

LA-UR-12-25548

Approved for public release; distribution is unlimited.

Title: Remote Detection of NO₂ Stable Isotopes

Author(s): Clegg, Samuel M.
Nowak-Lovato, Kristy Lynne
Fessenden-Rahn, Julianna E.
Obrey, Stephen J.
Currier, Robert P.

Intended for: Program Meeting at PNNL



Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

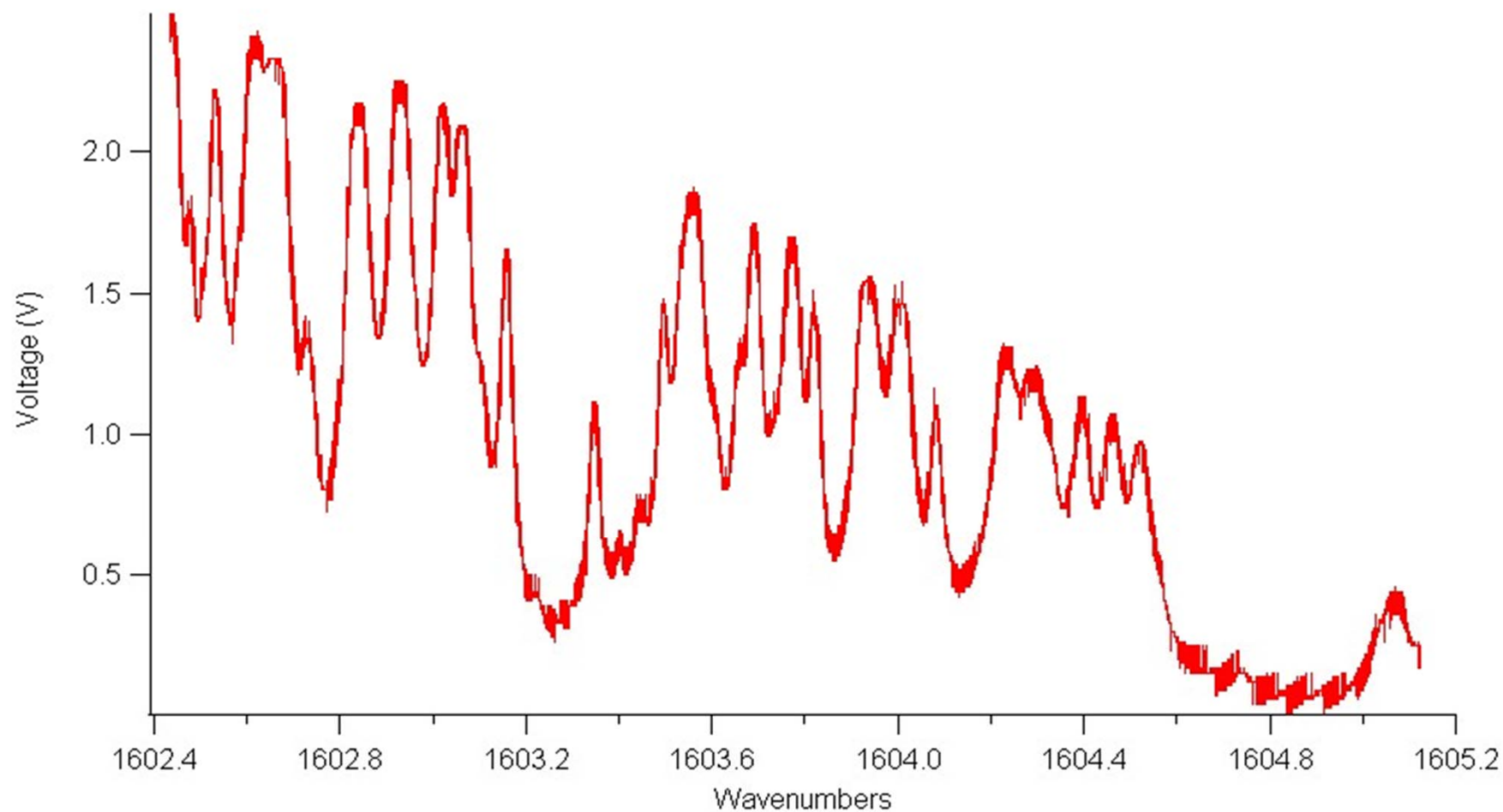
Remote Detection of NO₂ Stable Isotopes

Sam Clegg, Kristy Nowak-Lovato, Julianna Fessenden, Robert Carrier and Steven Obrey

