

Terahertz (THz) Measurements of Liquids by a vacuum compatible ATR accessory

1. Introduction

Characterized by wavelengths longer than the mid-infrared region, the far-infrared region is also referred to as the terahertz region. In recent years, this region has been used to evaluate crystal polymorphs for pharmaceuticals and semiconductor device materials, as well as for archaeological research applications, including the study of inorganic pigments. Light in the far-infrared region (terahertz waves) corresponds to hydrogen bonding and Van der Waals forces believed to hold the key to an understanding of the functional expressions of and structural changes in biological molecules in liquids, as well as absorption energy in hydrophobic interactions. Calculations, generally theoretical, have been applied for such purposes in the past, but using light in the far-infrared region should allow the acquisition of important experimental information regarding such behavior.

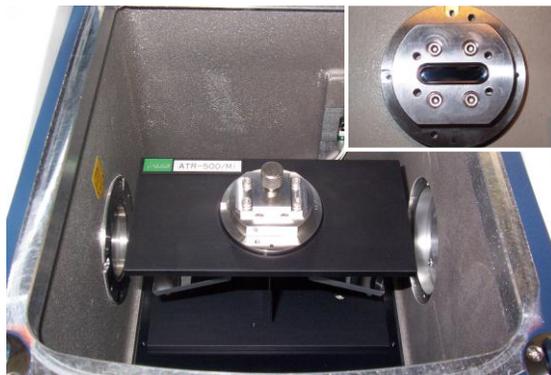


Figure 1: ATR-500/Mi + ATR crystal plate
(Upper right: Prism and liquid cell)

The transmission method is commonly used for measurements in the far-infrared region but is not suitable for measurements of samples with significant absorption in the far-infrared region. For measurements of liquid samples such as biological molecules in an aqueous solution, cell thickness must be reduced to about 10 μm or less to avoid the effects of solvent absorption. This makes it difficult to directly measure gel-state materials or biological samples, like protein solutions. ATR measurements utilize infrared light focused into a crystalline prism which penetrates slightly into the sample when the sample and the prism are in intimate contact. The method allows easy measurements of samples with good contact characteristics, such as liquids and gel-state materials, simply by placing the sample on the prism. Although the effects of moisture vapor are more pronounced in the far-infrared region than in the mid-infrared region, maintaining the interferometer and sample chamber in a vacuum during measurements reduces the effects of the water bands, but depressurizing the sample chamber to a vacuum causes liquid samples to vaporize, preventing ATR sample measurements of the sample. The liquid triple-reflection ATR crystal plate for the THz (far-infrared) region that can be mounted on the ATR-500/Mi, used for these measurements, is configured to allow sealing of the ATR crystal area. This keeps the liquid from vaporizing when the sample chamber is depressurized and enables simple ATR measurements. The Si prism in the ATR accessory can provide a penetration depth of approximately 2 μm at 1000 cm^{-1} and approximately 10 μm at 200 cm^{-1} .

To verify the relationship between hydration and ions in various aqueous electrolyte solutions, Far-IR ATR measurements of pure water and various salt water solutions were performed using the JASCO FT/IR-6300FV, and a liquid triple-reflection ATR accessory. The results of these measurements are outlined below.

2. Measurement Conditions

System: FT/IR-6300FV

Measurement Method: ATR method (Triple-reflection)

Resolution: 2 cm^{-1}

Accumulations: 128

Accessory: ATR-500/Mi + liquid triple-reflection ATR crystal plate (for Far-IR)

Sample: pure water, 2 or 5 mol/L- Sodium chloride and Potassium chloride solution, 2 mol/L- Calcium chloride solution

3. Results and discussions

ATR measurements were performed of pure water in the mid-infrared and far-infrared regions. The results obtained by applying ATR corrections to the measured spectra are shown in Figure 2. The measurement conditions are given in Table 1. As shown in Table 1, the FT/IR-6000 series allows changes in the light source and beam splitter based on measurement frequency, enabling measurements across a broad spectral range. A peak near 600 cm^{-1} potentially assigned to the absorption resulting from the intermolecular motion of water is shown in Figure 2. Another peak was observed near 180 cm^{-1} (yellow border in Figure 2), which is assigned to hydrogen bonding. The change in the behavior of the peak near 180 cm^{-1} resulting from the solute type was also measured.

