

In Operando Optical Measurements of Sodium Battery Electrolytes

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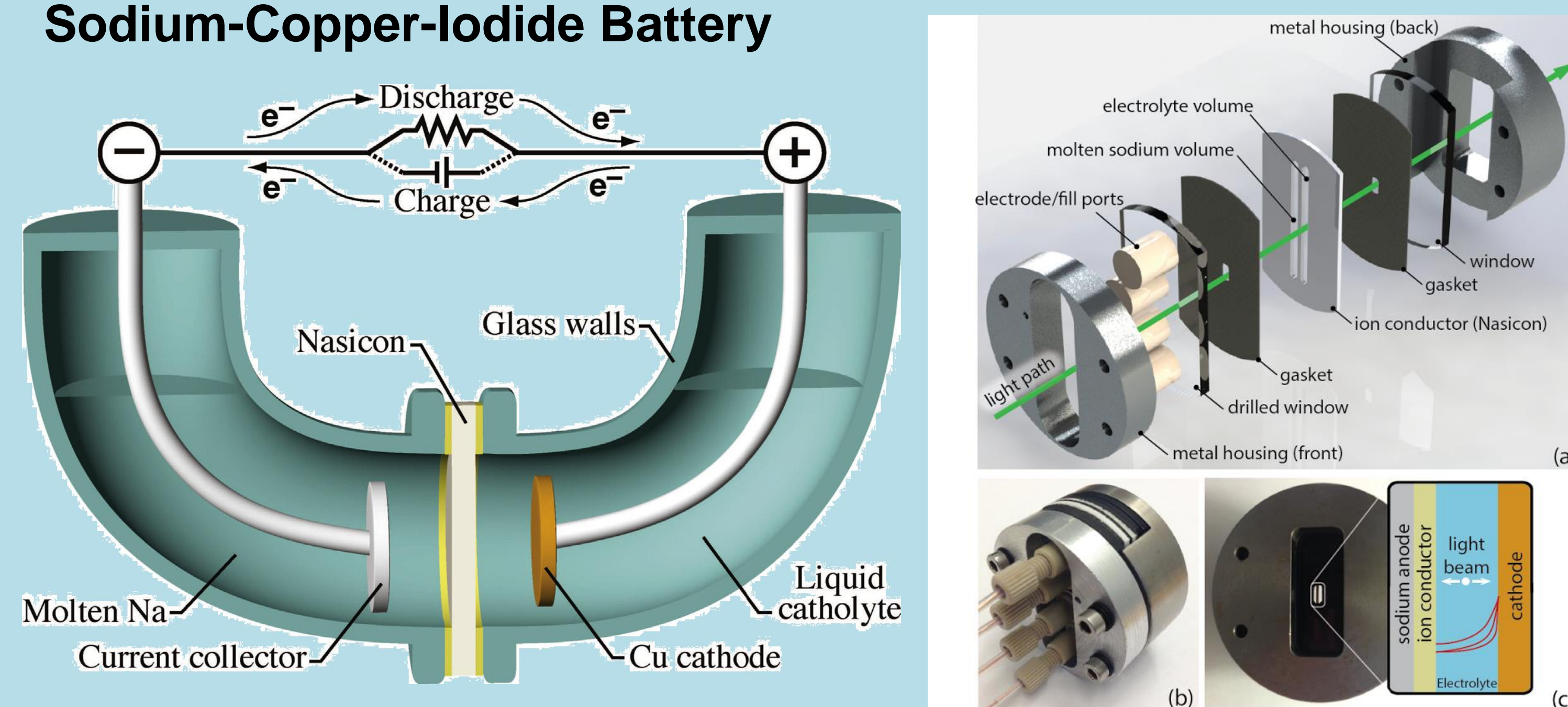
Computational Battery Chemistry Models

Chemical processes that govern the charging and discharging behavior of batteries are typically understood based on computational models tailored to fit reaction potentials of the species present in the battery cell. These models are derived from current and voltage measurements taken during operation, and while they provide valuable insight they can be subject to ambiguity. In the case of the Sodium-Copper-Iodide secondary battery, Cathode chemistry is assumed to be dominated by the CuI_2^- species. However, the model used can accommodate alternative reaction pathways, including a CuI centric cathode reaction.

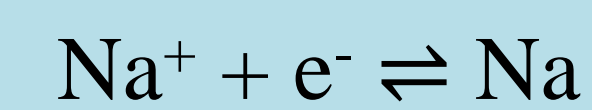
Real Time Observation of Battery Chemistry

By using a specially designed battery cell equipped with optical windows, it is possible to take spectroscopic measurements of operating electrolytes in order to physically observe the formation and transport of chemical species responsible for charge and discharge mechanics. This technology is modular, and can be used to study various battery designs and spectral ranges in order to determine optimal electrolyte compounds and operating conditions to minimize or eliminate the formation of unwanted species during battery cycling.

