Direct Headspace Analysis of VOCs in Water by FT-MRR

(*Fourier Transform - Molecular Rotational Resonance*)

Brent J. Harris [a,b], Justin L. Neill [a], Matt T. Muckle [a], Robin L. Pulliam [a], Dave A. McDaniel [a], Roger L. Reynolds [a], Brooks H. Pate [a,b]

 [a] 770 Harris St. Suite 104B, Charlottesville, VA 22903, [b] Department of Chemistry University of Virginia – Charlottesville, VA

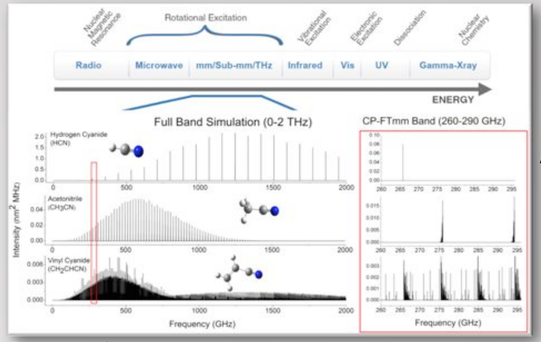
FT-MRR Spectroscopy for Chemical Analysis

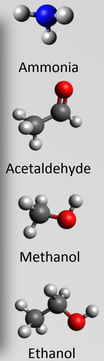
Of SMALL, POLAR, VOLATILES

$$I = MR^2$$

Rotational spectroscopy is high resolution and structure specific. No chemical separation is necessary. The rotational spectrum can be calculated with a high degree of accuracy based on the molecule's *mass distribution*.

SMALL (less than 150 amu)

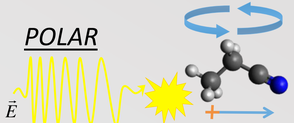




There are two effects as the molecule gets heavier:

1) The rotational energy levels get closer, spreading the population thinner (weaker emission)
2) Conformers and vibrationally excited modes contribute distinct spectra (weaker emission, dense spectra

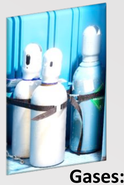
POLAR



Stronger coupling between the electric field of the excitation light and the oscillating dipole means stronger signals.

VOLATILE

High resolution MRR spectroscopy require freely rotating molecules at reduced pressure (10^{-4} atm). Only 1mL of STP gas is required.



Gases:
Cylinder purity
Process control, feed gas
Airborne contaminants

Liquids:
Headspace
Solutions
Reaction monitoring

Solids:
Residual Solvent
Identification
TGA

FT-MRR New Spectroscopy for Analytical Applications

FUNDAMENTAL ADVANTAGES

Selectivity	MRR is *high resolution*, no complex chemometrics required	*Direct Analysis No chromatography*
Structure Specificity	MRR spectra are unique to the moments of inertia of a rotating molecule. Any mass re-distribution shifts the spectrum.	*Isomers, Conformers, Isotopologues, Enantiomers*
Sensitivity	The chirped-pulse Fourier transform technique maximizes the measurement duty cycle and excitation efficiency.	*In Minutes: f mols, 100s ppb 10^5 Dynamic Range*
Precision	Very stable millimeter wave light sources produce consecutive spectra that are reproducible to < 0.5%	*On line monitoring Method transfer*
Simplicity	No lasers or complicated optics. The highly stable light field is digitally generated, detected, and analyzed	*Direct Automated Easy Operation*
Multi-Species Sensing	Excitation and detection are digitally controlled for full-band and targeted monitoring of multiple species in a mixture	*One instrument, many molecules Reprogrammable*
Breadth of Application	MRR is a non-destructive, low pressure gas measurement (10^{-4} atm)	*Solvents Airborne Toxins Gas Mixtures*

Spectroscopy AND Sensitivity

Predicted Detection Limits

Molecules of Interest	Detection Limit (40 seconds, pmol)	Residual Solvent Class 3	Detection Limit (40 seconds, pmol)
Acetonitrile*	0.02	**Formic Acid**	**0.28**
Carbonyl Sulfide*	0.04	**Dimethyl sulfoxide**	**0.41**
Ethylene oxide*	0.05	**Acetone***	**1.5**
Trifluoromethane	0.09	**Ethanol***	**1.6**
Acrylonitrile*	0.11	**Acetic Acid**	**2.8**
Propionitrile*	0.14	**Methylethyl ketone**	**3.7**
Acetaldehyde*	0.20	**2-propanol***	**4.2**
Nitric Acid	0.16	**Ethyl formate**	**4.5**
Formaldehyde (in water)*	0.26	**1-propanol***	**10**
Propyne*	0.33	**2-butanol**	**11**
Methyl isocyanate*	0.38	**Ethyl acetate**	**23**
Chloroacetonitrile*	0.66	**1-butanol**	**32**
Methanesufonyl chloride*	0.71	**Diethyl ether**	**62**
Nitrous Oxide*	1.26	**Anisole**	**80**
1-Butyne*	2.9	**3-methyl-1-butanol**	**140**
Nitrogen Dioxide	8.6	**tert-butylmethyl ether**	**370**
Methyl acetate	11	**Methylisobutyl ketone**	**372**

