

Onset detection of solid-state phase transition in estrogen-like chemical via terahertz transmission spectroscopy

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Solid-state phase transition onset in an endocrine-disrupting estrogen-like chemical (1,4-naphthol) is detected using terahertz transmission spectroscopy. The appearance of two absorption peaks and the sudden upsurge of terahertz-radiation power at 210 K indicate the onset of the solid-state phase transition. Differential scanning microscopy reveals a first-order phase transition at around 240 K while temperature-dependent x-ray diffraction analysis shows the occurrence of such phenomenon also at around 240 K. This demonstrates the sensitivity of the terahertz spectroscopic technique to phase transition since it provides a signal before such phenomenon actually occurs. © 2004 American Institute of Physics. [DOI: 10.1063/1.1812366]

The progress of terahertz (THz) technology has been enormous over the past several years. Several works have been published wherein biological samples show specific frequency-dependent absorption and dispersion in the THz regime.¹⁻⁴ Direct measurement of intramolecular dynamics in dye molecules⁵ and the nondestructive imaging of chemical compounds⁶ have also been conducted. Recently, it was found that the 1,4-dihydroxynaphthalene (1,4-naphthol) exhibited an absorption peak at around 0.4 THz in room temperature. Such peak was ascribed to some interaction between THz radiation and hydrogen bonds that link into chains the adjacent molecules in the isomer.⁷ Naphthol was selected in such study because very little attention has been given to its electronic absorption in the far infrared while several works have already been conducted in the mid-infrared region.⁸⁻¹⁰

Responses of organic materials to THz radiation with changing temperature have led to the observation of conformational changes. In the study of charge transfer organic crystal, it was reported that by irradiating the tetrathiafulvalene-*p*-chloranil sample with laser pulses not simply did conformational change occur but rather a structural phase transition took place.¹¹ Since this finding is significant from the viewpoints of chemistry and physics, an alternative technique with increased sensitivity for the detection of phase transition in organic/biological materials is thus warranted.

This letter reports the use of THz-radiation spectroscopy in detecting solid-state phase transition onset in 1,4-naphthol, a biochemical known to exhibit estrogen-like behavior, i.e., it can mimic natural hormones.^{12,13} The results here will show that THz spectroscopy is a valuable technique and a sensitive probe in detecting phase transition.

The sample was prepared using 150 mg of 1,4-naphthol (C₁₀H₆(OH)₂) powder with 99.9% purity. The powder was

pressed into a pellet with a diameter of 10 mm and a thickness of 1 mm. The pellet was placed in a copper sample holder, which was attached to the cold finger of a cryostat. The cryostat had a 10-mm-diam window equipped with a special quartz glass for THz transmission spectroscopy. The spectroscopic setup here is similar to that in Ref. 7 except in this case a 2.5 T magnet was used.

The plot of the absorption spectra of 1,4-naphthol at various temperatures is shown in Fig. 1(a). The absorption peak at 4 K is relatively sharp and well defined compared to the distorted and broad peak at 300 K. This can be explained by considering the anharmonicity of the vibrational potentials.¹ In an environment of extremely low temperature, thermal population of vibrational potential occurs only in the

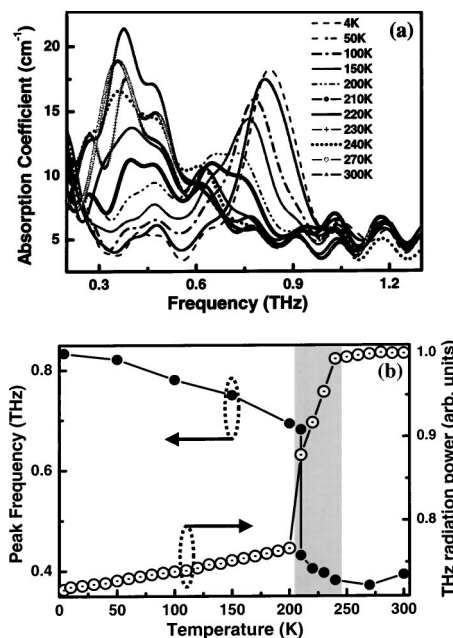


FIG. 1. Temperature-dependent (a) absorption spectra and (b) absorption peak frequency and transmitted THz radiation power of 1,4-naphthol. The gray rectangle in (b) signifies the temperature range with which solid-state phase transition occurred.

