

# FAR-IR DIAMOND ATR SPECTROSCOPY

## INTRODUCTION

Historically, ATR spectroscopy has not been commonly used in the far-IR (FIR) due to several factors. A limited choice of appropriate ATR crystals was available. Small KRS-5 crystals could be used down to  $200\text{cm}^{-1}$ . But KRS-5<sup>1</sup> is a soft material with a short lifetime for ATR measurements of solids. Si could also be used as an ATR crystal, for measurements below  $350\text{cm}^{-1}$ . FIR measurements are highly susceptible to interference from water. So the spectrometer in which the ATR accessory was installed needed to be well purged or evacuated. Because the sample compartment needed to be opened between sample and background single beam spectra, these measurements were impractical on a routine basis.

Several developments over the past ten years have made which improve the practicality of FIR-ATR measurements. The development of micro-ATR spectroscopy in the early 1990s resulted in the routine use of diamond as an ATR crystal. Diamond is an extremely hard and chemically inert material, suitable for use as an ATR crystal for virtually any sample. Diamond also offers a wider spectral range at the far end of the infrared range, i.e. from  $1600\text{cm}^{-1}$  to the FIR. In addition, the accessories available began to be available with integral purge enclosures,

so the sample and background spectra could be recorded without interruption of the purge<sup>2</sup>. This convenient feature increased the potential for FIR ATR spectroscopy. In addition to the aforementioned, there have been developments in technology which improved the S/N of commercial spectrometers, making these types of measurements more practical on a routine basis.

This note demonstrates the use of diamond ATR for FIR measurements. Four powdered samples were examined using FIR ATR spectroscopy.

## EXPERIMENTAL

Four different powders were examined. The silicon dioxide was a ~400 mesh,  $2\mu\text{m}$  AOS Powder, S.A., 99.5% Silicon (IV) oxide (Alfa Aesar, CAS#1631-86-9). The  $\text{KMnO}_4$  was powdered and acquired from J.T. Baker Chemical Co. (CAS#7722-64-7). The calcium sulfate used was  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 99% from Alfa Aesar, CAS#10101-41-4. The sugar used was a non-chemical grade confectioner's sugar.

Spectra were obtained using the MVP2/Pro series ATR accessory (similar to that shown in Figure 1) with a type IIIA diamond ATR crystal. A 56 in-oz Slip-Clutch was used with the MVP2/Pro to compress the sample against the ATR crystal. The accessory was installed in an FTIR spectrometer equipped



Figure 1. An MVP2/Pro Series Diamond ATR Accessory.

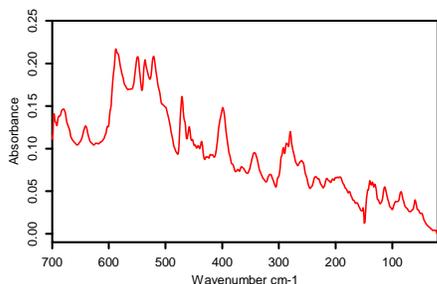


Figure 2. ATR Spectrum of Confectioner's Sugar.

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with a pyroelectric detector, a halogen source and a mylar beam splitter for operation in the far-IR. Spectra were collected from 2000 to 0  $\text{cm}^{-1}$  using 128 scans at a resolution of 2  $\text{cm}^{-1}$ .

The accessory was installed in the spectrometer and its purge seals were extended to completely enclose the beam path. The spectrometer and the accessory were then purged for 28 hours to eliminate interference from water vapor.

The ATR crystal was cleaned and the solvent was allowed to evaporate. Then the single background spectrum was collected. A small quantity of the sample was placed on the center of the ATR crystal. The sample was compressed against the crystal using the 56 in-oz Slip-Clutch and then the sample spectrum was collected. All four samples were measured using the same procedure.

## RESULTS AND DISCUSSION

Figure 2 shows the FIR diamond ATR spectrum of confectioner's sugar. This spectrum exhibits peaks at 48, 54, 59, 65, 75, 85, 98 and 113  $\text{cm}^{-1}$  in the tera-hertz region. These bands are virtually identical to those observed in icing sugar by Tribe and coworkers.<sup>3</sup>

Figure 3 is the ATR spectrum of silicon dioxide. This spectrum shows distinct

bands around 690  $\text{cm}^{-1}$  and 390  $\text{cm}^{-1}$  which compare favorably with the bands previously reported for  $\alpha$ -quartz.<sup>4</sup>

Figures 4 and 5 show the spectra of calcium sulfate and potassium permanganate respectively. Both have well-resolved bands in the FIR spectra.

## CONCLUSION

This study demonstrates that the diamond ATR spectroscopy can be used effectively to examine materials in the FIR spectral region. Both organic and inorganic materials can be studied, provided that the spectrometer and ATR accessory are well purged.

## REFERENCES AND NOTES

1. KRS-5 was commonly used for ATR but less widely used due to its toxicity.
2. U. S. Patent 5,177,561.
3. William R. Tribe, David A. Newnham, Philip F. Taday, and Michael C. Kemp, Terahertz and Gigahertz Electronics and Photonics III, Jennifer Hwu, ed., SPIE Proc., Vol. 5352 (SPIE, Bellingham, WA 2004).
4. Kazuo Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part A: Theory and Applications in Inorganic Chemistry*, 5<sup>th</sup> ed. (John Wiley and Sons, Inc., New York, 1997).

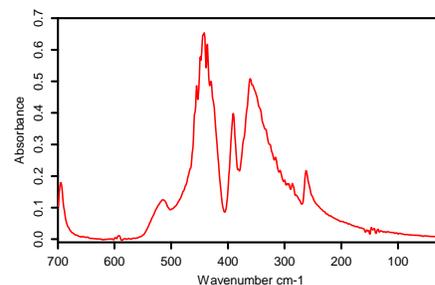


Figure 3. ATR Spectrum of SiO<sub>2</sub>.

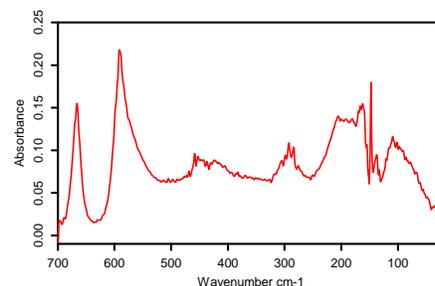


Figure 4. ATR Spectrum of CaSO<sub>4</sub>·2H<sub>2</sub>O.

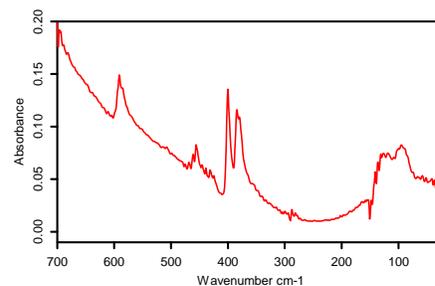


Figure 5. ATR Spectrum of KMnO<sub>4</sub>.



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