

Temperature-dependent low-frequency vibrational spectra of sodium magnesium chlorophyllin

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Abstract— Terahertz time-domain spectroscopy has been used to investigate the vibrational spectra of polycrystalline sodium magnesium chlorophyllin - one of the natural derivatives of chlorophyll - over the temperature range 88 K–298 K. A number of well-resolved absorption peaks were observed in the frequency range 0.2–2.5 THz, which are interpreted as originating from mixed character of intramolecular and intermolecular vibration modes. As the temperature is increased, the observed absorption features resolve into broader peaks. The peak centered at 1.83 THz shifts towards higher frequencies, indicating that for this feature, significant intermolecular anharmonicity exist.

I. INTRODUCTION

THE sodium magnesium chlorophyllin (Chl-Mg-Na) is a costless, readily available, and fairly stable metal-porphyrin derivative obtained from simple saponification of chlorophyll-*a*. It is widely used as a food additive, pharmaceutical material, and in other fields. This molecule is composed of a porphyrin ring with a magnesium central ion, and three sodium carboxylate groups (–COONa) connected to the porphyrin ring. Moreover, Chl-Mg-Na can be potentially used as a calibration standard for terahertz (THz) spectroscopy instruments to potentially estimating the chlorophyll contents in plants leaves at THz frequencies [1]. Observing the temperature dependence of the low-frequency vibrational spectra of polycrystalline Chl-Mg-Na can play a decisive role in the assignment of the features originating from mixed character of intramolecular and intermolecular vibration modes observed in molecular crystals. These vibrations modes have frequencies significantly lower (≤ 6 THz) than intramolecular vibrations [2-7]. At 0 K, the motions of atoms around the equilibrium minima are well described by a harmonic potential. In the presence of anharmonicity of the vibrational potentials it is expected that increased temperature will lead to a redshift of vibrational transition frequencies with a broadening of the line profile [3-5]. Recently, the low-frequency vibrational spectra were explored in chlorophyll species by means of THz time-domain spectroscopy (THz-TDS) measurements [8-11], FTIR and surface-enhanced Raman spectroscopy experiments.

In this work, we present temperature dependent THz spectra of polycrystalline Chl-Mg-Na. Investigating the relationship between the low frequency vibrational features of Chl-Mg-Na and temperature is critical for future simulations and assignments of the modes involved in natural chlorophylls and

chlorophyll derivatives THz spectra at room temperature.

II. RESULTS

THz spectra were measured by THz-TDS using a Teraview spectrometer in a transmission configuration. In order to record the temperature dependence of the spectral features the samples were mounted in liquid nitrogen cooled cryostat. Figure 1 shows the temperature dependence of the absorbance spectra of a pellet prepared by mixing Chl-Mg-Na powder with HDPE powder, from 88 K to 298 K. For this mixed pellet, the low-temperature spectra have three well-defined features (P1, P2, and P3 at 1.44, 1.83, and 1.98 THz, respectively). We did not observe spectral features of interest in the region below 1.0 THz. As the sample temperature is increased, all these features become broader. The weaker peak P3 at 1.98 THz is no more detectable above 240 K while the close-by stronger peak P2 also broadens. The extraction of features parameters, *i.e.*, central frequency, amplitude, and linewidth, has been performed by fitting each of the spectra with a multipeak fit using a Lorentzian function.

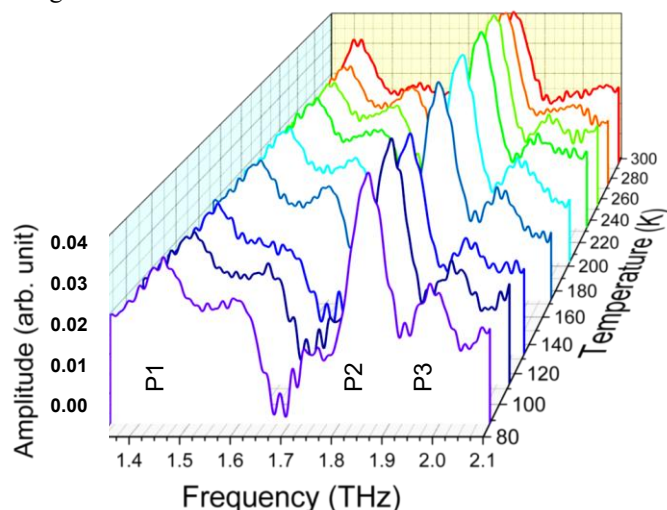


Figure 1. Absorbance spectra of a pellet containing 17.2 wt-% of Chl-Mg-Na in HDPE (total weight 79.2 mg) at temperatures from 88 K to 298 K. The spectra are normalized and background corrected. At room temperature, the peaks P1, P2, and P3 fall at 1.44 THz, 1.83 THz and 1.98 THz, respectively.