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lowest energy level with spacings equivalent to THz energy. However, at higher temperatures population also occurs at other vibrational levels, which causes the broadening feature in the lower frequency portion of the absorption spectrum. As the temperature is increased to 200 K, steady shift of the absorption peak toward lower frequency coupled with a decrease in absorption intensity are observed. Such shift is typical for molecules in hydrogen-bonded networks¹⁻³ implying that the absorption peak observed here is due to intermolecular hydrogen bonding. This absorption feature suggests that the observed low-energy vibrational mode is strongly coupled to the lattice and that the molecule undergoes conformational change. Since a change in temperature can also lead to an electronic redistribution in the hydroxyl (OH) functional group, π -electron cloud-hydrogen-bond interaction can possibly occur. This interaction is possible due to the presence of the π -electron cloud in the naphthalene ring. As the temperature is varied, delocalization of the π electrons can take place thereby causing a certain degree of conformational change with respect to the orientation of the O-H bond to the plane of the aromatic ring. It should be noted here that this interaction is inter-related to the change in hydrogen bonding since according to Gutman,¹⁴ the change in the hydrogen bonding can also be regarded as a redistribution of electrons in the functional group due to the lability of the electron lone pair, which in the case of naphthol is the oxygen lone pair. Thus, the change in hydrogen bonding is primordial to spectral change.

By increasing the temperature to 210 K, two broad peaks with almost equal amplitudes are manifested. One peak is observed below 0.6 THz (peak 1) while the other above 0.6 THz (peak 2). Further increasing the temperature to 300 K, peak 1 appears to settle at a particular position while its amplitude continuously increases. In conjunction with this, peak 2 shifts slightly toward lower frequency that it seems to superpose with peak 1 thereby forming a broader and distorted peak. Aside from the superposition of the two peaks, the influence of thermal energy is also a factor that needs to be considered since its effect becomes significant at these temperatures. To make sure that the manifestation of the two peaks with almost the same amplitude at 210 K is not merely due to the effect of pressure induced during sample preparation, pellets were prepared and pressed at different pressures (to a maximum pressure of 25 MPa). Based on the results obtained, at 210 K the two peaks are still observed indicating that such occurrence is not an artifact due to the effect of pressure induced during sample preparation.

In general, a continuous shift of absorption peak as a function of temperature would indicate conformational change.⁴ However, a discontinuous evolution of absorption peak due to temperature change would entail a different explanation. To exemplify this uncharacteristic behavior, a plot of the absorption peak frequency and transmitted THz radiation versus temperature is shown in Fig. 1(b). Initially the peak frequency shifts monotonically toward lower frequency accompanied by a continuous decrease in peak amplitude as the temperature is increased from 4 to 200 K. Then at 210 K, two broad peaks of almost equal amplitudes are observed and as plotted in Fig. 1(b) two different frequency points at a particular temperature. Here, it should be pointed out that the plot emphasizes the nonconstant evolution of the peak frequency and not a sudden change of peak frequency position.

Aside from this, it should be stressed that although the

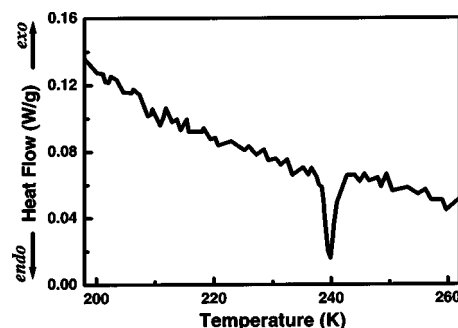


FIG. 2. DSC plot showing an endothermic peak at 240 K. Within the limitation of the instrument's resolution, no hysteresis is observed.

spectra at 200, 220, 230, and 240 K appear to be double peaked, the amplitudes of the low and high frequency peaks observed at each of these temperatures are distinctively different and that the behavior of the main peak (one with the highest amplitude) for each temperature reading is considered in the plot. Since the superposition of the peaks and influence of thermal energy distorts the spectra making the determination of the peak position difficult, plot smoothing is applied in order to approximate the position of the main peak. Such method is applicable due mainly to the distinct difference in the amplitude of the peaks. As for the THz-radiation power dependence, initially a steady increase of transmitted THz-radiation power is observed until 200 K. At 210 K, a sudden upsurge of THz radiation power is seen and later stabilized at around 240 K. These results cannot be explained by simply considering conformational change. A possible explanation is the occurrence of solid-state phase transition and that the onset of such phenomenon is at around 210 K. It should be pointed out that no hysteresis is observed in the measurement of the THz radiation power.

Differential scanning calorimetry (DSC) is conducted to verify this notion. Figure 2 shows that as the temperature is increased from 133 to 273 K, a peak at around 240 K is observed corresponding to an endothermic reaction. This confirms the occurrence of solid-state phase transition. Since a latent heat is absorbed, such phase transition is a first-order type. Also, the phase transition is reversible since the endothermic peak is observed at the same temperature upon heating and cooling the sample.

