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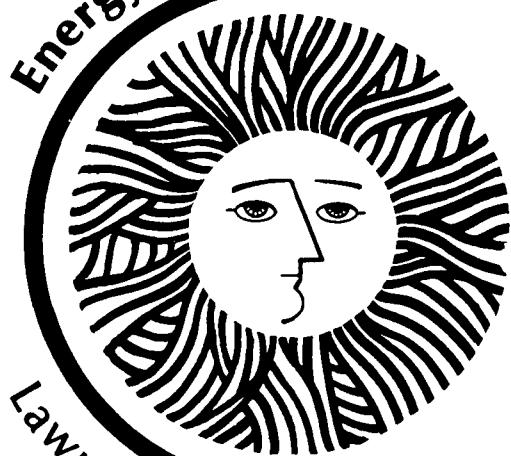
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L. Gundel and T. Novakov*

August 1978

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IDENTIFICATION OF THE OPTICALLY ABSORBING COMPONENT
IN URBAN AEROSOLS *

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Aerosol particles may play a significant role in modifying the local and global climate, and therefore it is important to study the optical properties of these suspended particulates. The overall effect of aerosol particles in heating or cooling the earth's surface depends critically on the relative magnitude of their scattering and absorption coefficients.^{1,2} In the past the effects of aerosols were thought to be due almost entirely to their scattering properties, but more recently it has been realized that the absorptivity of these particles is large. Therefore much more attention has been given to the imaginary index of refraction in heat balance calculations as well as in visibility degradation.^{3,4} To model the effects of fossil fuel combustion on climate and visibility, it is important to establish the nature of these absorbing species. In this letter we will describe the application of Raman spectroscopy and an optical attenuation technique to show that the high optical absorptivity of urban particulates and particles produced directly from various combustion sources is due to "graphitic" carbon, one component of combustion-produced soot, which also contains a complex mixture of organics.

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Raman spectroscopy is a highly selective method of analysis which, until recently, has not been applied to the characterization of air pollution particulates.⁵⁻⁷ The technique can often be used to make unambiguous identifications since different chemical species have characteristic vibrational modes and therefore characteristic Raman spectra. The Raman spectroscopy apparatus uses a Coherent Radiation argon ion laser producing 1 W of power at 514 nm. The laser beam is 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 is collected and imaged by an f/1 lens onto the slit of a 1-m Jarrell Ashe double monochromator equipped with two 1180-grooves/mm gratings blazed at 5000 Å. The output of the spectrometer is detected by an FW130 photomultiplier cooled to -20°C and used in a photon-counting mode. The pulses, after appropriate shaping, are counted and displayed on a multichannel analyzer. A computer-controlled grating drive made by RKB, Inc., allows a given spectral region to be scanned many times and added to the memory of the multichannel analyzer, greatly improving the signal-to-noise ratio. In order to minimize heating effects, the highly absorbing samples used in these experiments are rotated at 1800 rpm by a motor, which increases the area illuminated by the laser beam by a large factor with almost no loss in signal level. The focal spot of the laser is located approximately 5 mm below the axis of rotation so that the effective illuminated area is an annulus of radius 5 mm and width 2 mm, resulting in the low power density of $\sim 1 \text{ W/cm}^2$.

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. It is evident that the spectra of activated carbon, diesel exhaust, automobile exhaust, and the ambient sample are very similar, with the positions of the two Raman modes coincident to within $\pm 10 \text{ cm}^{-1}$, the estimated experimental error. The ambient sample was collected as part of the RAPS program in St. Louis, Missouri; however, the same Raman modes are also evident in every urban sample studied, including samples collected in Buffalo, New York, and Berkeley, Fremont, and Anaheim, California. Koenig et al.⁹ have studied the Raman spectrum of activated carbon and have identified the modes near 1600 cm^{-1} and 1350 cm^{-1} as being due to phonons propagating within "graphitic" planes. The close correspondence of the spectra in Figure 1 indicates the presence of physical structures similar to activated carbon in both source and ambient samples. These graphitic species are formed directly in combustion, and throughout the text we shall use the term "graphitic" soot to describe them.

