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

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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/CIO_y, CIO dimer (Cl_2O_2), and ClO_x/HO_y cycles are suggested to operate. Infrared spectroscopy is one of the methods used to measure CIO in the stratosphere [Menzies 1979 and 1983; Mumma et al. 1983]. To aid the quantification of such infrared measurements we have measured the CIO ground state fundamental band intensity.

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

The CIO band intensity and CIO + CIO + 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.

**CIO v = 0 - 1 Band Intensity Measurement**

The CIO 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 CIO v = 0 - 1 band intensity of $S = 11.8 \pm 2 \text{ cm}^{-2} \text{atm}^{-1}$ 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 $S = 11.3 \pm 2.0 \text{ cm}^{-2} \text{atm}^{-1}$ in good agreement
with the experimental values. Kostiuk et al. [1986] using infrared laser
heterodyne spectroscopy to monitor CIO have recently reported a CIO band
intensity of $S = 4.9 \text{ cm}^{-2} \text{atm}^{-1}$ at 298 K, about a factor of 2.4 lower than
the other measurements.

The discrepancy among the CIO band intensity measurements is
significant and has a direct effect on the interpretation of quantitative
atmospheric and laboratory infrared CIO measurements. In order to resolve
this discrepancy we measured the v = 0 - 1 band intensity of the CIO radical
using directly calibrated [CIO]. The CIO spectra were recorded at 0.004
$\text{cm}^{-1}$ resolution over the CIO concentration range $4 \times 10^{12}$ to $1.4 \times 10^{13}$
molecule cm$^{-3}$ using two different chemical sources of CIO, Cl + O$_3$ and NO +
OCIO. Spectra were recorded at a total pressure of $\leq 0.4 \text{ torr}$, M = He. A
sample CIO spectrum recorded during these measurements is shown in figure 1.
Figure 1 CIO radical infrared absorption spectrum. The spectrum was recorded at 0.004 cm\(^{-1}\) resolution in 50 coadded scans. [CIO] = 1.35 \times 10^{13}\text{ molecule cm}^{-3}.

A preliminary value of the measured integrated band intensity is $I = 9.15 \pm 1.5 \text{ cm}^{-2} \text{ atm}^{-1}$ at 296 K. A $N_2$ collisional broadening coefficient of $\gamma_0 = 0.093 \pm 0.018 \text{ cm}^{-1} \text{ atm}^{-1}$ 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 CIO radicals will also be discussed.

**CIO + CIO Reaction Product**

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

\begin{align*}
\text{CIO} + \text{CIO} + \text{M} &\rightarrow \text{Cl}_2O_2 + \text{M} \quad (1) \\
\text{Cl}_2O_2 + \text{h}_\nu &\rightarrow \text{Cl} + \text{ClO}0 \quad (2) \\
\text{ClO}0 + \text{M} &\rightarrow \text{Cl} + \text{O}_2 + \text{M} \quad (3) \\
2(\text{Cl} + \text{O}_3) &\rightarrow \text{ClO} + \text{O}_2 \quad (4) \\
\text{NET} &\rightarrow 2\text{O}_3 \rightarrow \text{3O}_2 \quad (5)
\end{align*}
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, \( \text{Cl}_2\text{O}_2 \), 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, \( \tau \approx 20 \) hours. The UV absorption spectrum, photolysis rate and reactivity of \( \text{Cl}_2\text{O}_2 \) 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].

REFERENCES


