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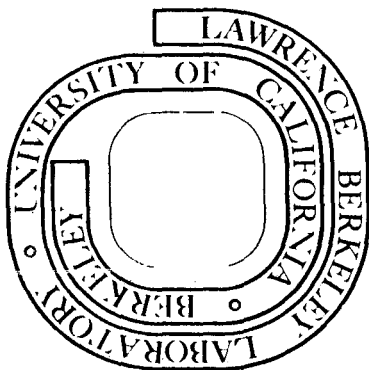
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July 1976

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APPLICATION OF RAMAN SCATTERING TO THE CHARACTERIZATION
OF ATMOSPHERIC AEROSOL PARTICLES*

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Airborne particulates play a major role in the air pollution problem. They are responsible for acid rain, reduced visibility, and, in certain size ranges, are deposited in the lungs where they can cause a variety of adverse health effects. Considerable effort has been expended in the analysis of these particulates. Such techniques as wet chemistry, X-ray fluorescence, infrared spectroscopy, and ESCA have been used rather extensively. Yet there are still great uncertainties as to the chemical form and origin of many of the particulate species. In this letter we would like to report on our preliminary studies to explore the feasibility of characterizing particulate pollutants by means of Raman spectroscopy. We believe that this is the first attempt to apply this spectroscopic technique in this area of research. The samples studied were, among others, diesel exhaust particles, automobile exhaust particles (unleaded fuel, no catalytic converter), and several ambient air samples. The spectra from these samples were compared to those of polycrystalline graphite and activated carbon which were used as references.

The experimental set-up included a Coherent Radiation argon ion laser operating with 1 W of power at 5145 \AA . The laser beam was focused by a 75-mm focal length cylindrical lens to a spot $.06 \text{ mm} \times 2 \text{ mm}$ on the sample surface, and the backscattered radiation was collected and imaged by an f/3.4 lens onto the slit of a Jarrell Ashe double monochrometer. 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 photon pulses, after appropriate pulse 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 were EDM 3 grade polycrystalline graphite obtained from POCO Graphite, Inc., NORIT A activated carbon obtained from Pfanstiehl Labs, 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 1974 Pinto, and an ambient sample collected in 1975 as part of EPA's RAPS program in St. Louis, Missouri. The latter sample was collected on a 1.2- μ millipore filter using a dichotomous sampler¹ and was in the small size range fraction. The diesel and car exhaust samples were removed from the filter and transferred to an aluminum flat. This technique allowed one to obtain excellent Raman spectra of the particulates without interference from the large fluorescence of the filter material. This technique could not be applied to the ambient sample because of insufficient loading, and therefore in this case the Raman spectrum was obtained directly from the particles on the millipore filter substrate.

In Fig. 1 we show the Raman spectrum obtained from automobile exhaust. Similar spectra were observed for diesel exhaust, activated carbon, and polycrystalline graphite with the dominant features of the spectrum occurring between 1200-1700 cm^{-1} . For polycrystalline graphite

a strong line is also observed at $\sim 2700 \text{ cm}^{-1}$ which we associate with a C-H vibration. In the ambient sample, where the signal to noise is severely limited by the large fluorescence background, the only lines that were clearly seen above the noise level were also in the $1200\text{--}1700 \text{ cm}^{-1}$ spectral region. In Fig. 2 we show the Raman spectrum for the various samples in this region.

Koenig et al.² have measured the Raman spectrum of a single crystal of graphite 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} varies inversely with the crystallite size, L_a , as obtained from X-ray data. More recently, Solin et al.³ have shown that this ratio tends to saturate for crystallite sizes less than 40 \AA . The identification of the 1350 cm^{-1} mode is uncertain, but Koenig et al. 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.

It is evident from Fig. 2 that the spectra of activated carbon, diesel exhaust, automobile exhaust, and the ambient sample are very similar. The positions of the two Raman modes in these spectra are coincident to within $\pm 10 \text{ cm}^{-1}$ which is the estimated experimental error. Since the phonon frequencies are a sensitive probe of the lattice, we suggest that these spectra give strong evidence for the existence of physical structures similar to activated carbon in the samples we have studied. This is not

surprising since activated carbon is also produced in a combustion process.

Using the available results from the literature,² 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 $\approx 50 \text{ \AA}$ in size, while the ambient sample appears to have crystallite sizes of $\approx 100 \text{ \AA}$. We would expect such structures to have very large internal surface area.

