



Light-induced Difference Terahertz Spectroscopy

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Abstract. Visible/near-infrared laser-induced difference spectroscopy based on a time-domain terahertz system has been developed, and used to study copper pathencyonine. We find that the absorption peak of this molecule at 1.08 THz changes significantly under 790 nm laser excitation, suggesting that we have observed the first evidence of vibrational mode changes in the THz range induced by visible/near-infrared light.

Key words: Difference spectroscopy, pathencyonine, terahertz spectroscopy, time-domain

1. Introduction

Infrared (IR) difference spectroscopy has been widely used for the investigation of biological systems [1]. The technique consists of recording spectra from a sample before and after applying an external perturbation, such as illumination. The difference between the spectra is then calculated, and only modes that change in intensity or frequency are isolated. Signals originating from modes which are unaffected by the perturbation are subtracted out. This method is particularly effective in probing minor structural changes associated with individual bonds of chromophores and proteins [2–5].

The most common difference spectroscopy system is based on Fourier transform infrared (FTIR) spectroscopy. In the mid-IR, the dynamic range is around 10^5 at a fixed delay and frequency. In the far-IR, however, the poor performance of FTIR spectrometers, owing to the lack of suitable sources and detectors, makes it impractical to develop an FTIR difference spectroscopy system. In contrast, terahertz (THz) time-domain spectroscopy has a dynamic range of over 10^8 in the far-IR region owing to the ability to achieve time-resolved coherent detection [6–8]. This makes THz time-domain systems attractive for differential spectroscopy and in this paper, we report the development and application of such a visible/near-infrared (NIR) laser-induced difference spectroscopy system.

2. Experiment

Visible/NIR laser-induced differential THz spectroscopy was developed from a THz time-domain spectrometer [9]. Figure 1 shows the experimental arrangement

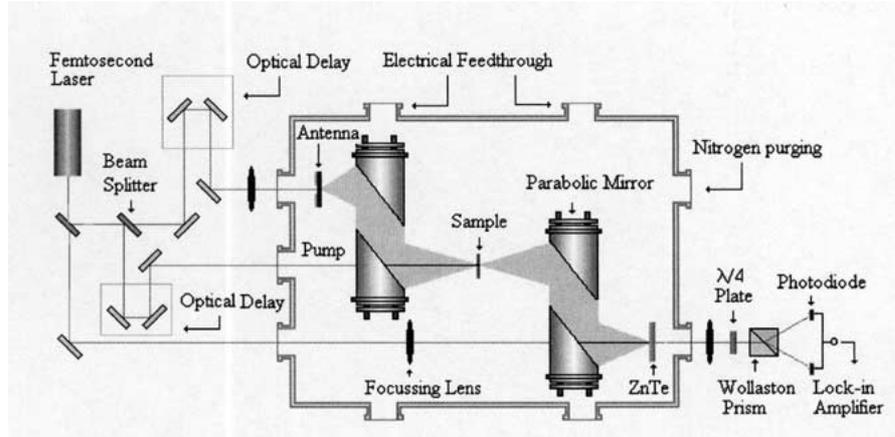


Figure 1. Schematic representation of a light-induced differential THz time-domain spectroscopy system.

which is similar to that used for visible-pump-THz-probe experiments [10–12]. In brief, a Ti:sapphire laser (Femtolasers Productions) provides visible/NIR pulses of 12 fs duration at a centre wavelength of 790 nm. The output from this laser is split into three parts: a 250 mW beam is used for THz generation using a biased semi-insulating-GaAs emitter, a 250 mW beam is used to excite the sample with a focus diameter of 300 μm , and the remaining 25 mW serves as the probe beam for electro-optic detection with a 1-mm-thick ZnTe crystal. The whole system is purged with dried nitrogen in order to eliminate absorption by water vapor in the beam path.

For recording the difference spectrum, we first measured the time-resolved field variation, $E(t)$, of the transmitted THz pulse through the sample in its ground state. We next measured $E(t)$ through the excited sample (1 ps after visible/NIR laser excitation). Fourier transforms of $E(t)$ gave both the amplitude $A(f)$ and the phase $\varphi(f)$ of the field components in the frequency domain. The differential spectrum of the sample was then calculated using the following equations:

$$\begin{aligned}\Delta(\alpha \cdot d) &= -20 \cdot \log[A_e(f)/A_g(f)] \\ \Delta(n \cdot d) &= [\varphi_e(f) - \varphi_g(f)] \cdot c/2\pi f\end{aligned}\quad (1)$$

where d is the sample thickness, and the subscripts g (ground state) and e (excited state) represent measurements of the sample in the absence and presence of visible/NIR laser excitation, respectively.

