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Publication Date

1976-06-01

Presented at the Air Pollution Control
Association Annual Meeting, Portland, OR,
June 27 - July 1, 1976

LBL-5215

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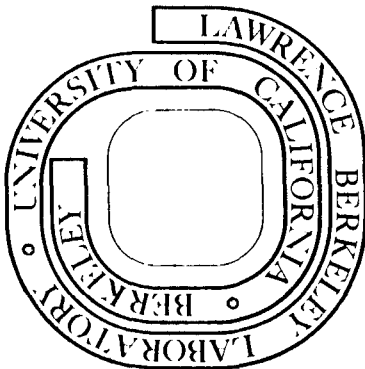
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June 1976

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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Paper presented at the Air Pollution Control Association
Annual Meeting, Portland, Oregon, June 27-July 1, 1976.

Chemical Characterization of Aerosol Species Produced
in Heterogeneous Gas-Particle Reactions*

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*This work was done with support from the U.S. Energy Research and Development
Administration and the National Science Foundation.

Abstract

The body of information presented in this paper is directed to those interested in the chemical characterization of aerosol particle species and their formation in heterogeneous gas-particle reactions. X-ray photoelectron spectroscopy, infrared, and Raman spectroscopy have been applied to study ambient, source-enriched, and laboratory-generated aerosols. The principal conclusions reached in the course of this study are: In addition to ammonium salts such as ammonium nitrate and ammonium sulfate, particulate ammonium may also appear in a volatile form independent of sulfate and nitrate. Studies of laboratory-generated aerosols indicate that the oxidation of SO_2 on soot particles results in the formation of sulfate salt-like species. Their hydrolysis product readily forms ammonium sulfate, however, in reaction with gaseous ammonia. Measurements on source-enriched particles confirm the presence of nitrate produced in nonphotochemical gas-particle reactions. Raman spectroscopic results indicate that physical structures similar to activated carbon are present in ambient and source emission particles.

Introduction

Sulfur, nitrogen, and carbon compounds constitute up to 80% of the dry mass of air pollution aerosol particles. It is therefore important to understand the chemical mechanism responsible for their formation. Furthermore, it is important to examine the relative importance of homogeneous (gas-phase) and heterogeneous (gas-particle) reactions in the formation of major aerosol species. Most studies in the past have emphasized the gas-phase photochemical reactions; considerably less effort has been devoted to studies of nonphotochemical heterogeneous reactions. However, such reactions seem to be important because episodes of heavy aerosol pollution do occur under typically nonphotochemical conditions. Under these conditions the aerosol particles should consist of primary particles and secondary species produced in nonphotochemical, probably gas-particle, reactions.

Because most of the air pollution is caused by the combustion of fossil fuels, it is of interest to investigate the chemical interactions between combustion-generated primary particles and principal gaseous pollutants. We have undertaken a study of the surface chemical and catalytic reactions on soot particles because they are the inevitable particulate products of even seemingly complete combustion. Furthermore, the chemical properties of soot particles are similar to activated carbon, which is a well-known catalytically and surface chemically active material.¹ Soot particles² are formed as the result of pyrolysis, polymerization, and condensation of gases and vapors produced in the incomplete combustion of fossil fuels. Soot particle diameters may range from about 100 Å to several microns. Each individual particle, however, consists of a number of small crystallites about 20 to 30 Å in diameter. The crystallites consist of several layers which exhibit the hexagonal graphitic structure.

In addition to carbon, soot particles contain about 1 to 3% hydrogen and 5 to 15% oxygen by weight.³ Oxygen associated with soot particles is located in surface carbon-oxygen complexes, typically of the carboxyl, phenolic hydroxyl, and quinone carbonyl type.⁴ The nature and the abundance of these surface complexes depend upon the combustion regime. Therefore, soot particles from different sources may differ not only in their physical properties such as size, but also in their surface chemical reactivity. An extreme case would be lamp black or carbon black. This material consists of relatively large particles and has a very low oxygen-to-carbon ratio. Fine soot particles which are invisible to the naked eye, on the other hand, have a much higher oxygen-to-carbon ratio. In this sense, fine soot particles can be regarded as an oxidized form of carbon black.

Before proceeding to outline the experimental results and their implications, we shall first briefly review some of the conclusions reached earlier on the chemical characterization using X-ray photoelectron spectroscopy (ESCA)⁵ of ambient aerosols and aerosol species produced in surface chemical and catalytic reactions involving fine soot particles and SO₂, NO, and NH₃.

The speciation of atmospheric aerosol particles is an important task because many of their environmental effects will depend on their specific chemical and physical state. Furthermore, it is important to determine the chemical compounds and species as they actually exist in the aerosol form

and not as they may appear in aqueous solutions. Most analyses of pollution aerosol particles, however, have employed wet chemical methods which only reflect 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^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+) ions,⁶ and suggested that the most likely combinations of these ions are ammonium nitrate, NH_4NO_3 , and ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$.⁷ In addition to these, nitric acid⁸ and sulfuric acid^{9,10} are also suspected to exist under certain circumstances. Wet chemical methods are of no use for insoluble aerosol species. Nondestructive physical methods are therefore preferred for chemical characterization of collected particles. X-ray photoelectron spectroscopy is one such method. For example, the 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.¹¹ These species are not soluble in water or solvents such as benzene¹² and therefore could not be detected by wet chemical methods.

Detailed ESCA and other studies of some 400 ambient air samples, collected at various places in California, 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: a) nitrate (as nitrogen) is usually a relatively minor fraction of the total particulate nitrogen; b) 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^{12,13}; c) a group of reduced nitrogen species of the amine, amide, and nitrile type^{11,12} occurs in concentrations similar to ammonium; d) the principal chemical form of sulfur is sulfate, which we find exists primarily as sulfuric acid adsorbed on particles; e) in addition to sulfate, sulfides are observed¹⁴ at some locations in concentrations comparable to, although always less than, sulfate; and, f) most of the particulate carbon appears in a neutral chemical state¹² (i.e., non-oxygenated) compatible with both condensed hydrocarbons and with primary combustion-generated carbonaceous material.

Our experiments demonstrate that soot particles, in the presence of moisture, reduce NO to NH_3 which in turn reacts with the surface carbon-oxygen complexes yielding reduced nitrogen species identical to those observed in ambient particles.¹² Ammonium species are produced at ambient temperatures, while amine, amide, and nitrile complexes are produced at elevated temperatures.

At ambient temperatures surface carboxyl and phenolic groups will react with ammonia to form carboxyl-ammonium or phenolic-ammonium salts. Ammonia may also physically adsorb by hydrogen bonding to these same functional groups.

At elevated temperatures ammonia will react by a nucleophilic substitution reaction with carboxyl groups to produce an amide, which may become a nitrile by further dehydration. Alternatively, carboxyl and phenolic hydroxyl ammonium salts may dehydrate at elevated temperatures to produce amides and/or nitriles, and amines, respectively.

We have also demonstrated in a number of experiments that combustion-produced particles are efficient catalysts for SO_2 oxidation to sulfate in humid air.¹⁵ In this respect, soot behaves in an identical fashion to carbon.^{16,17,18} SO_2 oxidation on carbon is preferentially a low temperature reaction. The sulfate formed on carbon is water soluble, yielding an acidic solution. Desorption studies show that the sulfuric acid produced ends up adsorbed on soot particles.

We observed that the catalytic oxidation of SO_2 on carbon particles,¹⁵ analogous to SO_2 oxidation on activated carbon, exhibits a pronounced saturation effect. For a given carbon particle concentration (surface area) and SO_2 concentrations above the saturation limit, the amount of sulfate formed will be practically constant, independent of the increase in the gaseous SO_2 concentration. It is believed that the saturation is caused by the self-poisoning of the carbon particle surface with the adsorbed sulfate product, i.e., sulfuric acid. This saturation behavior can in principle account for the systematic correlation between sulfate and particulate carbon which has been observed, thus far without exception, at different locations.