Los Alamos National Laboratory

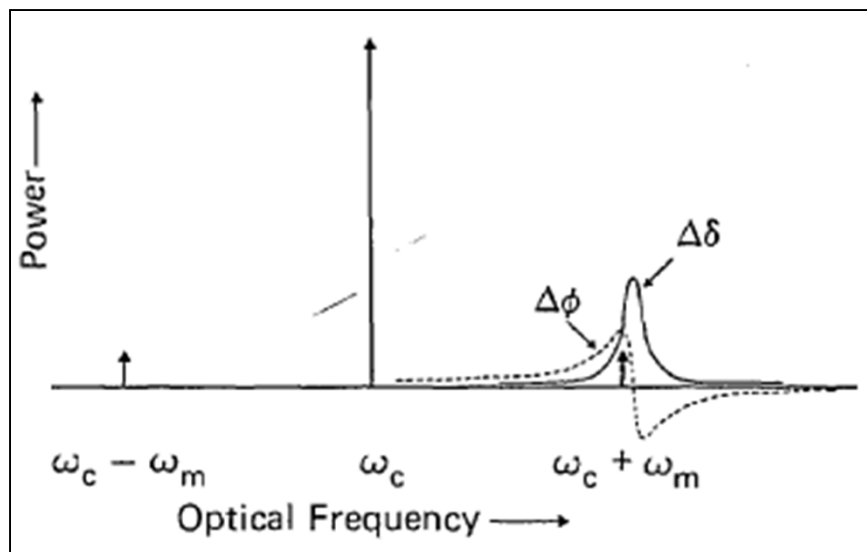
October 17-18, 2012

$^{15}\text{NO}_2$ Spectrum

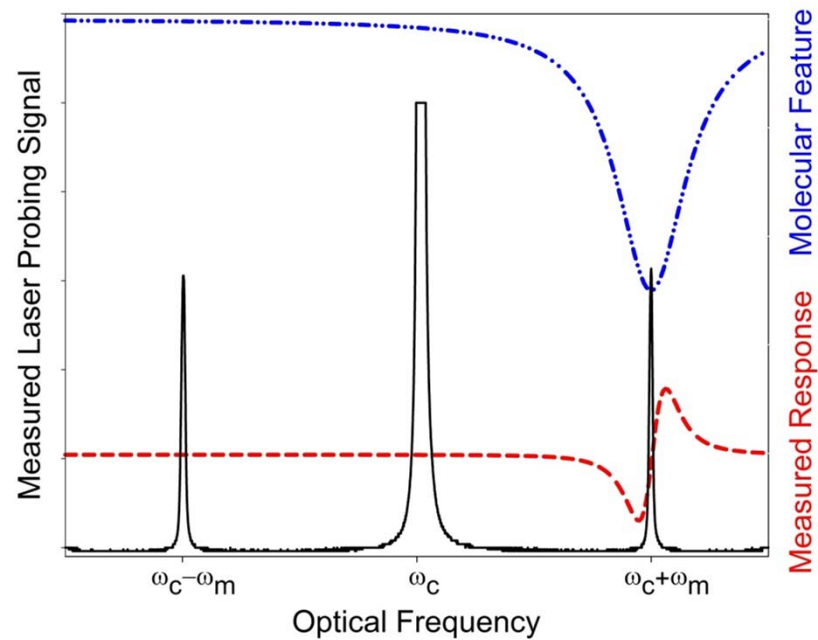


