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INFRARED AND PHOTOELECTRON SPECTROSCOPIC STUDY
OF SO₂ OXIDATION ON SOOT PARTICLES

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ABSTRACT

Results obtained by means of x-ray photoelectron spectroscopy and internal reflection infrared spectroscopy demonstrate the feasibility of heterogeneous oxidation of sulfur dioxide on soot particles in air. Sulfuric acid formed in this process can be neutralized on basic surface sites of soot particles, resulting in the formation of carbonium and/or oxonium sulfate. Hydrolysis of these salts into cyclic hemiacetals and sulfuric acid is expected.
INTRODUCTION

Novakov et al. (1) have recently demonstrated that combustion generated air suspendable carbonaceous (soot) particles are an efficient catalyst for the oxidation of SO$_2$ to sulfate, and suggested that this heterogeneous oxidation is important from the air pollution standpoint. X-ray photoelectron spectroscopy (XPS or ESCA) and wet chemical methods were used to characterize the product of SO$_2$ oxidation. The results of XPS analysis demonstrate that the oxidation state of the SO$_2$ oxidation product is 6+, i.e., sulfate, while wet chemical analyses show that the sulfate associated with soot particles is water soluble, and that it contributes to the acidification of water when dissolved. The question about the actual state of chemical bonding of sulfate associated with soot particles remains open, however. Namely, measurements of the type employed do not by themselves distinguish between, for example, liquid sulfuric acid, sulfuric acid adsorbed on soot particles, sulfate salts, etc. 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. The combination of these two techniques produced much more information than either of them used separately.
It is an established fact that XPS provides valuable information about solid surfaces, giving a measure of the charge states (oxidation states) \((2,3)\) of the elements which constitute the surface species. A parallel application of infrared spectroscopy should provide direct information on the molecular structure of the adsorbed species and the catalytic substrate itself.

It is difficult to apply the infrared transmission technique to the study of soot particles because of their large infrared absorption\((4)\) and high scattering losses. The technique of internal reflection spectroscopy, however, allows for efficient utilization of the incident light, without appreciable scattering losses. This makes it especially useful for the type of research described in this paper.

In this paper, we describe the results which demonstrate the heterogenous oxidation of \(\text{SO}_2\) on soot particles, and which furthermore show that the sulfuric acid, formed in this process, can be neutralized on basic surface sites of soot particles, resulting in the formation of carbonium and/or oxonium sulfate.

Because this research deals with catalytic and surface reactions of soot particles, a short summary of the known chemical properties of soot is in order at this point. For the purpose of clarity we shall, although somewhat arbitrarily, define "soot" as the combustion produced, air suspendable carbonaceous particles of relevance to air pollution. Much of the work in the past, however, has dealt with carbon blacks and charcoals, which we shall refer to
as "activated carbon". The differences between soot and activated carbon are related to particle size, surface to volume ratio, amount of surface oxygen complexes, surface area etc. (For example, soot can be regarded as "oxidized" carbon black.) The differences in their catalytic and adsorptive properties, are quantitative and not qualitative, however. We shall, therefore, assume that relevant results obtained in studies with activated carbon also apply to airborne soot.

Soot particle emissions result from the pyrolysis, polymerization and condensation of combustion produced gases (5,6). Small soot particles may agglomerate into larger aggregates, stuck together in a rather open network. Each individual soot particle consists of a large number of small crystallites 20 to 30 Å in diameter (7,8). These consist of several carbon layers with hexagonal graphite structure. The layer planes are randomly stacked in the crystallites. The distance between neighboring carbon atoms is 1.42 Å, i.e., similar to graphite. The interlayer spacing in soot is about 3.6 Å, that is, larger than in graphite (3.35 Å), indicating that the planes are held together by relatively weak Van der Waals forces.

Soot particles and activated carbon surfaces contain many exposed defects, dislocations and discontinuities in the layer planes, which may be regarded as active sites. Surface carbon atoms located at these sites, because of residual valencies, show a strong tendency to chemisorb other molecules. Thus, because of reactions with water
and oxygen during the process of combustion, 5 to 15% oxygen and
1 to 3% hydrogen (by weight) (9) may become incorporated into soot
particles. One may, therefore, regard soot as a complex three-
deimensional organic polymer, rather than merely as an amorphous
form of elemental carbon.