Figure 2 summarizes the temperature dependence of the central frequency and amplitude of the features. For P2, the significantly decrease in frequency from 1.86 down to 1.83 THz (Fig. 2a) and its amplitude variation of about 30% (Fig. 2b)

when the temperature increases, indicate that significant intermolecular anharmonicity is involved with this feature. The feature P1 at 1.44 THz shows a smaller decrease, while P3 at 1.98 THz does not display significant shift or change in amplitude with temperature change.

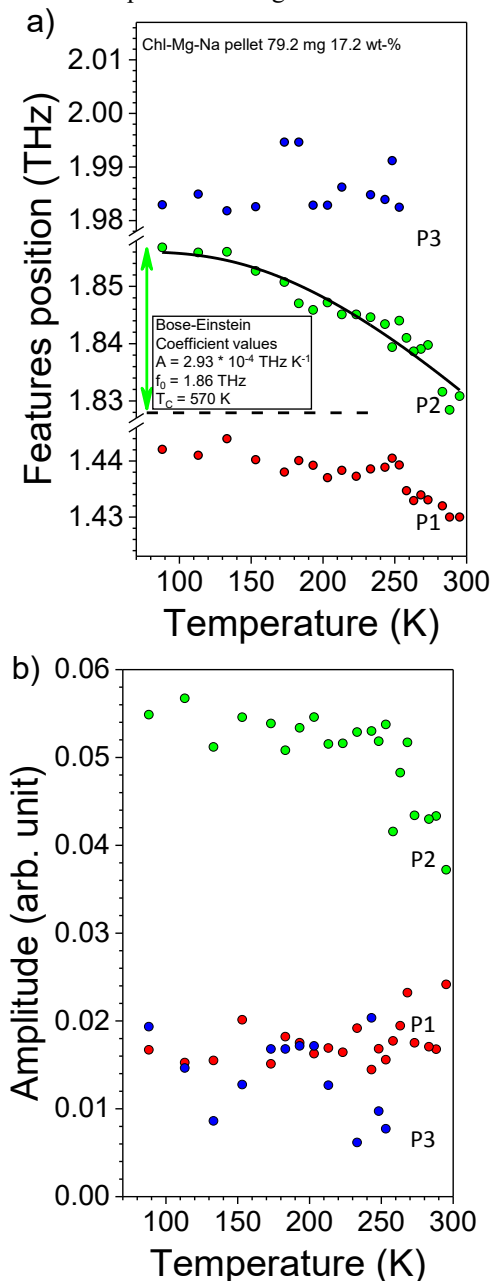


Figure 2. a) Frequency position of the three well-resolved absorption features P1 (red dots), P2 (green dots), and P3 (blue dots) versus temperature for the Chl-Mg-Na pellet (17.2 wt-% of Chl-Mg-Na in HDPE, total weight 79.2 mg) determined by a multippeak-fit using Lorentzian function of the spectral data. The black solid line is calculated for the feature P2, using Bose-Einstein distribution. Inset: Fitting parameters of the Bose-Einstein distribution. b) Amplitude of the three absorption features.

A Bose-Einstein distribution has been used to model the temperature dependence of P2. The frequency shift was fitted by $f(T) = f_0 - AT_c / (e^{T/T_c} - 1)$, where f_0 is the central frequency of the vibration mode at 0 K and A is a constant. T_c is a characteristic temperature related to the phonon bath of the

mode [12]. Figure 2a shows the best-fit result. The agreement is reasonably good over the entire temperature range with the fitting parameters shown in the inset of Fig. 2a.

Further work has been done to study the mixed character of intramolecular and intermolecular vibrations of Chl-Mg-Na without studying the temperature dependence [11]. This was carried out by introducing a small amount of water to the material to change the molecular environment and alter the intermolecular vibrational modes. The results of these experiments demonstrated that the change of the central frequency and amplitude of the 1.83 THz peak was drastic when compared to other peaks. This behaviour also suggested significant intermolecular anharmonicity for the P2 feature.

In conclusion, the low-frequency vibrational aspects of the Chl-Mg-Na molecular crystal were probed by means of temperature-dependent THz-TDS spectra. The decrease of frequency of the feature at 1.83 THz when the temperature increases is attributed primarily to the effect of intermolecular anharmonicity. Further study on low temperature measurement to few Kelvin and accurate simulations are now required in order to fully interpret the thermally induced shifts of the low-frequency peaks. Furthermore, chlorophyll derivatives such as Chl-Mg-Na represent prototype systems for the study of low-frequency vibrations in crystalline, amorphous and dissolved forms of less stable natural chlorophylls in plant leaves.

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