Fundamental FMS

From G.C. Bjorklund Optics Letters, 5, 15, 1980



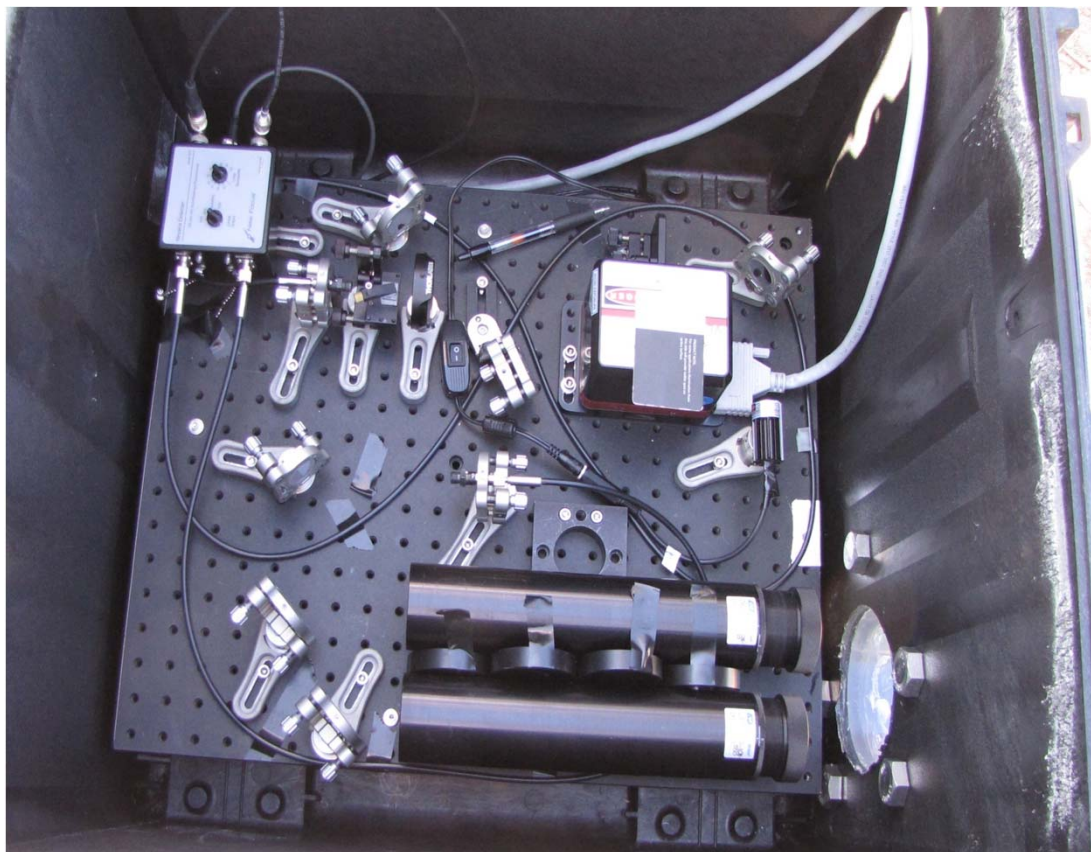
From LANL in situ instrument



$$\omega_c = 1607 \text{ nm}$$