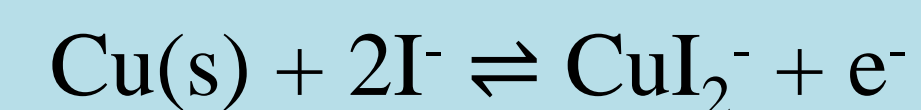
Sodium-Copper-Iodide Battery



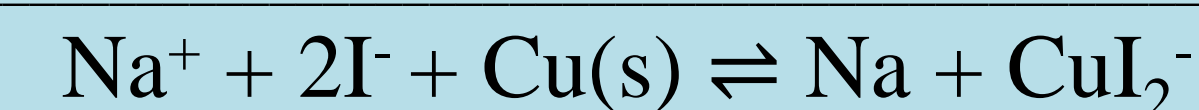
Anode-NASICON Surface Chemistry:



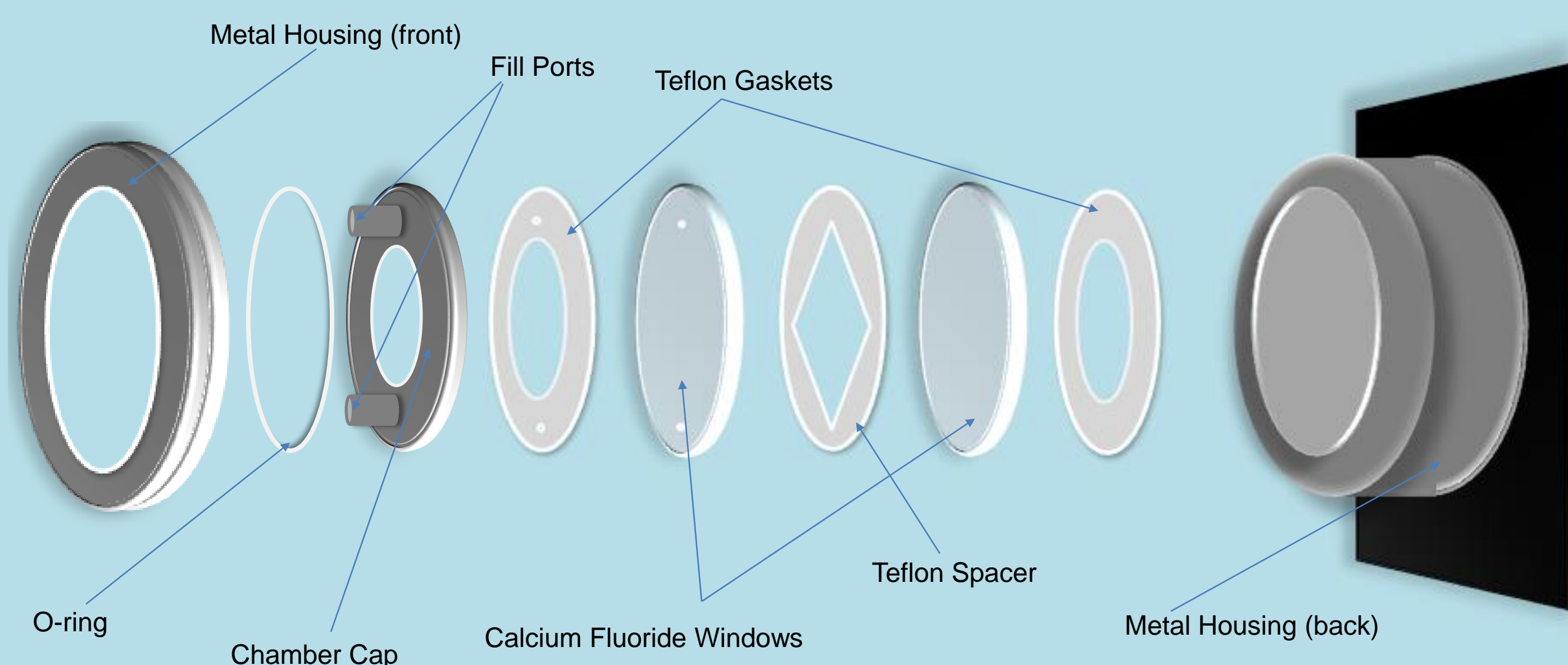
Copper Cathode Surface Chemistry:



