CAUSES OF ARTIFACTS IN THE INFRARED SPECTRA OF POWDERS

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ABSTRACT

Infrared (IR) spectra of powder dispersions are prone to artifacts. Understanding the conditions under which artifacts are produced in laboratory spectra, allows intrisic features in IR spectra of dust in astronomical enviroments to be distinguished. The types of problems that can occur are illustrated by examples of SiC, SiO_2 (quartz), and two chain silicates. Position, width, maximum absorbance, as well as relative intensity are all altered by sampling conditions (film thickness, i.e. path length, and the percentage of the total area that the sample effectively covers) but to degrees dependent on the strength of the band. As thickness increases above $\leq 0.1\mu$m, strong bands, e.g. Si-O stretching in the 10μm region, become increasingly rounded and flat-topped, due to light leakage around the particles. The absorbance depends on the amount of *sample coverage.* The observed smooth, near featureless, 10μm profiles of astronomical dusts could be thus be produced by sub-micron-sized crystalline silicates (see also Bowey & Adamson 2000a;b). The 10μm region is expected to be problematic for species indentification when the dust cloud is dense or has large grains. Care must be taken in interpreting this region and the intense peaks near 20-25μm. Due to the large variation of extinction coefficients among the various IR peaks in silicates, for a dust or dispersion, particles creating optically thin spectra in the mid-IR are not the same particles that create the far-IR patterns.

Key words: IR spectra, artifacts, crystalline silicates, amorphous features, SiC, dust size

1. INTRODUCTION

It is common knowledge that IR spectra of solids dispersed in a medium are prone to artifacts of sampling (Horak & Vitek 1978). Considerable efforts have been made to quantify the dependence of IR spectra on variables such as particle size and shape (e.g. O'Donnell 1994) , and of the effect of the transmitting medium (e.g. Dorschner et al. 1978). However, a key issue has been underrecognized, namely, that the dispersion not only transmits light through particles, it also can have particles nearly completely blocking the light, and inevitably has *open areas* where no particle lies in the beam and all the light of the source is transmitted. Thus, the spectrum contains a mixture of optically thin and optically thick components over different frequency ranges.

It is essential that artifacts in laboratory data be understood because controls cannot be exerted during observational astronomy. The sample of stardust cannot be diluted, particle size cannot be adjusted, and the proportions of phases in a mixture cannot be altered. Because identification of species in a dust is an important goal, it is crucial to know how relative intensities of peaks from a single phase are affected. For silicates, optically thin conditions for most intense bands require thicknesses of $\sim 0.1\mu$m, (e.g., Hofmeister 1995) which is the average grain size expected for the interstellar medium (Mathis et al. 1977). Thus, artifacts are possible for all but the most dilute and finest-size dust clouds.

This paper gives examples of artifacts purposefully created in the laboratory by (1) varying thickness, while holding sample coverage roughly constant and maximum, and (2) varying the area of sample coverage for constant sample thickness, and (3) varying both simultaneously. The observations are generallized and implications for identification of silicate dust from astronomical observations are discussed.

2. EXPERIMENTAL

Single-crystals of α-SiC were purchased from Alpha/Aesar (catalogue no. 36224). This specimen consists of hexagonally shaped platelets of up to 300μm diameter and $\sim$1-10 μm thick. Quartz from Lisbon, Portgual, jadeite from New Idria, California, and tremolite from Canaan, Connecticut have near endmember chemical compositions.

Films of varying thickness were created through compression of rough powers (μm sized) in a diamond anvil cell (DAC); see Hofmeister et al. (1989) for details. Slight irregularities in the thickness (e.g. wedging), and small cracks, are inevitable. Crushing removes the lateral grain boundaries, making optical path length (sample thickness) the only variable. Mid-IR spectra (450 to 4000 cm^{-1}) were obtained at 2 cm^{-1} resolution using a liquid-nitrogen cooled HgCdTe detector, a KBr beamsplitter and an evacuated Bomem DA 3.02 Fourier transform interferometer; far-IR spectra of the films were collected using a liquid-He cooled bolometer. Reference spectra were collected from the empty DAC . Single-crystal mid-IR spectra at 1cm^{-1} resolution were acquired using a Spectratech IR microscope. Far-IR spectra of finely ground sample dispersed in petroleum jelly on a polyethelene card were collected at 4cm^{-1} resolution with a DTGS detector. The reference was the polycard.

3. EFFECT OF SAMPLE THICKNESS

Quartz (SiO_2) was used as a test case because its mid-IR spectrum is relatively simple, yet it has features common to silicate minerals: a very intense band in the Si-O stretching region (8-10μm) with a sharp and a broad shoulder, and less intense bands at longer wavelength.

