Terahertz Spectroscopic Analysis of the Vermilion Pigment in Free-Standing and Polyethylene-Mixed Forms

Ji Eun Lee, Howon Lee, Jangwon Kim, Taek Sun Jung, Jae Ha Kim, Jonghyeon Kim, Na Yeon Baek, You Na Song, Han Hyoung Lee, and Jae Hoon Kim*

ACCESS | 📊 Metrics & More | 📖 Article Recommendations

ABSTRACT: Terahertz spectroscopy can be utilized as an effective nondestructive identification tool for the study of artist's pigments. Consequently, extensive measurements have been conducted on representative pigment species, and a few terahertz spectral databases have been constructed. However, the reported spectra were often acquired from pigment samples mixed with polyethylene at room temperature with low resolution, which often led to low-quality spectra with unresolved overlapping lines further broadened due to thermal effects. Here, we present our study of vermilion (HgS, mercury sulfide) as an illustration of how we can overcome such difficulties by studying free-standing oil-paint samples at room temperature and then by performing low-temperature measurements on polyethylene-mixed samples to minimize line broadening due to thermal effects. Our results identify clearly resolved absorption peaks due to lattice vibrations of vermilion at 40.4, 44.5, and 89.9 cm^{-1} at 2 K. The temperature dependence of the peak shift and line broadening reveals anharmonic characteristics of these lattice vibrational modes. Our approach will definitely suggest new ways to improve and enhance existing terahertz spectral databases of ancient and modern pigments toward actual analysis, diagnosis, and conservation of heritage artworks.
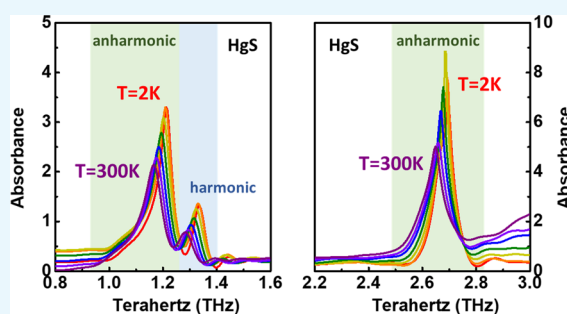
INTRODUCTION

Terahertz spectroscopy has recently established itself as a highly effective tool for studying historical and modern pigments.[1] The technique is nondestructive, a critical requirement for conservation and restoration of invaluable artworks, and is not hindered by the presence of fluorescence that often hampers Raman spectroscopy of pigments. Furthermore, due to its low-frequency nature, terahertz spectroscopy can unambiguously differentiate various pigment species by revealing their intermolecular vibrational modes (lattice modes and librational modes) rather than intramolecular vibrational modes (rotational-vibrational modes). This approximate description is quite useful in cases where the constituent molecules move nearly as rigid bodies. The intermolecular modes lie essentially in the terahertz range of 0.1−3 THz, while the intramolecular modes appear at higher frequencies in the mid-infrared range where molecular species common to many pigments exhibit rather similar absorption features.

