NANO-IR OPTICAL CONSTANTS AND MODEL OF FAR-FIELD SPECTRA FOR LINK BETWEEN FAR-FIELD AND NEAR-FIELD SPECTRAL FEATURES. O. L. Koren¹, T. D. Glotch¹, I. Vararathanjan¹, M. Tsuneto¹, X. Chen¹, L. Flores¹, Stony Brook University.

Introduction: Near-field infrared (nano-IR) imaging and spectroscopy is an ideal technique for mineral identification and analysis due to its ability to characterize and identify fundamental vibrational modes of minerals, glasses, and organics with a high signal to noise ratio (>50). Nano-IR instruments can achieve a spatial resolution of 20 nm or less by using atomic force microscopy (AFM). Analysis of nano-IR data can be challenging due to differences from traditional infrared spectroscopic data caused by strong probe-sample interactions in the near-field [1]. We look to find a link between the near-field and far-field spectral features to provide insight on future nano-IR analysis.

Methods: For direct comparisons between near and far-field spectra, amorphous glasses are optimal because spectra can be taken at any orientation and there are relatively few features to compare. The 6 glass samples chosen for this study include basalt, andesite, dacite, obsidian, rhyodacite, and rhyolite compositions. The samples were polished and near-field infrared spectra were taken using the neaspec neaSNOM nano-FTIR instrument in the Center for Planetary Exploration at Stony Brook University. This instrument covers the spectral range from 1.54 - 15.4 μm at 3.3 cm⁻¹ spectral sampling, comparable to that of typical laboratory mid-infrared (MIR) far-field spectral sampling. Traditional far-field reflectance spectra were acquired using a Nicolet iN10MX FTIR microscope with a deuterated triglycine sulfate (DTGS) detector [6]. The spectra produced by the micro-FTIR and the nano-IR can both be used to calculate the real (n) and imaginary (k) indices of refraction of each glass sample.

Several different methods can be used to calculate the optical constants from nano-IR data that provide quantitative predictability. These methods include a reversed finite-dipole model, a conformal mapping method, and a generalized spectral method [2]. The main difference between these methods is the modeled approximated shape of the AFM tip used to collect the nano-IR spectra. The reversed finite-dipole model approximates the tip as a spheroid [3] whereas the generalized spectral method approximates the tip as a prolate spheroid [4]. The conformal mapping method however approximates the tip as a cone [5].

Using the reversed finite-dipole method a program can be developed to calculate n and k. The near-field can be modeled as a finite dipole with two point charges, Q_0 and -Q_0. Q_0 is a point near the sample surface that induces near-field interaction that polarizes the spheroid. By approximating the charge redistribution as a point charge, Q, and a uniform charge distribution -Q, on the spheroid, a solution can be found. The resulting relationship is

\[ E_{\text{scat}} \propto (1 + r_p^2) \alpha_{\text{eff}} E_{\text{inc}} \]  

(1)

where \( r_p \) is the fresnel reflection coefficient for p-polarized light and \( \alpha_{\text{eff}} \) is the effective polarizability [3]. The program can estimate the parameters of a Lorentz oscillator model and uses them in a finite dipole model for tip-sample interaction to calculate the dielectric constant, \( \varepsilon = \varepsilon_1 + \varepsilon_2 \) and \( \varepsilon_b \) and \( \varepsilon_\alpha \) can then be used to calculate the \( n \) and \( k \) values[7]:

\[ n = \left( \frac{1}{2} \left[ \left( \varepsilon + \varepsilon_2 \right)^{1/2} + \varepsilon_\alpha \right] \right)^{1/2} \]  

(2.1)

\[ k = \left( \frac{1}{2} \left[ \left( \varepsilon + \varepsilon_2 \right)^{1/2} - \varepsilon_\alpha \right] \right)^{1/2} \]  

(2.2)

This code utilizes a 1-dimensional convolutional neural network system where different kernel widths capture different peak widths.

The optical constants calculated can be used to model far-field spectra. This can provide a direct comparison to the measured far-field spectra and inform us more on the fundamental differences between near- and far-field spectra. Using the far-field spectra collected by the micro-FTIR we can directly compare optical constants derived from nano-IR measurements with those derived from traditional reflectance measurements. The far-field modeled spectrum can be calculated using the Fresnel equation. When the angle of incidence is equal to zero, the Fresnel equation simplifies to [8]:

\[ R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \]  

(3)

Comparing the spectra will help infer how accurate the near-field optical constant calculation is. The more similar the spectra, the more accurate the calculation.

Results: Nano-IR images and spectra of each glass sample were collected using both silica and gold
standard as reference. These references were found to be functionally identical and therefore the silica standard has been used for analysis of this study. Figure 1 compares the amplitude of the nano-IR measurements to the reflectance of the micro-FTIR measurements.

The shapes of the nano-IR and micro-FTIR spectra in Figure 1 are somewhat similar with strong peaks around 1000-1100 cm⁻¹. The peaks of the far-field spectra are observed at higher wavenumbers than the near-field spectra. The far-field spectra also show more defined, narrow peaks compared to the broad peaks of the near-field spectra.

We observe trends in both the near-field and far-field showing peaks at higher wavenumbers with higher silica content.

Figure 2: Two plots of the near-field and far-field optical constants, the left plot displays the real index of refraction (n) and the right plot displays the imaginary index of refraction (k).

Figure 2 compares the optical constants calculated by the near and far-field spectra of the obsidian sample. The near-field calculations displayed in this plot were calculated using the reverse finite-dipole method. There are clear similarities between the near and far-field calculations with room to further improve the model.

Figure 3 displays the measured far-field reflectance and the modeled far-field reflectance calculated from the near-field optical constants of the obsidian glass. The peaks do match up at the same wavelength but the features are not completely modeled, notably the shoulder between 1200-1300 cm⁻¹.

Conclusions and Future Work: Being able to make connections between the near and far-field can help us better understand measurements and quantitatively link near-field measurements with bulk far-field spectra, including telescopic and spacecraft-based infrared remote sensing measurements.

Following success using the reverse finite dipole method to calculate the n and k values, additional calculation methods will be considered for comparison. This includes the conformal mapping method or a generalized spectral method.

Nano-IR will be a particularly useful technique for analysis of samples returned from asteroid 162173 Ryugu because of its ability to characterize hydration states and nano-scale mineralogy and organics. The nano-IR instrument is also non-invasive and it can provide high spatial resolution analyses of small samples/grains/dust particles. Conclusions drawn from this analysis will address one of the main goals of the Hayabusa2 mission: the formation of Ryugu and the conditions of the early solar system.

References: