Laboratory Measurement Of Air Broadened Linewidths In Support Of EOS-MLS

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Objectives

This program addresses immediate requirements of the EOS-MLS program with laboratory measurements of all the linewidths necessary for the interpretation of returned MLS data. These include transitions of the free radicals OH, HO_2, and BrO. Other molecular transitions include several near 2.5 THz of H_2O and O_3 and weak transitions of O_2. In the past, we have supplied frequencies, transition moments and linewidths to the MLS science team under another existing laboratory program. However, the extensive list of necessary measurements and the large range of frequencies have required an accelerated program in order to successfully complete the measurements prior to launch. The program reported upon here is directed mainly toward the measurements in the 600 GHz and 2500 GHz range and other more difficult measurements of radicals and weak transitions. These are addressed in the order of the priorities set forth in the MLS list of requirements within each frequency region. Linewidth measurements are compared to available data for these molecules in the infrared region and to theoretical calculations.

Measurements made in this laboratory have always been made available to the HITRAN database and that practice will be continued. Any incidental improvement of line positions will be also included in the continuously updated versions of the JPL Submillimeter, Millimeter, and Microwave Spectral Line Catalog. After the immediate requirements of the MLS program have been met, we will carry out corroborative measurements of related transitions to assure consistency of the data set and facilitate comparisons with theory and measurements of other investigators. This will also continue to improve the status of the submillimeter and far infrared data bases of linewidths in anticipation of still more advanced versions of MLS and related instruments.

Accomplishments to date

The measurements which will be discussed in this report required a number of improvements and modifications to existing equipment in order to achieve the accuracy and precision required by the EOS-MLS science team. These upgrades also facilitated related measurements which are supported under existing programs. This report will describe the instrumental upgrades, improvements in the data analysis, the status of each required measurement, and the status of related work which has been facilitated by this program.

Instrumental upgrades

The primary experimental achievement is the implementation of solid-state millimeter and submillimeter wave sources that create a stable, reliable and simple spectrometer. A computer controlled data-acquisition card that allows simultaneous measurements of temperature and pressure along with the spectrum has been implemented. Four types of temperature controllable free-space cells