In this paper we will describe recent ESCA measurements performed on a number of ambient and source-enriched aerosol particles with special emphasis on the sulfate and ammonium containing species. These analyses involve measurements of the ESCA chemical shift augmented by the determination of relative concentrations and volatility of particulate species. We will also present some results on the chemical characterization of secondary species, such as sulfate and nitrate produced in nonphotochemical gas-particle reactions. These analyses were performed by both ESCA and infrared spectroscopy. Finally, the use of Raman spectroscopy to determine the presence of active "graphitic" soot particles in source and ambient air particles will be discussed.

Results and Discussion

Chemical Characterization of Aerosol Particles by Means of ESCA

The capability of ESCA for a 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,¹⁹ in the summer of 1973; and the other, in St. Louis, Missouri,²⁰ in the summer of 1975.) The peak positions corresponding to NH_4^+ , $-\text{NH}_2$, 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.

These results demonstrate that ammonium sulfate in the aerosols can easily be distinguished from other forms of sulfate such as the one found in the West Covina case. However, wet chemical analyses²¹ performed on West Covina samples collected simultaneously with the ESCA samples resulted in

ammonium 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.^{12,13} That these volatile losses are not caused by the volatilization of ammonium sulfate is evidenced by the St. Louis case, where no volatile losses were observed. Similarly, ammonium nitrate (negligible in these samples) and ammonium bisulfate were found to be stable in vacuum for the periods of time usually required to complete the analysis. Therefore, 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)²² are shown as a function of the sample vacuum exposure time. Obviously, the ammonium peak intensity decreases with the vacuum exposure time of the sample. The amino-type nitrogen species intensity remains constant, however. The amount of nitrate in this sample was negligible compared to 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 of the 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. 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 plotted as a function of the sample vacuum exposure time. From inspection of this figure, it is evident that in addition to the cases of practically stoichiometric ammonium sulfate (samples 913 and 914) there are those 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 been shown to have volatility properties similar to those observed in ambient particulates.¹² Another possibility is that these species could be due to ammonium halides which are also volatile in vacuum. More experimental work is necessary in order to assign and evaluate these as well as other volatile ammonium species.

Chemical Characterization of Sulfate Produced by SO₂ Oxidation
on Soot Particles

In order to gain a more complete understanding of the state of chemical bonding of the sulfate produced catalytically on soot particles, we have applied both photoelectron and internal reflection infrared (IRS) spectroscopy to the analysis of sulfate associated with soot.

Photoelectron spectra were obtained with an AEI-200 photoelectron spectrometer utilizing Al K_α (1486.6 eV) radiation. IRS measurements were obtained by means of a Perkin-Elmer 621 infrared spectrophotometer equipped with a Wilks IRS attachment. Interaction of SO₂ with soot particles was studied either in a static regime, i.e., with soot particles precollected on a filter with subsequent exposure to SO₂ at room temperature, or in a flow system by introducing SO₂ downstream from a propane flame.

Photoelectron spectra representing the sulfur (2p) and carbon (1s) regions of propane soot particles produced by a Bunsen burner are shown in Figure 5a. The S (2p) photoelectron peak at a binding energy of 169 eV corresponds to sulfate. The C (1s) peak appears essentially as a single component line and corresponds to a substantially neutral charge state consistent with the soot structure. It is of interest to note that even the combustion of very low sulfur content fuels (0.005% by weight) results in the formation of an easily detectable sulfate emission.

The specific role of soot particles as a catalyst for the oxidation of SO₂ is demonstrated with the aid of Figure 5b. Here we show the S (2p) and C (1s) photoelectron peaks of soot particles, generated in analogous manner as before, but exposed to additional SO₂ in a flow system. A marked increase in the sulfate peak intensity, relative to carbon, is evident. The atomic ratios of sulfur to carbon in Figures 5a and 5b are about 0.15 and 0.50 respectively.

Figures 6a and 6b show infrared spectra between 1500 and 500 cm⁻¹ of the samples used for ESCA analyses (Figures 5a and 5b, respectively). Figure 6c shows the spectrum in Figure 6b expanded by a factor of 5. The spectrum of an aqueous solution of ammonium sulfate is shown in Figure 6d for comparison. The absorption band near 1400 cm⁻¹ is due to an ammonium vibration while the bands near 1080 cm⁻¹ and 615 cm⁻¹ are due to the ν₃ and ν₄ vibrations of the sulfate ion. It is obvious from the figure that exposure of the soot sample to SO₂ increases the sulfate absorption band. It is also clear that the spectra of ammonium sulfate and sulfate associated with soot are very similar. In contrast, these spectra are dissimilar to those of a 1N solution of H₂SO₄ and an aqueous solution of ammonium bisulfate shown in Figures 7a and 7b respectively.

It is possible to explain the observed differences in the IR absorption spectra of the various sulfate species by considering the major dissociation products of these compounds and their symmetry properties. Sulfuric acid is a strong acid. Its first ionization in water is virtually complete: $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+$. Its second ionization constant in water is 1.2×10^{-2} (at 25°C). The dominant species in 1N sulfuric acid are therefore,

hydrogen sulfate anions (HSO_4^-) and hydronium ions (H_3O^+). Ammonium bisulfate will completely dissociate in water to form an ammonium cation and again a hydrogen sulfate anion: $\text{NH}_4\text{HSO}_4 \rightarrow \text{NH}_4^+ + \text{HSO}_4^-$. The principal species in an aqueous solution of ammonium bisulfate are, therefore, ammonium cations and hydrogen sulfate anions. In contrast, ammonium sulfate will completely dissociate in aqueous solution into ammonium cations and sulfate anions.

The observed frequencies of different sulfate anions and their assignment on the basis of a group theoretical analysis²³ are listed in Table I. An inspection of these data shows that the spectra of sulfate species produced by catalytic oxidation of SO_2 closely match the spectrum of the sulfate anion SO_4^{2-} but not the hydrogen sulfate anion HSO_4^- . This would indicate that oxidation of SO_2 on soot particles results in the formation of sulfate salt-like species with tetrahedral structure. The soot particle surface must in that case provide relatively strong basic sites for the neutralization of sulfuric acid.

As previously mentioned, the sulfate associated with soot particles is water soluble. The product of its hydrolysis behaves like sulfuric acid because it easily forms ammonium sulfate in reaction with gaseous ammonia. This is illustrated in Figure 8. In Figure 8a the N (1s) and S (2p) ESCA regions of a soot sample exposed to SO_2 are shown. Here again, the solid bar represents the ammonium intensity expected if the entire sulfate were ammonium sulfate. It is seen that the nitrogen content of this sample is low compared to sulfate. In Figure 8b the ESCA spectrum of a soot sample exposed first to SO_2 and subsequently to NH_3 in humid air is shown. It is obvious that ammonium sulfate is the principal form of sulfate in the sample.

Formation of Nitrate in Gas-Particle Reactions

There are many indications that nitrates can be produced in heterogeneous nonphotochemical reactions. We have confirmed the presence of substantial nitrate concentrations by means of infrared spectroscopy and ESCA in the following cases: a) soot particles from propane-benzene combustion in air; b) exhaust particulates from an internal combustion engine; c) airborne particles collected in a highway tunnel; and d) activated carbon exposed to NO in humid air.

Infrared samples were mixed thoroughly with potassium bromide powder and pressed into pellets. The spectra between 1450 and 1300 cm^{-1} for the various samples are shown in Figures 9a, b, c, and d. In Figure 9e the spectrum of ammonium nitrate is shown for comparison. In all cases an intense and sharp band is found at $1385 \pm 5 \text{ cm}^{-1}$. This band corresponds to the ν_3 asymmetric stretching vibration of the NO_3^- anion. The broader band located at 1400 cm^{-1} is due to the ν_4 vibration of the NH_4^+ cation, and its intensity relative to the nitrate absorption band varies considerably from sample to sample. Parallel measurements have been made using ESCA. These spectra verify the presence of nitrates in all the samples except the one taken in the tunnel where a large observed ammonium peak made the observation of the nitrate peak difficult.

Because all the above samples originate in distinctly nonphotochemical situations, we assume that the oxidation of NO to NO_2 occurs in the dark.

