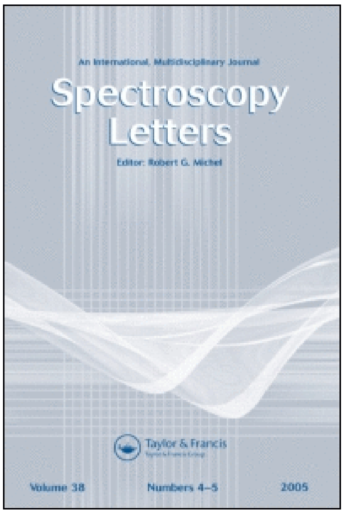

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Normalizing Infrared FT Photoacoustic Spectra of Solids

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NORMALIZING INFRARED FT PHOTOACOUSTIC SPECTRA OF SOLIDS

Key Words: Photoacoustic Spectroscopy, Infrared, Carbon.

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INTRODUCTION

Photoacoustic spectroscopy (PAS) has only recently emerged as a tool for the investigation of the vibrational spectra of condensed matter and surface adsorbates. Qualitative infrared (IR) photoacoustic spectra of various solid materials have been reported both dispersively[1-5] and in the Fourier transform mode.[6-11] In order to obtain quantitative information from a photoacoustic spectrum (as would be needed to monitor kinetics of surface reactions or for analytical purposes) it is necessary to convert the single beam spectrum into a double beam spectrum by ratioing against the spectral profile of the source radiation as it impinges on the sample. This is called source normalization.

According to the composite piston model for the generation of the photoacoustic signal,[12-13] the spectral irradiance may be garnered from any sample which exhibits photoacoustic saturation throughout the entire spectral region of interest. The criterion for saturation is that[14] $\mu_s \sim 10\ \mu_\alpha$, where μ_s is the thermal diffusion length of the material and μ_α is the optical absorption length. Another method of obtaining the source irradiance is to find a material that has a flat absorption over the region of interest. In this case saturation is not a necessary condition for being a black body. In the visible region, it would seem that any black substance would be suitable. However, Lochmuller and coworkers[15] in their investigation of various types of manufactured carbons observed notable discrepancies between various types of carbon when ratioed against the signal output of the pyroelectric detector of a commercial PAS instrument. They found that Norit A decolorizing carbon reproduces the detector output most faithfully, and as such is the best material with which to normalize visible dispersive photoacoustic spectra.

In the mid-IR region (4000-1000 cm^{-1}) Low and Parodi[5] investigated various types of carbon in order to determine whether they were suitable to normalize dispersive IRPA spectra. Their findings were that the use of carbon (in any form or manufacture) in normalizing IRPA spectra is questionable. This is not surprising when one considers the nature of infrared absorbances since even amorphous carbon exhibits certain bonding characteristics that give rise to nonuniform absorbances in the mid-infrared.

Rapid scan Fourier transform photoacoustic spectroscopy (FTPAS) adds another complication to finding an appropriate reference material. The rapid scan motion of one of the interferometer mirrors gives rise to the modulation that produces a photoacoustic signal according to the relationship below:

$$f = 2 \cdot \text{velocity of mirror (cm/sec)} \cdot \bar{\nu}\ (\text{cm}^{-1})$$

where $\bar{\nu}$ is the energy of each spectral element given in wavenumbers. Thus, convoluted into the photoacoustic signal is a modulation dependence along with a wavenumber dependence, since each spectral element is modulated at a different frequency. This complication is absent from the step-and-integrate FT photoacoustic spectrometer.[16] Another consequence of using rapid scan motion as the modulation source is suggested by the results of the "composite piston" model of signal generation: Different modulation frequencies probe different depths in the sample. This has a profound influence when this technique is used to examine inhomogeneous or layered samples which are optically transparent.[12] That is, different modulation frequencies probe different depths in the sample. The fact that the wavenumber axis of a FTPA spectrum is also a modulation frequency axis means a single FTPA spectrum will be probing slightly different sample depths over the entire spectral range because the thermal diffusion length μ_s varies inversely with modulation frequency. The consequence is a factor of 10 difference in the modulation frequency within the range of 4000-400 cm^{-1}.

The purpose of the present investigation is to determine the best method for normalizing FT infrared photoacoustic spectra. In order to achieve this end the spectra of eight different manufactured carbon samples were obtained at three different scanning speeds, chosen to coincide with modulation frequencies commonly encountered in microphonic photoacoustic experiments (< 1000 Hz). These spectra are then compared with the output of a deuterated triglycinesulfate (DTGS) pyroelectric detector which is standard on the Nicolet FTIR instrument in our laboratory.

EXPERIMENTAL

The carbon samples used were Norit A (MCB); Norit A, Acid Washed (Pfanstiehl Laboratories, Inc.); Pittsburgh Activated Carbon, Graphite (Sargent-Welch); XC-3003 carbon pellets (Union Carbide); Nuchar C-190-N (Eastman); Charcoal woodpowder (MCB); and Darco G-60 (J. T. Baker Chemical Co.). Only samples taken from freshly opened bottles were used, and all spectra of the same sample were measured in a period less than one hour to minimize sample contamination due to physical adsorption. Once installed the sample cell was not moved in order to prevent complications arising from minor displacements. All carbon samples, except for XC-3003 pellets, were <74 µm in diameter (200 mesh). The XC-3003 pellets were ~ 1 mm in diameter.

