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Synchrotron infrared photoacoustic spectroscopy

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The use of synchrotron radiation (SR) as a far- and mid-infrared source in the measurement of photoacoustic Fourier transform infrared spectra of solids is demonstrated for the first time in this work. Initial experiments were performed at beamline U10A at the National Synchrotron Light Source, Brookhaven National Laboratory. For synchrotron photoacoustic spectroscopy to be feasible, it must yield results superior to those obtained with a conventional thermal (Globar®) source; accordingly, SR and Globar® photoacoustic spectra recorded under similar conditions were compared in detail. The intensities of SR far-infrared photoacoustic spectra were found to be consistently greater than the corresponding Globar® spectra. At shorter wavelengths, SR always underfills the effective aperture (or, alternately, sample size); SR is a superior source in a spectral region that is a function of this aperture. The high wave number limit of this region exhibits a power-law dependence on aperture size. This investigation also showed that the entire mid-infrared photoacoustic spectrum is more intense using SR and apertures smaller than approximately 0.5 mm.
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I. INTRODUCTION

The utilization of synchrotron radiation (SR) as an alternative to traditional thermal radiation sources in infrared spectroscopy has been documented by several research groups.[1–6] Beginning with the Daresbury Synchrotron Radiation Source in the UK, a substantial number of infrared beamlines have been built in the last 20 yr at synchrotron facilities in several countries; more are planned or already under development. Many of these beamlines are dedicated to infrared microspectroscopy, and are designed to take advantage of the intrinsically high radiance (radiant power per unit area per unit solid angle) of SR in the mid-infrared. Other beamlines are optimized for far-infrared spectroscopy, in recognition of the fact that SR is more intense than conventional Globar® and Hg arc blackbody sources at longer wavelengths.[4,5] Both mid- and far-infrared beamlines are being designed at the Canadian Light Source, currently under construction at the University of Saskatchewan.

The number of infrared SR experiments performed with common (macro) sampling accessories is still relatively small,[7,8] primarily because the advantages of SR rapidly diminish as solid angle increases. In commercial Fourier transform infrared (FT-IR) spectrometers, the beam diameter at the sample position is commonly about 1 cm; depending on wavelength, SR may not be superior to thermal radiation in experiments utilizing IR beams of this size. Thus the choice between the two radiation sources is a question of both aperture (or sample) size and the spectral region to be investigated.

In this work, SR and thermal radiation sources are compared in the context of mid- and far-infrared photoacoustic (PA) spectroscopy, where the IR beam is usually slightly focused to about 5 mm. Significantly smaller beam sizes were also investigated in this study. The PA technique is of interest because it permits characterization of difficult samples such as carbonaceous solids and clay minerals, which frequently are not amenable to traditional sample preparation procedures. PA spectroscopy also affords the possibility of depth profiling of layered or inhomogeneous samples. The two primary objectives of the current investigation, which has also been briefly described in an extended abstract,[9] are as follows: first, to demonstrate the feasibility of PA infrared SR spectroscopy; and second, to determine whether this technique yields results superior to those from conventional PA infrared spectroscopy, either in the far- or mid-infrared regions.

II. EXPERIMENT

Experiments were performed at beamline U10A on the vacuum ultraviolet (VUV) ring at the National Synchrotron Light Source, Brookhaven National Laboratory. This beamline is equipped with an evacuable Bruker IFS 66v/S FT-IR spectrometer. This instrument can be operated with both mid- and broadband far-infrared beamsplitters (7000–400 and 650–30 cm^{-1}, respectively), utilizing either a standard thermal (Globar®) source or SR from the VUV ring. Both sources of infrared radiation were used in this feasibility

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TABLE I. Samples analyzed in this work.

Sample	Region (cm^{-1})
Glassy carbon	30–1000
Carbon-filled rubber	30–6000
Clay	400–6000
Hydrocarbon coke	400–6000

study. An MTEC 100 PA cell and preamplifier were interfaced with the spectrometer to allow measurement of PA infrared spectra.