Urban and combustion source particulates collected on various filter media have a gray or black appearance. The "graphitic" species identified by Raman spectroscopy are the most likely candidate for explaining this coloration. To test this hypothesis, we have developed an optical attenuation technique to quantitatively measure various properties of the absorbing species. The optical attenuation

apparatus compares the transmission of a 633-nm He-Ne laser beam through a loaded filter relative to that of a blank filter (Fig. 2). The loaded filters are placed in the beam with the loaded side towards the laser: after multiple scattering through the filter substrate, the light is collected by an $f/1$ lens and focused on a photomultiplier tube. The data presented in this paper were obtained from particles collected on Millipore or quartz fiber substrates, but the optical attenuation measurement can be made with a wide variety of filter media. This technique is based on a principle similar to that of the opal glass method used by Weiss et al.⁴ and measures the absorbing rather than the scattering properties of the aerosol. Since the real parts of the refractive indices of the filter media and the particulates are approximately equal, the addition of a few monolayers of nonabsorbing particles is expected to be a small perturbation on the transmission properties of the filter. We have verified that this is indeed the case for a Millipore filter loaded with $20 \mu\text{g}/\text{cm}^2$ of nonabsorbing $3\text{-}\mu\text{m}$ NH_4HSO_4 aerosols. Also heat treatment and solvent extraction experiments have shown that one can remove from a filter substrate most of the mass of the aerosol that is responsible for scattering without appreciably affecting the optical attenuation. We therefore throughout the text shall attribute the optical attenuation measured in the above fashion to the absorbing component in the aerosol.

Using this apparatus we have studied the temperature stability and solubility of the absorbing species in ambient and source particulate samples. Our results show that these species have high

temperature stability with only minimal oxidation up to 400°C¹⁰ and are essentially insoluble in a wide variety of solvents.^{4,10} We have also shown, using a spectrophotometer, that to within 20% over the visible spectral region, the optical attenuation has a $1/\lambda$ wavelength dependence characteristic of a constant imaginary index of refraction.^{4,10}

All these results strongly suggest that the absorbing species in urban and source particulate samples is "graphitic" soot. A direct substantiation of this hypothesis is provided by comparing the integrated intensity of the 1600 cm^{-1} Raman mode with the optical attenuation of the same filter sample. These measurements have been done on acetylene soot samples, which were essentially pure carbon with only trace amounts of metallic impurities; highway tunnel samples; and ambient samples collected in Berkeley and Fremont in the San Francisco air basin and Anaheim in the Los Angeles air basin. The results shown in Figure 3 indicate that within experimental error there is a direct correspondence between the optical attenuation and the Raman intensity or "graphitic" soot content for all samples studied, despite widely different chemical compositions (e.g., for a given optical attenuation, the Pb and Fe concentrations vary by more than a factor of 100). The only reasonable explanation is that the optical attenuation is due to the "graphitic" soot content of the collected particulates.

In summary, we have shown that the species responsible for the high optical absorptivity of particulate samples has high temperature

stability in air, is insoluble in a variety of solvents, and absorbs uniformly throughout the visible region. We have also demonstrated that the amount of the absorbing species is directly proportional to the "graphitic" soot content as defined by Raman spectroscopy. All these results taken together indicate that the high optical absorptivity of both ambient samples collected in urban environments and various source particulate samples is due to the "graphitic" component of the aerosol. The effects of these species on physical and chemical processes^{11,12} in the atmosphere require further investigation.

Acknowledgment

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Figure Captions

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 sampler⁸ 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.
2. Schematic of optical attenuation apparatus.
3. Plot of integrated Raman intensity of the 1600 cm⁻¹ mode versus percent optical attenuation at 633 nm for ambient, acetylene soot, and tunnel samples.