The PAS sample cell employed was designed in our laboratory. The sample was loaded to a depth of 1 cm to avoid heat transfer to the bottom of the cell. The cell is fabricated from stainless steel and is polished to minimize light scattering. The cell inside diameter is 1 in, dictated by the radius of the infrared beam at the sample surface, as measured by the color change of a heat sensitive liquid crystal (Edmunds Scientific). The acoustic channel is 1 mm in diameter and extends 15 mm to the microphone, which is sealed to the sample cell by an "O" ring. This distance prevents stray light from impinging on the microphone. The Helmholtz resonance of the cell was calculated to be > 10,000 Hz by the appropriate boundary value equation.[17] A NaCl sample beam window was sealed to the cell by means of an "O" ring. A Nicolet 7199A FTIR spectrometer was used for all spectral measurements with mirror velocities of 0.058 cm sec^{-1} corresponding to a frequency f = 464 Hz at 4000 cm^{-1} and 46.4 Hz at 400 cm^{-1} (VEL = 1); 0.074 cm sec^{-1}, f = 592 to 59.2 Hz (VEL = 4), and 0.088 cm sec^{-1}, f = 704 to 70.4 Hz (VEL = 6). The horizontal output beam from the interferometer was reflected downward by a 1" diameter gold coated pyrex mirror (Newport Research Corp.) mounted 45° to the horizontal. (The mirror has a flat ~ 97% reflectivity over the mid-IR range.) The photoacoustic signal was detected by a B & K Model 4165 condenser microphone operated with a Type 2804 power supply. The signal passes through a preamplification stage using a Model 2619S B & K preamplifier. Since we cannot use a lock-in amplifier, it was necessary to enclose the microphone and preamplifier in an air tight aluminum casing to reduce the effects of ambient room noise and decrease data acquisition time. The signal passes through A.C. coupled circuitry to remove the large D.C. offset of the microphone signal and then passes through an initial amplification stage. Afterwards it is processed identically to the signal of one of the standard pyroelectric detectors which are built into the Nicolet instrument. Spectra were recorded at 8 cm^{-1} resolution (2048 data points) with a sample spacing of 632.9 nm (He-Ne laser wavelength). This corresponds to a total mirror stroke of 0.13 cm. There is a consequent 1.1 msec interval between data points at VEL = 1, 0.86 msec at VEL = 4, and 0.72 msec at VEL = 6. The interferograms were phase corrected and apodization was performed by the Happ-Genzel method before being transformed into the photoacoustic spectrum.

RESULTS AND DISCUSSION

Figures 1-8 give the FTIRPA spectra of eight varieties of carbon at the three different scanning velocities mentioned in the

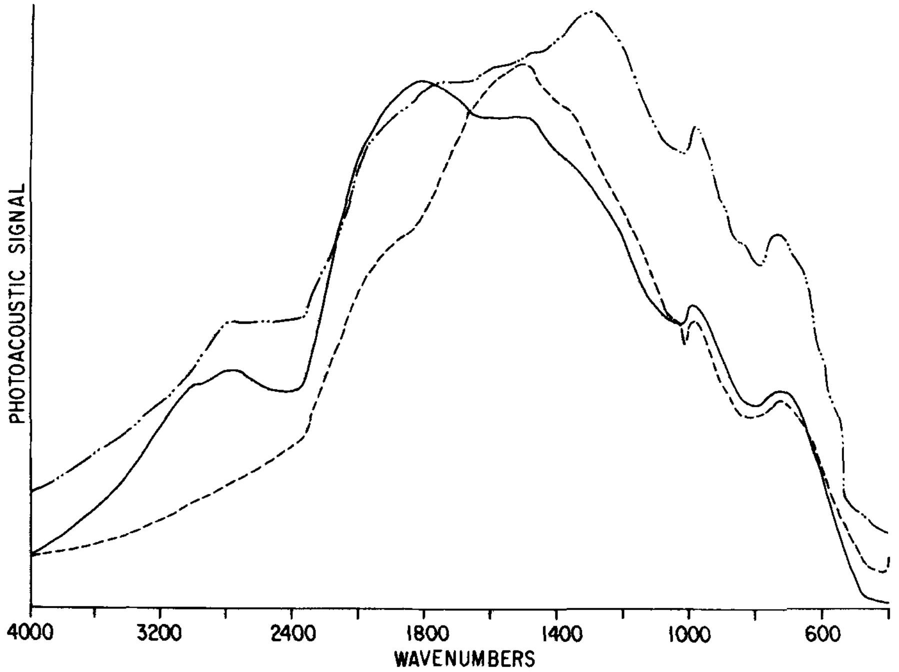

Fig. 1. Photoacoustic spectra of Norit A (Pfanstiehl Laboratories, Inc.), VEL = 1 —·· — ; VEL = 4 ——— ; VEL = 6 - - - .

experimental section. Figures 9-12 plot the different carbon samples scanned at the same velocities. There are several striking aspects of these spectra. For example, none of the carbon samples examined exhibited a spectrum independent of scanning speed. Graphite, charcoal woodpowder and Darco G-60 showed the least scan speed dependence of the eight carbon samples. A spectrum of the empty cell (Figure 13) was obtained to verify that the cell window or other components were not

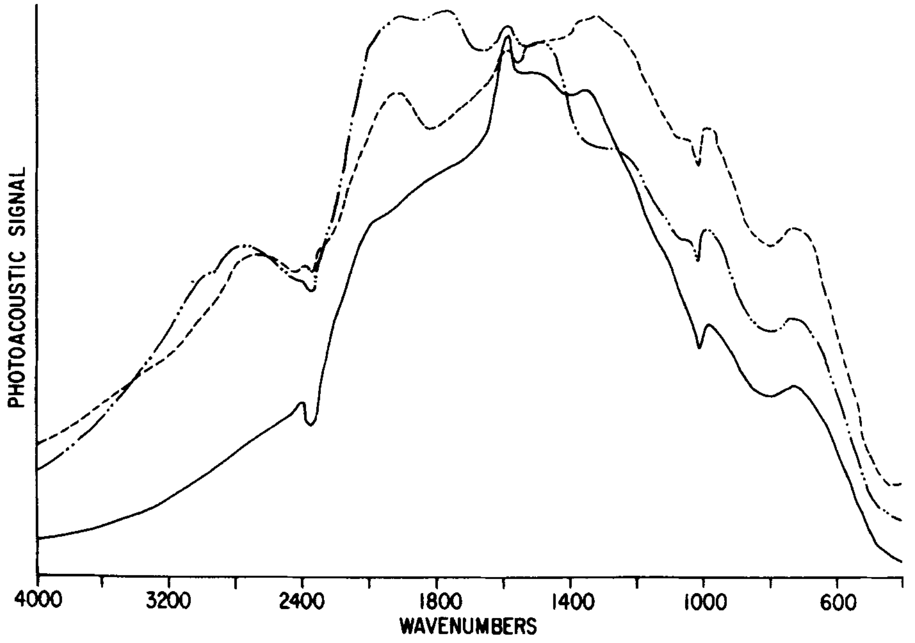

Fig. 2. PA spectra of Norit A (MCB), VEL = 1 - - - ; VEL = 4 —··— ; VEL = 6 ——— .

contributing significantly to the PA signal. Atmospheric CO_2 (2387 cm^{-1} and 667 cm^{-1}) and H_2O (1600 cm^{-1}) are clearly present. Their respective absorptions are slightly wavelength shifted compared to literature transmission spectra because they have not been source compensated.

