# Low Temperature Air Oxidation of Caking Coals: Fourier Transform Infrared Studies

P. C. PAINTER, M. M. COLEMAN, R. W. SNYDER, O. MAHAJAN,* M. KOMATSU,† and
P. L. WALKER, JR.

*Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania*

Fourier transform infrared spectroscopy has been used to characterize the oxidation of a coking coal. The results demonstrate that the most important initial products of oxidation are carbonyl and carboxylic acid groups. Bands associated with car-bon-oxygen single bonds, as in ethers or phenols, do not become prominent until the later stages of the oxidative process. Upon reaction with potassium in tetrahydrofuran a number of changes in the spectrum of both the oxidized and unoxidized coal become apparent. This reagent cannot be considered specific for cleavage of ether bonds, but can also lead to products usually associated with air oxidation.

Index Headings: Fourier transform infrared spectroscopy; Analysis, for oxidation of coal.

## INTRODUCTION

Recent work in this laboratory has involved the application of Fourier transform infrared spectroscopy (FT-IR) to the structural characterization of coal.[1-5] It has been established that this technique is particularly sensitive to small changes that occur in the initial stages of the oxidation of polymeric materials.[6] In a preliminary study[5] we noted an equivalent sensitivity to the chemical changes occurring upon the oxidation of coal. This work involved the characterization of channel samples along an exploration adit through a high volatile coking coal seam.[5] Samples near the mouth and end of the adit were fairly extensively oxidized, as measured by free-swelling index and the appearance of infrared bands characteristic of various carbonyl and carboxylic acid groups. Some of these bands were only revealed after subtraction of the spectrum of a relatively unoxidized sample, obtained from the center of the seam, from the spectra of samples obtained from the periphery. The detection of such oxygen containing functional groups by FT-IR is in disagreement with results based on chemical methods of analysis. Wachowska et al.[7] determined that there was no change in carbonyl content when oxidizing Balmer 10 coal at 100°C. Furthermore, carboxyl groups were not detected in the oxidized material by an ion-exchange method using calcium acetate. However, these authors did determine that, upon reaction of the oxidized coal with potassium in tetrahydrofuran (THF), there is a large increase in dilation, suggesting that the formation of ether linkages plays a key role in the loss of swelling behavior and associated coking properties.

It is possible that coal oxidized by exposure for long time periods at the edge of a seam differs in structure from coal oxidized at elevated temperatures in the laboratory. Alternatively, infrared spectroscopy may be far more sensitive to the presence of carbonyl and carboxyl groups than chemical methods. In this paper we will report on the application of FT-IR to the characterization of coal oxidized in the laboratory. In addition, we will examine the structural changes that occur upon reaction with potassium in THF.

## I. EXPERIMENTAL

The coal used in this study was a highly coking coal (HVA bituminous) having a free swelling index of eight. The samples were originally obtained from the lower

Kittanning seam (PA), and the proximate and ultimate analysis of the −60 mesh fraction of the coal is given in Table I. This coal is designated PSOC 337 in the Penn State/ERDA coal data base. All samples were stored in sealed containers under nitrogen. Grinding and sieving procedures were performed in a glove box, also under a nitrogen atmosphere. The 200 by 250 mesh fraction was used for this study.

The coal was oxidized by spreading about 3 g uniformly in a ceramic boat, which in turn was placed in a horizontal tube furnace. As a guide to the degree of oxidation of the coal, the weight gain of the coal on a dry mineral matter free basis was determined. This weight gain is presented in the following discussion as percent oxygen uptake. Samples with an oxygen uptake of 1.4, 3.3, and 6.7% were used in this study.

Samples were treated with potassium in THF using the method of Sternberg et al.,[8] as described by Wachowska et al.[7] As we will demonstrate below, this procedure apparently leads to oxidation of the coal. We originally thought that this might occur in the final drying step, performed at 70°C. Consequently, for some experiments we modified the procedure by drying under vacuum at ambient temperatures.

Spectra were recorded on a Digilab 15B FT-IR instrument. Four hundred co-added interferograms were used to obtain spectra with a resolution of 2 cm$^{-1}$. Most samples were prepared for infrared analysis by forming standard KBr disks. In addition, certain samples were also prepared by grinding into fluorolube, so that the —OH stretching region of the spectrum could be examined without interference from water absorbed on the KBr.

