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CHEMICAL CHARACTERIZATION OF ATMOSPHERIC AEROSOL PARTICLES USING RAMAN SPECTROSCOPY *

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ABSTRACT

The Raman spectra of ambient and source-enriched samples have been obtained. These spectra indicate that "graphitic soot" and $(NH_4)_2SO_4$ are major species in the samples studied. The complementary nature of the infrared and Raman spectroscopy is emphasized, and the high selectivity and nondestructive character of the Raman technique are discussed.

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I. Introduction

In order to make a better assessment of the origin and the environmental effects of airborne particles, it is important to explore new techniques for their chemical characterization. The use of vibrational spectroscopy for chemical analysis is well known. Both the infrared and Raman scattering techniques are often used in a complementary fashion to determine the vibrational structure and the chemical species in question. The infrared technique is used in the analysis of ambient aerosol particles (see, for example, Cunningham et al., 1974). The Raman scattering technique has been applied to laboratory-generated aerosol particles (Rosasco et al., 1975; Stafford et al., 1976; Wright and Krishnan, 1973); however, the technique has only recently been applied to pollution particulate samples (Rosen and Novakov, 1976). In this paper we will assess the Raman scattering method, which is presently in its early stages of development but seems to hold considerable promise as a nondestructive, sensitive, and highly selective technique for the characterization of aerosol particles. The present state of the art of the technique will be discussed, and the Raman spectra of both source-enriched and ambient samples will be presented. In the samples studied, the spectra indicate the presence of "graphitic soot" of very small crystallite size as well as $(NH_4)_2SO_4$ as major species. We will compare the infrared and Raman techniques and will discuss possible future developments.

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II. Experimental Techniques

A schematic of the experimental setup is shown in Figure 1. The setup included a Coherent Radiation argon ion laser operating with 1 W of power at 5145 Å. The laser beam was focused by a 75-mm focal length cylindrical lens to a spot .06 mm x 2 mm on the sample surface via a small mirror, and the backscattered radiation was collected and imaged by an f/3.4 lens onto the slit of a 1-m Jarrell Ashe double monochromator equipped with two 1180-grooves/mm gratings blazed at 5000 Å. The incident polarization of the laser was perpendicular to the slit of the spectrometer, and no analysis of the scattered polarization was made. The output of the spectrometer was detected by an FW130 photomultiplier cooled to -20°C and used in a photon-counting mode. The pulses, after appropriate shaping, were counted and displayed on a multichannel analyzer. In order to minimize heating effects, the highly absorbing samples used in these experiments were rotated at 1800 rpm by a motor. In this way one can increase the area illuminated by the laser beam by a large factor with almost no loss in signal level. The focal spot of the laser was located approximately 5 mm below the axis of rotation so that the effective illuminated area was an annulus of radius 5 mm and width 2 mm which yielded a rather low power density of $\sim 1.5 \text{ W/cm}^2$.

The samples used in these experiments included diesel exhaust collected on a glass fiber filter, automobile exhaust collected on a glass fiber filter from a number of cold starts of a poorly tuned automobile, ambient samples collected in 1975 as part of EPA's RAPS program in St. Louis, Missouri, and a number of pure compounds. The ambient samples were collected on a $1.2-\mu$ Millipore filter using a dichotomous sampler (Loo et al., 1976) and were in the small size range fraction. The diesel and automobile exhaust samples were removed from the filter and transferred to an aluminum flat. This technique could not be applied

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to the ambient samples because of insufficient loading, and therefore in this case the Raman spectrum was obtained from the particles on the Millipore filter substrate. The filters were mounted in a plastic holder which was especially designed for the dichotomous sampler (Loo et al., 1976) but proved to be quite convenient for mounting on the motor described above.

The spectra from these source-enriched and ambient samples were compared to those of E.D.M. 3 grade polycrystalline graphite, NORIT A activated carbon, ammonium sulfate, ammonium bisulfate, and sulfuric acid, which were used as references. The graphite specimens were obtained from POCO Graphite, Inc. and the activated carbon from Pfanstiehl Labs. The ammonium bisulfate was obtained from Matheson, Coleman and Bell and was of reagent grade, and the ammonium sulfate and sulfuric acid were obtained from Mallinckrodt Inc. and were also of reagent grade.