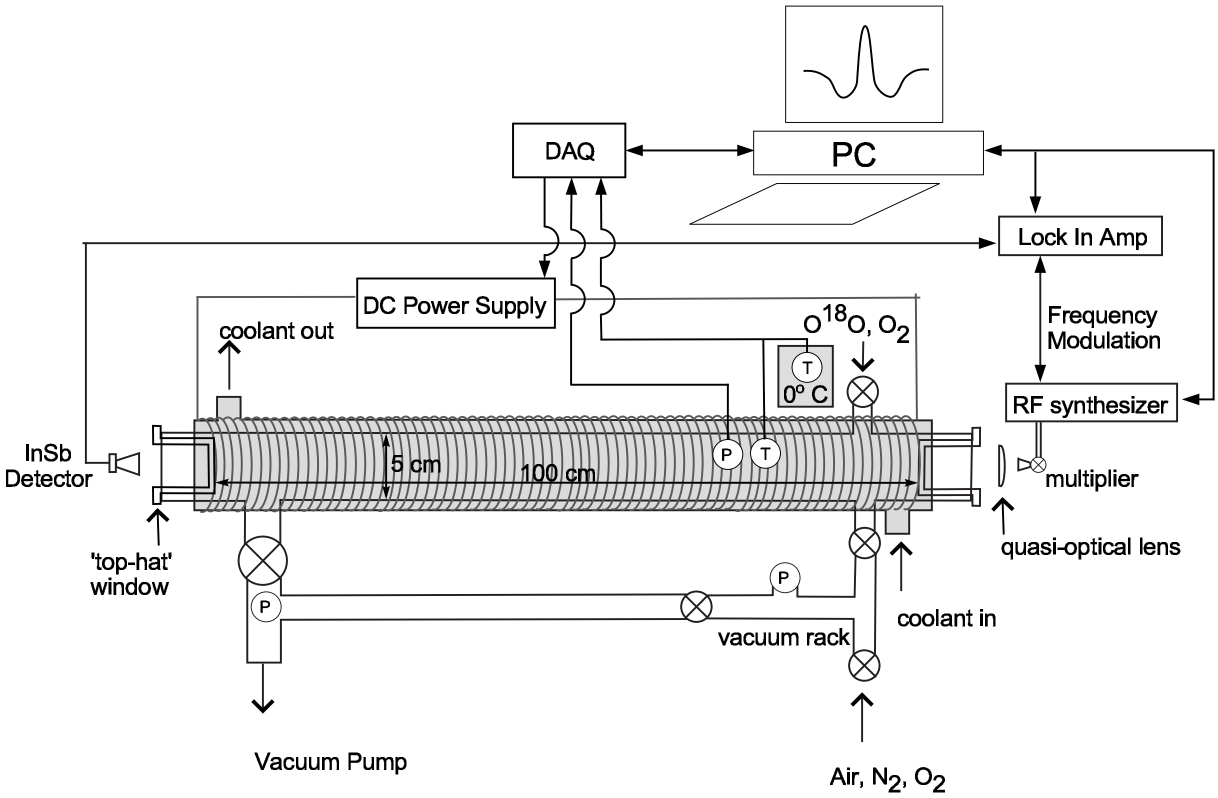

Figure 1: The experimental setup for measurement of $O^{18}O$ linewidth parameters.

have been built for the demanding experimental needs of observing the variety of chemicals found in the MLS radiometric bands. These include a fast flow, Zeeman modulated cell for radical and other highly reactive species; a slow flow cell for less reactive species, a special leak tight cell for long averaging of the $^{18}O^{16}O$ spectrum, and a large diameter cell for FIR sideband and emission measurements. Software has been written that allows rapid inter-comparison of the broadening measurements at the same workstation at which the spectra are recorded. This new system allows efficient collection of statistically relevant data sets, rather than relatively sparse data sets commonly used to determine temperature dependent rotational half-width parameters. The software, which provides real time analysis of the data, allows experimental problems to be more quickly detected and corrected. In the past data acquisition and analysis were done serially, with analysis usually following a full day of data acquisition. Devices have been made available by the JPL Submillimeter Wave Advanced Technology (SWAT) team (Oswald, *et al.,* 1998) that have allowed us to make spectroscopic measurements with multiples of directly synthesized frequencies from stable solid state sources. Thus, problems associated with source instability have been virtually eliminated. Use of the Balloon OH radiometer as a sideband source has allowed frequency and linewidth measurements in the entire EOS-MLS THz bandwidth.

Data analysis

As was the case with our previous linewidth measurements, we have used the convolution method described by Pickett (Pickett, 1980). This method allows one to determine the pressure broadening due to a foreign gas without precise knowledge of the instrumental lineshape or of the concentration of the broadened molecule. The experimental spectrum $S(\nu, p)$ at the pressure p is given by

$$S(\nu, p) = \int_{-\infty}^{\infty} S_r(\nu', p')L(\nu - \nu', p - p')d\nu,$$

where $S_r(\nu, p')$ is a reference spectrum taken at a lower pressure p' and $L(\nu, \Delta p)$ is a Lorentzian function the width of which is that caused by the additional broadening gas. The advantage of the method is that the information regarding instrumental effects, Doppler broadening, and all sources of pressure broadening common to both the low- and high-pressure samples is contained in the reference spectrum. The convolution method allows the additional pressure broadening to be readily determined in the regime where it is comparable to other contributions to the linewidth. For example, if $S_r(\nu, p')$ is a Gaussian, $S(\nu, p)$ will be a Voigt profile. The requirements for the method to be valid are that the absolute pressure of the broadened molecule remain constant as the foreign gas is varied, that the absorption of the reference spectrum be linear at the line center and that the power and instrument function be constant over the broadened line profile. The method has been tested against other techniques in an inter-laboratory comparison(Goyette, *et al.*, 1998).