## II. RESULTS AND DISCUSSION

The infrared spectrum (plotted in absorption) of coal oxidized to the extent of 1.4% $O_2$ uptake is compared to the spectrum of the same sample prior to oxidation in Fig. 1. The major difference in the two spectra is the appearance of a weak shoulder near 1695 cm$^{-1}$ in the spectrum of the oxidized sample. In addition, the intensity of the aliphatic C—H stretching modes near 2900 cm$^{-1}$ appears to decrease upon oxidation. FT-IR is a particularly powerful tool for accentuating such subtle changes through the use of the digital subtraction rou-

TABLE I. Proximate and ultimate analysis of raw coal.

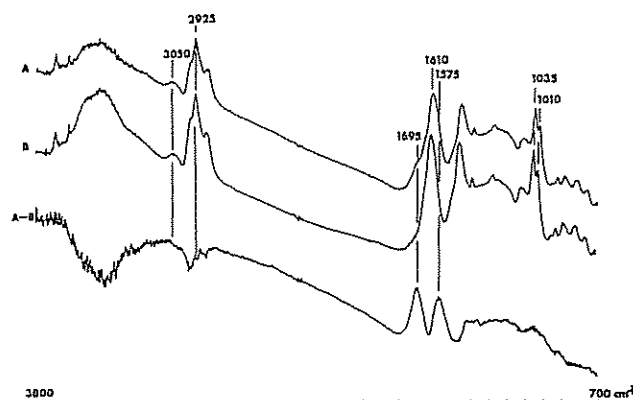| Constituent | Wt (%) |
|---|---|
| *Proximate analysis* | |
| | PSOC-337 |
| Ash (dry basis) | 8.5 |
| Volatile matter (daf) | 38.2 |
| Fixed carbon (daf) | 61.8 |
| *Ultimate analysis (daf)* | |
| | PSOC-337 |
| C | 84.9 |
| H | 5.8 |
| N | 1.6 |
| S (organic) | 0.70 |
| O (by difference) | 7.0 |



FIG. 1. A, infrared spectrum of oxidized coal (PSOC 337), 1.4% oxygen uptake; B, infrared spectrum of fresh coal (PSOC 337); A − B, difference spectrum.

tine. Fig. 1 also shows the difference spectrum obtained by subtracting the spectrum of the unoxidized sample from that of the oxidized. The criteria used to determine the "correct" degree of subtraction was the elimination of the kaolinite bands at 1035 and 1010 cm$^{-1}$, since this clay should be relatively unaffected by low-temperature oxidation. It can be seen that this subtraction results in the elimination of the aromatic C—H stretching mode near 3050 cm$^{-1}$ and the aromatic C—H out-of-plane bending mode between 700 and 900 cm$^{-1}$. This is to be expected in that direct oxidative attack of the aromatic nuclei is unlikely under the oxidation conditions used in this study and confirms the choice of the kaolinite bands as a subtraction standard.

In contrast to the aromatic C—H bands, the aliphatic C—H stretching modes near 2900 cm$^{-1}$ appear negative, or below the baseline, demonstrating a loss in CH$_2$ groups upon oxidation. This observation is not particularly novel, as methylene groups in the benzylic position are well known to be sensitive to oxidation and are probably the initial site of oxidative attack.[5, 9] However, the difference spectrum reveals new detail in the 1700 to 1500 cm$^{-1}$ region of the spectrum. The 1695 cm$^{-1}$ band, which appeared as a weak shoulder in the original spectrum of the oxidized coal, is now resolved as a separate band. Furthermore, a prominent new band near 1575 cm$^{-1}$ is now revealed in the difference spectrum. This band is not detectable in the original spectrum. The 1695 cm$^{-1}$ absorption is probably due to an aryl alkyl ketone, while the 1575 cm$^{-1}$ mode can be assigned to an ionized carboxyl group, COO$^-$.[10, 11] Clearly, at only 1.4% oxygen uptake, these bands represent the major products of oxidation. Weak, broad residual adsorption between 1200 and 1300 cm$^{-1}$ in the difference spectrum could possibly be due to C—O bonds, as in phenols or ethers, but it would be difficult to identify any separately resolved bands assignable to functional groups of this type. Nevertheless, bands that can be assigned to such groups do appear at higher levels of oxidation. For example, Fig. 2 compares the infrared spectrum of a coal sample, oxidized to give 6.7% oxygen uptake, to the spectrum of the unoxidized sample. The difference spectrum, obtained using the same subtraction criteria described above, is also shown in this figure. A prominent difference band can now be observed near 1200 cm$^{-1}$, as well as the strong 1695 cm$^{-1}$ and 1575 cm$^{-1}$ bands. In addition, a weak shoulder near 1765 cm$^{-1}$ can now be resolved. This band