This fingerprinting capability of terahertz spectroscopy is highly advantageous in efficient identification of ancient and modern pigments. Consequently, a number of representative pigments, such as azurite,[2−6] malachite,[3−5,7] verdigris,[5,7] and magenta,[8,9] have been extensively studied in the terahertz range, and a few spectral databases have been established at various institutes around the world.[10] However, in these data sets, most often, only transmission spectra are given, which include rather distorted spectral features of individual absorption lines. In fact, for accurate spectral analysis, both the absorption coefficient α (equivalently, the extinction coefficient k) and the refractive index n are needed for each pigment species. Furthermore, most existing terahertz databases of pigments contain only room-temperature spectra where a substantial broadening of all spectral lines is inevitable. This is especially relevant to our efforts to connect the experimental data to density functional theory (DFT) calculations frequently performed on crystal structures stabilized at absolute zero without consideration of thermal broadening.[5,9,11,12] Consequently, closely spaced or nearly overlapping absorption lines are not amenable to accurate mode assignments based on DFT. Additionally, the anharmonic nature of some lattice vibrational modes predicted by DFT needs to be unveiled experimentally in the absence of thermal broadening at elevated temperatures. All these
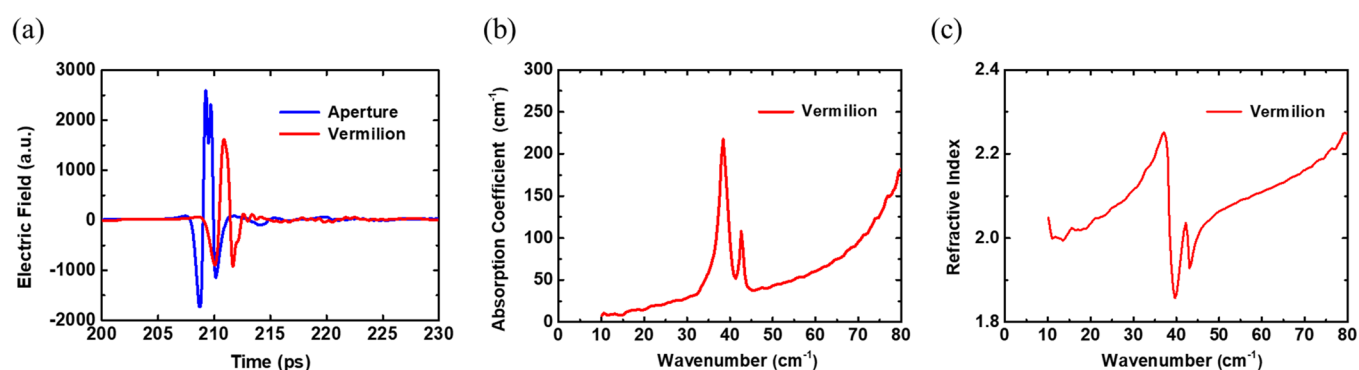
Figure 1. (a) Terahertz electric field waveforms transmitted through the reference aperture (blue) and vermilion oil paint (red) in free-standing sample form. (b) Terahertz absorption coefficient spectrum of vermilion oil paint in free-standing sample form. (c) Terahertz refractive index spectrum of vermilion oil paint in free-standing sample form.
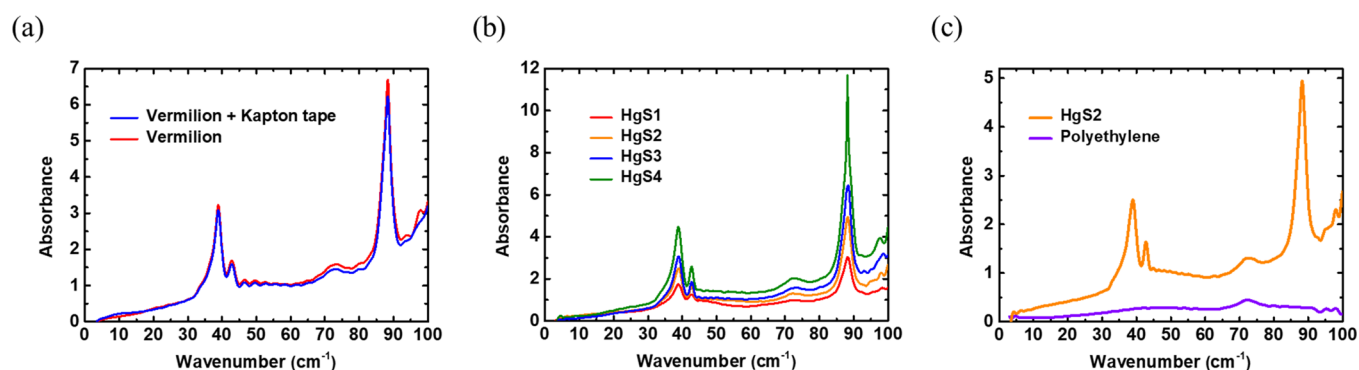