With the exception of Darco G-60 and Pittsburgh Activated Carbon (Figures 4 and 7) all carbon samples measured at VEL = 1 produce broader absorption profiles than in the spectra at higher

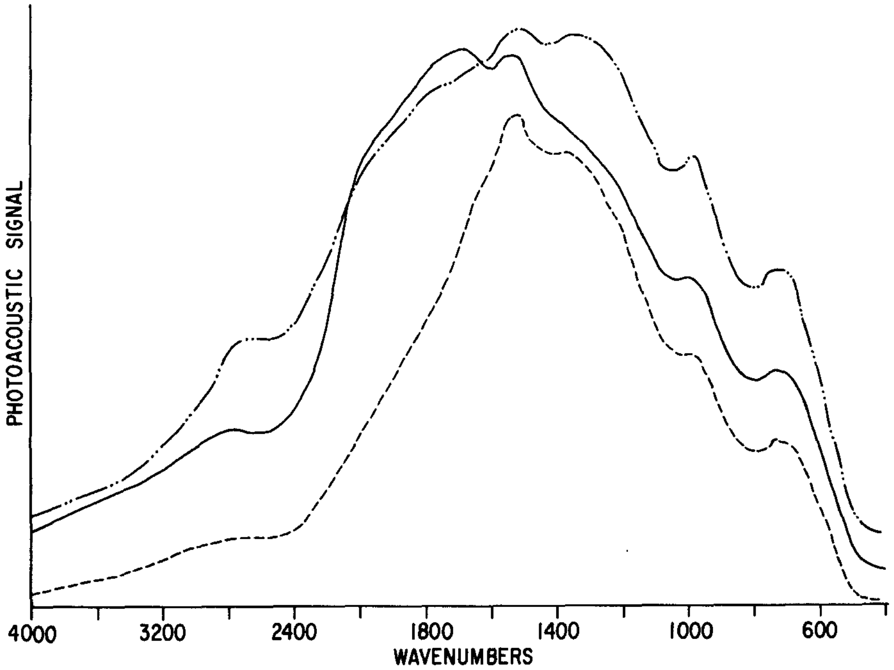

Fig. 3. PA spectra of Charcoal woodpowder (MCB), VEL = 1 —··— ; VEL = 4 ——— ; VEL = 6 - - - .

velocities. For the exceptions a spectrum taken at VEL = 4 was only slightly broader than the one taken at VEL = 1. These measurements were taken at 50% of peak amplitudes.

From Figures 9-12, it is apparent that different carbon samples scanned at the same speed more closely resemble each other than do spectra of the same sample run at different speeds, with the exception of Norit A (MCB) and Nuchar C-190-N scanned at VEL =

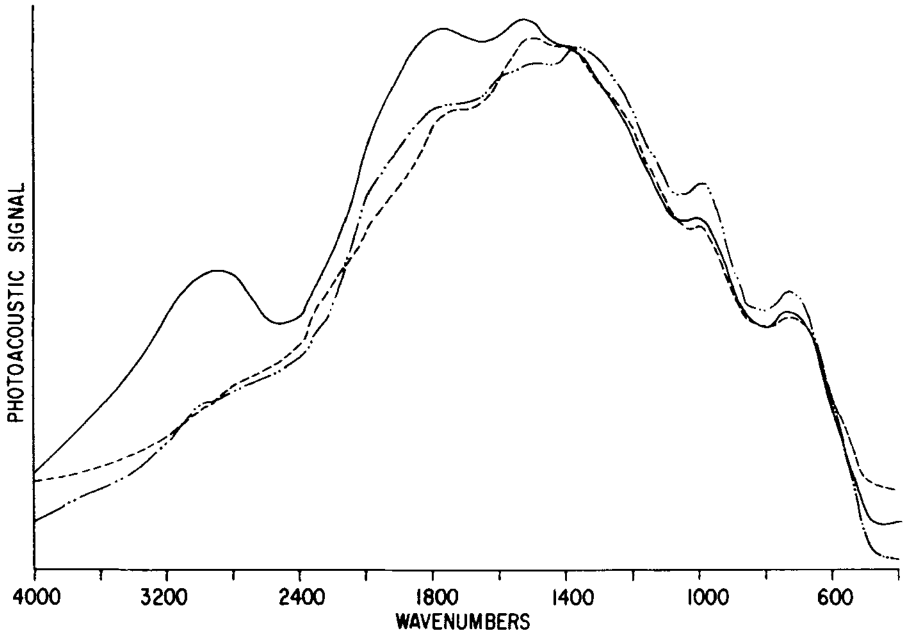

Fig. 4. PA spectra of Darco G-60 (J.T. Baker Chemical Co.), VEL = 1 —··— ; VEL = 4 ——— ; VEL = 6 - - - .

1. The spectra of these two exceptions are much more structured at VEL = 1 than at VEL = 4 and VEL = 6, where they closely resemble the spectra of the other carbons. All the spectra are most faithfully reproduced in the region below 1200 cm^{-1}.

