Experimental and calculated terahertz spectra of naphthalene and 1,4-dihydroxynaphthalene in the 0.5 – 6 terahertz region

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Abstract. Far infrared (IR) spectra of naphthalene and 1,4-dihydroxynaphthalene (1,4-naphthol) were measured in the region from 0.5 to 6.3 THz at room temperature using a GaP THz wave generator. Quantum chemical calculations were performed to obtain normal mode coordinates and frequencies for an isolated molecule case of naphthalene and 1,4-naphthol.

1. Introduction
The terahertz (THz) frequency region is becoming important since characteristic parameters of various materials are distinct in this region. To date, spectroscopic applications of THz radiation have already been extended to characterization of chemical and biological samples. Our group has already demonstrated that THz spectroscopy can be used in identifying various naphthol isomers [1]. We also have reported the temperature dependence THz transmission spectroscopy of 1,4-dihydroxynaphthalene (1,4-naphthol) in the 0.2- to 1.5 THz. Such spectroscopic measurements detected the onset of solid-state phase transition of the isomer [2]. In this work, we report the experimental and quantum mechanical calculation results of naphthalene and 1,4-naphthol in the THz region. We have chosen 1,4-naphthol because it is a good model in understanding hydrogen-bonded molecules and has a relatively simple structure. Using difference frequency mixing, we obtained a THz spectrum from 0.5 – 6 THz using a GaP crystal, where the experimental spectra were compared to semi-empirical calculations.
2. Experimental

2.1. Sample preparation
The samples were prepared by obtaining naphthalene (Aldrich, 99%, scintillation grade) and 1,4-naphthol (TCI, 95%). Each of the samples was grounded and mixed together with polyethylene (Aldrich, ultrahigh molecular weight, surface modified). From this, 300 mg of PE and 15 mg of the sample were taken and pressed to form a pellet with approximately 20 mm diameter and 1 mm thick. It was then wedged with an angle of 2° to avoid interference fringes. A reference sample was also prepared with 300 mg PE of the same size.

2.2. GaP THz generator
Nishizawa and coworkers developed a GaP THz generator based on difference-frequency generation (DFG) of widely tunable coherent THz waves via excitation of a phonon-polariton mode GaP crystal [3-6]. Using the GaP THz generator as a light source, a THz spectrometer was constructed also by the Nishizawa’s group [7]. Figure 2 shows a schematic figure of the GaP THz spectrometer. The pump beam for DFG was fed from β-BaB$_2$O$_4$ (BBO) based optical parametric oscillator (OPO) pumped with the 355 nm line from a Q-switched Nd:YAG third harmonic generation laser with a repetition rate of 10 Hz. The energy of the pump beam was 4 mJ with a 3 mm beam diameter at a pulse width of 6 ns. The linewidth was less than 0.075 cm$^{-1}$ in tuned range (1035-1064 nm). The signal beam was the 1064 nm fundamental beam of the Nd:YAG laser, of which linewidth was less than 0.003 cm$^{-1}$. The energy of the signal beam was also 4 mJ with a 3 mm beam diameter at a pulse width of 11 ns. The two beams were combined with a very small angle to fulfill the phase-matching condition at each frequency. The measurement frequency range was from 0.5 to 6.3 THz with using liquid helium-cooled Si-bolometers as THz detectors. Double beam construction was employed in order to reduce the effect of laser intensity fluctuations. The THz beam was divided into two beams. One of the beams was guided through a pellet mounted in a cryostat equipped with a plastic window transparent for the THz wave, and the other was directly guided to each detector. The transmittance spectra were measured in 5 GHz steps with a spectral resolution of less than 1.5 GHz (0.05 cm$^{-1}$). Details of the GaP THz spectrometer can be found in elsewhere [7].

Figure 1. A schematic diagram of the experimental setup for the THz wave generation using a GaP crystal.

2.3. Semi-empirical calculations
The THz transmission plots were compared with spectra obtained by the quantum mechanical calculation. We used Austin Model 1 (AM1), which is a semi-empirical method to obtain the low frequency vibrational modes. A graphic user interface, Facio (ver.10.1.1) [8], was used to call PCGAMESS version [9,10] of the GAMESS (US) QC package [11] to perform such calculations.

3. Results and Discussion
The left figure in Figure 2 is the experimentally obtained absorption spectrum and the results of the semi-empirical calculation for naphthalene sample. The experimentally obtained absorption spectrum
shows a dominant peak at 5.28 THz. To assign the vibrational mode of this absorption peak, we compare the spectrum with the calculation results. We surmised that the dominant peak at 4.95 THz of the calculated spectrum is the absorption peak which is also observed in the experiment. The difference in their frequency between the experiment and calculation may be due to the fact that the model used in the calculation is for an isolated molecule placed in a vacuum, while in the case of the experiment the molecule is placed in the structure of a polycrystalline of naphthalene in room temperature. Furthermore, the theoretical level of the calculation is too low to predict the vibrational frequencies in the THz region accurately. The related vibrational mode of this absorption is a butterfly motion of the naphthalene ring as shown in the inset.

![Inset Image](image)

**Figure 2.** Experimentally obtained absorption spectra and results obtained by the semi-empirical calculation of naphthalene (left) and 1,4-naphthol (right). The atomic displacement of the butterfly motion of naphthalene is shown in the inset.

On the other hand, the right figure in Figure 2 is the experimentally obtained spectrum and calculated results of 1,4-naphthol. Five peaks are observed at 2.49 THz, 2.91 THz, 3.73 THz, 4.87 THz, and 5.70 THz. A dominant peak in the experimental spectrum was at 5.70 THz while the calculation shows a dominant peak at 5.74 THz. We assigned the motion for the peak as the butterfly motion from the atomic motions along the normal coordinate, the same absorption peak previously observed in the experimental absorption of naphthalene (5.28 THz). We infer that the higher frequency shift is due to contribution of the motion of the OH bond to the normal coordinate. It is interesting to note that 1,4-naphthol has resonance frequency in the higher-frequency side though it has a larger mass than naphthalene due to the hydroxyl group. The absorption peak at 3.55 THz in the calculated spectrum, which may corresponds to the 3.73 THz peak in the experimental spectrum, has a vibrational mode with mixed motion of a butterfly vibration of the naphthalene ring and an out-of-plane OH wagging vibration, which is out-of-phase each other. However, further studies are needed to be able to accurately assign these vibrational modes. Isotope substitution shift and/or calculation including periodic structure of the crystalline state are needed. This also shows that the isolated molecule model is insufficient in predicting the vibrational frequencies in the THz region.

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