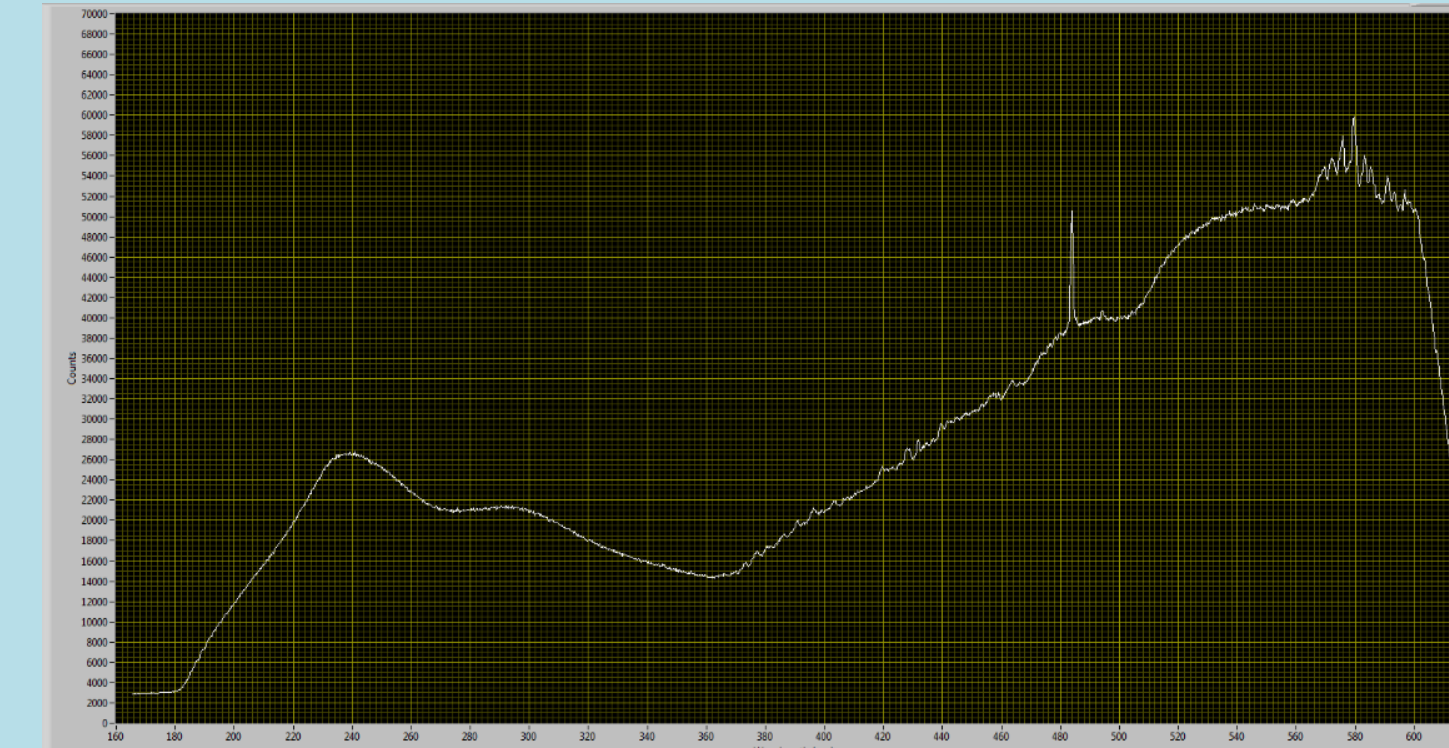
Overall Reaction:



Experimental Cell For Fundamental UV Data



Fundamental Spectroscopy

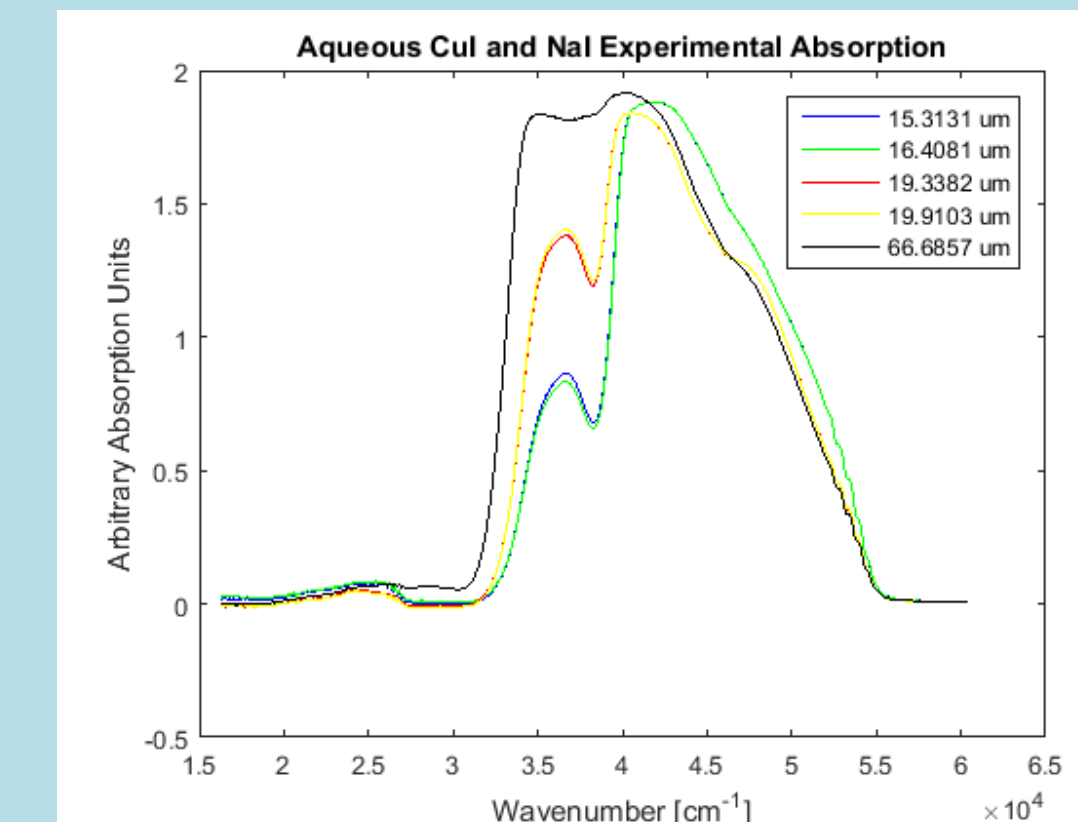


Experimental Transmission Spectrum in the UV-Visible wavelength range for aqueous solution of 0.045M CuI and 2.65M NaI (to serve as Intensity spectrum, I). This solution is used to produce the CuI_2^- species.

