# Absolute Infrared Band Strength Measurement of the CIO Radical by Fourier Transform Infrared Spectroscopy

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High-resolution (0.005 cm<sup>-1</sup>) Fourier transform infrared (FTIR) spectra of the  $X^2\Pi_i - X^2\Pi_i$ (1–0) rovibrational bands of <sup>35</sup>Cl<sup>16</sup>O and <sup>37</sup>Cl<sup>16</sup>O were obtained in 1 Torr of helium carrier gas. ClO radicals were produced in a discharge-flow chemical reactor containing White-type optics. During acquisition of the FTIR spectra, a diode array spectrometer was used to monitor the ClO concentration by observing the  $A^2\Pi_i - X^2\Pi_i$  electronic band in the ultraviolet. After measuring the strengths of approximately 830 individual infrared lines from several spectra, a total band strength,  $S_v = 13.1 \pm 1.1$  cm<sup>-2</sup> atm<sup>-1</sup>, and a first Herman–Wallis coefficient,  $\alpha = (4.12 \pm 0.62) \times 10^{-3}$ , were determined. The fundamental transition moment calculated from the band strength was  $-(3.9 \pm 0.2) \times 10^{-2}$  D. © 1988 Academic Press, Inc.

#### INTRODUCTION

The chlorine monoxide radical is an important participant in the catalytic destruction of ozone in the earth's stratosphere. Numerous attempts have been made to determine atmospheric concentration profiles of ClO by remote sensing using microwave (1, 2)and infrared spectroscopy (3-5), and by in situ methods based on the chemical conversion of ClO to Cl (6, 7). Previous infrared field studies of ClO have utilized laser heterodyne spectroscopy from both ground-based and balloon-borne platforms (3-5). The interpretation of these infrared studies in terms of atmospheric concentrations has been complicated by the lack of a consistent data base from which to evaluate the absolute band strength of the fundamental  $X^2 \Pi - X^2 \Pi$  band centered near 844 cm<sup>-1</sup>.

Previous values reported for the ClO v(1-0) band strength range between 4.9 and 32.4 cm<sup>-2</sup> atm<sup>-1</sup>. The highest values were mainly theoretical predictions from early ab initio calculations (8, 9). However, even laboratory experiments which used diode laser or laser heterodyne techniques to measure the frequency and strength of a few individual rovibrational lines (10-13) did not agree well. Some of the variability in the experimental studies may be due to differences in the methods used to measure the absolute ClO concentration. Two recent approaches to the problem have used concentration-independent methods. One of these used a Herman–Wallis factor (14) retrieved from the Fourier transform infrared (FTIR) band spectrum of ClO to calculate the v(1-0) transition dipole (15). Molecular beam electric resonance was used in another study to obtain electric dipole moments for ClO which were combined with relative intensity data to yield the fundamental transition moment (16).

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In the work reported here, we have coupled high resolution FTIR measurements with UV measurements of ClO in order to measure directly the  $X^2\Pi-X^2\Pi$  (1–0) infrared band strengths of the <sup>35</sup>Cl<sup>16</sup>O and <sup>37</sup>Cl<sup>16</sup>O isotopomers. High-resolution Fourier transform infrared spectra of approximately 125 absorption lines were recorded at several ClO concentrations. ClO concentrations were obtained from electronic band spectra recorded by diode array spectroscopy in the UV region. This represents an improvement over previous experiments which used single UV wavelengths to determine ClO concentrations. Concentration measurements based on a single UV wavelength suffer from possible interferences from reactant O<sub>3</sub>, OClO, or Cl<sub>2</sub>. In this work, the absolute ClO UV cross sections were also remeasured with the diode array spectrometer prior to the infrared experiments.

The  ${}^{2}\Pi$  system of ClO is similar to that of OH in that they are both inverted spin doublets with the  ${}^{2}\Pi_{3/2}$  state lower in energy than the  ${}^{2}\Pi_{1/2}$  state. Both subbands exhibit  $\Lambda$  doubling but only the splittings in the  $\Pi_{1/2}$ - $\Pi_{1/2}$  transitions are resolvable with FTIR instrument capabilities. An interesting feature of the infrared spectrum is the presence of the O branch since ClO has electronic orbital angular momentum. A detailed treatment of the infrared spectroscopy of such diatomic molecules is available elsewhere (17). The ClO ground state rotational energy levels and v(1-0) transition frequencies have been previously determined (18, 19). Our FTIR analysis allowed us to measure the first coefficient,  $\alpha$ , of the Herman-Wallis factor. This parameter is an indication of the extent of rotation vibration interaction in the molecule, an effect that is relatively small for ClO. It manifests itself as an intensity variation other than that expected solely from the Boltzmann distribution and Hönl-London factors, and is measurable for absorption lines with high J values. We have addressed the reliability of approximating a linear dipole moment function for CIO and inferring a band strength solely from the first Herman-Wallis coefficient, a method used previously for HCl (20).