Beam current in the VUV ring normally varies between about 400 and 1000 mA, depending on the elapsed time (up to approximately 5 h) since the most recent injection into the ring. Since PA detection is a zero-baseline technique that produces absorption spectra, intensities of PA infrared SR spectra are observed to vary linearly with this current. To permit comparison of data obtained at different times, SR spectra were normalized to a beam current of 700 mA. This means that the SR signal levels reported here in the comparisons with the Globar® source can be equaled or exceeded 50% of the time. It should be noted, that this is a slight modification of usual practice on this beamline, in which spectra are normalized to a beam current of 1000 mA.

PA infrared spectra were recorded for the following samples: carbon-filled rubber, glassy carbon, clay, and coke residue from thermal treatment of aromatic hydrocarbons. These samples are listed in Table I, together with the spectral region covered for each. When appropriate, circular brass apertures with diameters ranging from 0.5 to 3 mm were placed directly over the samples to reduce the size of the infrared beam. To avoid edge effects the central 3 mm of each aperture was milled out, leaving a thickness of only 100 μm.

The PA cell was purged with helium gas for several minutes prior to the measurement of each spectrum. It should be noted that the He used in these experiments had an unusually high concentration of water vapor; a PA cell that has been purged with He should in fact yield no measurable signal from vapor phase species. The presence of this level of water vapor is generally not desirable in PA spectroscopy, because it adversely affects the signal-to-noise ratio. Because of the data analysis methods used in this work, however, it does not affect the conclusions.

Double-sided interferograms were recorded in rapid-scan mode, in both forward- and backward-scan directions, using the lower mirror velocities on the IFS 66v/S. The most commonly used velocity corresponds to a modulation frequency of 2.2 kHz at the wave number of the reference HeNe laser (15 800 cm^{-1}). The nominal resolution of the spectra was 6 cm^{-1}. Phase correction, apodization, and Fourier transformation were carried out with OPUS, standard Bruker software that controls the spectrometer. Spectra of residual water vapor in the PA cell, which make an unwanted contribution to PA spectra obtained with the Globar® source, were obtained separately by placing a piece of aluminum foil between the aperture and sample, preventing the infrared beam from impinging on the solid. These spectra were subsequently subtracted from the corresponding PA spectra of the solids to obtain results free from these interfering absorption bands. Subtraction of spectra obtained in this way also corrected for the non-negligible signal arising from the brass aperture itself.