Figure 2. (a) Terahertz absorption spectra of vermilion-polyethylene (PE) pellet HgS3 with Kapton tape (blue) and without Kapton tape (red) on the sample backside. (b) Terahertz absorption spectra of vermilion-polyethylene (PE) pellet samples (HgS1, HgS2, HgS3, and HgS4) with varying vermilion:PE weight ratios ranging from 1:20 to 1:23 (see Table 1). The absorption of HgS4 clearly shows clipping and distortion associated with the third absorption peak at 88.1 cm^{-1}. (c) Absorbance spectra of the vermilion-PE pellet HgS2 and a pure polyethylene pellet.

problems can be solved by performing temperature-dependent measurement and analysis of absorption peaks and their spectral lineshapes. In this context, a recent terahertz study on the amino acid glycine also stresses the importance of low-temperature measurements on intrinsic samples.[13,14]

Here, we report on our terahertz spectroscopic study of vermilion (HgS, mercury sulfide), a representative pigment possessing a set of signature absorption bands in the terahertz range. A recent DFT calculation performed by Kleist and Korter[12] predicted three absorption peaks at 35.08, 46.52, and 90.61 cm^{-1}, which were assigned to the lattice vibrational modes of the transverse optical (TO) type corresponding to A$_2$, E, and E symmetries, respectively. Previous experiments indeed detected the presence of these three absorption peaks near the corresponding frequencies.[7,12,15−17] However, the two lowest modes were not clearly resolved in some early measurements performed at low resolution due to the much weaker intensity of the second peak, which even led to some doubt about the reality of this peak itself. The detailed nature of intrinsic lineshapes and line broadening has not been seriously discussed either. We have effectively resolved these issues by performing temperature-dependent terahertz time-domain spectroscopy (THz-TDS), which yielded accurate spectra of the refractive index and absorption coefficient of vermilion. Our new analysis identified clearly distinguished double-peak features at 38.4 and 42.6 cm^{-1} in vermilion at room temperature, consistent with the aforementioned DFT calculations, and assisted us in understanding the nature of

their lineshapes and broadening mechanisms. Overall, our results demonstrate an effective method for characterizing detailed low-frequency spectral features of representative pigments by using terahertz time-domain spectroscopy with temperature control, thereby indicating ways to help construct an improved terahertz database of ancient and modern pigments.

■ RESULTS AND DISCUSSION

Free-Standing Sample and Room-Temperature Spectra. Figure 1a shows the terahertz electric field waveforms transmitted through the reference aperture (blue) and vermilion oil paint (red) in free-standing sample form. The corresponding absorption coefficient and refractive index spectra are presented in Figure 1b and Figure 1c, respectively. These spectra represent intrinsic optical characteristics of vermilion in the terahertz range. The refractive index of vermilion is about 2 in the terahertz range, and there is a 20% variation across the band of dispersion corresponding to the two strong absorption peaks at 38.4 and 42.6 cm^{-1} at room temperature that appear in the extinction coefficient. The accurate value of the refractive index should be useful in determining the real-space thickness of a vermilion layer from terahertz reflection imaging of actual artworks. The two strong peaks at 38.4 and 42.6 cm^{-1} are clearly distinguished in our experiment carried out with a resolution of 0.43 cm^{-1}. According to a recent DFT calculation, the transverse optical modes corresponding to A$_2$, E, and E symmetries should
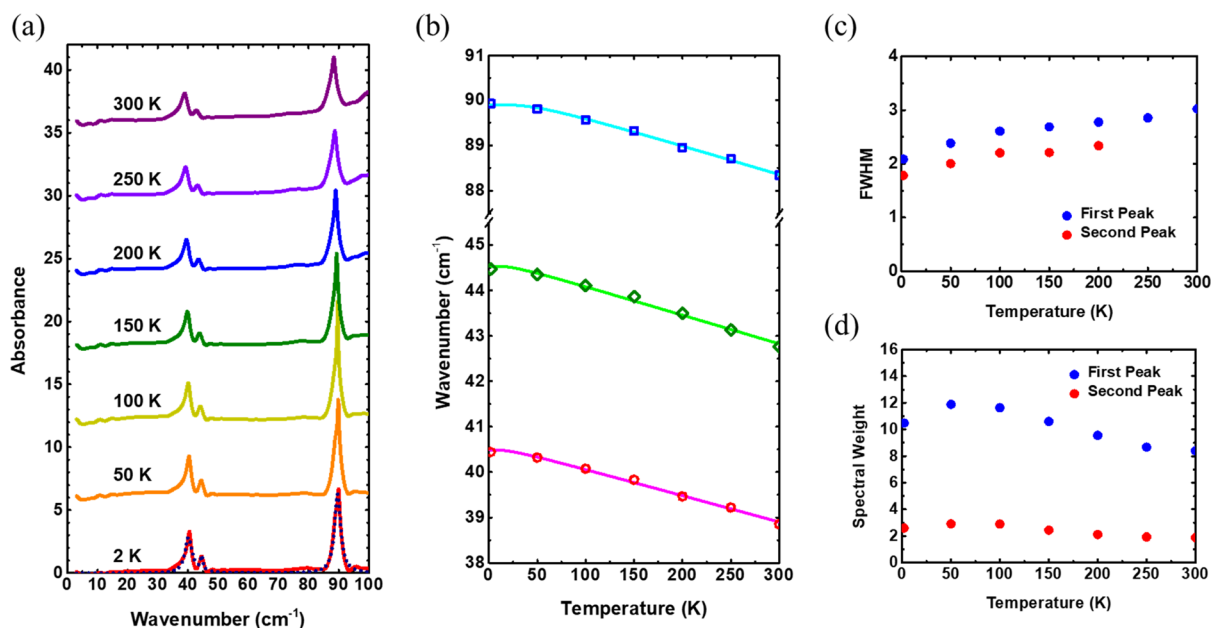
Figure 3. (a) Terahertz absorption spectra of vermilion-polyethylene (PE) pellet HgS3 over the temperature range of 2−300 K normalized against those of a reference pure PE pellet. Spectra were systematically shifted vertically for clarity. For the 2 K spectrum, its Lorentzian fit (dotted line) is also given. (b) Temperature dependence of the peak positions of the three major absorption lines (symbols) with anharmonic decay model fits (solid lines). At 2 K, the three main peaks are found at 40.4, 44.5, and 89.9 cm^{-1}. The three peaks redshift with increasing temperature and appear at 38.8, 42.8, and 88.3 cm^{-1} at 300 K. Note a break in the vertical scale. (c) Temperature dependence of the linewidths (FWHM: full width at half-maximum) of the first two major absorption peaks (symbols). For the second peak, the linewidths at 250 and 300 K cannot be reliably determined (see text). (d) Temperature dependence of the spectral weight of the first two major absorption peaks (symbols).

appear at 35.08, 46.52, and 90.61 cm^{-1}, respectively.[12] The two experimentally observed peaks at 38.4 and 42.6 cm^{-1} fairly well match these DFT predictions. The spectral weight of the 38.4 cm^{-1} peak is at least 4 times stronger than that of the 42.6 cm^{-1} peak. The power-law type background absorption is probably due to scattering loss commonly found in inhomogeneous media, and it masks the 88.1 cm^{-1} peak of vermilion that is found in our measurements on an optimized pellet sample HgS3 (Figure 2a).

