

Pressure Broadening of ClO by Nitrogen

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The temperature and pressure dependence of linewidths for the $J = \frac{1}{2} - \frac{3}{2}$ and $J = \frac{3}{2} - \frac{5}{2}$ transitions of ClO have been determined by microwave spectroscopy. The widths for both transitions are found to be the same within experimental error. The width parameter for nitrogen broadening is 3.35 ± 0.17 MHz/torr at 317 K and 4.44 ± 0.23 MHz/torr at 218 K.

INTRODUCTION

The importance of ClO as a catalytic species in stratospheric ozone depletion is of current interest. A ClO distribution in the upper atmosphere has been modeled by a number of workers (see, for example, Logan *et al.* [1978]). Measurement of volume mixing ratios of stratospheric ^{35}ClO is now performed by means of aircraft-based and ground-based microwave emission spectrometers [Waters *et al.*, 1979; Parrish *et al.*, 1981]. The profiles obtained by analysis of the $J = \frac{3}{2} - \frac{5}{2}$, $J = \frac{1}{2} - \frac{3}{2}$, $J = \frac{1}{2} - \frac{1}{2}$ and $J = \frac{1}{2} - \frac{1}{2}$ transitions at 167 GHz, 204 GHz, 241 GHz, and 278 GHz, respectively, are sensitive to the value of the pressure broadening parameter γ used in the collisional lineshape function. Waters *et al.* [1979] estimated $\gamma = 4.2$ MHz/torr, for ClO ($\mu = 1.24D$) by linear interpolation of values for HF ($\gamma = 4.86$ MHz/torr, $\mu = 1.8D$) and CO ($\gamma = 3.16$ MHz/torr, $\mu = 0.11D$). This paper describes the determination of γ for ClO at 207 K and 278 K, by N_2 line broadening of the $J = \frac{1}{2} - \frac{3}{2}$ and $J = \frac{1}{2} - \frac{1}{2}$ transitions of $v = 0$ $^2\Pi_{1/2}$ ^{35}ClO .

EXPERIMENTAL DETAILS

The submillimeter source used in these measurements was frequency stabilized klystron whose output is multiplied by a diode multiplier. Frequency measurements and stabilization was achieved by comparison of the klystron output with some multiple of X band (8–12 GHz) oscillator as shown in Figure 1. The X band source is phase-locked by a commercial phase-lock loop stabilizer and is counted by a frequency counter. A sample of the klystron output and the X band are fed into a harmonic mixer, and the resulting IF is coupled into a 1120–1220 MHz amplifier. A portion of the IF is sampled and displayed by the spectrum analyzer and the remainder is passed to double balanced mixer. Here a synthesized frequency of 1060 MHz to 1160 MHz down-converts the IF to produce a 60 MHz signal for the phase-lock synchronizer. The phase-lock synchronizer uses a digital phase-frequency detector described by Pickett [1977] which provides a nearly linear phase-voltage output over a range of nearly $\pm 2\pi$.

Detection was achieved by use of an InSb hot electron bo-

lometer. The detected signal was demodulated by a lock-in amplifier and converted into digital form. Typically signal averaging was performed by adding the digitized signal into memory over four upward and four downward sweeps of 256 discrete frequency points, with a lock-in amplifier time constant of 0.3 s. The spectrum was displayed continuously on an oscilloscope during acquisition. After completion of the specified number of sweeps the spectrum was stored on magnetic disk for future data analysis. On the basis of previous work [Pickett *et al.*, 1980], the detection sensitivity is 10^{-7} cm^{-1} .

The free-space absorption cell consists of a quartz tube with a cooling jacket surrounded by eight germicidal lamps each capable of producing 5 W of mercury-line radiation. The lamps are contained within an aluminum jacket which confines the harmful UV radiation and, when purged with dry N_2 , provides a means of preventing frost buildup on the exterior of the cell walls. The sample volume is 3 cm in diameter and 50 cm in length. The cell is cooled by circulating spectroscopic grade methanol through a 10 foot (~ 3 m) copper coil immersed in a dry ice-isopropanol bath. The chilled methanol passes through the photolysis cell jacket into a dewar reservoir where the temperature is monitored. The circulation of methanol past the photolysis lamps was rapid enough that there is less than a 4 K measured temperature differential between the inlet and outlet of the cooling jacket. The end windows of the sample cell were Teflon lenses maintained at room temperature. Mathematical modeling of the temperature gradients in the cell showed that there is a sharp gradient of approximately 2 cm width near the junction of the end caps on the cell with the cooling jacket. Therefore approximately 10% of the sample cell length is at room temperature while the rest of the cell is within 4 K of the measured temperature.