### EXPERIMENTAL DETAILS

As shown in Fig. 1, the 15-cm-diameter room temperature flow tube was equipped with White-type optics. The infrared path length was 42.56 m. Infrared spectra of ClO were recorded at 0.005 cm<sup>-1</sup> full width at half-maximum unapodized resolution with a Bomem DA3.002 Fourier transform interferometer and an externally mounted Cu: Ge detector at liquid helium temperature. A narrow band-pass filter centered at 11.5  $\mu$ m and cooled to liquid helium temperatures was used in front of the detector. With 100 to 200 interferograms coadded per spectrum, a peak-to-peak signal-to-noise ratio of approximately 50:1 was obtained for the strongest absorption peaks. Typical acquisition times were five to eight hr per spectrum. For each spectrum, 90 to 150 lines were recorded between 790 and 900 cm<sup>-1</sup>. The strongest ClO transitions corresponded to absorptions of approximately 26%. A typical infrared absorption spectrum of ClO is shown in Fig. 2.

The apparatus was configured such that the UV/visible beam was directed parallel to the axis of the infrared beam, approximately 1.5 cm from the flow tube wall. In this way the optical density of ClO in the column traversed by the infrared beam was independently monitored. The source of the UV/visible beam was a  $D_2$  lamp positioned at the downstream end of the flow tube. After a single pass through the 152-cm cell,



FIG. 1. Schematic Diagram of FTIR/fast flow reactor system.

the beam was dispersed by a grating spectrometer onto a diode array detector (PARC 1461/1412 OMA III). The amount of reactant O<sub>3</sub> or OCIO was measured with the spectrometer centered at 275 or 350 nm, respectively. In each case, Cl atoms were added until the measured absorbance for the reactant went to zero. The ClO ( $A^2\Pi_i - X^2\Pi_i$ ) spectrum centered at 275 nm was then recorded at frequent intervals during acquisition of the infrared spectrum to ensure that the ClO concentration remained constant (±5%). The diode array spectrometer facilitated the rapid (12 sec) acquisition of UV spectra with a bandwidth up to 80 nm.

ClO was produced in a fast flow reactor using one of the following source reactions,

$$Cl + O_3 \rightarrow ClO + O_2$$
(1)  

$$k_{298} = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \sec^{-1} (21)$$

or

$$Cl + OClO \rightarrow 2ClO$$
 (2)  
 $k_{298} = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \sec^{-1} (22).$ 

Chlorine atoms were produced by flowing  $Cl_2/He$  mixtures through two 2450 MHz microwave discharges situated on opposite sides of the reactor sidearm. OCIO or O<sub>3</sub> was introduced through a sliding injector positioned downstream of the discharges. Approximately half of the 12 slm helium carrier gas flow was introduced in the sidearm, resulting in a residence time in the sidearm of approximately 20 msec. The balance of the helium was introduced in the main flow tube. At a total pressure of about 1 Torr, the flow tube residence time was approximately 0.1–0.15 sec. The walls of both the sidearm and flow tube were coated with halocarbon wax to minimize radical wall loss.



FIG. 2.  $X^2\Pi - X^2\Pi$  infrared absorption spectrum of ClO ([ClO] =  $5.78 \times 10^{13}$  molecules cm<sup>-3</sup> in 1 Torr helium; 100 coadds; Hamming apodization function). (a) Entire  $X^2\Pi - X^2\Pi$  band (b) expanded cm<sup>-1</sup> scale showing  ${}^{2}\Pi_{3/2} - {}^{2}\Pi_{3/2} - {}^{37}Cl^{16}O$ ,  ${}^{35}Cl^{16}O$  *R*-branch transitions and resolved  $\Lambda$  doublets of the  ${}^{2}\Pi_{1/2} - {}^{2}\Pi_{1/2}$  ${}^{35}Cl^{16}O$  *R*-branch transitions.

Reactions 1 and 2 were carried out in the flow tube sidearm under conditions of excess atomic chlorine ( $[Cl]_0 > 1 \times 10^{14}$  molecule cm<sup>-3</sup>). Under these conditions the residence time in the sidearm was sufficiently long to permit the O<sub>3</sub> or OCIO to

be converted completely to ClO. When  $O_3$  was used as the ClO precursor, it was observed that the ClO yield was less than that expected from stoichiometric conversion when  $[O_3]_0$  was greater than about  $2 \times 10^{13}$  molecule cm<sup>-3</sup>. A possible explanation involves the production of vibrationally excited ClO from reaction 1 with subsequent reactions resulting in the secondary removal of ClO:

$$Cl + O_3 \rightarrow ClO (v > 0) + O_2$$
 (1a)

$$ClO(v > 2) + Cl \rightarrow Cl_2 + O$$
(3)

$$O + CIO \rightarrow CI + O_2 \tag{4}$$

$$ClO(v > 0) + O_3 \rightarrow Cl + 2O_2$$
(5)

$$\operatorname{ClO}(v > 0) + \operatorname{ClO}(v \ge 0) \rightarrow \operatorname{products.}$$
 (6)

Reactions 3, 5, and 6 are known to be quite slow for ClO (v = 0) but might be important if ClO were vibrationally excited. With the helium flow rates used in the present experiments these processes as well as vibrational relaxation would be complete in the sidearm. Therefore we would not expect ClO hot bands to be observed in the FTIR spectra.