For low-temperature measurements to be described later, we need a polyethylene (PE) matrix to stabilize vermilion at low temperature and Kapton tape to affix the vermilion-PE pellets onto a copper sample holder. To check if these additional components add any spectral features in the terahertz range, we performed additional room-temperature terahertz transmission measurements on HgS3 with and without Kapton tape (Figure 2a). From this, we conclude that Kapton tape does not modify the absorption spectrum in any serious way. This information is important when we examine the low-temperature spectra of vermilion-PE pellet samples. To acquire robust absorption spectra of highly absorbing samples, we should carefully avoid clipping of absorption peaks and distortion of their lineshapes that arise from a very small transmissivity level near a strong absorption peak. This amounts to optimization of the vermilion-PE weight ratio of our pellet samples. Figure 2b shows the absorption spectra of our four vermilion-PE pellet samples with varying vermilion-PE weight ratios. The HgS1 and HgS2 samples were prepared with a vermilion:PE weight ratio of 1:23 but with thicknesses of 1.7 and 3.2 mm, respectively, and HgS3 and HgS4 were prepared with a weight ratio of 1:20 and thicknesses of 3.4 and 5.1 mm, respectively. The weight ratio and thickness were selected in such a way that all three major absorption peaks of vermilion in the terahertz range of 0.1−3 THz can be clearly observed. The absorption

spectrum of HgS4 actually exhibits clipping and distortion associated with the 88.1 cm^{-1} peak. This is due to a very low level of transmissivity at this frequency, which was about 0.01% in our experiment. In fact, the absorption spectrum shows a needle-like narrowing near the peak, which distorts the entire lineshape, hampering reliable analysis based on, e.g., Lorentzian fitting. For this reason, we adopted HgS3 for our low-temperature study, which does not seem to possess anomalous features such as those found in HgS4. The absorbance of a pure PE pellet with a thickness of 2.76 mm was measured separately to determine the origin of the small band found between 70 and 75 cm^{-1}. As shown in Figure 2c (purple), a small peak at 72 cm^{-1} was observed in the pure PE pellet, which shows that the small peak at 72 cm^{-1} present in our vermilion-PE pellet samples comes from the PE component.

Low-Temperature Spectra. We now move on to the discussion of low-temperature spectral data. Figure 3a shows the temperature-dependent terahertz absorption spectra of vermilion:PE pellet HgS3 measured over the temperature range of 2−300 K. In the absence of any structural phase transitions, we do not observe the appearance of new modes or splitting of the existing modes. As expected, the first two major absorption peaks are now more clearly distinguished as their intensities grow and their linewidths narrow as the temperature is lowered. Our low-temperature data removes any doubt about the presence of the second peak. Figure 3b shows the temperature dependence of the frequency positions of the three major absorption peaks. All three peaks blueshift monotonically with decreasing temperature. The observed temperature dependence is quite consistent with the anharmonic decay model, as shown by the excellent fits in Figure 3b (solid lines).[13,14,18] In addition, Figure 3c shows the temperature dependence of the linewidths (FWHM, full width

at half-maximum) of the first two major absorption lines. Their monotonic increase with increasing temperature is again consistent with the anharmonic decay model, although the detailed functional form (i.e., linear vs exponential) cannot be identified with data limited to the temperature range below 300 K. For the second peak, its linewidths at 250 and 300 K cannot be readily determined as it overlaps substantially with the first peak at these elevated temperatures. Unfortunately, the linewidth analysis of the third peak turned out to be difficult due to its rather anomalous lineshape. We also estimated the strength of the first two major peaks as a function of temperature. Figure 3d shows the temperature-dependent spectral weight of the first and second peak. The spectral weight essentially increases as the temperature is reduced as expected. The spectral weight is extracted from the experimental absorbance data by numerical integration.

Our low-temperature data provide us with a valuable opportunity to examine the intrinsic lineshapes of the relevant lattice vibrational modes independent of thermal broadening. Figure 3a shows our lineshape analysis of the 2 K absorption spectrum of vermilion. As shown, the first and third absorption peaks cannot be fitted to a Lorentzian function, which confirms that these two modes possess substantial anharmonic characteristics. We tried Voigt and Gaussian fits, neither of which could reproduce the experimentally measured lineshapes of these two peaks in a satisfactory manner. It will be useful to compare our findings with the DFT analysis of the corresponding modes in vermilion as given by Kleist and Korter,[12] although anharmonicity was not explicitly mentioned in their work. In contrast, the second peak can be reasonably well fitted to a Lorentzian function, even at low temperatures. We note that the second mode involves mostly the displacement of the Hg atom roughly along the b axis without a relatively large displacement of the S atom. This rather simple vibrational pattern may lead to a Lorentzian lineshape. In comparison, the highly complex vibrational patterns of the first and third peaks involving both the Hg and S atoms in large displacements through narrow crystallographic channels[12] probably result in their anharmonic characteristics and anomalous lineshapes, as shown in our low-temperature spectra. More research is needed to further clarify this point.