Pressure was measured with a Mensor quartz spiral manometer at the exit of the cell. Pressure was also monitored at the inlet to the cell with a thermocouple gauge. Comparison of the two gauges under static conditions and the slow-flow conditions of the experiment showed less than 1 mtorr differential pressure for flow conditions. The manometer measurements are accurate to 5 mtorr.

There are several methods by which ClO may be produced in the laboratory. However, the most successful scheme we

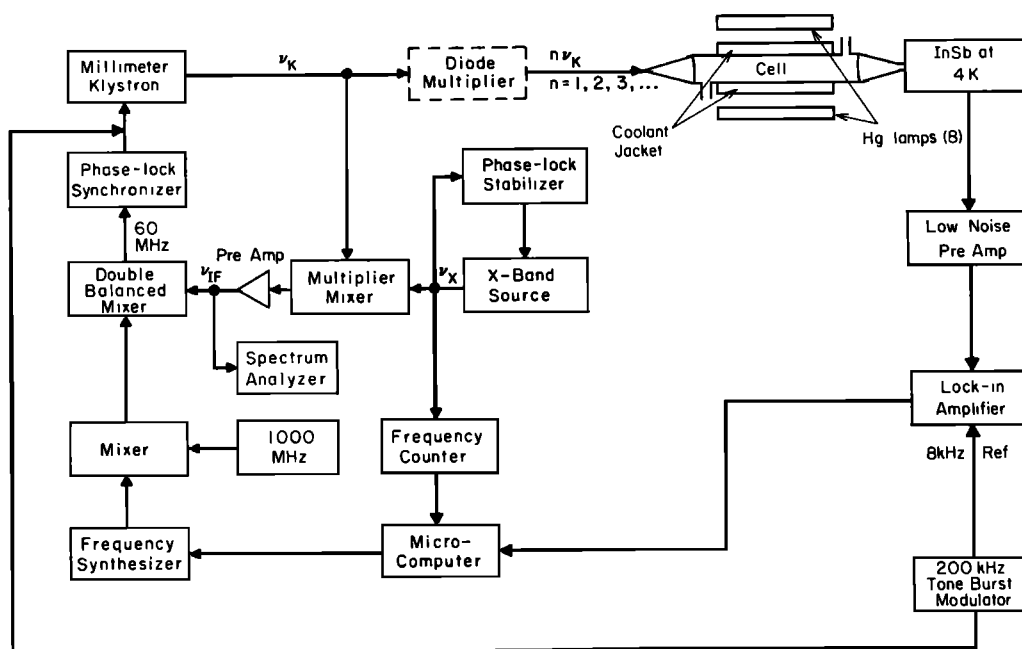
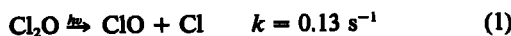


Fig. 1. Block diagram of submillimeter spectrometer.

have found is the photolysis of Cl₂O by mercury-line radiation at 253.7 nm [Watson, 1977]:



The effective first-order rate constant is based on 40 W of 253.7 nm radiation over 425 cm² surface area and an absorption cross section for Cl₂O at this wavelength of 1.9×10^{-18} cm². The chlorine atom generated in (1) reacts quickly with Cl₂O molecule to produce another ClO and Cl₂:

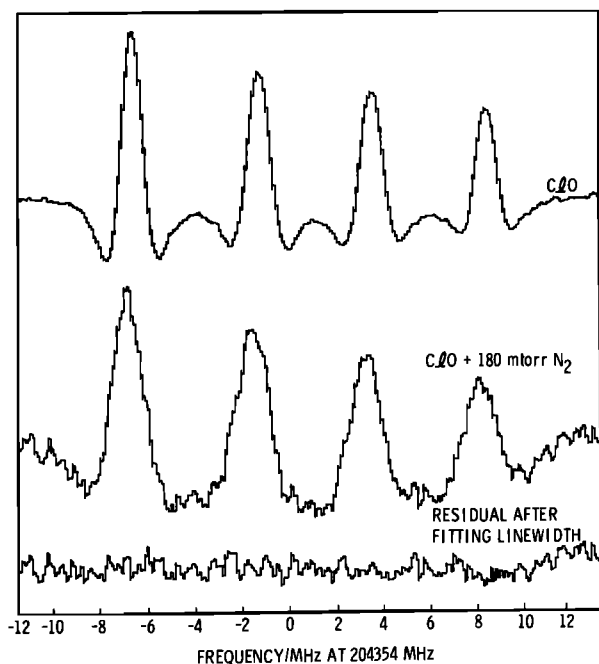
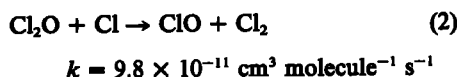


Fig. 2. Experimental profiles for ClO broadening by nitrogen at 204 GHz. The lower two curves have the same vertical scale.

