Molecular Rotational Resonance (MRR) spectrometers for

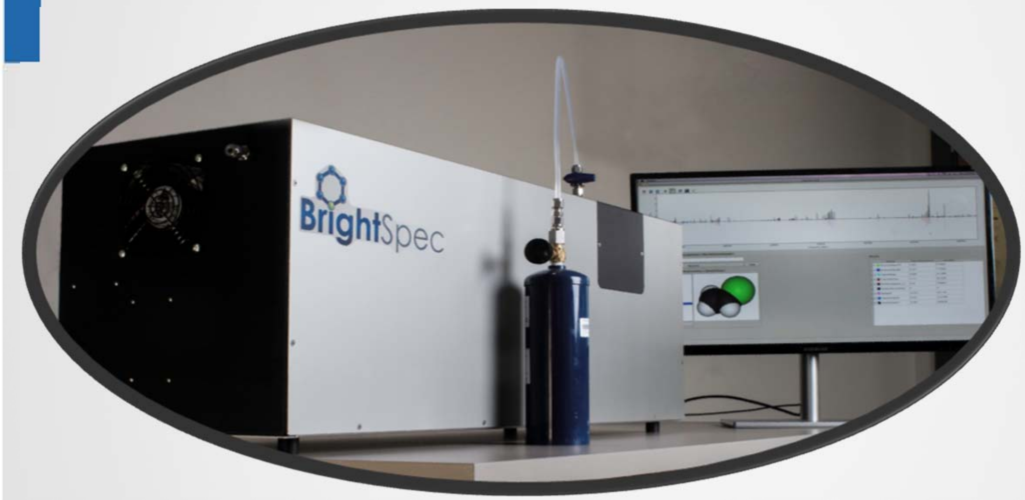
TRACE LEVEL VOC DETECTION

AND CHEMICAL SENSING

22 slides total

February 14th, 2014
EPFL THz

BrightSpec
Instruments and Analytical Services



Direct quantitative analysis of complex gas mixtures

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BrightSpec

VDI

DMPI
Dominion MicroProbes, Inc

VIBRATESS, LLC
THz Spectroscopy & Biosensors

NRAO

ALMA
Atacama Large Millimeter / submillimeter Array

North American ALMA Science Center

Applications of Fourier Transform Molecular Rotational Resonance (FT-MRR) Spectroscopy

The simplicity of FTIR, the power of Mass Spec

Direct Analysis of Complex Mixtures

Impurities in gases, Environmental analysis, Semicon processes

Reprogrammable Sensors for Multispecies Monitoring

Residual solvent analysis, Genotoxicity testing, Environmental Monitoring

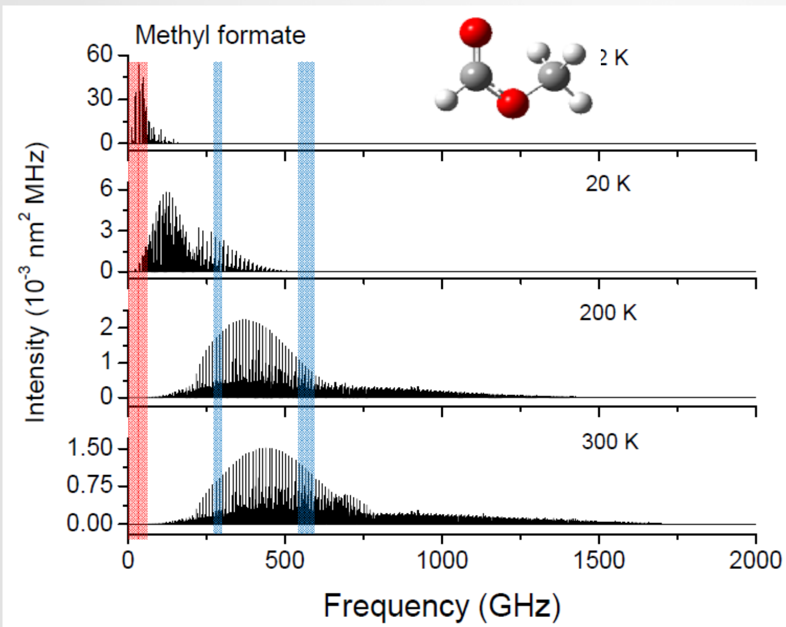
Dedicated Chemical Sensors

Water (humidity), ammonia, formaldehyde, NO

Basics of Molecular Rotational Resonance (MRR) Spectroscopy

Spectrum Directly Tied to 3D Geometry: $T_{rot} = \frac{L^2}{2I}$

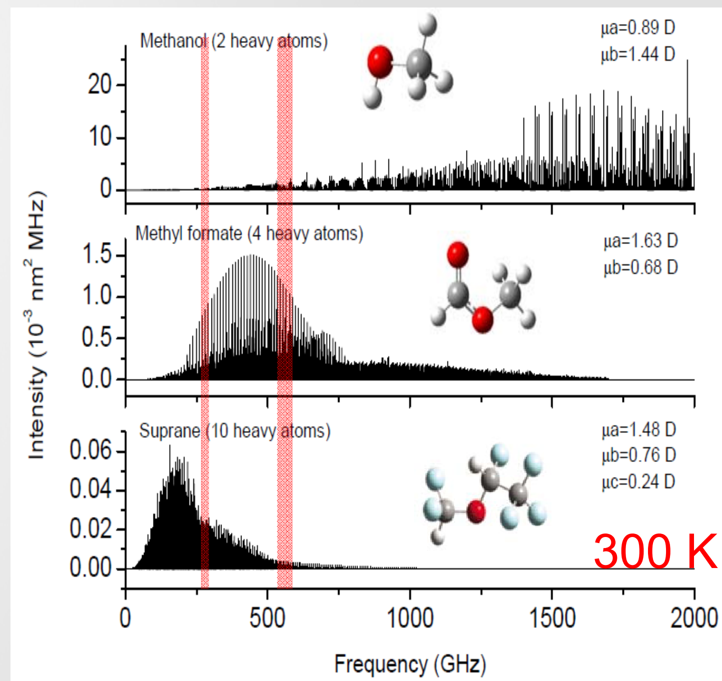
The Effect of Temperature



260-290 GHz CP-FT Spectrometer

3-8 Heavy Atoms at Room-Temperature

The Effect of Molecular Size



Chemical Analysis by Molecular Rotational Spectroscopy

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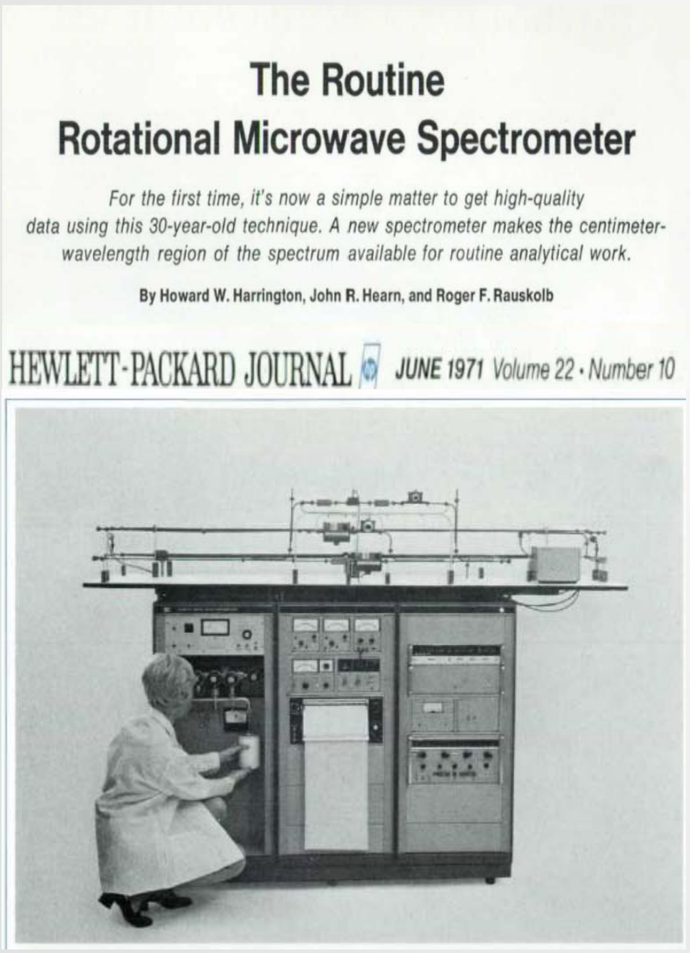
Spectroscopy and its Applications