CONCLUSIONS

In conclusion, we presented an effective way to determine the refractive index and extinction coefficient of vermilion at room temperature by performing terahertz time-domain spectroscopy (THz-TDS) on free-standing samples and a series of low-temperature measurements to reliably examine the temperature dependence of the positions and linewidths of the three major absorption peaks of vermilion in the terahertz range. We were able to resolve an existing controversy on the low-frequency double-peak structure and identify possible anharmonic characteristics of these vibrational modes by a lineshape analysis at low temperatures. Our results should be useful for informative terahertz reflection imaging of artworks and for an enhanced terahertz database of artist's pigments to be utilized in the analysis, diagnosis, and restoration of cultural heritage materials.

MATERIALS AND METHODS

Sample Preparation. We prepared two types of vermilion (HgS, color index number: PR106) samples. The first type is

vermilion oil paint (Extra Fine Artists' Oil Color Series, Holbein, H215) in free-standing form used for room-temperature measurements. This first type of sample will mimic vermilion layers after their brushwork on the surface of actual artworks. To mount these free-standing oil paint samples, a circular aperture of a depth of 0.42 mm and a diameter of 0.5 mm was cut out from a copper plate and then filled with vermilion oil paint, which stayed within the aperture space during room-temperature measurements owing to its high innate viscosity. The second type is a vermilion pigment (Holbein, PG209) mixed with polyethylene (PE) powder and pressed into tablet form. The tablets were subsequently pressed under a weight of 10 tons for 1 min into pellet form prior to their low-temperature terahertz transmission measurements. The PE matrix was there to stabilize vermilion in the low-temperature vacuum environment without disrupting the absorption features of vermilion in the terahertz range. A reference pellet of pure PE was also prepared under the same conditions. The thicknesses of the pellets were measured with a micrometer, and they ranged from 1.7 to 5.1 mm. More details on these pellet samples (HgS1, HgS2, HgS3, and HgS4) are given in Table 1.

Table 1. Our Second Type Sample of Vermilion Mixed with Polyethylene (PE) Powder in Pellet Form Prepared for Low-Temperature Measurements[a]

sample number	vermilion weight (mg)	polyethylene weight (g)	vermilion:PE weight ratio	thickness (mm)
HgS1	44	1.05	1:23	1.7
HgS2	44	1.05	1:23	3.2
HgS3	55	1.10	1:20	3.4
HgS4	55	1.10	1:20	5.1

[a]The sample number, the vermilion weight, the PE weight, and their weight ratios are listed along with the thicknesses of the pellets used (HgS1, HgS2, HgS3, and HgS4).

Terahertz Measurements. Room-temperature terahertz transmission measurements were conducted on a Teraview TPS3000 (Teraview Ltd., UK) in the frequency range of 0.1−3 THz. A femtosecond laser delivered 70 fs pulses centered at a wavelength of 800 nm at a repetition rate of 80 MHz. Terahertz radiation was generated and detected by photoconductive switches fabricated on low-temperature grown GaAs. Low-temperature terahertz transmission measurements were carried out with a TERA K15 (Menlo Systems GmbH, Germany) equipped with a helium closed cycle magneto-optical cryostat of a SpectromagPT (Oxford Instruments Ltd., UK). A femtosecond laser delivered 90 fs pulses centered at 1560 nm with a 100 MHz repetition rate. The terahertz radiation was produced by an InGaAs photoconductive emitter, and two TPX (polymethylpentene) lenses were used to collimate and focus the radiation onto the sample. A similar setup was used in the detection path in the reverse order with an InGaAs photoconductive receiver. The SpectromagPT system provided a capacity to control the temperature from 1.5 to 300 K and the magnetic field from 0 to 7 T. All measurements were carried out in dry nitrogen or in vacuum to remove the water vapor absorption. Our terahertz time-domain spectroscopy (THz-TDS) technique employed in both spectrometers yielded raw data in the form of time-dependent waveforms of the electric field, and these were converted into complex-valued functions of frequency through Fourier

