

# Modeling of inter and intra-molecular interactions of 1,4-dihydroxynaphthalene in the 0.5- to 6 terahertz region

C. Ponseca<sup>a,b</sup>, A. Quema<sup>a</sup>, G. De Los Reyes<sup>a</sup>, E. Estacio, H. Murakami, S. Ono<sup>c</sup>, N. Sarukura, R. Pobre<sup>d</sup>, R. Quiroga<sup>d</sup>, T. Tanno<sup>e</sup>, T. Sasaki<sup>e</sup>, K. Suto<sup>e</sup>, J. Nishizawa<sup>e</sup> and K. Tominaga<sup>f</sup>

## INTRODUCTION

The spectroscopic investigation of biological substances has been extensively performed to understand intermolecular dynamics and vibrations of these molecules in the terahertz (THz) frequency regime[1]. For complex molecules such as these, and especially for hydrogen-bonded systems, an in-depth investigation is warranted to probe the conformational or structural changes that could occur; thereby modifying a molecule's toxicity and carcinogenic property [2,3]. As such, it is also imperative that quantum mechanical and or semi-empirical calculations be used to predict intra and intermolecular vibrational modes with relatively high accuracy. Some low-frequency intermolecular modes are still very difficult to explain from the first principles and the complexity of such many body problems require extremely high computational cost. On the other hand, semi-empirical models, which have been regarded to be less accurate compared with ab initio calculations present an inexpensive, alternative calculation tool. In general, semi-empirical methods are modified versions of the Hartree-Fock theory using experimental corrections in order to improve performance. A semi-empirical treatment in modeling a complex molecule, thus, necessitates actual experimental data to complement the results and to ensure their validity. In a previous work, the THz absorption spectrum of naphthol in the 0.1-1.1 THz region was studied. The unique absorption spectra of each of the isomeric configurations were obtained and were attributed to the nature of the molecular structures [3]. However, due to the limited THz bandwidth, other relevant absorption peaks that may have been present at higher frequencies were not investigated. Moreover, the explanations were not supported by numerical simulations. In this paper, we present semi-empirical calculations on the THz absorption spectra of 1,4 di-hydroxynaphthalene (1,4-naphthol). Naphthol was chosen for this study because it is a good model in understanding hydrogen-bonded molecules and the intermediate complexity of its structure does not require high computational cost. The results are then verified by THz absorption spectroscopy data in the 0.5- to 6-THz region.

Figure 1.a shows chemical structure of the unit cell of 1,4 naphthol. One unit cell is composed of 4 naphthol molecules arranged in a Pnma orthorhombic space group. [4]. A graphic user interface, Facio [6], was used to run PCGAMESS version of the GAMESS (US) QC package

[7,8] to perform semi-empirical calculation using Austin Model (AM1). All the calculations were performed on a desktop computer; and no parallel computation was utilized. Actual THz absorption spectroscopy was then performed to validate the simulation results. Samples were prepared by pressing high purity naphthol mixed with polyethylene. Figure 1.b shows a schematic of the experimental setup for the difference frequency generation (DFG) of a THz wave in GaP crystal. The  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> based optical parametric oscillator (OPO) provided the tunable source from 1050-1063 nm. Tunable DFG is accomplished in the GaP crystal with along with another 1064 nm beam from the fundamental line of a Nd:YAG laser [5].

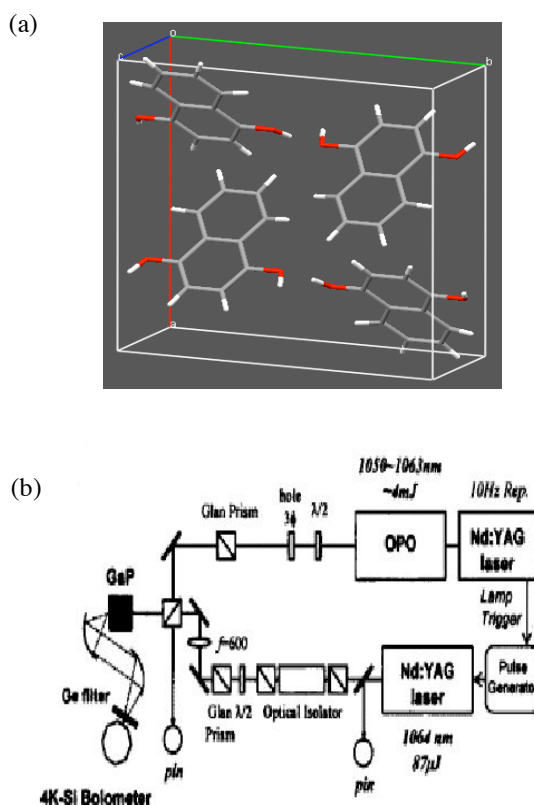


Figure 1. (a) Chemical diagram of unit cell of 1,4-naphthol, (b) Schematic diagram of GaP THz generator

