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and T. Novakov*

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IDENTIFICATION OF PRIMARY PARTICULATE CARBON AND SULFATE SPECIES BY 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 $(\text{NH}_4)_2\text{SO}_4$ are major species in the samples studied. Also, a direct correspondence is observed between the optical absorptivity and the intensity of the "graphitic" Raman modes for a variety of source and ambient particulate samples. These preliminary data may indicate that the absorptivity is due to "graphitic" soot for the samples studied.

APPLICATION OF RAMAN SCATTERING TO THE CHARACTERIZATION OF POLLUTION PARTICULATES.

In order to better assess the origin and the environmental effects of airborne particles, it is important to explore new techniques for their chemical characterization. During the last year, we have successfully obtained Raman spectra of both ambient and source-enriched particulate samples. As far as we know, this is the first application of this method to the characterization of pollution particulate samples (1,2)*. Although the Raman scattering technique is in its early stages of development, it seems to hold considerable promise as a nondestructive, sensitive, and highly selective method for the characterization of pollution particulates.

The Raman spectra between 900 and 1950 cm^{-1} of ambient, automobile exhaust, and diesel exhaust particulates are compared with the spectra of activated carbon and polycrystalline graphite in Figure 1. The close correspondence of the spectra 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.

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 2 we show the Raman spectrum of a heavily loaded ($\approx 400 \mu\text{g}/\text{cm}^2$) sample collected in St. Louis, Missouri, in the spectral region between 900 and 1700 cm^{-1} after subtraction of the fluorescent background. The elemental composition of this sample as determined by X-ray fluorescence (3) is shown in Table I. The spectrum was obtained with a scan speed of 0.5 $\text{\AA}/\text{min}$, an integration time of 2 min/ch, and a slit width of 3 \AA (10 cm^{-1}). The spectral lines characteristic of "graphitic" soot are again evident. However, a sharp line is also observed near 976 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 1. The improvement is due to the longer integration times used in this scan and the smaller

*Numbers in parentheses designate references at the end of the paper.

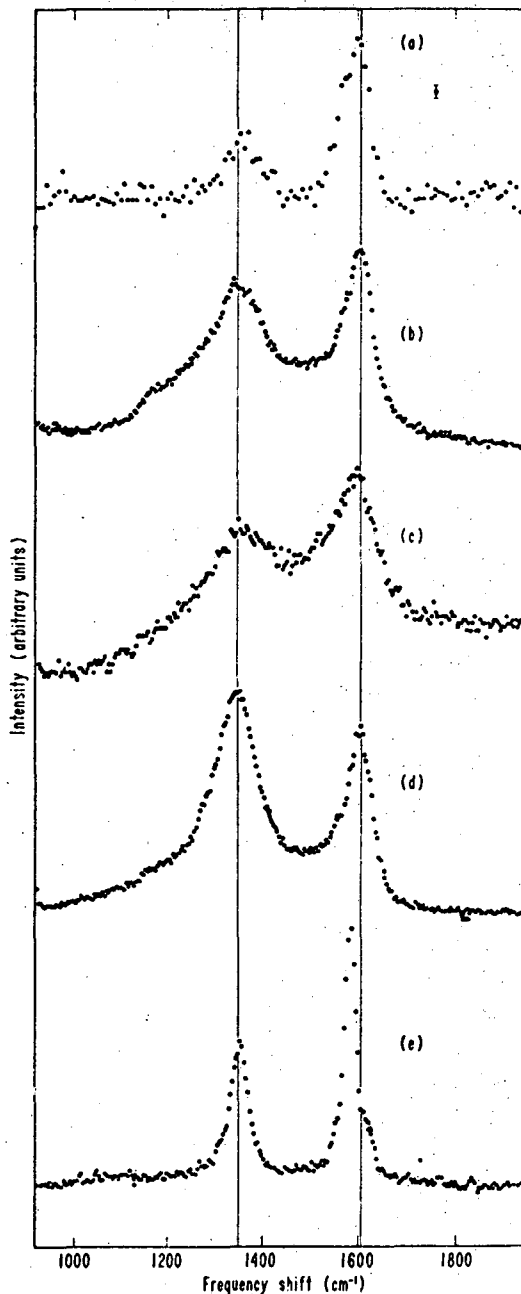


Figure 1. Raman spectra between 920 and 1950 cm^{-1} of
 a) Ambient sample collected in 1975 as part of EPA's RAPS program. The sample was collected on a dichotomous sampler and was in the small size range fraction.
 b) Automobile exhaust collected from a number of cold starts of a poorly tuned automobile using lead-free gas and having no catalytic converter.
 c) Diesel exhaust.
 d) Activated carbon.
 e) Polycrystalline graphite.