Under all reaction conditions, the bimolecular disproportionation of ClO,

$$ClO + ClO \rightarrow Cl + ClOO$$
 (6a)

$$\rightarrow$$
 Cl + OClO (6b)

$$\rightarrow Cl_2 + O_2 \tag{6c}$$

$$k_{298} = 1.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} (23),$$

resulted in a ClO concentration gradient of less than 10% along the flow tube axis. First-order ClO wall loss would be expected to produce an additional axial gradient of less than 10%, based on previous flow tube studies of ClO (24). However, even if a significant axial ClO concentration gradient were present, the band strength determination would not be affected because the ultraviolet and infrared beams probed the same reaction volume.

OCIO was produced by flowing  $Cl_2/He$  through a column of NaClO<sub>2</sub> packed with glass beads. Ozone was generated in an ac discharge in pure O<sub>2</sub> using a commercial ozonizer (Wellsbach T-816). The flow exiting the ozonizer (2% O<sub>3</sub> in O<sub>2</sub>) was passed directly into the flow tube.  $Cl_2$  (Alphagaz) and O<sub>2</sub> (VBA Cryogenics) had stated purities of 99.99%. The helium purity was 99.995%. All gases were used without further purification. Solid sodium chlorite was obtained from Kodak.

Prior to the infrared experiments, the absorption cross sections of CIO at 253.7 and 257.7 nm were calibrated with the diode array spectrometer set at an effective resolution of approximately 0.3 nm. With the diode array spectrometer centered at 325 nm, it was possible to obtain the UV absorption spectrum of OCIO. Since the absolute cross sections of OCIO have been previously reported (25) for the entire 240- to 480-nm range, our differential absorbance measurements in the structured region could be converted to OCIO concentrations. Known concentrations of OCIO were titrated with

excess atomic chlorine to produce ClO (reaction 2). The absorbance of ClO as a function of OClO concentration was determined from a series of such titrations.

## DATA ANALYSIS

## **Concentration Measurements**

From the electronic absorption spectra recorded while taking infrared spectra, the ClO optical density in the flow tube was calculated for each experiment. UV spectra of ClO and  $O_3$  recorded with the diode array spectrometer are shown in Fig. 3. Both the differential absorption cross sections in the structured region and the cross sections determined at 253.7 and 257.7 nm in the continuum were used to determine the ClO absorbance.

Infrared spectra from 790–900 cm<sup>-1</sup> were obtained for ClO concentrations ranging from  $1.14 \times 10^{13}$  to  $5.73 \times 10^{13}$  molecule cm<sup>-3</sup>. The total cell pressure including the helium carrier gas was approximately 1 Torr. Figure 4 illustrates the linear increase in equivalent width for three individual lines (*e* and *f* components combined) over this concentration range. The equivalent width values in Fig. 4 represent the average strengths from a total of seven different infrared spectra. Generation of ClO by two different methods did not produce ClO at different rotational temperatures and hence the infrared line intensities from the two different sources were indistinguishable.

## Infrared Linestrengths

After Fourier transformation of the coadded interferograms, the resultant absorption spectra were convolved with a sinc instrumental lineshape function, a combination Voigt-Lorentzian profile, and a "medium" (26) apodization function. A nonlinear least-squares fitting program, developed by Brown *et al.* was used to fit for linestrengths and line positions. The details of the fitting routines have been described previously (27). The input parameters for the fitting programs included the experimentally measured concentration and path length. The linestrengths from each spectrum were all normalized to 296 K and averaged before doing the band strength analysis.



FIG. 3. UV absorption spectra of ClO and  $O_3$  obtained with diode array spectrometer at 0.3-nm resolution.



FIG. 4. Beer's law plot of ClO infrared line intensities. Each point includes both e and f components of an *R*-branch transition and is the average equivalent width from several spectra. These linestrengths must therefore be divided by two to use in Eq. (7). The average values combine data from the vibrational spectra of ClO produced by two different chemical methods (Cl and O<sub>3</sub>; Cl and OClO).

