Pressure Broadening of ClO by N_2 and 0_2 near 204 and 649 GHz and New Frequency Measurements between 632 and 725 GHz.

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Abstract -- The N_2 and O_2 pressure broadenings of the ClO transitions near 204 and 649 GHz have been measured between 200 and 300 K. Oxygen broadening has been measured for the transitions near 278 GHz. The accuracy of the derived air broadening is comparable to that for the air broadening of stable species and is estimated to be within $\approx 3\%$ over the entire temperature range. These transitions are currently being used for satellite, balloon, and ground based monitoring of atmospheric ClO, respectively. Some new frequency measurements are reported in the 632 to 725 GHz range. These are in good agreement with previous measurements and predictions,

INTRODUCTION

The Microwave Limb Sounder[1] (MLS) has been monitoring global ClO from Earth orbit aboard the Upper Atmospheric Research Satellite since September, 1991. When laboratory measurements of ClO pressure broadening were first obtained in anticipation of this effort[2], the existence of large quantities of relatively low altitude ClO in the polar regions was unknown. Since becoming operational, MLS has detected large amounts of lower stratospheric ClO during the polar winters and has shown a high correlation between enhanced ClO and severe ozone depletion over the Antarctic'. Error analyses of MLS retrievals[3] indicated shown that the uncertainty of the earlier ClO linewidth parameters could contribute even greater uncertainty in the determination of lower stratospheric ClO. Therefore, we have remeasured the N_2 broadening of the $J = 11/2 - 9/2$ transitions centered near 204,352 GHz used by MLS and measured the O_2 broadening for the first time in the 200-300 K temperature range. Similar measurements have been made for the $J = 35/2 - 33/2$ transitions centered near 649.448 GHz which arc used by a balloon borne submillimeter limb sounder[4]. Oxygen broadening measurements at 295 K arc included for the $J = 13/2 - 11/2$ transitions near 278,631 GHz which arc used for ground based measurements[5]. These measurements significantly improve the accuracy of the spectroscopic parameters used for retrievals of atmospheric ClO from millimeter and submillimeter remote sensing data. *The 204 GHz results reported in this paper have been used in all publications on ClO by the MLS team and in the production of all MIS' data sets now being released for general scientific use.*

EXPERIMENTAL STUDIES

The millimeter spectrometer used for these measurements has been described by Birk et al.[6] Many of the experimental details for the pressure broadening experiment have been given by Oh and Cohen.[7] Only the specific differences between these experiments and those in Ref. 7 will be described here.

Power at 204, 278 or 649 GHz was obtained from klystrons driving a Schottky diode multiplier to obtain second, third or sixth harmonic. Tone burst modulation[8] was used. At the lower frequencies it was possible to compensate for baseline drift by turning off the ClO generation and obtaining baselines which could be subtracted from both reference and broadened spectra. At 649 GHz the baseline drift was insignificant.

Pickett[8] has shown that pressure broadening due to a foreign gas maybe determined by a convolution method which dots not require 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 advantages of this method and the requirements for the results to be valid has been reviewed in Ref. 7. The convolution method as it is used here contains the assumptions that all hyperfine components of a transition have the same pressure broadening and that the resulting feature is a simple sum of its broadened components.

Unlike the ozone experiment described in Ref. 7, the gases were mixed as they entered the observing region. The ClO was produced by a microwave discharge through a Cl_2-O_2 mixture in a 7 mm id. quartz tube and carried into the cell via an approximately 3 cm section of 1 cm id. glass tube the last 2 cm of which pass through the cell's cooling jacket. The broadening gas was introduced via an identical glass tube directly opposite the ClO entrance to the 7.5 cm. diameter 80 cm long cell. The gases then flowed the entire length of the cell to the outlet. At the flow rates used, the pressure gradient along the length of the sample ccl] was insignificant. Because ClO is highly reactive, methods of producing the molecule and premixing it with broadening gas gave considerably poorer signal to noise ratios than the method which produced it just prior to its introduction into the observing region. However, the derived parameters did not seem to be functions of either the mixing scheme or the differential pressure. This gives confidence in the assumption that the gases arc well mixed throughout the observing region.

