The UV absorption of ClO
Part 1. The $^2I^g-^2I^u$ spectrum at wavelengths from 285–320 nm studied by cavity ring-down spectroscopy

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The UV absorption of ClO at wavelengths between 285 and 320 nm has been investigated using cavity ring-down spectroscopy. This wavelength region spans the (0,0) to (7,0) bands of the $^2I^g_3/2-X^2I^u_3/2$ transition. The previously unobserved $^2I^g_3/2-X^2I^u_3/2$ (0,0) and (1,0) absorption bands have been recorded with rotational resolution, and spectra of the (2,0) to (6,0) bands of the $^2I^g_1/2-X^2I^u_1/2$ transition are shown for the first time. Analysis of the spectra gives refined band origins and rotational constants for the $^2I^g$ $v'$ levels and reveals a strong $v'$ dependence in the linewidths of rotational features. The lifetimes of the $^2I^g_3/2$ $v'$ = 0–2 and $^2I^g_1/2$ $v'$ = 2–4 levels are revised from previous estimates, and the lifetimes of $^2I^g_1/2$ $v'$ = 5 and 6 levels have been determined. The deduced predissociation rates for $^2I^g_3/2$ $v'$ = 3–7 confirm earlier studies. The lifetimes of vibrational levels of the two spin–orbit components of the $^2I^g_0$ state are markedly different. No evidence of $J$-dependence in the predissociation is found, in contrast to the corresponding $^2I^g_1/2$ state of the IO radical.

1. Introduction

The chlorine monoxide radical, ClO, was first identified spectroscopically from emission bands in a chlorine-enriched flame, and, in an early demonstration of the flash photolysis technique, Norrish and Porter reported the first UV absorption spectrum of ClO. The enormous significance of the ClO radical became apparent with the realisation that stratospheric chlorine atoms were a more efficient contributor to the destruction of stratospheric ozone than nitric oxide. Molina and Rowland subsequently demonstrated that production of chlorine from stratospheric photolysis of chlorofluorocarbons (CFCs) is a serious global environmental hazard. Ozone reacts with chlorine to produce ClO via:

$$\text{O}_2 + \text{Cl} \rightarrow \text{ClO} + \text{O}_2$$

and thus a knowledge of the properties, concentrations, photochemistry and reactions of ClO is crucial to an understanding of atmospheric chemistry. The chlorine catalysed destruction of ozone centres on reaction (1) followed by a second reaction to release the chlorine atom for further chemical processing. ClO is fairly unreactive towards other major atmospheric constituents and its principal route for chemical destruction is by reaction with other radicals such as oxygen atoms and NO, the concentrations of which vary strongly with altitude.

The tropospheric chemistry of chlorine compounds differs greatly from that in the stratosphere. Although CFCs are tropospherically inert, there are many natural and man-made halogen compounds that are more labile. It is now strongly believed that chlorine (in a variety of forms) is a major contributor to the oxidation of chemical species in the marine troposphere. A study by Spicer et al. concluded that concentrations of chlorine molecules were close to a hundred times higher than suggested by chemical models, and thus cannot be explained by known reactions of chlorine species. An understanding of the photochemistry of all chlorine containing molecules at wavelengths longer than 290 nm, corresponding to tropospheric wavelengths, is thus required, and photochemical production of ClO has been proposed as a possible new source to account for the deficit of chlorine species in existing models.

The best simulations of marine boundary layer tropospheric chemistry suggest the presence of high mixing ratios of ClO. ClO absorbs weakly at tropospheric wavelengths via the $^2I^g_0-X^2I^u_0$ ($\Omega = 1/2$ or $3/2$) transition. This absorption shows a long vibrational progression in the UV, but the (0,0) and (1,0) absorption bands have never been observed with rotational resolution because of the rapid fall of the absorption cross-section from a maximum at $\lambda \sim 275$ nm as the wavelength increases. Transitions in the $^2I^g_3/2-X^2I^u_3/2$ system are even weaker than for the $^2I^g_1/2-X^2I^u_1/2$ transition because the $X^2I^u_3/2$ component lies $320$ cm$^{-1}$ above the $X^2I^u_1/2$ state and thus the $v'=0$, $X^2I^u_3/2$ population is $\sim 21\%$ that of the corresponding level in the $X^2I^u_3/2$ component at 298 K. Consequently, there is a lack of information concerning the lifetimes of ClO radicals excited into the lowest vibrational levels of both components of the $^2I^g_0$ state, yet absorption to these levels coincides with the rapid rise in tropospheric solar actinic flux at wavelengths from 290–320 nm.