can be assigned to an ester. The ester carbonyl group usually appears near 1740 cm$^{-1}$, but when an electron-withdrawing group such as an aromatic ring is attached to the ester single bonded oxygen, this band is shifted to near 1765 cm$^{-1}$.[5, 10, 11]

These spectral changes closely parallel those observed in a previous study of the variation in oxidation of coal according to position in a seam.[5] Consequently, the formation of carbonyl and carboxyl groups is apparently a general phenomenon during oxidation. This conclusion contradicts the results of some chemical methods of characterizing oxidation products, where no change or carboxyl or carbonyl content was detected.[7] However, we believe the spectroscopic results presented here are unequivocal. Furthermore, these results also demonstrate that C=O functional groups are the main product in the critical early stages of the oxidation. Bands characteristic of ether and phenolic C—O bonds only become prominent in the difference spectra at higher degrees of oxidation.

A number of studies[7, 9] have concluded that the formation of ether cross links are critical to loss of coking ability. For example, it has been observed that the swelling behavior of coking coal can be partially regenerated by treating with potassium in THF, a reagent that should cleave C—O bonds but not C—C bonds. We therefore considered it valuable to apply FT-IR to the characterization of the chemical changes occurring upon reaction of potassium in THF with oxidized coal. The spectrum of an oxidized coal (3.3% oxygen uptake) is compared to the spectrum of the same sample treated with potassium in THF in Fig. 3. We were surprised by the observation that this treatment apparently leads to an increase in the degree of oxidation of the sample, as measured by the increased intensity of the shoulder near 1695 cm$^{-1}$. This is confirmed by the difference spectrum, shown in the same figure, which is remarkably similar to the difference spectra shown in Figs. 1 and 2. The criteria for obtaining this difference spectrum differs from that used previously, in that, because kaolinite is lost from the sample during the course of the reaction, it is no longer a suitable subtraction standard. Instead, we subtracted the aliphatic C—H modes near 2900 cm$^{-1}$ to the baseline. Because of the weak intensity of this band, this subtraction is only approximate. Nevertheless, the carboxyl band, now appearing near 1580 cm$^{-1}$, is again revealed.
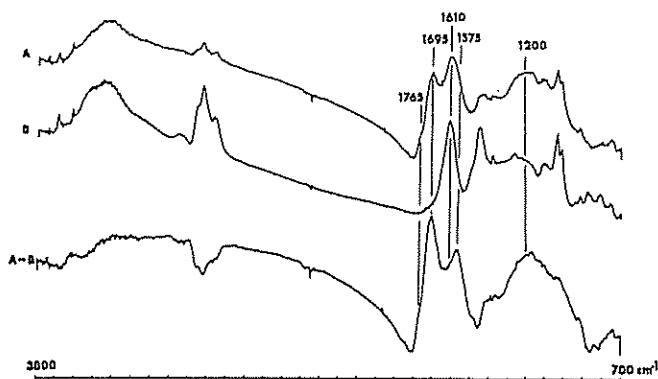


FIG. 2. A, infrared spectrum of oxidized coal (PSOC 337), 6.7% oxygen uptake; B, infrared spectrum of fresh coal; A − B, difference spectrum.
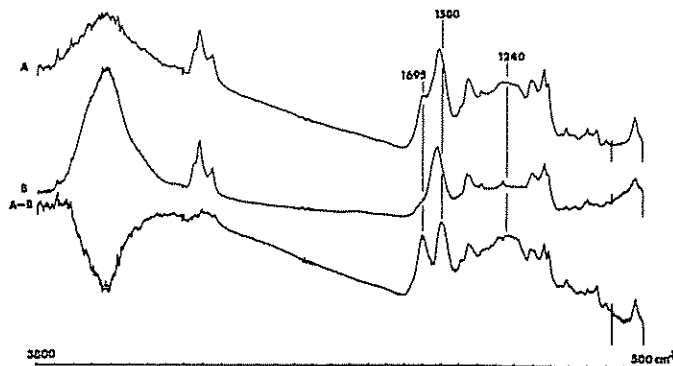


FIG. 3. A, infrared spectrum of oxidized coal (3.3%, oxygen uptake) after treatment with potassium in THF; B, infrared spectrum of oxidized coal (3.3% oxygen uptake); A − B, difference spectrum.

