

Low-frequency dynamic of ATP and its related compounds studied by terahertz time-domain spectroscopy

Feng Zhang,¹ Ohki Kambara,² Keisuke Tominaga^{1,2}

¹Graduate School of Science, Kobe University

²Molecular Photoscience Research Center, Kobe University

Introduction

There has been considerable interest in both the experimental and theoretical investigation of the low-frequency motion associated with molecules and molecular aggregates in condensed phases. Vibrational motions with resonance frequencies in the terahertz (THz; 1 THz = 10¹² Hz) frequency range are characterized by weaker potential forces and/or larger reduced masses, which are in sharp contrast to vibrations localized within a molecule with resonance frequencies in the mid infrared region.¹⁻⁶ In this work we report our recent activities on the application of THz time-domain spectroscopy (TDS) to condensed phases on biologically important small molecules such as adenosine triphosphate (ATP) and its related compounds to investigate low-frequency dynamics and inter- and intramolecular interactions. We especially focused our attention to temperature dependence and hydration effect on the THz spectra of these compounds.

We have measured the low-frequency spectra of ATP and its related compounds such as adenine and adenosine. In the metabolic processes ATP is used as an energy source to convert it back into its precursors. Therefore, ATP is continuously recycled in organisms. Two phosphoanhydride bonds in an ATP molecule are responsible for the high energy content of this molecule. Structural fluctuation of these bonds can be investigated by THz-TDS.

Results and Discussion

In the series of our THz studies we display the experimental results as the reduced absorption cross section (RACS) defined as,

$$\begin{aligned}\sigma_R(\tilde{\nu}) &\equiv \frac{\beta hc \tilde{\nu}}{(1 - e^{-\beta hc \tilde{\nu}})} n(\tilde{\nu}) \sigma(\tilde{\nu}) \\ &= \frac{2\pi^2 c N_A}{3\epsilon_0 N} \beta \tilde{\nu}^2 \int_{-\infty}^{\infty} dt e^{-i2\pi\tilde{\nu}t} \langle \mathbf{M}(0)\mathbf{M}(t) \rangle\end{aligned}$$

where $\sigma(\tilde{\nu})$ is the absorption cross section, $n(\tilde{\nu})$ is the refractive index, $\beta = 1/k_B T$, N is the number of molecules, $\mathbf{M}(t)$ is the total dipole moment of the system, and the other symbols have usual meanings.¹⁻⁶ RACS is a physical quantity defined per mole of molecule. At high

temperatures, $\sigma_R(\tilde{\nu}) \approx n(\tilde{\nu})\sigma(\tilde{\nu})$.

We measured THz spectra of adenine, adenosine, adenosine monophosphate (AMP) sodium salt, ATP magnesium salt, and ATP disodium salt at room temperature as shown in Figure 1. The samples are dried in a vacuum desiccator for one hour. Adenine and adenosine have a band at 55 cm^{-1} and 37 cm^{-1} , respectively. The RACS intensities below 35 cm^{-1} for the two molecules, where there is no resonant band observed, are typical for other organic molecules in the non-resonant THz frequency region.

Interestingly, the three phosphate compounds have a large intensity of the RACS in the THz frequency region compared to those of adenine and adenosine. As can be seen in the figure, it is found that addition of one phosphate group to adenosine makes the RACS intensity significantly large. However, the difference between AMP and ATP is rather small. Furthermore, we can see a clear difference between the ATP disodium salt and ATP magnesium salt. We, therefore, suggest that the large increase in the RACS intensity by addition of the phosphate group results from the presence of both anionic phosphate group and counter cation. This pair makes a large dipole moment in the molecule, and, consequently, the RACS intensity becomes significantly large.

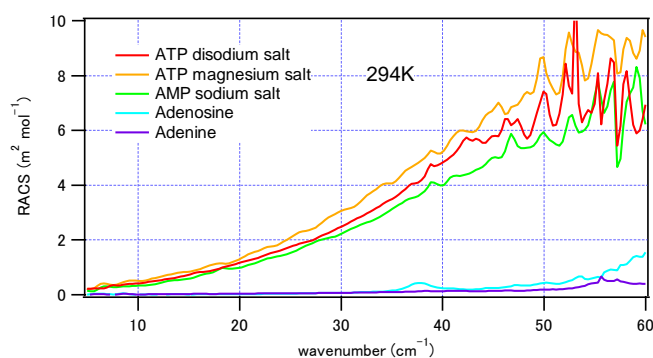


Figure 1. Reduced absorption cross section (RACS) of adenine, adenosine, AMP sodium salt, ATP magnesium salt, and ATP disodium salt at room temperature. All the samples are dried.

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