Frequency	Molecular Energy Levels	Commercial Techniques
RF (<1 GHz)	Nuclear Spin in Magnetic Field	NMR, MRI
MW (9-90 GHz)	Electron Spin in Magnetic Field	EPR/ESR
MW-THz (2-2000 GHz)	Overall Molecular Rotation	NONE
IR (100-4000 cm^{-1})	Molecular Vibration	FTIR, NDIR diode laser
UV-VIS (100-800 nm)	Electronic Excitation	Fluorimeters, Imaging, LIBS, Raman microscopy
X-rays (< 100 nm)	Inner Core Electron Excitation	X-ray emission for chemical analysis

Requirements for Analytical Chemistry


The Routine
Rotational Microwave Spectrometer

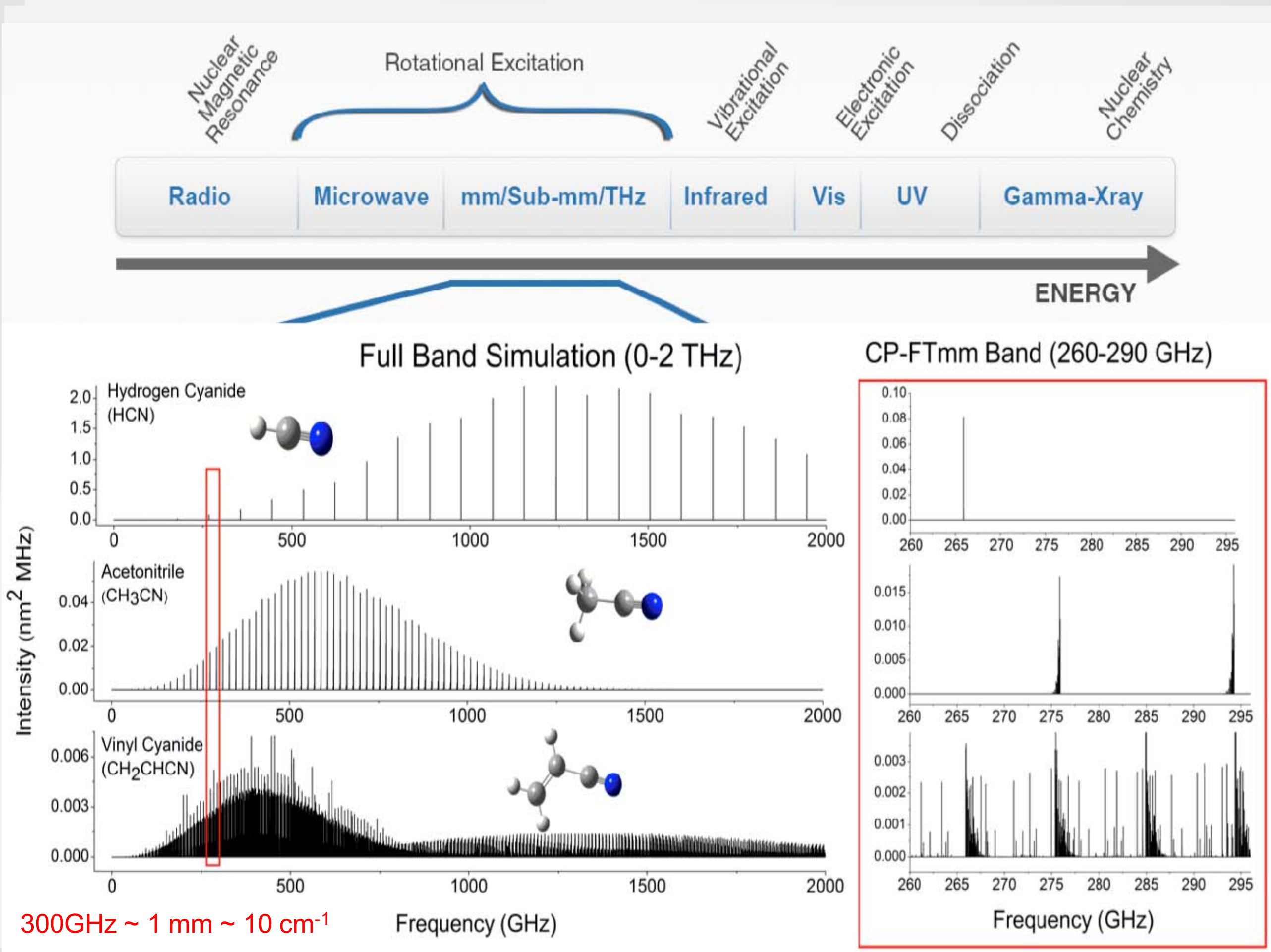
For the first time, it's now a simple matter to get high-quality data using this 30-year-old technique. A new spectrometer makes the centimeter-wavelength region of the spectrum available for routine analytical work.

By Howard W. Harrington, John R. Hearn, and Roger F. Rauskolb

HEWLETT-PACKARD JOURNAL JUNE 1971 Volume 22 • Number 10

1) Room-temperature operation
2) Compact instrument
3) Standard electrical requirements
4) Automated library analysis
5) Ability to make chemical identification

Molecular Rotational Resonance



Chemical Selectivity:

(mass distribution and Inertia)

Direct Mixture Analysis

(high spectral resolution)

High Sensitivity

(BrightSpec CP-FT)

