Application Note AN M122

Carbonate Minerals and Other Samples Studied by Far IR ATR Spectroscopy

Introduction

The far IR or THz spectral region, which lies below $400\,cm^{-1}$, is important for the study of inorganic substances which involve vibrations of heavier atoms. External or lattice vibrations, which are sensitive to crystal structure and polymorphism, can be seen also for both inorganic and organic solid samples. However it was not always that straightforward to obtain high quality far IR spectra, due to inherent weak sources and rather insensitive room temperature detectors, but the latest technical developments now make it much easier. In particular, the INVENIO R and VERTEX 70v FTIR spectrometers offer a wide band mid to far IR beamsplitter and detector combination to access the complete spectral range in one go (BRUKER FM option). There is an automatic beamsplitter changer for the VERTEX 80v vacuum spectrometer which enables unattended multi range spectroscopy without breaking the spectrometer vacuum which would otherwise disturb the measurement.

The traditional solid sample preparation for the far IR is to use pressed polyethylene discs or Nujol mulls in transmission mode. ATR (Attenuated Total internal Reflectance) is a very popular technique in the mid IR because neat samples can be studied without any time consuming preparation which may also change the nature of the sample. Furthermore, certain ATR sampling accessories can operate in the

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Far IR	INVENIO R and VERTEX 70v
Minerals	A225/Q ATR accessory
Polymorphs	Advanced ATR correction
Inorganics	Second derivative
Crystal lattice modes	Solid state FIR beamsplitter
BRUKER FM FIR-MIR option	OPUS Curve Fit

far IR because of their all reflective optics. However ATR spectra show differences with spectra recorded in transmission mode and this is particularly true in the far IR at longer wavelengths and inorganic samples with higher refractive index. The purpose of this application note was to study an already well characterised set of carbonate samples in order to demonstrate the ease of the ATR measurement and compare the ATR data with some recent transmission results (see reference 1). Other sample types were investigated too to demonstrate the type of information revealed by access to the far IR range.

Experimental

Three powder carbonate samples ($CaCO_3$, $BaCO_3$ and $MnCO_3$) were used as received from Sigma Aldrich. A VERTEX 70v vacuum FTIR spectrometer was set up with the standard air cooled mid IR source, solid state FIR beamsplitter and far IR room temperature DLaTGS detector. A Bruker single crystal diamond ATR unit (Platinum ATR) was installed in the sample compartment. The measurement parameters were set to resolution 4 cm⁻¹, zero filling 4 to give roughly 1 point per cm⁻¹ and mirror velocity 2.5 kHz. Approximately half an hour of measurement time was used and the spectra reported here are the result of three independent measurements to maximise signal to noise so that the second derivative function could be applied to estimate better both the number of overlapping peaks and their location, although useable standard spectra can be obtained after scanning for just a few minutes. The use of an optional Hg arc lamp would improve signal to noise below ca 100 cm⁻¹. The optimum solution for the far IR is to use a vacuum spectrometer to remove efficiently the interference of water vapour absorption. However, alternatively an effective and stable dry air or nitrogen purge leads also to good results. A background measurement of the clean crystal was taken and then a small amount of neat powder was applied to the crystal and pressed down using the clamp.

Advanced ATR correction software

The OPUS FT-IR software contains an advanced ATR correction function (see reference 2), which has most input parameters fixed by the type of ATR accessory used. For the Platinum ATR, we use:

- Refractive index of the ATR crystal (diamond = 2.4)
- The angle of incidence (45 degrees)
- The number of reflections (nominally 1)

In addition, the sample refractive index needs to be entered and this can often be looked up in tables.
Fine tuning of the number of reflections, which means entering a non integer value is possible. In other words, this parameter may not simply be the actual number of reflections but an effective value brought about by the approximation in the ATR depth of penetration equation and experimental factors such as the convergence of the light and coverage of the ATR crystal. In the software algorithm, this parameter is used to estimate the sample absorption index k. The Kramers-Kronig transform is then used to estimate the real refractive index n of the sample. Therefore the 'number of reflections' will eventually influence n and cause band shifts. This has been described before in reference 3 where an effective number of reflections parameter was introduced for measurements of liquids by ATR.