To get an insight into the structural change transpiring during the phase transition, temperature-dependence x-ray diffraction analysis (XRD) is performed. Room temperature XRD reveals that the sample is polycrystalline. Figures 3(a) and 3(b) show the XRD patterns at 50 and 300 K, respectively. In Fig. 3(a), the peaks centered at 16.7° (peak IA) and 25.0° (peak IB) are marked by a closed triangle and closed circle, respectively. The open triangle and open circle marked the peaks centered at 14.7° (peak IIA) and 23.6° (peak IIB), respectively. In Fig. 3(b), the closed triangle and closed circle are ascribed to peaks IA and IB. To clearly demonstrate the behavior of the 2θ peaks mentioned earlier, their temperature dependence is plotted in Fig. 3(c) using the same symbols as in Figs. 3(a) and 3(b). It can be seen here that peaks IA and IIA gradually shift toward lower 2θ while peaks IB and IIB remained almost constant as the temperature is increased to 230 K. As the temperature is further increased to 240 K, peaks IA and IIA exhibit an abrupt shift toward lower 2θ value. This event is simultaneous with the disappearance of peaks IIA and IIB. Clearly, such manifes-

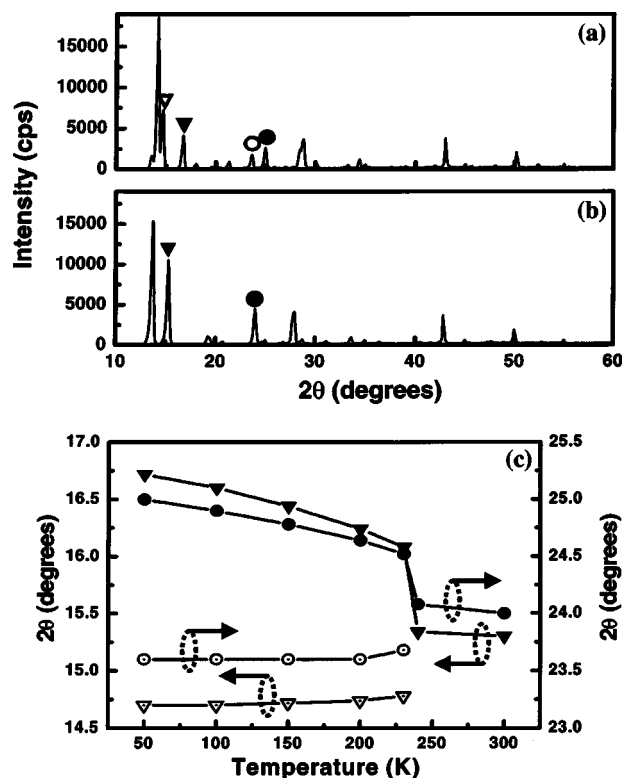


FIG. 3. XRD pattern of the sample at (a) 50 K and (b) 300 K. (c) Temperature dependence of the characteristic XRD peaks of 1,4-naphthol. These peaks are indicated by the same symbols used in (a) and (b). Whether the temperature was increased or decreased during the measurement, the same set of data was obtained indicating no hysteresis.

tation is not simply a conformational change but rather a phase transition. At room temperature, the crystal structure of 1,4-naphthol was determined to be orthorhombic $Pnma$ with four molecules in a cell of dimensions $a=12.67$, $b=12.95$, $c=4.80$ Å.¹⁵ Using a single crystal four-axes x-ray diffractometer, a more detailed description of the phase to which the sample transforms into can be determined. Such analysis is under way.

Here a remark on the difference of phase transition temperature observed by THz spectroscopy and that of DSC and XRD is presented. As the temperature is increased from 4 to 200 K, the molecule undergoes conformational change wherein possible hydrogen bond stretching may have occurred. At 210 K, a certain threshold of the hydrogen bonds is attained and it starts to break. This breaking of hydrogen bonds would then lead to the creation of free radicals, which would then look for new atoms to bond with. The breaking and reformation of bonds occurs simultaneously at this tem-

perature. This then would usher in the start of the phase transition until such phenomenon is completed at 240 K. It is likely that the phenomenon detected by the THz spectroscopy is merely the onset of the phase transition and not the actual phase transition itself since the operating energy range of THz spectroscopy is much lower than that of the energy required for the actual phase transition to occur. Lastly, the further broadening of the low frequency peak with increasing temperature might have been hindered because the molecule may have used some of the thermal energy for phase transition to occur.

In summary, it has been shown that solid-state phase transition in 1,4-naphthol indeed occurs at around 240 K, as shown by both DSC and XRD measurements. THz transmission spectroscopic analysis reveals that it can detect the onset of such phenomenon, which in this case is at around 210 K. This indicates that transmission spectroscopy in the THz region is a valuable tool and a sensitive technique in detecting solid-state phase transition since it provides a signal before the actual occurrence of such phenomenon.

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