III. Results and Discussion

The Raman spectrum of automobile exhaust between 90 and 3830 cm⁻¹ is shown in Figure 2. It was obtained with a scan speed of 12.5 Å/min, an integration time of 0.1 min/ch, and a slit width of 3 Å (\sim 10 cm⁻¹). The spectrum consists of two intense lines located near 1350 and 1600 cm⁻¹ and a weak line at 1700 cm⁻¹. The apparent line at 3150 cm⁻¹ is an artifact due to the transmission characteristics of the Raman spectrometer, and the sharp lines denoted by an asterisk are grating ghosts. Spectra with similar features are observed for diesel exhaust, activated carbon, and polycrystalline graphite. For the graphite sample, an intense line is also observed at \sim 2700 cm⁻¹, which we associated with

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a C-H vibration. For ambient samples the signal to noise is severely limited by a large fluorescence background. The only peaks clearly seen above the background with an integration time of 0.2 min/ch and a slit width of 8 Å (\sim 25 cm⁻¹) are again in the 1200 to 1700 cm⁻¹ spectral region. In Figure 3 we show the Raman spectra for various samples in this region. The frequencies of the two Raman modes in the ambient, automobile exhaust, diesel exhaust, and activated carbon samples are coincident to within the experimental error, which is estimated to be \pm 20 cm⁻¹ for the ambient sample and \pm 10 cm⁻¹ for the other cases. For the polycrystalline graphite sample, the lines are narrower, and the 1600 cm⁻¹ mode is shifted to lower frequencies. These shifts and changes in line shape are not presently understood.

Tuinstra and Koenig (1970) have measured the Raman spectrum of a graphite single crystal as well as that of polycrystalline graphite and activated carbon. In a single crystal, only the Raman mode near 1600 cm⁻¹ is observed; and from a group theoretical analysis, it has been assigned to the k = 0 E_{2g} phonons of the graphite lattice. The mode near 1350 cm⁻¹ appears only in samples which are not perfectly ordered, and its intensity relative to the one near 1600 cm⁻¹ was found to vary inversely with the crystallite size, L_a , as obtained from X-ray data (Tuinstra and Koenig, 1970). More recently, Solin and Kobliska (1974) have shown that this ratio tends to saturate for crystallite sizes less than 40 Å. The identification of the 1350 cm⁻¹ mode is uncertain, but Tuinstra and Koenig (1970) suggest that it may be due to an A_{1g} phonon which is normally Raman inactive but is active in this case due to a breakdown of the k selection rules by the small crystallites in the sample. Another

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possible explanation for this mode, which is also consistent with the experimental data, is that it is due to surface species on the small crystallites found in these samples.

The close correspondence of the spectra shown in Figure 3 strongly suggests the presence of physical structures similar to activated carbon in both source-enriched and ambient samples. These graphitic species are presumably of primary origin, and throughout the text we shall use the term "graphitic soot" to describe them. The fact that the two modes near 1600 cm^{-1} and 1350 cm^{-1} tend to dominate the Raman spectrum indicates that "graphitic soot" is a major species and may be the principal species in the samples we have studied. One could in principle use the Raman scattering data to quantify these species. However, this would require a more detailed analysis which would have to take into account the short optical absorption length which could cause saturation of the signal, as well as particle size effects (Chew et al., 1976).

Using the results of Tuinstra and Koenig (1970), we can estimate the crystallite sizes in the various samples from the intensity ratios of the two observed Raman modes. The automobile exhaust and diesel exhaust samples have roughly the same peak intensity ratio, yielding crystallites of ≈ 50 Å in size, while the ambient sample appears to have crystallite sizes of ≈ 100 Å.

Typically about 10% of the weight in the small particle size fraction $(\leq 2.4 \ \mu)$ of the ambient samples studied is sulfur. Therefore if the Raman cross section for sulfur species is comparable to that of "graphitic soot," we would expect to observe such species. In Figure 4 we show the Raman spectrum of a heavily loaded ($\approx 400 \ \mu g/cm^2$) St. Louis sample in the spectral

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region between 900 and 1700 $\rm cm^{-1}$ after subtraction of the fluorescent background. The elemental composition of this sample as determined by X-ray fluorescence (Jaklevic et al., 1976) is shown in Table I. This spectrum was obtained with a scan speed of 0.5 Å/min, an integration time of 2 min/ch, and a slit width of 3 Å (10 cm⁻¹). The spectral lines characteristic of "graphitic soot" are again evident. However, a sharp line is also observed near 976 $\rm cm^{-1}$, which we assign to sulfate species. The lines denoted by an asterisk are due to grating ghosts. This spectrum clearly has better signal to noise than that of the ambient spectra shown in Figure 3. The improvement is due to both the longer integration times used in this scan and the smaller slit widths which tend to enhance the sharper features of the spectrum relative to the broad fluorescence background. The position of the sharp line was compared with that of the v_1 vibration of $(NH_A)_2SO_A$ which was used as a standard. The peak position was coincident to within $\pm 2 \text{ cm}^{-1}$, which is the estimated experimental error. This suggests that the line is indeed due to $(NH_{4})_{2}SO_{4}$. It is clear from Figure 5, which shows the Raman spectra of sulfuric acid, ammonium bisulfate, and ammonium sulfate, that the Raman technique is highly selective and can certainly distinguish between these species. For sulfate salts like $CaSO_A$ and $PbSO_A$, the spectral changes are smaller; but the sharpness of the spectra allows one to detect small shifts and therefore discriminate between the various compounds (Wright and Krishnan, 1973).