The lowest total pressures used for reference spectra were between 0.100 aud 0,200 mbar. It is estimated that no more than a few percent of this mixture was ClO. As a result any changes in the contribution of self broadening as a function of production efficiency arc unimportant in the analysis, Up to 0.73 mbar of broadening gas was added for the lower frequency measurements ant] up to 2.6 mbar for the measurements at 649 GHz. Samples diluted with broadening gas were also used as references for those at higher total pressure. Consistent results were obtained irrespective of the reference. No trends in effective broadening coefficients or in the distribution of the residuals were observed as functions of pressure. Thus, the assumptions regarding the widths and the summing of the individual hyperfine components appear to be adequate for the conditions used and the transitions studied in this work.

Fig. 1 shows examples of reference and presure broadened spectra as well as the residuals after subtracting the convolution of the reference from the broadened spectra. Fig. 2 is a plot of differential Lorentzian linewidth versus differential pressure for a large number of possible differences from a series of measurements on the J = 35/2 – 33/2 transitions.

Frequency measurements were made at ≈ 50 mbar total pressure and with less modulation than was used for the pressure broadening measurements.

RESULTS AND DISCUSSION

The N_2 and O_2 broadened widths, W, in MHz are given by $W = \gamma(T)P$ where P is the pressure in millibar. Table 1 contains the experimentally determined $\gamma(T)$'s for both the J = 11/2 – 9/2 and J = 35/2 – 33/2 transitions. For the J = 15/2 – 13/2 transition a value of 2,018 MHz/mbar was determined for O_2 broadening at 295K. The $\gamma(T)$'s in Table 1 are plotted in Fig. 3 along with the best fits to the equation

$$\gamma(T) = \gamma_0(296/T)^x.$$

The values of γ_0 and x are given in Table 2. As in Ref. 7 the uncertainties are estimated to be about 3% for γ and 10% for x.

The previously measured N_2 broadenings by Pickett, et al[2], at 204 GHz were 3.33(17) and 2.51 (14) MHz/mbar at 218 and 317 K. These compare well with new calculated values of 3.26 and 2.59 MHz/mbar at the same temperatures. The consistency is quite encouraging in view of the very different experimental setup now being used. in particular, the old method generated ClO by photolysis in the observing region of Cl_2O already diluted with N_2. The method employed here uses ClO generated in a Cl_2 - O_2 discharge and diluted with the broadening gas as it enters the observing region. The fact that the 295K O_2 broadening of the J = 15/2 - 13/2 transition is close to that of the J = 11/2 — 9/2 transition is also consistent with the finding in Ref. 2 that the N_2 broadenings were similar. Calculated broadenings of the 649 GHz feature also agree with preliminary measurements of Radford and Chance[8] to within their experimental uncertainties.

Most of the discussion regarding precision and accuracy from our recently published paper on O_3 linewidths[2] applies to these measurements as well, It is unlikely that any predicted air broadening coefficient for either the 204 or 649 GHz ClO transitions will be in error by more that 3% over the entire range of stratospheric temperatures.

Because the sensitivity of the spectrometer is considerably greater than it was at the time ClO was last measured in this laboratory, several transition frequencies were remeasured and several others were measured for the first time in the 632 -725 GHz range. No differences of significance to atmospheric observations were found and no physically meaningful changes were required of the previous] y published molecular parameters[10,11] were required to accommodate the new measurements. q'able 3 contains the newly measured frequencies whi ch arc determined from the peaks of the observed features, For transitions were no F quantum number is given, the frequency is the peak of an unresolved quartet of the four strongest $\Delta F = 1$ transitions. These are used along with other available data [10–12] for the JPL Microwave, Millimeter and Submillimeter Spectral Line Catalog[13].

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Table 1. Experimentally determined pressure-broadening coefficients γ(MHz/mbar) for C1O.