Following the first tentative assignment of the ClO $^2I^g_3/2-X^2I^u_3/2$ transition from flame emission, investigations identified nineteen vibrational bands in emission, but with an uncertain vibrational assignment (the bands are now known to involve transitions to $\nu''=4$ to $\nu''=14$ levels of the ground electronic state). The proposed labelling of the vibrational bands was in error by one quantum of $v'$, and this error was propagated through the literature until corrected by Coxon.

With the advent of flash photolysis, the absorption of ClO radicals could be recorded with a consequent reduction in spectral congestion compared to flame emission studies. Porter obtained spectra of the (3,0) to (22,0) bands of the $^2I^g_1/2-X^2I^u_1/2$ transition, but the spectral resolution was insufficient to allow analysis of the rotational structure. The
A$^{1}\Pi_{1/2}$ dissociation limit was estimated and the A$^{2}\Pi_{1/2}$ state vibrational levels were shown to converge to a limit corresponding to formation of electronically excited atomic oxygen atoms together with Cl($^3P$) atoms. This conclusion was confirmed by higher resolution studies that revealed predissociation of the vibrational bands.\textsuperscript{12} Durie and Ramsay\textsuperscript{13} reported a rotational analysis of the CIO A$^{1}\Pi_{1/2}$ - X$^{1}\Pi_{1/2}$ (4,0) to (24,0) vibrational bands, with the exception of the very diffuse (6,0) and (7,0) bands. The (4,0) to (12,0) bands of the A$^{1}\Pi_{1/2}$ - X$^{1}\Pi_{1/2}$ transition were also observed,\textsuperscript{1,3} but without rotational analysis. Both the A$^{1}\Pi_{1/2}$ and A$^{2}\Pi_{1/2}$ components were demonstrated to correlate asymptotically with Cl($^3P_{1/2}$) and O($^3D_{3/2}$) atomic products.\textsuperscript{13} Analysis of a combination of absorption\textsuperscript{14} and emission\textsuperscript{15} data produced a refined set of rotational and vibrational constants for the X$^{3}P^{o}$ and A$^{3}P^{o}$ states of CIO. The absorption study was the first attempt to quantify the linewidths of the rotational structure in the vibrational bands, though the difficulties in measuring linewidths, and hence lifetimes, from photographic plate spectra led to later re-investigations. The (2,0) to (25,0) bands of the A$^{1}\Pi_{1/2}$ - X$^{1}\Pi_{1/2}$ transition were recorded, but the (2,0) band was far too weak for a proper analysis of linewidths and rotational structure. The (7,0) band was fully characterised for the first time.\textsuperscript{14} These two studies provided a superior estimate of the dissociation limit of 38051 $\pm$ 3 cm$^{-1}$ (defined relative to $v'$ = 0 of the X$^{3}\Pi_{3/2}$ state), suggesting that $v'$ = 25 was the highest bound level of the A$^{2}\Pi_{1/2}$ state. Rotational linewidths were generally too broad at low $v'$ to study either A-doubling or the two main distinct isotopeomers, 35ClO and 37ClO, separately. The emission study enabled an estimate of the linewidths (1.0 - 1.4 cm$^{-1}$) and hence lifetimes of rotational levels of $v'$ = 0, and suggested that predissociation dominated the depopulation of this vibrational level.