For all the samples studied the absolute maxima of the PA spectra shift from lower wavenumbers at VEL = 1 (all maxima within the range 1380 cm^{-1} to 1300 cm^{-1}) to higher wavenumbers when scanned at VEL = 4 and VEL = 6. The absorption maxima of carbon

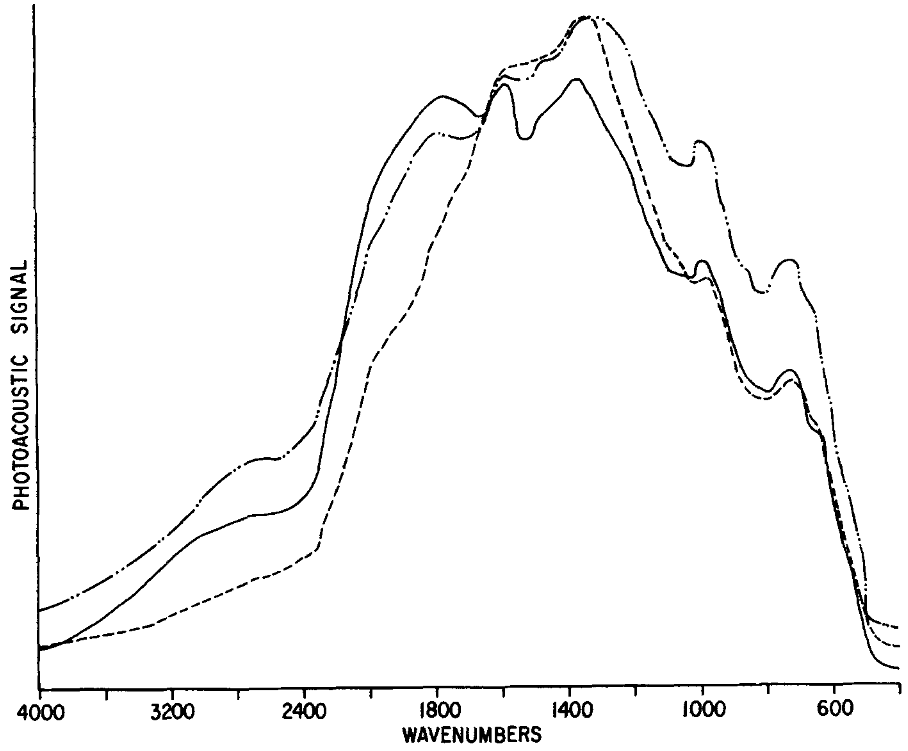

Fig. 5. PA spectra of Graphite (Sargent-Welch), VEL = 1 —··— ; VEL = 4 ——— ; VEL = 6 - - - .

samples scanned at VEL = 4 usually were shifted to a greater spectral frequency than for the same sample run at VEL = 6, but the spread between the two never exceded 160 cm^{-1} (for charcoal woodpowder 1525 cm^{-1} at VEL = 6, 1680 cm^{-1} at VEL = 4) centered around 1550 cm^{-1}. Again Nuchar C-190-N and Norit A (MCB) are anomalous because of their greater degree of spectral structure.

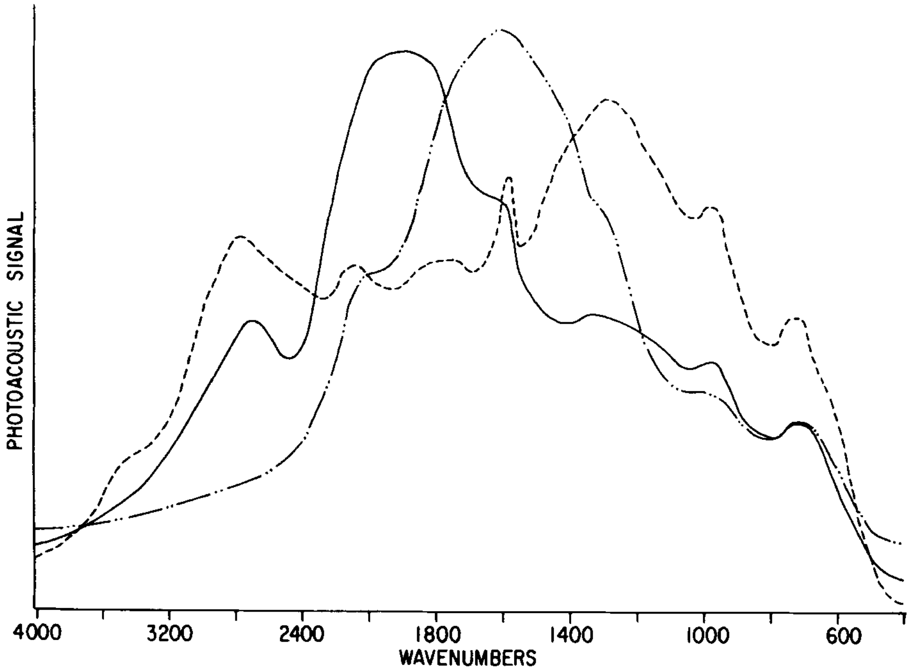

Fig. 6. PA spectra of Nuchar C-190-N (Eastman), VEL = 1 - - - ; VEL = 4 ——— ; VEL = 6 —··— .

Figure 14 represents the response spectra of the Nicolet DTGS detector at four different scanning velocities ranging from 0.160 cm sec^{-1} at VEL = 15 to 0.440 cm sec^{-1} at VEL = 30. Velocities lower than 0.160 cm sec^{-1} could not be recorded because the signal produced is greater than the analog-to-digital converter will accept, and a convenient means of adequately attenuating the infrared beam was lacking. Figure 14 indicates that the spectral response of the DTGS detector is independent of mirror velocity.