$T(K)$	J = 11/2 – 9/2 204.3519 GHz		J = 35/2 – 33/2 649.4481 GHz	
	$\gamma(N_2)$	$\gamma(O_2)$	$\gamma(N_2)$	$\gamma(O_2)$
295	2.68 2.74	1.98	2.23	1.73
263	2.89	2.16	2.44	1.86
248	—	—	2.58	L92
233	3.14	2.33	2.76	2.08
218	—	—	2.87	2.17
203	3.41	2.51	3.08	2.32

Table 2. ClO pressure-broadening parameters for N_2 and 0_2.

$\gamma(T) = \gamma_0(296/T)^x$ Parameter	$J = 11/2 - 9/2$ 204.3519 GHz	$J = 35/2 - 33/2$ 649.4481 GHz
$\gamma_0(N_2)$/MHz/mbar	2.69	“ 2.22
$x(N_2)$	0.62	0.87
$\gamma_0(O_2)$/MHz/mbar	1.99	1.70
$x(O_2)$	0.63	0.79
γ_0(Air)/MHz/mbar	2.54	2.11

Table 3. New C1O Frequency Measurements

J'	F'	J''	F''	Ω	e, f	^{35}ClO $v = 0$	^{35}ClO $v = 1$	^{37}ClO $v = 0$	^{37}ClO $v = 1$
35/2		33/2		3/2	e	649445.250(50)†	643222.888(70)	638495.670(50)	632430.716(100)
35/2		33/2		3/2	f	649451.072(50)†	643228.593(70)	638501.182(50)	632436.108(100)
35/2	18	33/2	18	3/2	e	649410.243(70)			
35/2	18	33/2	18	3/2	f	649417.910(70)			
35/2	17	33/2	17	3/2	e	649435.790(70)			
35/2	16	33/2	16	3/2	e	649457.477(100)			
35/2	16	33/2	16	3/2	f	649460.981(70)			
35/2		33/2		1/2	e	650629.260(100)	644379.202(100)	639617.875(50)	
35/2		33/2		1/2	f	651298.581(100)	645043.513(100)	640276.026(50)	
39/2		37/2		3/2	e	723439.314(50)†			
39/2		37/2		3/2	f	723446.513(50)†			
39/2		37/2		1/2	e	724793.426(100)			
39/2		37/2		1/2	f	725461.299(100)			