## Absolute Infrared Band Strength

The band intensity  $S_v$  is given by the following equation (28),

$$S_{\rm v} = \frac{S_i \cdot Q_{\rm r} \cdot \nu_0}{\nu_i \cdot L_i \cdot \exp(-E_r''/kT) \cdot [1 - \exp(-\nu_i/kT)] \cdot F},\tag{7}$$

where  $S_i$  is the line intensity,  $\nu_i$  is the line frequency,  $\nu_0$  is the band origin,  $L_i$  is the Hönl-London factor,  $Q_r$  is the lower state rotational partition function, k is the Boltzmann constant, T is the temperature,  $E_r''$  is the lower state rotational energy, and F is the Herman-Wallis factor. The Hönl-London factors,  $L_J$ , for the CIO molecule are as follows (29),

*P* branch: 
$$L_J = \frac{J^2 - \Omega^2}{J}$$
 (8)

R branch: 
$$L_J = \frac{(J+1)^2 - \Omega^2}{J+1}$$
 (9)

Q branch: 
$$L_J = \frac{\Omega^2(2J+1)}{J(J+1)}$$
, (10)

where  $\Omega = \frac{3}{2}$  or  $\frac{1}{2}$ .

In the band strength analysis, the  ${}^{2}\Pi_{3/2} - {}^{2}\Pi_{3/2}$  and the  ${}^{2}\Pi_{1/2} - {}^{2}\Pi_{1/2}$  subbands were treated separately for each of the two most abundant isotopomers,  ${}^{35}Cl^{16}O$  and  ${}^{37}Cl^{16}O$ . The band center frequencies and lower state rotational energies were provided by Kakar *et al.* (18) based on previous microwave measurements. The band centers, partition functions, and isotopic abundances used in the data reduction are summarized in Table I.

The linestrengths and other factors in Eq. (7) were fitted to a function,  $S_v \cdot F(m)$ , where the Herman-Wallis factor F(m) was of the form,

$$F = 1 + \alpha m \tag{11}$$

Parameters Used in Calculation of Band Strength and Transition Dipole					
	<sup>35</sup> Cl <sup>16</sup> O		<sup>37</sup> Cl <sup>16</sup> O		
	<sup>2</sup> Π <sub>3/2</sub>	<sup>2</sup> II <sub>1/2</sub>	<sup>2</sup> Π <sub>3/2</sub>		
$\nu_0^{a} (cm^{-1})$	842.5653143	839.2884373	835.4862066		
Q <sub>r</sub> (296 K) <sup>b</sup>	809	809	823		
Isotopic abundance	0.7535	0.7535	0.2441		
$Q_{\rm v}^{\rm b}$	1.016	1.016	1.017		

TA	BL	E	1
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\* Calculated by Cohen from microwave measurements (18).

<sup>b</sup> For method of calculation see Gillis and Goldman (19).

with m = -J for the P branch, m = J + 1 for the R branch, and m = 0 for the Q branch. A graph of  $S_v \cdot F$  as a function of m did not indicate any curvature, so a quadratic term in m was not included.  $S_v$  was determined as the m = 0 intercept of the fitted line. The linear graph for the  ${}^{35}Cl^{16}O {}^{2}\Pi_{3/2} - {}^{2}\Pi_{3/2}$  transitions is shown in Figs. 5a, 5b. The other subbands with fewer data points or with data only for small |m| were fitted with F = 1 since there was no slope evident in the graphs. This was the case for the  ${}^{37}Cl^{16}O {}^{2}\Pi_{3/2} - {}^{2}\Pi_{3/2}$  data shown in Fig. 5a and the  ${}^{35}Cl^{16}O {}^{2}\Pi_{1/2}$  $^{2}\Pi_{1/2}$  data in Fig. 5b.

The square of the dipole moment matrix element,  $\mu$ , was found by direct substitution of the experimental value for  $S_{\rm v}$  into the following equation:

$$|\mu^{2}| = \frac{S_{v} \cdot 3hc \cdot Q_{v} \cdot T}{8\pi^{3} \cdot \exp(-E_{v}'/kT) \cdot \nu_{0} \cdot 273.15 \cdot n \cdot C}.$$
 (12)

Here,  $Q_v$  is the vibrational partition function,  $E_v^{v}$  is the lower state vibrational energy, T is the temperature, C is the isotopic abundance, n is the degeneracy, h is Planck's constant, and c is the speed of light in a vacuum.

#### RESULTS

#### Ultraviolet Data

The data from the titrations of OCIO with Cl atoms are presented in Fig. 6. The ClO cross sections at individual wavelengths were calculated from the slopes of the graphs divided by twice the UV path length. The factor of two arises from the stoichiometry of reaction 2. ClO cross sections of  $(4.20 \pm 0.21) \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> at 253.7 nm and  $(4.91 \pm 0.37) \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> at 257.7 nm were obtained. These particular wavelengths were chosen in order to compare our cross sections with previous measurements. Since they are in the continuum region there should be no instrumental resolution effects. The results at 257.7 nm are in good agreement with those of Clyne and Coxon (30), who obtained a value of  $4.85 \times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> using a discharge-flow/absorption method in which ClO radicals were titrated with atomic oxygen and NO. Our value at 253.7 nm is also in agreement with the 4.28  $\times 10^{-18}$  cm<sup>2</sup> molecule<sup>-1</sup> value reported by Mandelman and Nicholls (31) whose relative CIO spectrum was normalized at 257.7 nm to the Clyne and Coxon cross section.



