

High Dynamic Range in Broadband Monitoring of OCS Rare Isotopes

Introduction

For gas monitoring applications in manufacturing process control and environmental analysis, analytes are often measured within a complex mixture where high abundance components can cause significant crosstalk during detection. Pure rotational spectroscopy is an inherently high resolution technique, making it ideal for mixture characterization. With typical resolving power ($\nu/\Delta\nu$) of $>10^5$, and typical device bandwidths of up to 10% of the center frequency, rotational spectrometers can yield more than 10,000 independent data channels. In many cases, pure samples are equilibrium mixtures of different forms of the molecule (isotopes, conformers, vibrationally excited modes) and, since each involve a change in the mass distribution, they each yield a distinguishable rotational spectrum. BrightSpec spectrometers offer linear response over 5 orders of magnitude. A "pure" sample of OCS is used to benchmark the dynamic range of a single, 5 minute broadband measurement by analyzing the rare isotopes in natural abundance.

OCS also serves as an example of a common sulfur bearing toxin that is used in many industrial processes. The electronics industry has fueled the development of OCS gas sensors because the molecule causes metal corrosion and is the focus of failure analysis, for example, in semiconductor manufacturing. OCS is a very favorable molecule for rotational spectroscopy because the simple, linear rotor simplifies the rotational spectrum and reduces the number of accessible angular momenta states (the partition function). Although it is not that polar of a molecule, the energy levels are well populated in the room temperature millimeter wave spectrum.

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 downconverts 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. OCS gas (295124 Aldrich, $\geq 97.5\%$) was introduced to the spectrometer measurement cell without purification in the amount of 3 mTorr. The full band spectrum in high dynamic range mode was acquired with 100,000 signal averages (about 5 minutes). Main OCS isotope levels compared to the spectrometer noise level are $> 1,000,000:1$.

Table 1: OCS Rare Isotopes

	<u>% abundance</u>	<u>ratio to main</u>	<u>ppm</u>
OCS	~94%		
OC ³⁴ S	4.00000%	1 : 24	41,100
O ¹³ CS	1.00000%	1 : 94	10,640
OC ³³ S	0.74000%	1 : 127	7,800
¹⁸ OCS	0.20000%	1 : 470	2,100
O ¹³ C ³⁴ S	0.04000%	1 : 2350	425
¹⁷ OCS	0.03500%	1 : 2690	372
OC ³⁶ S	0.01670%	1 : 5630	178
¹⁸ OC ³⁴ S	0.00834%	1 : 11,270	89
O ¹³ C ³³ S	0.00831%	1 : 11,310	88
¹⁸ O ¹³ CS	0.00211%	1 : 44,550	2

Results and Discussion

Fig 1. Is a full band measurement of OCS and highlights the dynamic range and the complexity of the OCS spectrum which includes vibrationally excited states (2 are visible next to the main OCS lines in the 1x view). Across the bandwidth of the spectrometer there are three transitions of OCS. The spectral redundancy is an important characteristic of the OCS spectrum considering the fact that line overlap could be a possibility if OCS were to be measured in a complex mixture. Large bandwidth is a key design parameter of BrightSpec spectrometers in order to ensure multiple lines are accessible for detection. Smaller molecules have a more sparse spectrum and, may not have lines with appreciable intensity in the 260 -290 GHz band (for example, nitric oxide), so BrightSpec has also designed a small molecule detector which operates from 520 – 580 GHz. For rotational spectroscopy, spectral intensity and frequency are both indicators for molecular assignment, which means there are 6 parameters (2 parameters, 3 lines each) for OCS detection confidence. All of the isotopologues detected in this 5 minute fullband measurement are listed in Table 1.

The baseline in the vertically expanded scale of Fig. 1 seems confused, however it is a very high resolution data set that cannot accurately be captured in a single figure. Much of

