Terahertz Time-domain Spectra of Inter- and Intramolecular Hydrogen Bonds of Fumaric and Maleic Acids

Yuko Ueno,* Rakchanok Rungsawang, Isao Tomita, and Katsuhiro Ajito
NTT Basic Research Laboratories, 3-1 Morinosato Wakamiya, Atsugi 243-0198

(Received June 12, 2006; CL-060677; E-mail: ueno@aecl.ntt.co.jp)

The inter- and intramolecular hydrogen-bonding modes of two steric isomers, namely fumaric acid and maleic acid, are observed by using terahertz time-domain spectroscopy (THz-TDS). The intermolecular modes observed with fumaric acid crystals are inactivated by incorporating the molecules in the nano-sized pores of a mesoporous silicate (SBA-16) due to the separation of the molecules, whereas the intramolecular modes of maleic acid of the crystal and the incorporated samples are similar.

THz-TDS has been used to study low-frequency vibrational modes and weak molecular interactions such as hydrogen bonds in the 0.1–3.0 THz (3–100 cm^{-1}) region, corresponding to the lower end of the far-infrared (FIR) region.[1] Intra- and intermolecular hydrogen bonds are important in that they stabilize the structures of many biological molecules. The THz-TD absorption spectra of DNA[2] and amino acids[3] have revealed that specific resonance patterns can be identified as the vibrational modes of intermolecular hydrogen-bond networks. The assignment of the THz peaks by using theoretical models has not agreed sufficiently well with experimental results because the theoretical models did not take account of crystalline conditions or hydrogen-bonding effects.[4] Although recent theoretical predictions of the THz modes of crystalline samples have been improved by using solid-state density functional theory calculations,[5] it is still difficult to distinguish experimentally between intramolecular and intermolecular modes since they have very similar frequencies.

This paper proposes a way to distinguish between intra- and intermolecular modes by incorporating target molecules in nano-sized spaces in porous materials to reduce the concentration/density of the intermolecular hydrogen bonds of the sample. We have recently found that a mesoporous silicate (SBA-16) has excellent transparency up to 4.3 THz and is thus applicable to THz-TDS.[6] Moreover, a wide variety of target molecules can be incorporated in the pores of mesoporous silicates because the pore size and structure of mesoporous silicates are tunable, and they are easy to produce.[7] Here, we examined the THz-TD absorption spectra of simple steric isomers, namely, fumaric (FA) and maleic (MA) acids and maleic anhydride (MAH). FA is the trans isomer of butenedioic acid and its two carboxylic acid groups form an intermolecular hydrogen bond while MA is the cis isomer and the two carboxylic acid groups form intramolecular hydrogen bonds. MAH has a cyclic structure and forms no inter-/intramolecular hydrogen bonds.

The samples were prepared as follows. Cubic symmetrical SBA-16 was synthesized by using triblock copolymer EO_{70}-PO_{100}-EO_{70} (BASF Corporation: Pluronic P127; $M_\text{w} =$ 12,600) as a template agent.[8] About 20 mg of SBA-16 was soaked in 0.2 mL of >0.5 mmol/L methanol solution of FA (Kanto Kagaku) and MA (Kanto Kagaku), respectively. The samples were then stirred vigorously, filtered, washed with methanol, and dried well in air at room temperature. The FA and MA samples in SBA-16 were packed in a cavity of a plastic cell. The optical path length and thickness of the plastic walls were both 1 mm in order to provide a sufficient path length to eliminate the effect of the multiple reflection that occurs between the two surfaces of the sample disk (etalon artefacts[9]) in the spectra. The FA, MA, and MAH sample reference pellets were prepared by crushing the crystals into powder and then mixing 23.22, 11.61, and 9.81 mg of FA, MA, and MAH with 76.78, 88.39, and 90.19 mg of PE powder, respectively. The mechanically measured pellet thickness was 1.4 ± 0.2 mm. The THz-TD absorption spectra were measured by using a THz-TDS2004 (Aispec) combined with a 10 fs NIR pulse laser (Integral Pro, FEMTOLASERS). The optical set-ups and experimental conditions are described elsewhere.[10] Since heat-induced frequency shifts and resonance broadening are generally observed for THz peaks,[2,3] we measured the THz spectra at room temperature (293 K) and 77 K to observe the spectral properties in detail.

