Absolute absorption cross sections at high resolution in the $A^2\Pi_t - X^2\Pi_t$ band system of CIO

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Chlorine monoxide (CIO) has been produced at temperatures near 315 K in a fast-flow system at total pressures (of argon diluent) in the range 1.0–2.0 mm Hg. The transmittance of ultraviolet radiation has been determined with a spectral resolution of 0.0054 nm for all $^{35}\text{ClO}$ $\nu'$=0 $A^2\Pi_{3/2}$ – $X^2\Pi_{3/2}$ sub-band in the range 3 $\leq \nu' \leq 12$ (305.9–274.9 nm). The CIO column density obtained with 8 or 12 traversals of the radiation along an 80 cm cell was in the range 1.0–2.0 $\times 10^{17}$ cm$^{-2}$.

The experimental transmittance profiles for each sub-band have been reproduced closely by synthetic spectrum calculations. The parameters required as input to the programs were optimized by nonlinear least-squares techniques. The fitted (Lorentzian) linewidths are on average more than double those previously reported from visual estimates of linewidths on photographic plates. The fitted band strengths lead to a well-defined electronic transition moment variation for the $A - X$ system of CIO, which is in excellent agreement with an earlier determination by Mandelman and Nicholls from spectra at lower resolution (0.22 nm) with unresolved rotational structure.

On a produit du monoxyde de chlore (CIO), à des températures voisines de 315 K dans un système à écoulement rapide, sous des pressions totales (d’argon diluant) situées dans l’intervalle 1,0–2,0 mm de Hg. La transmittance du rayonnement ultraviolet a été déterminée avec une résolution spectrale de 0.0054 nm pour toutes les sous-bandes $\nu' = 0$ $A^2\Pi_{3/2}$ – $X^2\Pi_{3/2}$ de $^{35}\text{ClO}$, dans l’intervalle $3 \leq \nu' \leq 12$ (305,9–274,9 nm). La densité de la colonne de CIO obtenue avec 8 à 12 traversées du rayonnement dans une cellule de 80 cm allait de 1,0 à 2,0 $\times 10^{17}$ cm$^{-2}$.

Les profils de transmittance obtenus expérimentalement pour chaque sous-bande correspondent étroitement avec les spectres synthétiques calculés. Les paramètres requis pour les programmes de calcul étaient optimisés par des techniques de moindres carrés non linéaires. Les larges de raies (lorentziennes) qu’ont déterminées sont en moyenne plus que deux fois supérieures à celles qui ont été rapportées antérieurement à partir d’estimations visuelles sur des plaques photographiques. Les intensités des bandes donnent pour le système $A - X$ de CIO une variation de moment de transition électronique qui est en excellent accord avec une détermination antérieure effectuée par Mandelman et Nicholls d’après des spectres de résolution moindre (0,22 nm) où la structure rotationnelle n’était pas résolue.

[Traduit par le journal]


Introduction

The first spectroscopic observation of CIO was reported by Pannetier and Gaydon (1) in 1948. These authors observed nineteen red-degraded CIO $A \rightarrow X$ emission bands from a hydrogen–oxygen flame containing small amounts of chlorine. The emission spectrum was due to thermal population of low-lying vibrational levels of the $A$ state, which is the lowest known bound electronic state of CIO. The assignment of the flame bands to CIO was confirmed a few years later by Porter and Wright (2) in the first application of the technique of flash photolysis; the same $A - X$ transition was observed in absorption following photolysis of mixtures of chlorine and oxygen. Subsequently, a large number of investigations concerned with both the positional and the intensity spectroscopy of CIO ($A \leftrightarrow X$) have been performed. In recent years, considerable interest in the $A \leftrightarrow X$ system has arisen owing to the possibility of spectroscopic detection and measurement of CIO concentrations in the stratosphere. Direct chemical analysis, as well as the predictions of chemical and transport models, have indicated that significant steady-state concentrations of CIO exist at stratospheric altitudes, owing at least in part to photolysis of man-made chlorofluoromethanes.