ClO can react with itself to form a variety of products and is also rapidly photodissociated by the mercury light. Numerical simulation of the photochemistry using the recommended rate constants of Watson [1977] suggest that number densities of 5×10^{12} cm⁻³ of ClO would be produced. The observed signal strength obtained is consistent with this estimate.

The approach to measuring linewidths involved first measuring a low-pressure reference spectrum in the Doppler broadened regime. This spectrum contains all the information concerning instrument response and spectral modulation line-shapes in addition to the Doppler contribution to the width. Higher pressure spectra are then obtained by adding the appropriate partial pressure of nitrogen and recording the spectrum under the same spectral resolution and modulation depth conditions present in the low pressure spectrum. This results in isolating the pressure induced width information when comparison is made between the spectra. The values of the pressure broadening coefficient are obtained by use of a Lorentzian convolution/fitting procedure developed by Pickett [1980]. In this work the reference spectrum was taken at pressures below 20 mtorr and well within the Doppler limit. This is done so any changes in reaction chemistry on addition of nitrogen would not change the reference line profile. In fact there did appear to be a small quenching of ClO production when nitrogen was introduced. Since the Voigt profile is a convolution of a Lorentz profile and a Gaussian profile, the convolution procedure permits comparison of Doppler broadened reference spectra with higher pressure spectra which are further into the collision-broadened regime.

RESULTS

The upper spectrum in Figure 2 shows a typical low pressure (30 mtorr) spectrum for the 11/2-9/2 transitions of ClO. An example of the $J = 15/2-13/2$ measurements is given in a previous publication [Pickett, 1980]. The spectrum was recorded by tone-burst modulation with a tone frequency of 200 kHz. The lower spectrum in Figure 2 demonstrates the effect of addition 180 mtorr of N₂ to the absorption cell. There are

TABLE 1. ³⁵ClO Line Frequencies Observed for ²Π_{3/2}, v = 0 Vibronic State

J'	J''	F'	F''	P'	P''	Frequency, MHz		
11/1	9/2	7	6	-1	1*	204346.000(23)†		
		7	6	1	-1	204346.000(23)†		
		6	5	-1	1	204351.630(20)		
		6	5	1	-1	204352.220(20)		
		5	4	-1	1	204356.860(20)		
		5	4	1	-1	204357.480(30)		
		4	3	-1	1	204362.557(20)†		
		4	3	1	-1	204362.557(20)†		
		15/2	13/2	9	8	-1	1	278627.115(27)
				9	8	1	-1	278628.137(14)
8	7			-1	1	278630.099(14)		
8	7			1	-1	278631.219(31)		
7	6			-1	1	278632.647(22)		
7	6			1	-1	278633.783(23)		
6	5			-1	1	278635.570(40)		
6	5			1	-1	278636.580(160)		

* Parity of λ doubling levels under inversion (assuming a ²Σ⁺ interacting state).

† Unresolved.

eight distinct lines resulting from nuclear quadrupole splitting and λ doubling of resulting hyperfine lines. However, under these conditions the λ doublets are not resolved for the 204 GHz multiplets. The transition frequencies are listed in Table 1. The line positions are consistent with predictions based on lower frequency work of *Kakar et al.* [1978]. Calculated intensities and frequencies for the lines of ClO are listed on the Jet Propulsion Laboratory Submillimeter, Millimeter, and Microwave Spectral Line Catalogue [*Poynter and Pickett*, 1980].

Several measurements of linewidth were made at various temperatures and pressures with incident power less than 10 μW cm², thus avoiding power saturation. Data are given in Table 2. Confidence limits for individual fits of the lineshapes are not given since large correlation between the width and area parameters leads to excessively small uncertainties. In principle, one might expect that there would be some F dependence to the linewidths. However, the procedure used here assumes equal linewidths for each component and superposition of the lineshapes for each component. Examination of the residuals of the fit in Figure 2 shows that these assumptions are correct to within the accuracy presently available. The higher temperature measurements on the 278 GHz transition of ClO is uncertain by 10 K because the measurements were made in an earlier cell which was not thermally controlled. In general the 278 GHz data have larger error bars due to the smaller multiplet splittings which make the transition harder to observe under nitrogen broadening. The pressure broadening coefficients for both transitions are plotted in log-log fashion in Figure 3.