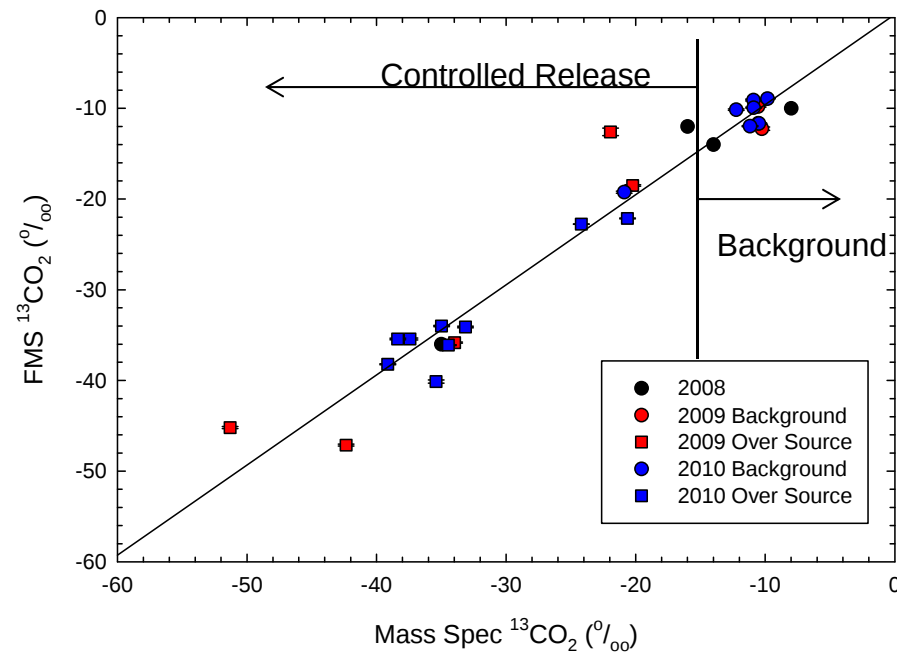
$$\omega_m = \pm 2 \text{ GHz}$$

LANL – FMS Program



CO₂ FMS Field Results

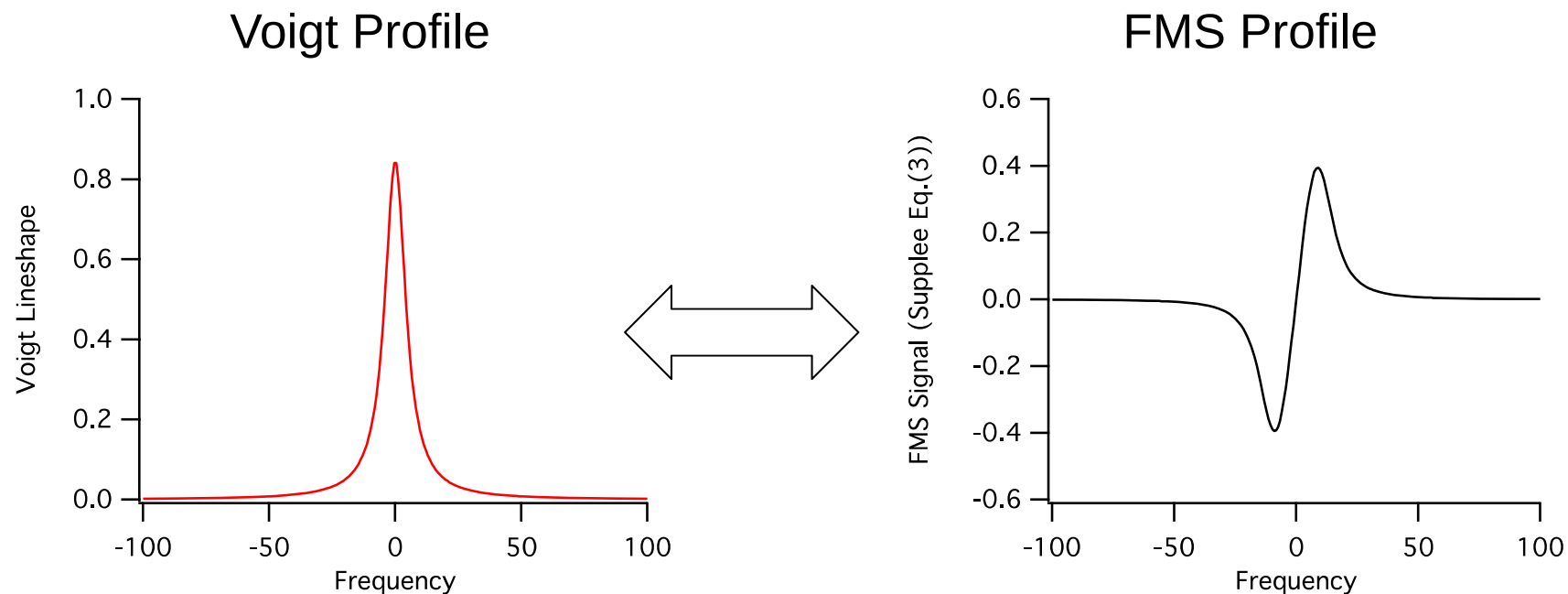
In Situ Field Results