It appears that the most reliable and least equivocal determination of an absolute absorption cross section for the ($A - X$) electronic transition of CIO is still that given by the 1968 publication of Clyne and Coxon (3). These authors performed a careful room-temperature chemical titration of CIO with nitric oxide in a fast-flow system at total pressures near 2 mm Hg. The reported molar decadic extinction coefficient, $\epsilon = 1270$ dm$^3$ mol$^{-1}$ cm$^{-1}$ at $\lambda = 257.7$ nm, gives a cross section ($\sigma$) at this wavelength of $\sigma = 4.86 \times 10^{-18}$ cm$^2$. Since absorption at 257.7 nm occurs in the continuum region of the CIO ($A \leftrightarrow X$) transition, the measured cross section is not subject to error arising from finite instrumental resolution. Clyne and Coxon also obtained an apparent cross section near the head of the 11–0 band, which is the strongest transition in the banded region. In a later publication, Coxon (4) presented an approximate

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deconvolution analysis of the band head data in an attempt to provide reliable calculated absorption cross sections for rotationally-resolved bands at longer wavelengths (3–4, 4–0, and 5–0 bands).

Several investigators using a variety of techniques have subsequently collated absorption data which attempt to establish the wavelength dependence of the absolute cross section (or electronic transition moment) in both the continuum and banded regions. In the earliest of these studies, Johnston et al. (5) employed the molecular modulation method with a spectral slit width of 0.2 nm. Most of the data were obtained in the continuum (λ < 262.8 nm). In a later study, Mandelmann and Nicholls (6) produced CIO in a room-temperature flow system from the rapid reaction of atomic chlorine with ozone. With a similar instrumental resolution (0.22 nm spectral slit width), the data obtained by these authors in the banded region thus included the effect of convolution with a fairly broad slit function. However, using planimetric techniques to obtain integrated band absorptions (which required corrections for overlap), it was possible to obtain absolute oscillator strengths for individual bands. Using Franck–Condon factors based on the revised A state vibrational numbering (7, 8), the radial variation of the CIO (A → X) electronic transition moment was then experimentally determined for the first time. While this was an important advance, the authors stated the need for high resolution data in order to perform a more rigorous analysis. Mandelmann and Nicholls also presented a useful summary of their own (apparent) cross section with those of earlier investigators; all the then available data were normalized to Clyne and Coxon’s (3) continuum cross section at 257.7 nm. Yet another low resolution study was published soon after by Jourdain et al. (9), in this case however, the normalization procedure against Clyne and Coxon’s apparent cross section near the head of the 11–0 band was less satisfactory. On the other hand, Jourdain et al. did take some account of the elevated temperature which were found in flows of CIO radicals; an increase over ambient temperature is expected on account of the exothermicity of the CIO decay reaction.

Two other studies which reported independent estimates of absolute cross sections, not referenced to Clyne and Coxon’s (3) data, are worth noting. In the work of Wine et al. (10), absorbances were obtained in a point-by-point fashion using a tunable narrow-band dye laser. While these are the only data prior to the present work to be obtained from a rotationally resolved spectrum, the measurements were obtained over a very limited range of wavelength which covered just a few lines of the A – X system of CIO. The data indicate that a small increase in transition moment occurs with increasing intermolecular separation, in accord with a quite sophisticated ab initio calculation. Any further data acquisition should be for rotationally-resolved spectra, as described in the present work.

Experimental procedures

Preparation of chlorine dioxide

CIO₂ was prepared in a glass vacuum system using the method of Bray (15). A slurry of 18 g of potassium perchlorate, 60 g of oxalic acid, and 9 mL of distilled water was warmed slowly to 60°C. The gaseous product (CO₂ and CIO₂) was swept rapidly from the reaction chamber with a continuous flow of nitrogen gas. In this way the presence of a high partial pressure of CIO₂ product was precluded, and hence the chance of an explosion minimized. The gaseous mixture was passed through a phosphorous pentoxide drying tower, and then through a dry ice – acetone trap at −78°C. This permitted collection of a fairly pure solid CIO₂ product; the major impurity was water. Small amounts of water are of no consequence in the formation and kinetic behaviour of CIO in our system, and water is optically transparent in the spectral regions of interest. After evacuation of the system, the solid CIO₂ was allowed to vaporize into two 10 L flasks; the yield of CIO₂, as measured on a glass spiral gauge, was typically 70 mm Hg. The gas was stored as a 1:1 mixture with argon diluent, and was not significantly decomposed even after several days.