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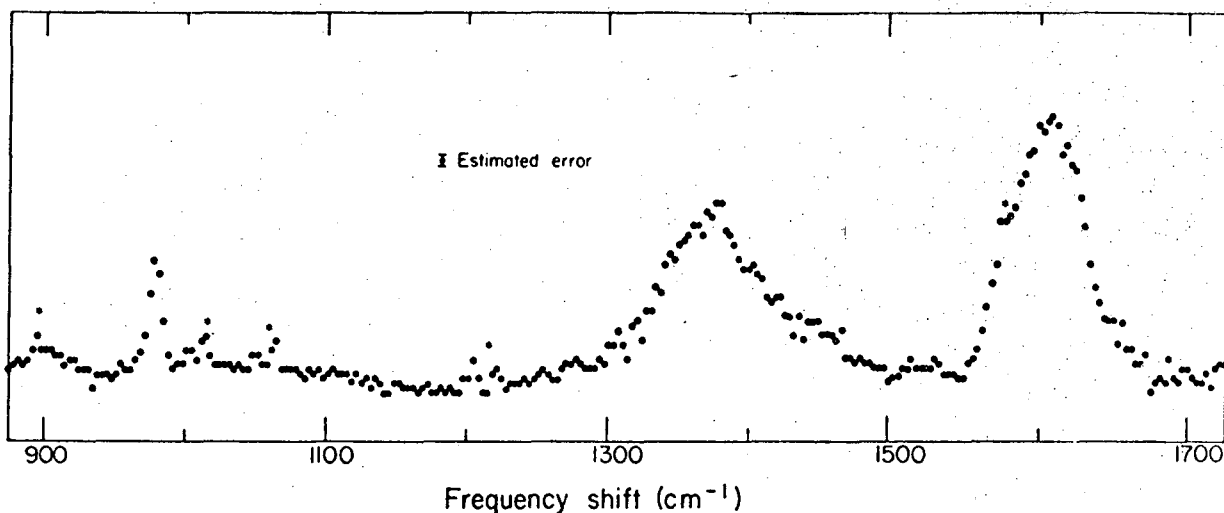


Figure 2. Raman spectrum of an ambient sample collected in 1975 as part of EPA's RAPS program in St. Louis, Missouri. The sample was collected on a dichotomous sampler and was in the small size range fraction. The spectrum was obtained with a slit width of 3 \AA ($\sim 10 \text{ cm}^{-1}$) and integration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

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 ν_1 vibration of $(\text{NH}_4)_2\text{SO}_4$, 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 $(\text{NH}_4)_2\text{SO}_4$. It is clear from Figure 3, 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_4 and PbSO_4 , the spectral changes are smaller; but the sharpness of the spectra allows one to detect small shifts and therefore discriminate among the various compounds (4).

Table 1 - Elemental Composition of the Ambient Sample Whose Raman Spectrum is Shown in Figure 2.^a

Element	Nanogram/cm ²	Element	Nanogram/cm ²
Al	729	Ni	27
Ar	96	P	250
As	2	Pb	4,091
Br	389	Rb	6
Ca	650	S	45,781
Cl	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
K	1,084	Zn	505
Mn	82		

^aData obtained using the X-ray fluorescence analyzer developed by Jaklevic et al. (3).

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

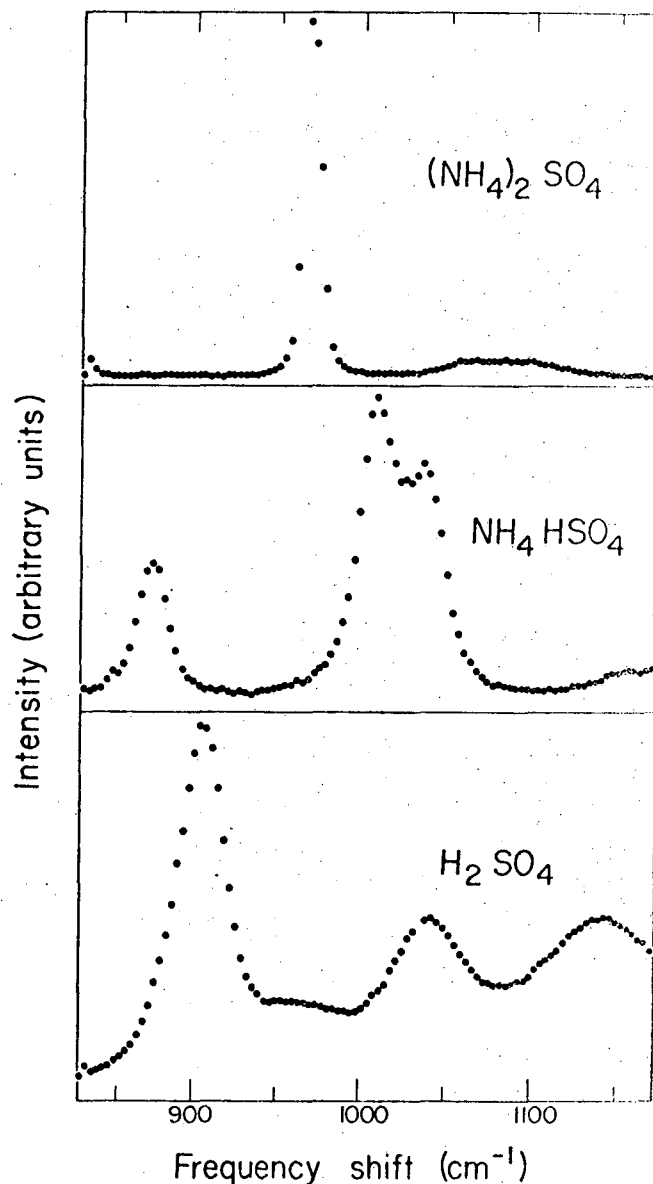


Figure 3. Raman spectra of various compounds.