Since the Raman and infrared techniques are complementary methods for vibrational analysis, parallel application of these techniques to the same sample should be useful. A comparison of the spectra should allow more definite assignments to be made. It is also clear that certain species would be detected more sensitively by one or the other technique. In most cases the Raman lines are sharper than the corresponding infrared modes, and therefore the Raman technique should have better selectivity. However, one should not overemphasize this point since the infrared lines can indeed be very sharp, as demonstrated for the surface nitrate species observed by Cunningham et al. (1974). It should also be noted that the Raman scattering technique can be applied nondestructively without any sample preparation to particles collected on a filter medium or on impactor stages.

The major problem associated with the Raman scattering scheme is the large fluorescence background which limits the sensitivity of the technique. In its present stage of development, the technique has only been applied successfully to heavily loaded samples. The most straightforward way of improving the signal to noise is to reduce the fluorescent background. Our initial attempts in this direction have included changing the excitation frequency from 5145 to 7525 Å in order to avoid electronic transitions, and using a pulsed laser to try to discriminate against the fluorescence on the basis of the difference between the fluorescent and Raman lifetimes. These approaches have not yielded a significant reduction in the background. Other methods for reducing the background are being pursued; however, even if the fluorescence level cannot be reduced, one should be able to improve the sensitivity of the technique considerably by using a better signal-averaging method. One such method would be to use some type of multichannel data collection system which would allow simultaneous detection of a broad spectral region with high resolution and would in principle improve the signal to noise by a large factor.

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IV. Acknowledgment

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VI. Table and Figure Captions

Table I. Elemental composition of ambient sample whose Raman spectrum is shown in Figure 4.

Figure 1. Schematic of experimental setup (not to scale). The elements of the apparatus are labeled in the following way: F - 30-Å interference filter, M1 - mirror, L1 - 75-mm focal length quartz cylindrical lens, M2 - small mirror, L2 - f/3.4 collection lens, PMT - photomultiplier tube, PCE - photon-counting electronics, and MCA - multichannel analyzer.

Figure 2. Raman spectrum of automobile exhaust in the spectral region between 90 and 3830 cm⁻¹. The sample was collected from a number of cold starts of a poorly tuned automobile using lead-free gas and having no catalytic converter. The slit width for this scan was 3 Å $(\sim 10 \text{ cm}^{-1})$ and the integration time was 0.1 min/ch. The lines identified with an asterisk are due to grating ghosts.

Figure 3. Raman spectra between 920 and 1950 cm^{-1} of

- a) Ambient sample collected in 1975 as part of EPA's RAPS program. The sample was collected on a dichotomous sampler and was in the small size range fraction. The slit width was 8 Å (\sim 25 cm⁻¹) and the integration time was 0.2 min/ch.
- b) Automobile exhaust collected from a number of cold starts of a poorly tuned automobile using lead-free gas and having no catalytic converter.
- c) Diesel exhaust.
- d) Activated carbon.

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e) Polycrystalline graphite.

The slit width for samples b-e was $3 \text{ Å} (\sim 10 \text{ cm}^{-1})$, and the integratime was 0.1 min/ch.

Figure 4. Raman spectrum of an ambient sample collected in 1975 as part of EPA's RAPS program in St. Louis, Missouri. The sample was collected on dichotomous sampler (Loo et al., 1976) and was in the small size range fraction. The spectrum was obtained with a slit width of $3\text{ Å}(\sim 10 \text{ cm}^{-1})$ and an integration time of 2 min/ch. The lines denoted by an asterisk correspond to grating ghosts.

Figure 5. Raman spectra of $(NH_4)_2SO_4$, NH_4HSO_4 , and H_2SO_4 in the spectral region between 850 and 1150 cm⁻¹. These spectra were obtained with a slit width of 3 Å (~ 10 cm⁻¹).

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Element	Nanogram/cm ²	Element	Nanogram/cm ²
A1	729	Ni	27
Ar	96	р	250
As	2	Pb	4,091
Br	389	Rb	6
Са	650	S	45,781
C1	95	Sc	565
Cr	13	Se	22
Cu	135	Si	1,593
Fe	1,034	Sr	2
Ga	0	Ti	112
Hg	13	· · · V	38
К	1,084	Zn	505
Mn	82		

Table I. Elemental composition of ambient sample whose Raman spectrum is shown in Figure 4.^a

^aData obtained using the x-ray fluorescence analyzer developed by Jaklevic et al. (1976).



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Figure 5

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