

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, HO₂, and BrO. Other molecular transitions include several near 2.5 THz of H₂O and O₃ and weak transitions of O₂. 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 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. Three types of free-space cells 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, and a special leak tight cell for long averaging of the $^{18}\text{O}^{16}\text{O}$ spectrum. Software has been written that allows rapid inter-comparison of the broadening measurements at the same workstation at which the spectra are recorded. The efficiency of the spectrometric system allows expedient 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 virtually 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 Astronomy Team and the Submillimeter Technology Development 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.

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

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

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

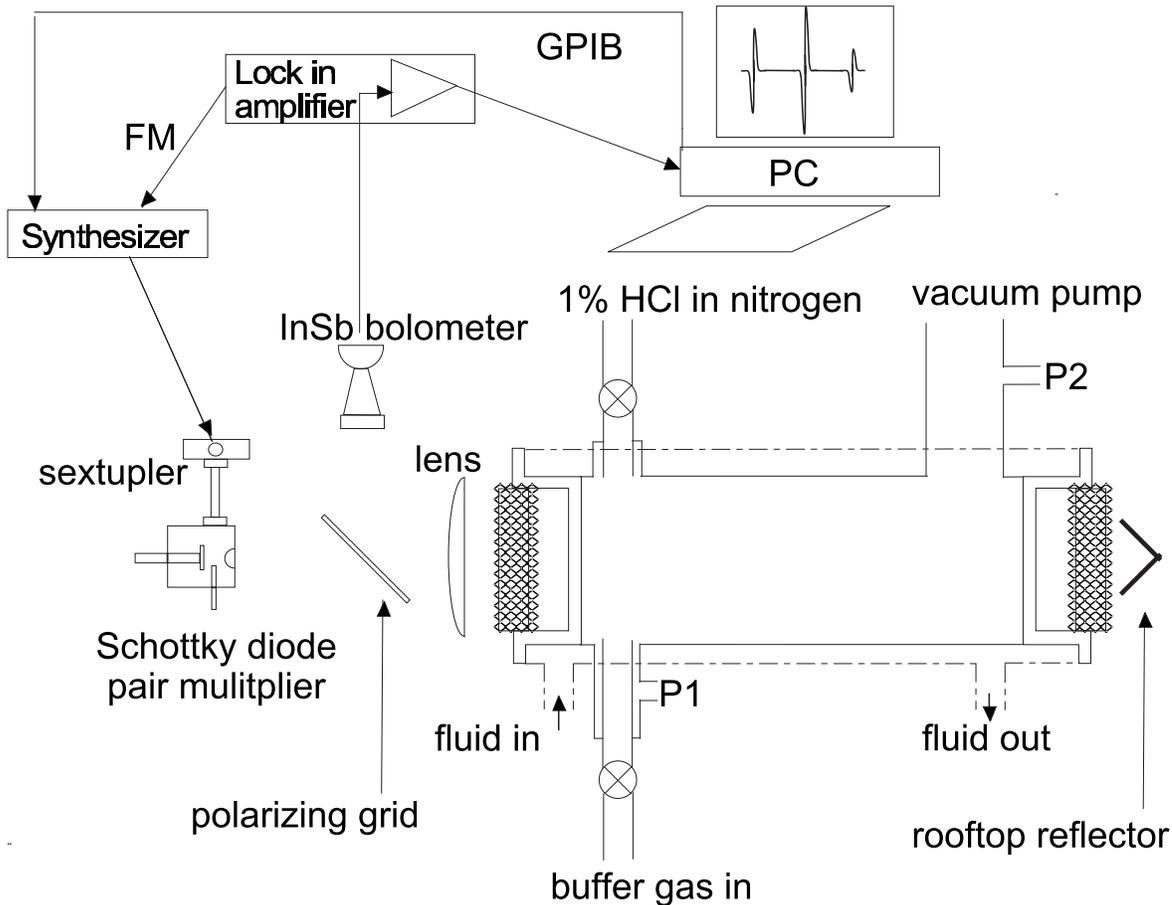


Figure 1: The experimental setup for measurement of HCl $J = 1 \leftarrow 0$ lineshape parameters. Not shown are the connections of the pressure gauges, P1 and P2, to the computer and the thermocouples.

to the parameters and because it 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

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

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 in press, preliminary results, and to be done in this calendar year.

MLS Highest Priority Linewidth Requirements

- [HCl line at 625.9 GHz.](#)
- [O₃ lines at 235.7, 237.1, 242.3, 243.5, and 625.4 GHz.](#)
- [BrO lines at 624.8 and 650.2 GHz.](#)
- [¹⁸O¹⁶O line at 233.9 GHz.](#)
- [HO₂ lines at 649.7 and 660.5 GHz.](#)
- 2.5 THz lines of OH, O₂, and H₂O and O₃ .

