

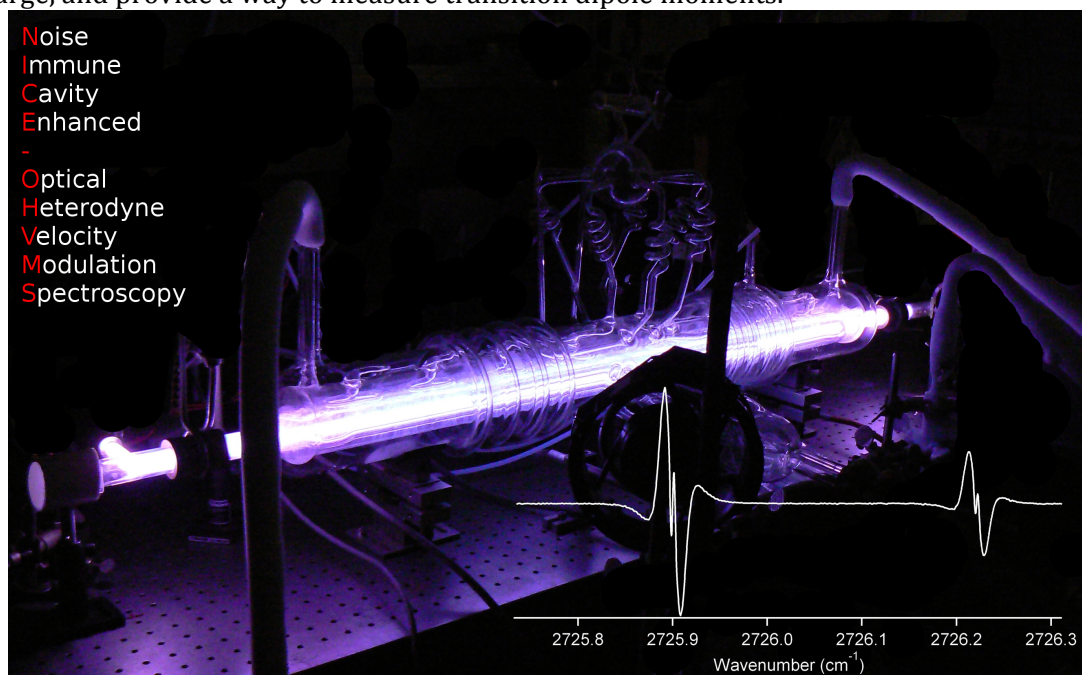
## Advances in Sensitive, Accurate, Precise, Ion Spectroscopy through Noise Immune Cavity Enhanced Optical Heterodyne Velocity Modulation Spectroscopy

James N. Hodges<sup>1</sup>, Adam J. Perry<sup>1</sup>, Charles R. Markus<sup>1</sup>, Paul A. Jenkins II<sup>1</sup>, G. Stephen Kocheril<sup>1</sup>, Benjamin J. McCall<sup>2</sup>

<sup>1</sup>*Department of Chemistry, University of Illinois, Urbana, Illinois*

<sup>2</sup>*Department of Chemistry and Departments of Astronomy and Physics, University of Illinois, Urbana, Illinois*

Noise immune cavity enhanced optical heterodyne velocity modulation spectroscopy (NICE-OHVMS) is the implementation of velocity modulation spectroscopy with cavity enhanced optical heterodyne spectroscopy. NICE-OHVMS combines the advantages of pathlength and power enhancement of the cavity, reduced  $1/f$  noise as a result of heterodyne modulation, and ion selectivity due to velocity modulation. Our lab developed this technique to measure molecular ion transitions with high precision, which allows us to support astronomical observations and challenge the predictive power of ab initio theory. Our spectrometer consists of an optical parametric oscillator (OPO) and a low finesse external optical cavity, which contains a liquid nitrogen cooled positive column discharge cell.<sup>[1]</sup> The sensitivity of the spectrometer is approximately  $10^{-9} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ . Coupling our OPO into a cavity results in a tremendous amount of power, about 10 to 12 watts, which allows us to optically saturate ion transitions. Optical saturation results in Lamb dips in the spectra which can be fit with a high degree of frequency precision. When the OPO is referenced to an optical frequency comb, we can determine transition frequencies with an uncertainty of 500 kHz to a few MHz depending on the signal to noise ratio of the Lamb dip. We have measured transitions from a variety of ions including  $\text{H}_3^+$ ,  $\text{HeH}^+$ ,  $\text{HCO}^+$ ,  $\text{CH}_5^+$ , and  $\text{OH}^+$ ,<sup>[2,3]</sup> and have successfully reduced the errors on these linecenters by two orders of magnitude. Additionally, ongoing work is focused on describing NICE-OHVMS lineshapes, in order to infer the saturation parameter, which can be used to better understand the relaxation rates in a positive column discharge, and provide a way to measure transition dipole moments.



### References

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- [3] A.J. Perry et al. J. Chem. Phys. (2014), 141, 101101.