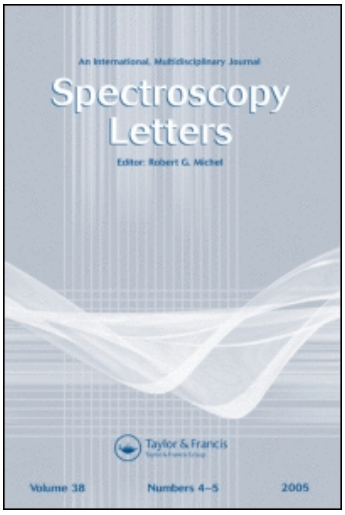

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Normalizing Infrared Photoacoustic Spectra of Solids

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NORMALIZING INFRARED PHOTOACOUSTIC SPECTRA OF SOLIDS

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Key Words : Photoacoustic Spetroscopy, Infrared, Photothermal Beam Deflection Spectroscopy

INTRODUCTION

Infrared spectra of infrared detectors were measured in order to contribute to our understanding of the normalization of photoacoustic spectra of solids[1] . Such spectra are usually "source-compensated," i.e., normalized to account for differences in source emission at different wavelengths, and such compensation or normalizing is done by comparing the single-beam spectrum of the sample to the emission spectrum of the source measured with a detector or, more commonly, to the single-beam spectrum of a carbon material of some sort which is taken to be a flat black absorber. We showed, however, that this assumption was not generally valid because different carbons gave different spectra and, because of the variability of carbons, concluded that it would be better to avoid

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carbons and use direct measurements of the exciting source to compensate spectra.[2] That statement was not further amplified partly because we did not know how absolute direct measurements might be made. These conclusions were supported by Riseman and Eyring[3], who measured IR Fourier transform photoacoustic spectra of various carbons and found not only that the spectra differed but that each individual carbon would give rise to varying spectral responses depending on the scan speed of their interferometer. In also concluding that no form of carbon was suitable for source normalization they suggested that "...a more easily standardized normalization method for FTIRPAS would employ a double beam in space arrangement where a fraction of the incoming beam is directed into the DTGS [deuterated triglycine sulfate] detector, or any detector whose response function closely matches that of an ideal photoacoustic black body absorber, "[3] i.e., the DTGS or some other detector is used to measure the source spectrum directly.

Using a DTGS detector for normalizing spectra leads to useful results, but cannot be fundamentally correct because the source spectrum obtained in this fashion depends on the absorptive properties of the detector itself. To investigate this, the spectra of real detectors were measured.

EXPERIMENTAL

The housing of each of three high quality ($D^* > 10^{10}$) complete DTGS detector assemblies was cut away to expose the detector flakes. An assembly was then mounted in the sampling area of an IR-FT photothermal beam deflection (PBD) spectrometer[4] in the manner shown schematically in Fig.1. IR radiation coming from the interferometer was focussed onto the surface of the black paint covering the detector flake and the assembly was positioned and adjusted so that the instrument's probe laser beam passed between the detector's electrical leads (they are not shown in Fig.1) and grazed the painted surface. The photothermal effect at the surface causes the gas over it to warm; the resulting changes in the refractive index in the gas causes the probe beam to deflect (the mirage effect[5]) and this deflection is measured and results in the IR-PBD spectrum, as described elsewhere[4]. Spectra were recorded at 8 cm^{-1} resolution using 1000 scans. Some results are shown in Fig.2, the arbitrary ordinates being displaced.

RESULTS

The trace marked S in Fig.2 indicates the over-all photothermal response of a high-temperature charcoal frequently used in this laboratory as standard, as well as the responses S_A, S_B and S_C (not shown individually)

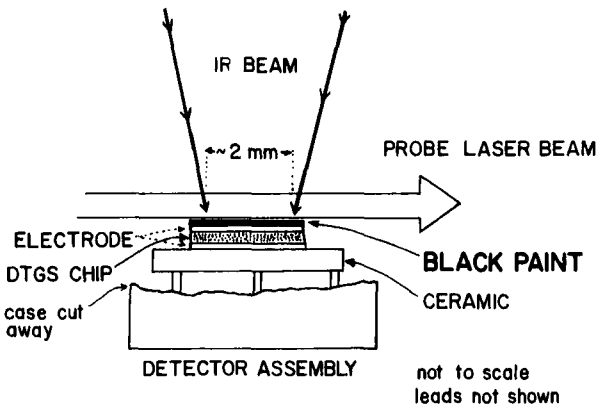

Fig.1 Schematic experimental arrangement

of each of the detector surfaces. The four traces are indistinguishable by visual observation at low ordinate scale expansion, especially in a small printed figure, thus indicating than the four surfaces are very closely matched, suggesting that any of the four materials and spectra could be properly used to normalize the photoacoustic or PBD spectra of other solids which do not absorb strongly.