Oxygen associated with soot or activated carbon is
located in surface carbon oxygen complexes. Different kinds of
such complexes have been postulated (10). Experimental evidence
shows that these complexes may be acidic and basic in character.
The chemical nature of these surface groups determines the catalytic
and absorptive behavior of soot.

Carbon is the most abundant element in air pollution
particles and much of it is emitted in the form of soot as a primary
pollutant. (11) In spite of the fact that the catalytic and surface
chemical properties of activated carbon are well known, heterogeneous
catalysis of gas phase reactions on soot particles has received
very little attention. Indicative of such catalytic activity, for
example, is the presence of unpaired electrons (12,13) on activated
carbon as well as on soot. It has also been demonstrated that these
substances may act separately as electron donors (14) and acceptors
(15).

Of special importance to the topics of this paper are a
number of studies on the catalytic oxidation of \( \text{SO}_2 \) on activated
carbon. Low temperature \( \text{SO}_2 \) oxidation on activated carbon
(wood charcoal) has been studied, among others, by Davtyan et al. (16, 17), who found that surface oxides, easily formed at 20°C, are responsible for the catalytic oxidation of \( \text{SO}_2 \). These surface oxides are in equilibrium with gas phase oxygen and are easily removed from the carbon surface by vacuum (at 20°C). All other surface "oxides" apparently are not participating in the catalytic oxidation of \( \text{SO}_2 \).

In the absence of water vapor, the final product of \( \text{SO}_2 \) oxidation is believed to be \( \text{SO}_3 \), which is retained on the carbon surface at low temperature. \( \text{SO}_3 \) will partially desorb at elevated temperatures, however.

The product of \( \text{SO}_2 \) oxidation on activated carbon in the presence of water vapor remains on the surface in the form of \( \text{H}_2\text{SO}_4 \). The amount of \( \text{H}_2\text{SO}_4 \) formed increases with the concentration of water vapor until a limiting, or saturation amount of \( \text{H}_2\text{SO}_4 \) is produced. The saturation limit depends on the partial pressure of gas phase oxygen. The carbon catalyst is apparently self-poisoned by the product of \( \text{SO}_2 \) oxidation. Catalytic activity of activated carbon can be restored, however, by the removal of \( \text{H}_2\text{SO}_4 \) from its surface.

We have recently demonstrated (1) that air suspendable combustion produced soot particles are, in analogy to activated carbon, an efficient catalyst for the oxidation of \( \text{SO}_2 \) in air.
In addition to soot particles, oxygen and water vapor in the air were found to be essential for the catalytic oxidation of SO₂. Similarly as in the case of activated carbon, soot catalyzed SO₂ oxidation also shows a prominent saturation behavior. We have furthermore experimentally demonstrated that for constant relative humidity and SO₂ exposure, the sulfate yield relative to carbon increases with the inherent O:C ratio on the soot particle substrate before its reaction with SO₂ (34). Apparently, the relative efficiency of sulfate formation is related to the active surface area of the soot catalyst. Because of the high surface to volume ratio of soot particles, the (sulfate) S to carbon (atomic) ratio can be as high as about 0.5:1. Sulfate species produced catalytically on soot particles are essentially nonvolatile in vacuum at room temperature, indicating that the oxidation product of SO₂ is in the form of adsorbed, surface bonded sulfuric acid.
II. Experimental Methods

X-ray photoelectron spectroscopy (2), also known as ESCA (Electron Spectroscopy for Chemical Analysis), is the study of kinetic energies of photoelectrons expelled from a sample irradiated with monoenergetic x-rays. The kinetic energy of a photoelectron $E_{\text{kin}}$, expelled from a subshell $i$, is given by $E_{\text{kin}} = h\nu - E_i$, where $h\nu$ is the x-ray photon energy and $E_i$ is the binding energy of an electron in that subshell. If the photon energy is known, the determination of the photoelectron kinetic energy provides a direct measurement of the electron binding energy, which is the main observable in this type of spectroscopy.

The electron binding energies are characteristic for each element, while the photoelectron intensity is related to the concentration of atoms of that element in the active sample volume. This enables the method to be used for elemental analysis. The binding energies are not, however, absolutely constant, but they are modified by the valence electron distribution, so that the binding energy of an electron subshell in a given atom varies when the atom is in different chemical environments. These differences in electron binding energies are known as the "chemical shift".

In the early stages of photoelectron spectroscopy, it was realized that the chemical shifts can be related to the oxidation state. Subsequent studies have shown that the binding energy shifts are correlated to a high degree with the effective charge which the atom possesses in the molecule. Therein lies the usefulness of chemical
shifts in the analysis of unknown molecular structures.