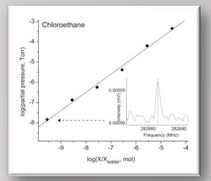
* Experimentally measured at BrightSpec Labs

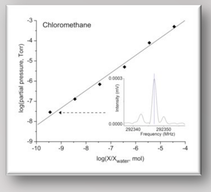
Composition of solution headspace

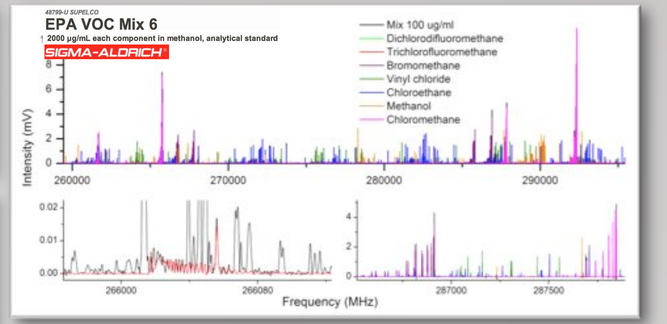
Experimental:

1) A standard sample of each component of VOC Mix 6 dissolved in methanol was diluted 1:10 in water. (20 – 500 ug/mL)
2) A standard sample of EPA VOC Mix 6 was diluted to 1:20 in water. (each component 100 ug/mL)
3) 1mL of each solution was injected through a septum into an evacuated glass vial.
4) After 10 minutes of equilibration at room temperature, the FT-MRR spectrum is recorded for each sample by drawing 10 mTorr of headspace into the spectrometer sample cell via a needle connected to the vacuum transfer line.

Results: Dynamic Range 10^5



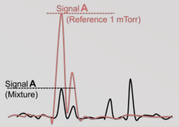




With 50,000 independent data channels, the high resolution FT-MRR spectrum enables high dynamic range, direct mixture analysis. High sensitivity results can be obtained in 5 minutes for broad searches (above) or in 40 seconds for targeted detection (left). Linearity is retained across a dynamic range of 10^5.

Quantitation in liquid-vapor equilibrium:

1. Reference measurement of A



2. Linearly extrapolate: A in mixture

$$\frac{Signal_{mixture}}{Signal_{reference}} = Partial\ Pressure\ (P_A)$$

3. Apply Henry's Law $P_A = k_{H_A} X_A$

X_A = *mole fraction A in solution*

Solvent 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

For comparison, the EPA method 624 for VOC detection in water lists GC/MS purge and trap detection limits on the order of 0.5 – 1 ug/L. The EPA 624 method requires approximately 60 minutes. The FT-MRR detection technique offers time savings and simplicity. The volatiles here were measured by a direct headspace measurement without heating, trapping, or salt enhancements and with a total measurement time 10 times faster than the established EPA method.

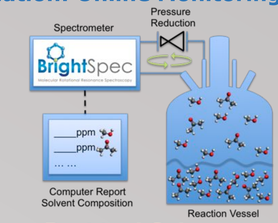
Implications and Applications

MIXTURE ANALYSIS WITHOUT A CHEMICAL SEPARATION:

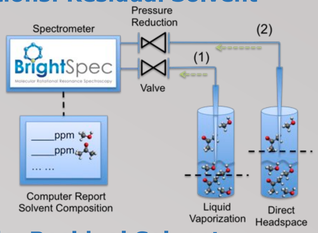
- 10 times higher sample throughput
- Reduction in consumables cost (no columns or carrier gases)
- Reduction in resource intensive calibration
- Turn key, automated operation (minimal training)

Vapor phase monitoring is important to many processes in chemical manufacturing. FT-MRR promises new analytical capability enabled by molecular structure selectivity, high sensitivity, high resolution and operational simplicity.

Formulation: Online Monitoring



Solutions: Residual Solvent



Solids: Residual Solvent