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MEASUREMENTS OF THE ClO RADICAL VIBRATIONAL BAND INTENSITY AND THE ClO + ClO + M REACTION PRODUCT

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James B. Burkholder, John J. Orlando, Philip D. Hammer, and Carleton J. Howard, NOAA Aeronomy Laboratory, R/E/AL2, 325 Broadway, Boulder, Colorado 80303 and Cooperative Institute for Research in Environmental Sciences University of Colorado, Boulder, Colorado and Aaron Goldman, Department of Physics, University of Denver, Denver,Colorado 80208

There is considerable interest in the kinetics and concentrations of free radicals in the stratosphere. Chlorine monoxide is a critically important radical because of its role in catalytic cycles for ozone depletion. Depletion occurs under a wide variety of conditions including the Antarctic spring when unusual mechanisms such as the BrO_x/ClO_x, ClO dimer (Cl_2O_2), and ClO_x/HO_x cycles are suggested to operate. Infrared spectroscopy is one of the methods used to measure ClO in the stratosphere [Menzies 1979 and 1983; Mumma et al. 1983]. To aid the quantification of such infrared measurements we have measured the ClO ground state fundamental band intensity.

The high ClO concentrations and the low stratospheric temperatures found in the Antarctic increase the liklihood of Cl_2O_2 formation and possible ozone destruction through the ClO dimer cycle. Little is currently known about the chemistry and photochemistry of Cl_2O_2. We have therefore studied the ClO + ClO + M reaction product to characterize the Cl_2O_2 infrared and UV absorption spectra.

The ClO band intensity and ClO + ClO + M reaction product measurements are made using a flow tube reactor coupled to a fast flow multipass absorption cell. The absorption cell is optically coupled to a high resolution Fourier transform spectrometer (FTS) (Bomem, Model DA3.002) for infrared absorption measurements. A UV spectrometer is also optically coupled to the absorption cell for simultaneous UV absorption measurements on the gas sample.

ClO v = 0 - 1 Band Intensity Measurement

The ClO radical infrared line intensities were first measured by Rogowski et al. [1978] and Margolis et al. [1978] using tunable diode laser spectroscopy. The results from these two experiments are in good agreement and give a ClO v = 0 -1 band intensity of $S = 11.8 \pm 2\ \mathrm{cm^{-2} atm^{-1}}$ at 298 K. This band intensity value and all subsequent band intensity values discussed include contributions from both chlorine isotopes and electronic spin states. A subsequent Herman Wallis analysis of data from our laboratory [Burkholder et al. 1987] gave $S = 11.3 \pm 2.0\ \mathrm{cm^{-2}\ atm^{-1}}$ in good agreement with the experimental values. Kostiuk et al. [1986] using infrared laser heterodyne spectroscopy to monitor ClO have recently reported a ClO band intensity of $S = 4.9\ \mathrm{cm^{-2} atm^{-1}}$ at 298 K, about a factor of 2.4 lower than the other measurements.

The discrepancy among the ClO band intensity measurements is significant and has a direct effect on the interpretation of quantitative atmospheric and laboratory infrared ClO measurements. In order to resolve this discrepancy we measured the v = 0 -1 band intensity of the ClO radical using directly calibrated [ClO]. The ClO spectra were recorded at 0.004 $\mathrm{cm^{-1}}$ resolution over the ClO concentration range 4×10^{12} to 1.4×10^{13} molecule $\mathrm{cm^{-3}}$ using two different chemical sources of ClO, Cl + O_3 and NO + OClO. Spectra were recorded at a total pressure of ≤ 0.4 torr, M = He. A sample ClO spectrum recorded during these measurements is shown in figure 1.

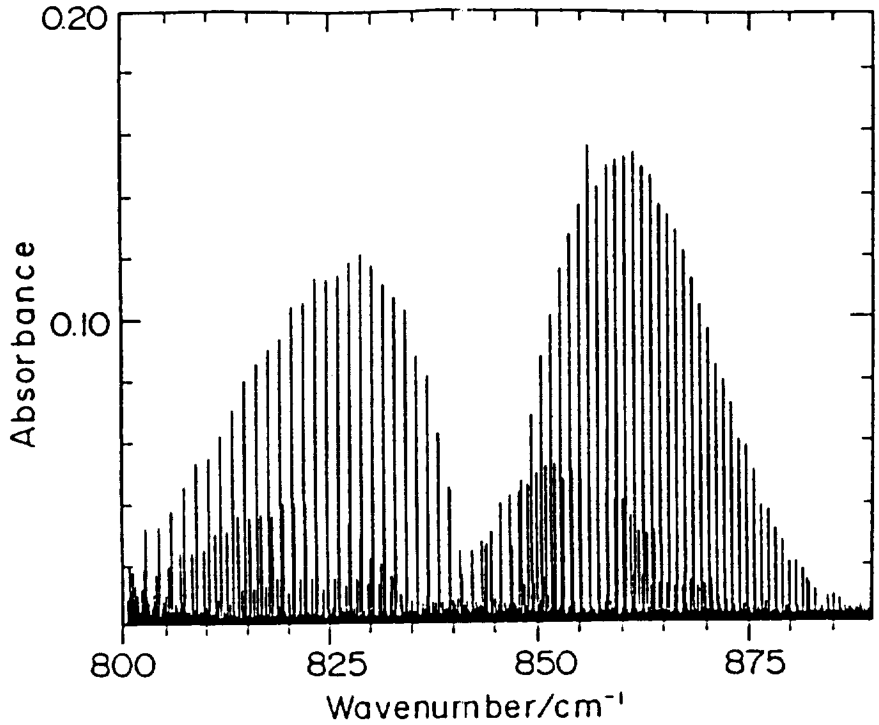

Figure 1 ClO radical infrared absorption spectrum. The spectrum was recorded at 0.004 cm^{-1} resolution in 50 coadded scans. [ClO] = 1.35 x10^{13} molecule cm^{-3}.

A preliminary value of the measured integrated band intensity is S = 9.15 ± 1.5 cm^{-2} atm^{-1} at 296 K. A N_2 collisional broadening coefficient of γ^0 = 0.093 ± 0.018 cm^{-1} atm^{-1} was also determined from spectra recorded at higher pressure, 10 torr N_2. The discrepancy between our FTS band intensity measurements and those of Kostiuk et al. [1986] will be discussed. A source of systematic error in the use of the Cl + O_3 reaction as a quantitative source of ClO radicals will also be discussed.

ClO + ClO Reaction Product

Molina and Molina [1987] have discussed the ClO dimer cycle:

$ClO + ClO + M \rightarrow Cl_2O_2 + M$ (1)

$Cl_2O_2 + h\nu \rightarrow Cl + ClOO$ (2)

$ClOO + M \rightarrow Cl + O_2 + M$ (3)

$\underline{2(Cl + O_3 \rightarrow ClO + O_2)}$ (4)

NET $2O_3 \rightarrow 3O_2$ (5)

and suggested that it may play an important role in the Antarctic ozone depletion. At the temperature, pressure and [ClO] observed in the lower Antarctic stratosphere, the self reaction of ClO to form the dimer, Cl_2O_2, is significant. At these temperatures, 190 - 210 K, the ClO dimer ,assuming a bond energy ~16.5 kcal mole^{-1}, would have a long thermal decomposition lifetime, τ ~ 20 hours. The UV absorption spectrum, photolysis rate and reactivity of Cl_2O_2 therefore need to be understood to determine the significance of the ClO dimer cycle. Infrared and UV absorption measurements of the ClO + ClO + M reaction products will be presented. Our observations will be compared with the recent measurements of Molina and Molina [1987].

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