We postulated that the increased oxidation of the sample might occur in the final stage of the reaction procedure, where the coal is dried at 70°C.[7, 8] Consequently, we modified the procedure so that the final product was dried under vacuum at room temperature. The results remained the same. For example, the spectrum of the unoxidized coal is compared in Fig. 4 to the spectrum of the same sample after reaction. Again a carbonyl band appears as a shoulder near 1695 cm$^{-1}$. However, there is also an apparent decrease in intensity of the band near 1265 cm$^{-1}$ (which was not observed in the spectra of samples dried at 70°C; for example, see Fig. 3), suggesting that some C—O bonds are being cleaved. The reaction of coal with potassium in THF therefore appears more complex than considered in previous studies and does not lead to cleavage of C—O bonds alone. It is important to note that Wachowska et al.[7] detected an increase in oxygen content of both fresh and oxidized coal upon reaction, an increase that manifests itself in our study as an increase in carbonyl and carboxylic acid groups.

It is possible that these groups are formed by a molecular rearrangement following cleavage of ether type linkages. Nonetheless, we believe this type of mechanism at best only contributes a fraction of the new carbonyl groups. If Fig. 4 is examined carefully it will be observed that there is an apparent decrease in intensity of the aliphatic C—H stretching modes near 2920 cm$^{-1}$. A loss of methylene groups is more evident in the decrease in the intensity of the methylene CH$_2$-bending mode near 1450 cm$^{-1}$, relative to the 1610 cm$^{-1}$ band.

Coal oxidized to a higher degree (6.7% oxygen uptake) has already lost most of its CH$_2$ groups, as can be seen by an inspection of the spectrum shown in Fig. 5, so that the spectrum of this sample subsequent to reaction with potassium in THF, also shown in this figure, does not show any further changes in the bands characteristic of this group (near 2900 and 1450 cm$^{-1}$). There is, in addition, no apparent increase in the intensity of the carbonyl band near 1695 cm$^{-1}$ relative to the 1610 cm$^{-1}$ band. This observation adds further support to the observations made above that, in addition to cleavage of C—O bonds, potassium in THF results in carbonyl formation, probably through an oxidative attack on methylene units.

Fig. 5 also indicates that there is a loss in ether bonds upon reaction by a decrease in absorption near 1260 cm$^{-1}$. More intriguing, however, is the decrease in inten-

FIG. 5. A, infrared spectrum of oxidized coal (6.7% oxygen uptake) after treatment with potassium in THF; B, infrared spectrum of oxidized coal (6.7% oxygen uptake); A – B(1), difference spectrum 1; A – B(2), difference spectrum 2.

sity of the shoulder near 1765 cm$^{-1}$, assigned above to an ester bond. This decrease can be revealed more clearly by subtracting the spectrum of the untreated from that of the treated sample. Bands due to groups that have disappeared upon reaction should then appear negative. Because we were unsure of the correct degree of subtraction, two difference spectra, with different degrees of subtraction, are presented in Fig. 5. It can be seen that, in addition to the band at 1765 cm$^{-1}$, a second negative band appears near 1735 cm$^{-1}$. This latter band is not visible in the original oxidized spectrum, presumably due to its proximity to the strong 1695 cm$^{-1}$ mode. Bands near 1735 cm$^{-1}$ can also be assigned to esters, but in this case there would not be an aromatic group attached to the single bonded oxygen. These observations can reasonably be interpreted as a cleavage of ester C—O bonds upon reaction with potassium in THF.