Franck-Condon factors and r-centroids were calculated for 35ClO and 37ClO transition bands with $v'$ = 0-2 and $v''$ = 0-23, and absorption cross-sections were derived from the combined absorption and emission studies.\textsuperscript{16} A previously unreported linewidth of 1.7 cm$^{-1}$ was used for the rotational features of the (2,0) band, and the rotational linewidth for the (1,0) band was estimated as $>7$ cm$^{-1}$. In the first laser measurements of CIO spectra, Wine et al.\textsuperscript{17} determined the absorbances of rotational lines of the (9,0) band and found them to be incompatible with previously calculated absorption cross-sections, suggesting that existing linewidth estimates\textsuperscript{18} were too low by a factor of nearly two. Re-measurements of the (3,0) to (12,0) bands confirmed these suspicions,\textsuperscript{18} and the most recent investigation of linewidths in the A$^{1}\Pi_{1/2}$ - X$^{1}\Pi_{1/2}$ (7,0) to (23,0) vibrational bands\textsuperscript{19} agrees with the revised measurements for the (7,0) to (12,0) bands.

Only two studies to date have addressed the rotational analysis of vibrational bands of the A$^{1}\Pi_{1/2}$ - X$^{1}\Pi_{1/2}$ transition.\textsuperscript{14,15} Rotational constants were derived from the (2,0), (3,0), (4,0), (9,1), (2,1) and (2,2) bands in absorption and the (0,5) and (0,6) bands in emission, but linewidth data were presented for just the (2,1), (3,0), (4,0) and (9,0) bands. All these bands displayed considerably narrower linewidths than the corresponding bands in the A$^{2}\Pi_{1/2}$ - X$^{2}\Pi_{1/2}$ system, but the results must be regarded with caution since the spectra were recorded using photographic plates.

As a consequence of the weak CIO absorption at $\lambda > 305$ nm, all previous studies have failed to resolve clearly the absorption bands to longer wavelength than the (2,0) band: the Franck-Condon factor for the (2,0) band was estimated to be $\sim$ 20 times larger than that for the (0,0) band.\textsuperscript{19} CIO in the A$^{1}\Pi_{1/2}$ state is known to suffer predissociation in all levels from $v' = 3$ to the dissociation limit, but the lifetimes of the vibrational levels are strongly $v'$ dependent. Comparison with the IO radical in the A$^{1}\Pi_{1/2}$ state is instructive: here the lifetimes of the vibrational levels up to $v' = 5$ vary by nearly two orders of magnitude, with $v' = 2$ the longest lived.\textsuperscript{20} Thus, the lifetimes of the $v' = 0$ and $v' = 1$ levels of the A$^{1}\Pi_{1/2}$ state of CIO cannot confidently be extrapolated from measurements of the lifetimes of the higher $v'$ bands in the absence of detailed knowledge of the predissociation mechanism, and lifetimes of A$^{1}\Pi_{1/2}$ $v'$ levels also remain uncertain.

To resolve outstanding questions concerning the predissociation of the low $v'$ levels of the A$^{2}\Pi_{1/2}$ state, we have applied the method of cavity ring-down spectroscopy (CRDS),\textsuperscript{21,22} an ultrasensitive laser absorption technique, to measure high-resolution absorption spectra of the lowest vibrational bands of the A$^{1}\Pi_{1/2}$ - X$^{1}\Pi_{1/2}$ and A$^{1}\Pi_{1/2}$ - X$^{2}\Pi_{1/2}$ transitions. The work presented here concentrates on measurements of the lifetimes of CIO subsequent to photoexcitation via bands lying at wavelengths greater than 285 nm. This paper is arranged as follows: in Section 2 we describe the CRDS experiment used in this study, then absorption spectra and data analysis are presented in Section 3. In Section 4, comparison is made with previous studies and the Rydberg-Klein-Rees (RKR) procedure is applied to determine the A$^{1}\Pi_{1/2}$ potential energy curve. A detailed theoretical interpretation of the results of this and previous studies is given in the companion paper.\textsuperscript{24}

2. Experimental

The cavity ring-down apparatus used in our experiments has been described in detail previously\textsuperscript{25} and only the details relevant to CIO measurements will be given here. The output of a Nd: YAG (Quantel YG680) pumped dye laser (Spectra Physics PDL-3) was frequency doubled in a KDP crystal to generate wavelengths between 285 and 320 nm. The UV radiation pulses, of energy 1 - 2 mJ, were injected into a 1.5 m long glass vacuum tube through one of a pair of high reflectivity mirrors that form the ring-down cavity. The output ring-down signal, with a 1/e time of $\sim$ 7 ms for an evacuated cavity, was detected by a photomultiplier tube. Two sets of high-reflectivity mirrors with maximum reflectivity at centre wavelengths of 290 nm (Virgo Lightning Optical Corp.) and 325 nm (Research ElectroOptics) were used to record CRD spectra of CIO.