The slope of the curve is such that the presence of room temperature gas in the end of the cell changes the linewidth by 2% and is partially compensated by the temperature gradient in the methanol coolant between the inlet and the measurement point at the outlet of the cooling jacket.

DISCUSSION

The best fit to the data for the 204 GHz multiplet in Figure 3 yields a temperature exponential of -0.75 ± 0.2 . Using the arguments found in *Townes and Schawlow's* [1975] book, this temperature exponential implies $n = 5$ for a $1/r^n$ interaction potential. This is intermediate between dipole-quadrupole ($1/r^5$) and dipole-induced dipole ($1/r^6$) interactions for ClO-N₂ collisions. It is risky to base the temperature exponential on two temperatures and indeed the functional form of a Tⁿ dependence of linewidth on temperature is based on very inexact arguments. Nonetheless it is interesting to note that the dependence obtained is reasonable.

TABLE 2. Linewidth Measurements

Temperature, K	N ₂ Pressure, mtorr	Linewidth Parameter MHz/torr	
218 ± 4	204 GHz Multiplet		
	115	4.37	
	180	4.70	
	235	4.26	
		4.44 ± 0.23*	
	317 ± 4	86	3.08
		100	3.23
		170	3.54
		181	3.40
		295	3.49
		3.35 ± 0.19*	
207 ± 4	278 GHz Multiplet		
	50	3.34	
	90	4.10	
	120	5.09	
		4.18 ± 0.88*	
	317 ± 4	70	3.07
		95	4.29
		144	3.56
			3.64 ± 0.61*
	363 ± 10	95	2.86
151		2.49	
174		2.86	
400		2.44	
		2.66 ± 0.23*	

* Average.

and dipole-induced dipole ($1/r^6$) interactions for ClO-N₂ collisions. It is risky to base the temperature exponential on two temperatures and indeed the functional form of a Tⁿ dependence of linewidth on temperature is based on very inexact arguments. Nonetheless it is interesting to note that the dependence obtained is reasonable.

The values obtained here do not alter the conclusions of *Waters et al.* [1979] and were actually used in the analysis of ground-based atmospheric measurements [*Parrish et al.*, 1981]. The values reported here should be useful for future measurements of ClO in both the microwave and infrared regions. We expect that the results should be transferable to in-

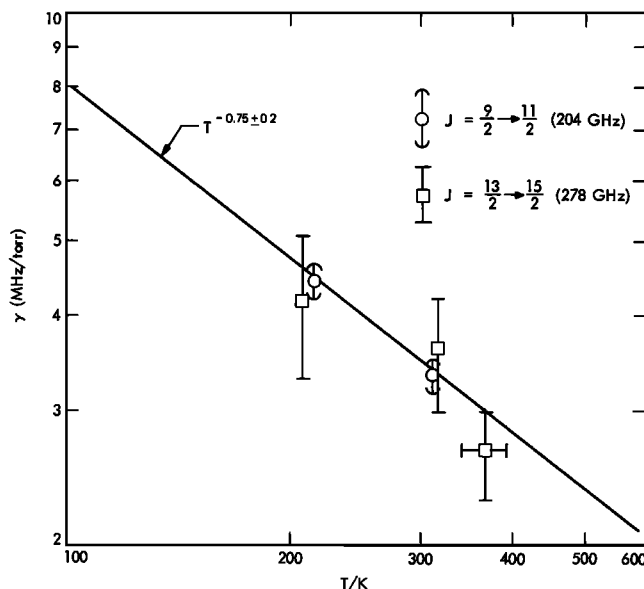


Fig. 3. Temperature dependence of ClO line broadening by nitrogen.

frared transitions involving similar J values. This contention is based on the fact that collisional broadening in both microwave and infrared regions is dominated by rotational energy transfer. The rotational energy transfer in ground and excited vibrational states is different mainly by subtle changes in the vibrational averaging of the interaction potential, and should be the same to within 5%. (Currently the measurements reported here form the basis for the linewidths quoted on the Air Force Geophysics Laboratory infrared tapes for the current listing on ClO.)

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