FIG. 5. (a) Herman–Wallis plot for  ${}^{2}\Pi_{3/2} {}^{-2}\Pi_{3/2}$  lines of both CIO isotopomers. The parameters retrieved from the fit are given in Table II. (b) Same as (a) with  ${}^{35}\text{Cl}{}^{16}\text{O}{}^{2}\Pi_{1/2} {}^{-2}\Pi_{1/2}$  lines included for comparison.

## Infrared Data

Since the  ${}^{2}\Pi_{1/2}$  (v = 0) levels lie about 320 cm<sup>-1</sup> above the  ${}^{2}\Pi_{3/2}$  levels, approximately 80% of the room temperature ClO population is located in the latter. Therefore, the absorption lines from the  ${}^{2}\Pi_{3/2}$  ground state are the stronger of the two.



FIG. 6. UV data from the titrations of OCIO with Cl atoms used to determine CIO UV absorption cross sections; that is,  $\sigma_{CIO} = \text{slope}/2l$ , where l = UV path length.

In Fig. 5a,  $S_v \cdot F$  is plotted against *m*, for the <sup>35</sup>Cl<sup>16</sup>O <sup>2</sup> $\Pi_{3/2}$ -<sup>2</sup> $\Pi_{3/2}$  subband. The most extensive and precise fit for  $S_v$  and *F* using Eq. (7) was obtained from these data. The retrieved band strength is 10.03 ± 0.12 cm<sup>-2</sup> atm<sup>-1</sup> and  $\alpha = (4.12 \pm 0.62) \times 10^{-3}$ . The band strength is the m = 0 intercept in Fig. 5a, while  $\alpha = \text{slope}/S_v$ . The data for the <sup>2</sup> $\Pi_{3/2}$ -<sup>2</sup> $\Pi_{3/2}$  subband of <sup>37</sup>Cl<sup>16</sup>O are also included in Fig. 5a. The contribution to the total band strength retrieved from this graph is 3.08 ± 0.03 cm<sup>-2</sup> atm<sup>-1</sup>. The data did not fit preferentially to any functional form of *F*, so  $\alpha$  was not determined. The ratio of the band strengths for the two isotopomers is 3.26 which is within 5% of the theoretical estimate based on their relative abundances. By adding the band strengths of the two isotopomers, we arrive at a total band strength,  $S_v = 13.11$  cm<sup>-2</sup> atm<sup>-1</sup>.

A separate analysis of the <sup>35</sup>ClO <sup>2</sup> $\Pi_{1/2}$ -<sup>2</sup> $\Pi_{1/2}$  band gave a value of  $S_v = 10.51 \pm 0.26$ . However, it can be seen from Fig. 5b that these data do not differ significantly from those of the stronger <sup>2</sup> $\Pi_{3/2}$ -<sup>2</sup> $\Pi_{3/2}$  subband. There is inherently more error in measuring linestrengths for the weaker <sup>2</sup> $\Pi_{1/2}$ -<sup>2</sup> $\Pi_{1/2}$  transitions so there is less precision in the data and no  $\alpha$  value was determined. Furthermore, most of the  $\Lambda$  doublets were resolved but were not exactly equal in intensity so there are two data points for every m value. This contributed to the scatter in Fig. 5b. Only four measured lines were assigned to the <sup>37</sup>Cl<sup>16</sup>O <sup>2</sup> $\Pi_{1/2}$ -<sup>2</sup> $\Pi_{1/2}$  transitions so these lines were not used in the band strength determination.

Several lines in the Q branch of the <sup>35</sup>Cl<sup>6</sup>O band were resolved. Since these lines were very weak they could not be measured accurately and therefore were not included in the final analysis. These lines would not affect the overall fit for  $S_v$  and F.

The dipole moment matrix elements calculated for the  ${}^{35}Cl^{16}O$  and  ${}^{37}Cl^{16}O$  ${}^{2}\Pi_{3/2} - {}^{2}\Pi_{3/2}$  bands, using Eq. (12) are  $-3.94 \times 10^{-2}$  D and  $-3.85 \times 10^{-2}$  D, respectively, while for the  ${}^{35}ClO {}^{2}\Pi_{1/2} - {}^{2}\Pi_{1/2}$  band, it is  $-4.04 \times 10^{-2}$  D. The same errors associated with the band strengths can be applied to the dipole moment values. The different subbands give essentially the same dipole moment. The weighted average is  $-(3.9 \pm 0.2) \times 10^{-2}$  D.