The flow system

The gas-flow system for production of CIO is depicted schematically in Fig. 1. A 40 mm diameter Pyrex tube of 80 cm length is pumped with a 60 L s⁻¹ pump (Lehboyl Heraeus S60A). At each end of the flow tube, a Brewster window unit is attached via a flange arrangement and O-ring seal. This facility permits removal of the quartz windows for cleaning of interior surfaces, and for coating the walls of the flow tube with 10% phosphoric acid solution. Phosphoric acid effectively tempers the walls of the tube against chlorine atom recombination. Chlorine (Matheson, C.P. grade) mixed with a large excess of argon diluent was admitted to the flow tube via a fine control valve, and the total flow rate of the mixture was regulated to about 1.5 mm Hg at full pumping speed. Total pressures could be measured at either end of the flow tube using a silicone oil manometer. The mixture of chlorine and argon was passed through a 2450 MHz microwave discharge operating at about 0.5 mW and about 100 W. The discharge cavity was located about 10 cm upstream of the flow tube. Small amounts of CIO₂–argon mixtures were added to the discharge products, namely, atomic chlorine and a small amount of undissociated chlorine, immediately prior to entry of the gas flow into the flow tube. Formation of CIO in the rapid reaction

CI + CIO₂ → CIO + ClO₂

was effectively complete before the gas mixture entered the flow tube. The total column density of CIO along the flow tube was typically 2 × 10¹⁴ cm⁻².

Optical arrangement

Continuum radiation (from a 500 W xenon arc lamp, mounted in an air-cooled housing (Oriel 6140) and operated with a stabilized power supply (Oriel 8540) at currents near 28 A, was focused at a point immediately adjacent to the full mirror of a White cell arrangement of concave mirrors. This arrangement of one full and two half-mirrors in a focal length of 1 mm, was mounted external to the flow cell. The more efficient arrangement of an internal mirror assembly was precluded by the highly corrosive nature of the chlorine–oxygen mixtures. The White cell arrangement permitted multiple traversals of the continuum radiation along the length of the absorption cell (flow tube). In most experiments, 5 or 12 traversals were employed. In the initial work, the mirrors were coated with a multilayer dielectric to maximize reflectance at wavelengths near 300 nm. However, in the later work, a simple magnesium fluoride protective coating was
found to be equally satisfactory. The beam of radiation emerging from the multiple traversal system was focussed with a cylindrical lens on the entrance slit (10 mm wide) of a 1.26 m scanning spectrometer (Spectra 269). The spectrometer is equipped in order to measure a 2400
/m line-to-line interferometer which gratin (Jobin-Yvon) and a sensitive detector (RCA C31034A Ge/As photomultiplier) mounted in a radio frequency (RF) shielded, thermoelectrically cooled housing (Products for Research).

A small portion of the beam of radiation undergoing multiple passes above the absorption cell was split off and collected after only three traversals. This sample of the radiation beam was used to monitor the CIO column densities, and was focussed after passing through a narrow band interference filter (Corion, 282.4 nm, 0.7 nm) on the Orte/Te photocathode of a solar-blind photomultiplier (EMI G200311). The CIO column density determination was made by reference to the extinction coefficient reported by Clyne and Coxon (3) at 257.7 nm. A small reliable correction was applied to take into account the difference between the weighted average transmission wavelength and the interference filter (258.4 nm) and the 257.7 nm wavelength used in ref. 3.