The ring-down cavity was combined with a gas flow system for the production of CIO radicals. Chlorine atoms were formed by passing a 5% mixture of Cl$_2$ in Ar through a microwave discharge and subsequent reaction with a flow of 2% O$_3$ in O$_2$ produced CIO, with secondary production of OCIO enhanced at large ratios of O$_3$ to Cl$_2$. Typical operating pressures in the flow system were 100 mTorr of the 2% O$_3$ in O$_2$ and 200 mTorr of the 5% Cl$_2$ in Ar. Both ozone and chlorine absorb over the wavelength range of the experiments: at the short wavelength end, the absorption cross-section for ozone is comparable with that of CIO and is about an order of magnitude higher than that for Cl$_2$. At longer wavelengths there is increasing Cl$_2$ absorption but decreasing ozone and chlorine absorb over the wavelength range of the experiments: for the dye laser fundamental was obtained by a KDP crystal, was directly proportional to the absorption coefficient length of the ring-down rate coefficient (which is directly proportional to the absorption coefficient). Wavelength calibration of the dye-laser fundamental was obtained by simultaneously recording an I$_2$ laser induced fluorescence (LIF) spectrum.

3. Results

CRD spectra of the CIO A$^{1}\Pi_{1/2}$ - X$^{1}\Pi_{1/2}$ transition were recorded over the range 31200 to 34800 cm$^{-1}$. The bands corre-
spond to excitation from the $v' = 0$ level of the $X^2\Pi_{3/2}$ component of the ground state to $v' = 0$–7 of the $A^2\Pi_{3/2}$ state, and from the $v' = 0$ level of the $X^2\Pi_{1/2}$ component to $v' = 2$–6 of the $A^2\Pi_{1/2}$ state. In addition, several hot bands were also observed. Sample experimental spectra are shown in Figs. 1–5. As a consequence of predissociation of both $\Omega$ components of the $A^2\Pi_{1/2}$ state, the bands exhibit a wide range of spectral linewidths and varying degrees of resolved rotational structure.

The rotational structure within vibrational bands was modelled in a Hund’s case (a) basis using the diatomic simulation program PGOPHER and allowed for both $^{35}\text{ClO}$ and $^{37}\text{ClO}$ absorptions in their appropriate natural abundances. Simulations used an $N^2$ Hamiltonian (the full form of which is given in ref. 26) and a rotational temperature of 300 K. The ground state constants $B_\nu$, $D_\nu$, and $T_\nu$ for $v' = 0$ and $v' = 1$ were taken from Maki et al.$^{27}$ while $X^2\Pi$ state $A$-doubling constants and spin-orbit-splitting constants were taken from Coxon.$^{28}$ Spectral analysis involved floating the upper-state constants $B_\nu$, $D_\nu$, and $T_\nu$ in a least-squares fitting procedure in order to reproduce the measured line positions, or, in the case of partially unresolved structure, the band contours. $A^2\Pi$ state spin–orbit constants ($A_\nu$) were only derived for vibrational levels in which both $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$ components were analysed, i.e., for $v' = 2$–6. For the ground state spin-

![Fig. 1](image1.png)

**Fig. 1** CRD spectra of the ClO $A^2\Pi_{3/2}$–$X^2\Pi_{3/2}$ absorption bands (a) $(0,0)$ and (b) $(1,0)$. For each spectrum, the lower trace is the experimental recording and the upper trace is a simulation performed using the method described in the text. In (b) the simulation includes partial overlap with the $(3,1)$ hot band (which also overlaps and masks the $(1,0)$ band). Combs above the spectra indicate the rotational assignments of the spectral lines for $^{35}\text{ClO}$. The position of the $R$-branch bandhead for $^{37}\text{ClO}$ is also indicated. In this and subsequent figures, the $T = 300$ K simulations include a Gaussian line-shape component of FWHM 0.08 cm$^{-1}$ (laser linewidth). In addition, line-shapes contain a Lorentzian component of FWHM (a) 1.2 cm$^{-1}$ and (b) 2.65 cm$^{-1}$. The spectrum in (a) is partially overlapped by an OCIO absorption (see text) which causes apparent differences between the simulated and experimental spectral intensities in the vicinity of the bandhead.