The experimental results are summarized in Table II. A complete v(1-0) ClO line list including frequencies, ground state rotational energies (18), and linestrengths is available from the authors.

Infrared $v(1-0)$ ClO Band Parameters						
	<sup>35</sup> Cl <sup>16</sup> O		<sup>37</sup> Cl <sup>16</sup> O			
	<sup>2</sup> Π <sub>3/2</sub>	<sup>2</sup> Π <sub>1/2</sub>	<sup>2</sup> П <sub>3/2</sub>			
$S_v (cm^{-2} atm^{-1})^a \alpha^a \mu (debye)^a$	$10.03 \pm 0.84 (4.12 \pm 0.62) \times 10^{-3} -(3.94 \pm 0.2) \times 10^{-2}$	$10.51 \pm 1.05$ -(4.04 ± 0.3) × 10 <sup>-2</sup>	$3.08 \pm 0.26$ -(3.85 ± 0.2) × 10 <sup>-2</sup>			
No. lines fitted	122	29	88			

TABLE II

*Note.* Total band strength:  $13.1 \pm 1.1 \text{ cm}^{-2} \text{ atm}^{-1a}$ ; average transition moment:  $-(3.9 \pm 0.2) \times 10^{-2} \text{ D.}^{a}$ <sup>a</sup> Total estimated error limits.

#### DISCUSSION

The measurement of CIO concentrations by diode array spectrometry, in the absence of any interfering species, enabled us to directly measure the infrared band strength of CIO. From fitting measured linestrengths to Eq. (7), the total fundamental band strength for both isotopes was determined to be  $13.11 \pm 0.12$  cm<sup>-2</sup> atm<sup>-1</sup>. The m = 0intercept obtained from the graphs of  $S_v \cdot F$  versus m was not very sensitive to the functional form of F used for the fit. Based on an analysis of our experimental methods, we find the overall uncertainty  $(\pm 1\sigma)$  in the band strength to be  $\pm 8.4\%$ . This value includes errors in determining the CIO concentration, uncertainties in the UV cross sections of OCIO used in our calibrations  $(\pm 3.5\%)$  (25), and limitations associated with our graphical analysis of the titration data and the residuals from the  $S_v$  determination using Eq. (7). Our final band strength is thus  $13.1 \pm 1.1$  cm<sup>-2</sup> atm<sup>-1</sup>.

Table III compares the CIO band strength reported here to previous values. Some of the numbers have been revised since they were originally published. For example, the original ab initio value reported by Langhoff *et al.* (8) was 32.4 cm<sup>-2</sup> atm<sup>-1</sup>. In a more recent theoretical study of the dipole moment function of CIO by Pettersson *et al.* (32), a value of  $12 \pm 2$  cm<sup>-2</sup> atm<sup>-1</sup> was calculated. We assume that the diode laser measurement of  $30 \pm 10$  cm<sup>-2</sup> atm<sup>-1</sup> reported by Menzies *et al.* (10) was improved upon, since Margolis *et al.* (11) subsequently reported a value of  $11.9 \pm 2.2$  cm<sup>-2</sup> atm<sup>-1</sup>. Without knowing the full experimental and analytic details, we cannot speculate about the reason for the 30 cm<sup>-2</sup> atm<sup>-1</sup> value, but the authors did report a large uncertainty in that figure.

Our data are in excellent agreement with the tunable diode laser data reported by Rogowski *et al.* (12). They measured the strengths of nine lines in the  ${}^{35}$ Cl<sup>16</sup>O

Reference	Method	Band strength cm <sup>-2</sup> atm <sup>-1</sup>
Menzies et al. (1977)	Tunable diode laser	30
Margolis et al. (1978)	Tunable diode laser	11.9
Rogowski et al. (1978)	Tunable diode laser	9.2ª
Gillis and Goldman (1981)	Theory	11.8 <sup>b</sup>
Langhoff et al. (1977)	Ab initio	32.4
Komornicki and Jaffe (1979)	Ab initio	23
Kostiuk et al. (1986)	Laser heterodyne	4.9
Burkholder et al. (1987)	FTIR/Herman-Wallis	11.3
Pettersson et al. (1986)	theory	12
Yaron et al. (1988)	Molecular beam electric resonance	c
Burkholder et al. (1988, unpublished)	FTIR	9.68
This work	FTIR	13.1

#### TABLE III

ClO  $X^2 \Pi_i - X^2 \Pi_i v(1-0)$  Infrared Band Strength

<sup>a</sup> This "average" band strength is apparently only for the  ${}^{35}Cl^{16}O$  isotopomer. Scaling this value gives a total of 12.2 cm<sup>-2</sup> atm<sup>-1</sup>.

<sup>b</sup> Normalized to the data of Rogowski et al. (12).

<sup>c</sup> Reported  $\mu = -(3.4 \pm 0.5) \times 10^{-2}$  D; combined with relative intensity data of Burkholder et al. (15).