Because of the low energy of photoelectrons produced by Mg or Al x-rays, which are most commonly used, the effective escape depth for their emission without suffering inelastic scattering is small. Recent studies (18) have given electron escape depths of 15 to 40 Å for electron kinetic energies between 1000 and 2000 eV. This renders the ESCA method especially surface sensitive and thus useful in the surface chemical studies.

Photoelectron spectra reported in this paper were obtained with an AEI-200 photoelectron spectrometer utilizing Al Kα (1486.6 eV) radiation. The spectrometer pressure was ≤10⁻⁸ torr during measurements. Photoelectron peak energies were referenced to the carbon (1s) binding energy of 285 eV. The carbon peak is almost entirely due to the soot content in samples.

Because of the high infrared absorption cross section and scattering losses, it is difficult to apply the infrared transmission technique to the study of soot particle surfaces. The technique of internal reflection spectroscopy (IRS) (19), however, allows for an efficient utilization of the incident light, without appreciable scattering losses. When a beam of infrared light, which propagates in a high refractive index medium, undergoes total reflection at the interface with a lower refractive index material (i.e. the sample), an evanescent wave is set up in the latter medium, which propagates parallel to the interface. If the lower index medium is infrared absorbing, then the evanescent wave will be attenuated and the reflection
will no longer be total. This is known as the attenuated total i.r. reflection. With a conventional i.r. monochromator an absorption spectrum of the sample can be obtained. The penetration of the evanescent wave is usually only a small fraction of its wavelength, thus allowing a selective study of surface species. The IRS method is especially convenient for the analysis of filter collected particles because of its nondestructive nature.

The general theory behind the IRS technique has been discussed in detail by Fahrenfort (20) and Harrick (19). IRS has been recently applied to the identification of surface oxygen functional groups on activated carbon by Mattson et al. (21).

IRS measurements reported in this work were obtained by means of a Perkin-Elmer 621 infrared spectrophotometer equipped with a Wilks Model 9 IRS attachment. A KRS-5 (Thallium bromoiodide) crystal, 2 mm thick, 200 mm wide and 52.5 mm long was used. The crystal was polished between each run. An incidence angle of 60° was used, which produces about 30 reflection events.

Soot particles used in this study were generated with a conventional Bunsen burner using propane or propane saturated with benzene vapor as fuel. The propane (Matheson) was either of research or instrument grade with an assayed purity of 99.99 and 99.5% respectively. Both propane grades did contain about 0.005% sulfur by weight. Benzene (Mallinckrodt) also contained the same percentage of sulfur.
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 the flame. The filters used to collect soot particles were of silver membrane type (Flotronics) with pore sizes of 5.0 or 0.8 µm.
III. Experimental Results

Photoelectron spectra representing the sulfur (2p) and carbon (1s) regions of propane soot particles produced by a Bunsen burner are shown in Figure 1a. The S (2p) photoelectron peak at a binding energy of 169 eV corresponds to sulfate. C (1s) peak appears essentially as a single component line and corresponds to a 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 easily detectable sulfate emission. Several competing mechanisms, including the oxidation on soot particles, may be responsible for the conversion of trace amounts of sulfur in fuel to particulate sulfate. The specific role of soot particles as catalyst for the oxidation of SO$_2$ is demonstrated with the aid of Figure 1b. Here we show the S (2p) and C (1s) photoelectron peaks of soot particles, generated in analogous manner as before, but exposed to additional SO$_2$ in a flow system. A marked increase in the sulfate peak intensity, relative to carbon, is evident. The atomic ratio of sulfur to carbon corresponding to Figures 1a and 1b are 0.16 and 0.51 respectively, for this particular experiment.

The IRS spectrum in the wave number region from 1500 to 500 cm$^{-1}$ of the same sulfate on soot sample, whose XPS spectrum is shown in Figure 1b, is represented in Figure 2a, and with expanded
scale in Figure 2b. In Figure 2c the IRS spectrum of an aqueous solution of ammonium sulfate is shown for comparison. The absorption band at about 1400 cm\(^{-1}\) is due to the vibration of the ammonium cation. The IRS spectra of 1N sulfuric acid and an aqueous solution of ammonium bisulfate are shown in Figure 3a and 3b, respectively.