The primary difference in data handling is that all data points derived from the convolution method at the different temperatures and differential pressures are fitted simultaneously to the equation

$$\gamma(T, \Delta p) = \gamma_0 \Delta p \, (296/T)^n \qquad (1)$$

where γ_0 is the pressure broadening coefficient at 296K and n is the temperature exponent. Because this method allows individual measurements at each temperature and pressure to contribute equally to the parameters and because if allows for proper incorporation of uncertainties of the experimental parameters, it results in more realistic uncertainties than one would obtain by first determining a series of γ's at various temperatures and then determining n and γ_0. A similar expression

$$\delta(T, \Delta p) = \delta_0 \Delta p \, (296/T)^s \qquad (2)$$

is fitted for the line shifts. Shift and width parameters derived from the convolution method are not highly correlated since the width is an even function of frequency and the shift is an odd function.

Overview of measurement status

The most urgently required measurements are listed below with the current status of the work indicated as follows: completed and published, completed, and in progress.

MLS Highest Priority Linewidth Requirements

- HCl line at 625.9 GHz.
- O_3 lines at 235.7, 237.1, 242.3, 243.5, and 625.4 GHz.
- BrO lines at 624.8 and 650.2 GHz.
- $^{18}O^{16}O$ line at 233.9 GHz.
- HO_2 lines at 649.7 and 660.5 GHz.
- 2.5 THz lines of OH, O_2,and H_2O and O_3 .

MLS High Priority Linewidth Requirements

- O_3 lines at 239.1, 231.3, 248.2, 249.8, and 250.0 GHz.
- CO line at 230.5 GHz.
- CH_3CN lines near 183.9, 202.3, 624.8, 626.4,and 660.7 GHz.
- HOCl line at 635.9 GHz.
- HCN line at 177.3 GHz.

This program has been concerned primarily with transitions above 600 GHz as well as the $^{18}O^{16}O$ line at 233.9 GHz and the low frequency lines in the cluttered CH_3CN spectrum. The other lower frequency transitions are being addressed by another program, but with instrumental improvements that have been implemented under this program. Details of the results for molecules that have been addressed by this program and that have been published are in the following section. These species as well as molecular parameters that have not been published yet have been given to the MLS Science team(contact: William Read) and are included in the forward model-retrieval algorithm. Of the molecules in progress, the THz measurements are nearing completion and are also discussed below, HO_2 requires further inter-comparison of results with those of the Amano group which also collaborated on the BrO measurements.

Measurements and Results for Individual Species

HCl

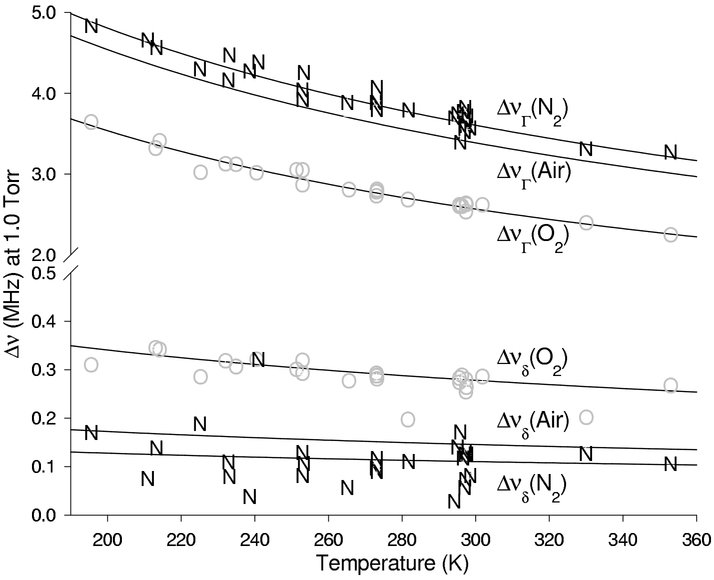

Figure 2: A comparison of average lineshape parameters from individual runs (N = N_2, O = O_2) and the parametric fit (solid lines) to individual spectral comparison data points.