 ${}^{2}\Pi_{3/2} - {}^{2}\Pi_{3/2}$  subband. Their reported average band strength of 9.2 cm<sup>-2</sup> atm<sup>-1</sup> given in Table III apparently includes only the  ${}^{35}$ Cl  ${}^{16}$ O transitions, and therefore the total band strength would be 12.2 cm<sup>-2</sup> atm<sup>-1</sup>. For purposes of comparison to our results, their actual measured linestrengths were considered. Using Eq. (7) to calculate  $S_v$ values from their data (at 300 K), and fitting graphically for  $S_v \cdot F$ , the m = 0 intercept is 9.43 ± 1.48 cm<sup>-2</sup> atm<sup>-1</sup>. Scaling this value to include the bands of both isotopic species gives a total CIO band strength of  $12.52 \pm 2$  cm<sup>-2</sup> atm<sup>-1</sup>. Since the data are at small m values and are quite scattered, taking an average of the  $S_v$  values (or fitting  $S_v \cdot F$  with F = 1) is also valid. The  ${}^{35}$ Cl  ${}^{16}$ O contribution is then  $11.34 \pm 1.4$  cm<sup>-2</sup> atm<sup>-1</sup>, implying a total band strength of  $15.1 \pm 2$  cm<sup>-2</sup> atm<sup>-1</sup>. The UV cross section at 257.7 nm which Rogowski *et al.* used (4.85 × 10<sup>-18</sup> cm<sup>-2</sup> molecules<sup>-1</sup> (30)) was very close to our value of  $4.91 \times 10^{-18}$  cm<sup>-2</sup> atm<sup>-1</sup>, so the CIO concentration was determined in a manner consistent with our experiment.

Gillis and Goldman (19) calculated the relative line intensities of the entire ClO band. They then set the sum of the linestrengths which Rogowski et al. provided equal to the sum of the strengths of the same J-level transitions in their calculation. This served to calibrate their band strength. The relative intensities measured by Rogowski et al. adhere to those predicted by Gillis and Goldman to within  $\pm 12\%$  overall which is reasonable considering the uncertainty of the measured strengths was  $\pm 20\%$ . Intensity variations due to a Herman-Wallis factor were not included, but Gillis and Goldman estimate that setting the rovibrational transition probability equal to unity in the Einstein A coefficient caused an error in the line intensities of about  $\pm 12\%$ . The band strength obtained by Gillis and Goldman from summing the individual calculated line intensities was 11.8 cm<sup>-2</sup> atm<sup>-1</sup> at 296 K. This is in good agreement with our reported value. It is worthwhile to note that the band strength reported from the tunable diode laser data of Margolis et al.,  $11.9 \pm 2.2$  cm<sup>-2</sup> atm<sup>-1</sup>, was obtained from four values, calculated individually from different linestrengths. In units of  $cm^{-2} atm^{-1}$ , the band strengths were R(6.5), 12.4; R(13.5), 12.8; R(7.5), 13.6; and R(8.5), 8.63. In this case, the authors' error limits are very meaningful, because the majority of the band strengths are actually higher than the 11.9 average and are within the uncertainty range of our reported value.

Direct FTIR measurements of the CIO band strength were recently made by Burkholder *et al.* with the unpublished result of  $9.68 \pm 1.5$  cm<sup>-2</sup> atm<sup>-1</sup>(33). This is slightly lower than any of the experimental results discussed above.

One experimental value which is significantly lower than the other direct measurements is the 4.9 cm<sup>-2</sup> atm<sup>-1</sup> value reported by Kostiuk *et al.* (13) from their laser heterodyne measurements. Two possible systematic errors could have occurred in their experiments. Infrared O<sub>3</sub> linestrengths were used to determine the amount of excess O<sub>3</sub> in the infrared path. The contribution from ozone (30–80%) was then subtracted from the total UV absorbance to give the CIO contribution. Since the O<sub>3</sub> UV cross section is approximately three times that of CIO in the continuum region, an error in estimating the amount of unreacted O<sub>3</sub> would result in an erroneous absorbance. The final infrared band strength would be too low if the CIO concentration inferred from the absorbance were too high. Since the experiments were done at total pressures of 5–6 Torr, formation of (CIO)<sub>2</sub> also needs to be considered, that is,

$$CIO + CIO + M \rightarrow (CIO)_2 + M$$
 (13)

$$k_{298} = 4 \times 10^{-32} \text{ cm}^6 \text{ molecules}^{-2} \text{ sec}^{-1} (\text{ for } M = \text{He}) (34).$$

The extent of dimer formation would depend on the flow rates and thus on the residence times in the cell as well as on the buffer gas. Although the dimer absorbs strongly in the UV (peak maximum = 240 nm (35)), it is difficult to verify its presence in a reaction system, even with broad band FTIR spectroscopy. Like O<sub>3</sub>, it could lead to erroneous CIO concentrations.