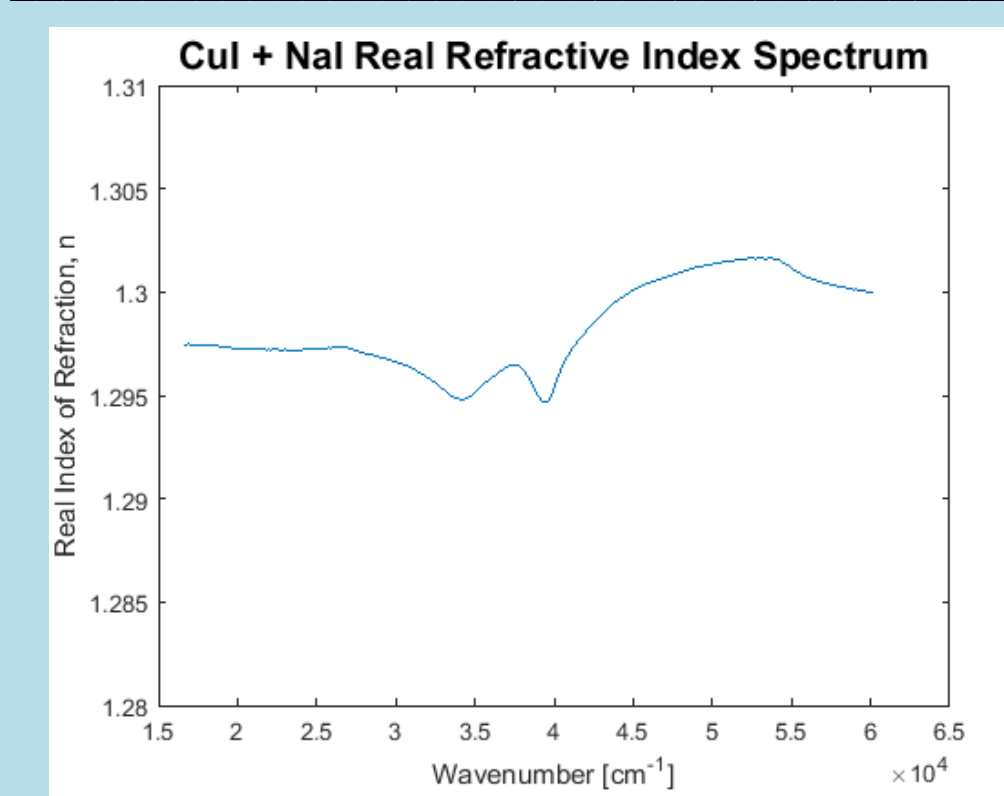
Experimental Absorption Spectra (EAS):