![Fig. 2](image2.png)

**Fig. 2** CRD spectra and simulations of the $(0,0)$ absorption band for the (a) $A^2\Pi_{3/2}$–$X^2\Pi_{3/2}$ and (b) $A^2\Pi_{1/2}$–$X^2\Pi_{1/2}$ transitions in ClO. In (a) the simulation includes the overlapping $(4,1)$ hot band. The simulations include a Lorentzian component of FWHM (a) 2.7 cm$^{-1}$ and (b) 0.85 cm$^{-1}$. These spectra clearly demonstrate a marked dependence of the lifetime on the spin–orbit component of the $A^2\Pi$ state.

![Fig. 3](image3.png)

**Fig. 3** CRD spectra and simulations of the $(3,0)$ absorption band for the (a) $A^2\Pi_{3/2}$–$X^2\Pi_{3/2}$ and (b) $A^2\Pi_{1/2}$–$X^2\Pi_{1/2}$ transitions in ClO. In (a) the simulation includes the overlapping $(4,0)$ hot band. The simulations include a Lorentzian component of FWHM (a) 5.45 cm$^{-1}$ and (b) 2.65 cm$^{-1}$. In this and subsequent figures, combs of rotational line assignments are not given since the structures of the bands are very similar to those in Figs. 1 and 2.

orbit constant, we used \( A_0 - o \) from ref. 28 because \( A_0 \) and the \( A \)-doubling constant, \( o \), are highly correlated parameters. The \( A \)-doubling constants in the \( \Delta \Pi \) state were set to zero since line-broadening prevents the effects of \( A \)-doubling being observed. Table 1 lists the values of the constants derived from this fitting procedure. Rotational constants derived from the fits were found to vary slightly with the choice of linewidth used in the spectral simulation. Errors quoted on the spectroscopic constants thus represent the variation of values of constants derived from fits over the range of spectral linewidths that can reproduce the observed band contours or lineshapes.

Band origins were fitted to determine vibrational parameters. For the \( \Delta \Pi_{1/2} \rightarrow \Delta \Pi_{3/2} \) transition, \( T'_{v} \) values for \( v' = 0 \) to 25 were fitted using data from this study and from a previous spectroscopic investigation.\(^{14}\) A polynomial fit including terms up to \((v' + \frac{1}{2})^3\) was necessary to reproduce the variation of \( T'_{v} \) with \( v' \). For the \( \Delta \Pi_{3/2} \rightarrow \Delta \Pi_{1/2} \) transition, \( T_{v} \)

**Table 1** Spectroscopic constants for the \( \Delta \Pi_{n} \) states of CIO derived from fits to the experimental data as described in the text\(^a\)