MLS High Priority Linewidth Requirements

- [O₃ lines at 239.1, 231.3, 248.2, 249.8, and 250.0 GHz.](#)
- [CO line at 230.5 GHz.](#)
- CH₃CN 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 ¹⁸O¹⁶O line at 233.9 GHz and the low frequency lines in the cluttered CH₃CN 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 accepted for publication are in the following section. In those cases (HCl, BrO and O₃) the MLS Science team (contact: William Read) has been provided with the pre-prints of the manuscripts and the parameters have been included in the forward model-retrieval algorithm. Of the molecules in progress, ¹⁸O¹⁶O is nearing completion and is also discussed below, HO₂ requires further intercomparison of results with those of the Amano group which also collaborated on the BrO measurements.

Measurements and Results for Individual Species

HCl

The lowest rotational transition, $J = 1 \leftarrow 0$, of hydrogen chloride lies in the lower sideband of the 640 GHz radiometer. No previous studies have examined its temperature dependent linewidth. 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.

Table 1: Linewidth and lineshift parameters^a for H³⁵Cl.

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 .

A manuscript [Drouin, 2003a] reporting the parameters and describing the methodology in detail has been accepted for publication in the Journal of Quantitative Spectroscopy and Radiative Transfer (JQSRT). Furthermore, a the recommended halfwidth value has been submitted to HITRAN. The results are summarized in Table 1

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 on-board 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 (~ 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.

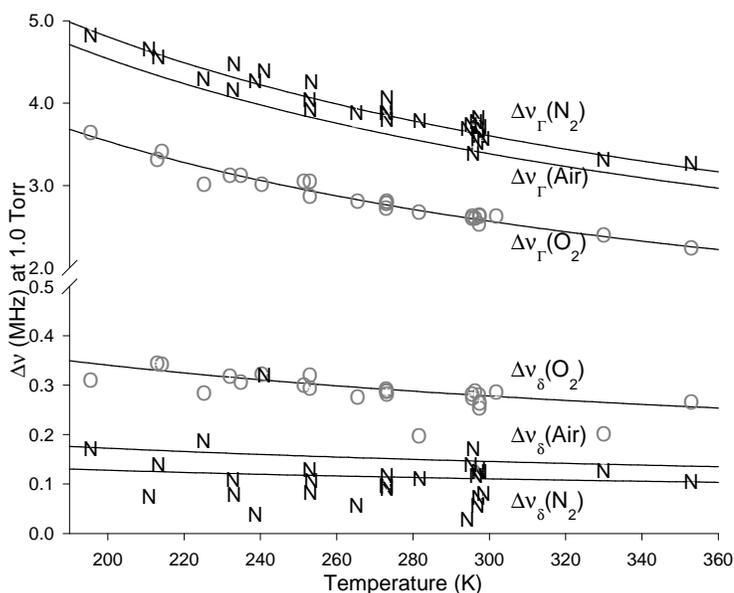


Figure 2: A comparison of average lineshape parameters from individual runs (N = N₂, O = O₂) and the parametric fit (solid lines) to individual spectral comparison data points.

Table 2: Linewidth parameters of BrO.

Gas	624.77 GHz		650.17 GHz	
	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)

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 N₂ and O₂ values.

The results have been accepted for publication in JQSRT [Yamada, 2003]. The HITRAN database does not list BrO.

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 has been accepted for publication in JQSRT [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

¹⁸O¹⁶O

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 $^{18}\text{O}_2$ and $^{16}\text{O}_2$.

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 is now complete, with over 1000 air-broadened comparative data points. 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].

Future Plans

The mechanical and analytical tools necessary to measure the remaining species in the millimeter and submillimeter regions are all in place. Measurements of hypochlorous acid, sulfur dioxide and methyl cyanide in the 180, 240 and 640 GHz regions are expected to be 'routine' and will be made concurrently with the THz measurements described next.

In order to expedite the FIR measurements, we will make use of the capabilities of the existing OH radiometer which has observed stratospheric OH from balloon. The radiometer will essentially operate as a laser sideband spectrometer that will cover exactly the same spectral window as the MLS THz instrument. This spectrometer will utilize the existing planar Schottky diode mixer as a tunable sideband generator. The existing optics and limb-scanning mirror will be used to couple the laser and its sidebands out into a free-space cell. At the opposite end of this cell will be complimentary optics focusing the laser and sidebands onto a second planar Schottky diode that begins a chain of frequency down conversions ultimately ending with lock-in detection of the frequency modulated sideband.

All data recorded and analyzed prior to August, 2003, will be entered into the retrieval algorithm prior to launch. It is anticipated that all of the THz measurements will be completed by this time as well as the aforementioned GHz measurements. During the remaining funding period focus will be on any of these measurements that may require further refinement. Measurements on nitric acid above 600 GHz have been recently requested by the MLS team and may extend past August. Work on hydroperoxy radical, HO_2 , will continue in order to facilitate comparisons with the results of other laboratories, to incorporate the techniques used for $^{18}\text{O}^{16}\text{O}$, 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 January '04, and these will be directly determined through interaction with the MLS science team.

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¹Paper based on results from this program