Raman Spectroscopy of Lithium Hydride Corrosion: Selection of an Appropriate Excitation Wavelength to Minimize Fluorescence.

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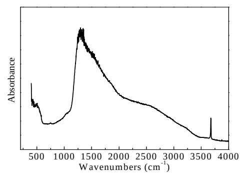
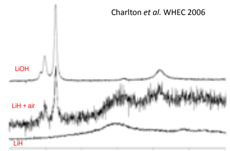
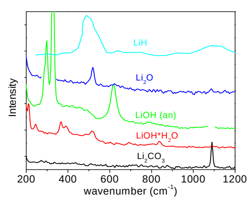
Introduction

- The recent interest in a hydrogen-based fuel economy has renewed research into metal hydride chemistry.
- Many of these compounds react readily with water to release hydrogen gas and form a caustic.
- Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT) has been used to study the hydrolysis reaction. The LiOH stretch appears at 3670 cm^{-1}.





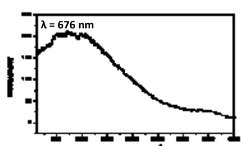
- Raman spectroscopy is a complementary technique that employs monochromatic excitation (laser) allowing access to the low energy region of the vibrational spectrum (<600 cm^{-1}).
- Weak scattering and fluorescence typically prevent Raman from being used for many compounds.
- The role of Li_2O in the moisture reaction has not been fully studied for LiH. Li_2O can be observed by Raman while being hidden in the Infrared spectrum.



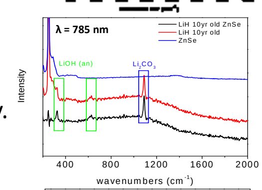
Fluorescence

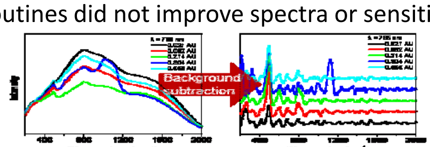
- The significant feature in the Raman spectrum of LiH at most excitation wavelengths is fluorescence.
- As a result, high concentrations of LiOH or Li_2CO_3 are required to be observed.


Highly corroded LiH

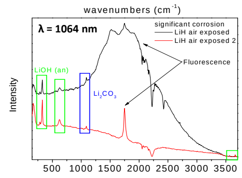


- Baseline correction and exotic deconvolution routines did not improve spectra or sensitivity.



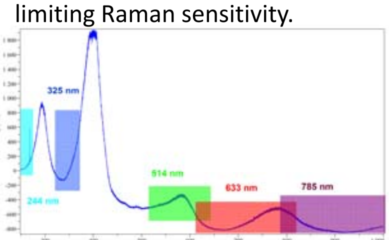


- FT-Raman (λ = 1064 nm), which typically is used to overcome fluorescence resulted in two distinct fluorescence features.



Photoluminescence

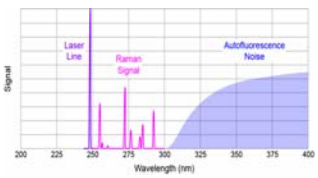
- Absorbed laser photons are spontaneously emitted from LiH at specific wavelengths.
- The intensity of these photons is much greater than Raman scattering limiting Raman sensitivity.



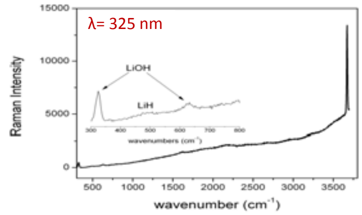
- The Raman spectral region (100-4000 cm^{-1}) is highlighted for multiple excitation wavelengths in order to pick the best laser probe.
- UV wavelengths offer high intensity and low luminescence.

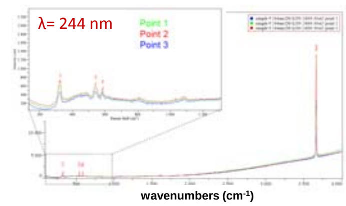
UV Raman

- Excitation with a UV (<400 nm) laser has been shown recently to effectively overcome autofluorescence in many organic and biological compounds.
- The energy gap between the UV excitation and initiation of autofluorescence is such that the entire Raman scattering spectrum can be observed free of obstruction.

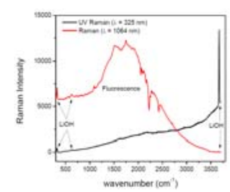


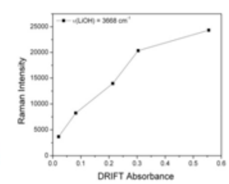
- Raman intensity is also much stronger since intensity is proportional to $1/\lambda^4$. Stretching and phonon vibrations for LiOH observed.





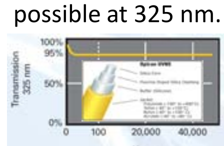
- UV excitation removes fluorescence even compared to FT-Raman.
- LiOH concentration can be easily correlated for both Raman and Infrared intensity.

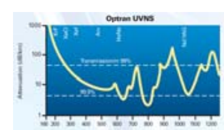


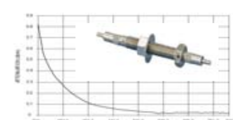


Fiber Optic Delivery

- Due to pyrophoricity concerns, spectroscopy within a controlled environment is desired. This can be achieved through fiber optics.
- Advances in UV fibers and optical filters make fiber optic delivery possible at 325 nm.







- Renishaw, Inc. designed a UV fiber optic Raman probe for use in environmental enclosures.

In Situ Hydrolysis

- Compacted LiH was exposed to 100 %RH air for 1 day.
- The UV Raman probe measured spectra every minute.
- Both Li_2CO_3 and LiOH grew in intensity

$$LiH + H_2O \rightarrow LiOH + H_2(g)$$
$$LiOH + CO_2 \rightarrow Li_2CO_3 + H_2(g)$$

- Fluorescence bleached away over time
- Heating the sample (350 ºC) under vacuum converts LiOH to Li_2O which is observed by Raman directly.