It is of interest to note that the IRS spectrum of the sulfate associated with soot particles resembles that of ammonium sulfate, but not sulfuric acid or ammonium bisulfate. In the following section we will propose an explanation for this observation, by considering the principal species present in these samples and their normal vibrational modes.

In our experiments the soot samples were collected on silver filters, which can react with sulfuric acid produced catalytically on soot or by hydrolysis of the surface sulfate species. Silver sulfate could, in principle, interfere with the characterization of sulfate associated with soot particles. It was found, however, that this interference does not represent a serious problem even with thin soot deposits and does not affect the conclusions reached in the course of this work. Actually, the IRS spectrum of silver sulfate is sufficiently different from that of sulfate on soot, that the two can be easily distinguished.

The IRS spectrum of silver sulfate (analytical grade, supplied by Bryant Laboratories, Inc.) is shown in Figure 4a. The characteristic absorption frequencies of silver sulfate are labeled
A and A' in the figure. The IRS spectrum of a thin soot sample, exposed to \( \text{SO}_2 \) and collected on a silver membrane filter, is shown in Figure 4b. The absorption bands of sulfate associated with soot are labeled B and B'. The coexistence of the two sulfates in this sample is evident from the figure.

We have also studied the thermal stability in vacuum of sulfate on soot, ammonium sulfate and ammonium bisulfate. The experimental procedure consisted of measuring XPS spectra at gradually increasing sample temperature. It was found that sulfate produced catalytically on soot particles desorb in vacuum in a unique way which is different from stoichiometric compounds such as ammonium sulfate and ammonium bisulfate. In Figure 5 the sulfate concentrations on these samples are plotted against the sample temperature. For comparison, we also show a desorption graph for a typical urban ambient air sulfate sample.

These results demonstrate that ammonium bisulfate remains stable in vacuum up to about 100°C, after which it decomposes rapidly. Ammonium sulfate decomposes at temperatures above about 110°C. The slight initial rise in sulfate intensity for ammonium sulfate can be attributed to fractional release of ammonia, which leaves more exposed sulfur atoms in the surface layer. In contrast to these two cases, the thermal desorption of sulfate associated with soot particles, and interestingly enough of ambient particulate sulfate, does not exhibit a definitive decomposition or desorption temperature. Its desorption is monotonic. We will discuss these experiments in the next section in more detail.
IV. Discussion

It is possible to explain the observed differences in the i.r. absorption spectra of various sulfate species, (22,23,24) by considering the major dissociation products of these compounds and their symmetry properties.

Let us first consider the major species in aqueous solutions of sulfuric acid, ammonium bisulfate and ammonium sulfate. 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 secondary ionization constant in water is $1.2 \times 10^{-2}$ (at 25°C). Therefore, a 1N aqueous solution of sulfuric acid should contain about 0.011 and 0.489 g ion/l of $\text{SO}_4^{2-}$ and $\text{HSO}_4^-$, respectively. The dominant species in 1N sulfuric acid are therefore, hydrogen sulfate anions ($\text{HSO}_4^-$) and hydronium ions ($\text{H}_3\text{O}^+$).

Ammonium bisulfate will completely dissociate in water to form an ammonium cation and again a hydrogen sulfate anion: $\text{NH}_4\text{HSO}_4 \rightarrow \text{NH}_4^+ + \text{HSO}_4^-$. Hydrogen sulfate ion is in equilibrium with sulfate and hydronium ions according to the secondary ionization constant of sulfuric acid, giving a ratio of $\text{HSO}_4^-$ to $\text{SO}_4^{2-}$ of about 9. The principal species in 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 cation and sulfate cation.
The differences in the dissociation products of sulfuric acid and ammonium bisulfate on the one hand, and ammonium sulfate on the other, are reflected in their i.r. absorption spectra. Namely, free \( \text{SO}_4^{2-} \) ion belongs to the high symmetry point group \( T_d \). Of the four fundamental vibrational modes, only \( v_3(T_2) \) and \( v_4(T_2) \) are infrared active. For monodentate sulfate compounds (\( \text{HSO}_4^- \) can be regarded as such) and bidentate compounds (such as pure \( \text{H}_2\text{SO}_4 \)) the symmetry is lowered to \( C_{3v} \) and \( C_{2v} \), respectively. Lowering of symmetry results in the removal of degeneracy giving rise to new infrared active vibrational modes. The totally symmetric and nondegenerate \( A_1 \) species associated with the \( T_d \) point group will remain the same for the \( C_{3v} \) point group. Because the characters are the same for symmetry elements common to both the \( T_d \) and the \( C_{3v} \) point groups, the doubly degenerate \( E \) of \( T_d \) will become \( E \) of \( C_{3v} \). Triply degenerate species \( T_2 \) of \( T_d \), however, will split into a totally symmetric \( A_1 \) and a doubly degenerate \( E \) vibrational mode, as the result of change in symmetry to \( C_{3v} \). With the lowering of symmetry from \( T_d \) to \( C_{2v} \), all degeneracies are removed so that \( A_1 \) of \( T_d \) becomes \( A_1 \) of \( C_{2v} \), \( E \) of \( T_d \) resolves into the sum of \( A_1 + A_2 \) and \( T_2 \) of \( T_d \) splits into \( A_1 + B_1 + B_2 \). The results of such symmetry analysis are summarized in Table I.