First, we compared the THz absorption spectra of FA molecules incorporated in the pores of SBA-16 (dotted lines) and of their polyethylene (PE) pellets as the reference bulk samples (solid lines) in the 1.5 to 4.0 THz region (Figure 1, the lower panel). The THz spectra of FA in SBA-16 and the crystal sample are significantly different. Some characteristic peaks were clearly observed in the 2.8–3.7 THz region with the crystal samples at both temperatures and the peaks of FA shifted to higher frequencies with lowering the temperature. These peaks were not detectable with the samples in SBA-16 even at 77 K. Therefore, the THz peaks of FA can be assigned as the intermolecular hydrogen-bonding mode, which is inactivated by the incorporation of the molecules into the nano-sized pores of SBA-16 due to the separation of the molecules. Some FA molecules may exhibit intermolecular interactions in SBA-16, even so, the concentration of those molecules must be much lower than that of the crystal sample.

Then, we compared the THz absorption spectra of MA and MAH (Figure 1, the upper and the middle panels). In contrast to the THz spectra of FA, the spectral features of MA are similar for the samples in SBA-16 and the crystals in PE pellets, although the spectral features were rather unclear at 297 K due to the heat effects as we described previously. These peaks can be assigned as the intramolecular hydrogen-bonding modes, because the THz absorption spectra of FA were completely different from those of MA. Moreover, if the MA peaks are derived from something other than the intramolecular hydrogen bond, such as the interaction between the molecular layers, it is difficult to explain the striking reduction in the absorption intensities of all the peaks of MAH. The peaks of MA shifted to higher

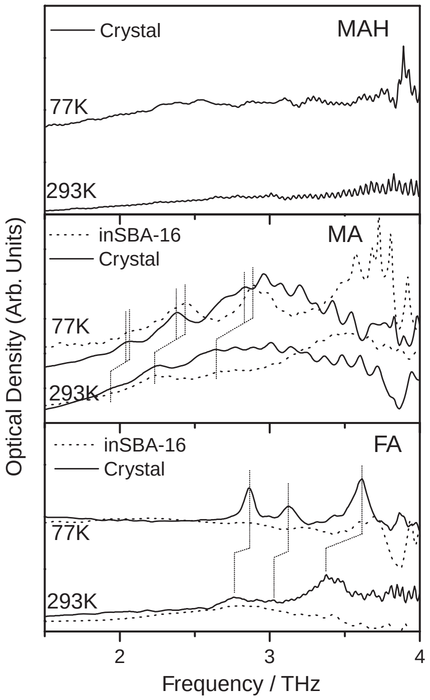

Figure 1. THz-TD absorption spectra of MAH, MA, and FA (from top to bottom): in SBA-16 (solid lines) and PE pellets of crystals (dotted lines). The peak positions are labeled with the thin dotted lines.

frequencies with lowering the temperature in both the SBA-16 and PE pellets. It is also noteworthy that the peak positions of MA in SBA-16 at 77 K were slightly higher than those of the PE pellet. This indicates that incorporating MA molecules in the pores has a similar effect to lowering the temperature.

To investigate the molecular structures of FA and MA in SBA-16 in detail, we also measured the micro-Raman spectra of FA and MA molecules incorporated in the pores of SBA-16 and crystals as reference bulk samples (Figure 2). The Raman bands of FA and MA in SBA-16 were clearly observed as well as those of the crystal samples. Therefore, the disappearance of the THz peaks of FA in SBA-16 is not likely to be due to the low concentration of the incorporated molecules. The FA and MA spectra in SBA-16 were almost the same as those of the crystals, although a slight broadening and shifting of some bands were observed with the SBA-16 spectra. The results indicate that incorporating FA/MA molecules in the nano-sized pores of SBA-16 slightly changes the molecular structures of FA/MA and that the FA/MA molecules incorporated in SBA-16 interact with silanol groups (Si–OH) on the SBA-16 surface.

