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LETTER TO THE EDITOR

Anomalous enhancement of the surface IR modes in photoacoustic spectroscopy of SiO₂ particles

Mohindar S Seehra and Raghoottama S Pandurangi

Department of Physics, West Virginia University, Morgantown, WV 26506, USA

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Abstract. A comparative study of the intensities of the IR modes in the photoacoustic and FTIR spectroscopy of amorphous and crystalline SiO₂ particles is presented. It is observed that in photoacoustic spectroscopy of amorphous SiO₂, IR modes of surface species are enhanced by over an order of magnitude compared to the bulk IR modes of SiO₂. This effect, though not yet understood, may find applications in surface science.

Since the publication of the Rosencwaig–Gersho theory of the photoacoustic effect in solids in 1976 [1], a great deal of attention has been paid to the development of photoacoustic spectroscopy (PAS) into an analytical technique for condensed matter studies, especially when combined with the modern Fourier transform infrared (FTIR) spectrometer [2–8]. PAS has now been applied to a variety of experimental situations [2, 3] and it is particularly suitable for opaque powders and for cases where sample preparation (e.g. mixing with KBr as is usually done in FTIR spectroscopy) is not desirable. Another area of interest is the depth profiling feature of PAS, which is studied by varying the modulation frequency of the incident radiation [2–8]. The one-dimensional Rosencwaig–Gersho theory for non-porous samples has been extended to other cases [9–12]. Recently it has become known [11, 12] that for porous samples with porosity ϵ , the IR modes are enhanced by a factor proportional to ϵ . This enhancement is due to the pressure wave set up in the interstitial gas in the porous sample and this enhancement has been reported by a number of groups [12–14].

In this Letter we report the observation of anomalously large enhancement of the PAS signal for certain surface IR modes on the surface of amorphous silica particles. This observation differs from the previous reports in that certain surface modes are enhanced by over an order of magnitude compared to the bulk IR modes. Although the reasons for this enhancement of the surface IR modes in PAS are not understood at present, this observation may open up new approaches to the study of surfaces. Results of these initial observations are given in this Letter.

Experimental studies reported here were carried out on an FTIR spectrometer (Mattson Instruments, Model Cygnus 100) equipped with an MCT detector. The same instrument was used for PAS studies in conjunction with an MTEC (Model 100) PA cell. The sample cell and the spectrometer are continuously flushed with dry, CO₂-free air obtained by the use of Balston Instruments Air Dryer Filter System (Model 75-60). Usually data were collected for 32 scans at 4 cm⁻¹ resolution, although both scan and resolution can be varied. For FTIR studies, samples were mixed with IR-grade KBr and

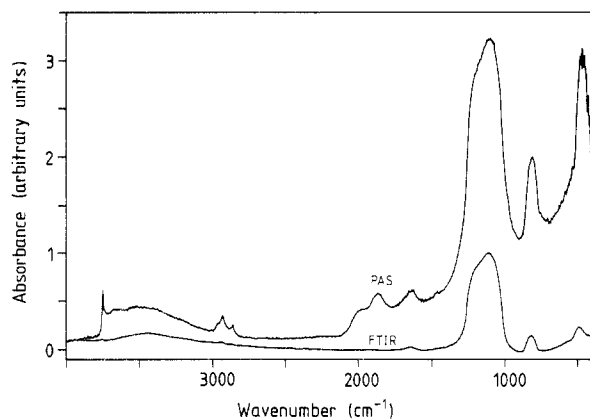


Figure 1. Spectrometer recording (32 scans at 4 cm^{-1} resolution) of the photoacoustic spectra (PAS) and FTIR spectra of a-SiO₂ particles of mass 0.9 mg.

pelletised. For PAS, no sample preparation is necessary and data are ratioed against dry carbon black [4, 5].

Two kinds of silica (SiO₂) particles were studied in this work: 'Min-U-Sil' which is crystalline quartz (c-SiO₂) of average particle size $\sim 5\ \mu\text{m}$ and 'Cab-O-Sil' which is amorphous silica (a-SiO₂) of average particle size $\approx 0.05\ \mu\text{m}$. The specific surface areas, as measured by BET adsorptometry, are $5\ \text{m}^2\ \text{g}^{-1}$ and $200\ \text{m}^2\ \text{g}^{-1}$ for c-SiO₂ and a-SiO₂, respectively, and the corresponding porosities ε are 0.79 and 0.97, respectively. All spectra reported here were taken at room temperature.

In figure 1, the recorded absorbance of a 0.9 mg sample of a-SiO₂, both by the FTIR and PAS techniques, is shown against wave numbers from $400\ \text{cm}^{-1}$ to $4000\ \text{cm}^{-1}$. (Only 0.9 mg of sample is used because spectra for small masses are not saturated.) In a separate paper [15], we discuss the significance of various peaks in the spectra. Here it suffices to say that peaks near 500 , 800 and $1100\ \text{cm}^{-1}$ are bulk IR modes of the SiO₂ lattice whereas the surface modes include the sharp peak at $3745\ \text{cm}^{-1}$ due to OH stretching of the surface silinol group (Si-OH) group, the broad band between 3000 – $3700\ \text{cm}^{-1}$ due to H-bonded impurities and the $2900\ \text{cm}^{-1}$ group of bands due to C-H stretching of aliphatic surface impurities. These surface modes, due to adsorption of aliphatic impurities and water vapour, decrease in intensity and eventually disappear upon heating the sample [15]. In figure 2, FTIR and PA spectra of 0.9 mg of c-SiO₂, taken under exactly similar conditions, are plotted. We now examine the major features of these spectra.