†Remeasurement

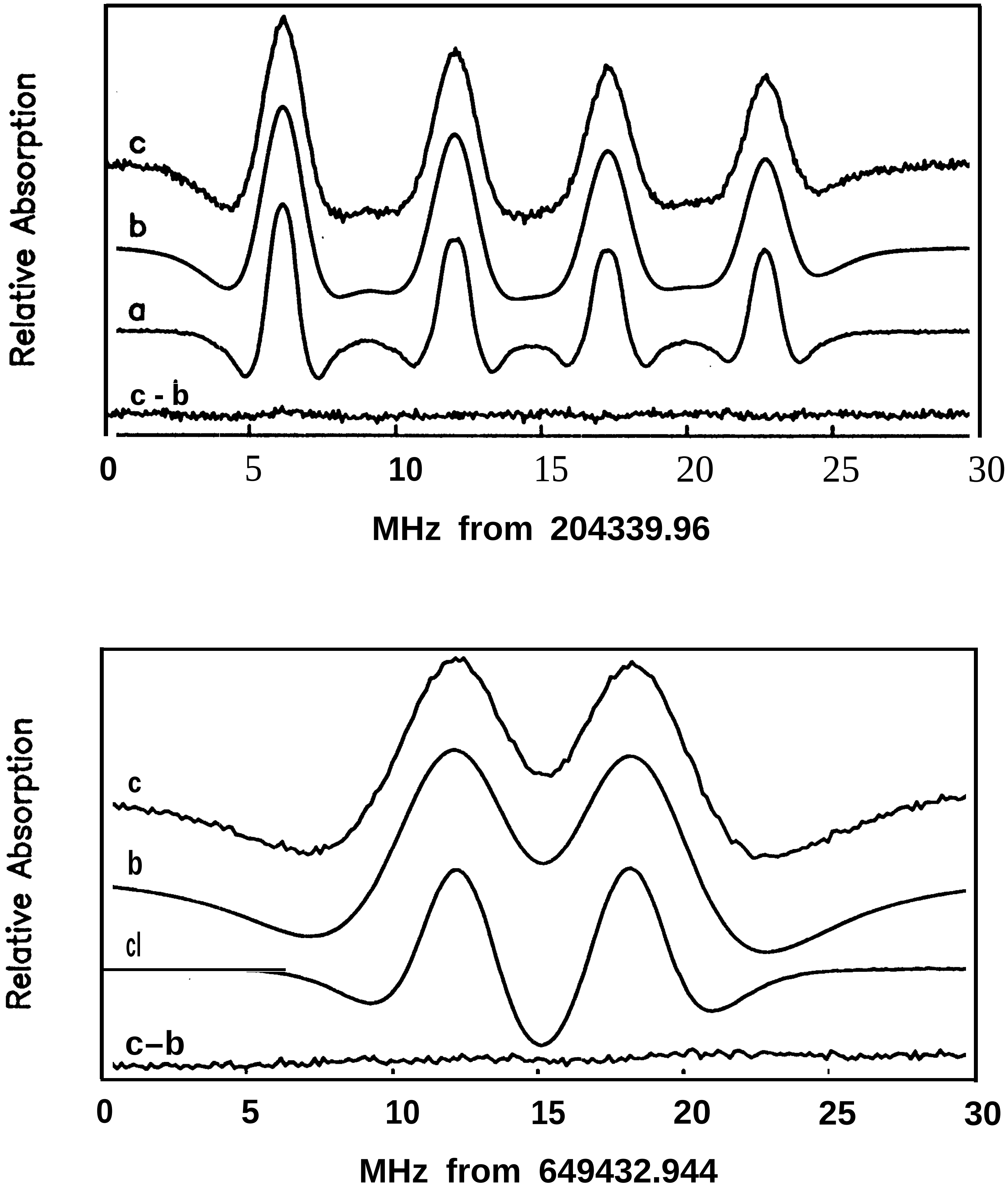
Figure Captions

Fig. 1. Top-CIO near 204 GHz broadened by N_2 at 295 K. (a.) C1O reference at a total pressure of all gases of 0.107 mbar. (b.) Reference convoluted with a 0.809 MHz wide Lorentzian. (c.) C1O + additional 0.303 mbar N_2. The residual (c-b) is on the same scale as trace (c). The reference (a) is reduced by a factor of 7. Bottom - C1O near 649 GHz broadened by N_2 at 263 K. (a.) C1O reference at a total pressure of all gases of 0,331 mbar. (b.) Reference convoluted with a 3.016 MHz wide Lorentzian. (c.) C1O + additional 1.252 mbar N_2. The residual (c-b) is on the same scale as trace (c). The reference (a) is reduced by a factor of 20.

Fig. 2. Lorentzian linewidth vs. differential pressure for N_2(n) and 0_2(o) broadening of C1O, $J = 35/2 - 33/2$, at 248 K. A total of 48 differential pressures among ten spectra are plotted for N_2 and 58 differential pressures among eleven spectra for O_2.

Fig. 3. A log–log plot of γ vs temperature. The dashed and solid lines are plots of γ vs T using the parameters in Table 2 for the $J = 11/2 - 9/2$ and $J = 35/2 - 33/22$ transitions, respectively. The experimental points in Table 1 for N_2 and 0_2 broadening are indicated by N and O. The vertical bars correspond to $\pm 2\%$ of $\gamma(T)$.

Fig. 1.