3.1. Band broadening

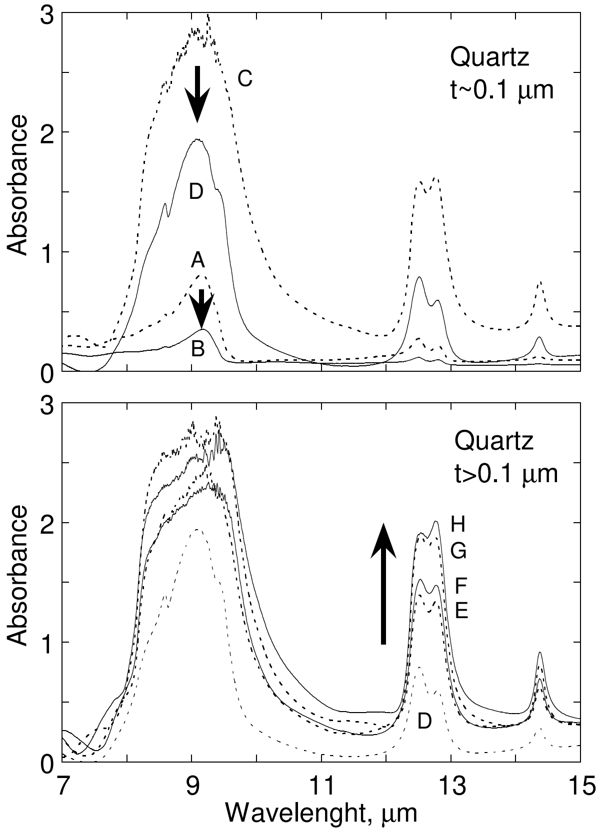

Figure 1. Spectra of Lisbon quartz compressed in a DAC. Top, effect of thinning the sample (heavy arrows). Bottom, effect of adding sample. Films **A**,**B**,**D** *are* $\sim 0.1\mu$m *thickness. Thickness of* **E**-**F** *are in the submicron range, and show artifacts in intensity, position, and width.* **C** *and* **D** *have artifacts mostly in width.*

Spectra in the top part of Figure 1 are recognizably those of quartz. Only the thinnest films give spectra (**A** and **B**) free of artifacts. **C** and **D** show broadening of the intense Si-O stretch near 9.2μm, due to the increase in prominence of the shoulders on both sides. For **C**, the broadest of the three shoulders merges with the main peak. The pair of bands near 12.5 and 12.8μm do not change in width. However, as the sample thickens, the 12.8μm peak becomes the more intense of the doublet and the intensity of the doublet becomes larger in proportion to the main band at 9.2μm. **A**-**D** indicate that absorbance (A) should be below 1 to avoid artifacts. For $1 \leq A \leq 2$, positions are unaffected, except for the shoulder near 9.5μm, but widths and intensities vary widely.

3.2. Changes in apparent intensity and wavelength shifts

Spectra **E** to **H** in Figure 1 were acquired after sequential additions of quartz to the existing film (**D**) in the DAC. The non-linear response is apparant as the film thickness approaches a substantial fraction of 1μm. In addition, the featureless regions become less transparent. Although the weak peaks give a recognizable quartz pattern, for $A \leq 2$, the main band looses features indicative of crystalline quartz, becoming rather flat topped. The sharp feature near 8.6μm disappears in the process. Although the shoulders near 8.3 and 9.6μm grow, the intensity of the main band is nearly constant. Due to the steep rise of the main peak at short wavelengths, but a sloping profile at long wavelengths, the position of the main band shifts to longer wavelengths as thickness increases. The next most intense peak at 12.5μm shows a non-linear change in intensity, relative to the weakest peak in this region at 12.9μm when $A \simeq 2$.

3.3. Effect of film imperfections

If the films were perfect, with no light from cracks and no wedging, then the intensities would increase proportionately, until the strongest peak is opaque (i.e., any light transmitted is below the level of detection). At this point the peak would be perfectly flat and at the maximum value allowed by the software (typically 2 or 4 is used for transmissions below the detection limit). As the sample is thickened, the width of the flat region would increase until the shoulders merge with the flat top. The width of the band would increase, because the observed spectrum is the truncation at constant absorbance (e.g., 2) of a peak that has constant full width at half maximum, but whose true absorbance, is much larger, as determined by the path length.

For the case at hand, the imperfect film "leaks" light through cracks in the film, and is wedged; this results in a 9.2μm main band with a rounded top. Here, some growth in intensity is due to the increase in the wavelength range over which the peak is opaque (i.e. when $A > 2$).

