IARPA MORGOTH'S CROWN: Summary of Phenomenology That Affects Infrared Spectral Signatures

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Summary of the Physical Basis of Variations in Infrared Spectroscopic Signatures

The specific details of reflectance spectra depend on (1) intrinsic material physical properties that govern the light/matter interactions in that material and (2) extrinsic geometric properties of the material, its surroundings, and the illumination and viewing angles. Intrinsic effects explored within this report include material properties that are dependent on thermodynamic state and molecular level interactions (specifically those due to adsorption onto a substrate, varying degrees of hydration, and interactions within solutions). Important extrinsic factors include particle size effects, optically thin material mixtures, sample morphology dependence, and illumination and viewing geometries:

- Thermodynamic State: When temperature or pressure variations result in either molecular conformational changes or phase changes, the shape and location of spectral features can change dramatically. For mixtures of reacting species, the temperature dependence of the reaction's equilibrium constant will lead to adsorption spectra variations driven by the mixture's changing composition. Materials with anharmonic intermolecular potentials experience shifts in spectral feature locations and changes in feature widths as temperature and pressure vary.
- Molecular Level Interactions: All forms of molecular level interactions introduce changes in the location and shape of a compound's spectral features. Additionally, the novel interactions provided by the secondary species (whether the substrate, solvent, or sorbed water molecules) can lead to the appearance of new spectral features or to the disappearance of some features due to bonding geometries. Relative concentrations of the participating species affect both the quantitative and qualitative nature of spectral feature variations.
- Extrinsic Factors: The scattering optical depth of a sample depends on the density and spatial-scale of inhomogeneities in the media. The absorption optical depth depends on the total amount of the media that light waves are able to propagate through. Higher density, smaller-scale inhomogeneities tend to increase overall sample reflectance, while the corresponding change in spectral feature depth and width depends on whether the material is optically thick or thin on the spatial scale set by the inverse of the inhomogeneity density.

Non-monotonic feature depth/width changes can occur as the inhomogeneity density varies monotonically. For mixtures involving optically thin component media, the mixture spectrum typically evolves non-linearly between the pure component spectra as a function of mixture composition and it is not uncommon for the mixture spectrum to not be bounded by the component spectra over at least some wavelength range. Variations in spectral contrast and overall spectral shape typically are present as illumination and viewing angles change.

The attached report from the MITRE Corporation provides a detailed literature review of the underlying physical phenomenologies for variations in infrared spectroscopic signatures.