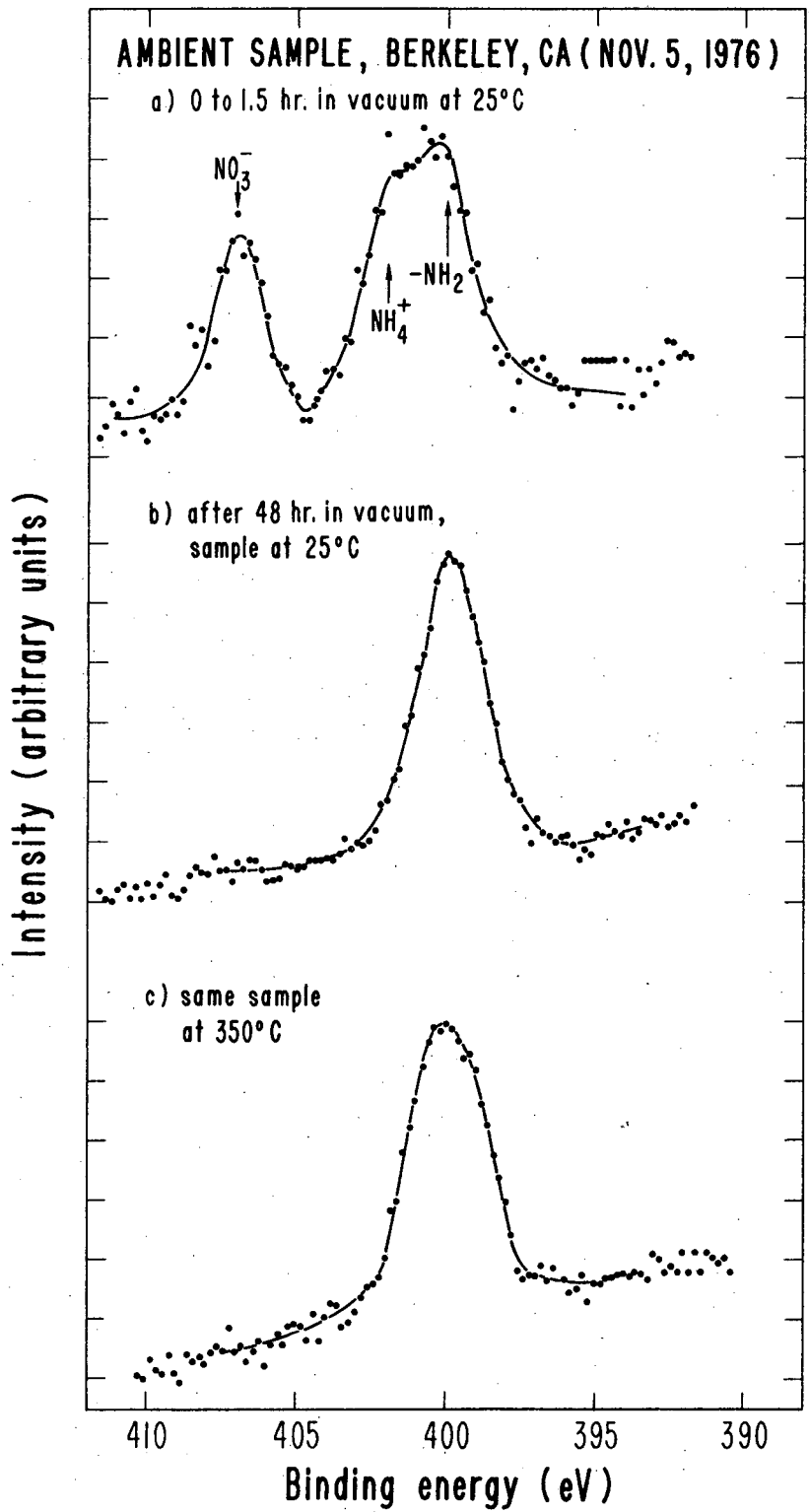
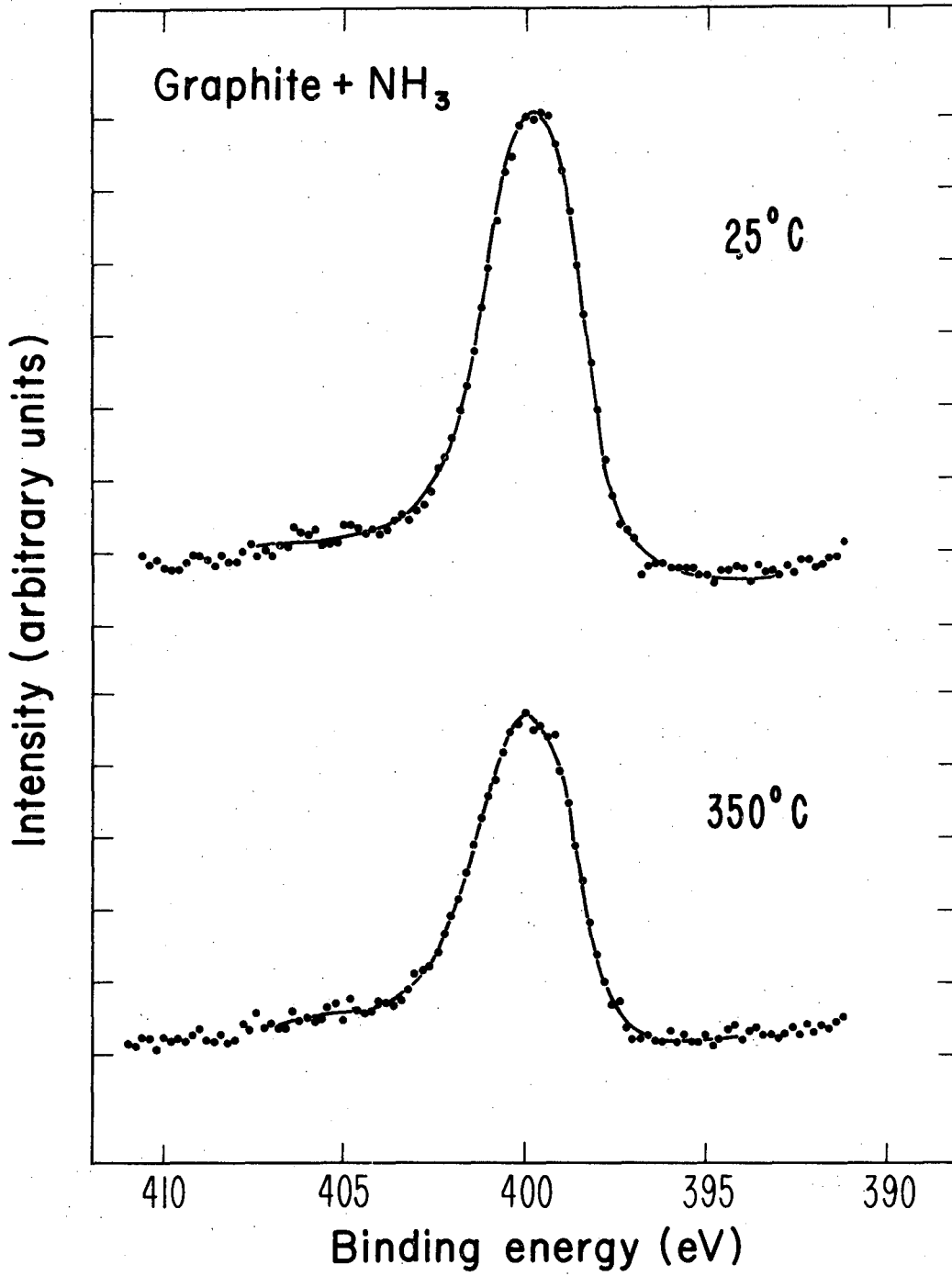


Figure 7



XBL 774-909

Figure 8

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