The behavior is not unique to quartz, or even silicates, as the same effect occurs in olivines, garnets, pyroxenes, SiC, nanocrystals of AlN, water, and carbonates.

4. COVERAGE AND "STRAY" LIGHT EFFECTS

We studied single-crystals of α-SiC because of the simplicity of its spectrum (one major IR band) and sample availability. Figure 2 shows that artifacts are caused by masking the image rather than by placing the sample in physical contact with a pinhole aperature.

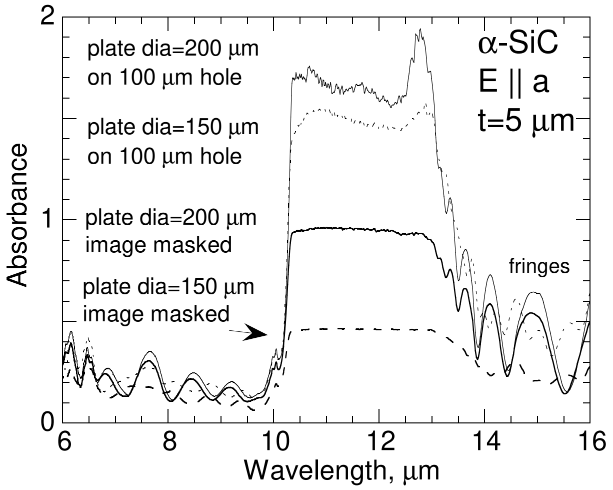

Figure 2. IR absorption spectra of two plates of 5μm thick α-SiC crystals with the a-axis parallel to the direction of light propogation. Uppermost solid line, spectrum of a plate, 200μm in diameter, placed on a pinhole of 100μm diameter. Lower solid line, spectrum of the same 200μm plate, on KBr, but with the image masked such that a diameter of 100μm is ostensibly sampled. Dotted line, spectrum of a plate, diameter of 150μm, placed on a pinhole of 100μm diameter. Dashed line, spectrum of the same 150μm plate, on KBr, but with the image masked such that a diameter of 100μm should be sampled. Peaks near 6μm are overtones. Interference fringes seen are related to reflections from the parallel faces. The true absorbance of the main peak is extremely large, but the back reflection, whose intensity depends on wavelength, causes some features between 10 and 13μm .

For the samples in contact with an aperature, the absorbance is about 2, partially due to software algorithms, and also because these highly reflective plates have an internal bounce plus a reflection which feeds back into the interferometer. With image masking, the artificially low absorbance becomes increasingly lower as the effective diameter of the mask approaches the sample diameter. Thus, absorbance in a dispersion is determined by the open path.

The variation in maximum absorbance occurs because light diffracted through the mask strikes an annulus of larger diameter than the area intended for observation. This phenomena is documented in the literature on IR microscopy. Developers of the first instrument of this kind (Messerschmidt 1995) have tried to remedy them by masking the image before and after the sample. Even this does not completely eliminate stray light from regions not intended for sampling (Reffner et al. 1997).

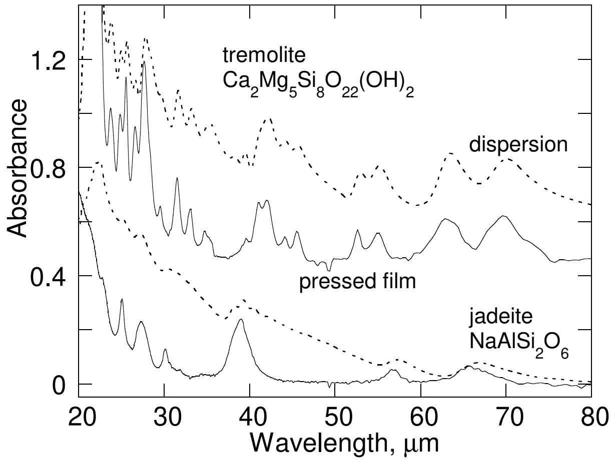

Figure 3. Far-IR pectra of chain silicates. Solid lines, films formed by compression in a DAC. Dotted lines, dispersion spectra with similar intensity for the lowest frequency bands. Films are sub-μm thickness. Dispersion are mg spread over a cm-sized area. The tremolite thin film was multipled by 3 and offset by 0.3 absorbance units for clarity. The polyethelene has an interfering band near 23μm. Some interference with wate vapor is indicated by the down-pointing small, sharp peaks near 50μm.