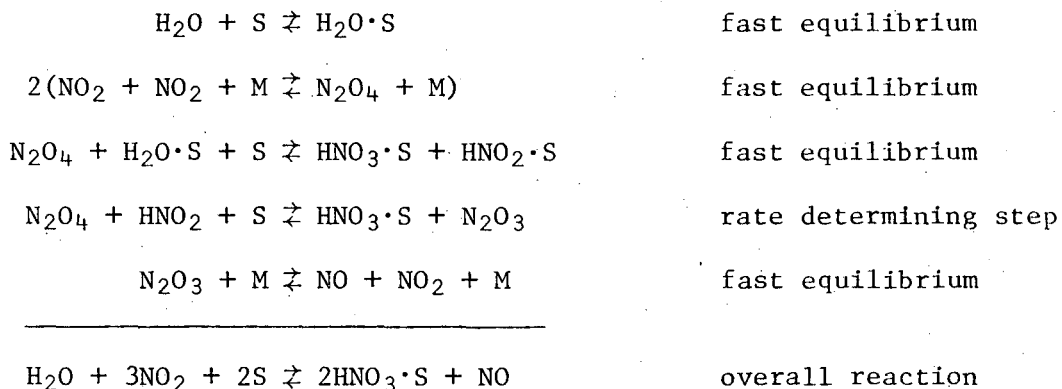
Actually, it is known that NO can be catalytically oxidized to NO₂ by activated carbon and other solids.²⁴ NO₂, once formed, could react with water in a heterogeneous reaction to produce nitric acid. The reverse reaction, i.e., the destruction of nitric acid by nitric oxide, 2HNO₃ + NO surface 3NO₂ + H₂O, has been studied,²⁵ and the following rate law was proposed:

$$\frac{d(\text{NO}_2)}{dt} = k(\text{HNO}_3)(\text{NO})(\text{NO}_2).$$

The equilibrium constant for the reaction is known, and by assuming the microreversibility of the reaction, we have derived the following rate equation for the formation of HNO₃:

$$\frac{d(\text{HNO}_3)}{dt} = k' \frac{(\text{NO}_2)^4(\text{H}_2\text{O})}{(\text{HNO}_3)},$$

where k' is the rate constant and is a function of the nature of the particle surface, k' = f(S). S represents the number of "active" sites on particle surfaces. Using this rate law as a guide, we propose the following step-by-step mechanism:



Here M represents any third body, and HNO₃·S represents the adsorbed HNO₃, H₂O·S adsorbed water, etc.

Characterization of Particulate Carbon

In order to assess the importance of the proposed soot-catalyzed reactions, it is important to determine the chemically active primary carbon in the carbonaceous fraction of ambient and source-enriched aerosol particles. In this section we will present the results of ESCA and Raman spectroscopic measurements aimed at this goal.

Photoelectron spectra of ambient particles show that carbon (1s) photoelectron peak appears essentially as a single peak with a binding energy corresponding to a neutral charge state, compatible with either elemental carbon or hydrocarbons. Chemically shifted carbon peaks due to oxygen bonding, when observed, are generally of low intensity as compared with the main neutral charge state carbon peak. Such measurements tend to rule out

carbonates and highly oxygenated hydrocarbons--expected from photochemical reactions--as the major forms of particulate carbon.

Unfortunately, because of the nature of the chemical bonding in hydrocarbons, they cannot be distinguished from soot-type carbon by ESCA chemical shift under realistic sample conditions. We therefore had to employ other supplementary measurements to estimate the relative abundance of soot in airborne particles. This was achieved in one series of experiments by comparing the carbon ESCA peak intensity with the sample at normal operating temperature of 25°C to the peak intensity obtained with the same sample at 350 to 400°C. The difference between the low and high temperature runs should give the fraction of the volatile carbon compounds, under the assumption that organic compounds formed in atmospheric reactions will have vapor pressures above 10^{-6} torr, i.e., order of magnitudes higher than the spectrometer pressure, at the temperatures employed. We have performed such measurements on a number of ambient samples and have found that in these samples, up to 80% of the total carbon is nonvolatile and of essentially neutral core charge.

During the last year we have performed preliminary studies to explore the feasibility of characterizing particulate carbon by means of Raman spectroscopy. We believe that this is the first attempt to apply this spectroscopic technique in this area of research. The samples studied, among others, were polycrystalline graphite, activated carbon, diesel exhaust particles, automobile exhaust particles (unleaded fuel, no catalytic converter), and several ambient air samples.

The major features of the Raman spectra are two intense lines at about 1350 cm^{-1} and 1600 cm^{-1} . In the ambient samples, where the signal-to-noise is severely limited by the large fluorescence background, the only lines that were clearly seen above the noise level were also in this spectral region. In Figure 10 we show the Raman spectra of the various samples in the region between 1200 to 1700 cm^{-1} .

In perfectly ordered single-crystal graphite specimens, only the Raman mode near 1600 cm^{-1} is observed and from a group theoretical analysis has been assigned to the $k = 0, E_{2g}$ phonons of the graphite lattice.²⁵ The mode near 1350 cm^{-1} appears only in samples which are not perfectly ordered, and its intensity relative to that of the one near 1600 cm^{-1} varies inversely with the crystallite size, L_a , as obtained from X-ray data.

It is evident from Figure 10 that the spectra of activated carbon, diesel exhaust, automobile exhaust, and ambient samples are very similar. The positions of the two Raman modes in these spectra are coincident to within $\pm 10\text{ cm}^{-1}$, which is the estimated error. Since the phonon frequencies are a sensitive probe of the lattice, we suggest that these spectra give strong evidence for the existence of physical structures similar to activated carbon in the samples studied.

Using the available results from the literature, we can estimate the crystallite sizes in the various samples from the intensity ratios of the two observed Raman modes. The ambient, diesel exhaust and automobile exhaust

particles appear to have roughly the same peak intensity ratio, indicating a crystallite size between 50 and 100 Å.

These results indicate that physical structures similar to activated carbon are present in exhaust and ambient samples. The fact that the two observed modes are the dominant features of the Raman spectrum may indicate that "graphitic" soot is the major component in these samples. However, the large intensity of these modes may be due just to their large Raman cross section. Quantitative interpretation of these results will have to await a more detailed analysis.

Conclusions

ESCA analysis on ambient samples allows for a straightforward differentiation of different forms of atmospheric sulfate and ammonium containing species. The following distinctly different cases have been identified.

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

The anions corresponding to the volatile ammonium species cannot be identified with certainty at this time, however.

ESCA and infrared analyses indicate that oxidation of SO_2 on soot particles results in the formation of sulfate salt-like species with tetrahedral structure. The product of its hydrolysis behaves like sulfuric acid and it readily forms ammonium sulfate in reaction with gaseous ammonia.

ESCA and infrared measurements on source-enriched particles confirm the presence of nitrate produced in heterogeneous nonphotochemical reactions. A step-by-step mechanism is proposed to account for this observation.

Results obtained by means of Raman spectroscopy indicate that physical structures similar to activated carbon are present in ambient and source emission particles.

References

1. For a review of catalytic and surface chemical properties of activated carbon see: S. Berkman, J. C. Morrell, and G. Egloff, Catalysis, Reinhold, New York, 1940; and J. S. Mattson and H. B. Mark, Jr., Activated Carbon, Marcel Dekker, New York, 1971.
2. See, for example, J. B. Edwards, Combustion--Formation and Emission of Trace Species, Ann Arbor Science, Ann Arbor, 1974, and references therein.
3. A. Thomas, Comb. and Flame 6: 46 (1972).
4. H. P. Boehm, Advan. Catal. Relat. Subj. 16: 179 (1966).
5. For application of ESCA to aerosol analysis see T. Novakov, Proc. 2nd Joint Conf. on Sensing of Environ. Pollutants, Instr. Soc. of America, Pittsburg, 1973, p. 197.
6. C. E. Junge, Atmospheric Chemistry and Radioactivity, Academic Press, New York, 1973.
7. G. M. Hidy and C. S. Burton, Int. J. of Chem. Kinetics, Symposium 1: 509 (1975).
8. D. F. Miller and C. W. Spicer, J. Air Pollut. Contr. Assoc. 25: 940 (1975).
9. R. J. Charlson et al., Science 184: 156 (1974).
10. P. T. Cunningham et al., Chemical Engineering Division--Environmental Chemistry Annual Report, Argonne National Laboratory Report ANL-75-51 (1975).
11. T. Novakov, P. K. Mueller, A. E. Alcocer, and J. W. Otvos, J. Colloid Interface Sci. 39: 225 (1972).
12. S. G. Chang and T. Novakov, Atmos. Environment 9: 495 (1975).
13. B. R. Appel, J. J. Wesolowski, E. Hoffer, S. Twiss, S. Wall, S. G. Chang, and T. Novakov, Intern. J. Environ. Anal. Chem. 4: 169 (1976).
14. N. L. Craig, A. B. Harker, and T. Novakov, Atmos. Environment 8: 15 (1974).
15. T. Novakov, S. G. Chang, and A. B. Harker, Science 186: 259 (1974).
16. J. Siedlewski, Intern. J. Chem. Eng. 5: 608 (1965).
17. O. K. Davtyan and Yu. A. Tkach, Zh. Fiz. Khim. 35: 992 (1961).
18. K. Yamamoto, M. Seki, and K. Kawazoe, Nippon Kagaku Kaiski 7: 1268 (1973).
19. Samples courtesy of C. W. Spicer, Battelle Memorial Institute, Columbus, Ohio.