The lowest rotational transition, $J = 1 \leftarrow 0$, of hydrogen chloride lies in the lower sideband of the 640 GHz radiometer. No previous submillimeter studies had examined the temperature dependence of the lineshape parameters. Remote sensing measurements by Stachnik *et al.* (Stachnik, *et al.,* 1992) have indicated the need for a lineshift parameter for proper fitting of line profiles observed from balloon. Lineshape measurements of hydrogen chloride have been completed. Both linewidth and lineshift parameters were determined. After the spectrometer was equipped with an elevated temperature control bath (290 - 350 K) the lineshape in the 290 - 350 K region was first predicted with the 195-295 K data, and then verified with corroborative measurements. The full analysis with expanded temperature data significantly reduced the correlation between the parameters. A manuscript (Drouin, 2003a) reporting the parameters and describing the methodology in detail has been published. Furthermore, the recommended halfwidth value has been submitted to HITRAN. The results are summarized in Table 1

Table 1: Linewidth and lineshift parameters[a] for $H^{35}Cl$.

Half-width parameters	Nitrogen	Oxygen	Air[b]
γ_o (MHz/Torr)	3.639(7)	2.595(5)	3.420(7)
n	0.71(3)	0.79(1)	0.73(3)
$\chi_{\gamma,n}$	0.4010	0.4425	0.4097
2σ(180 K)	4.3%	2.4%	3.9%
Lineshift parameters			
δ_o (MHz/Torr)	0.111(3)	0.280(1)	0.146(3)
s	0.36(19)	0.50(3)	0.4047
$\chi_{\delta,s}$	0.3687	0.4047	0.3763
2σ(180 K)	22.1%	4.2%	17.8%

[a] Parameters are defined in eqns 1 and 2. The units of γ and δ are MHz/Torr in all tables.

[b] These values are determined from a fit to the calculated function $\sum_i c_i\gamma_{0,i}(296/T)^{n_i}$, where $c_{N_2} = 0.79, c_{O_2} = 0.21$, errors are propagated linearly. The correlation coefficients are given by χ.

BrO

The bromine monoxide radical has two transitions in the upper and lower sidebands of the 640 GHz radiometer of EOS-MLS. A similiar radiometer called SMILES, to be included in the Japanese Experiment Module onboard the International Space Station, will observe the very same transitions. In the interests of recovering the most accurate linewidth parameters for this radical species this group collaborated with the Japanese spectroscopy group at Ibaraki University.

Measurements at JPL covered the temperature range 220 - 300 K, which extends below the point ($\sim$ 240 K)where significant amounts of the radical and its reactants begin to condense on the spectrometer cell walls. Extension of the measurements into this temperature range required a strong, stable signal and minimal baseline distortion which was only achieved using the multiplier technology available at JPL (Oswald, *et al.,* 1998).

Because of the somewhat different data collection and analysis methods used at the two institutions, the combined analysis of JPL and Ibaraki data does not take advantage of the parametric fitting procedure. Parameters from equivalent (weighted linearized least-squares) analyses of the individual data sets agree within 3σ. Reported parameters are from the combined analysis of laboratory data. The results have published (Yamada, 2003). The HITRAN database will list BrO in its forthcoming version, rotational transition frequencies, as well as linewidth parameters for this listing will be based on analyses from this laboratory.

Table 2: Linewidth parameters of BrO.