One drawback to the sample preparation technique used to obtain all the above spectra, namely grinding in KBr, is that water absorbed by this alkali halide masks the O—H stretching bands of the coal. We managed to circumnavigate this problem by grinding in fluorolube using the glass plate technique described by Brady.[12] Nevertheless, we still have problems, the most difficult of which is the strongly sloping baseline, as shown by the spectrum of the unoxidized sample presented in Fig. 6. This problem can be overcome to some extent by use of standard baseline correction procedures available on computerized instruments. The baseline-corrected spectrum is presented in the same figure, and it can be seen that the broad OH stretching mode centered near 3300 cm$^{-1}$ is much better defined. Fig. 7 compares the spectra of the unoxidized, oxidized (6.7% oxygen uptake), and oxidized plus treated with potassium in THF coals, all with baselines corrected in the same manner. It can be seen that there is only a slight increase in —OH groups upon oxidation, in contrast to the conclusions of some previous studies,[9] but a more substantial increase is found after treatment with potassium in THF. This is due to the formation of —OH groups by hydrolysis subsequent to the cleavage of ether and ester C—O bonds.

The results presented above strongly suggest the involvement of carbonyl and carboxyl groups in the loss of coking properties. One of the most important remaining tasks is to formulate a mechanism by which these func-
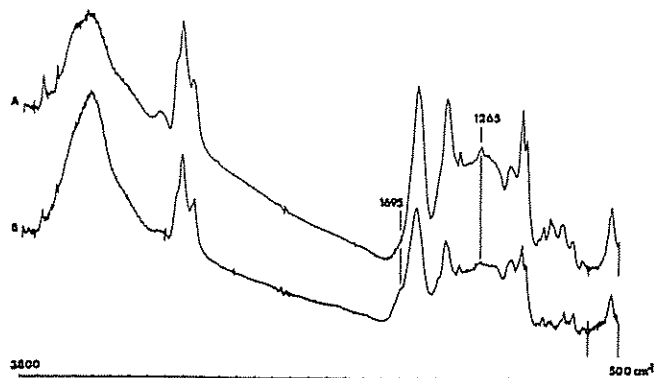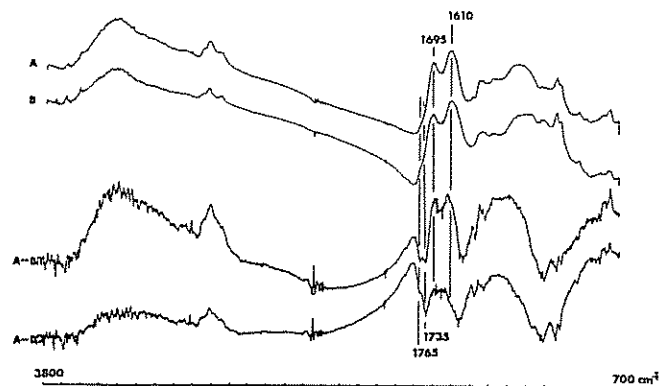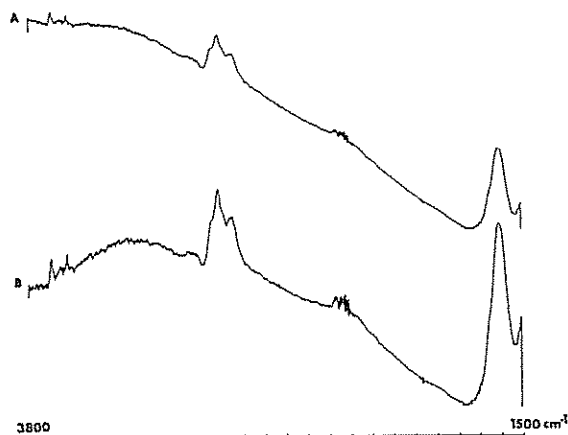
FIG. 4. A, infrared spectrum of fresh, unoxidized coal; B, infrared spectrum of unoxidized coal after treatment with potassium in THF.

FIG. 6. A, infrared spectrum of fresh unoxidized coal ground in fluo-rolube; B, same spectrum as A after baseline correction.
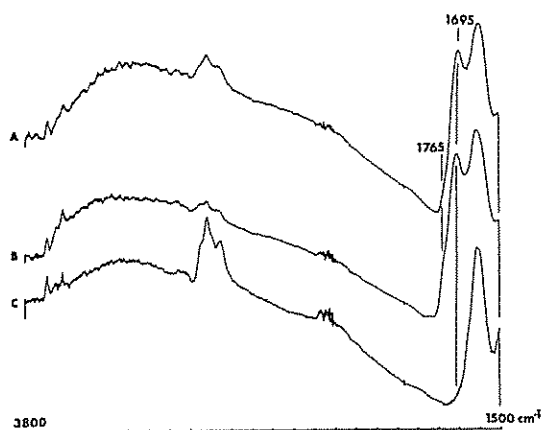