$$-\log(I/I_0)$$

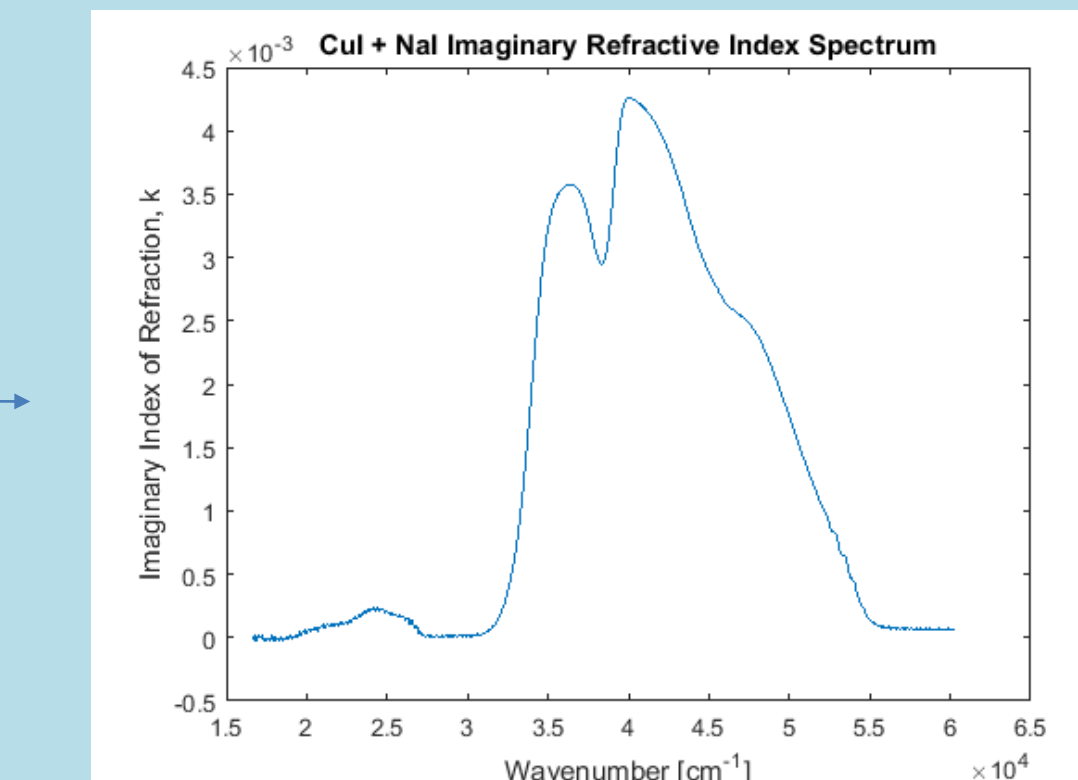
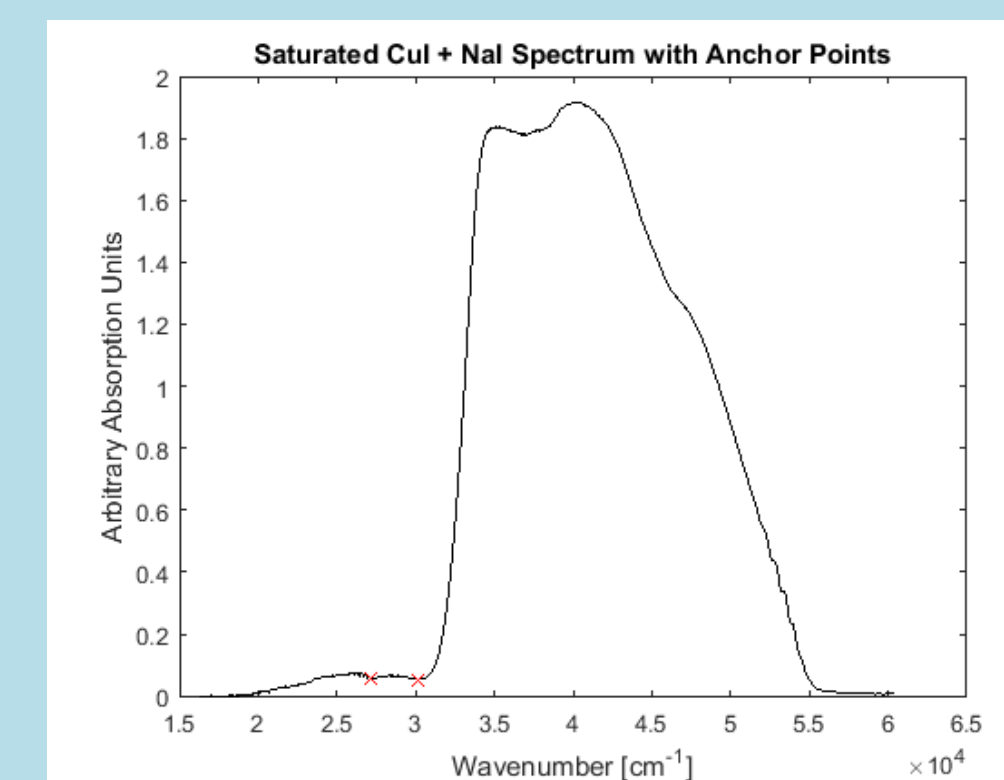
These are not true absorbance spectra, as not all signal attenuation is caused by absorption. Some reduction is due to reflection, and some to unknown, variable effects.



A series of programs originally written by J.E. Bertie and modernized by C. Dale Keefe make use of the Kramers-Kronig (KK) dispersion relations to produce true absorbance spectra from experimental.



According to the KK dispersion relations, when a medium has optical loss (or gain) its refractive index becomes complex. The real part of the refractive index can be used to calculate reflection, and is used to subtract this source of reduction in transmitted light intensity.



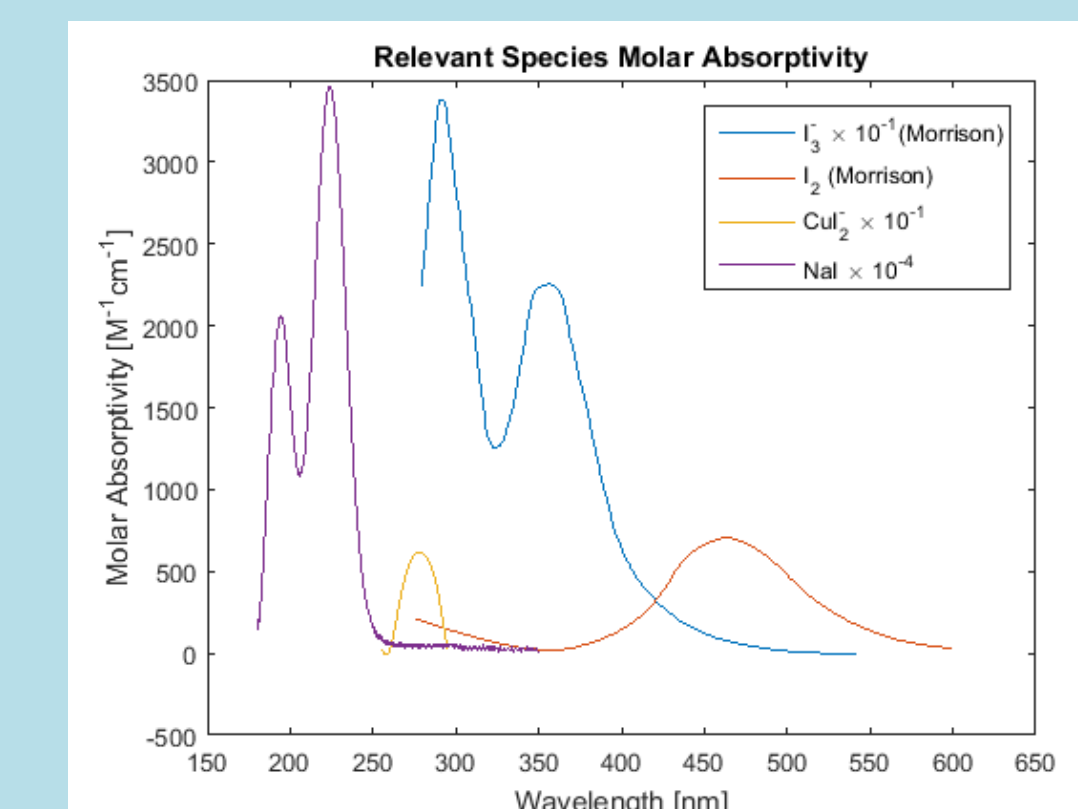
A long path length is chosen from the data set so that a portion of the baseline appears to have significantly non-zero absorption. Keefe's program uses the real index of refraction to calculate and subtract the signal due to reflection, then divides out the path length to produce linear absorption coefficients at anchor points (local minima along the baseline) chosen by the user. These values are used in the calculation of the imaginary refractive index (k) spectra for all path lengths in the data set.