For the carbonate samples, the number of reflections was adjusted to match the reference calcium carbonate (calcite) band at 228.0 cm⁻¹ giving a value of 0.56. Therefore we have estimated this parameter in an empirical way. To give an idea of the sensitivity of band shift to this parameter, the peak moves to 228.6 cm⁻¹ at 0.50 and 227.4 cm⁻¹ at 0.62. The value of 0.56 was then applied directly to barium and manganese carbonates.
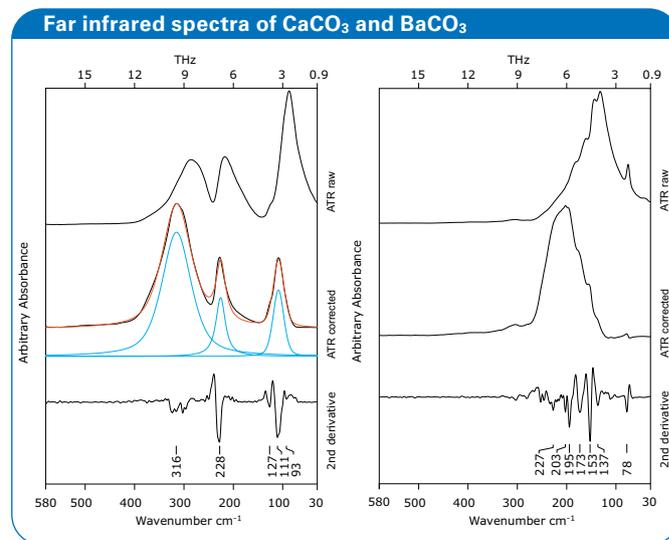
Fig. 1 (left): Far IR spectra of neat calcium carbonate. Top: the raw ATR result as an absorbance spectrum (for y scale see text). Middle: after the advanced ATR correction has been applied (for parameters see text). Blue curves are individual peaks using the Curve Fit function in OPUS/IR and the red curve is the sum. Bottom: the second derivative of the middle spectrum which was used to estimate the number of peaks and position. In all three plots, the y scale is arbitrary for better display purposes.

Fig. 2 (right): Far IR spectra of neat barium carbonate.

Results and Discussion

The lowest internal fundamental vibration of the carbonate anion occurs at ca 700 cm⁻¹, so all bands seen in the far IR are lattice vibrations.
Figure 1 shows the calcium carbonate (calcite) spectrum. The top plot shows the uncorrected spectrum in absorbance units with three major bands at 87, 217 and 286 cm⁻¹. The intensity of this spectrum reached greater than 1 absorbance even with a single reflection ATR accessory. Upon ATR correction (see middle spectrum), using a sample refractive index of 1.6, there are large changes in band intensities with the longer wavelength features reducing in intensity as expected and peak shifts with the major bands moving upwards to 111, 228 and 316 cm⁻¹. This corrected spectrum shows generally good agreement with the transmission result over the whole wavenumber range (see table 1) although a shoulder at 360 cm⁻¹ is not so distinct. The

Table 1: Peak positions

CaCO₃ meas. [cm⁻¹]	CaCO₃ Ref 1 [cm⁻¹]	BaCO₃ meas. [cm⁻¹]	BaCO₃ Ref 1 [cm⁻¹]	MnCO₃ meas. [cm⁻¹]	MnCO₃ Ref 1 [cm⁻¹]
93	98	78		153	
111	110	137	137	160	160
127 (sh)		153	155	172	177
228	228	173	182	203	205
316	319	195		209	
	360	203	205		308
		227	230	328	
		694			352

Peak positions (cm⁻¹) for CaCO₃, BaCO₃ and MnCO₃ and comparison with literature transmission values (reference 1).

Far infrared spectra of MnCO₃ and ascorbic acid

Fig.3 (left): Far IR spectra of neat manganese carbonate

Fig.4 (right): Far IR spectra of ascorbic acid. Top: raw ATR result as an absorbance spectrum (for y scale see text). Bottom: corrected ATR spectrum, number of reflections =1. The y scale is arbitrary for display purposes.

bottom trace in the plot shows the second derivative curve of the corrected ATR spectrum. Negative features in this plot indicate possible single bands and a peak pick is also shown. There seems to be a clear shoulder at 127 cm⁻¹ in our data.