<table>
<thead>
<tr>
<th>Band</th>
<th>( T_{v}/\text{cm}^{-1} )</th>
<th>( B_{v}/\text{cm}^{-1} )</th>
<th>( D_{v} \times 10^{9}/\text{cm}^{-1} )</th>
<th>( T'_{v}/\text{cm}^{-1} )</th>
<th>( A_{v}/\text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0)</td>
<td>( \Omega = 1/2 )</td>
<td>31483.79(50)</td>
<td>0.4418(1)</td>
<td>2.64(83)</td>
<td>1.24(2)</td>
</tr>
<tr>
<td>(1,0)</td>
<td>( \Omega = 1/2 )</td>
<td>31987.62(150)</td>
<td>0.4339(1)</td>
<td>0.23(25)</td>
<td>2.65(35)</td>
</tr>
<tr>
<td>(2,0)</td>
<td>( \Omega = 1/2 )</td>
<td>32674.11(150)</td>
<td>0.4303(1)</td>
<td>3.39(83)</td>
<td>0.85(15)</td>
</tr>
<tr>
<td>(3,0)</td>
<td>( \Omega = 1/2 )</td>
<td>32476.48(150)</td>
<td>0.4281(1)</td>
<td>1.30(25)</td>
<td>2.7(2)</td>
</tr>
<tr>
<td>(4,0)</td>
<td>( \Omega = 1/2 )</td>
<td>32949.52(150)</td>
<td>0.4187(1)</td>
<td>0.025(25)</td>
<td>5.45(35)</td>
</tr>
<tr>
<td>(5,0)</td>
<td>( \Omega = 1/2 )</td>
<td>33063.22(150)</td>
<td>0.4160(1)</td>
<td>3.81(31)</td>
<td>3.05(15)</td>
</tr>
<tr>
<td>(6,0)</td>
<td>( \Omega = 1/2 )</td>
<td>33406.74(5)</td>
<td>0.4120(1)</td>
<td>0.023(25)</td>
<td>4.15(25)</td>
</tr>
<tr>
<td>(7,0)</td>
<td>( \Omega = 1/2 )</td>
<td>33844.83(5)</td>
<td>0.3972(1)</td>
<td>6.2(83)</td>
<td>8(1)</td>
</tr>
<tr>
<td>(0,0)</td>
<td>( \Omega = 1/2 )</td>
<td>33471.1(150)</td>
<td>0.3912(1)</td>
<td>2.2(25)</td>
<td>6.35(35)</td>
</tr>
<tr>
<td>(0,1)</td>
<td>( \Omega = 1/2 )</td>
<td>34672.71(150)</td>
<td>0.3832(1)</td>
<td>10(5)</td>
<td>52.3(92)</td>
</tr>
</tbody>
</table>

\( a \) Errors are estimated from the reproducibility of constants from fits to more than one spectrum and from variation in the constants with the range of linewidths tolerated in the spectral simulations and fits. The quoted errors span all values of constants thus obtained and, in all cases, exceed errors arising from fits to a single spectrum for a single linewidth. The errors refer to the last significant figure on the quoted constants. \( A_{v} \) values are derived from the \( T_{v} \) values (where the latter values were measured for both \( \Delta \Pi \) components) and the ground-state spin-orbit splitting from ref. 28 and quoted errors are the sum of errors in all these terms. \( \dagger \) Constrained to be zero. \( \ddagger \) These values were constrained, and the band was analysed just to obtain a linewidth estimate.  

the laser bandwidth (previously measured levels. smooth variation of with v because it deviates slightly from the equilibrium parameters because it is less sensitive to the rotational linewidths. The constants, but also makes the values of constants returned from inevitably reduces the precision in derived rotational constants.

Simulations were performed with a variety of rotational line-profiles and the derived values are insensitive to the precise FWHM chosen for the Gaussian function. The bands show no evidence of function. We conclude that the primary interaction of the state is judged not to be induced by A poses of comparison with A absorption, we used a ratio of to which A band centred at 317.21 nm. To minimise the absorption cross-section increases up to 351.30 nm and gradually drops off to longer wavelength. This overlapping absorption greatly complicates the recording of spectra of the very weak A-X transition (0,0) band because of a strong underlying OCIO band centred at 317.21 nm. To minimise the OCIO absorption, we used a ratio of O3 to Cl2 which favoured the production of Cl2 over OCIO. This method was partially successful for the (0,0) band, but for the A-X transition (1,0) band, the OCIO absorption dominates to the extent that the CIO spectrum could not be analysed.

4. Discussion
The improved sensitivity of CRDS over conventional absorption spectroscopies is clearly demonstrated by the observation of the A-X transition (1,0) and (0,0) absorption bands of CIO, which have previously escaped detection. The results also illustrate how CRDS provides an alternative and complementary technique to LIF detection of weak electronic absorptions, since LIF fails to detect CIO A-X bands because of the rapid A-X state predissociation.