Relative Absorption
c
b
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0
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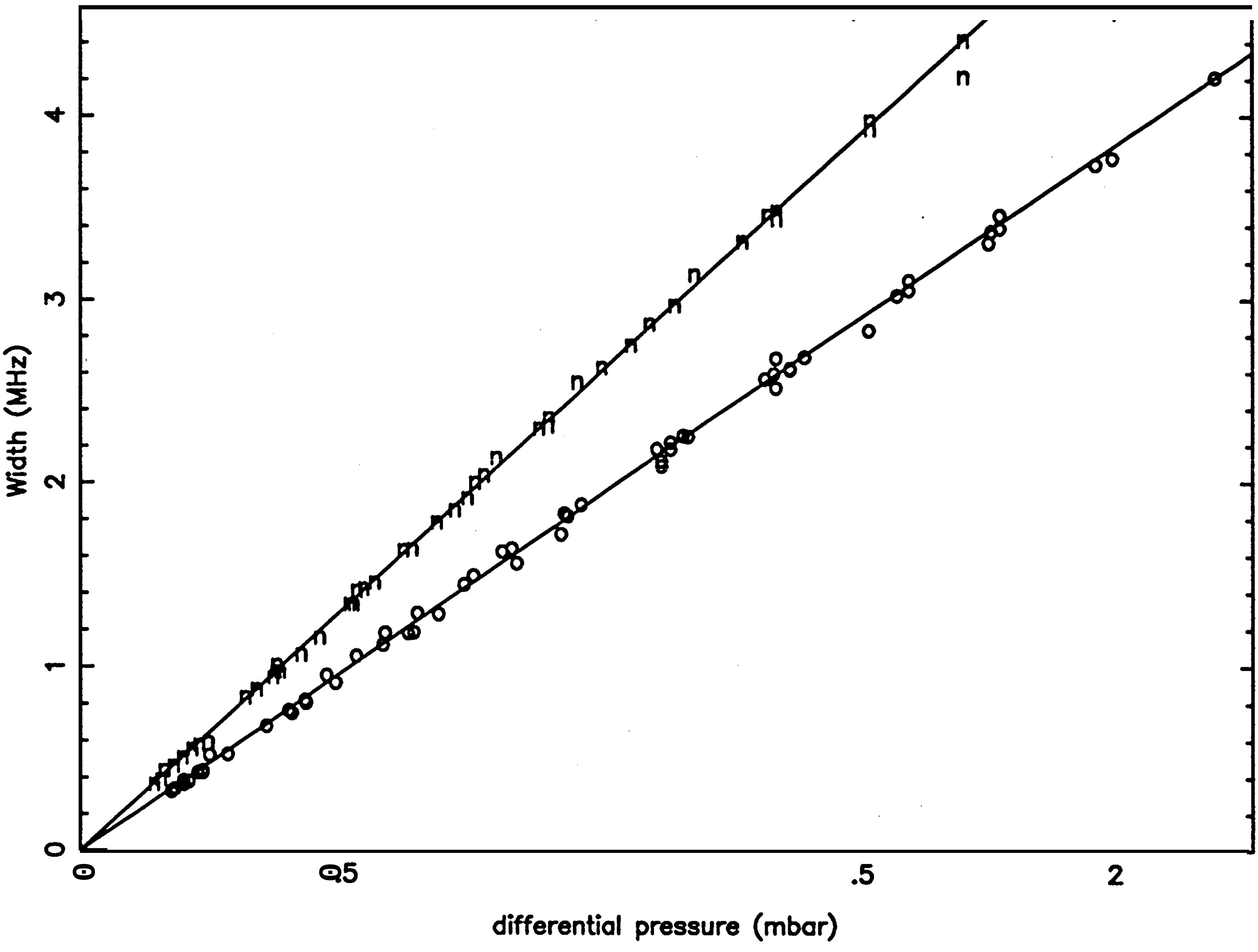
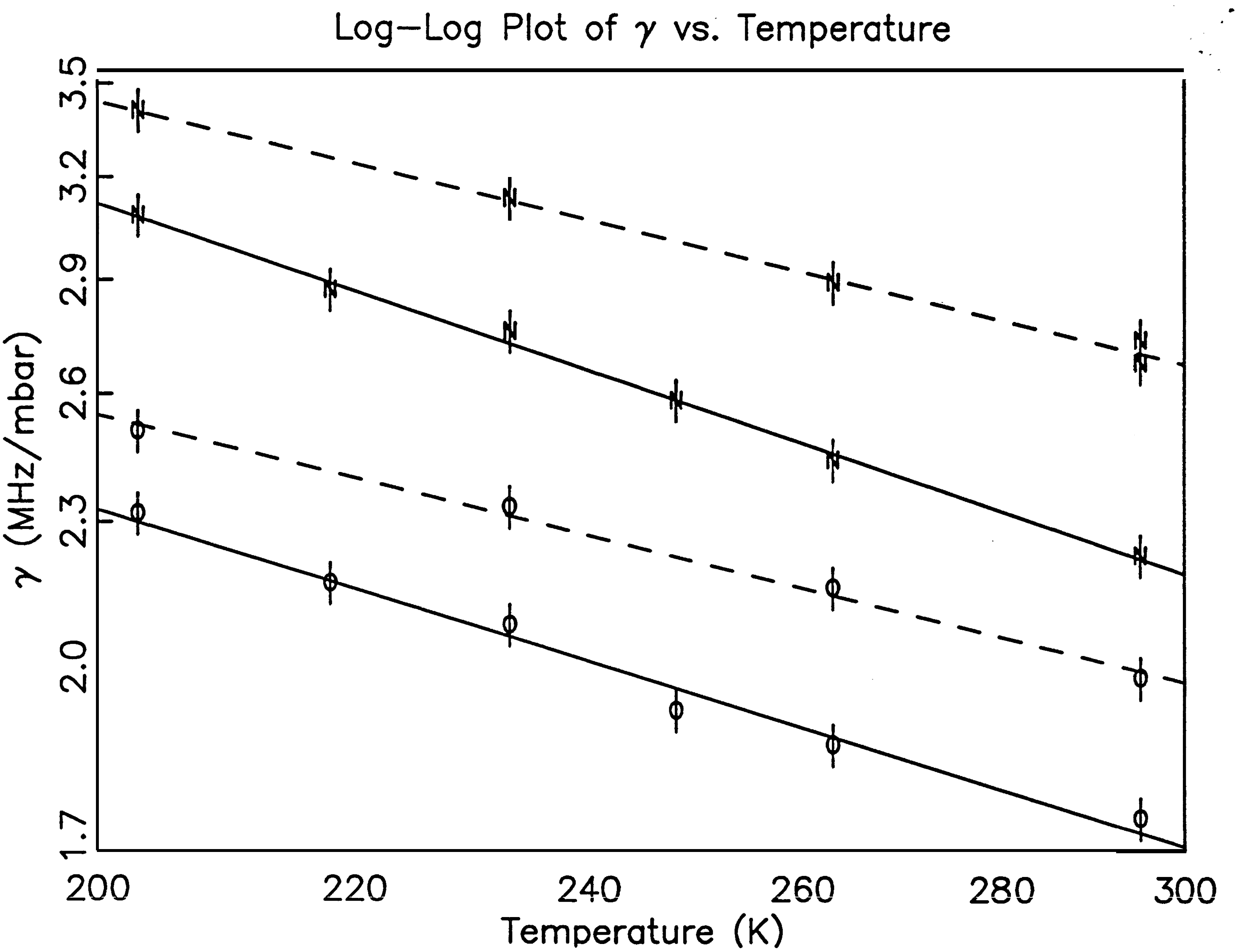
MHz from 649432.944

ClO (649 GHz) broadening by N2 and O2 at 248 K




Log–Log Plot of γ vs. Temperature
γ (MHz/mbar)
3.5
3.2
2.9
2.6
2.3
2.0
1.7
200
220
240
260
280
300
Temperature (K)