Fourier Transform Molecular Rotational Resonance (FT-MRR) Spectroscopy

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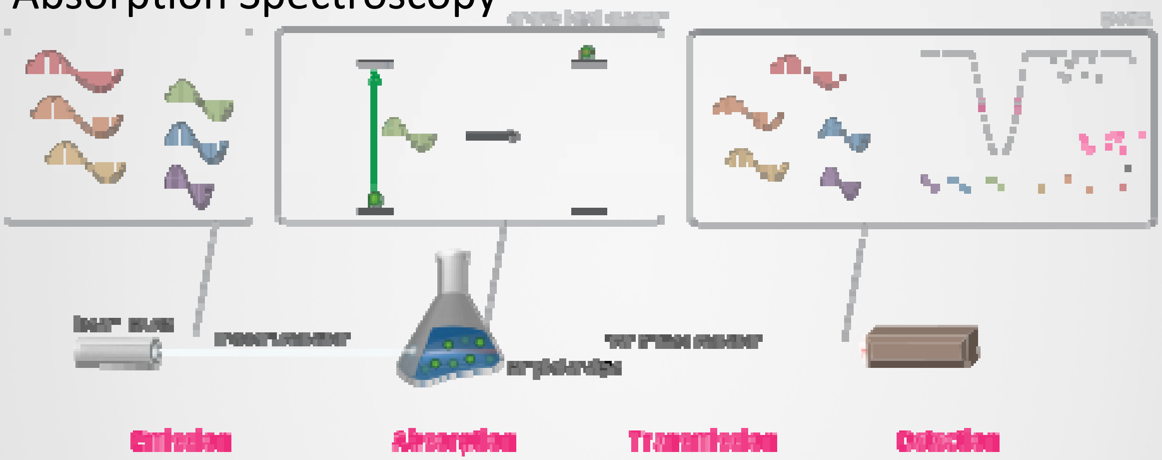
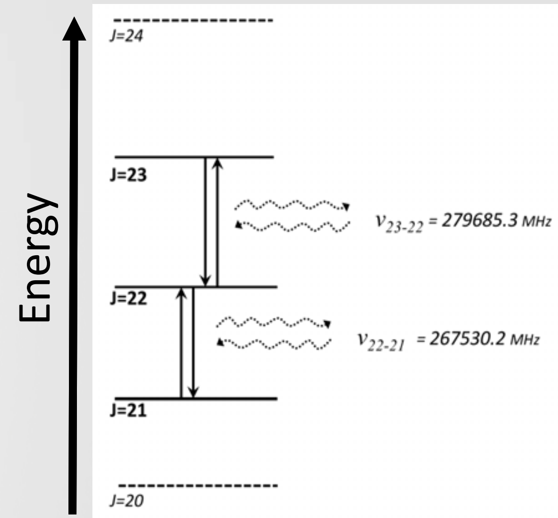
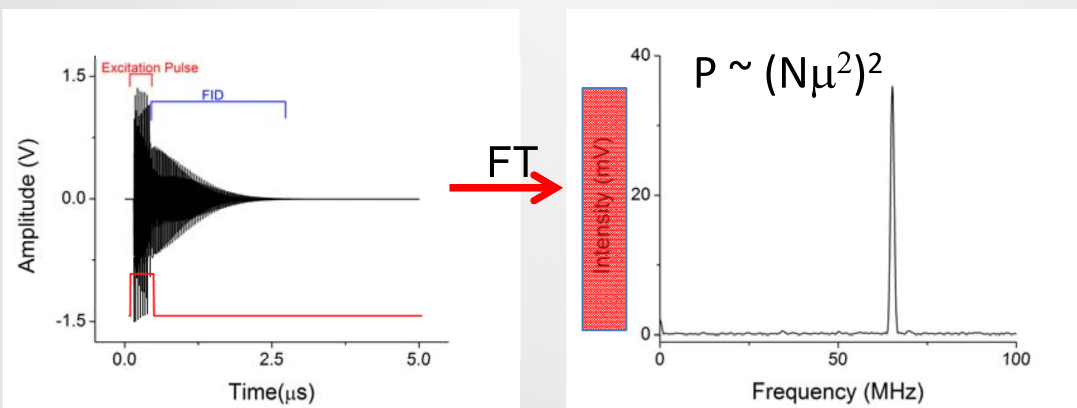
Absorption Spectroscopy



Jon Chui, Wikipedia

OCS Level Diagram



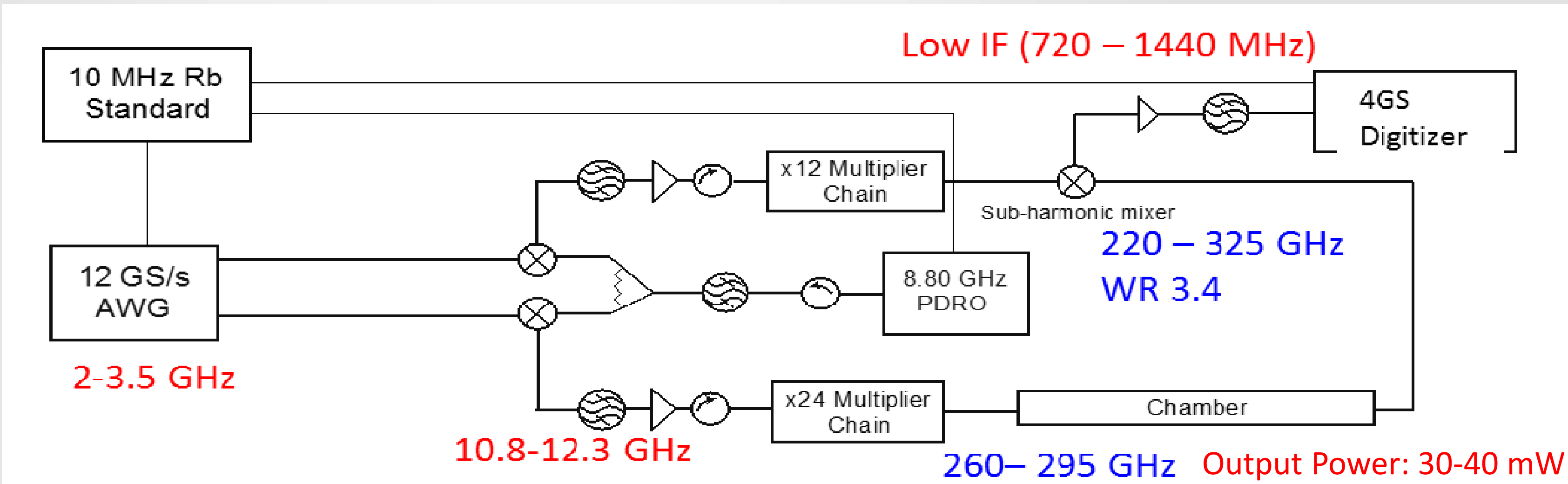


Don't detect against a light source

Can make efficient use of high power mm-wave sources

Offers unique capabilities for spectrum analysis (FT-NMR)

A Spectrometer Based on Solid State Electronics



Key Features: 1) Tailored Excitation Pulses using Arbitrary Waveform Generator

Agilent M8190A, 12-bit

2) High Peak Power, High Bandwidth Active Multiplier Chain Sources

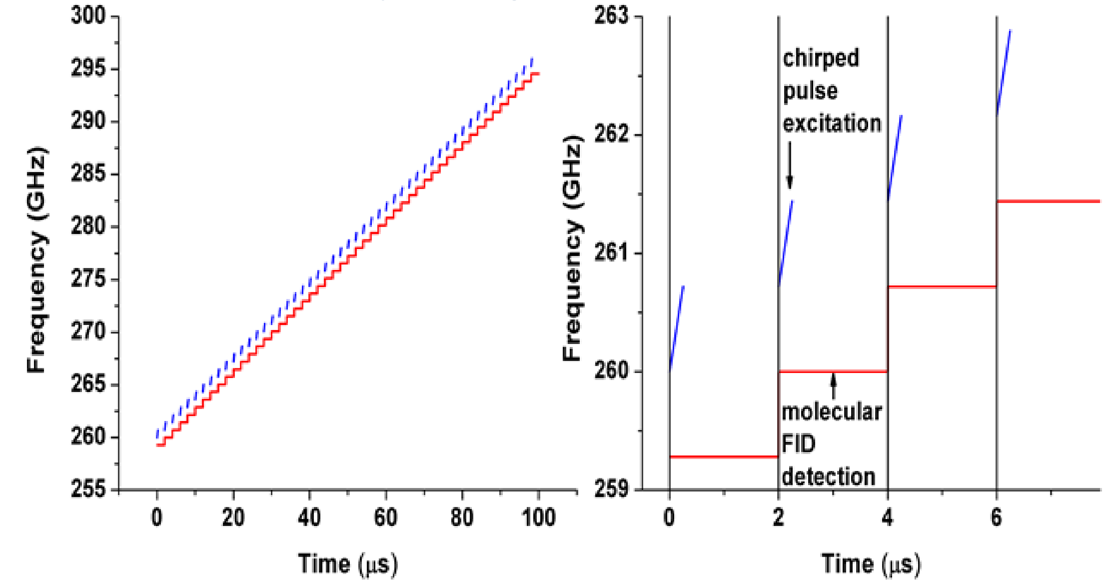
VDI High Efficiency Multipliers

3) High Speed Digitizer with FPGA Signal Accumulation (16M averages)

Agilent Acqiris U1084A, 8-bit

Chirped Pulse Waveform for Real-Time FT-MRR Spectroscopy

Schematic Pulse Spectrogram



Chirped Pulse Advantages

1) Delivers maximum pulse energy to the sample for any given excitation bandwidth.