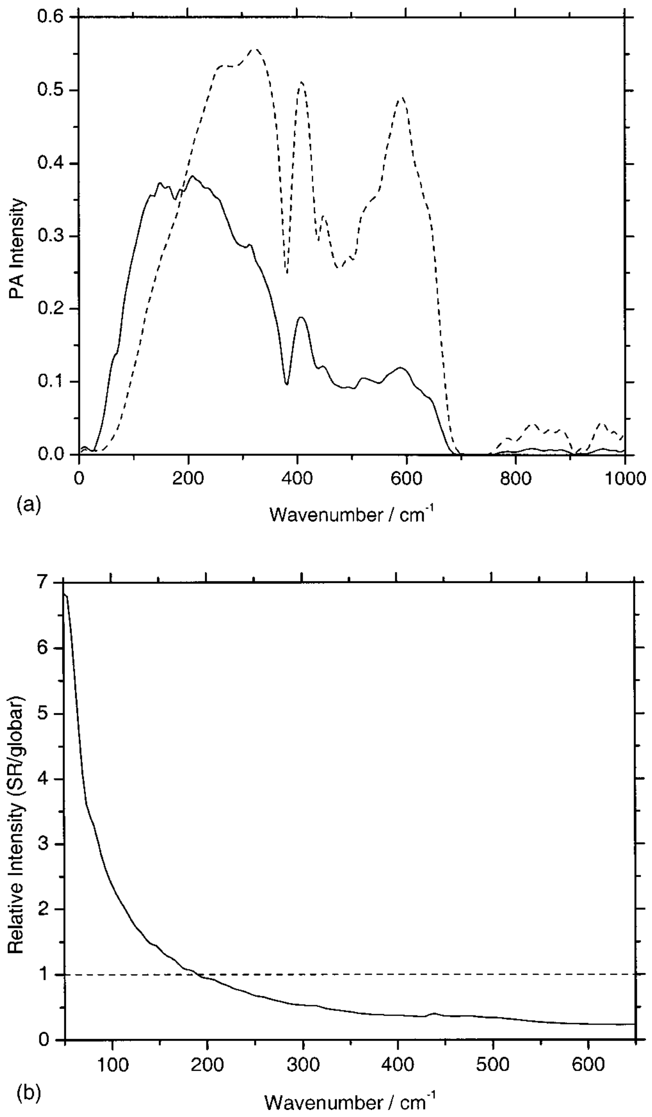

FIG. 1. (a) Far-infrared PA spectra of glassy carbon, obtained with two different sources of infrared radiation. Solid line, synchrotron radiation (SR); dashed line, Globar®. (b) Ratio of the SR spectrum in (a) to the Globar® spectrum. The dashed line at 1.0 is drawn as an aid to the reader.

III. RESULTS

A. Far-infrared spectra

Figure 1(a) compares a far-infrared PA spectrum for glassy carbon, obtained using SR (solid line), with the corresponding Globar® spectrum (dashed line). These spectra were recorded with no aperture above the sample and correspond to an infrared beam size of 5 mm, although it should be pointed out that the SR underfills this aperture. Glassy carbon does not give rise to specific absorption bands in the far- and mid-infrared regions; instead, the features in this figure are due to the choice of optical components [e.g., the broadband far-infrared (FIR) beamsplitter] and the presence of residual water vapor in the PA cell.

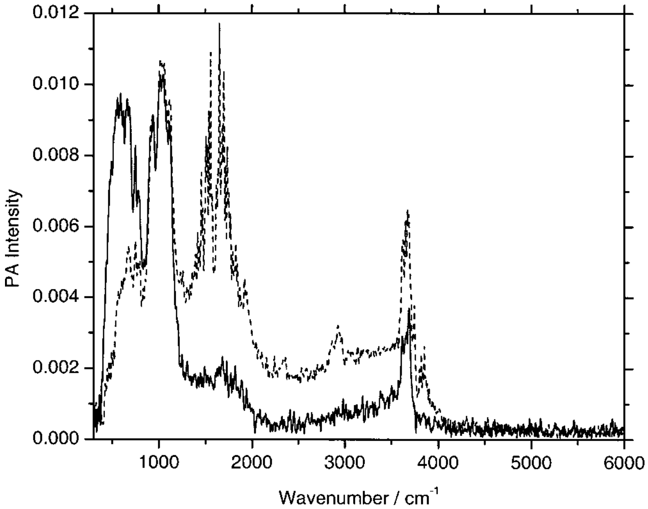

FIG. 2. Mid-infrared PA spectra of common clay, obtained with a 1 mm beam. Solid line, synchrotron radiation (SR); dashed line, Globar®.

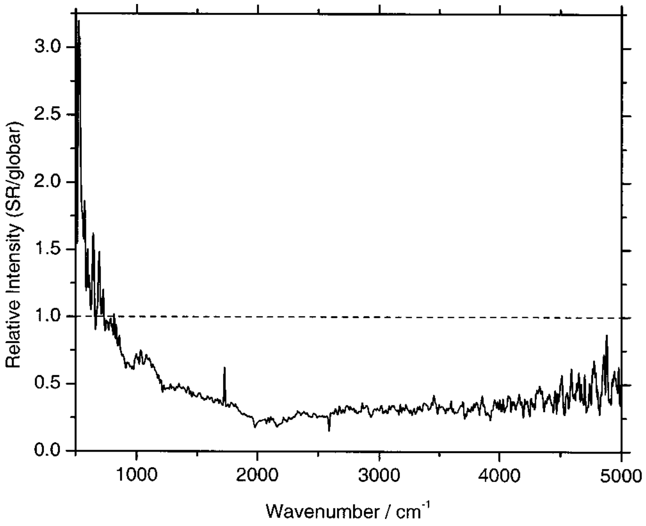

FIG. 3. Ratio of SR PA spectrum of carbon-filled rubber to the corresponding Globar® spectrum, obtained with an aperture of 2 mm. The dashed line at 1.0 is drawn as an aid to the reader.