The data in Figure 2 indicate that all spectra of SiC particles by Anderson et al. (1998) are affected by stray light (diffracted and/or from incomplete sample coverage). The sizes of $\sim$2 to 40μm examined are all opaque from 10.5 to 13 microns; Speck et al. (1999) show that submicron films are needed for transparancy. Transmission in this interval shows substantial light leakage. Because their samples have a size distribution and the grains are round and thus transmit some light from the edges and between grains, their spectral profiles are rounded, not step-like as shown here, and vaguely resemble the intrinsic absorption pattern of SiC. The conclusions of Anderson et al. (1998) of the grain size effects in SiC spectra are questionable, because the primary variable in their experiment is the amount of stray light from gaps between grains, sample edges and the diffraction annulus.

5. ARTIFACTS IN DISPERSIONS AND FILMS

Here we use chain silicates to compare techniques for absorption measurements because these minerals have a large number of modes in the far-IR. A lower resolution was used for the films to avoid diffraction fringes[1].

[1] Lower resolution causes artificial broadening of the peaks. A change in resolution will not effect this discussion since the same resolution is used for each measurement (see Bowey et al. (2000) for further discussion of resolution). Tremolite (Figure 3) has a multitude of narrow bands which are only resolved in high resolution spectra.

Overall, the spectra obtained by the dispersion and compressed film methods (Figure 3) are similar. One difference is the steeper rise towards short wavelengths in the dispersions. The difference is stronger for jadeite, and is due to it having a more intense band in the O-Si-O bending region near 20μm. Due to this rise, the peaks seem to shift to longer wavelengths. Flat topping is seen for the peak near 40μm, which is the most intense peak in the far-IR for jadeite. The most intense peak in tremolite at 30μm is similarly reduced in relative absorbance. Relative intensities are not preserved between the two methods for tremolite: this may be an orientational effect related to the tendency of tremolite to form shards.

6. CONDITIONS FOR OPTICALLY-THIN FEATURES

For peaks in the Si-O stretching region to be free of artifacts requires very thin samples. The maximum thickness for garnets was determined by two methods. (1) Single-crystals were thinned by ion milling until optically thin for all peaks (McAloon & Hofmeister 1993). Scanning electron microscopy pictures of two samples of $Ca_3Al_2(SiO_4)_3$ indicate thicknesses of $\sim$ 0.1μm (Hofmeister 1995). (2) Comparison of absorptivity calculated from reflectance to measured absorbance of films and crystals gives thicknesses of $\sim$0.17 to 0.21μm for these same samples and for $Ca_3Fe_2(SiO_4)_3$. Since garnet and olivine both contain isolated silicon tetrahedra, similar thicknesess are probably required for both minerals. These thicknesses are probably adequate for all silicates since the relief is similar in the optically-thin spectra of many silicate films.

The weakest far-IR peaks can be detected in the submicron films and dispersions if the signal-to-noise ratio is high. However, to resolve these bands thicknesses can be $\sim$ 20μm for olivine (Hofmeister 1987) and garnets (McAloon & Hofmeister 1993).

7. CONCLUSIONS

Artifacts (variation in peak position, width and relative intensity from intrinsic spectra) are produced in IR laboratory spectra of solids by

1. incomplete coverage of the aperture by the sample,
2. particles thick (or dense) enough to produce absorbances >1,
3. limitation of maximum absorbance to 2 or 4 by software routines (this is actually a result of the detector having a limited sensitivity).

These effects combine to create a size filter that depends on frequency for dispersions and dusts and decouples the information conveyed by the weak and strong peaks.

Intense peaks (bending and stretching modes of Si-O) are apt to have artifacts. Even in the sub-μm range, a rather featureless and broad peak was produced for quartz. Hence, a broad peak could indicate amorphous material that is optically thin, or crystalline silicates that approach being optically thick. A similar conclusion was reached by Bowey & Adamson (2000a) and (b) who deduced that a mixture of crystalline and amorphous silicates could fit the 10μm band of several objects. The 10μm region is expected to be problematic for species indentification when the dust cloud is dense or has large grains. Care must be taken in interpreting this region and the intense peaks near 20-25μm.

The weak peaks at long wavelength are less prone to artifacts and the patterns vary greatly among structures and with chemical composition: this region has great potential in interpreting dust spectra. Because of the large variation of extinction coefficients among the various IR peaks in silicates, for a dust or dispersion, particles creating optically thin spectra in the mid-IR are not the same particles that create the far-IR patterns. In observational astronomy, it is not necessary for the peaks in the mid- and far-IR regions to have the same proportionality as observed in the laboratory. Identical patterns would require indentical distributions of particle size and equal amounts of sample coverage. Hence, identification of minerals in the dust should be made through comparing groups of peaks with similar intensity.

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