Data acquisition

Except in early preliminary work, all data were obtained with the Spectra spectrometer operated under computer control. A block diagram of the computer—spectrometer configuration is shown in Fig. 1. The computer is a Digital MINC-11 laboratory computer with a PDP 11/23 processor and PXO2 dual floppy disc drive, and is equipped with several input—output (I/O) modules—two 16-bit parallel digital input modules, a 16-bit parallel output module, and a 12-bit analog-to—digital (A/D) converter module. All the modules are addressable with FORTRAN subroutines. Instructions are sent to and output is received from an electronic interface card through a serial interface (data rate 9600 b/s) during an experiment. Simple numerical procedures were adopted to transform the raw data to smoothed transmittances

\[ T(l) = \frac{1}{p} \int I(l) \, dl \]

where the parameter \( p \) has a value close to unity and \( I(l) \) are the normalized experimental transmittance vs modulated output of p = 0.97, for example, would indicate \( \frac{I(l)}{I(l)_{\text{opt}}} \) are smaller by 3% than those due to CIO (A \( \times \) X).

Theory

Since the aim of the present work was to infer absolute absorption cross section profiles from the experimental transmittance data, it is appropriate to review briefly the theoretical basis for the procedures we have adopted. The following sections show how an experiment on data which have been corrected for the absorption cross section of a diatomic electronic band system is expected to vary with frequency (or wavelength). Without such a framework for calculation of a cross section profile, it would not be possible to adopt the results of the present work for reliable predictions of CIO transmittances under conditions of temperature and concentration which differ from those of the laboratory work.

Absorption due to a single line

Initially, we consider a beam of radiation of intensity \( I_0 \) incident on a cell containing molecular absorbers. Denoting the concentration of CIO molecules in the cell by \( N \), the absorption coefficient \( \kappa \) and its frequency derivative \( \kappa' \) by \( \omega \), then

\[ I(l, \omega) = \exp (-\kappa(l) \omega \omega) \]

where \( I(l) \) is the intensity of transmitted radiation, and \( B_1 \) is the Einstein coefficient of induced absorption for the \( J = 1 \) transition. \( B_1 \) is given by

\[ B_1 = \left( \frac{8\pi}{3} \hbar c^2 \right) \sum_{\Omega} |P_{\Omega+1/2}|^2 / \Delta \]

and where, for electric dipole transitions, \( P_{\Omega+1/2} \) are the matrix elements of the electric dipole moment. The summation in [4] is over all degenerate components \( n \) and \( m \) of the lower and upper states. Equation [3] can be put in the form

\[ I(l, \omega) = \exp (-\tau(l) N \omega) \]

where \( N \) is the column density of absorbers (in all levels, not just the \( J = 1 \) level) and \( \tau(l) \), the absorption cross section, is given by

\[ \tau(l) = B_1 \omega \omega(l) / \sqrt{f(l)} \]

\( f(l) \) being the fraction of absorbers in the \( J = 1 \) level. Equation [5] suffices to define a transmittance in the case that the incident radiation has a constant intensity for a frequency interval about \( \omega_0 \) sufficient to cover the whole linewidth. However, in the case that transmittances are determined with a scanning spectrometer, exactly the opposite pertains; the intensity of incident radiation varies strongly (according to the instrumental slit function) within the absorption linewidth. It is then appropriate to take explicit account of the variation of cross section with frequency,

\[ \sigma_\omega(l, \omega) = \sigma_\omega(l) \omega_\omega(l) \]

where \( \omega_\omega(l) \) is the lineshape function which is normalized such that the integral over all frequencies is

\[ \int \sigma_\omega(l, \omega) \, d\omega = \omega_\omega(l) \]

When line broadening is due principally to predissociation in the excited state, as occurs for the \( A \times X \) band system of CIO, a Lorentzian function is appropriate. Accordingly, in this work, the lineshape function is given by

\[ \sigma_\omega(l, \omega) = \omega_\omega(l) / (1 + \omega^2 / \omega_\omega(l)^2) \]


\[ \sigma(v, T) = \sum \frac{a_v}{R_{\text{v}, r}^3} \rho_{v, r} \rho_{v', r'} \left( \frac{L(2J' + 1)}{Q(T)} \right) \]

where \( \rho_{v, r} \) and \( \rho_{v', r'} \) are the transition moments squared of \( v \) and \( v' \), respectively, and \( Q(T) \) is the partition function.