The ratio of the SR spectrum to the Globar® spectrum is plotted from 50 to 650 cm^{-1} in Fig. 1(b). The dashed line at 1.0 is drawn to facilitate interpretation of the data. It can be noted that the SR spectrum is more intense (i.e., the ratio is >1.0) than the Globar® spectrum at frequencies below about 200 cm^{-1}, whereas the Globar® spectrum is the stronger of the two at higher wave numbers. This result is noteworthy for two reasons: first, it shows that the intensity of the available SR at frequencies below 200 cm^{-1} (wavelengths greater than 50 μm) exceeds that of a standard thermal source, even for a relatively large infrared beam; and second, it confirms the feasibility of far-infrared PA spectroscopy, a technique that has received rather limited attention in the scientific literature.[10,11]

In addition to the results in Fig. 1, two sets of far-infrared PA spectra were obtained for carbon-filled rubber. In these experiments, an aperture was used to limit the beam size to 3 mm. The SR PA spectrum was more intense than the Globar® spectrum at frequencies up to 300 cm^{-1} in one experiment, and to 365 cm^{-1} in the other case. The results of these measurements are discussed further in the detailed comparison of SR and Globar® spectra later in this article.

B. Mid-infrared spectra

Figure 2 compares mid-infrared PA spectra of common clay (a layer silicate), obtained with the two sources of infrared radiation utilized in this investigation. Following the convention used in the previous figure, the solid line is the (uncorrected) SR spectrum, while the dashed line is the Globar® spectrum. These PA spectra were obtained with a 1 mm aperture placed above the sample. The spectrum arising from the aperture alone was not recorded; hence its contribution to the curves in Fig. 2 cannot be removed.

Inspection of Fig. 2 reveals that the SR spectrum is more intense than the Globar® spectrum at frequencies between approximately 300 and 1000 cm^{-1}. Importantly, for the smaller beam size of 1 mm, the spectral region in which SR is preferable to the Globar® includes a significant part of the mid-infrared. This region contains several bands due to silicon–oxygen stretching and other vibrations involving the heavier atoms (Si, Al, O) in the clay lattice.

The Globar® spectrum contains a series of prominent rotation–vibration bands due to water vapor between about 1400 and 1900 cm^{-1}. Analogous bands occur in the hydroxyl stretching region between 3600 and 4000 cm^{-1}, where O–H bands due to clay are also observed. The water bands are positive-going (absorptive) because water vapor is enclosed in the PA cell; by contrast, when the spectrometer contains water vapor the resulting bands are transmission-like, because energy is removed from the beam before it impinges on the PA sample cell.

A simple explanation can be put forward to account for the fact that the intensities of the water bands in the Globar® spectrum are much greater than in the SR spectrum. In the absence of optical and thermal saturation, PA intensity increases linearly with sample concentration. The infrared beam from the Globar® has a larger diameter (≈10 mm) and subtends a significantly larger solid angle than does the SR. Hence the volume of gas in the PA cell illuminated by infrared radiation is larger in the Globar® experiment, causing a stronger PA signal from water vapor. Although fortuitous, this effect favors the SR spectrum, simplifying its appearance and interpretation.

Further mid-infrared results are shown in Fig. 3, which depicts the ratio of the SR PA spectrum of carbon-filled rubber to the corresponding Globar® spectrum at an aperture size of 2 mm. Two salient points can be made with respect to this figure. First, the general appearance of the left-hand side of the graph is similar to Fig. 1(b), except that it is shifted to higher wave numbers. This is expected for smaller apertures. Second, the trend of the graph in Fig. 3 reverses at about 2000 cm^{-1}: the SR signal improves relative to the Globar® signal as frequency increases. This is due to the fact that the Globar® is a blackbody source, for which emitted energy diminishes rapidly at high wave numbers.