	624.77 GHz		650.17 GHz	
Gas	γ_0	n	γ_0	n
N_2	3.24 (5)	0.76 (5)	3.20 (7)	0.84 (7)
O_2	2.33 (6)	0.93 (7)	2.41 (6)	0.70 (7)

Ozone

Ozone spectra will be recorded in all but the 118 GHz radiometers of EOS-MLS. All temperature dependent linewidth parameters above 206 GHz were previously unmeasured with microwave techniques. The pressure induced broadening of a series of pure rotational transitions of ozone have been measured as a function of temperature. In addition to the transitions of interest to EOS-MLS, several additional transitions were partially investigated to extend comparison of the present work to existing infrared, FIR and mm-wave results as well as theory. The results of experiments were compared with calculations employing the complex semiclassical theory of Robert and Bonamy as part of a collaboration with J. Fischer and R. R. Gamache. This formed the basis of a paper which is now published (Drouin, 2003b). A list of recommended linewidth values have been submitted to HITRAN. The results for the lines most important to MLS are listed in Table 3

Table 3: Ozone pressure induced half-width parameters measured in air.

$J'_{K'_a,K'_c}$	J_{K_a,K_c}	Frequency/MHz	$\gamma_o(296)$	n	$\chi_{\gamma_o n}$	$2\sigma_{max}$[a]
$7_{1,7}$	$6_{0,6}$	249788.600	3.236(8)	0.674(9)	0.7767	2.3
$8_{3,5}$	$9_{2,8}$	244158.438	3.181(17)	0.749(18)	0.8103	3.8
$10_{2,8}$	$10_{1,9}$	249961.960	3.157(6)	0.675(7)	0.7079	2.1
$12_{0,12}$	$11_{1,11}$	243453.793	3.062(10)	0.685(14)	0.7435	2.9
$12_{2,10}$	$12_{1,11}$	242318.736	3.103(7)	0.663(8)	0.6934	2.1
$14_{2,12}$	$14_{1,13}$	237146.192	3.037(10)	0.693(10)	0.8123	2.6
$16_{1,15}$	$16_{0,16}$	231281.491	2.986(8)	0.710(9)	0.7352	2.3
$16_{2,14}$	$16_{1,15}$	235709.840	2.971(8)	0.677(9)	0.7718	2.3
$15_{4,12}$	$16_{3,13}$	247761.770	3.014(15)	0.685(14)	0.8368	3.2
$15_{6,10}$	$16_{5,11}$	625371.468	2.988(19)[b]	0.745(25)[b]	0.6539	4.5
$18_{2,16}$	$18_{1,17}$	239093.260	2.980(7)	0.692(8)	0.7529	2.2
$20_{2,18}$	$20_{1,19}$	248183.380	2.949(5)	0.680(5)	0.6754	1.8

[a] In percent at 180K.

[b] These values calculated from measured N_2 and O_2 values.

$^{18}O^{16}O$

The $N = 2 \leftarrow 0$ transition of isotopic molecular oxygen, located in the lower sideband of the 240 GHz radiometer, is a weak magnetic dipole transition. Since the species is uniformly mixed throughout the atmosphere, it is useful for determining the pointing of the MLS antenna. It is a rare and costly species which can be obtained commercially only in randomized samples containing 50% of the mixed isotope and 25% each of $^{18}O_2$ and $^{16}O_2$.

With anticipated long integration times and high cost of the purified gas sample, a static gas cell of 1 meter length was built. The cell, like the radical flow cells, was wrapped with square wire to allow Zeeman modulation of the spectra. Temperature dependent measurements of the oxygen transitions at 118 GHz and 425 GHz were done to verify the performance of the static cell at extreme temperature and streamline the Zeeman modulation control. At the extreme sensitivity levels required for data collection a multitude of noise sources were identified and minimized or eliminated.

Integration times of 15 - 20 minutes were typically used to obtain S/N of > 50. In order to remove any baseline effects which may manifest themselves over long integration times, a double modulation scheme was employed. The microwave source is frequency modulated and the computer provides Zeeman modulation by switching the Zeeman field on and off and storing the difference for each data point.