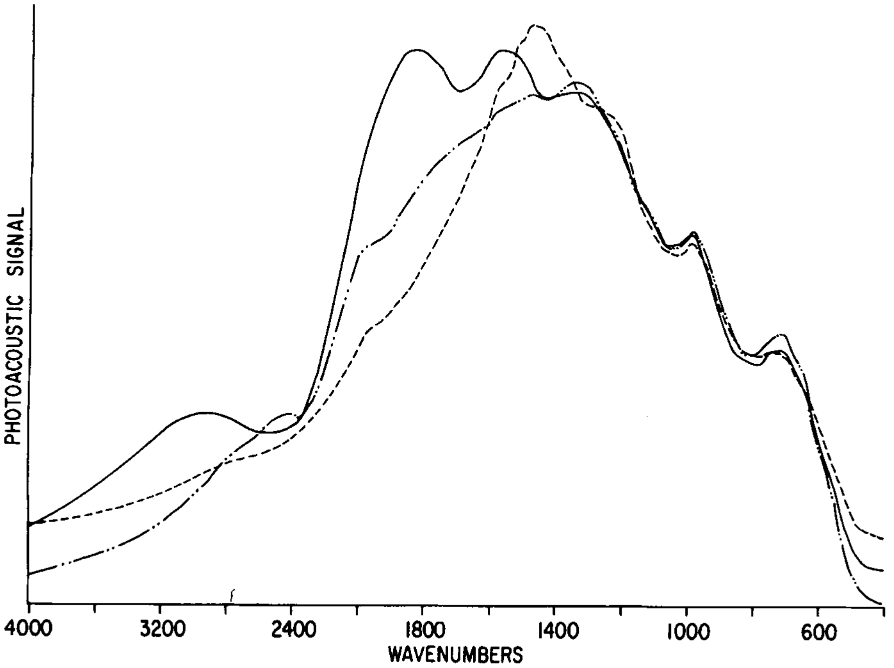

Fig. 7. PA spectra of Pittsburgh Activated Carbon, VEL = 1 —..— ; VEL = 4 ——— ; VEL = 6 - - - .

This detector exhibits a response independent of the spectral frequency, but changes linearly with modulation frequency in the same fashion as the photoacoustic signal from a true black body (saturated) absorber.[7] Thus the response curve of this detector will duplicate the output of the infrared source after passing through the interferometer.

In Figures 10 and 12 plotted along with the carbon sample spectra is the DTGS detector response, and in every case the spectra

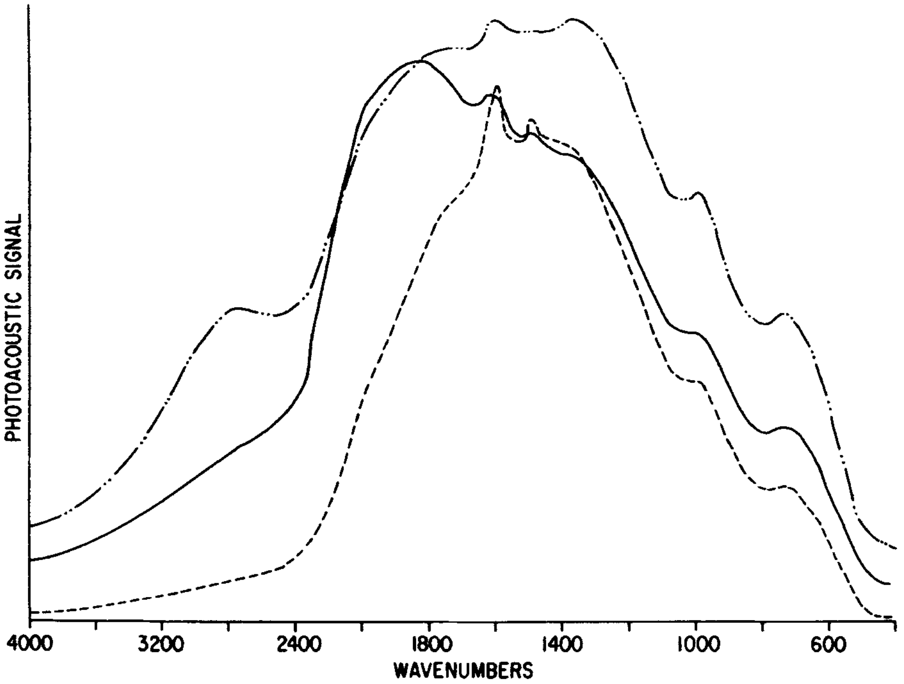

Fig. 8. PA spectra of XC-3003 pellets (Union Carbide), VEL = 1 —··— ; VEL = 4 ——— ; VEL = 6 - - - .

obtained at VEL = 1 most closely resemble the DTGS curve. Spectra at VEL = 4 were omitted for brevity. The DTGS detector response peaks at 1240 cm^{-1}, and its broad profile is very closely matched by charcoal woodpowder (maximum at 1275 cm^{-1}), Darco G-60 (maximum at 1340 cm^{-1}) and Graphite (maximum at 1300 cm^{-1}), although no one carbon would yield a horizontal line when ratioed against the DTGS detector.

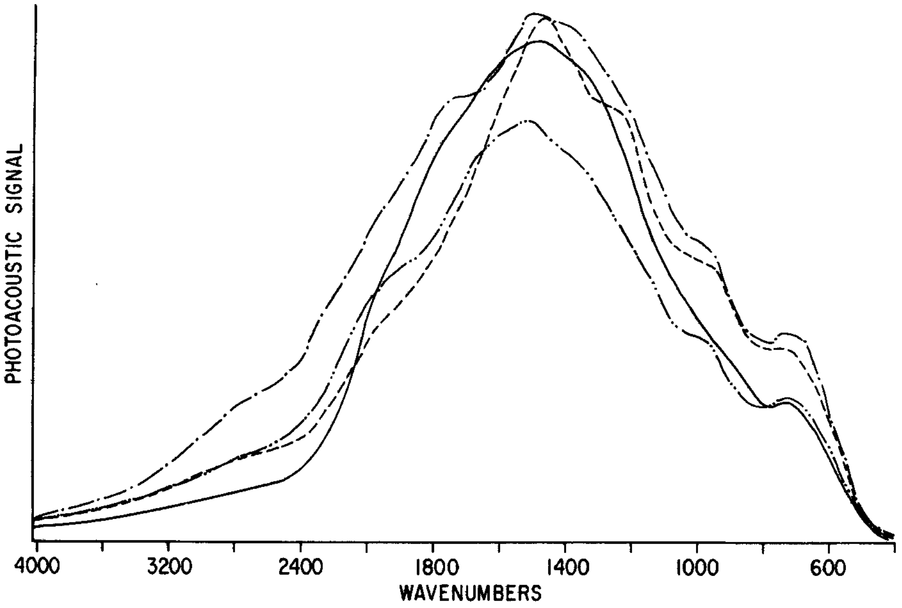

Fig. 9. PA spectra of four different carbons sampled at VEL = 6: Darco G-60 —·— ; Norit A (Pfanstiehl) —··— ; Pittsburgh Activated Carbon - - - ; XC-3003 pellets ——— .