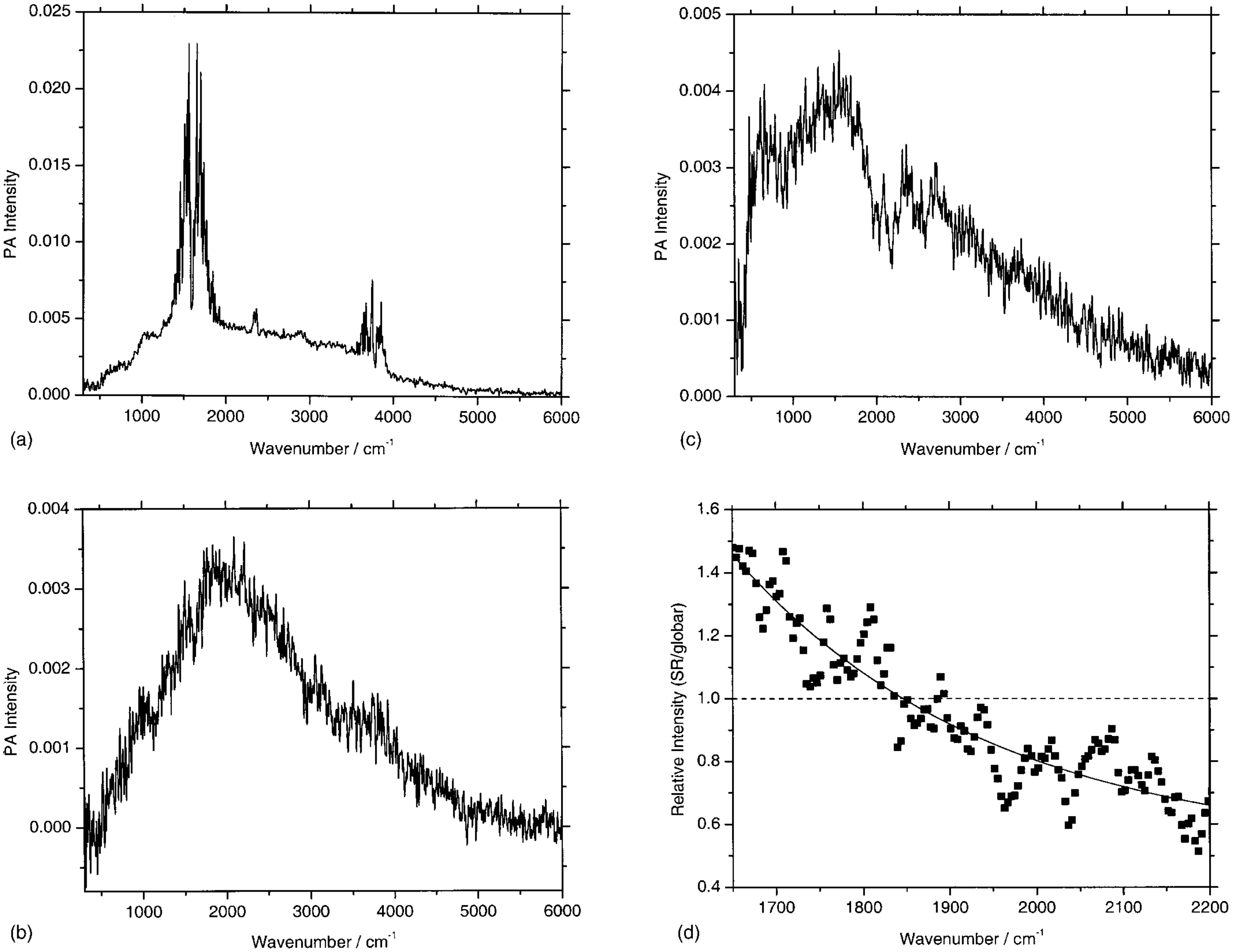

FIG. 4. Mid-infrared PA spectra of carbon-filled rubber, obtained with a 1 mm beam: (a) Globar® spectrum, (b) Globar® spectrum after subtraction of spectrum due to water vapor, (c) SR spectrum, and (d) ratio of spectrum in (c) to that in (b). The solid line in (d) is an experimental fit to the data; the dashed line at 1.0 intersects this curve at the frequency where SR and Globar® PA intensities are equal.