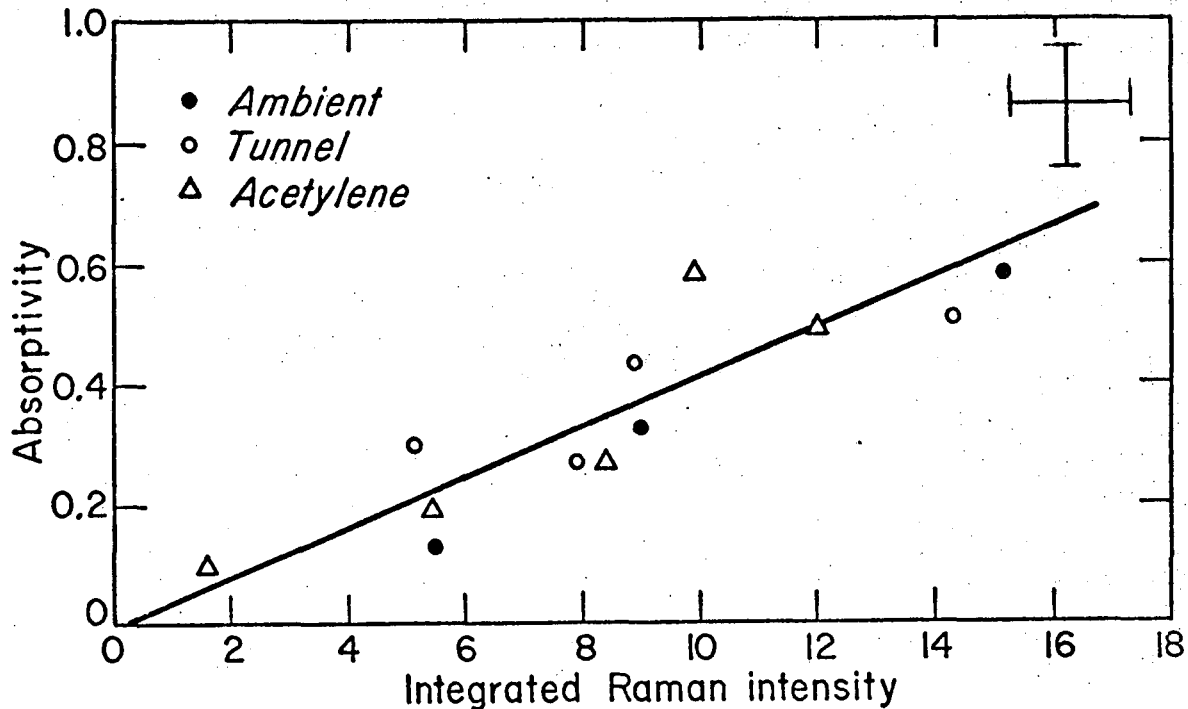


Figure 4. Plot of integrated Raman intensity of the 1600 cm^{-1} mode versus optical absorptivity at 6328 \AA for acetylene soot, tunnel, and ambient samples.

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. (5). 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 \AA 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.

RAMAN STUDY OF THE RELATIONSHIP BETWEEN OPTICAL ABSORPTIVITY AND "GRAPHITIC" SOOT CONTENT

The absorptivity of urban aerosol particles is quite high as evidenced by the grayish or blackish appearance of even lightly loaded particulate samples. The results in Paper 171 of this conference suggest that this absorptivity is due to the "graphitic" soot content of the aerosol particles. Since "graphitic" soot seems to offer a very attractive tracer for primary emissions, we would like to obtain more direct evidence that this is indeed the case. Our approach was to measure the Raman spectrum and absorptivity of the same sample and then to compare the integrated

intensity of the "graphitic" Raman mode near 1600 cm^{-1} with the optical absorptivity. These measurements were done on acetylene soot samples, highway tunnel samples, and ambient samples collected in Berkeley. The results are shown in Figure 4. Within experimental error these data show that there is a direct correspondence between the optical absorptivity and the Raman intensity for all samples studied. (For a description of the experimental technique for making the absorptivity measurements, see Paper 171.)

If we take the Raman intensity as a measure of the "graphitic" soot content of the aerosol particles, then these results clearly show that the optical absorptivity is also a quantitative measure of this species for the samples studied. The most obvious explanation for this correlation in these widely different samples is that the absorptivity is due to the "graphitic" soot component of the aerosol particles. In the future other source and ambient samples will be studied to see if the correspondence is generally valid.

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