20. Samples courtesy of T. Dzubay, EPA--National Environmental Research Center, Research Triangle Park, North Carolina.
21. C. W. Spicer, Battelle Memorial Institute, Columbus, Ohio, private communication.
22. C. D. Hollowell et al., Lawrence Berkeley Laboratory Report LBL-5214 (1976).
23. For details see S. G. Chang and T. Novakov, Lawrence Berkeley Laboratory Report LBL-4446 (1975).
24. M. N. Rao and O. A. Hougen, A.I.Ch.E. Symposium Series 48: 110 (1952).
25. J. H. Smith, J. Phys. Chem. 69: 1741 (1947).
26. F. Tuinstra and J. L. Koenig, J. Chem. Phys. 53: 1126 (1970).

Table I. Observed IRS fundamental vibrational frequencies of sulfate ions in the region 1500 to 500 cm^{-1} .

Origin	Main sulfur species	Pt. group	ν_1	ν_2	ν_3	ν_4
1N H_2SO_4	HSO_4^-	C_{3v}	885(S)	—	1040(S) 1160(S)	578(S) 605(M)
NH_4HSO_4 aqueous soln.	HSO_4^-	C_{3v}	860(S)	—	1035(S) 1162(S)	578(S) 605(M)
$(\text{NH}_4)_2\text{SO}_4$ aqueous soln.	$\text{SO}_4^{=}$	T_d	978(W)	—	1072(S)	612(M)
soot+ SO_2 in humid air	$\text{SO}_4^{=}$	T_d	960(W)	—	1080(S)	615(M)

Figure Captions

Figure 1. Nitrogen (1s) and sulfur (2p) regions in X-ray photoelectron spectra of two ambient samples. The peak positions corresponding to NH_4^+ , $-\text{NH}_2$, and SO_4^{2-} 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 differences 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 to 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. Carbon (1s) and sulfur (2p) photoelectron spectrum of:
 a) Soot particles produced by combustion of propane saturated with benzene vapor. The sulfur content of this fuel is 0.005% by weight.
 b) Soot particles generated in analogous manner to a, but exposed to additional SO_2 in humid air.

Figure 6. Infrared (IRS) spectra (between 1500 and 500 cm^{-1}) of:
 a) Soot particles produced by combustion of propane saturated with benzene vapor.
 b) Soot particles generated in an analogous manner to a but exposed to additional SO_2 in humid air.
 c) The same spectra shown in b but expanded by a factor of 5.
 d) Aqueous solution of ammonium sulfate. The absorption band at 1400 cm^{-1} is due to the ν_4 vibration of the NH_4^+ cation.

Figure 7. Infrared (IRS) spectra of:

- a) 1N sulfuric acid aqueous solution.
- b) An aqueous solution of ammonium bisulfate.

Figure 8. a) ESCA spectrum of sulfate produced by catalytic oxidation of SO_2 on soot particles. Note that the nitrogen content in this sample is low compared to sulfate.

b) ESCA spectrum of a soot sample exposed first to SO_2 (i.e., as in Figure 5a), and subsequently to NH_3 in humid air. Formation of ammonium sulfate is evident.

Figure 9. Infrared spectra between 1450 and 1300 cm^{-1} of:

- a) Soot particles from propane-benzene combustion in air.
- b) Exhaust particles from an internal combustion engine.
- c) Airborne particles collected in a highway tunnel.
- d) Activated carbon exposed to NO in humid air.
- e) Ammonium nitrate.

Figure 10. Raman spectra between 1200 and 1700 cm^{-1} of

- a) Ambient sample collected in 1962 in Buffalo, New York. The sample was collected with a hi-vol sampler on a glass fiber filter. Similar spectra were observed for samples collected from St. Louis in 1975 as part of the RAPS program.
- b) Car exhaust (unleaded fuel and no catalytic converter).
- c) Diesel exhaust.
- d) Activated carbon.
- e) Polycrystalline graphite.

The slit width for samples b-e was 3 Å, while for sample a 7-Å slits were used to improve signal-to-noise.

