

Interpreting the Low-frequency Vibrational Fingerprints of Crystalline Pigments

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Terahertz (THz) and low-frequency Raman spectroscopies are promising tools in art conservation and restoration. They provide non-invasive and non-destructive methods for revealing chemically specific data concerning the composition and condition of culturally or historically valuable objects. Experimental THz and Raman spectral databases of modern and ancient artists' pigments exist, but lack explanations for the origins of the unique spectral features. Rigorous assignment of the spectra in these pigment databases will aid their rational construction. Solid-state density functional theory (DFT) simulations can provide insight into these absorption features and the molecular and intermolecular forces that dominate them. In this study, two inorganic metal-containing pigments, mercury sulfide (vermilion) and lead (II, IV) oxide (minium), were investigated using a combination of THz time-domain spectroscopy, low-frequency Raman spectroscopy, and solid-state DFT to fully characterize the sub-200 cm^{-1} vibrations in these crystalline pigments. Complete assignment of both experimental spectra for each pigment was achieved via solid-state DFT simulations that revealed the significance of longitudinal optical/transverse optical (LO/TO) phonon splitting in providing high-quality spectral reproductions.