Finally, the transition moments squared can be resolved into electronic, vibrational, and rotational factors, and absorption cross section can be calculated for given experimental conditions; in [14], the parameters \( \rho_{v, r} \) are defined in terms of the band strength \( (\tau_{v, r}) \) by

\[ \rho_{v, r} = \nu_{v, r} \tau_{v, r} / \Pi_{v, r} \]

where \( \tau_{v, r} = (8r^3/3h\epsilon_d) \Pi_{v, r} \nu_{v, r} \) and \( \Pi_{v, r} \) are the rotational and vibrational transition moments, and constant band origins \( (\nu_{v, r}) \) are employed as an effective value of \( v \) over the small frequency ranges of each band.

**Synthetic absorption spectra**

In the previous section, it has been shown that [14] provides a prescription with which an absorption cross section profile for a banded molecular transition can be computed from a knowledge of the line positions, rotational line strengths, Franck-Condon factors, lineshape functions, electronic transition moments, and constant band origins. We now consider the use of [14] for the A'-X' system of CIO, and show how the theoretical cross sections can be employed in synthetic spectrum calculations.
v' = 0 and v' = 1 progressions of 12ClO (A = X) have been published by Coxon (4). Although the ν-chords have negligible (≤0.03%) isotope dependence, the Franck–Condon factors for 32ClO and 31ClO differ significantly. The Franck–Condon factors for 32ClO were calculated in the present work using the same methods and potentials as in ref. 2.

For the rotational line strengths (Sν), a Hund’s case (a) values as given by Kovač (20) for P, Q, and R branches were employed. The expressions

\[ S(ν) = \left( J^2 - \Omega^2 \right) / J \]

\[ S(ν) = \Omega(2J + 1)/\left(J(J + 1)\right) \]

are accurate to within 0.2% even at the highest J values (Jmax = 50).

Synthetic spectra

Two Fourier programs have been developed for the calculation of absorption cross sections and transmissions. The first program calculates the cross sections \( σ(ν, T) \) at an equally spaced set of points \( ν_{i} = ν_{1} \) in a frequency range \( cm^{-1} \), \( ν < ν < ν_{i} \) according to [4]. The step-size between the points \( ν_{j} \) was chosen as 0.20 cm⁻¹. The program calculates the contributions from all lines in the extended range \( ν_{i} ≤ ν < ν_{i+1} \). A contribution from the "tails" of lines outside the range of interest are ignored probably. The extension by 100 cm⁻¹ was known to be adequate since use of larger extensions led to changes in \( σ(ν, T) \) at all points which were less than 0.5%; the resulting transmitted intensities are then invariant to within 0.1%, well within the experimental uncertainty. In order to optimize run times, the contributions from each line are restricted to the frequency range to a multiple of linewidths between 2 and 25; for the most intense lines, 25 linewidths are used; for the weakest, 2 linewidths. In addition to the frequency range and step-size, data which must be provided are (i) temperature, \( T \); (ii) the linewidths of Lorentzian, linewidths \( (ν_{o}) \) arumed to have no J dependence and no Ω dependence (except where photographic estimates (11) of different linewidths for the two Ω components were available), (iii) the array of Franck–Condon factors \( 2ν_{o} \) for (v, ν = 0) and (iv), a set of parameters \( \nu_{o}, ν_{e}, ν_{e}' \), given in [16].

\[ \nu = 8.2232 - 40.32ν_{e}' (nm) \]

as a linear approximant for the variation of \( R_{i}^{2} \) in the range \( 0.160 ≤ ν ≤ 0.1725 nm \). Equation [23] was derived by fitting a subset of the ab initio results of Arnald et al. (13).