Since the band strength reported by Kostiuk *et al.* is much lower than other experimental values, the CIO column densities derived from their subsequent field data should be reevaluated.

Another approach to the ClO band strength problem was reported by Burkholder et al. (15). Their method does not require any concentration measurements, but an accurate determination of relative infrared line intensities at high J values is needed. Previous application of this method by Chackerian to the HCl molecule (20) yielded results in good agreement with experimental measurements (36). Chackerian compared relative rovibrational line intensities between the P and R branches of HCl to obtain the first Herman-Wallis coefficient for that molecule. His method used the theoretical expressions of Tipping and Ogilvie (37) for the Herman-Wallis factor and assumed a linear dipole moment function,  $\mu(r)$ , in the vicinity of the equilibrium internuclear separation. The approximation for the vibrational transition dipole in terms of the first Herman-Wallis coefficient,  $\alpha$ , is

$$\mu_{10} = -8 \left(\frac{B_{\rm c}}{\omega_{\rm c}}\right)^{3/2} \left(\frac{M_0}{\alpha_{10}}\right). \tag{14}$$

Here,  $M_0$  is the rotationless transition moment,  $B_e$  is the equilibrium rotational constant, and  $\omega_c$  is the harmonic frequency. When Burkholder et al. applied this treatment to relative rovibrational lines of CIO measured with a tunable diode laser, they obtained  $\alpha = (4.39 \pm 1.23) \times 10^{-3}$  and a band strength of  $17 \pm 9$  cm<sup>-2</sup> atm<sup>-1</sup>. They also obtained a value of  $\alpha = (5.63 \pm 0.47) \times 10^{-3}$  from their FTIR spectrum, which implied a band strength of  $11.3 \pm 2.0$  cm<sup>-2</sup> atm<sup>-1</sup>. From the analysis of the relative rovibrational linestrengths in our FTIR spectra of ClO we report a value of  $\alpha = (4.12)$  $\pm$  0.62)  $\times$  10<sup>-3</sup> which would correspond to a band strength of 21  $\pm$  7 cm<sup>-2</sup> atm<sup>-1</sup> if Eq. (14) is applied separately to each isotope and then the band strengths are totalled. The band strength obtained in this way from our FTIR data is only good to within  $\pm 33\%$  which includes the linestrength error limits. From Eqs. (12), and (14) it can be seen that  $S_v$  is proportional to  $(1/\alpha)^2$ . Thus a small uncertainty in  $\alpha$  has a large effect on  $S_{v}$ . Most of the uncertainty in our value of  $\alpha$  is attributed to the fact that the Herman-Wallis effect in ClO is a very small correction to the rigid rotor approximation. Accurate linestrength measurements for high J transitions are needed to accurately measure the coefficients. Our FTIR measurements extended to J = 35.5in the R branch of the  ${}^{2}\Pi_{3/2}$  -  ${}^{2}\Pi_{3/2}$  band of the main isotope, and to J = 29.5 in the P branch. At these J levels the effect of F on the intensities of the measured lines is  $\leq 15\%$ . A few lines beyond this were recorded but they were too weak to meet our minimum signal-to-noise criterion in the linestrength fitting analysis.

A further weakness in the application of the Herman–Wallis factor to the band strength determination for ClO is the extreme nonlinearity of the dipole moment function near the equilibrium internuclear separation,  $r_e(16, 32)$ . A cubic polynomial in  $(r - r_e)$  can best be used to describe the shape of the asymmetric curve which has a maximum in the vicinity of  $r_e(16)$ . This would invalidate the assumptions made in the derivation of Eq. (14) if the classical turning points in the function are at r values close to the maximum. Therefore, while Eq. (14) proved to be a good approximation for HCl it may not be sufficient to describe molecules such as ClO or OH. A more explicit determination of the fundamental transition moment for the v(1-0) band has recently been done by Yaron *et al.* (16). They measured the electric dipole moments of ClO in the (v = 0) and (v = 1) levels using molecular beam electric resonance. The dipole moments were combined with relative intensity data (15) to give  $\mu = -(3.4 \pm 0.5) \times 10^{-2}$  D which (using Eq. (14) for each isotope) corresponds to a total band strength of 9.8  $\pm 3$  cm<sup>-2</sup> atm<sup>-1</sup> at 296 K.

For molecules with strong infrared absorption features in regions where high Jvalue lines can be measured or for those with stronger rotation-vibration interactions, the method of Burkholder *et al.* and Chackerian may be acceptable for obtaining band strength values without concentration measurements. That type of band strength derivation is useful in at least approximating a band strength for cases where no concentration measurements are available. With the direct concentration measurements described in this paper and knowledge of the dipole moment function as a function of the vibrational state, CIO can now be used as a test case for comparing theoretical approximations for the band strength or transition dipole with experimental measurements.

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