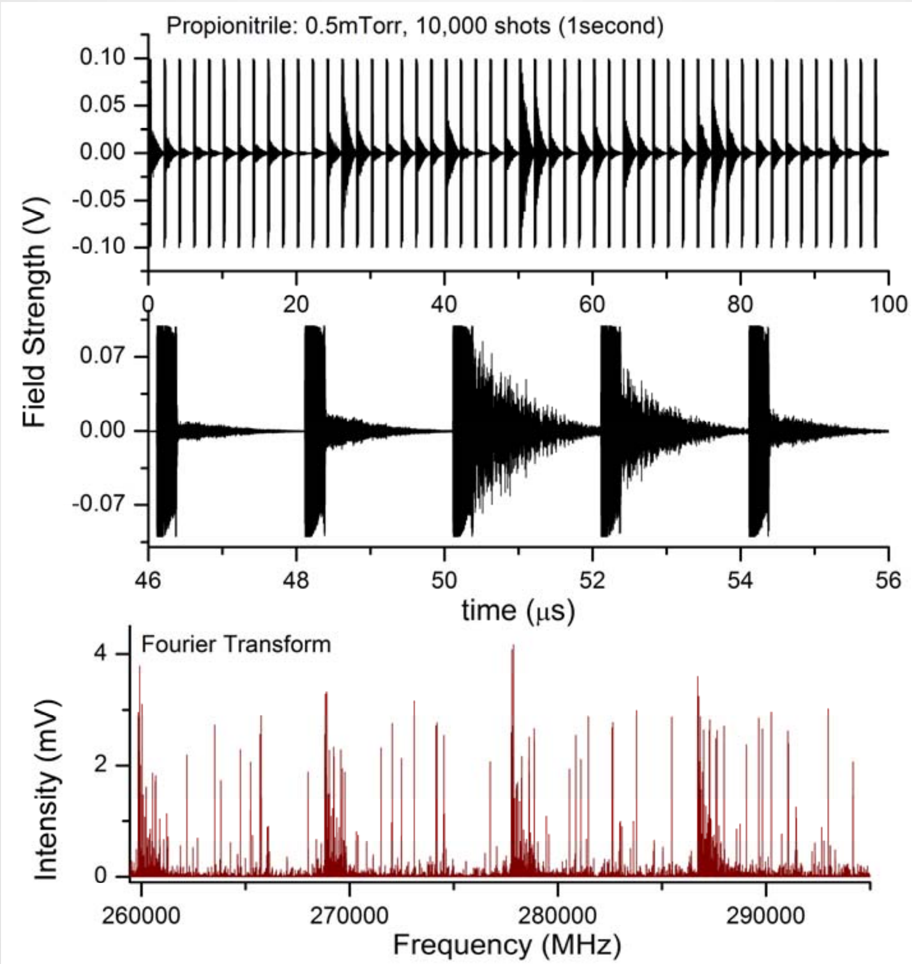
2) Bandwidth of the pulse is expanded by the AMC multiplication factor.

Separate AWG Channels Generate Chirp Segments (Blue) and Local Oscillator (LO) Frequency (Red) with Phase Reproducibility

*Justin L. Neill, Brent J. Harris, Amanda L. Steber, Kevin O. Douglass, David F. Plusquellic, and Brooks H. Pate, "Segmented chirped-pulse Fourier transform submillimeter spectroscopy for broadband gas analysis", Optics Express **21**, 19743-19749 (2013). [Highlighted in Spotlight on Optics]*

Chirped-Pulse Fourier Transform:

100 times more sensitive than absorption techniques



Segmented

(lowers performance requirements for digitizers)

Chirped Pulse

(add instantaneous bandwidth to utilize entire source power

Fourier Transform

(relieve pressure broadening in digital signal processing)

(enhance analysis time resolved analytical tools)

Near 100% Averaging Duty Cycle:
Record Length: 400,000 ; 8-bit

Basic Performance:

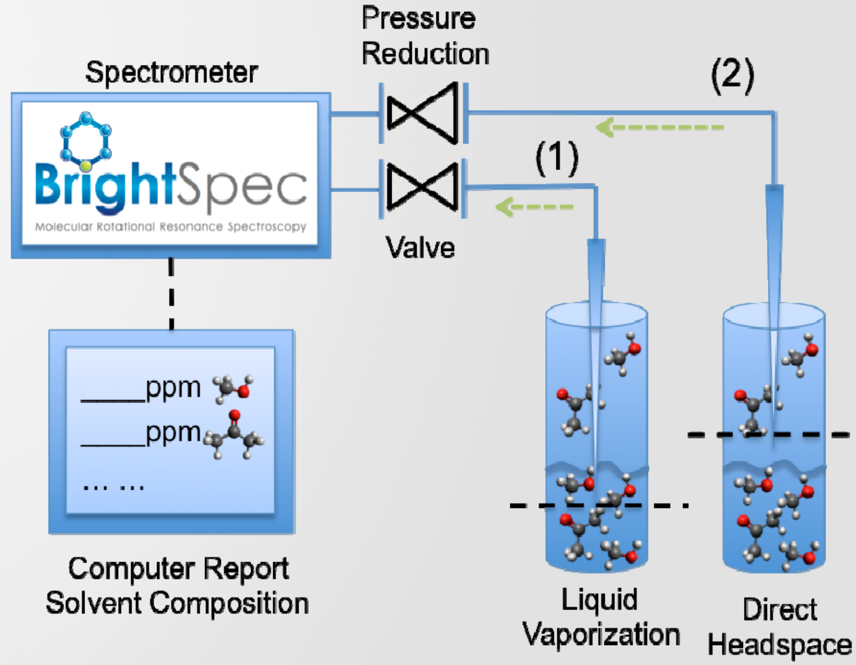
Chemical Niche:

1. Small (< 150 amu)
2. Polar
3. Volatile

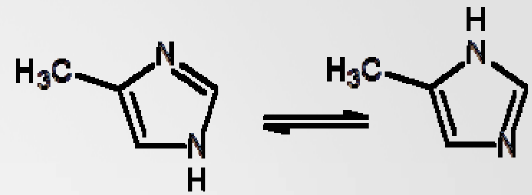
Forecasted Detection Limits for Class 3 Residual Solvents

	Molar Detection Limit (40 seconds) (pmol)
Formic Acid	0.28
Dimethyl sulfoxide	0.41
Acetone	1.5
Ethanol	1.6
Acetic Acid	2.8
Methylethyl ketone	3.7
2-Propanol	4.2
Ethyl formate	4.5
1-Propanol	10
Methyl acetate	11
2-Butanol	11
Ethyl acetate	23
1-Butanol	32
Diethyl ether	62
Anisole	80
3-Methyl-1-butanol	140
tert-Butylmethyl ether	370