transform. Both the refractive index n and the extinction coefficient k were reliably determined for our free-standing vermilion samples. For pellet samples for low-temperature measurements, only the absorption coefficients were extracted from their transmission spectra via the usual formula $\alpha = -(1/d)\ln(T)$, where α is the absorption coefficient, d is the thickness of the sample, and T is the transmissivity. For pellet samples, the corresponding refractive index was not considered as it will sensitively depend on the microstructure and the mixing ratio of PE.

AUTHOR INFORMATION

Corresponding Author

Jae Hoon Kim − *Department of Physics, Yonsei University, Seoul 03722, Republic of Korea;* ○ orcid.org/0000-0002-7840-3630; Email: super@yonsei.ac.kr

Authors

Ji Eun Lee − *Department of Physics, Yonsei University, Seoul 03722, Republic of Korea*

Howon Lee − *Department of Physics, Yonsei University, Seoul 03722, Republic of Korea*

Jangwon Kim − *Department of Physics, Yonsei University, Seoul 03722, Republic of Korea*

Taek Sun Jung − *Department of Physics, Yonsei University, Seoul 03722, Republic of Korea*

Jae Ha Kim − *Department of Physics, Yonsei University, Seoul 03722, Republic of Korea*

Jonghyeon Kim − *Department of Physics, Yonsei University, Seoul 03722, Republic of Korea*

Na Yeon Baek − *Graduate School of Cultural Heritage, Korea National University of Cultural Heritage, Buyeo 33115, Republic of Korea*

You Na Song − *CON-TECH, Korea National University of Cultural Heritage, Buyeo 33115, Republic of Korea*

Han Hyoung Lee − *CON-TECH, Korea National University of Cultural Heritage, Buyeo 33115, Republic of Korea*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.1c01336

Author Contributions

J.E.L. and Jonghyeon Kim designed the study and performed the terahertz transmission measurements. H.L. characterized the free-standing vermilion samples. Jangwon Kim and T.S.J. carried out the numerical simulations. J.E.L. and Jae Ha Kim analyzed the data. Y.N.S. and N.Y.B. prepared the vermilion samples. Jae Hoon Kim and H.H.L. guided the research. All authors read and approved the final manuscript.

Notes

The authors declare no competing financial interest.

ABBREVIATIONS

DFT, density functional theory; PE, polyethylene; THz-TDS, terahertz time-domain spectroscopy; TO, transverse optical; FWHM, full width at half-maximum

REFERENCES

(1) Fukunaga, K. *THz Technology Applied to Cultural Heritage in Practice*; Springer: Tokyo, 2016.

(2) Ha, T.; Lee, H.; Sim, K. I.; Kim, J.; Jo, Y. C.; Kim, J. H.; Baek, N. Y.; Kang, D.-i.; Lee, H. H. Optimal methodologies for terahertz time-domain spectroscopic analysis of traditional pigments in powder form. *J. Korean Phys. Soc.* **2017**, *70*, 866−871.

(3) Hong, T.; Choi, K.; Ha, T.; Park, B. C.; Sim, K. I.; Kim, J. H.; Kim, J. H.; Kwon, J. E.; Lee, S.; Kang, D. I.; Lee, H. H. Terahertz time-domain and Fourier-transform infrared spectroscopy of traditional Korean pigments. *J. Korean Phys. Soc.* **2014**, *64*, 727−731.

(4) Li, C. Y.; Shi, N. C.; Li, G. H.; Zhang, Z. W.; Gu, A.; Lei, Y.; Zhang, C. L. Study of the Traditional Chinese Pigments by Terahertz Time-Domain and Fourier-Transform Infrared Spectroscopy. *Appl. Opt.* **2017**, *10459*, 8.