The second program calculates the transmittance \( (I_{i}/I_{o}) \) at an equally spaced set of points \( (ν_{i}) \) in a region of wavelength, \( \lambda_{1} ≤ λ ≤ λ_{2} \). At each point \( i \), the transmittance is found from

\[ \frac{I_{i}}{I_{o}} = \exp \left[ -σ(ν)ν(ν') \right] \]

where \( J(ν, ν') \) is a function describing the frequency variation of the incident radiation centred at \( ν_{i} \) and integration is performed over all frequencies where \( J(ν, ν') \) is nonzero. Although the program permits calculation of absorbances for a column density which might vary (with frequency), in most calculations \( N(ν') \) was held constant. A "triangular slit function" has been adopted for \( J(ν, ν') \); denoting the width of this function at half-height by \( \lambda_{ν} \), [24] reduces at constant column density to

\[ \frac{I_{i}}{I_{o}} = \left( 1 + \frac{ν}{ν_{e}} \right) \exp \left[ -σ(ν)ν(ν') \right] \]

The value of \( \Delta ν \) was estimated by recording atomic emission lines of mercury from a low pressure discharge lamp under constant conditions (similar slit width, slit illumination) to those of the CO₂ absorbance experiments. Since the mercury linewidths are much less than the instrumental width, it was an excellent approximation to equate \( \Delta ν \) with the width at half-height of such emission lines. \( \Delta ν \) was typically 0.0054 nm, which is much less than the presociated linewidths of \( CO₂ = (0.05 nm) \), and compatible with the spectral slit width of 0.04 nm calculated for the 10 cm slit widths employed. Any error in \( \Delta ν \) is thus of little consequence.

The integrals of [25] were performed numerically using Simpson’s rule where \( σ(ν) \) is supplied to the program as a vector of points at equally spaced frequencies. Intermediate points used in the integration are found using a 4th order Lagrangian polynomial interpolation scheme.

Results

The experimental data described in this section are concerned with the specific wavelength ranges of each \( ν' = 0 \) sub-band of \( ν' = 1 \) sub-band of \( 32ClO \) in the range \( 3 ≤ ν' ≤ 12 \). A summary of the data is given in Table 1.

For the bands at short wavelengths \( (∣ν' > 6) \) the final results are for single experiments on a particular sub-band. For \( ν' = 6 \), however, the results of two or more independent experiments or sets of experiments are considered. The 3–0 band posed the greatest experimental difficulties. In this case, absorption is the least of any of the sub-bands, so that noise caused by lamp instability was particularly troublesome. Of the many experiments performed for the 3–0 band, Table 1 shows that we have used the averaged data of just three selected experiments in the final analysis.

Data analysis

The raw data (transmitted intensities \( I_{i} \), at equally spaced spectrometer wavelengths) are initially input to a computer program which (i) smooths the data, (ii) subtracts an estimated background of continuous absorption, and (iii) calculates transmittances (\( I_{i}/I_{o} \)) for a CIO column density of \( 2.00 × 10^{-17} cm^{-2} \) from least-squares profiles of \( I_{o} \) and [ClO]. The subsequent part of the analysis is a nonlinear least-squares fit of the normalized transmittances to the model described in previous sections. This nonlinear least-squares fit of the theoretical or synthetic absorption spectrum – can be calculated in terms of at most six adjustable parameters, which are to be optimized to obtain the best agreement, in the least-squares sense, with the experimental spectrum. The six parameters are (i) temperature, \( T \), (ii) linewidth \( (ν_{o}) \), of the \( 32ClO \) \( Σ_{π',π} ν' = 0 \) sub-band being considered, (iii) the parameter \( ν_{e}' \), defined by [15], of the same sub-band, (iv) the parameter \( ν_{e} \) used in [2] to take account of absorption as compared with the air wavelengths of the experimental data, the step-size, or the wavelength interval, between the individual points of the calculated spectrum. The last four parameters represent, in effect, an internal wavelength calibration provided by the ClO spectrum itself. Owing to such effects as the imperfection of the sine-bar drive mechanism of the spectrometer grating drive, and the use of vacuum wavelengths in the calculated spectra, as compared with the air wavelengths of the experimental data, the step-size which gives optimum agreement with experiment is not exactly the nominal 0.003 nm value which is used to increment the spectrometer parameter vector.