The traces marked S_A/S, S_B/S and S_C/S were obtained by ratioing the spectra of the detectors against the spectrum S of the reference carbon, shown at 40-50 - fold ordinate scale expansion. Some extensive overlapping of noise spikes in the high frequency region (brought about by the poor transmission of the instrument's beam splitter) were removed

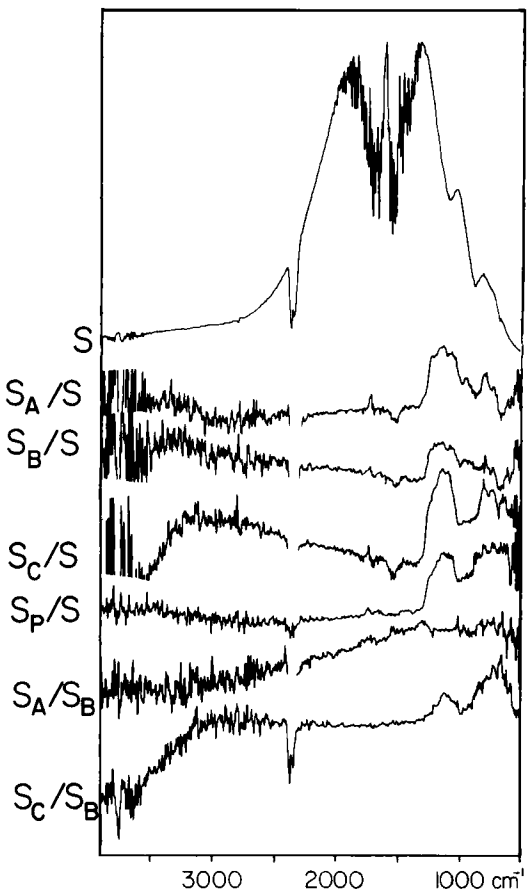

Fig.2 IR spectra of IR detectors

(literally,cut away; the figure was prepared by overlaying and pasting down the computer-drawn plots). Shown also is the spectrum S_P/S of 3M "black velvet" commercial paint (commonly used as anti-reflection, totally absorbing coating within optical instruments and on detector surfaces), compensated by ratioing against the spectrum S of the carbon standard. A small patch of the ceramic bearing the detector chip which was not obstructed by the leads had been painted and the spectrum of the painted patch was then recorded. The same spectrum was obtained when the paint had been deposited on an Al mirror.

Comparison shows the overall profiles of spectra S_A/S, S_B/S and S_C/S to differ, and all three show similar absorptions near 1200 and 700 cm^{-1}, which also appear in the spectrum S_P/S of the paint itself. If it may be tentatively assumed that spectrum S_P was correctly or reasonably correctly normalized, it is possible to attribute the discrete 1200 and 700 cm^{-1} features to the absorptions of the glass microspheres which are a constituent of the paint. If that assumption is extended to the other spectra, one is led to conclude that not only do the over-all photothermal responses of the detectors differ slightly over the entire spectral region, but each shows the characteristic absorptions of one component of the paint. If

that assumption is not valid, one can produce six compensated spectra, two of which are shown and labelled S_A/S_B and S_C/S_B, by using only the single-beam spectra of the detectors; all differ slightly.

DISCUSSION

The response of a thermal detector depends on its absorptive properties and to insure that all of the radiation striking the device is absorbed, the detector's surface is normally coated with a thin layer of a highly absorptive material, frequently a carbon-based paint. The absorptive layer is thus itself the primary sensor; energy absorbed by it is transferred to some secondary sensing material, e.g. a DTGS detector flake, the electrical or other properties of which change and can be observed. The response of the device is thus critically dependant on the properties of the absorptive sensor; the search for "black" absorbers has continued for many years, e.g.[6].

In the present case, the primary sensor is the paint layer and the secondary sensor the gas above that layer, as is the case with the Golay detector[7], and the photothermal responses of the layers differed slightly, implying that different results would be obtained with each detector. Although the number of samples examined was of necessity small, the results obtained with three detectors made the same way by the same vendor[8] tend to

support the contention that the use of DTGS or similar detectors is not the answer to the normalization problem. It seems probable that, although consistent results can be obtained in one laboratory, different laboratories using the same tye of detector, supposedly identical, would obtain slightly different results because of variations in detector manufacture, paint composition, paint texture, and so on. It is also probable that, even if detectors were identical, different laboratories would obtain different results with the proposed double-beam-in-space arrangement[3] which uses only a portion of the IR beam, because of differences in the geometries of the experimental arrangements. The IR source is never a point source, parallelism is not achieved, and there are multiple interferences, so that the IR beam coming from the interferometer is not homogeneous, but in practice this does not matter if the IR beam fills or underfills the detector. If the detector is overfilled, as in the proposed scheme, the results obtained differ slightly depending on which portion of the beam is sampled, so that the proposed scheme should be avoided. A true double-beam-in-space system with an exactly filled detector would be preferable although probably not practical in the IR range because the IR intensity is halved. Some other means of normalizing is needed.

Coufal[9] recently described the preparation of self-supporting carbon glass films and presented spectral and photoacoustic data which indicate that these films are an optimum choice as standard samples for photoacoustic spectroscopy with gas-coupled microphones. However, the data covered the 400-800 nm region and it is not certain how the films would perform in the IR range. Also, Murphy and Aamodt[10] have described the photothermophone, a device for absolute calibration of photoacoustic spectrometers, essentially consisting of an electrically conducting platinum black film which serves as spectrally black absorber and also as a uniform source for resistive heating. Within the measurement accuracy, the metal black was spectrally flat, based on comparisons to measurements with a pyroelectric detector and photoacoustic measurements of a carbon. However, the measurements were made in the visible region and, again, there may be some differences in the IR region : we have found the IR photothermal response of platinum blacks to vary below 1000 cm^{-1}, seemingly depending on the preparation conditions; this will be described elsewhere. It would seem that a proper normalization procedure for IR spectra has yet to be found.

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