The only previous study of band origins and rotational constants for the A-X transition of CO2 reported origins for bands from (2,0) upwards, and rotational constants for the (3,0) to (25,0) bands. The superior sensitivity of CRDS has allowed band origins and rotational constants for the (0,0) to (2,0) bands to be determined for the first time. In addition, the agreement between our data and those of the previous investigation for the (3,0) to (7,0) bands is excellent, but with one minor exception: the B constant for the (4,0) band is determined to be somewhat smaller than the previous study. The discrepancy may result from different treatments of the centrifugal distortion constant (D") in the two studies. Coxon and Ramsay did not float D" in their simulations of the band structure but instead used constrained values calculated from an RKR analysis. We opted to float D" (unlike stated otherwise in Table 1). Our derived D" values do not display a simple v dependence, contrary to the assumption of a small increase with v made for the constrained values in ref. 14. Precise values of D" are difficult to extract from the experimental data, however, because of the large linewidths, and because we are unable to measure transitions to very high rotational levels because of overlap between neighbouring vibrational bands. The erratic series of D" values could also be the result of perturbation of the A-X state by the numerous repulsive states that are responsible for the A-X state predissociation.

All the band origins and upper-state rotational constants for the A-X transition derived from this study,
For the transition, our linewidth measurements for the (3,0) and (4,0) bands are again larger than previous reports, and, in addition, we observe that the rotational features of the (3,0) band are sharper than those of the (4,0) band, in contradiction to the earlier work. Widths of lines in the (2,0) band are about twice those previously reported for the (2,1) band, consistent with known discrepancies. We suspect, therefore, that the previously reported (9,0) linewidth is a HWHM rather than FWHM value. We have estimated the linewidths of individual transitions within the (5,0) and (6,0) bands, but the accuracy is poorer than for other, less diffuse bands. We emphasise that the linewidths of the remaining unobserved bands cannot be extrapolated from those of their neighbours as there is no simple trend in the variation of linewidths with . Combining our data with those of other studies, we present the variation of linewidths with for vibrational levels of both components of the A state in Fig. 6. For the A component the linewidths show oscillations with vibrational quantum number at low and go through a maximum at before exhibiting a general decline towards large . The linewidths for the A component also show extensive variation with and, again, pass through an apparent maximum at for or 6. The figure clearly shows, however, a marked difference in the magnitudes of the linewidths for the two spin-orbit components of the A state, with linewidths for the larger component generally larger than for the same vibrational level of the component.

Coxon performed an RKR analysis of the data for the A and A components, but combined the two data sets in order to produce a composite potential energy curve. The non-trivial dependence of on , however, suggests that it would be prudent to calculate curves for the two states separately. In addition, a number of assumptions were made that are not borne out by the more complete data set presented here. For example, the smooth increase of with is questioned by our data set. Similarly, it was assumed that the difference between the rotational constants for the two spin-orbit components, , fell smoothly as increased. We thus caution against the use of eqn. (9) of ref. 14 to calculate the values of .

There has been some confusion over the exact definition of linewidth (FWHM or HWHM) used by Coxon and Ramsay. Later work by Barton et al. and McLaughlin et al. helped resolve any uncertainties for the (3,0) to (25,0) bands of the A-X transition, but these studies did not update the corresponding A-X measurements. To this existing body of data we add linewidth measurements for the (0,0) band, again provided by the emission data. The linewidths of rotational features of the (2,0) band are larger than those reported previously for the (2,1) band, but the discrepancy is consistent with the discrepancies found by other authors with regard to the values presented by Coxon and Ramsay.

Table 3  Turning points and energies of the vibrational levels in the A state of ClO from an RKR analysis of the results from this work and ref. 16

<table>
<thead>
<tr>
<th>v'</th>
<th>Energy/cm⁻¹</th>
<th>R_min/Å</th>
<th>R_max/Å</th>
<th>v'</th>
<th>Energy/cm⁻¹</th>
<th>R_min/Å</th>
<th>R_max/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>259.06</td>
<td>1.786</td>
<td>1.941</td>
<td>13</td>
<td>5401.26</td>
<td>1.593</td>
<td>2.642</td>
</tr>
<tr>
<td>1</td>
<td>763.69</td>
<td>1.742</td>
<td>2.014</td>
<td>14</td>
<td>5641.01</td>
<td>1.589</td>
<td>2.719</td>
</tr>
<tr>
<td>2</td>
<td>1252.38</td>
<td>1.715</td>
<td>2.070</td>
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* An eighth-order expansion was used for the vibrational parameters and a sixth-order expansion for the rotational parameters. The minimum of the RKR potential lies 31224.74 cm⁻¹ above v' = 0 of the X state and R = 1.855 Å. The parameters used to construct the potential are available from the authors on request.

