BrightSpec
Molecular Rotational Resonance Spectroscopy

Acrolein/Acrylonitrile Headspace Analysis and Conformer Specificity to Acrolein

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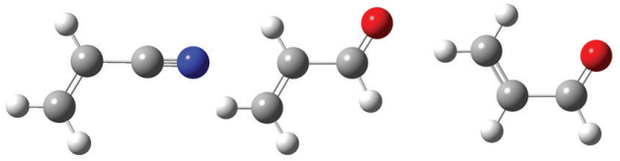
Introduction

Acrolein and acrylonitrile are common precursors in chemical manufacturing. Acrylonitrile is highly toxic and has regulated exposure limits important for its use in any pharmaceutical synthesis. Residual solvent analyses must meet stringent requirements for acrylonitrile content. Acrolein is combustion byproduct and common air pollutant that has not been identified as highly toxic. However, it is a heavily monitored molecule. There is an established EPA method 603 for composition analysis of Acrolein and Acrylonitrile in water.[1] Acrolein and acrylonitrile are low molecular weight, polar, volatile molecules that are very favorable for detection by rotational resonance spectroscopy. The Acrolein/Acrylontrile standard mixture for EPA method 603 is used in this study to benchmark BrightSpec's rotational spectrometers as a detector for direct analysis of the volatiles in water headspace. Since water has no rotational signature at room temperature in the bandwidth of the 260-295 GHz spectrometer, it does not interfere with the spectrum of the analytes.

Acrolein has two stable conformers shown in Fig 1. The *cis*-conformer exist in room temperature equilibrium at approximate 2% abundance compared to the more stable



Acrylonitrile *trans*-Acrolein *cis*-Acrolein

Fig 1: *Target species: acrylonitrile and cis/trans acrolein. Each give a distinct rotational spectrum and highlight structurally sensitive MMR spectroscopy.*

trans conformer.[2] Since the rotational spectrum is a unique fingerprint tied directly to the moments of inertia of the freely rotating molecule, it is specific to any change in mass distribution and, hence, specific to a molecular geometry. The *cis*-conformer of Acrolein can be distinguished in the vapor of the reference spectrum of Acrolein generated for this study. This communication highlights the specificity and sensitivity of BrightSpec's millimeter wave rotational spectrometers for the analysis of volatiles in a mixture. The measurement protocol can be software controlled to change the measurement mode from unbiased, fullband spectral analysis, to the more sensitive targeted analysis of specific analytes.

Experimental

The software controlled spectrometer consists of a millimeter wave light source which broadcasts an excitation pulse from 260-290 GHz, a heterodyne receiver which downcoverts the molecular free induction decay for digitization on a PCI card, and a computer. The measurement cell is a 65cm steel tube approximately 5cm in diameter and 1L in volume. A port is used to introduce gas and a separate port is used to evacuate gas by turbo pump. Pure liquid samples of Acrolein (O1679 Fluka) and Acrylontrile (110213 Aldrich) were each transferred to a glass sample holder, frozen with liquid nitrogen, and the air was evacuated. The glass sample holder is sealed by o-ring to a kyvar glass/metal sealed tube which mates with the measurement cell by Swagelok. After warming, the vapor pressure of the pure liquid is allowed to expand into the measurement cell to a pressure of 0.5 mTorr. The full band spectrum in high dynamic range mode was acquired (about 1.5 minutes). Typical signal levels compared to the spectrometer noise level for the Acrolein and Acrylonitrile reference spectra are > 20,000:1.

The EPA Acrolein/Acrylonitrile standard of 10,000µg/ml each in water was diluted in series with purified water (46871-U Supelco). The following concentrations were prepared: 1million µg/L, 1,000 µg/L, 100 µg/L, 10µg/L, 1µg/L. Spectra for fullband analysis were acquired in fullband high dynamic range mode in order to determine the optimal set of spectral lines for a targeted analysis tailored for the acrolein /acrylonitrile sample matrix. Each sample is frozen, the air evacuated, warmed to room temperature, and the vapor is allowed to expand into vacuum for direct measurement of the headspace without any chemical separation.

Results and Discussion

The reference spectra of acrolein and acrylonitrile are displayed in Fig 2. Though there are spectral similarities, the spectra are highly resolved. The cis-acrolein spectrum was recovered upon comparison of the acrolein reference spectrum to a simulated spectrum of cis-acrolein based on rotational constants measured in the low frequency rotational spectrum (Fig 3). Signal intensities for *cis*-acrolein are approximately 1% of trans-acrolein as a result of lower abundance in the headspace and a reoreintation of the dipole moment due to the structural change. [2]

For trace detection of acrolein and acrylonitrile in a mixture the excitation pulses are customized in frequency