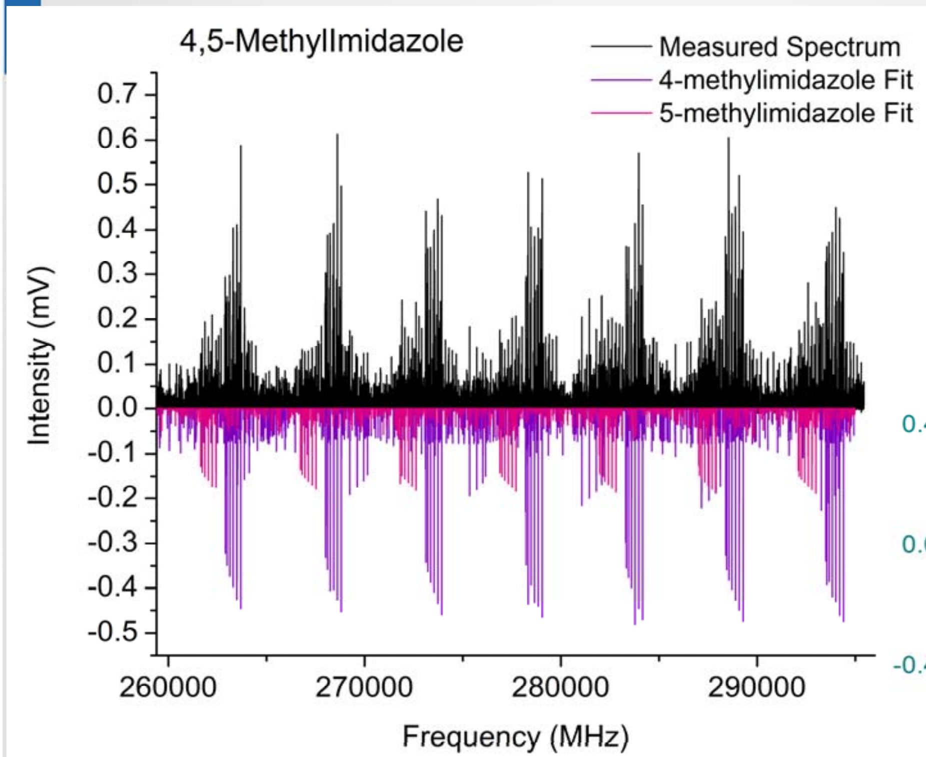
10 – 100 mTorr (10^{-4} atm)



Solid Samples:



4-methyl 5-methyl

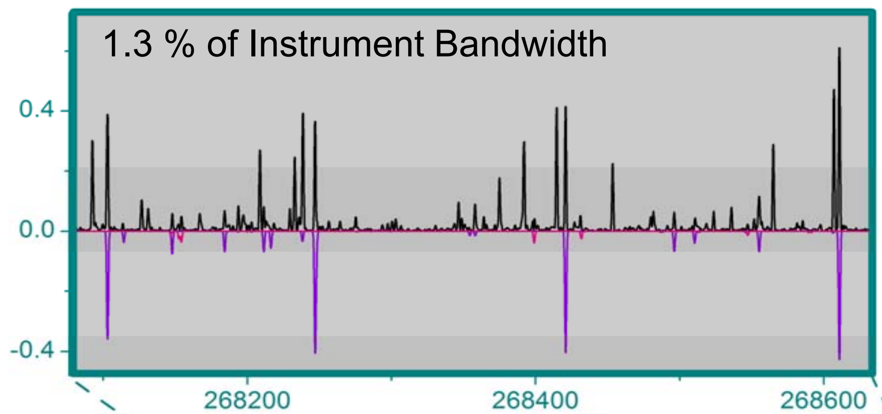


Sample Pressure: 5 mTorr (50 nmol)