The spectra of Norit A (Figure 15) obtained from two different vendors are observed to be vastly different in their photoacoustic response. The Norit A (MCB) shows the presence of discrete absorbances whereas the sample obtained from Pfanstiel Laboratories, Inc. does not. This may be attributable to any number of reasons but demonstrates that it would be impossible to choose a universal carbon reference material, just as Low and Parodi[5] have asserted.

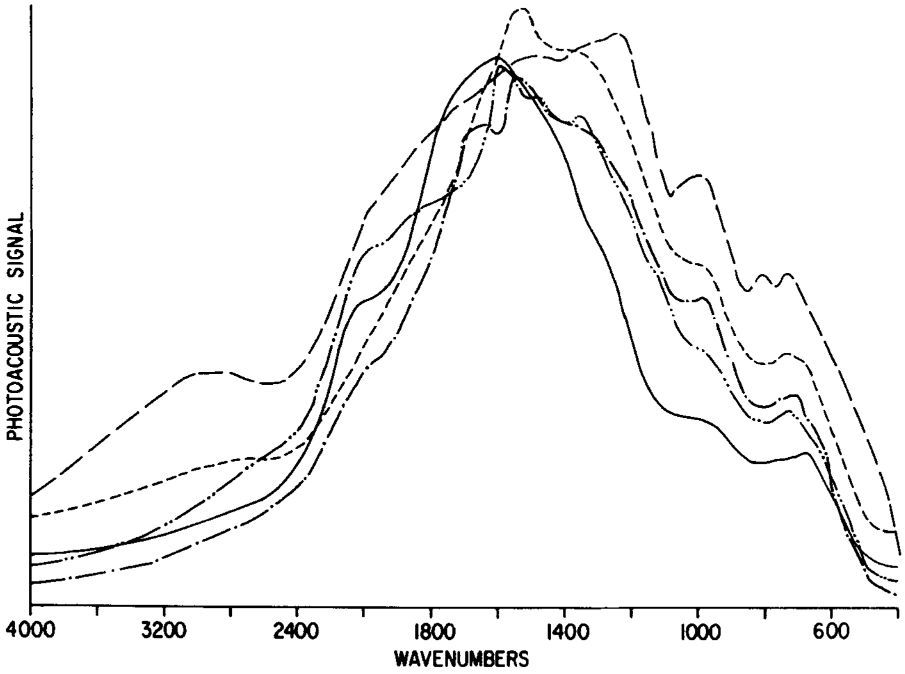

Fig. 10. PA spectra of four different carbons sampled at VEL = 6: Charcoal woodpowder - - - ; Nuchar C-190-N ——— ; Norit A (MCB) —··— ; Graphite —·— ; DTGS detector — — .

The profound velocity dependence of the spectra of all carbon samples is not very surprising. The results indicate that all the carbons studied are very strong infrared absorbers even though they are all less than ideal for producing photoacoustic background spectra. The spectra of individual carbons at the three different scanning velocities clearly illustrate one inconvenience of rapid scan FTPAS: This is the unique modulation

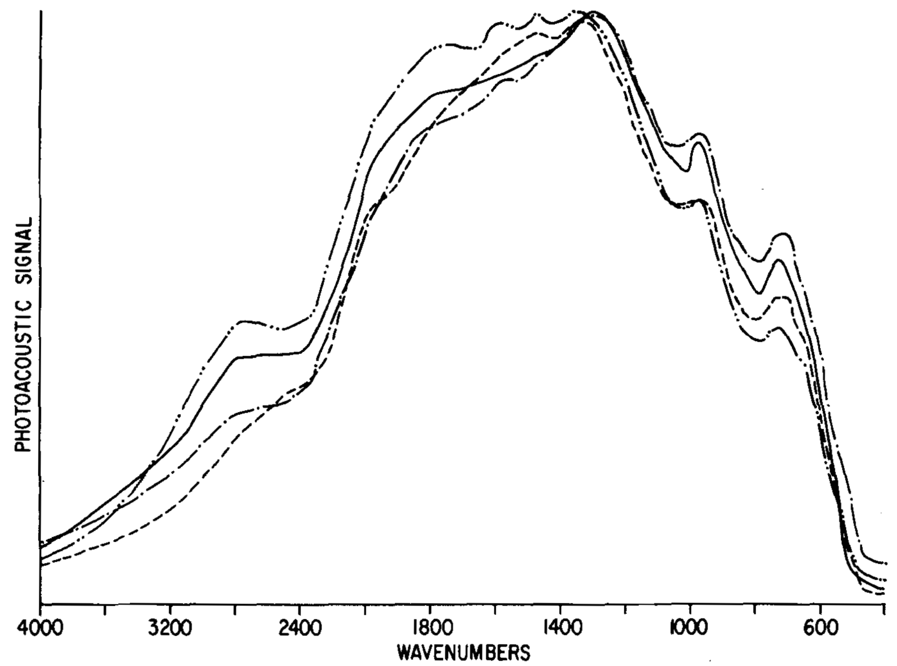

Fig. 11. PA spectra of four different carbons sampled at VEL = 1: Norit A (Pfanstiehl) ——— ; Pittsburgh Activated Carbon - - - ; XC-3003 pellets —··— ; Graphite —·— .

dependence of each spectral element. Not only does this mean that each spectral frequency is being probed at different thermal diffusion lengths, but also implies that in the case of strong absorbers such as carbon the signal is observed to advance through successive stages of saturation. Full saturation is achieved at modulation frequencies corresponding to less than 1200 cm^{-1}, i.e. frequencies less than ~150 Hz. The FTPA spectrum of carbon moves