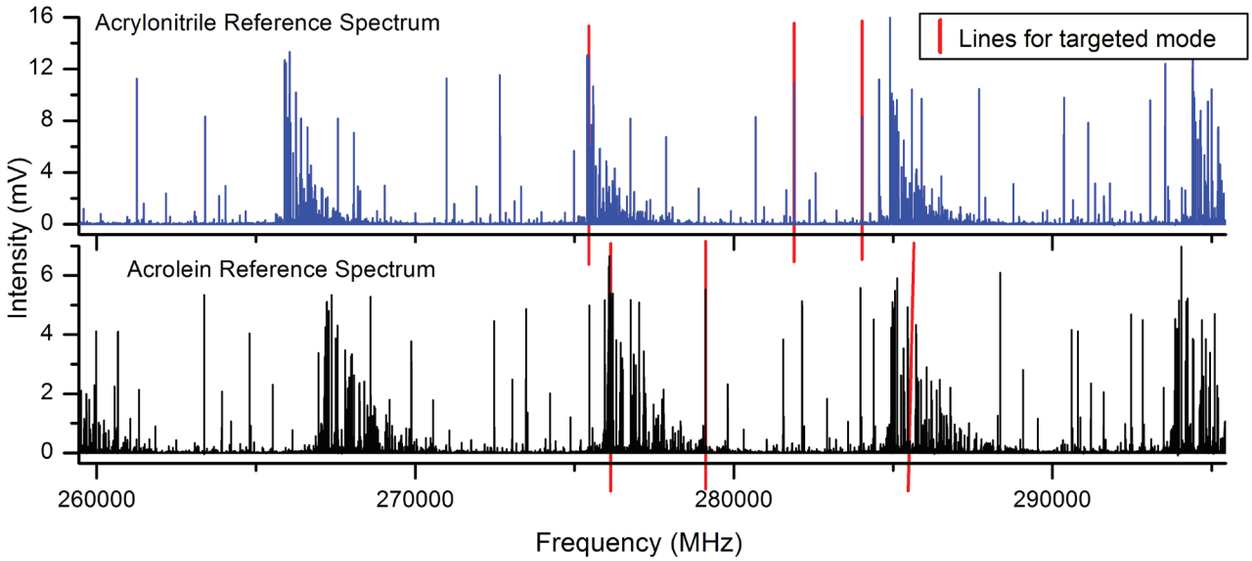


Fig 2: *The fullband spectra of acrylonitrile and acrolein. Strong, isolated lines are chosen for targeted detection mode which optimizes the spectrometer sensitivity for specific molecular signals in this matrix.*

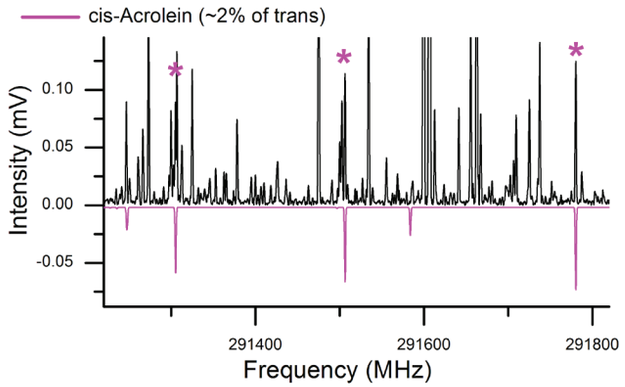


Fig 3: *The cis-acrolein assignment was made in the reference spectrum based on simulating the spectrum from literature values of the rotational constants measured by low frequency microwave spectroscopy and refining the parameters to include the BrightSpec frequencies.*

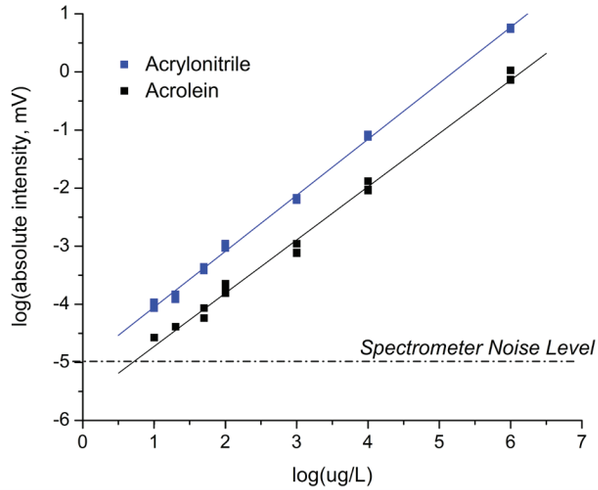


Fig. 4: *Signal levels across 6 orders of magnitude of concentration. The acrylonitrile signal is 2 times stronger and approximately 3 times more abundant in the headspace.*

and duration to optimally excite specific transitions and tradeoff bandwidth for enhanced sensitivity (targeted mode). Signal intensities of three lines for both acrylontirile and acrolein are plotted versus the concentration in the standard mixture dilutions in Fig 4. The plot shows a linear dynamic range of six orders of magnitude. Detection limits of 3µg/L for acrylonitrile and 12µg/L for acrolein are comparable to purge and trap GC/MS detection limits, yet the results presented here are a direct measurement of the headspace expansion into vacuum (Table 1). No other pre-conditioning was utilized. Measurements at these detection limits can be obtained in less than five minutes by BrightSpec MRR. Simple methods for enhancing the partial pressure of the analytes in the headspace such as the addition of salts, heating the sample, and drying the vapor can improve detection limits and keep the sampling protocol simple.

Table 1: Detection limits (3:1) in water by direct headspace measurement (5min)

Acrylonitrile	2.4 µg/L	1 nTorr
Acrolein	12 µg/L	5 nTorr

Table 2: Detection limits in gas

	1 min full band	5 min full band	40 sec target
Acrylonitrile	38 nTorr (2.3 pmol)	13 nTorr (0.8 pmol)	1 nTorr (60 fmol)
Acrolein	76 nTorr (4.6 pmol)	26 nTorr (1.5 pmol)	2 nTorr (120 fmol)

[1] EPA method 603 Acrolein and Acrylonitrile [2] Blom, C. E., Gassi, G., Bauder, A., JACS, 1984 (106), 7427