Figure 2 shows the same plots but for barium carbonate. This substance has a different crystal structure (aragonite) and the far IR spectrum is also remarkably different considering just the cation is exchanged. Before ATR correction there is a large broad and overlapping band with a maximum peak at 132 cm⁻¹. The maximum absorbance in this plot reached greater than 1.5. Standing out lower down is a clear and prominent band at 75 cm⁻¹. Upon ATR correction using the same refractive index of 1.6, this broad intensity moves to higher wave number peaking at 203 cm⁻¹ in agreement with the peak seen in transmission (see table 1). The 75 cm⁻¹ band reduces in intensity as expected and shifts to 78 cm⁻¹. It is possible that this band has been missed in the transmission work. A second derivative spectral analysis indicates a complicated overlap in the main band and some tentative suggestions are made as to the number and position of peaks present. However, in general the agreement with transmission data is very good for example the corrected ATR data also have clearly defined shoulder peaks at 137 and 153 cm⁻¹ (see table 1). Further, we see distinct shoulders at 173 and 195 cm⁻¹. The fundamental mode of the carbonate anion was also seen at 694 cm⁻¹ but is not shown in the plot. The plots for manganese carbonate are shown in figure 3 where again a refractive index of 1.6 has been used for correction. The maximum absorbance in the raw ATR data reached 1.7 with the main peak at 140 cm⁻¹. This peak moves to 160 cm⁻¹ upon ATR correction in good agreement with reference 1, see table 1. There appears to be a doublet at 203 and 209 cm⁻¹ corresponding to the 205 cm⁻¹ band in reference 1. Possibly six bands are overlapping creating a broad feature between 305 and 351 cm⁻¹.
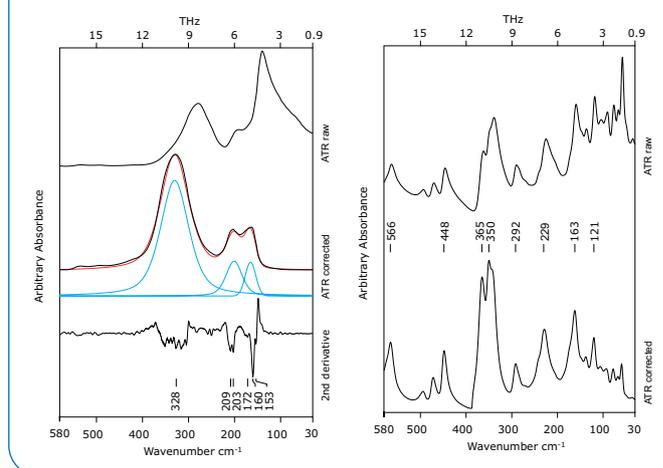
Further example measurements

The inorganic carbonate samples are a fairly severe test of the ATR correction routine since the absorbance is high and there are large changes in sample refractive index (dispersion). Therefore, it was of interest to look also at more standard samples. Ascorbic acid (Vitamin C) in the form of small crystals was chosen as a typical organic compound. DMSO-d₆, which has prominent far IR bands, was measured as an example for liquids.

Figures 4 and 5 show the uncorrected and ATR corrected far IR spectra of ascorbic acid and DMSO-d₆. The absorbance y values in the uncorrected spectra reach 0.4 for ascorbic acid and 1.2 for DMSO which has intense absorption below 100 cm⁻¹.

Table 2 shows that 'reflections = 1' works quite well for these standard samples. Going back to the carbonates, even using the value of 1 for CaCO₃ shifts the reference peak considerably in the right direction from 217 cm⁻¹ (uncorrected) to 226 cm⁻¹ (corrected). It is suggested that fine tuning of the 'number of reflections' is only necessary if more detailed agreement with transmission is desired. For the carbonate examples here, the same 'number of reflections' parameter worked well for all samples of this type. As a final example, cupric oxide powder (CuO) was measured which has various lattice modes in the far IR. In this case, the uncorrected spectrum shows distorted line shapes due to the higher sample refractive index >2 (see figure 6, where the maximum absorbance reaches 0.9).

Far infrared spectra of DMSO-d$_6$ and CuO

Table 2: Samples

Substance	Refractive index	Reference Bands [cm^{-1}]	Uncor-rected	ATR corrected, Reflections = 1
CaCO$_3$	1.6	228	217.5	225.7
Ascorbic acid	1.7	367	362.3	365.4
		448	446.4	448.5
		565	563.8	565.9
DMSO-d$_6$	1.5	263	263.9	265
		308	306	308.7

Uncorrected and corrected ATR data for calcium carbonate, ascorbic acid and DMSO-d$_6$ (fully deuterated dimethyl sulphoxide). Reference cm^{-1} values come from "Raman/Infrared Atlas of Organic Compounds", B Schrader, Second Edition, VCH, 1989.

Fig.5 (left): Far IR spectra of DMSO-d$_6$. Top: raw ATR result as an absorbance spectrum (for y scale see text). Bottom: corrected ATR spectrum, number of reflections =1. The y scale is arbitrary for display purposes.

Fig.6 (right): Far IR spectra of neat cupric oxide from top to bottom: raw ATR, corrected ATR and 2nd derivative data.

The ATR correction algorithm can 'symmetrise' the peak shape and when the second derivative is plotted out, the peak positions are seen at 538, 479, 322,165 and 150 cm^{-1}. These correspond to values of 523, 470, 322, 161 and 145 cm^{-1} from single crystal reflectivity experiments (reference 4).

Conclusion

A range of samples has been investigated in the far IR by the ATR technique, which offers simplicity in the sampling procedure. The ATR correction algorithm can be applied to transform the spectra so they more closely resemble transmission. This is important if ATR effects in the spectra need to be removed or if these types of ATR measurements need to be compared with transmission data, for example in reference library searching.

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