(5) Kleist, E. M.; Koch Dandolo, C. L.; Guillet, J. P.; Mounaix, P.; Korter, T. M. Terahertz spectroscopy and quantum mechanical simulations of crystalline copper-containing historical pigments. *J. Phys. Chem. A* **2019**, *123*, 1225−1232.

(6) Panzner, M. J.; Klotzbach, U.; Beyer, E., Torosyan, G.; Schmid, A.; Köhler, W. THz-Time-Domain Spectroscopy - A new tool for the analysis of artwork. In: Radvan, R.; Asmus, J. F.; Castillejo, M.; Pouli, P.; Nevin, A. (eds.) *Lasers in the Conservation of Artworks VIII*, pp.167−171. CRC Press (2010).

(7) Bardon, T.; May, R. K.; Jackson, J. B.; Beentjes, G.; de Bruin, G.; Taday, P. F.; Strlič, M. Contrast in Terahertz Images of Archival Documents-Part I: Influence of the Optical Parameters from the Ink and Support. *J. Infrared, Millimeter, Terahertz Waves* **2017**, *38*, 443−466.

(8) Squires, A. D.; Kelly, M. T.; Lewis, R. A. Terahertz Analysis of Quinacridone Pigments. *J. Infrared, Millimeter, Terahertz Waves* **2017**, *38*, 314−324.

(9) Squires, A. D.; Lewis, R. A.; Zaczek, A. J.; Korter, T. M. Distinguishing Quinacridone Pigments Via Terahertz Spectroscopy: Absorption Experiments and Solid-State Density Functional Theory Simulations. *J. Phys. Chem. A* **2017**, *121*, 3423−3429.

(10) http://www.thzdb.org/ (accessed Feb 25, 2021)

(11) Ruggiero, M. T.; Bardon, T.; Strlic, M.; Taday, P. F.; Korter, T. M. Assignment of the Terahertz Spectra of Crystalline Copper Sulfate and Its Hydrates Via Solid-State Density Functional Theory. *J. Phys. Chem. A* **2014**, *118*, 10101−10108.

(12) Kleist, E. M.; Korter, T. M. Quantitative Analysis of Minium and Vermilion Mixtures Using Low-Frequency Vibrational Spectroscopy. *Anal. Chem.* **2019**, *92*, 1211−1218.

(13) Allen, J. L.; Sanders, T. J.; Horvat, J.; Lewis, R. A. Anharmonicity-driven redshift and broadening of sharp terahertz features of α-glycine single crystal from 20 K to 300 K: Theory and experiment. *Spectrochim. Acta, Part A* **2021**, *244*, 118635.

(14) Sanders, T. J.; Allen, J. L.; Plathe, R.; Horvat, J.; Lewis, R. A. The 3, 5, 6, and 7 THz resonances of α-glycine. *Spectrochim. Acta, Part A* **2021**, *253*, 119544.

(15) Yang, Y.; Zhai, D.; Zhang, Z.; Zhang, C. THz Spectroscopic Identification of Red Mineral Pigments in Ancient Chinese Artworks. *J. Infrared, Millimeter. Terahertz Waves* **2017**, *38*, 1232−1240.

(16) Fukunaga, K.; Picollo, M. Terahertz Spectroscopy Applied to the Analysis of Artists' Materials. *Appl. Phys. A: Mater. Sci. Process.* **2010**, *100*, 591−597.

(17) Zallen, R.; Lucovsky, G.; Taylor, W.; Pinczuk, A.; Burstein, E. Lattice vibrations in trigonal HgS. *Phys. Rev. B* **1970**, *1*, 4058−4070.

(18) Kato, K.; Oguri, K.; Sanada, H.; Tawara, T.; Sogawa, T.; Gotoh, H. Determination of phonon decay rate in p-type silicon under Fano resonance by measurement of coherent phonons. *AIP Adv.* **2015**, *5*, No. 097152.