Figure 1

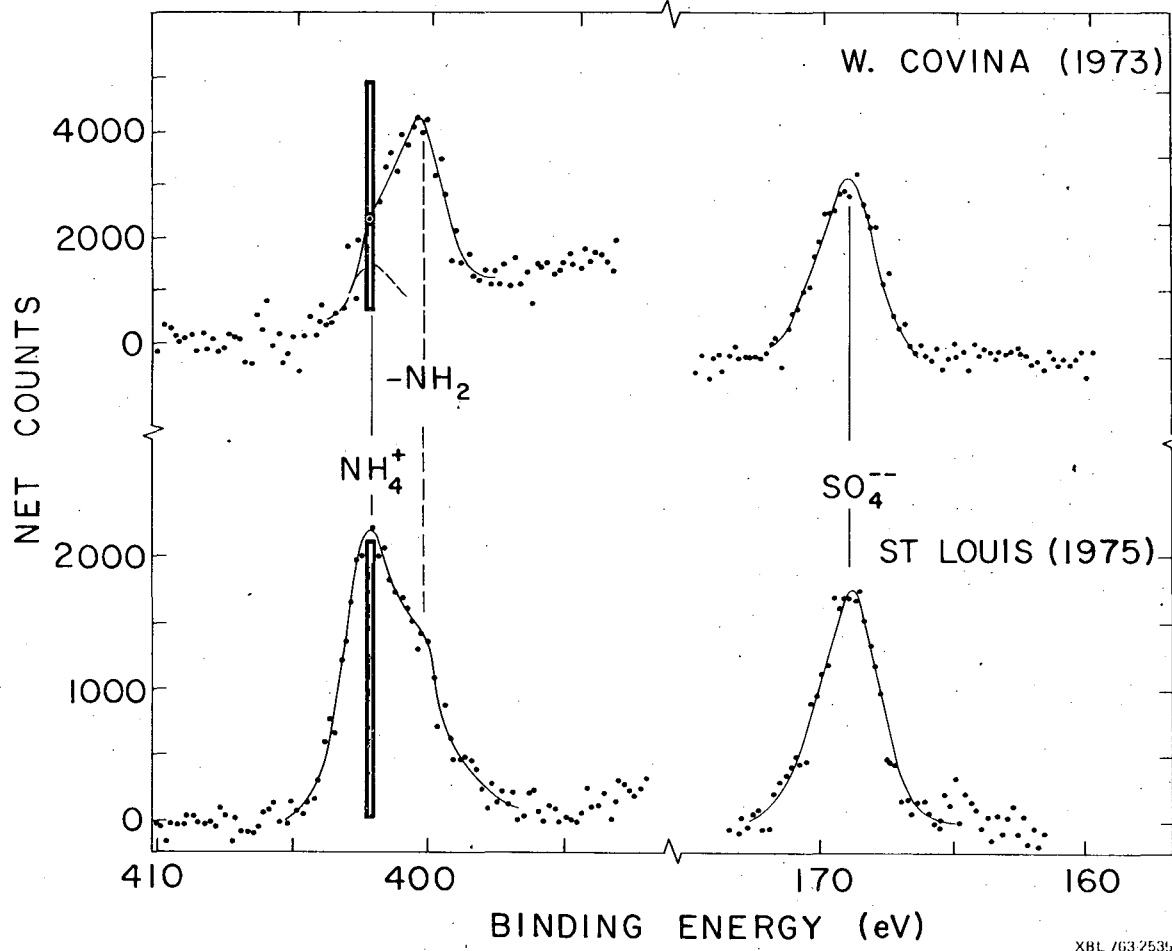
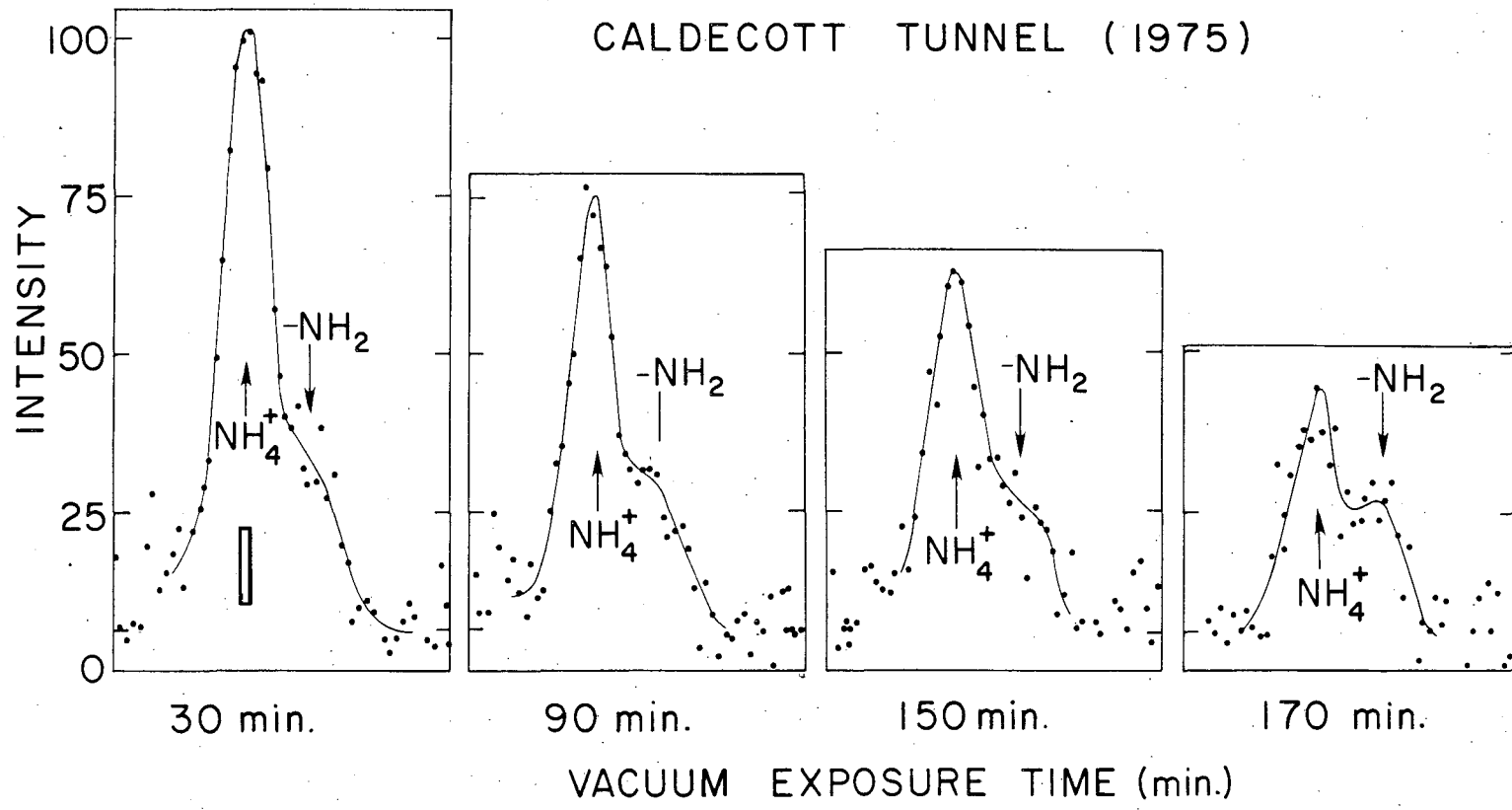