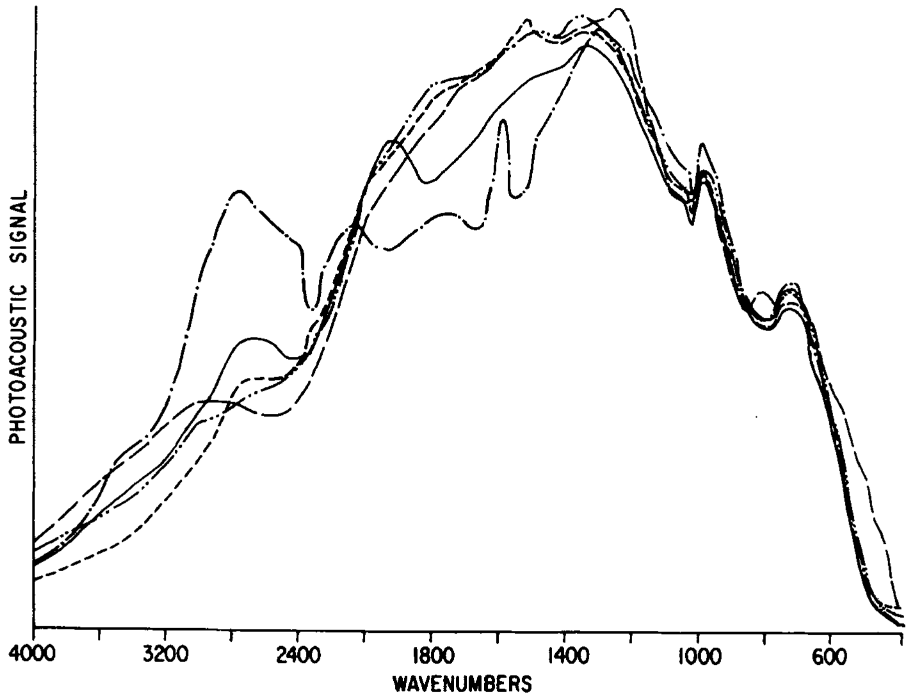

Fig. 12. PA spectra of four different carbons sampled at VEL = 1: Norit A (MCB) ——— ; Darco G-60 —··— ; Charcoal woodpowder - - - ; Nuchar C-190-N —·— ; DTGS detector — — .

out of full saturation toward the high wavenumber end (4000 cm^{-1}) of the mid-infrared spectrum. The reason the PA spectra of the same carbon sample at three different sampling velocities are most faithfully reproduced in the low wavenumber region and the greatest discrepancies occur at the high frequency end is that at the high frequency end the FTPA spectrum has moved out of the region of total saturation.

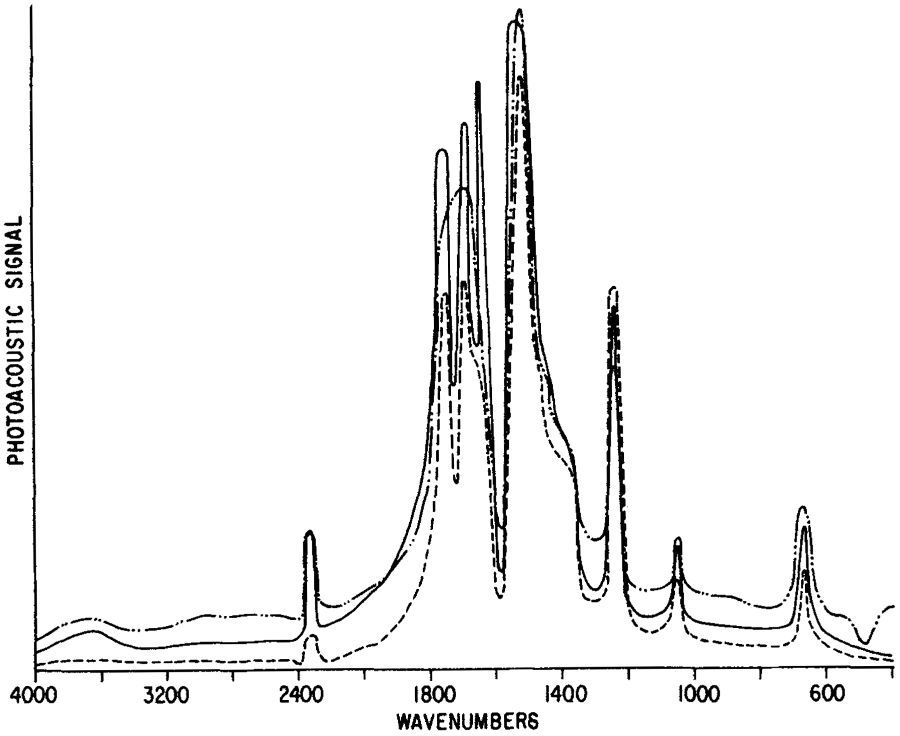

Fig. 13. PA spectrum of empty PA cell sampled at VEL = 1 —··— ; VEL = 4 ——— ; VEL = 6 - - - .

The above conclusions are substantiated by FTPA spectra of 5 mm thick polyethylene sheets. The spectrum of polyethylene should not be compromised by saturation effects because of the low extinction coefficients of this mid-infrared absorber.[7] The spectra run at the three different velocities (VEL = 1,4, and 6) are found to be absolutely congruent.