Measurement Time: 2 minutes

Signal to Noise: 1250:1

Quantitation Limit: 120 pmol



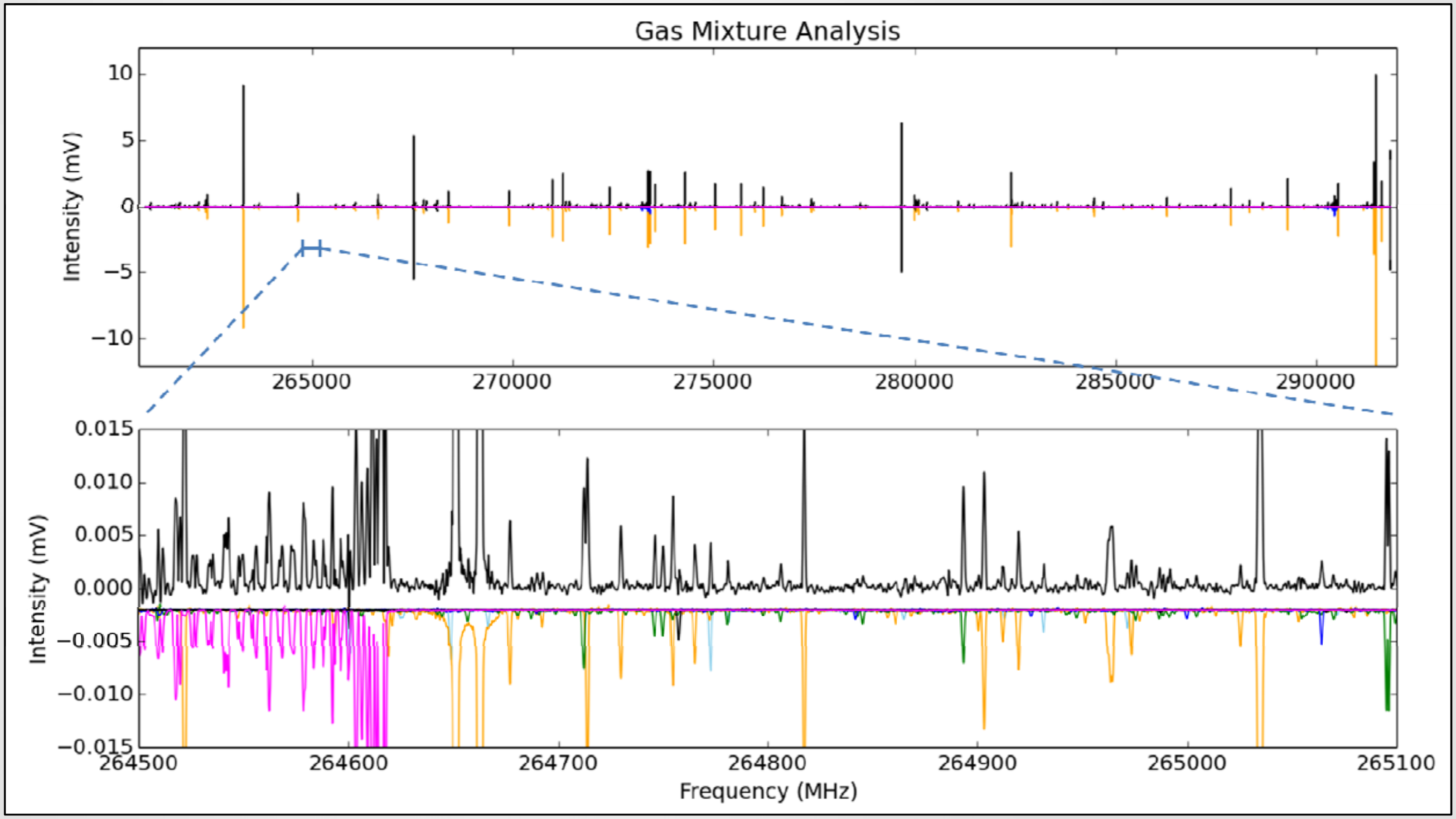
30 GHz Bandwidth

1MHz spectral line width

30,000 independent data channels

Direct Analysis

Gas Mixtures: No chromatography



Analysis of multicomponent mixtures with > 10,000 dynamic range in minutes

Quantitative Analysis

Complex Mixtures: No chromatography

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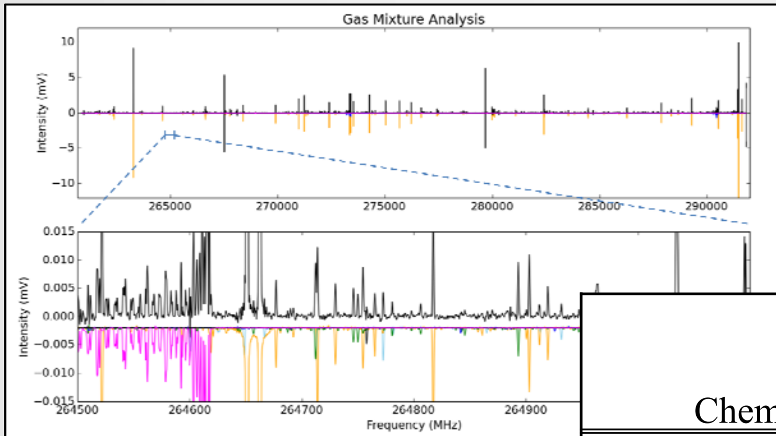


Automated Library Matching

Data acquisition and analysis in 2 minutes

Chemical	Expected Partial Pressure (mTorr)[1]	Observed Partial Pressure (mTorr)[2]	% Error
Ethylene Oxide	0.472 (± 8%)	0.493	2.34%
Chloroethane	0.079 (± 21%)	0.098	20.95%
Carbonyl Sulfide	0.211 (± 11%)	0.210	2.55%
Propyne	0.211 (± 11%)	0.238	10.39%
Trifluoroiodomethane	0.132 (± 15%)	0.099	26.41%
1-Butyne	0.026 (± 45%)	0.016	38.30%
Total	*1.13*	*1.154*	

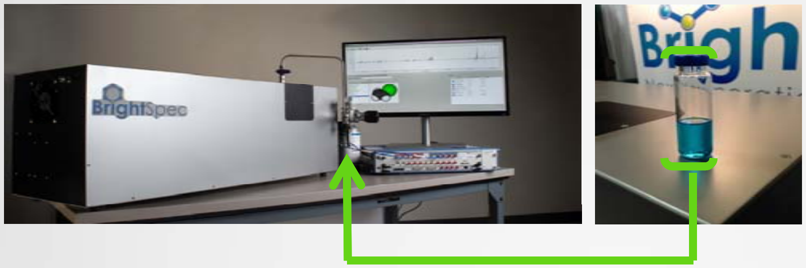
1) Expected partial pressure uncertainty was propagated from the accuracy of the pressure gauge (0.5 psi) used to prepare the mixture at a total pressure of 43 psi.

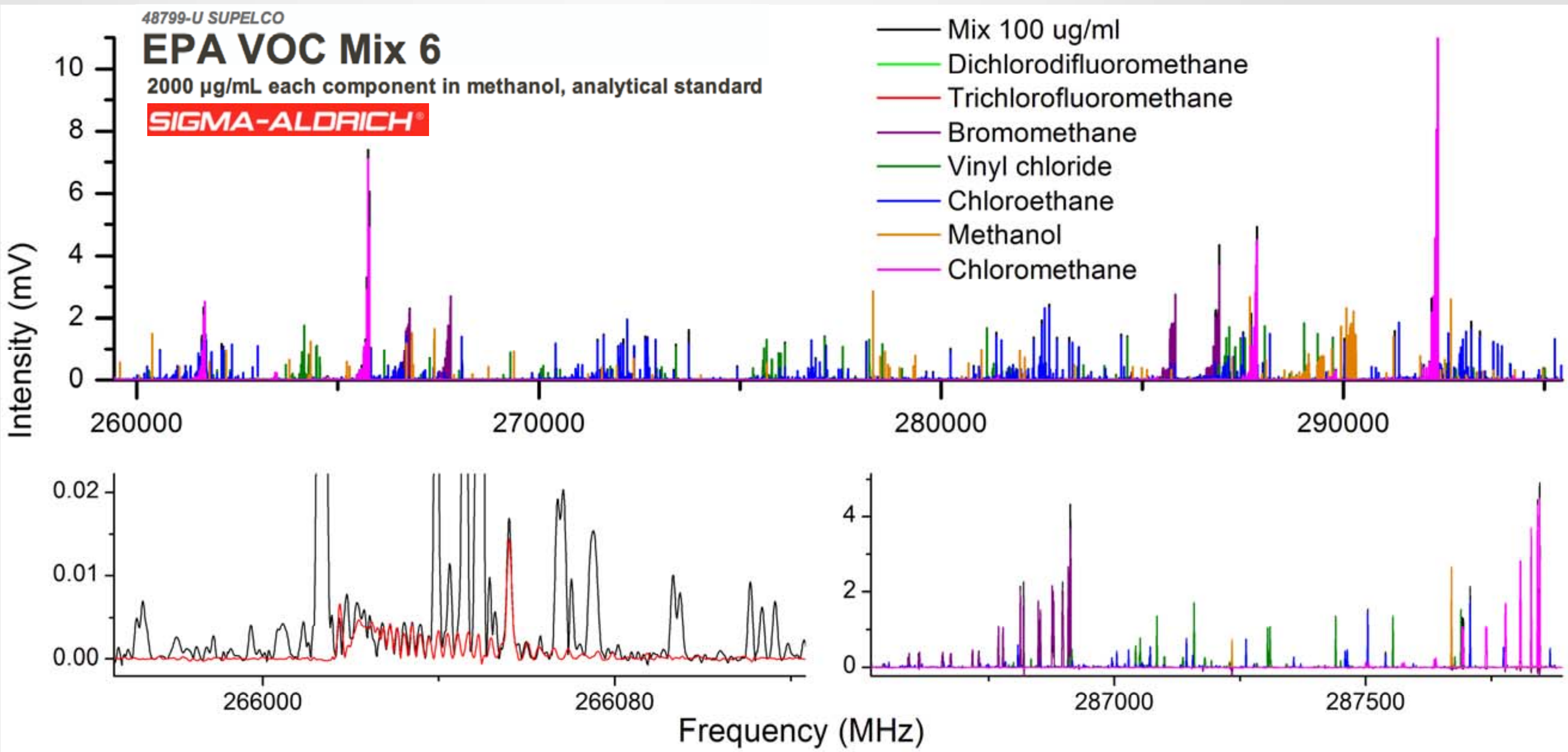
2) Observed partial pressure as returned by the matching algorithm.