Figure 2



19

Figure 2

XBL 763-2537

Figure 3

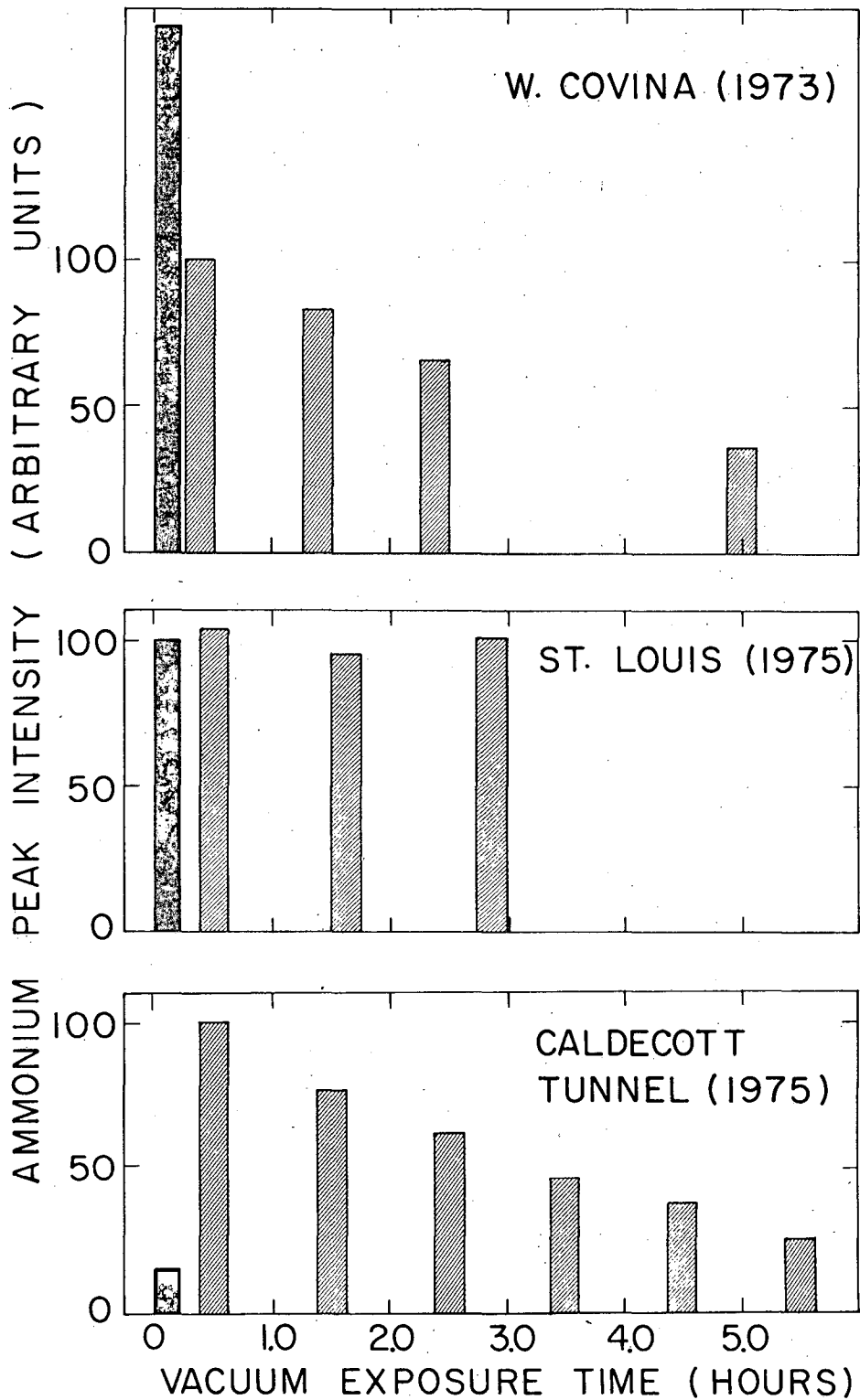
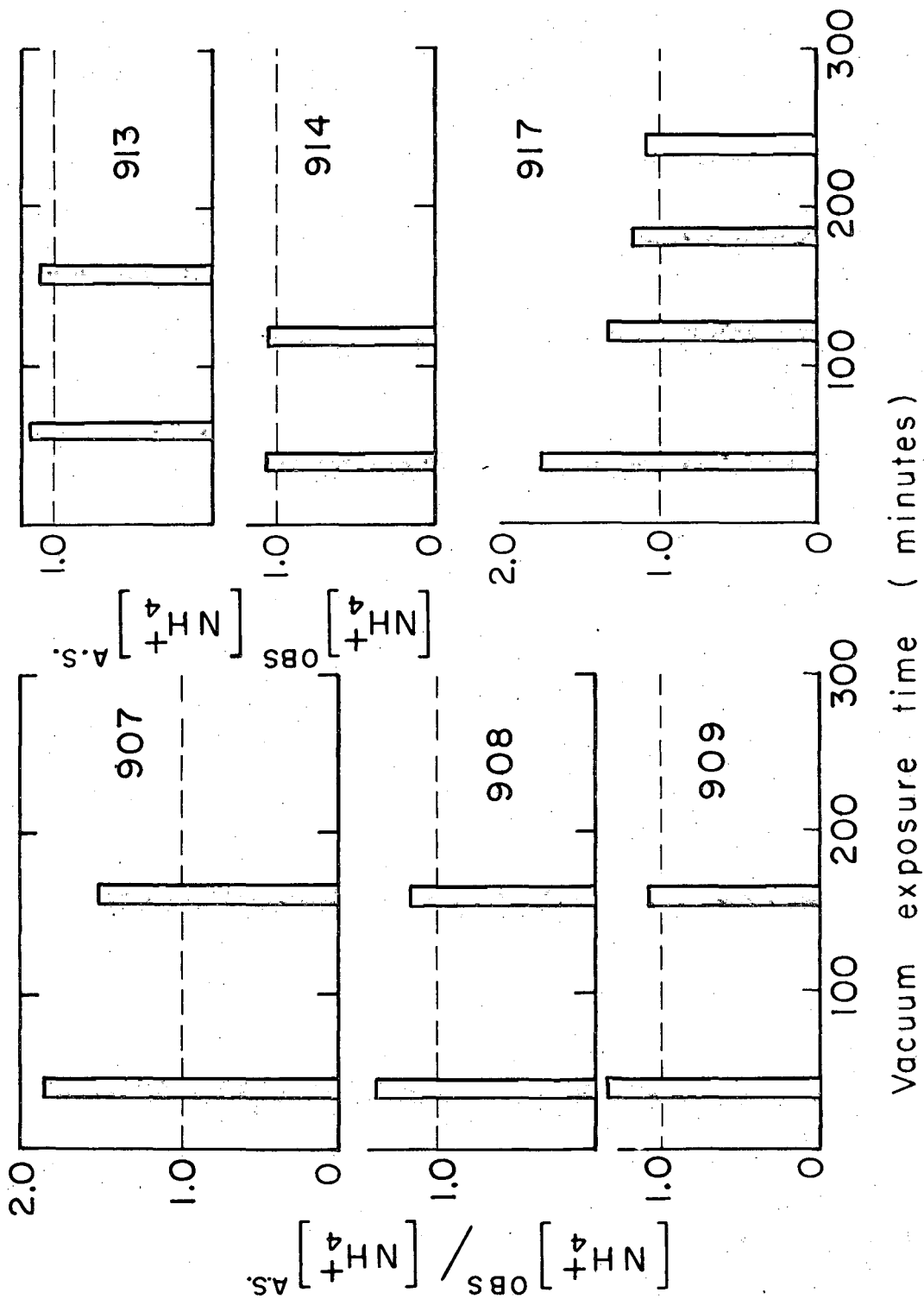
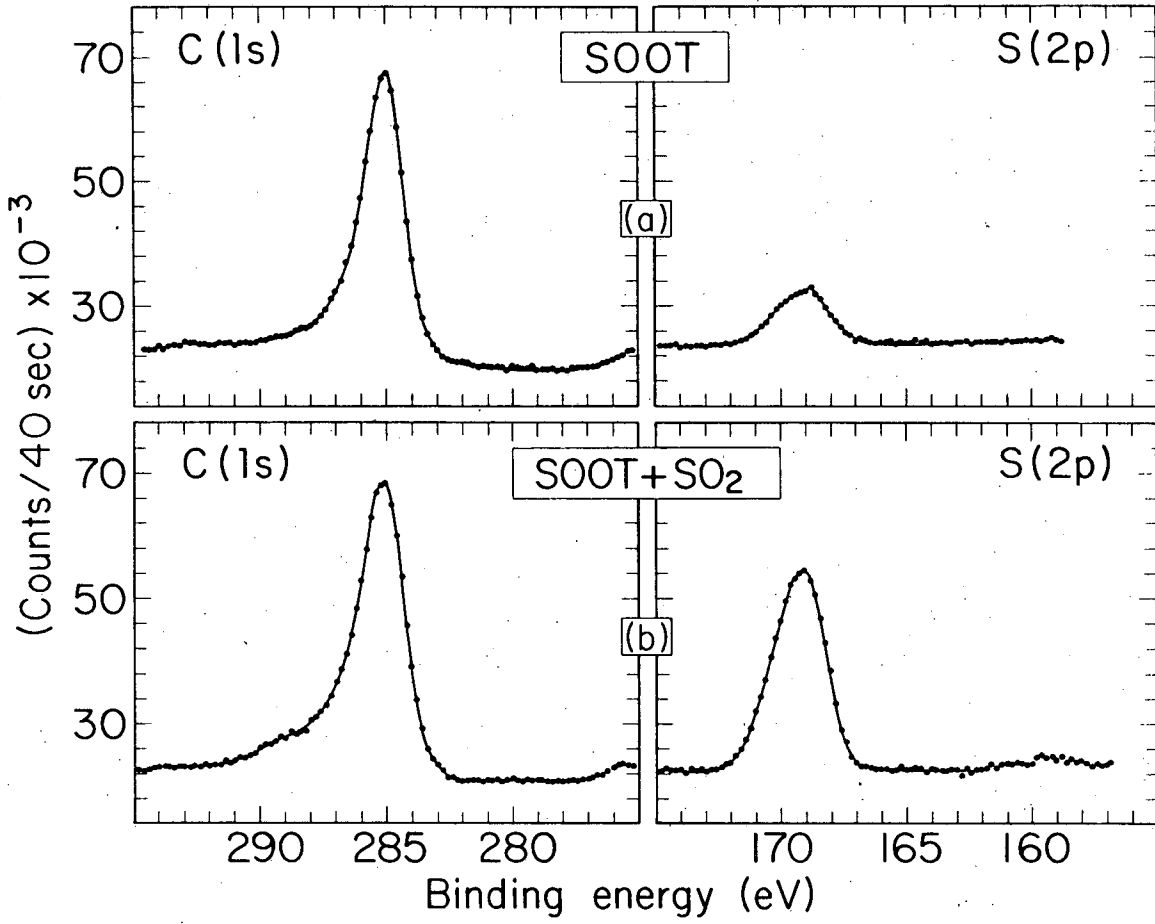