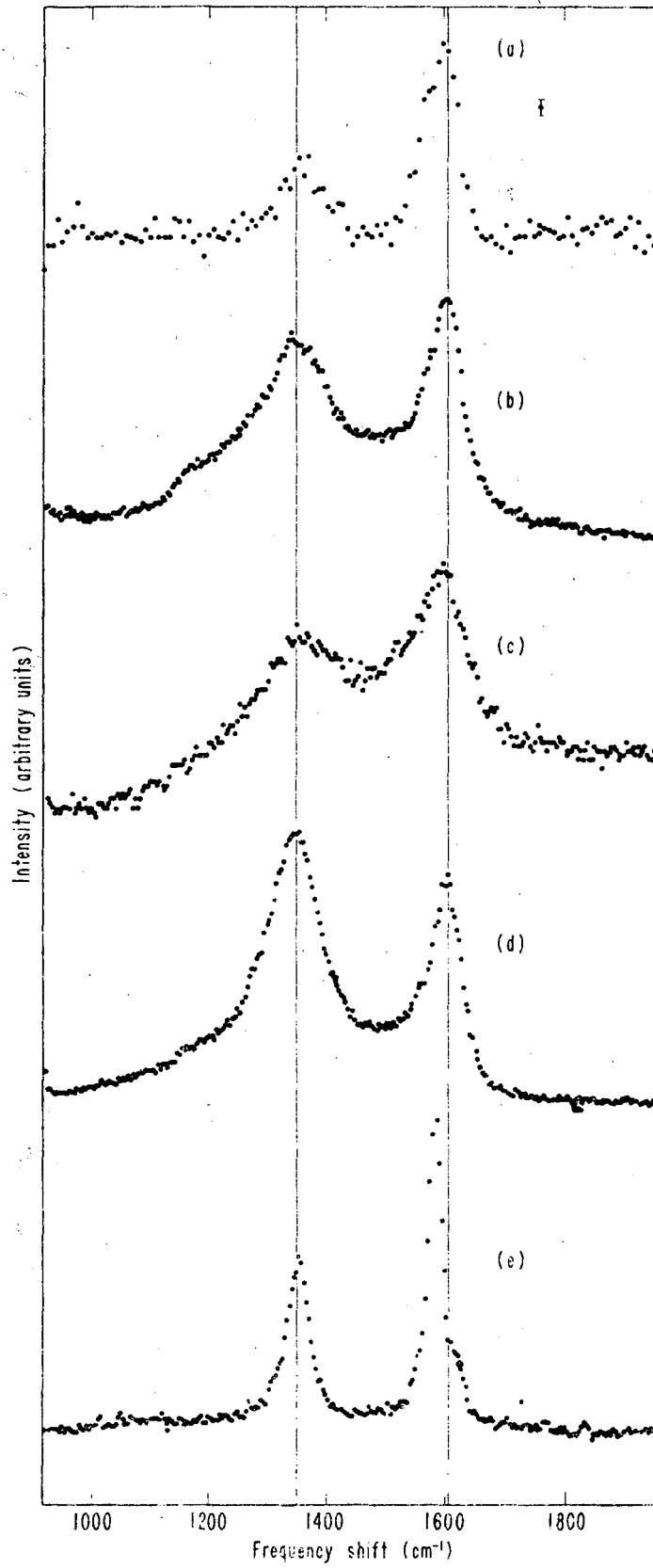
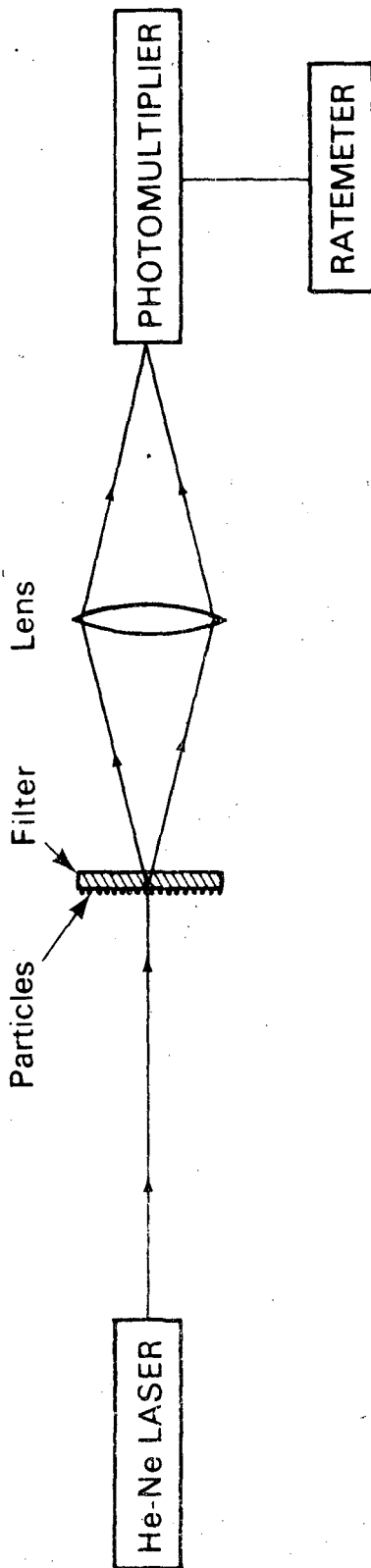
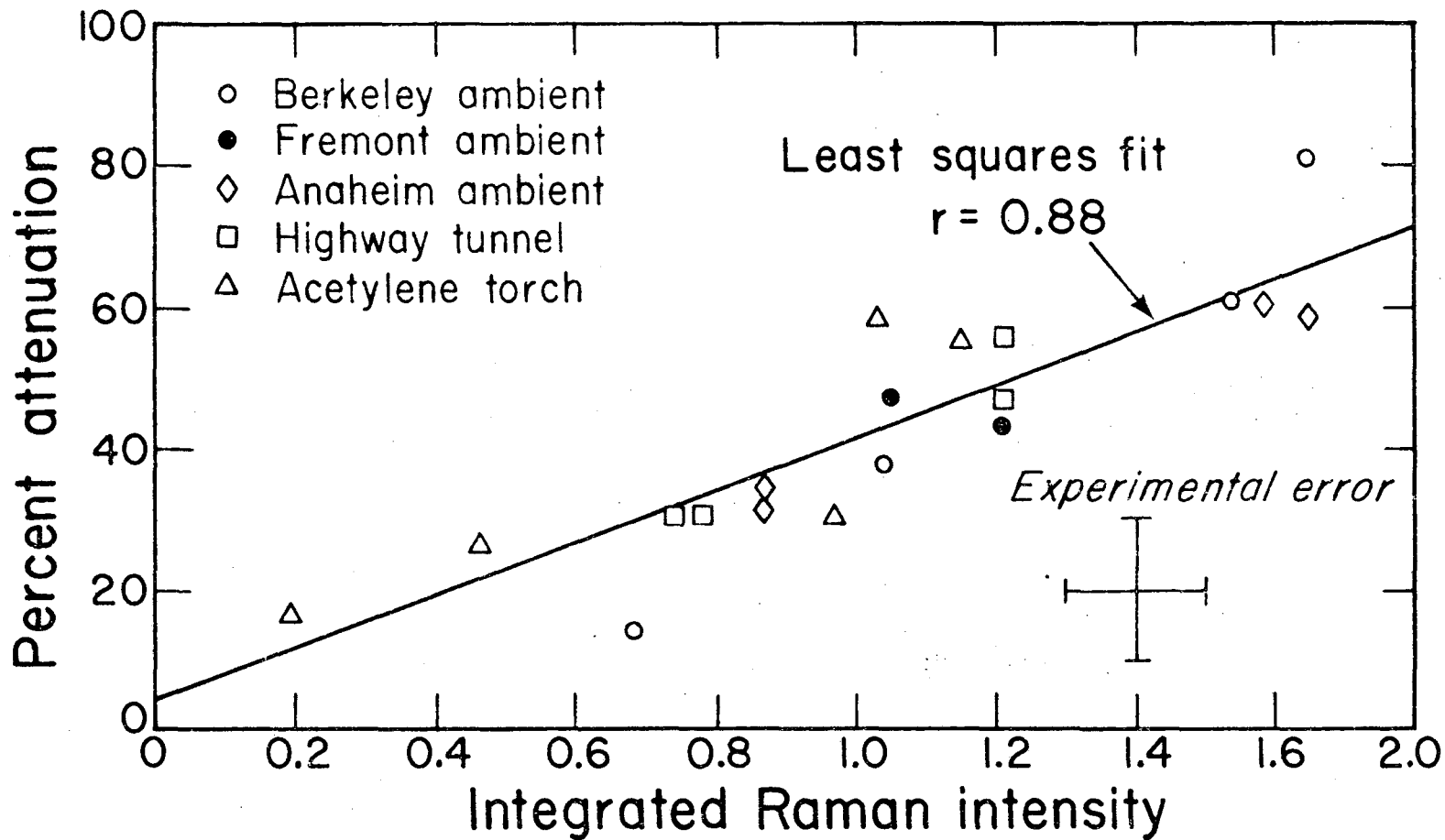


Figure 1



XBL 787-1361

Figure 2



XBL 782-177

Figure 3

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