Table 1 Measurement Conditions for Mid-IR and Far-IR region

Wavenumber [cm^{-1}]	Beam splitter	Light source	Detector
4000 - 400* ¹ (Green-lined)	Ge/KBr	High-intensity ceramic source	DLATGS (standard)
450 - 100* ² (Blue-lined)	5 μm Mylar	High-intensity ceramic source	Si bolometer (option)
110 - 20 (Red-lined)	25 μm Mylar	water-cooled mercury light source	

*1 The ATR PRO470-H (diamond prism) was used under normal atmospheric conditions.

*2 The S/N ratio is lower in the frequency range of 150 cm^{-1} and below.

The stack graph (Figure 3) shows the ATR spectra of these aqueous solutions near 180 cm^{-1} . Table 2 and Fig. 3 indicate the positions of the peaks assigned to hydrogen bonding. In all cases, the monovalent cation shifts toward the low frequency side compared to water, indicating a correlation between density and shift width. In the Potassium solution (K^+) the large ion radius shifts the peaksignificantly toward the low frequency side, as compared to the Sodium solution (Na^+). In an aqueous solution containing Calcium (Ca^{2+}), a bivalent cation, the peak shifts toward the high frequency side compared to water alone, behavior opposite that of the monovalent cation. This suggests that the ion radius, the electrical charge, and the water solution activity affect the hydrogen bonding energy.

As described above, using a liquid ATR accessory for measurements of solutions in a vacuum in the far-infrared region was confirmed to be highly effective in detecting slight changes in the behavior of aqueous solutions. Since significant differences between Na^+ and K^+ were verified in the measurements, we believe the liquid ATR accessory designed for the Far-IR region should find applications not just in the analysis of hydrogen bonding and intermolecular forces, but also the functions of and structural changes in molecules in solution, but for elucidating phenomena within biological organisms.

Reference: Miura, N. *et al.*, Proceedings of 2nd International Symposium on Portable Synchrotron Light Sources and Advanced Applications, 2007, 73-76.

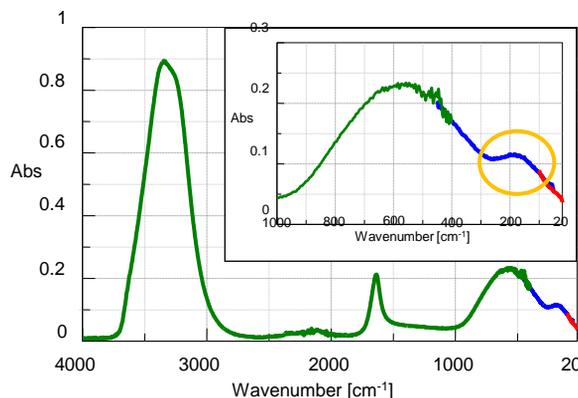


Figure 2: ATR spectra of pure water (Upper right: Enlargement below 1000 cm^{-1})

Table 2 Peak Shift of Each Sample

Sample (Valence)	Ion radius [nm]	Conc. [mol/L]	Peak top [cm^{-1}]	Peak shift [cm^{-1}]
H_2O	-	-	182.2	-
$\text{CaCl}_2\text{aq (+2)}$	0.114	2.0	187.1	+4.9
NaClaq (+1)	0.116	2.0	181.3	-0.9
		5.0	177.4	-4.8
KClaq (+1)	0.152	2.0	177.4	-4.8
		5.0	164.9	-17.3

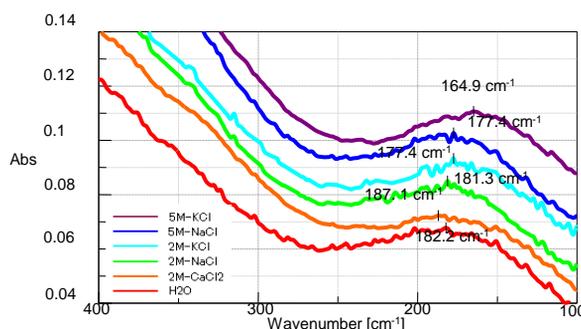


Figure 3: ATR spectra of Each Sample