Figure 4



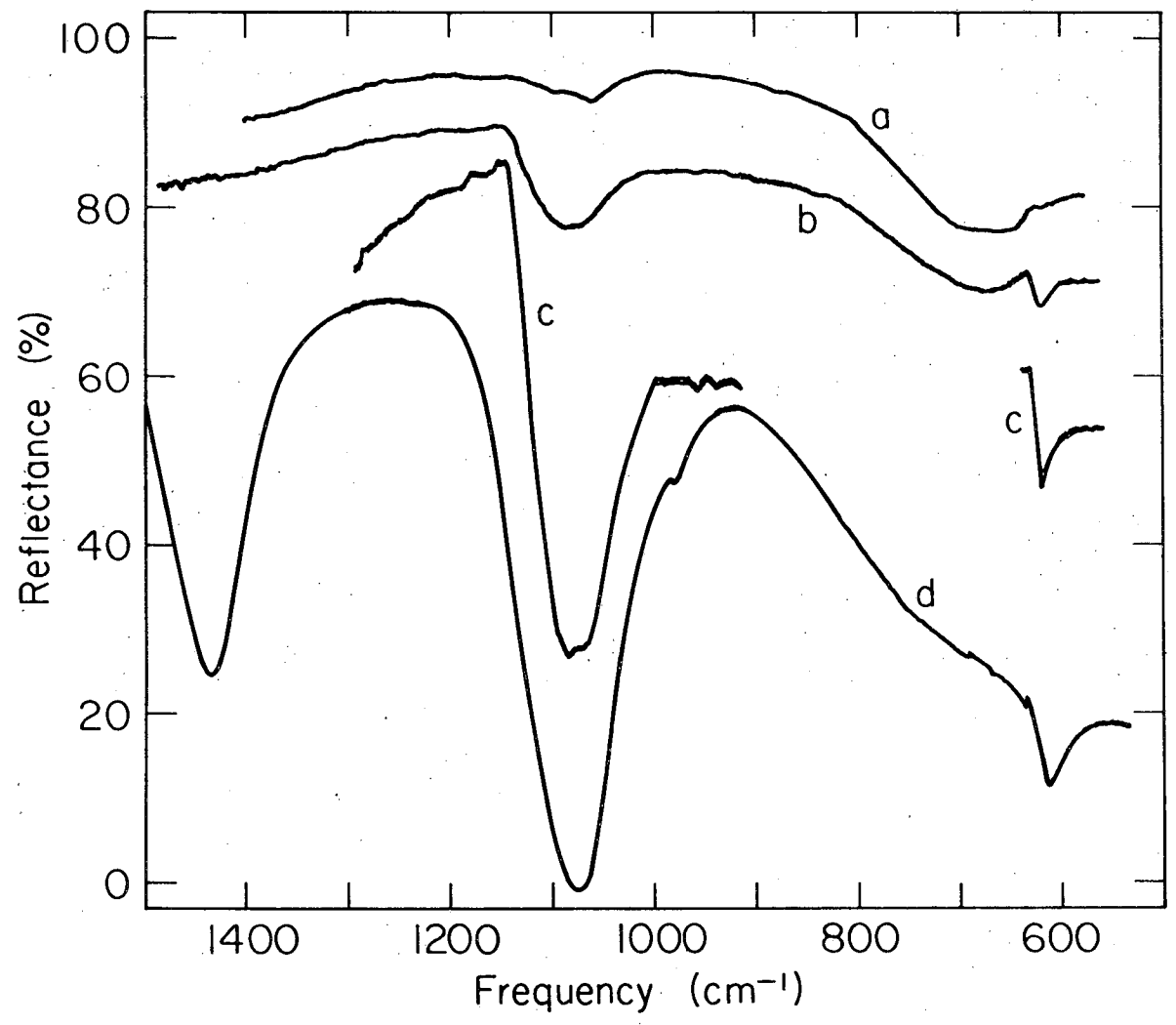
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Figure 5



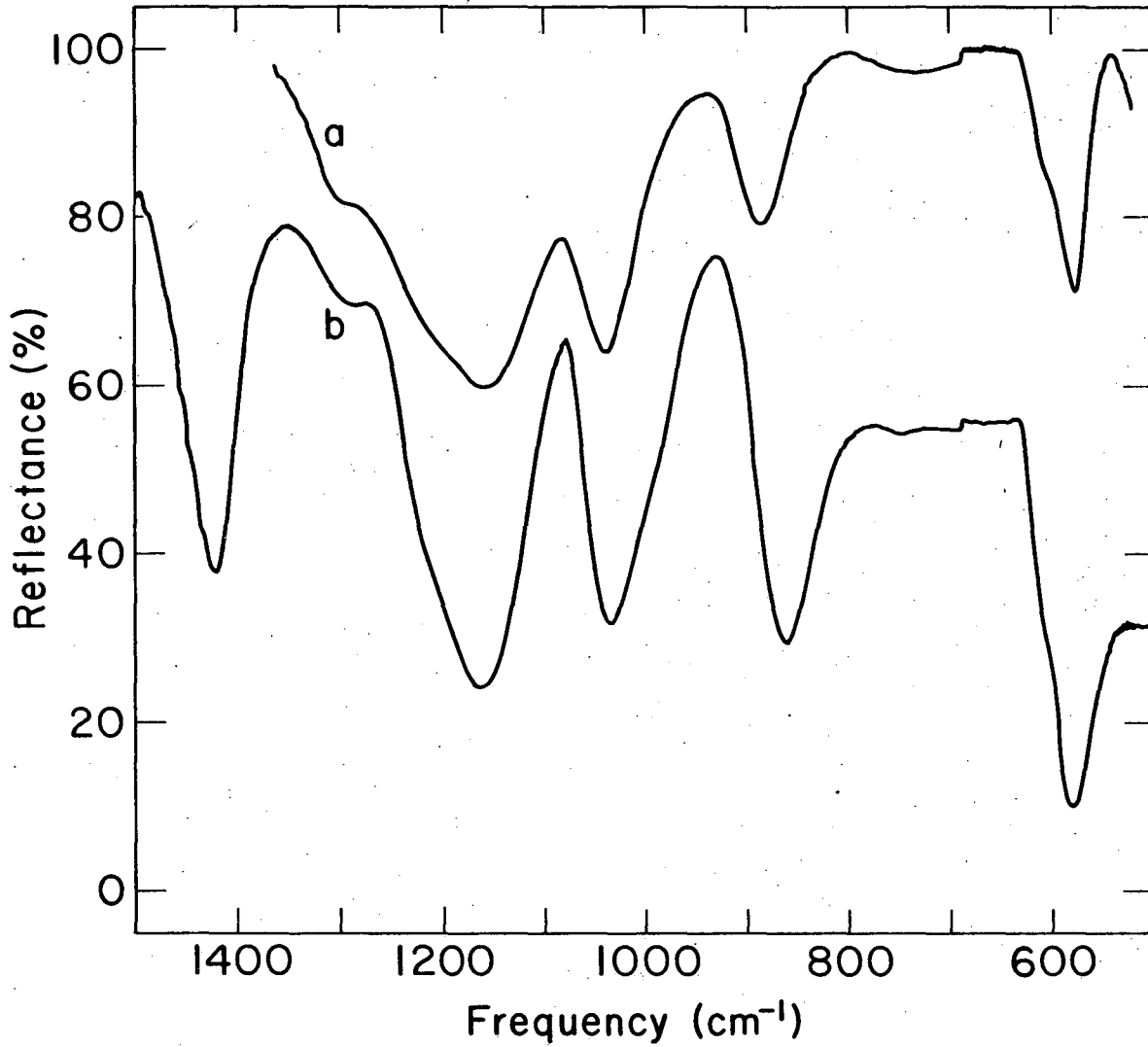
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Figure 6