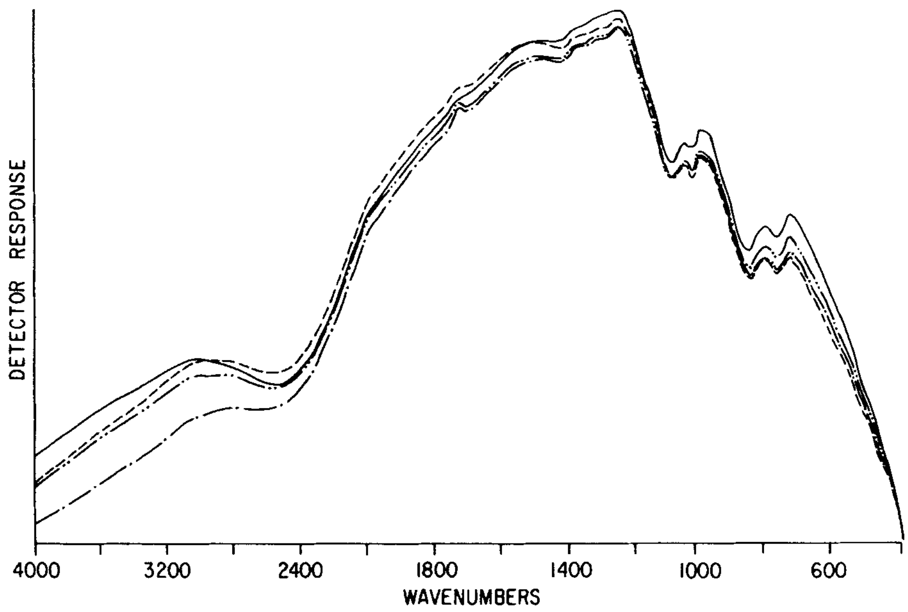

Fig. 14. DTGS detector response, sampled at: VEL = 15 - - - ; VEL = 20 —·— ; VEL = 25 —··— ; VEL = 30 ——— .

Thus, carbon in all varieties will be less suitable as a mid-infrared source reference material for rapid scan FTPA spectroscopy than for dispersive PA spectroscopy.

CONCLUSIONS

We have seen that no form of carbon is suitable for either dispersive[5] or FT photoacoustic source normalization at mid-infrared wavelengths.

A more easily standardized normalization method for FTIRPAS would employ a double beam in space arrangement where a fraction

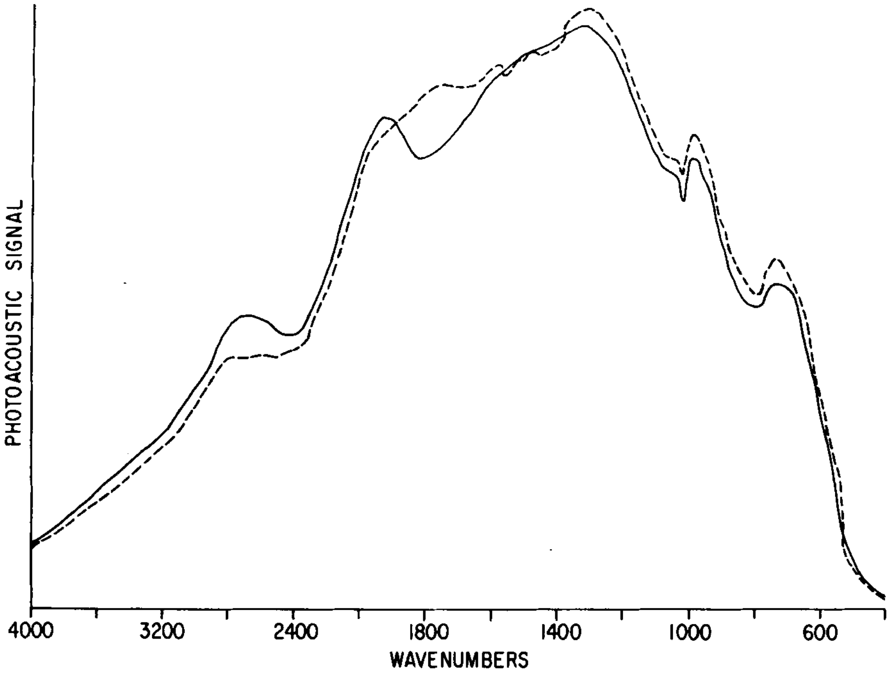

Fig. 15. PA spectra of Norit A at VEL = 1: Pfanstiehl Laboratories - - - ; MCB ——— .

of the incoming beam is diverted into the DTGS detector, or any detector whose response function closely matches that of an ideal photoacoustic black body absorber. The two signals (sample and reference) would then be ratioed before going to the data handling electronics. This technique would also correct for the noise of transient source fluctuations. The sensitivity of the DTGS detector at mirror velocities useful in taking microphonic PA data is so great that only 1% of the beam need be diverted to it thus retaining practically all of the throughput advantage of FT spectroscopy.

In examining any highly absorbing mid-infrared sample, such as coal, rapid mirror velocities must be employed in an FTPA spectral measurement so that saturation effects are not observed.

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REFERENCES

1. M. J. D. Low and G. A. Parodi, Infrared Phys., 20, 333 (1980).
2. M. J. D. Low and G. A. Parodi, Spectrosc. Lett., 11, 581 (1978).
3. M. J. D. Low and G. A. Parodi, Appl. Spectrosc., 34, 76 (1980).
4. M. J. D. Low and G. A. Parodi, J. Mol. Structure, 61, 119 (1980).
5. M. J. D. Low and G. A. Parodi, Spectrosc. Lett., 13, 663 (1980).
6. M. G. Rockley, Chem. Phys. Lett., 68, 455 (1979).

7. D. W. Vidrine, Appl. Spectrosc., 34, 313 (1980).

8. G. Laufer, J. T. Huneke, B. S. H. Royce, and Y. C. Teng, Appl. Phys. Lett., 37, 617 (1980).

9. M. G. Rockley and J. Paul Devlin, Appl. Spectrosc., 34, 407 (1980).

10. M. G. Rockley, D. M. Davis and H. H. Richardson, Science, 210, 918 (1980).

11. M. G. Rockley, Chem. Phys. Lett., 75, 370 (1980).

12. A. Rosencwaig and A. Gersho, J. Appl. Phys., 47, 64 (1976).

13. F. Alan McDonald, J. Opt. Soc. Am., 70, 555 (1980).

14. J. F. McClelland and R. N. Kniseley, Appl. Phys. Lett. 28, 467 (1976).

15. C. H. Lochmuller, R. Rohl and D. B. Marshall, Analytica Chimica Acta, in press.

16. L. B. Lloyd, R. K. Burnham, W. L. Chandler, M. M. Farrow and E. M. Eyring, Anal. Chem., 52, 1595 (1980).

17. J. Mathews and R. L. Walker, "Mathematical Methods of Physics", 2nd ed., W. A. Benjamin, Inc., Menlo Park, California, 1970, Chapter 8.

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