Terahertz ATR Spectroscopy to Sense Acetone in Water: Toward Biomarker and Contaminant Monitoring

Zahra Mazaheri [1,2,*], Anagha Ramankandath [1], Junaid Yaseen[1], Gian Paolo Papari[1], Can Koral[3], and Antonello Andreone[1, 2]

[3]Physics Department, University of Naples "Federico II", 80126, Napoli, Italy;
[4]National Institute for Nuclear Physics, Naples Unit, 80126, Napoli, Italy
[3]Department of Health Sciences, University of Basilicata, 85100, Potenza, Italy;

In this study, Attenuated Total Reflection (ATR) is combined with the Terahertz Time-Domain Spectroscopy (TDS) technique to provide a reliable method for measuring volatile organic compounds (VOCs). Acetone in water solution over the full concentration range (0-100%) was investigated. The complex function of the compound for different molar fractions was studied as a function of frequency and the intermolecular dynamics of the aqueous binary mixture analyzed using a double Cole-Cole (DCC) model.

Acetone, the smallest ketone, has high environmental and biomedical impacts, as it is highly used in laboratories and industries, as well as being a metabolic byproduct in humans [1]. Therefore, detection of acetone and understanding its dynamics with the environment is essential. Acetone is only a hydrogen-bond acceptor (aprotic molecule) that, can disrupt the existing O–H network of water, which leads to a sudden change in the dielectric response of pure water, even in small amounts. The terahertz (THz) band, which is highly sensitive to molecular relaxation and hydrogen-bond dynamics, makes spectroscopic techniques a powerful detection tool for such dynamics [3]. Using an ATR optomechanical design, with a sealed pool for the liquids as a sample holder at the top of a highly resistivity silicon, provides an opportunity to measure highly volatile compounds like acetone with high accuracy.

This study aims to investigate the intermolecular dynamics of the acetone aqueous solutions with different concentrations using THZ-ATR method. Measurements are carried out by using s-polarized THz pulses incident above the critical angle to the ATR prism at room temperature (T~25°C). The evanescent field interaction with the mixtures is probed, and real ($\varepsilon_1(\omega)$) and imaginary ($\varepsilon_2(\omega)$) parts of the dielectric response are retrieved at a frequency range of 0.2 to 1.6 THz. The experimentally achieved data were then fitted to the double Cole-Cole model (Eq. 1), showing a good agreement between model and experiment. Samples with different molar fractions (X_M%) were prepared in sealed conditions at room temperature to avoid acetone evaporation.

The double Cole-Cole model of dielectric response is [2]

$$\tilde{\varepsilon}(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_1}{1+(i\omega\tau_1)^{1-\alpha_1}} + \frac{\Delta\varepsilon_2}{1+(i\omega\tau_2)^{1-\alpha_2}}, \qquad (1)$$

where ε_∞ is the high-frequency permittivity, $\Delta\varepsilon_{1(2)}$ is the dielectric strength, ω is the angular frequency, and $0 \leq \alpha_{1\,(2)} \leq 1$ is the Cole-Cole broadening parameter.

Fig. 1 shows $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ of the mixtures, both the experimental data and the output of the fitting model at a fixed frequency (f = 0.6 THz) as a function of molar concentration. A sudden drop in both $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ is observed by adding only a small amount of acetone ($X_M \approx 0.8\%$), showing that ATR-THz spectroscopy is capable to detect subtle disruptions of the hydrogen-bond network due to the presence of an aprotic molecule. As the concentration changes, the dynamics of the mixture varies and can be described differentiating three regions: (i) water-rich region (0-25% X_M), where the acetone is introduced into the existing water network in small amounts and its aprotic nature leads to a sudden disruption of the existing O-H bonds [4]; (ii) intermediate region (25-60% X_M), in which acetone and water molecules interact via O-H band formation. Each acetone molecule can accept up to two O-H bonds from water molecules via its carbonyl oxygens. A milder dielectric response reduction is observed in this region by increasing the acetone concentration; (iii) ~~the~~ acetone-rich region (60-100% X_M), where the water molecules become the guest and water clusters are not present anymore. Here new O-H bonds are not forming anymore due to the aprotic nature of acetone, and the added acetone molecules interact through dipole-dipole interaction only [8]. In this region, we do not observe a noticeable change in the dielectric response of the mixtures as the concentration varies.

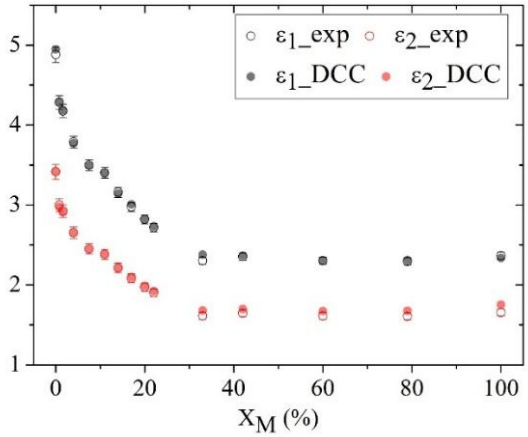

Figure 1. The comparison between the DCC model (full points) and the experimental data (open points) of the real (ε_1) and imaginary (ε_2) parts of the dielectric response of the water-acetone mixture as a function of concentration at 0.6 THz.

Contact: zahra.mazaheri@unina.it

References

1. G. A. Reichard *et al.*, “Plasma acetone metabolism in the fasting human,” J. Clin. Invest. *63*, 619–626 (1979).
2. K. S. Cole and R. H. Cole, “Dispersion and absorption in dielectrics I. Alternating current characteristics,” J. Chem. Phys. *9*, 341–351 (1941).
3. Z. Mazaheri, G. P. Papari, and A. Andreone, “Dielectric response of different alcohols in water-rich binary mixtures from THz ellipsometry,” Int. J. Mol. Sci. *25*, 4240 (2024).
4. Y. Marcus, “The structure of mixtures of water and acetone derived from their cohesive energy densities and internal pressures,” J. Mol. Liq. *320*, 112801 (2020).