Fig. 6 The experimentally determined v'-dependent Lorentzian linewidths (FWHM) of the A and A states of ClO. For the A data: solid circles are for this study; inverted open triangles are for data from Barton et al. (ref. 18); open triangles are for data from McLaughlin et al. (ref. 19). For the A data, solid squares are for this study.

measurements for the (0,0) band are in excellent agreement with the lifetime determined from emission data. The linewidths for the (1,0) band, again provided by the emission data are, however, a gross overestimate when compared to the current absorption spectrum value. The linewidths of rotational features of the (2,0) band are larger than those reported previously for the (2,1) band, but the disagreement is consistent with the discrepancies found by other authors with regard to the values presented by Coxon and Ramsay.

For the A-X transition, our linewidth values for the (3,0) and (4,0) bands are again larger than previous reports, and, in addition, we observe that the rotational features of the (3,0) band are sharper than those of the (4,0) band, in contradiction to the earlier work. Widths of lines in the (2,0) band are about twice those previously reported for the (2,1) band, consistent with known discrepancies. We suspect, therefore, that the previously reported (9,0) linewidth is a HWHM rather than FWHM value. We have estimated the linewidths of individual transitions within the (5,0) and (6,0) bands, but the accuracy is poorer than for other, less diffuse bands. We emphasise that the linewidths of the remaining unobserved bands cannot be extrapolated from those of their neighbours as there is no simple trend in the variation of linewidths with . Combining our data with those of other studies, we present the variation of linewidths with for vibrational levels of both components of the A state in Fig. 6. For the A component the linewidths show oscillations with vibrational quantum number at low and go through a maximum at before exhibiting a general decline towards large . The linewidths for the A component also show extensive variation with and, again, pass through an apparent maximum at for or 6. The figure clearly shows, however, a marked difference in the magnitudes of the linewidths for the two spin-orbit components of the A state, with linewidths for the larger component generally larger than for the same vibrational level of the component.

had some confusion over the exact definition of linewidth (FWHM or HWHM) used by Coxon and Ramsay. Later work by Barton et al. and McLaughlin et al. helped resolve any uncertainties for the (3,0) to (25,0) bands of the A-X transition, but these studies did not update the corresponding A-X measurements. To this existing body of data we add linewidth measurements for the (0,0) band, and find a trend of increasing with for . Although there is a dip at for 4, the trend is in contradiction to the previous analysis which suggested a fall in as increased. We thus caution against the use of eqn. (9) of ref. 14 to calculate the values of .

There has been some confusion over the exact definition of linewidth (FWHM or HWHM) used by Coxon and Ramsay. Later work by Barton et al. and McLaughlin et al. helped resolve any uncertainties for the (3,0) to (25,0) bands of the A-X transition, but these studies did not update the corresponding A-X measurements. To this existing body of data we add linewidth measurements for the (0,0) band, and find a trend of increasing with for . Although there is a dip at 4, the trend is in contradiction to the previous analysis which suggested a fall in as increased. We thus caution against the use of eqn. (9) of ref. 14 to calculate the values of .

Coxon performed an RKR analysis of the data for the A and A components, but combined the two data sets in order to produce a composite potential energy curve. The non-trivial dependence of on , however, suggests that it would be prudent to calculate curves for the two states separately. In addition, a number of assumptions were made that are not borne out by the more complete data set presented here. For example, the smooth increase of with is questioned by our data set. Similarly, it was assumed that the difference between the rotational constants for the two spin-orbit components, , fell smoothly as increased. We thus caution against the use of eqn. (9) of ref. 14 to calculate the values of .
and the Royal Society.

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References


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