Once the imaginary index spectra are resolved, they are converted to molar absorptivity (E) by the formula:

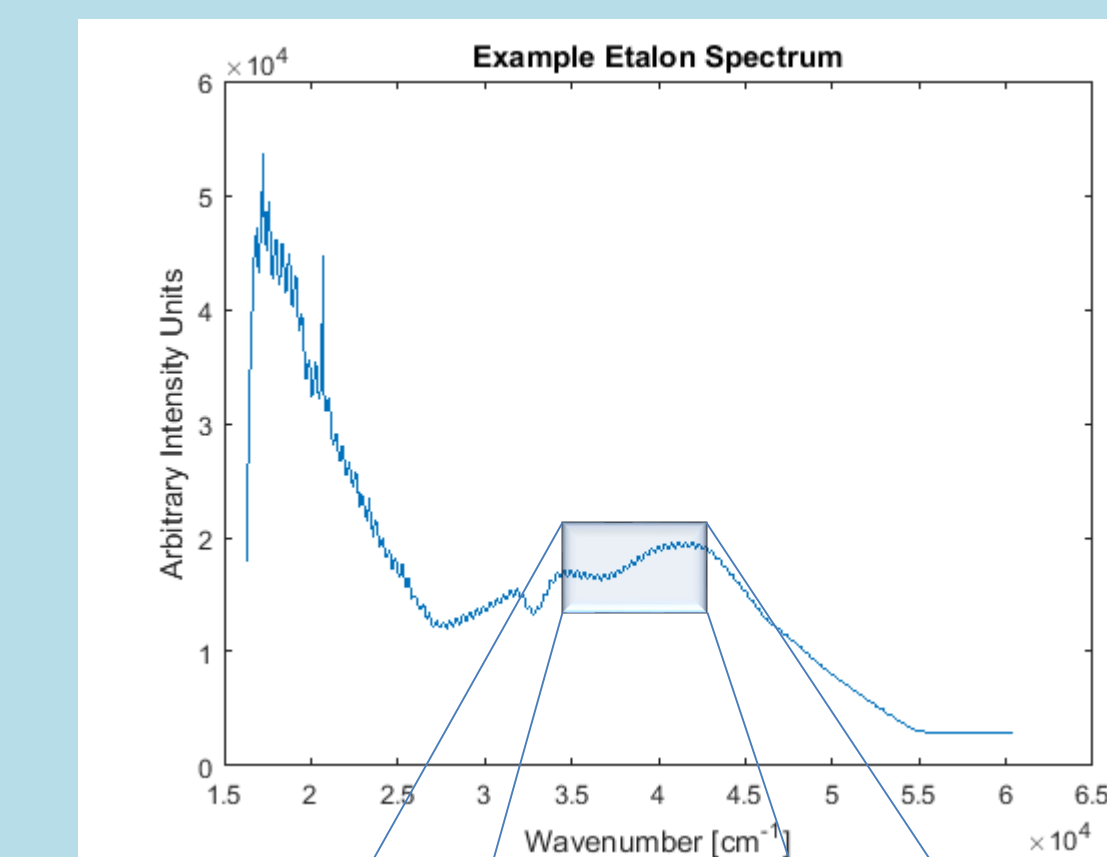
$$E(\omega) = 4\pi^2 \omega^2 k(\omega) / 2.303^2 C$$