C. Comparison of SR and Globar® PA infrared spectra

The results in the previous two sections show that the value of the highest infrared frequency at which an SR PA spectrum is at least as intense as the corresponding Globar® spectrum depends on the size of the infrared beam. In this section, the relationship between this "crossing frequency"—the point where the two spectra cross—and beam size is analyzed in more detail.

Data for carbon-filled rubber serve to illustrate the method. Figure 4(a) shows the entire mid-infrared PA Globar® spectrum, obtained with a 1 mm aperture. 132 scans were averaged in this experiment. As described above for clay, bands due to water vapor are prominent in the 1400–1900 and 3600–400 cm^{-1} regions of this spectrum; weaker CO_2 bands also appear near 2350 cm^{-1}. To model these features, a background spectrum was obtained by blocking the infrared beam just above the sample with Al foil, as explained in Sec. II. Subtraction of this background from the original Globar® spectrum in Fig. 4(a) yields the result in Fig. 4(b), in which the unwanted bands, as well as the graybody background from the aperture, are effectively removed. The SR spectrum, which does not require a similar correction, is illustrated in Fig. 4(c).

Because the spectra in Figs. 4(b) and 4(c) are noisy, visual inspection of a plot containing both curves tends to produce a rather subjective estimate of the crossing frequency. On the other hand, calculation of the ratio of these two spectra (SR/corrected Globar®) yields a more objective result; the ratio of the spectrum in Fig. 4(c) to that in Fig. 4(b) in the 1650–2200 cm^{-1} region is depicted in Fig. 4(d). The individual data points exhibit a scatter of about 0.1–0.2 units. A simple exponential curve fitted to these points intercepts the dashed horizontal line corresponding to a ratio of 1.0 at about 1850 cm^{-1}. This infrared frequency is therefore taken as the crossover point for PA spectra of carbon-filled rubber measured with the 1 mm aperture. In other words, the entire "fingerprint" region of the infrared is more intense in SR PA spectra than in Globar® spectra when the beam size is restricted to 1 mm.

A similar strategy was used to analyze several other sets of PA spectra where absorption by water vapor makes determination of crossing frequency difficult. In total, eight sepa-

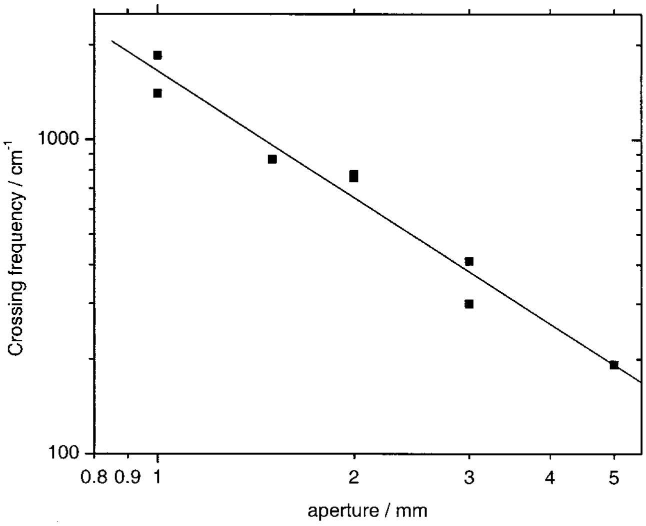

FIG. 5. Dependence of crossing frequency on aperture size. The crossing frequency is the wave number at which SR PA intensity equals Globar® PA intensity. The solid line is a least-squares fit to the data.