Data collection and analysis is now complete, with over 1000 air-broadened comparative data points. The data analysis indicates sufficient precision ($< 3\%$) is achieved in the 200-250 K range. The signal strength degrades with increasing temperature, and therefore the relative errors in the

250-300 K range increase above 3%. All results are consistent with the recent room temperature measurements of normal oxygen transitions by Krupnov *et al.*(Krupnov 2003). A manuscript has been prepared and will be submitted for publication soon.

Hypoclorous Acid

The reactive species hypoclorous acid has a singular linewidth measurement requirement for EOS-MLS near 635 GHz. Using the apparatus developed for isotopic oxygen measurements combined with the 600 GHz source available from the SWAT team this measurement was rapidly implemented. To insure accuracy and verify the high precision of the measurement, a series of HOCl transitions in the same Q-branch were also measured.

Sulfur Dioxide

This species has three linewidth requirements for EOS-MLS, which were each measured with sufficient accuracy using the apparatus designed for isotopic oxygen measurements.

Methyl Cyanide

Linewidth measurements for this species are nearing completion. This includes two clusters of transitions in the 600 GHz range and two more sets of transitions in the millimeter wavelengths. The data indicate important trends in the linewidth dependence on rotational state. The data quality is marginal for the lowest frequency measurements near 180 GHz. This is an issue of source capabilities and will be rectified when new measurements are made with a source designed for this spectral region.

2.5 THz measurements

In order to expedite the FIR measurements, we have made use of the capabilities of the existing OH radiometer which has observed stratospheric OH from balloon. The radiometer has now successfully operated as a laser sideband spectrometer that covers exactly the same spectral window as the MLS THz instrument. This spectrometer utilizes the existing planar Schottky diode mixer as a tunable sideband generator. The existing optics and limb-scanning mirror are used to couple the laser and its sidebands out into a free-space cell. This 2.2 m cell has been designed to accommodate the collimated 10 cm laser beam. Temperature control of the cell has been accomplished through submersion in a passively cooled alcohol bath that can be controlled to within 1 K at temperatures as low as 220 K. At the opposite end of this cell are refocussing optics and a tunable Fabry-Perot filter for single frequency filtration. The collimated beam is detected with a InSb bolometer at the frequency of the modulated sideband. This system has enabled temperature dependent measurements of OH and O_3 necessary for the THz MLS science. The O_2 measurement, however, remains beyond the reach of this experiment due to instability in the source power and frequency which limit the practical amount of integration time available for the experiments.

Future Plans

All data recorded and analyzed prior to August, 2003, have been entered into the retrieval algorithm for EOS-MLS, launch is currently scheduled for June 2004. This includes the HOCl, SO_2 and CH_3CN and $O^{18}O$ data which have not been published yet. Much of the current focus of this task is on improvements of the THz measurements. Although the OH and O_3 THz linewidths have been measured, the measurement uncertainties are considerable, and the O_2 measurement remains undone. To remedy this situation the present system is being converted into an emission apparatus that utilizes all of the Balloon OH instrument, namely the additional use of the onboard spectrometer and its filter banks. In this configuration the sensitivity will not be strongly dependent on pressure, as in the modulated sideband experiment. Instead, as the transition broadens at elevated pressures and reduced temperatures the wider filters will respond with equivalent sensitivities. For transitions off center from the channel, a synthesized local oscillator will be used to shift the responsivity of the filters to the appropriate center freuqency.

Measurements on nitric acid above 600 GHz have been recently requested by the MLS team will be accomplished under the continuing UARP task. Work on hydroperoxy radical, HO_2, will also continue in order to facilitate comparisons with the results of other laboratories, to incorporate the techniques used for $^{18}O^{16}O$, and assure that our measurements are entirely independent of the method of production. It is also possible that new priorities will arise after launch in June '04, and these will be directly determined through interaction with the MLS science team.

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[1] Paper based on results from this program