The observed frequencies of different sulfate anions and their assignment in the light of the foregoing discussion are listed in Table II. An inspection of these data shows that the spectra of
sulfate species produced by catalytic oxidation of SO₂ closely match the spectrum of sulfate anion SO₄²⁻ but not hydrogen sulfate anion HSO₄⁻. This would indicate that oxidation of SO₂ on soot particles results in the formation of sulfate salt-like species. The soot particle surface must in that case provide relatively strong basic sites for the neutralization of sulfuric acid. As stated previously, sulfuric acid is the product of SO₂ oxidation on activated carbon and can be regarded as the primary product of SO₂ oxidation on soot particles.

Actually, it is known that activated carbon may contain both basic and acidic surface functional groups (10). For example, exposure of carbon to oxygen at temperatures between 200° and 700°C produces acidic groups, such as carbonyl, lactone, phenolic hydroxyl, etc. Basic surface oxide groups are predominantly formed at temperatures either below 200°C or above 700°C. In reality, however, and especially in the case of combustion produced soot particles, there is no sharp transition temperature which separates the formation of acidic from basic groups. In the case of soot the two types coexist. The catalytic and adsorptive properties of soot particles will naturally depend on the nature and concentration of all surface oxides. In the following, we will consider several possibilities for the neutralization of sulfuric acid on soot particles.

Surface acidic groups, such as phenolic hydroxyl and
carboxyl, may form an oxonium salt with sulfuric acid: $C_x\text{OH} + H_2\text{SO}_4 \rightarrow C_x^+\text{OH}_2^+ + \text{HSO}_4^-$, where $C_x$ denotes the soot particle. Because of the weak basicity of these functional groups, however, a further transfer of a proton from the hydrogen sulfate anion is not favored. Soot particles must therefore provide stronger basic sites for the neutralization of sulfuric acid.

The existence of basic surface oxides on activated charcoal has been recognized for some time. Their structure is not fully understood, however. One important manifestation of basic sites stems from the observations of Burstein and Frumkin (25), who found that acids adsorb on activated carbon only in the presence of oxygen. The adsorption of acids on carbon is accompanied by liberation of hydrogen peroxide. Different surface structures have been proposed by Shilov and Chmutov (26), Frumkin, et. a. (27), Steenberg (28), and Garten and Weiss (29) in order to explain the phenomenon of acid adsorption on activated carbon. The concept of Garten and Weiss is apparently providing the most satisfactory explanation. According to these authors, oxygen is bound in a chromene like structure, i.e., a heterocyclic, oxygen containing ring, involving activated $>\text{CH}_2$ or $>\text{CHR}$ groups. The oxidation of the chromene group, in the presence of acid, will result in the formation of carbonium ion. Transfer of the positive charges is possible so that carbonium and oxonium ions are in resonance.
In the case of sulfuric acid, formation of carbonium and/or oxonium sulfate and hydrogen peroxide is to be expected.

In addition to this mechanism, Garten and Weiss (14) have also discussed the possibility that free radicals on activated carbon could contribute to the neutralization of acid and producing carbonium ions.

The process of neutralization of sulfuric acid on soot surface can be represented in the following way:
Carbonium and oxonium ions are weak bases (30) and consequently hydrolysis of their salts into cyclic hemiacetals (31) and sulfuric acid should be expected on exhaustive washing with water:
Differences in the heats of desorption of individual sulfate ions bound to surface sites reflect the nonuniformity of soot structure and could account for the observed monotonic desorption curve. Actually, soot particles do not have well defined molecular weight or structure. Each individual particle may possess some unique properties and features in terms of surface functional groups, free radicals, crystal structure, degree of unsaturation, etc. We are stressing the fact that the desorption behavior of typical urban air sulfate exhibits the same overall behavior as sulfate produced on soot. This is a further indication that soot particles are playing an important role in the atmospheric oxidation of SO₂.