Copper pathancyonine (CuPc) powder was obtained from Sigma-Aldrich (product #252980) and used without further purification. Samples were prepared by pressing CuPc powder into pellets of 8 mm diameter with a manual pellet maker.

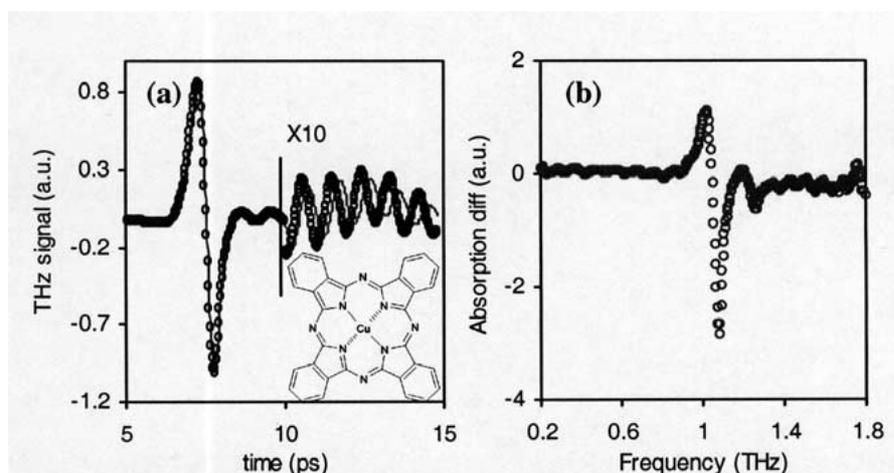


Figure 2. (a) THz transients after transmission through a CuPc pellet, measured with (line) and without (open circle) the pump laser beam. The signals after 10 ps are multiplied by a factor of 10 for clarity. The inset shows the molecular structure of CuPc. (b) Difference THz spectrum of a CuPc pellet calculated from the signals in (a).

3. Results and Discussion

Pathencyonines have excellent light harvesting capabilities, and their biomedical applications have been extensively investigated [13, 14]. The optical absorption of CuPc peaks at 678 nm and overlaps the spectrum of the visible/NIR laser pulse used in our experiments. Figure 2 (a) shows the THz transient transmitted through the CuPc sample measured in the presence and absence of visible/NIR laser excitation. The main THz pulses measured with and without laser excitation are almost identical, suggesting that most frequency components in the absorption spectrum do not change by excitation. However, the small ripples after the main pulse in the time domain are different, indicating that some THz absorption features are changed by the excitation. Figure 2 (b) shows the visible/NIR light-induced differential spectrum of a CuPc sample, calculated from the measured THz signals using the above equations. As expected, the difference spectrum is close to zero over most of the frequency range, however, strong spectral features appear at 1.08 and 1.26 THz. These features did not change as the delay between visible/NIR pump and THz probe was altered from -20 ps to 100 ps.

Previously, there have been reports of the use of visible-pump-THz-probe techniques for studying silicon [10], GaAs [11] and betaine [12]. For semiconductors, the observed absorption in the THz range is mainly a result of photo-generated electrons, whilst for betaine, the increase in the absorption is a result of the formation of hot ground-state molecules after a back electron transfer process. However, no fine spectral features were observed in any of these previous studies.

In contrast, the difference THz spectrum measured here clearly shows fine spectral features. To the best of our knowledge, this represents the first evidence of a vis-

ible/NIR light-induced vibrational mode change in the THz frequency range. The observed absorption features at 1.08 THz are likely to be related to a specific vibrational mode of the CuPc molecules. After visible/NIR laser excitation, the photo-generated electrons transfer from excited states to the ground state through non-radiative processes, causing a local temperature change. Since the low-frequency vibrational modes are sensitive to temperature changes [15], this local temperature change may cause differences in either the intensity or the frequency of the vibrational modes, which are then detected by the difference THz spectrometer. More experimental and theoretical work is needed to clarify this mechanism fully.

4. Conclusions

We have demonstrated that visible/NIR light-induced difference spectroscopy based on a THz time-domain system is a powerful tool for studying molecules of biomedical importance, such as CuPc. The measured difference spectrum shows clear features in the THz frequency range, suggesting that a specific vibrational mode of CuPc molecules is changed as a result of the visible/NIR laser excitation.

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