Background = -8 to -11‰

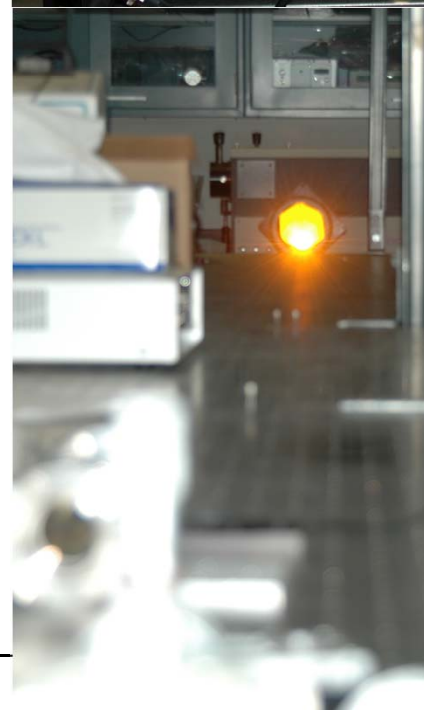
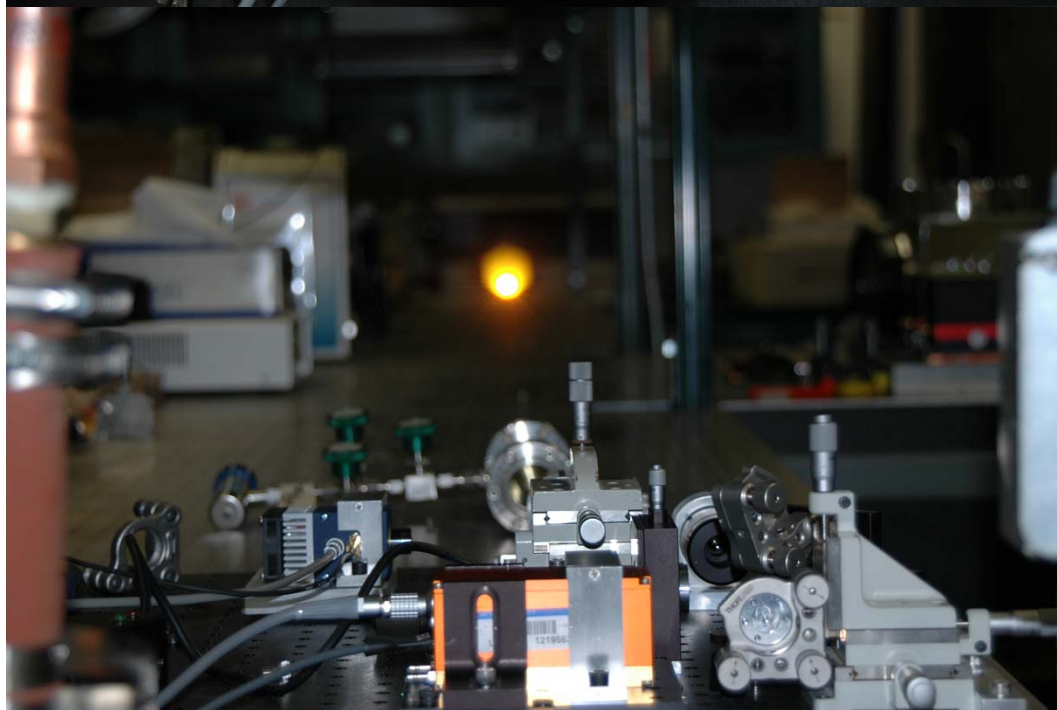
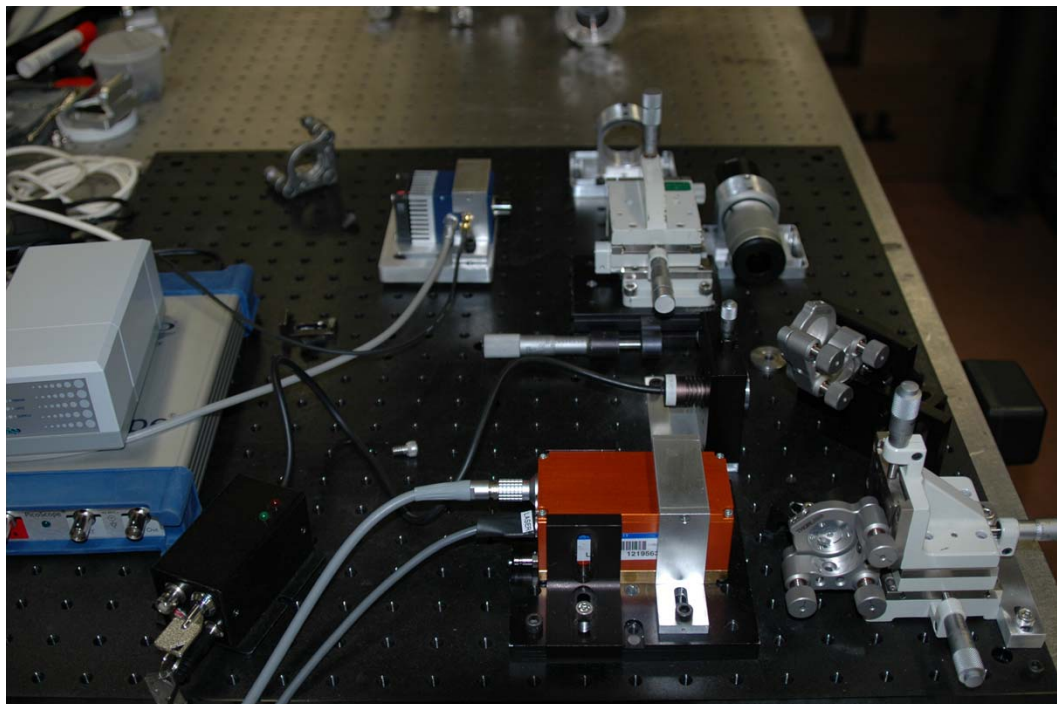
Seepage < -15‰