FIG. 7. Baseline corrected infrared spectra: A, oxidized coal (6.7% oxygen uptake); B, oxidized coal treated with potassium in THF; C, unoxidized coal.

tional groups result in changes, such as loss of swelling characteristics and the corresponding regeneration of this property upon reaction with potassium in THF. In this respect we believe that the detection of carboxyl groups by FT-IR is particularly significant. One possibility is a cross-linking mechanism analogous to that observed in ionomers (e.g., the Surlyn polymers manufactured by the E. I. DuPont de Nemours Company). Typically, these polymeric systems contain a small concentration (about 5%) of a carboxylic acid containing monomer (e.g., acrylic acid) copolymerized with a neutral monomer (e.g., ethylene). By incorporating a divalent cation such as $Ca^{++}$ or $Zn^{++}$, the chains become cross-linked through ionic salt bridges. This type of ionic cross link could occur in oxidized coal, providing that sufficient divalent cations are present. In addition, the regeneration of swelling behavior upon reaction with potassium in THF is readily explained by this interpretation. The

replacement of divalent cations with monovalent $K^+$ would break the ionic cross links. Alternatively, other types of ionic cross links are possible, depending upon the chemical nature and composition of the individual coal. For example, Sternberg et al.[13] have reported the presence of acid-base structures in coal. An ionic link between carboxylic acid and basic nitrogen groups could also explain the initial loss of swelling behavior upon oxidation and the subsequent regeneration in the presence of potassium ions. Naturally, these observations remain essentially speculative at the present time, but they do provide a framework within which we can explain the experimental observations.

## III. CONCLUSIONS

1. In the early stages of the oxidation of the HVA bituminous coal (PSOC 337) used in this study, the main oxygen-containing functional groups formed are carbonyl (probably aryl alkyl ketones) and carboxyl, $COO^-$. These are formed by attack of methylene groups, probably in the benzylic position. There is very little (if any) increase in intensity of bands assigned to C—O groups, as in ethers or phenolics, or O—H groups.

2. Only at higher degrees of oxidation is there a significant increase in intensity of bands that can be assigned to C—O groups.

3. Ester groups are also formed at higher degrees of oxidation.

4. Reaction of oxidized or unoxidized coals with potassium in THF does not specifically cleave C—O ether bonds, but also attacks esters. In addition, methylene groups are attacked at some point in the procedure and new carbonyl groups formed.

5. A mechanism for the loss of swelling behavior in oxidized coals is advanced. This mechanism involves the formation of ionic cross links between the carboxylic acid groups with divalent cations or between carboxylic acid groups and basic structures within the coal.

1. P. C. Painter, M. M. Coleman, R. G. Jenkins, P. W. Whang, and P. L. Walker, Jr., Fuel 57, 337 (1978).
2. P. C. Painter, M. M. Coleman, R. G. Jenkins, and P. L. Walker, Jr., Fuel 57, 125 (1978).
3. P. C. Painter, and M. M. Coleman, Fuel 53, 301 (1979).
4. P. C. Painter, Y. Yamada, R. G. Jenkins, M. M. Coleman, and P. L. Walker, Jr., Fuel 58, 293 (1979).
5. P. C. Painter, R W. Snyder, D. E. Pearson, and J. Kwong, Fuel 59, 282 (1980).
6. M. M. Coleman and P. C. Painter, J. Macromol. Sci. Rev. Macromol. Chem. C16(2), 197 (1978).
7. H. M. Wachowska, B. N. Nandi, and D. S. Montgomery, Fuel 53, 212 (1974).
8. H. W. Sternberg, C. L. Delle Donne, P. Pantages, E. C. Moroni, and R. E. Markby, Fuel 50, 432 (1971).
9. B. S. Ignasiak, D. M. Clugston, and D. S. Montgomery, Fuel 51, 76 (1972).
10. L. J. Bellamy, The Infrared Spectra of Complex Molecules (Methuen, London, 1954).
11. N. B. Colthup, L. H. Daley, and S. E. Wiberley, Introduction to Infrared and Raman Spectroscopy (Academic Press, New York, 1964).
12. L. E. Brady, J. Chem. Ed. 46, 301 (1969).
13. H. W. Sternberg, R. Raymond, and F. K. Schweighardt, Science 188, 49 (1975).