Novakov et al.⁴ have recently proposed that fine soot particles, which in many ways are similar to activated carbon, may play a major role in atmospheric chemistry. In order to assess the importance of the proposed soot-catalyzed reactions, it is important to determine the chemically active primary carbon in the carbonaceous fraction of ambient and source-enriched aerosol particles. Our results indicate that physical structures similar to activated carbon are present in diesel exhaust, automobile exhaust, and ambient samples. The fact that these features tend to dominate the Raman spectrum may indicate that graphitic "soot" is the primary species in the samples we have measured. However, the large intensity in these modes may be due just to their large Raman cross section, and therefore a quantitative interpretation of these results will have to await a more detailed analysis. Such an analysis will have to include measurements of the Raman cross section, optical absorption cross section, and take into account the little-understood particle size effects.

Acknowledgment

We would like to acknowledge B. M. Loo for providing samples that were collected as part of EPA's RAPS program.

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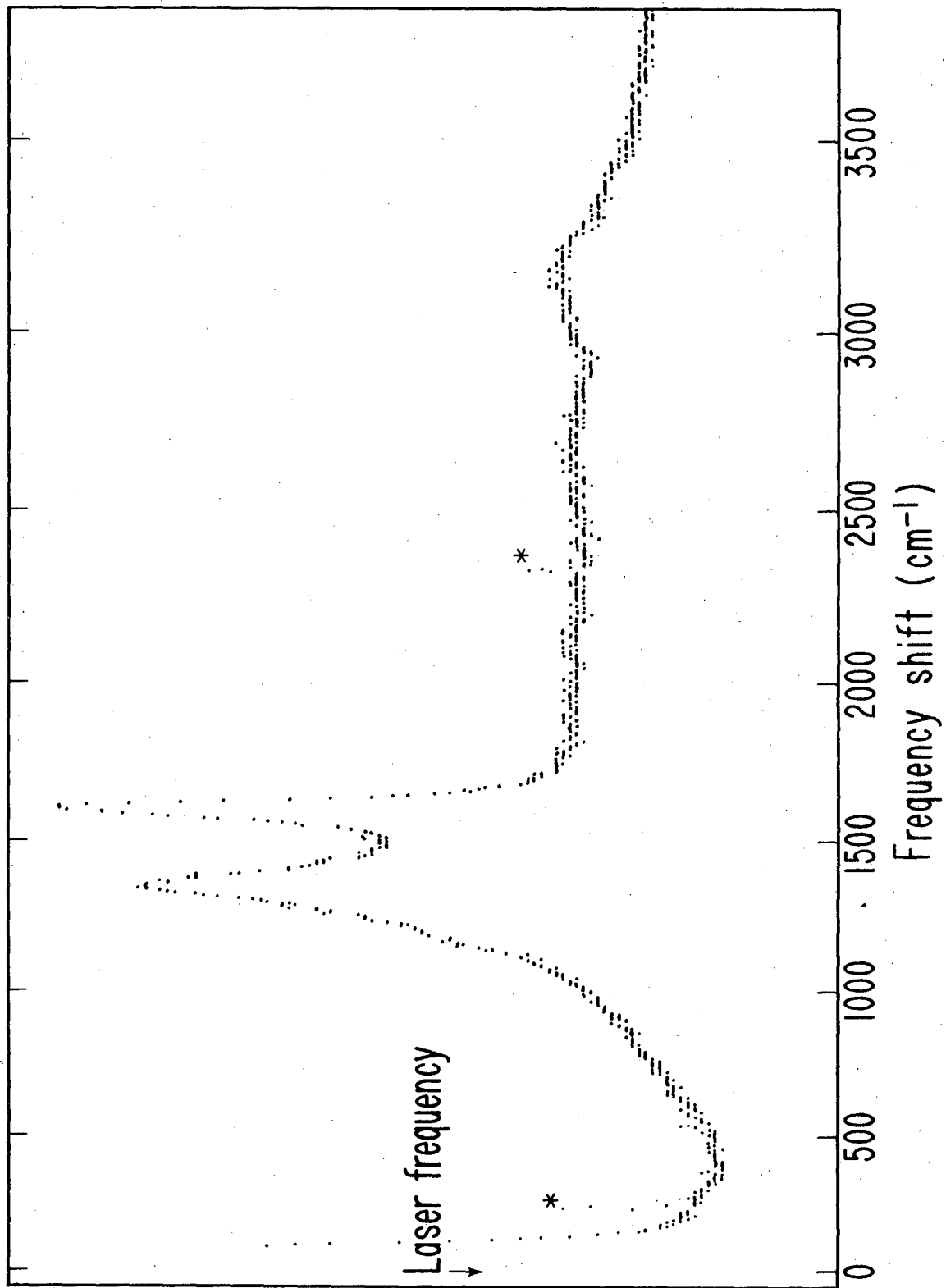
Figure Captions

Figure 1. 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 1974 Pinto using lead-free gas and having no catalytic converter. The slit width for this scan was 3 Å. The lines identified with an asterisk are due to grating ghosts.