Analysis of multicomponent mixtures with > 10,000 dynamic range in minutes

Headspace Analysis

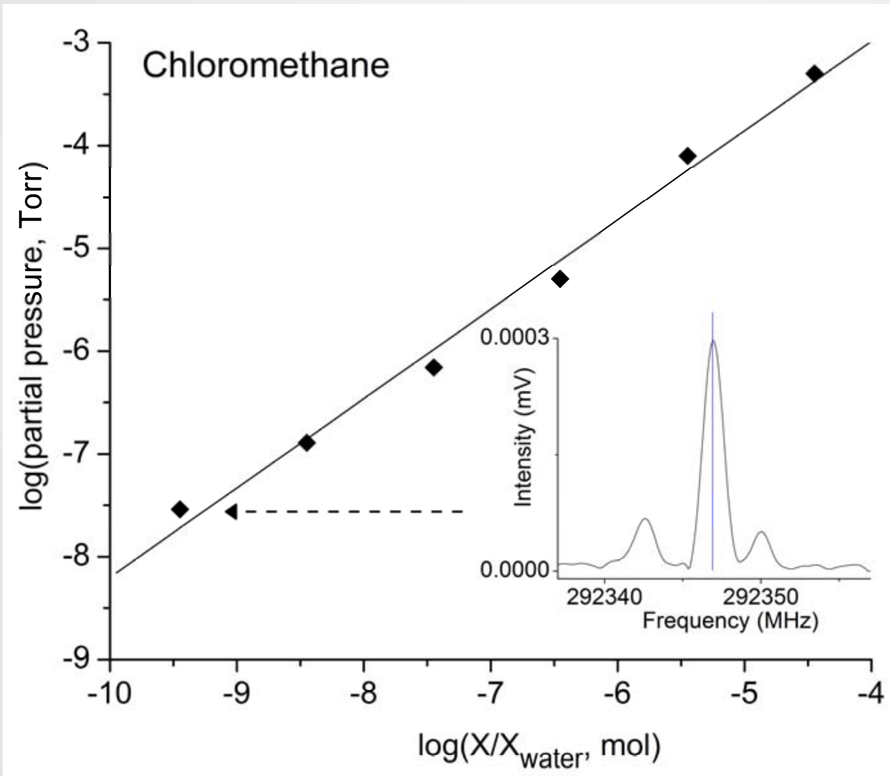
Complex Mixtures: No chromatography

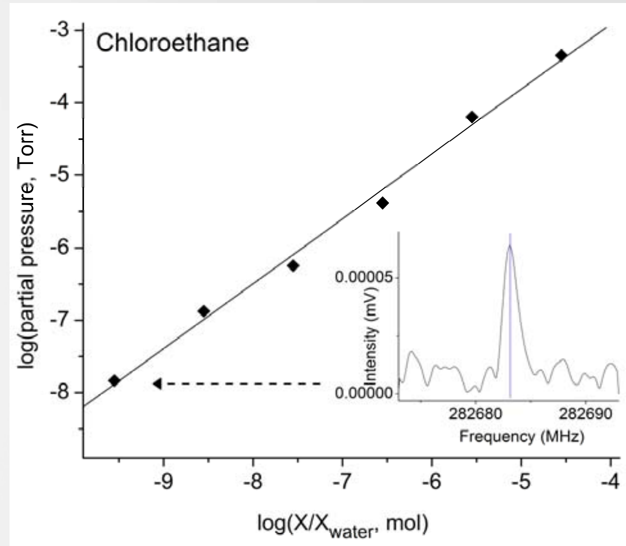




Headspace Analysis

Detection limits





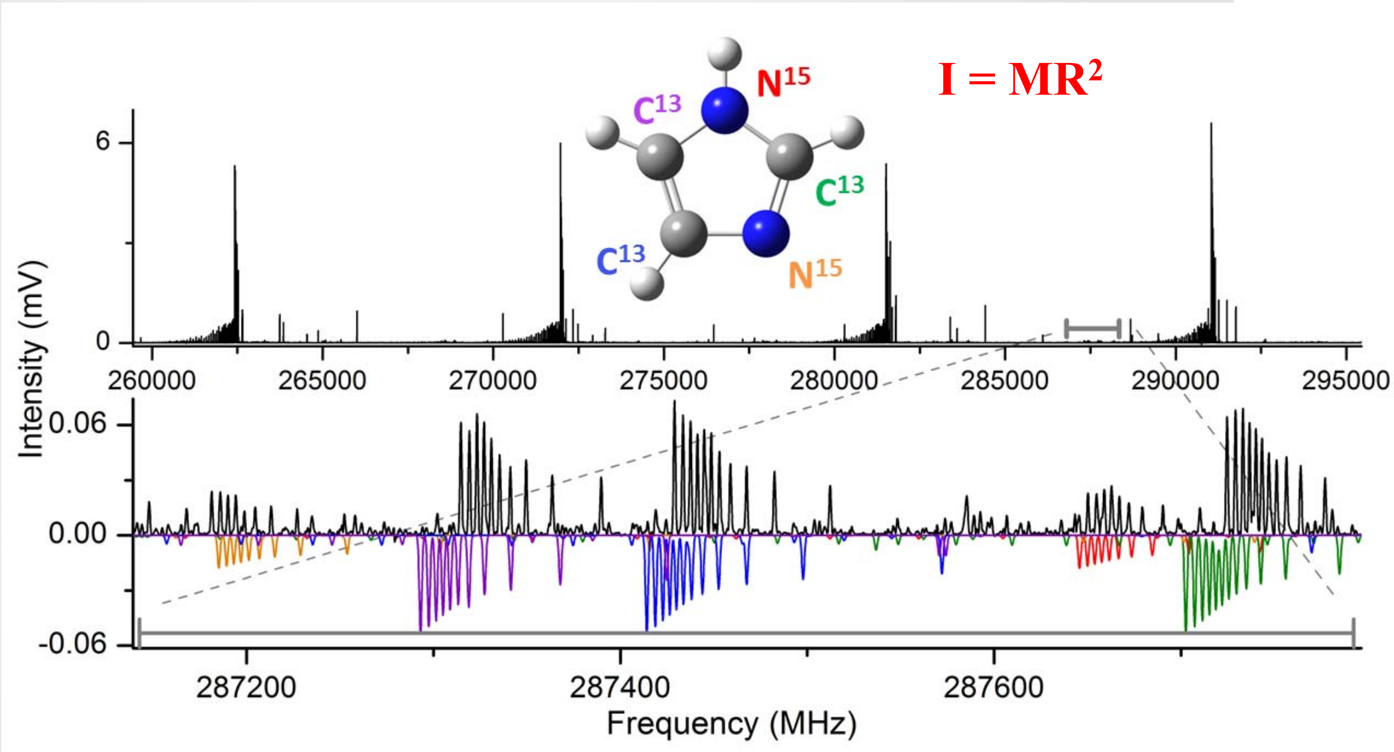
VOC mix #6 Detection Limits in Water

	Broadband (5min)	Targeted (40sec)
Chloromethane	0.005 ug/mL	0.1 ug/L
Bromomethane	0.022 ug/mL	0.8 ug/L
Chloroethane	0.026 ug/mL	0.5 ug/L
Vinyl Chloride	0.042 ug/mL	0.5 ug/L
Dichlorodifluoromethane	100 ug/mL	100 ug/L
Trifluorochloromethane	100 ug/mL	1000 ug/L

10^5 Linear Dynamic Range

Analysis Tools

Site-specific Isotope Analysis



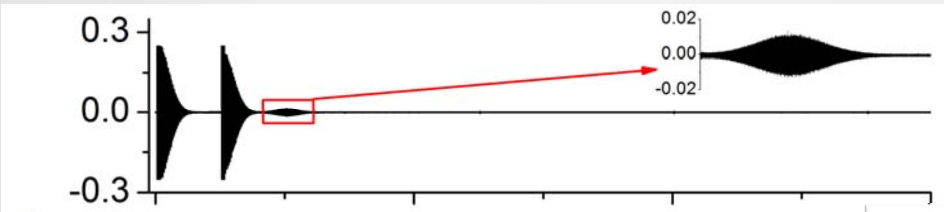
Sample Pressure:	5 mTorr (50 nmol)
Time:	2 minutes
S/N Ratio:	15,000:1
Quantitation Limit:	10 pmol