FMS Forward-Backward Modeling

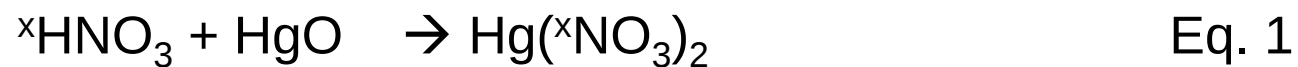


Voigt Profile accounts for both Temperature and Pressure Line Width

The Model Code was included in the 4th Quarter Report



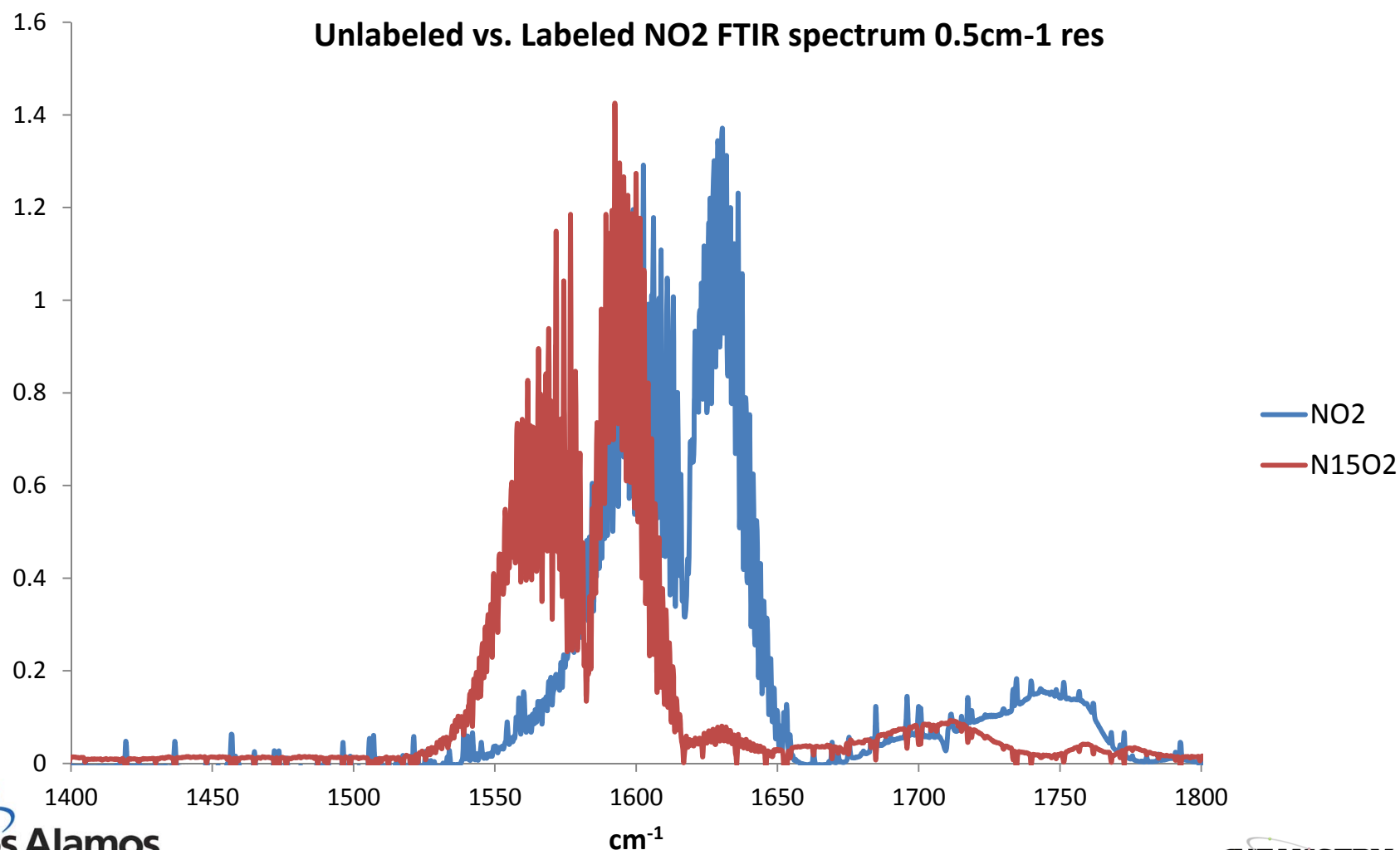
$^{14}\text{NO}_2$ and $^{15}\text{NO}_2$ Synthesis