An important point on the fitting procedure which requires emphasis is that the initial synthetic spectrum

\[ \begin{array}{cccc}
\text{Exp.} & ν' & \text{ν} & \text{Expt.} & \text{ν} & \text{ν} & \text{Expt.} & \text{ν} & \text{ν} \\
\text{ν} & \text{ν} & \text{ν} & \text{ν} & \text{ν} & \text{ν} & \text{ν} & \text{ν} & \text{ν} \\
1 & 3 & 0 & 5.66 & 309 & 0.969 & 2.433 & 3 & 4 & 0.095(1) & 312(2) & 0.956(1) & 2.572(6) & 3 & 4 & 0 & 4.09 & 323 & 0.958 & 2.531 & 5 & 5 & 6.00(10) & 315(2) & 0.959(1) & 2.642(5) & 5 & 5 & 5.99 & 0.970 & 2.542 & 6 & 6 & 10.00 & 321(3) & 0.993(3) & 3.057(9) & 6 & 6 & 10.00 & 315 & 0.949 & 2.822 & 7 & 7 & 5.21(17) & 314(4) & 0.927(3) & 2.771(15) & 7 & 7 & 5.21(17) & 314(4) & 0.927(3) & 2.771(15) & 9 & 9 & 0 & 4.76(8) & 321(3) & 1.010(7) & 3.036(12) & 9 & 9 & 0 & 4.76(8) & 321(3) & 1.010(7) & 3.036(12) & 10 & 9 & 9 & 5.15(8) & 324(3) & 1.014(6) & 3.104(9) & 11 & 10 & 5.63 & 307 & 0.977 & 3.146 & 12 & 11 & 3.58 & 315 & 0.956 & 3.014 & 13 & 12 & 3.75 & 322 & 0.974 & 3.096
\end{array} \]
Discussions

The present work represents the first comprehensive study of rotationally resolved absorption intensity in the $A^3\Pi \rightarrow X^3\Pi$ system of CIO. It has been shown that experimental transmission profiles can be reproduced very closely by calculated spectra after optimization of just a few adjustable parameters. Values of these parameters from a nonlinear least-squares procedure are listed in Table 2, together with estimated standard deviations for some of the bands studied. An immediate observation is that the fitted temperatures for individual bands are statistically well determined and show little variation from band to band, as is necessary and expected. In all cases, the fitted temperatures lie in the range 307–324 K; the mean value is 315 K. This higher than room-temperature result is in accord with the
directly measured temperatures reported by Jourdain et al. (9) for flows of ClO at concentrations very similar to those of the present work. Jourdain et al. found a maximum temperature of 351 K in the first centimeter of their cell; this was followed by a decay to room temperature in the next 15 cm. The initially large temperature is due to the (small) exothermicity of the rapid Cl + ClO reaction used to produce ClO. The slow decline to room temperature would be expected with the relatively large exothermicity of the ClO decay reaction. Although it is not strictly correct to adopt an effective single temperature for an ensemble of molecules at different local Boltzmann temperatures, the error in such an approximation is quite unimportant for the relatively small temperature differentials in the present work.

The parameter $p$ of Table 2, defined in [2], takes account of the presence of any background continuum absorption on which the individual $v^{'0}$ ClO ($A^{'0}X$) sub-bands might be superposed. This allowance for background absorption in the fitting procedure was introduced during the preliminary work on the $A^{'0}X$ and $A^{'0}X$ bands. It was found that agreement between calculated and experimental spectra without the background correction were quite unsatisfactory. It was reasoned that absorption due to molecular chlorine could be responsible for the observed effect. An increase in the concentration of molecular chlorine, over that which remains in the discharge products before addition of ClO, can be expected under certain conditions from the ClO decay reaction; an increase in [Cl$_2$] would not necessarily be reproducible, owing to variation, from one experiment to the next, in the efficiency of heterogeneous chlorine atom recombination on the flow tube wall. The absorption coefficient for the continuum ultraviolet (UV) system of Cl$_2$ has a maximum value near 30,000 cm$^{-1}$ (21). For the longest wavelengths of the present work (the 3$^0$ 0 band), $\epsilon$ (Cl$_2$) at room temperature is about 35 dm$^3$ mol$^{-1}$ cm$^{-1}$, whereas for the shortest wavelengths (the 12$^0$ 0 band at $\sim$36,500 cm$^{-1}$), $\epsilon$ (Cl$_2$) is only about 5 dm$^3$ mol$^{-1}$ cm$^{-1}$. An absorption of 4% as suggested by Table 2 for the longer wavelength bands would correspond to a Cl$_2$ column density of 2.3 x 10$^7$ cm$^{-2}$, very similar to ClO column densities which are observed after appreciable decay has occurred. It is not unreasonable, therefore, to expect a small percentage continuum absorption due to Cl$_2$ formation for the longer wavelength bands. For the bands in the midrange (7$^0$ 0, 8$^0$ 0, 9$^0$ 0), the values of $p$ are essentially unity; it would be necessary to assume that the experimental conditions for these bands were such that the flow tube wall had become sufficiently poisoned against atomic recombination. For the highest $v^{'0}$ bands, $p$ values are again significantly less than unity. In other preliminary