Finally, it is worth mentioning that hydrogen peroxide, liberated in the act of acid adsorption on soot, may play a role in the chemistry of a polluted atmosphere. For example, it may attack carbon in soot to produce additional acidic groups (32), which may affect the catalytic and surface chemical properties of soot; it may act as an oxidant for a number of organic and inorganic molecules; and, it may photodecompose to produce OH radicals which can initiate or participate in many important atmospheric gas phase reactions (33).
Acknowledgement:

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References


Table I. Correlation Table for $T_d$, $C_{3v}$, and $C_{2v}$.

<table>
<thead>
<tr>
<th>Point group</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$v_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_d$</td>
<td>$A_1$</td>
<td>$E$</td>
<td>$T_2(I)$</td>
<td>$T_2(I)$</td>
</tr>
<tr>
<td>$C_{3v}$</td>
<td>$A_1(I)$</td>
<td>$E(I)$</td>
<td>$A_1(I)$+$E(I)$</td>
<td>$A_1(I)$+$E(I)$</td>
</tr>
<tr>
<td>$C_{2v}$</td>
<td>$A_1(I)$</td>
<td>$A_1(I)$+$A_2$</td>
<td>$A_1(I)$+$B_1(I)$+$B_2(I)$</td>
<td>$A_1(I)$+$B_1(I)$+$B_2(I)$</td>
</tr>
</tbody>
</table>

($I$) indicates the infrared active modes.
Table II. Observed IRS fundamental vibrational frequencies of sulfate ions in the region 1500 to 500 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Origin</th>
<th>Sulfur species</th>
<th>Pt. group</th>
<th>(\nu_1)</th>
<th>(\nu_2)</th>
<th>(\nu_3)</th>
<th>(\nu_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NH}_4)(\text{HSO}_4) aqueous soln.</td>
<td>(\text{HSO}_4^-)</td>
<td>(\text{C}_3\text{v})</td>
<td>885(S)</td>
<td>-</td>
<td>1160(S)</td>
<td>605(M)</td>
</tr>
<tr>
<td>((\text{NH}_4)_2\text{SO}_4) aqueous soln.</td>
<td>(\text{SO}_4^{2-})</td>
<td>(\text{T}_d)</td>
<td>978(W)</td>
<td>-</td>
<td>1072(S)</td>
<td>612(M)</td>
</tr>
<tr>
<td>soot+(\text{SO}_2) in humid air</td>
<td>(\text{SO}_4^{2-})</td>
<td>(\text{T}_d)</td>
<td>960(W)</td>
<td>-</td>
<td>1080(S)</td>
<td>615(M)</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS:

Figure 1. (a) Carbon (1s) and sulfur (2p) photoelectron spectrum of soot particles produced by combustion of propane saturated with benzene vapor. The sulfur content of this fuel is 0.005% by weight. (b) Carbon (1s) and sulfur (2p) photoelectron spectrum of soot particles generated in analogous manner as in (a), but exposed to additional SO2 in humid air.

Figure 2. (a) Infrared (IRS) spectrum (from 1500 to 5000^-1) of soot particles exposed to SO2 in humid air. (b) Same as (a) with 5 x expanded reflectance scale. (c) IRS spectrum of an aqueous solution of ammonium sulfate. The absorption band at \approx 1400 cm^-1 is due to \nu_4 vibration of the NH4^+ cations. The assignments of other absorption bands are given in Table II.

Figure 3. (a) IRS spectrum of 1N sulfuric acid. (b) IRS spectrum of an aqueous solution of ammonium bisulfate.

Figure 4. (a) IRS spectrum of silver sulfate. (b) IRS spectrum of a thin soot sample exposed to SO2 in humid air. Silver sulfate (A and A) and sulfate associated with soot particles (B and B) coexist in this sample.

Figure 5. Thermal stability in vacuum of ambient sulfate, sulfate on soot particles, ammonium sulfate and ammonium bisulfate. The sulfate XPS peak intensities are plotted against the sample temperature.
Fig. 1
Fig. 4
Fig. 5
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