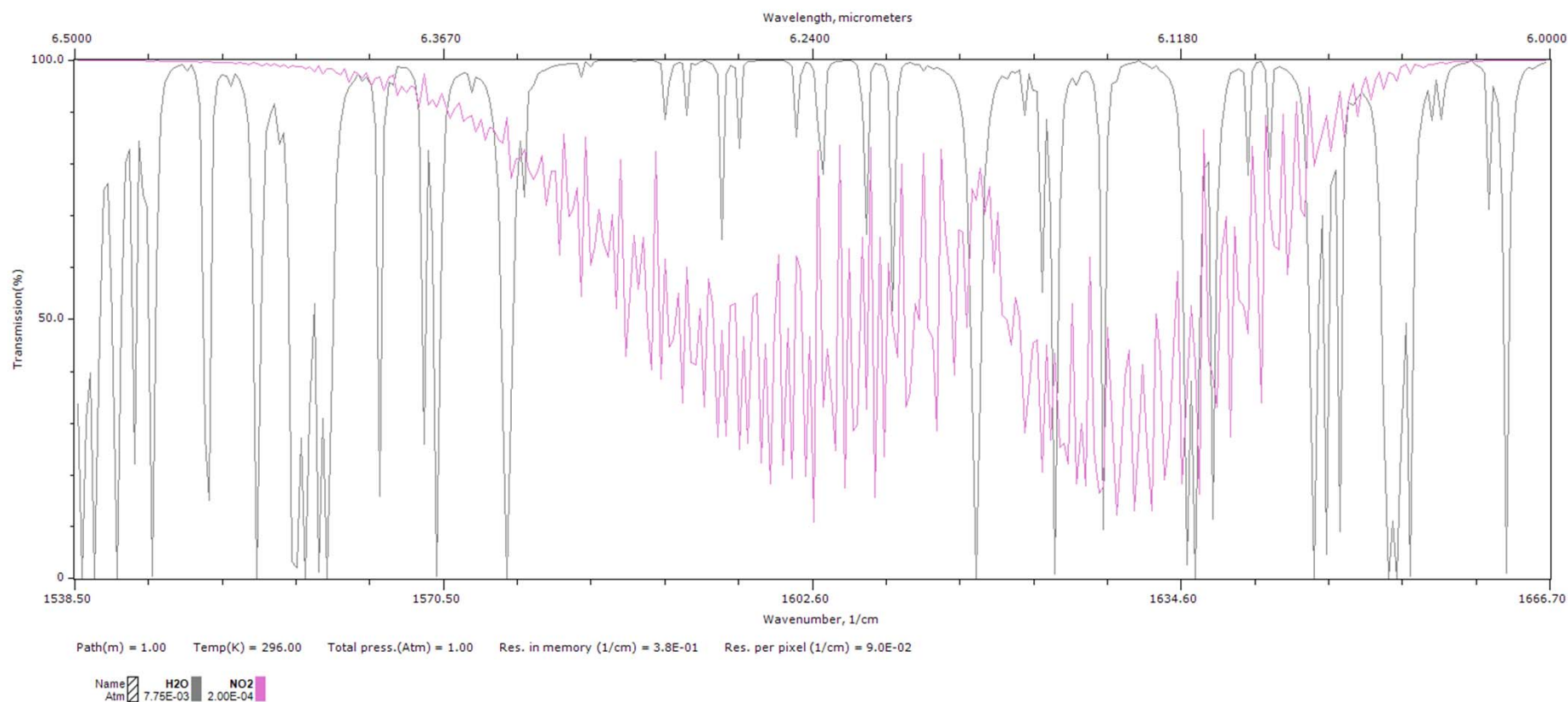
$x = 14 \text{ or } 15$

FTIR Validation of Synthesized NO₂

Unlabeled vs. Labeled NO₂ FTIR spectrum 0.5cm⁻¹ res



NO₂, H₂O Transmission Spectrum



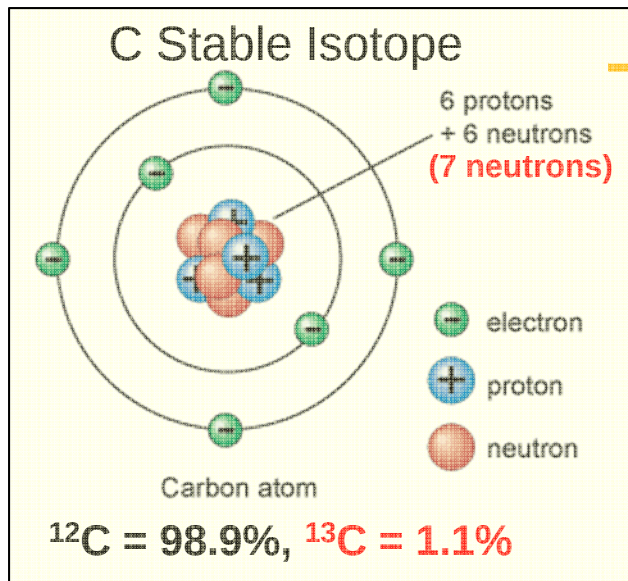
H₂O here is NOT a Problem!

Summary

- **Built and Tested a FMS Instrument**
 - Ready for Field Tests
- **Completed FMS Backward – Forward Model**
 - Determine the Concentration of a Species given the FMS Trace
 - Predict FMS Signal from a Sample for a given Instrument Setup
- **Successfully Synthesized $^{14}\text{NO}_2$ and $^{15}\text{NO}_2$.**