![Fig. 8. Radial dependence of the electronic transition moment squared in the A^1PI-X^1PI system of ClO](image)

![Fig. 9. Wavelength dependence of the absolute absorption cross section of the 2-0, $\Omega$ = 3/2 sub-band of ClO (A-X).](image)

![Fig. 10. Wavelength dependence of the absolute absorption cross section of the 3-0, $\Omega$ = 3/2 sub-band of ClO (A-X).](image)

![Fig. 11. Wavelength dependence of the absolute absorption cross section of the 4-0, $\Omega$ = 3/2 sub-band of ClO (A-X).](image)

![Fig. 12. Wavelength dependence of the absolute absorption cross section of the 5-0, $\Omega$ = 3/2 sub-band of ClO (A-X).](image)

from the fitted $\rho_{v^0}$ values. The $R_2^v(r)$ values are plotted in Fig. 8 as a function of $r$-centroid ($R_{v^0}$); also shown are experimental and theoretical values found by other workers. The excellent agreement of our results with those of Mandelman and Nicholls (6), not only in terms of the absolute magnitude of $R^2_r$, but also the variation with $r$-centroid, is particularly impressive. Our values are systematically larger by only 8%, which is within the approximately 5% error limits expected in the two experiments. The $R^2_v$ values in both experiments are direct determinations, and both depend on the same calibration of absolute [ClO]. With $R_v$ assumed to be linear, our data are represented by $R_v(r) = 1.19 - 14.4(r - r^*)$, where $R_v(r)$ is in atomic units, and $r^*$ is the ground state equilibrium bond length (in nm). Our results are perhaps to be preferred owing to the probability of underestimated corrections for band overlap in the spectroscopic method of ref. 6. The direct determinations of $R_v^2$ are systematically smaller than those found by Cooper (12) from a shock tube experiment. The latter work assumes that all emission is due to ClO, and that [ClO] can be calculated accurately from the shock tube parameters. The agreement of the results of ref. 12 with the sophisticated ab initio calculations of Arnold et al. (13) appears fortuitous. The reliability of the ab initio calculation is difficult to assess, but is unlikely to be better than 20-30%. In fact, the general agreement of the ab initio results with all the experimental data is a testimony to the quality of modern ab initio calculations.

We conclude this discussion with a presentation of
calculated cross section profiles for the $v' = 0$ sub-bands with $2 \leq v' \leq 5$ (Figs. 9–12). These bands are of special interest in terms of the possibility of spectrometric detection of CIO in the stratosphere. The cross section profiles are given at both 300 and 220 K. The linewidths of Table 2 and smoothed $R^2$ of Fig. 8 are used. For $v' = 2$, we assume a Lorentzian linewidth of $\delta_2 = 3.90 \text{ cm}^{-1}$, which is 2.3 times the value estimated by Coxon and Ramsay (11).

With the cross section profiles of Figs. 9–12, it is straightforward to calculate the transmittance spectra expected for stratospheric conditions. For a CIO column density of $N' = 10^{15} \text{ cm}^{-2}$, for example, transmittances of 99.92, 99.85, 99.70, and 99.50% would be expected near the heads of the $\Omega = 3/2$ $v' = 0$ sub-bands with $v' = 2$, 3, 4, and 5 respectively. Rotational structure would be clearly discernable for a spectral slit width of 0.02 nm, but would not be resolved for a larger width of 0.15 nm.

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