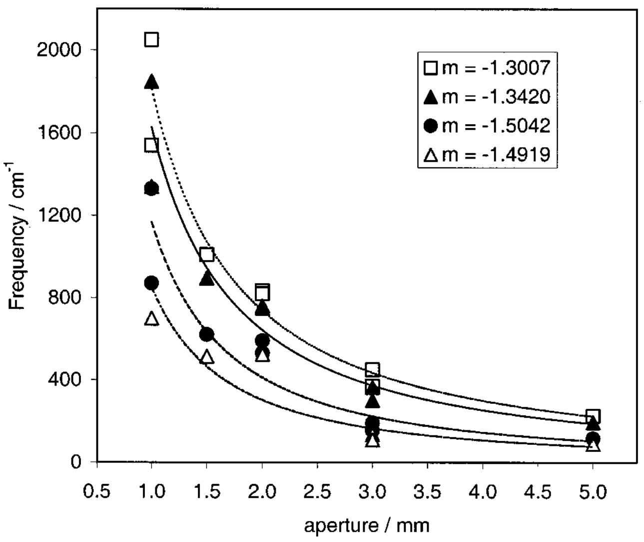

FIG. 6. Variation of frequency with aperture size for selected SR/Globar® intensity ratios. The curves represent power-law ($\nu \propto x^m$) fits to the experimental points (see legend). Ratios represented in this graph are 0.8 (open squares, dotted line), 1.0 (filled triangles, solid line), 2.0 (filled circles, dashed line), and 2.8 (open triangles, dash-dotted line).

rate comparisons of SR and Globar® PA spectra were performed in this work, the objective of these experiments being accurate observation of the dependence of crossing frequency on aperture size. In addition to the results for carbon-filled rubber described in the previous paragraphs, other spectra of rubber were analyzed, as were data for glassy carbon, clay, and coke.

Results of these calculations are depicted in Fig. 5, in which crossing frequency is plotted as a function of aperture size. Among the data displayed in this log–log plot are the values for glassy carbon and carbon-filled rubber that were described in the preceding paragraphs. A result derived from the clay spectra in Fig. 2 is not included, since an appropriate 1 mm background spectrum was not obtained.

As noted earlier, crossing frequency increases with diminishing aperture size; the rate of change appears to be much greater for apertures below approximately 2 mm, which is roughly the point at which the aperture begins to clip the SR beam. The straight line in Fig. 5 is a least-squares fit to the experimental points. The equation that describes this line is

$$\log \nu_c = -1.341\,98 \log x + 3.211\,78,$$

where ν_c is the crossing frequency (cm^{-1}) and x is the aperture size (mm). It is of interest to determine the aperture size at which ν_c equals 4000 cm^{-1}, which is commonly taken as the upper limit of the mid-infrared region. Substituting $\log(4000) = 3.602\,06$ into this equation, one obtains an aperture size of 0.51 mm. Hence this analysis leads to a significant prediction: the entire mid-infrared region should be more intense in SR PA spectra than in Globar® spectra for aperture (or sample) sizes less than 0.5 mm. Of course, far-infrared SR PA spectra are also more intense than the corresponding Globar® spectra at this relatively small beam size. These findings confirm the viability of both far- and mid-infrared SR PA spectroscopy, which was the main objective of this work. The results also define conditions under which SR is superior to a thermal source, which was the second goal mentioned in Sec. I.

The comparison of SR and Globar® PA spectra can be represented in a slightly different manner by generalizing the concepts discussed in the above paragraphs. The preceding analysis involves the characterization of the crossing frequency, defined as the point where SR and Globar® spectra have equal intensities for a particular aperture size; it is also desirable to determine the infrared frequencies at which the SR/Globar® ratio is significantly greater than unity. These frequencies define the spectral region where the use of SR in PA infrared spectroscopy offers a distinct advantage.