Where ω is the wavenumber and C is the concentration

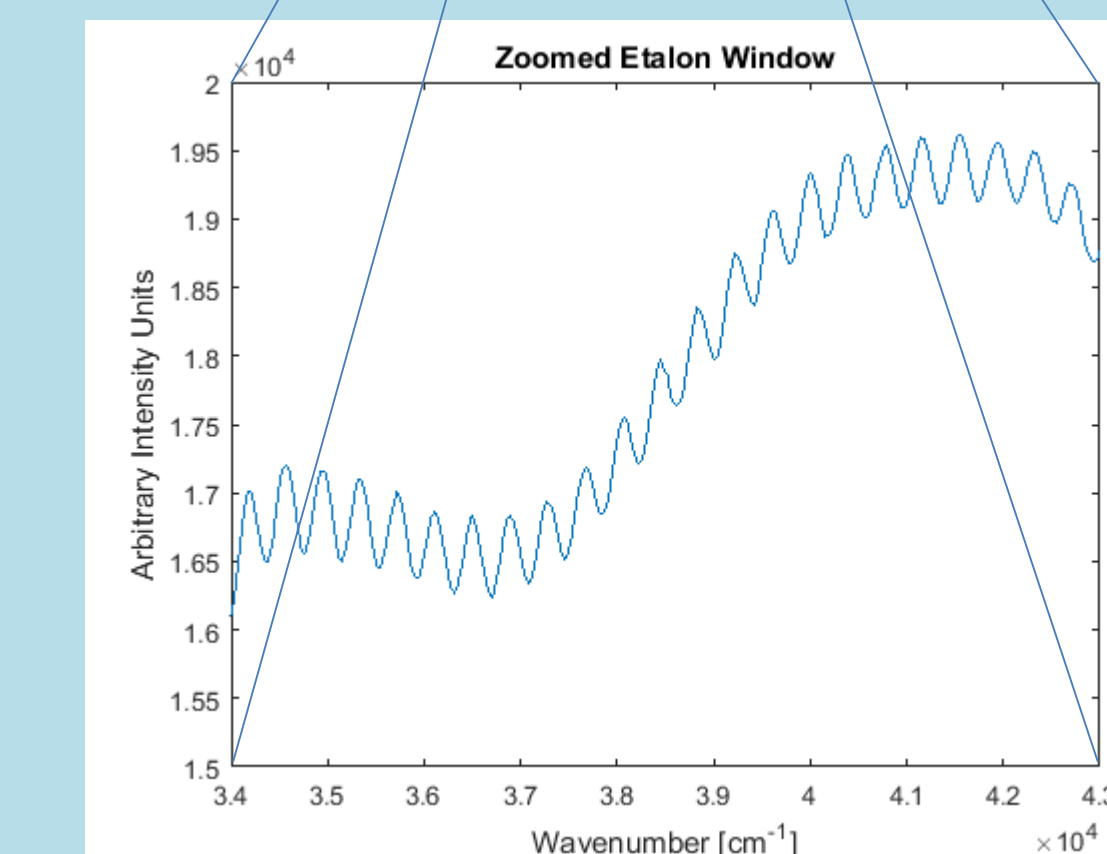
This was performed for the CuI and NaI mixture, as well as for NaI alone. The NaI spectrum was subtracted from the mixture to produce a CuI_2^- peak alone.



Precise Path length Resolution: Etalon



Signal saturation potentially occurs at path lengths not much longer than minimum allowed by equipment. Error from path length inaccuracies on the order of a single micron can propagate significantly. To rectify this, spectra of empty experimental vessel is taken before filling with sample.



Resulting signal is periodic in nature, due to interference caused by reflection between windows. If the wavelength of incident light is such that an integral number of waves fits in the distance spanned by reflection off both air-window interfaces ($3 \times \text{path length}$), signal resolves as a peak. If an integral number plus a half fits, signal resolves as a trough.

Peaks present in the etalon spectra correspond with interference fringes, and are separated by $1/2d$, where d is the path length.