Figure 2. Raman spectra between 1200 and 1700 cm^{-1} of

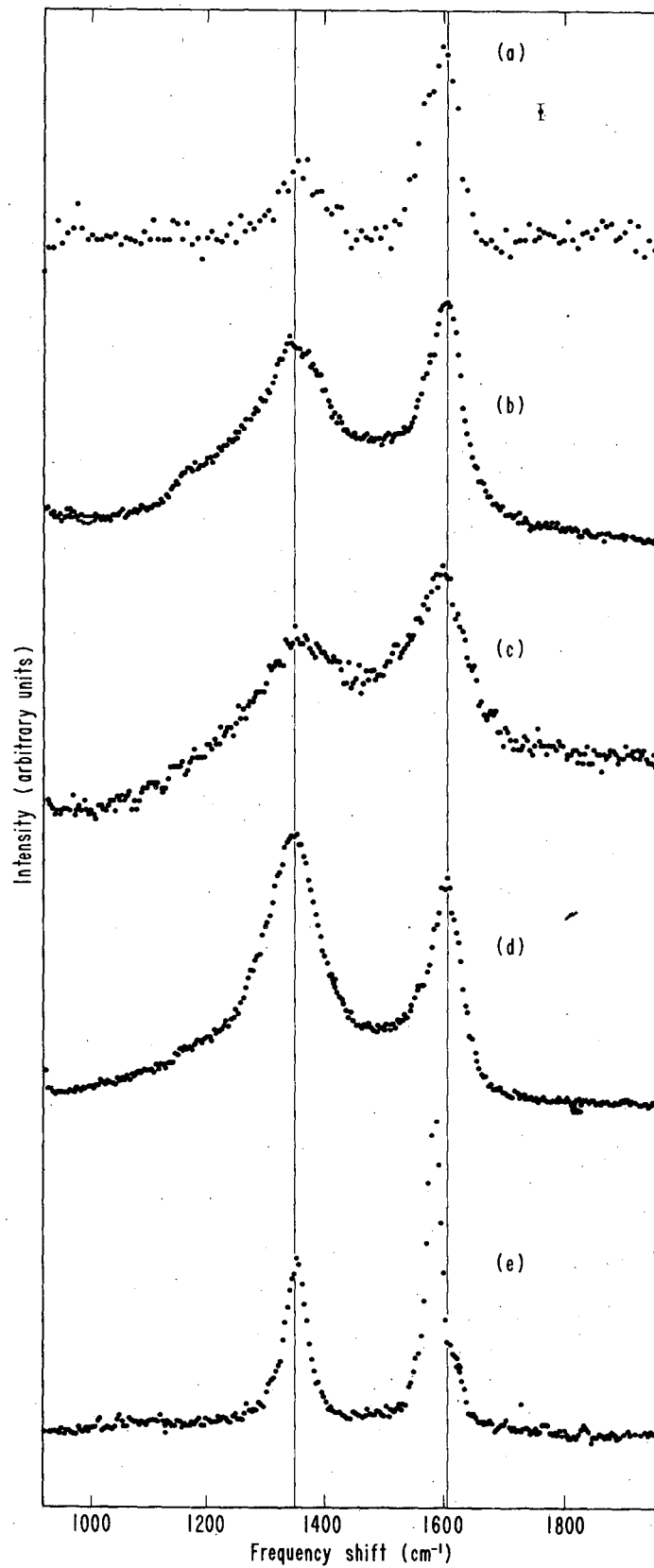
- a) Ambient sample collected in 1975 as part of EPA's RAPS program. The sample was collected on a dichotomous sampler¹ and was in the small size range fraction.
- b) Automobile exhaust collected from a number of cold starts of a poorly tuned 1974 Pinto using lead-free gas and having no catalytic converter.
- c) Diesel exhaust.
- d) Activated carbon.
- e) Polycrystalline graphite.

The slit width for samples b- was 3 Å; while for sample a, 7-Å slits were used to improve signal to noise.



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Fig. 1



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Fig. 2

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