The eight pairs of spectra obtained in this work were examined to ascertain the infrared frequencies that correspond to SR/Globar® ratios ranging from 0.8 to 2.8, at intervals of 0.2 units. Representative results are summarized in Fig. 6, which shows the variation of frequency with aperture size for SR/Globar® ratios equal to 0.8, 1.0, 2.0, and 2.8. Both frequency and aperture size are plotted on linear scales in Fig. 6, in contrast with the log–log plot discussed earlier. This linear presentation emphasizes the fact that frequency varies more rapidly for smaller apertures. For each ratio, the data were fitted by a power-law function of the form $\nu \propto x^m$, where ν denotes infrared frequency, x is aperture size, and m is analogous to the slope in Fig. 5. As noted in the legend to Fig. 6, m takes values of -1.3007, -1.342, -1.5042, and -1.4919 for the four respective ratios mentioned above.

Figure 6 makes it straightforward to determine the frequency intervals in which the SR/Globar® intensity ratio exceeds a particular value. For example, the curve corresponding to a ratio of 2.0 (dashed line) shows that a SR spectrum measured with an aperture of 2 mm is at least twice as intense as its Globar® counterpart at infrared frequencies up to 400 cm^{-1}; this interval extends to about 625 and 1160 cm^{-1} at apertures of 1.5 and 1 mm, respectively. This example shows how the information in this figure can be used to decide whether the choice of SR instead of a thermal source in a particular PA experiment is justifiable.

IV. DISCUSSION

The results of this investigation, believed to be the first successful attempt at measurement of SR PA infrared spectra, show that both mid- and far-infrared PA spectra of solids can indeed be obtained using synchrotron radiation instead of a thermal blackbody infrared radiation source. As might have been anticipated, the advantages of SR become greater as the wavelength increases and the effective sample size decreases, provided that the wavelength remains much smaller than this size. These observations should be taken into consideration during the design of future experiments in SR PA spectroscopy.

To place the current work in context, it should be mentioned that a PA detector was designed for x-ray absorption spectroscopy and adapted for far-infrared spectroscopy a number of years ago at the Photon Factory.[12] PA signals were observed in both regions, but no far-infrared spectra were displayed in the publication based on this research.

It is also appropriate to recall that several previous studies[1,2,6] have explored the question of beam diameter in SR infrared spectroscopy in detail. Moreover, Lobo *et al.*[5] presented graphical data that resembles Figs. 1 and 4 in this article. However, all these experiments used optical—rather than PA—detection. Determination of crossing frequency, as depicted in Figs. 4(d) and 5, is obviously an important part of the comparison of SR and thermal infrared sources; analogous experiments will be required when other macrosampling accessories are used in SR infrared spectroscopy. The present implementation of SR PA infrared spectroscopy suggests that these and other infrared sampling accessories will eventually be utilized successfully in conjunction with synchrotron radiation.

These experiments have been carried out with an unmodified PA cell, which utilizes a 2× mirror to focus the infrared beam before it impinges on the sample. Obviously, this mirror could be replaced, or other intermediate optics could be introduced, to produce tighter focusing. The amount of demagnification that could be achieved is limited by the solid angle the cell can accept, but for SR spot sizes of less than 100 μm should be feasible. This would allow the measurement of PA spectra of very small samples, possibly with dimensions smaller than the decay length of the thermal wave.

A final point should be made with respect to sample size in SR PA infrared spectroscopy. This investigation has shown that SR tends to surpass a Globar® source in a PA experiment as aperture size (or sample size) is reduced. Hence—even with the current focus size in the PA cell—there is no need to employ conventional PA sample cups, which contain approximately 10–100 mg of sample. A much smaller sample holder can be utilized, such as the single-particle and single-fiber microsampling accessories available from MTEC Photoacoustics. In fact, the use of these accessories has already been shown to produce improved signal-to-noise ratios in PA spectra obtained with a Globar® source.[13] Microsampling should be compatible with the small beam in a SR PA experiment, and produce spectra with less noise than those obtained in the present exploratory work.

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