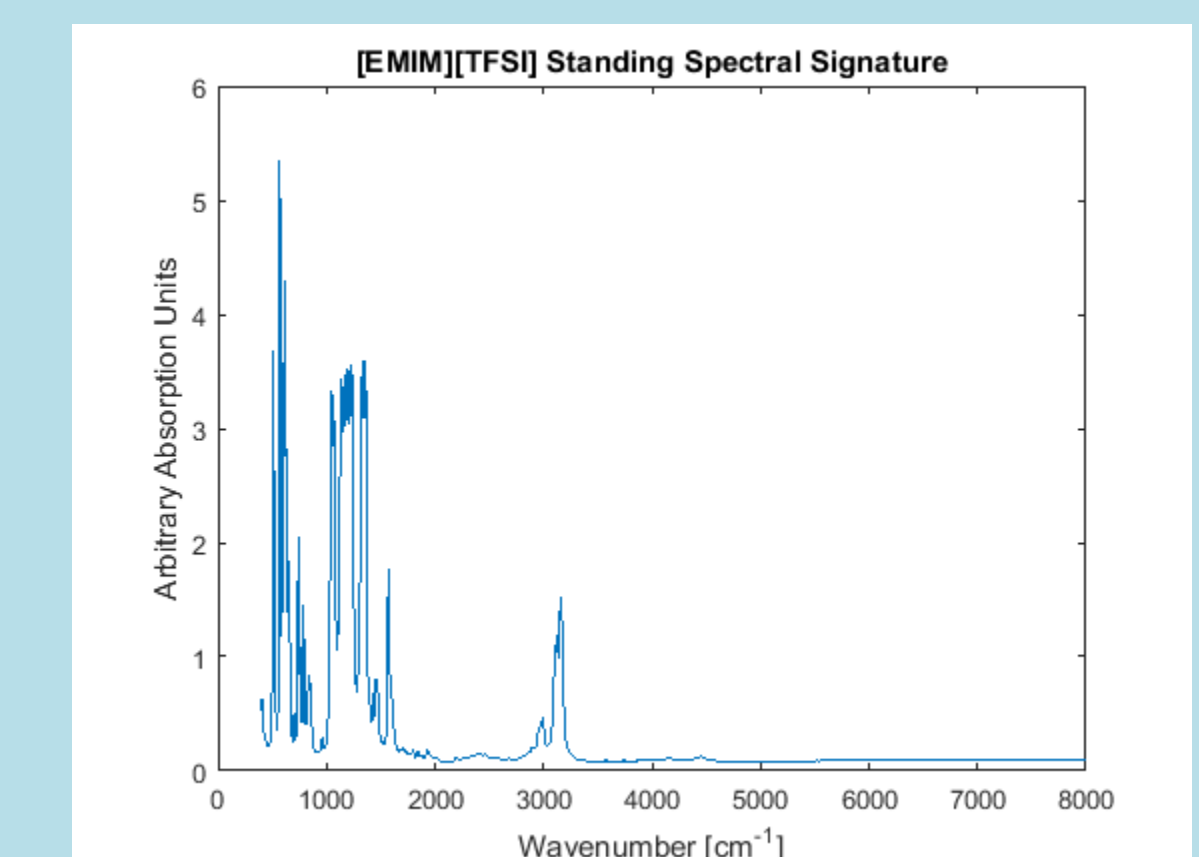
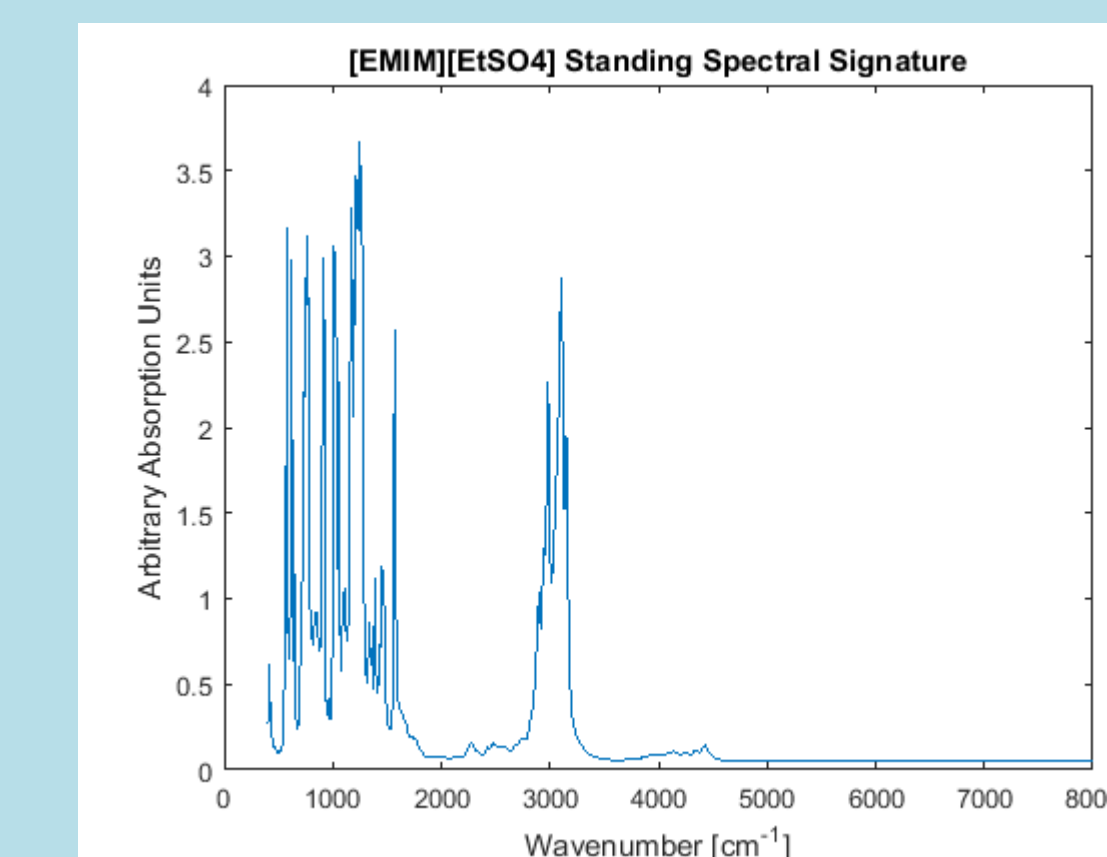
A wavenumber range with a clean periodic signal is selected, and the peaks within it are counted. Path length is then calculated as follows:

$$d = n/2r$$

Where n is the number of peaks, and r is the range where peaks are counted

Ongoing Ionic Liquid Research

Below are the steady state spectra for two examples of ionic liquids with potential applications as battery electrolytes. These spectra are in flux while present in an operating battery; peaks rise, fall and shift in a manner indicative of changes in species concentrations and formation of new species.



Another aim of research with the optical battery is to use laser spectroscopy, tuning the laser to wavelengths corresponding to absorption peaks for species of interest, such as CuI_2^- . In doing this, it will be possible to track transport of said species during battery operation, as well as obtain concentration gradients at various stages in the battery cycle. By better understanding the chemistry involved in sodium battery operation, it will be easier to improve the technology to a point where economical integration of such batteries into the grid becomes an attractive storage solution for renewable energy.

*Jason M. Porter, Christopher B. Dreyer, David Bicknese, Shubham Vyas, C. Mark Maupin, Joe Poshusta, Jerry Martin, Optical measurements of impurities in room-temperature ionic liquids. Journal of Quantitative Spectroscopy and Radiative Transfer, Volume 133, January 2014, Pages 300-310, ISSN 0022-4073

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