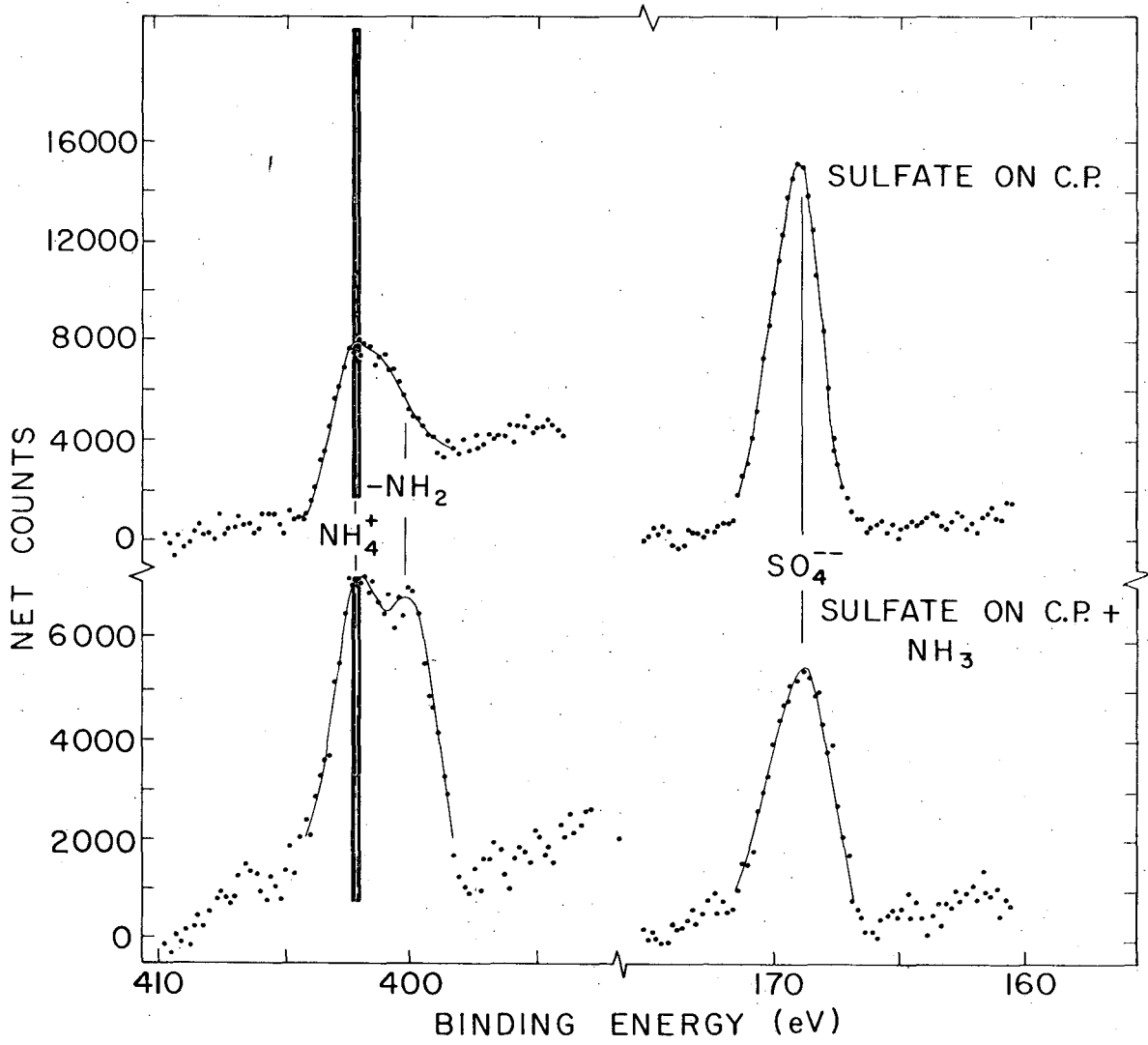
XBL763-2367

Figure 7



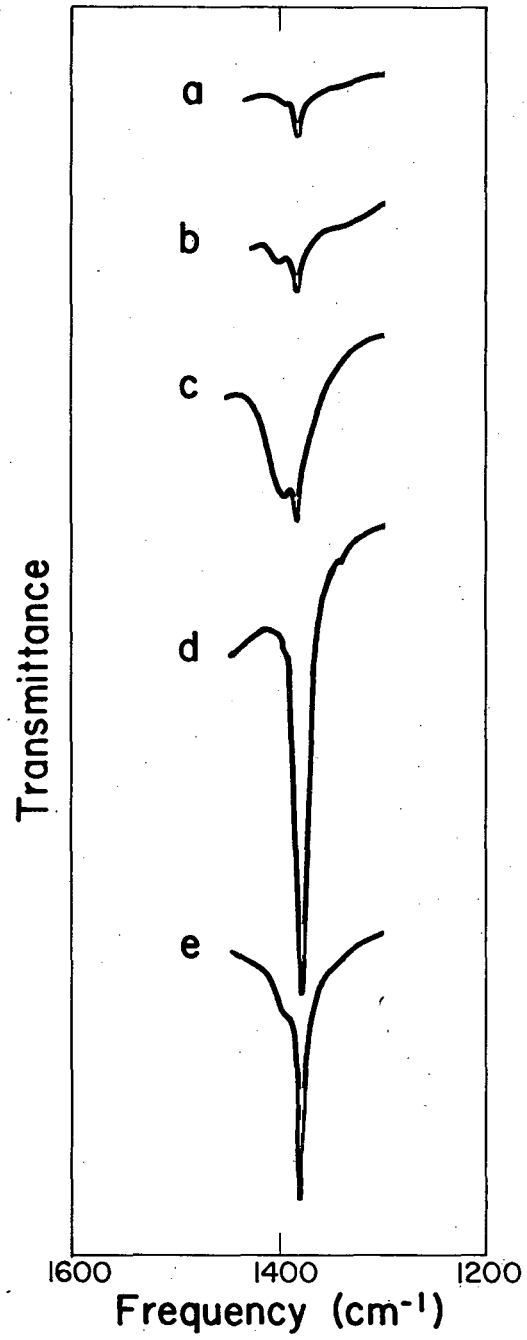
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Figure 8



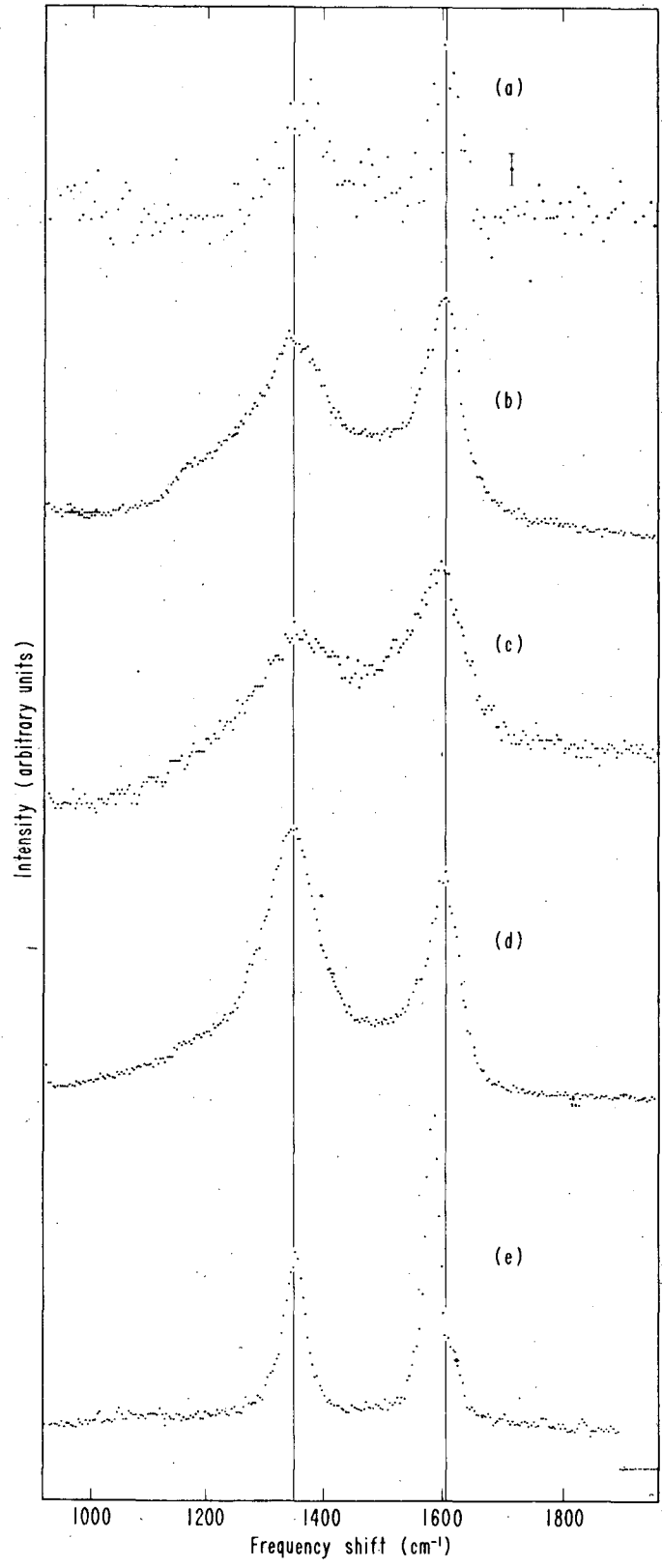
XBL 763253B

Figure 9



XBL 764-2612A

Figure 10



XBL 763-2481A

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