In summary, incorporating target molecules in nano-sized spaces in SBA-16 is effective in reducing the concentration/density of the intermolecular hydrogen bonds of the sample, and it is possible to distinguish intramolecular hydrogen-bonding modes from intermolecular modes. However, a detailed analysis of the THz spectra requires theoretical calculations as well as further experimental studies of other hydrogen-bonding systems.

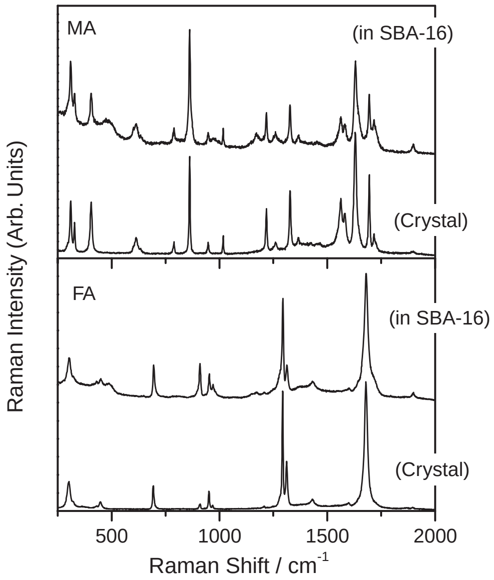

Figure 2. Raman spectra of MA and FA (upper and lower): in SBA-16, and crystal.

We thank the Wakate Project of NTT for financial support and Dr. Tsuneyuki Haga of NTT Microsystem Integration Laboratories and Dr. Keiichi Torimitsu of NTT Basic Research Laboratories for their encouragement.

References

1 For example: C. A. Schmuttenmaer, *Chem. Rev.* **2004**, *104*, 1759; S. Nishizawa, K. Sakai, M. Hangyo, T. Nagashima, M. W. Takeda, K. Tominaga, A. Oka, K. Tanaka, O. Morisawa, *Terahertz Optoelectronics, Topics Appl. Phys.*, ed. by K. Sakai, **2005**, Vol. 97, p. 203.
2 B. M. Fischer, M. Walther, P. U. Jepsen, *Phys. Med. Biol.* **2002**, *47*, 3807.
3 P. F. Taday, I. V. Bradley, D. D. Arnone, *J. Bio. Phys.* **2003**, *29*, 109; K. Yamamoto, M. H. Kabir, K. Tominaga, *J. Opt. Soc. Am. B* **2005**, *22*, 2417.
4 K. Yamamoto, K. Tominaga, H. Sasakawa, A. Tamura, H. Murakami, H. Ohtake, N. Sarukura, *Biophys. J.* **2005**, *89*, 22; R. Rungsawang, Y. Ueno, I. Tomita, K. Ajito, *J. Phys. Chem. B*, in press.
5 D. G. Allis, D. A. Prokhorova, T. M. Korter, *J. Phys. Chem. A* **2006**, *110*, 1951.
6 Y. Ueno, R. Rungsawang, H. Takenouchi, I. Tomita, K. Ajito, *Pacifichem 2005 Abstract, Nanoporous Materials: Synthesis and Applications-No. 1500.*
7 For example: C. T. Kresge, M. E. Leonowitz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710.
8 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024.
9 A. Dobroiu, M. Yamashita, Y. N. Ohshima, Y. Morita, C. Otani, K. Kawase, *Appl. Opt.* **2004**, *43*, 5637.
10 Y. Ueno, R. Rungsawang, I. Tomita, K. Ajito, *Anal. Chem.* **2006**, *78*, 5424.

Published on the web (Advance View) September 9, 2006; doi:10.1246/cl.2006.1128