## RESULTS AND DISCUSSION

Figure 2.a shows the calculated and experimental

THz absorption spectrum of naphthalene, which was used as a benchmark for the study. Both plots are in excellent agreement, showing a peak at  $\sim 5.28$  THz. This is ascribed to a butterfly-like motion about its shorter axis and has been identified as a natural vibrational mode. The inset illustrates the mode associated with this peak. Figure 2.b shows the results for the 1,4-naphthol sample, again showing excellent agreement of calculations and experiment. The position of the peak associated with the butterfly-like motion was shifted to 5.96 THz. This shift is attributed to an increase in the intramolecular interaction due to the hydroxyl bonds. Moreover, the semi-empirical model successfully predicted the shift. Furthermore, three other significant peaks located at 2.19 THz, 3.57 THz and 4.95 THz were identified. These features have been ascribed to modes arising from intermolecular interactions. These were assigned as vibrations due to the presence of OH bonds such as “breathing”, twisting, stretching, wagging, and a superposition of these motions.

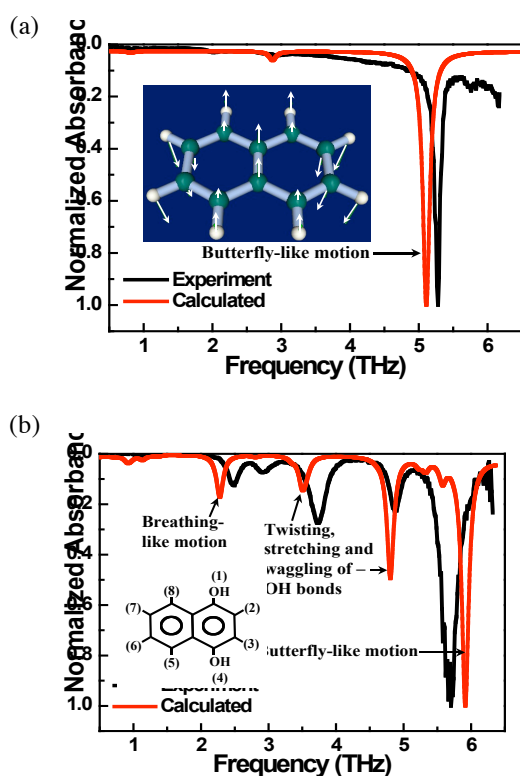


Fig. 2. Experimental THz absorption spectrum and semi-empirical calculation plot of (a) naphthalene and (b) 1,4 naphthol

## SUMMARY

In summary, semi-empirical calculations were employed in modeling the complex inter and intra-molecular interactions in 1,4 naphthol. In addition, actual THz absorption spectroscopy in the 0.5-6 THz region was conducted to validate the numerical simulations. Results have shown that the model can accurately predict the complex vibrational modes in an

intermediately complex biomolecule brought about by the presence of hydroxyl bonds.

## REFERENCES

- [1] Y. C. Shen, P. C. Upadhyaya, and E. H. Linfield, “Temperature-dependent low-frequency vibrational spectra of purine and adenine”, *Applied Physics Letters*, 82 14, 2350-2352 (2003).
- [2] R. H. Garrett and C. M. Grisham, *Biochemistry* (Saunders College, Fort Worth, TX, 1999), Chap. 1.
- [3] A. Quema, H. Takahashi, M. Sakai, M. Goto, S. Ono, N. Sarukura, R. Shioda, and N. Yamada, “Identification of Potential Estrogenic Environmental Pollutants by Terahertz Transmission Spectroscopy,” *Japanese Journal of Applied Physics, Part 2* 42, L932 (2003).
- [4] J. Gaultier, and C. Hauw, “Structure cristalline et moléculaire de la naphthohydroquinone-1,4,” *Acta Crystallographica*, 23(6), 1016-1024 (1967).
- [5] J. Nishizawa, K. Suto, T. Sasaki, T. Tanno, “A Comparative study of THz spectra,” *Proceedings of Japan Academy*, 81(B), 20-25 (2005).
- [6] M. Suenaga, “Facio: New Computational Chemistry Environment for PC GAMESS”, *Journal of Computer Chemistry, Japan*, 4(1), 25-32 (2005).
- [7] Alex A. Granovsky, <http://classic.chem.msu.su/gran/gamess>
- [8] A. V. Nemukhin, B. L. Grigorenko, A. A. Granovsky, “Molecular modeling by using the PC GAMESS program: From diatomic molecules to enzymes”, *Moscow University Chemistry Bulletin*, 45 (2), 75, 2004.

<sup>a</sup> Institute for Molecular Science

<sup>b</sup> The Graduate University for Advanced Studies

<sup>c</sup> Nagoya Institute of Technology

<sup>d</sup> De La Salle University

<sup>e</sup> Semiconductor Research Institute

<sup>f</sup> Kobe University