In c-SiO₂ ($5\ \mu\text{m}$ particles), the intensities of the lines in the FTIR spectra are slightly higher than those in the PA spectra. On the other hand, in a-SiO₂ ($0.05\ \mu\text{m}$ particles), all bands have enhanced intensities in PAS compared to those in FTIR (figure 1). The intensities (areas under the bands) of the various bands for both a-SiO₂ and c-SiO₂ are shown in table 1. The significant feature about this enhancement (as compared to FTIR) is that it is not uniform for all the bands. Whereas the bulk modes are only enhanced by a factor of between 2–5, the enhancement factor for the surface modes is over an order of magnitude larger. The largest observed enhancement (by a factor of over 60) is for the sharpest silinol peak at $3745\ \text{cm}^{-1}$. The broad band between 3000 – $3700\ \text{cm}^{-1}$ due to H-bonded impurities is behaving like a bulk mode in enhancement, presumably because it is comprised of many different kinds of H-bondings and these peaks overlap, giving rise to a broad band [15, 16]. The C-H stretching band of the impurities near $2900\ \text{cm}^{-1}$ is enhanced by a factor of about 20.

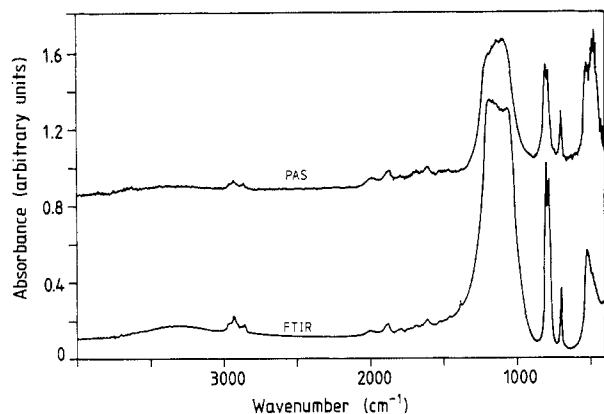


Figure 2. As in figure 1, except for c-SiO₂ particles. The base line for PAS has been shifted upward by 0.8 units for clarity.

Table 1. Intensities (area under the peaks) of the various bands in a-SiO₂ and c-SiO₂ particles. I_P and I_F refer to the intensities of the bands in PA and FTIR spectra, respectively. Listed band positions are approximate because the band positions are slightly different for a-SiO₂ and c-SiO₂ particles [15].

Band (cm ⁻¹)	a-SiO ₂			c-SiO ₂		
	I_P (cm ⁻¹)	I_F (cm ⁻¹)	I_P/I_F	I_P (cm ⁻¹)	I_F (cm ⁻¹)	I_P/I_F
3745	5.16	0.08	64.5	0.04	0.03	1.3
3700-3000	138.9	32.2	4.3	8.5	12.8	0.7
2960	13.7	0.7	19.6	4.0	5.6	0.7
1100	568.6	226.4	2.5	148.7	301.0	0.5
800	52.4	10.7	4.9	22.6	37.1	0.6

As was noted at the beginning of this Letter, some enhancement of the PAS signal over the FTIR signal is expected as the particle size is decreased because of the pressure signal from the interstitial gas trapped in the powder sample [12–14]. In the limit of weak absorption, this enhancement E may be written as [12]

$$E = 1 + \varepsilon A \quad (1)$$

where the factor A depends upon the properties of the gas in the PA cell and porosity ε is given by

$$\varepsilon = 1 - [\rho(\text{powder})/\rho(\text{solid})]. \quad (2)$$

In equation (2) $\rho(\text{powder})$ and $\rho(\text{solid})$ are respectively the densities of powder sample and the solid sample. For SiO₂ (quartz), $\rho(\text{solid}) = 2.65 \text{ g cm}^{-3}$. Earlier measurements have reported some enhancement of the PA signals as the particle size is decreased (thus increasing ε) [14]. However, the different levels of enhancement observed here for the surface and the bulk modes in PAS are significant new results which cannot be explained by equation (1). This difference in enhancement also cannot be due to different modulation frequencies for the lower and higher wave numbers inherent in PAS because this actually predicts a slightly lower signal at higher wave numbers [4, 5]. The other factor to consider

is the different surface areas of a-SiO₂ vis-a-vis c-SiO₂ particles. The surface area of a-SiO₂ is about 40 times greater than that of c-SiO₂. However, our observations cannot be due simply to more surface species in a-SiO₂ because if that were the case, larger signals should also have been observed in the FTIR spectra of the same particles. This is definitely not observed (figure 1). Hence we are led to conclude that these observations are specific to the PAS technique, and the effect is dependent on the particle size (hence surface area and ϵ). We are not able to advance an explanation for this effect at the present time. However we note that SERS (surface enhanced Raman scattering) and the anomalous enhancement observed here in PAS for surface modes may have some common features [17]. Further work is clearly warranted to understand the origin of this effect.

In summary, anomalously large enhancement of the surface IR modes in PAS is reported here. This effect may find extensive applications in the study of surfaces.

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