- **Obtained FMS and Absorption Spectra of neat and mixtures of $^{14}\text{NO}_2$ and $^{15}\text{NO}_2$.**
- **Determined that Atmospheric Water will not Interfere with the $^{14}\text{NO}_2$ and $^{15}\text{NO}_2$ Measurement.**

Backup

Stable Isotopes – Theory of Signature

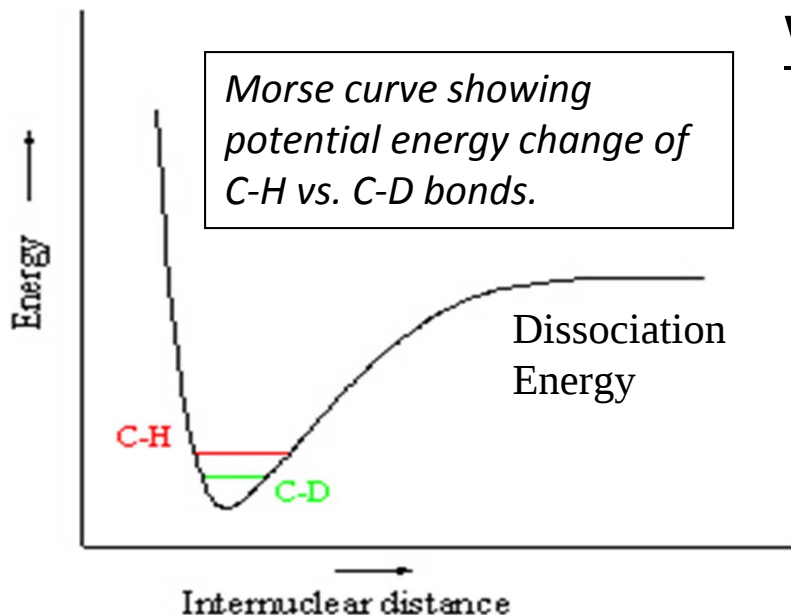


Stable Isotopes:

- exist in all molecules
- exist as ratio of heavy/light: $R = ^{15}\text{N}/^{14}\text{N}$
- chemical fingerprint (unique)
- not radiogenic/long lived

Why Signature Exists?:

- fractionation in chemical reactions
- partition into reactants/products
- due to bond strength differences



UNCLASSIFIED

Energy's NNSA