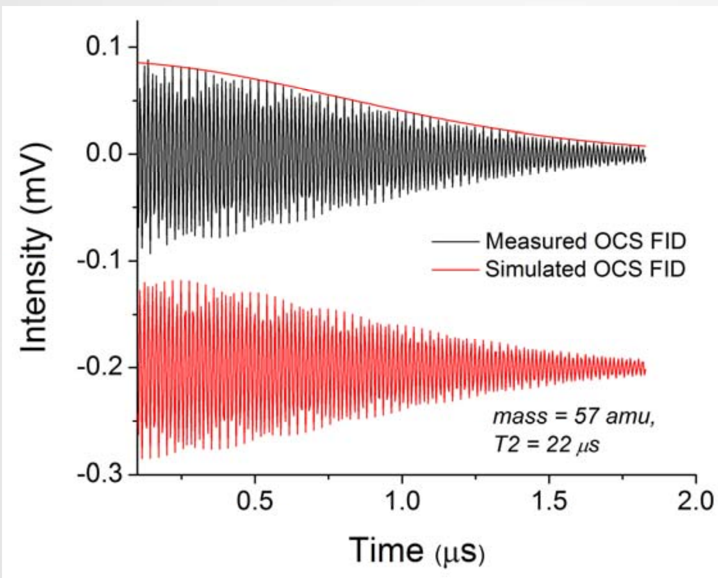
Site-Specific Isotopic Spectra are Predicted using an ab initio structure

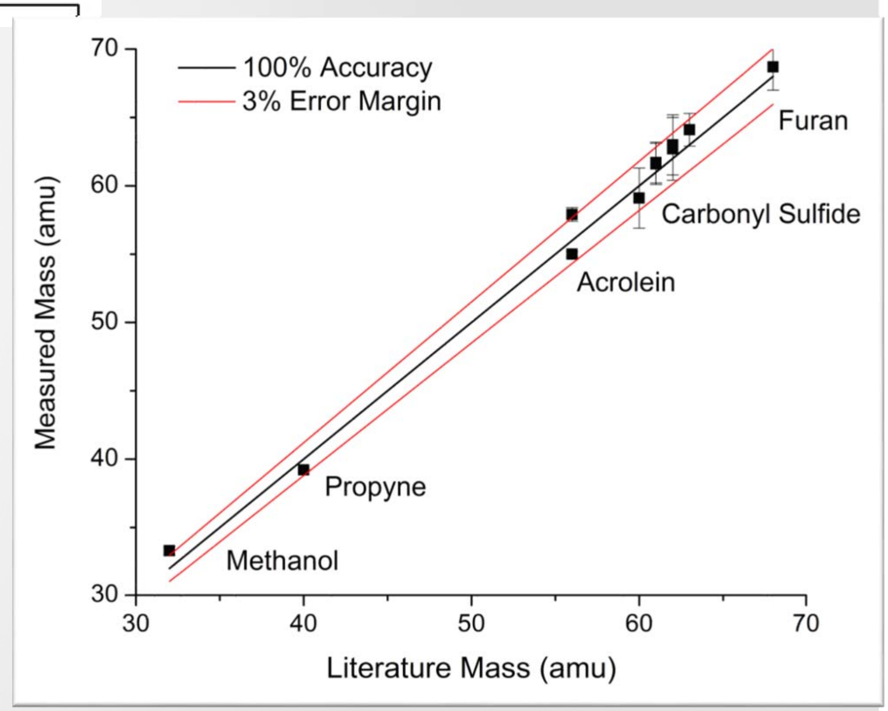
The intensity scale uses natural abundance of ^{13}C and ^{15}N

Analysis Tools:

Mass Estimation: Unknown Identification

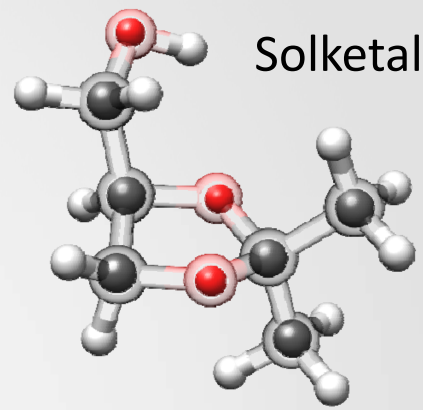


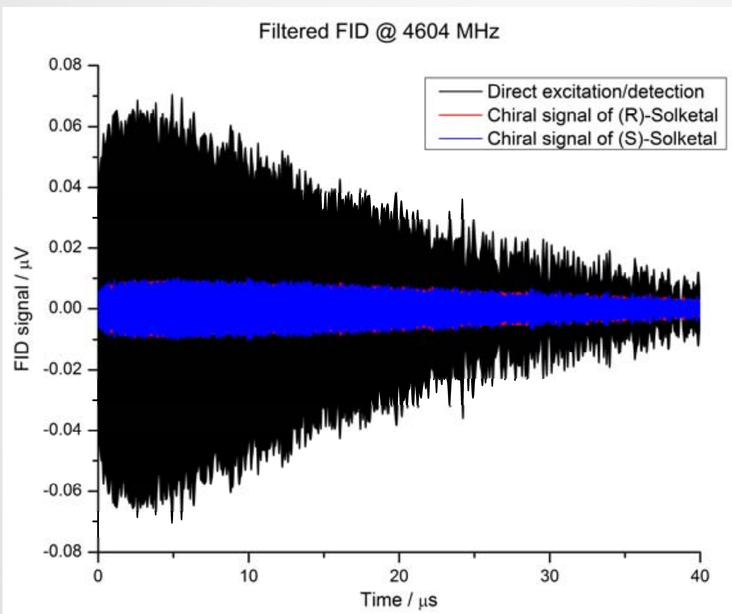


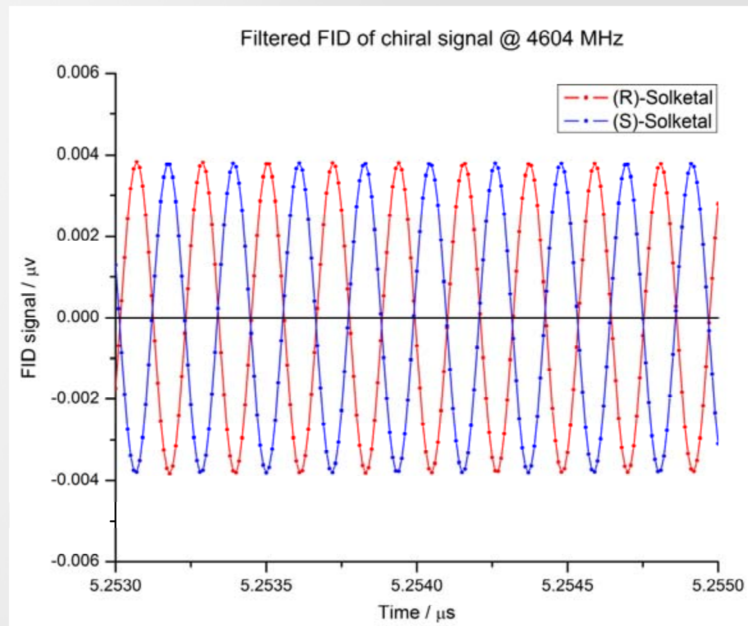


Analysis Tools

Enantiomeric Identification







* Cristóbal Pérez, Simon Lobsiger, Nathan A. Seifert, Daniel P. Zaleski, Berhane Temelso, George C. Shields, Zbigniew Kisiel, and Brooks H. Pate, “Broadband Fourier Transform Rotational Spectroscopy for Structure Determination: The Water Heptamer (Frontiers Article)”, Chem. Phys. Lett. **571**, 1-15 (2013).

How
would we work together

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