HIGH RESOLUTION ABSORPTION CROSS SECTIONS FOR THE A $^2\Pi$–X $^2\Pi$ SYSTEM OF ClO

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A narrow line laser has been used to measure absolute absorption cross sections for several rotational lines of the A $^2\Pi_{3/2}$–X $^2\Pi_{3/2}$ system of ^{35}ClO. Peak cross sections for the P(16.5–18.5) and R(19.5–21.5) lines of the 9–0 band are 10.0, 9.6, 8.6, 10.6, 10.3, and 9.2 × 10^{-17} cm², respectively. The estimated accuracy is ± 25%.

1. Introduction

The ClO molecule is believed to be an important intermediate in the catalytic destruction of ozone by chlorine-containing compounds [1]. A quantitative assessment of ozone depletion resulting from the injection of large amounts of chlorofluorocarbons into the atmosphere requires a knowledge of both numerous ClO formation–destruction rates and stratospheric ClO concentrations. While accurate rate constants for many of the significant kinetic processes are now available [2], the determination of stratospheric concentration profiles remains a difficult problem. Interest in UV absorption as a potential monitoring technique has increased considerably since recent attempts to observe ClO fluorescence proved unsuccessful [3, 4]. However, before application of this technique can become a reality, absorption cross sections must be known accurately. At present, only low resolution data is available [5,6].

High resolution cross sections are needed for several reasons: (1) high resolution measurements are inherently more sensitive since the sample can be probed

only where the absorption cross section is maximized, (2) only in the high resolution limit is the measured apparent cross section (i.e., the cross section computed under the assumption that *all* ClO molecules can absorb the incident radiation) independent of bandwidth, and (3) for monitoring purposes, high resolution makes it possible to distinguish ClO absorption from background O_3 absorption by simply tuning the spectroscopic probe on and off a line.

In this paper, we report ClO absorption cross sections which were measured using a frequency doubled tunable dye laser with a bandwidth of 0.015 Å (much narrower than the width of a single spectral line) as the spectroscopic probe.

2. ClO spectroscopy

The spectrum of ClO A $^2\Pi_i$– X $^2\Pi_i$ was first observed in emission from flames by Pannetier and Gaydon [7] and in absorption by Porter [8]. Vibrational and rotational assignments for the A $^2\Pi_i$ state were first given by Durie and Ramsay [9]. The recent work of Coxon and Ramsay [10,11] has resulted in a correction of the vibrational assignments, more accurate line frequencies, and estimates of linewidths. The re-

ported linewidths are constant within a band but vary from band to band over a range of 0.3 to 5 cm^{-1}, indicating that predissociation occurs from all vibrational levels with lifetimes in the picosecond range (thus explaining the inability of investigators to observe ClO fluorescence [3,4]). For our initial experiments, we have chosen to study the $A\,^2\Pi_{3/2}$--$X\,^2\Pi_{3/2}$ 9- 0 band. Although the 11--0 band has the largest Franck—Condon factor [12], the 9—0 band is expected to have the largest peak absorptions and best resolved spectrum; this is because the $P(J)$ and $R(J+3)$ lines exactly overlap (to within 0.005 Å), resulting in a spectrum which exhibits half the expected number of lines but double the expected peak intensities. Furthermore, overlap of the weaker $A\,^2\Pi_{1/2}$-$X\,^2\Pi_{1/2}$ system with the 9 -0 band is minimal. Over the spectral range 2822--2834 Å, only a few weak, high J lines of the $A\,^2\Pi_{1/2}$--$X\,^2\Pi_{1/2}$ 9—0 band are found; the intensities of these lines are negligible compared to the $A\,^2\Pi_{3/2}$–$X\,^2\Pi_{3/2}$ 9—0 line intensities. Since the spacing between adjacent rotational lines increases with increasing J, optimum resolution is obtained when studying high J levels. However, for $J'' > 12.5$ (at 300 K), line intensities decrease with increasing J

due to diminishing population in the ground state J'' levels. As a compromise between absorption intensity and resolution, we have focussed most of our attention on the R(19.5--21.5), P(16.5—18.5) lines. For completeness, measurements have also been made in the bandhead region.

3. Experimental

The experimental apparatus is shown schematically in fig. 1. It consists of two major components — a flow system for producing a known concentration of ClO and a laser system for producing a narrow line spectroscopic probe.

ClO was prepared by the reaction

$$Cl + O_3 \rightarrow ClO + O_2. \tag{1}$$

Chlorine atoms were generated by passing a Cl_2/He mixture through a microwave discharge, while ozone was generated using a commercial ozonizer and stored at 196 K in a U-tube packed with silica gel. Ozone (95% O_3, 5% O_2) was admitted to the flow tube through a movable injector which was positioned
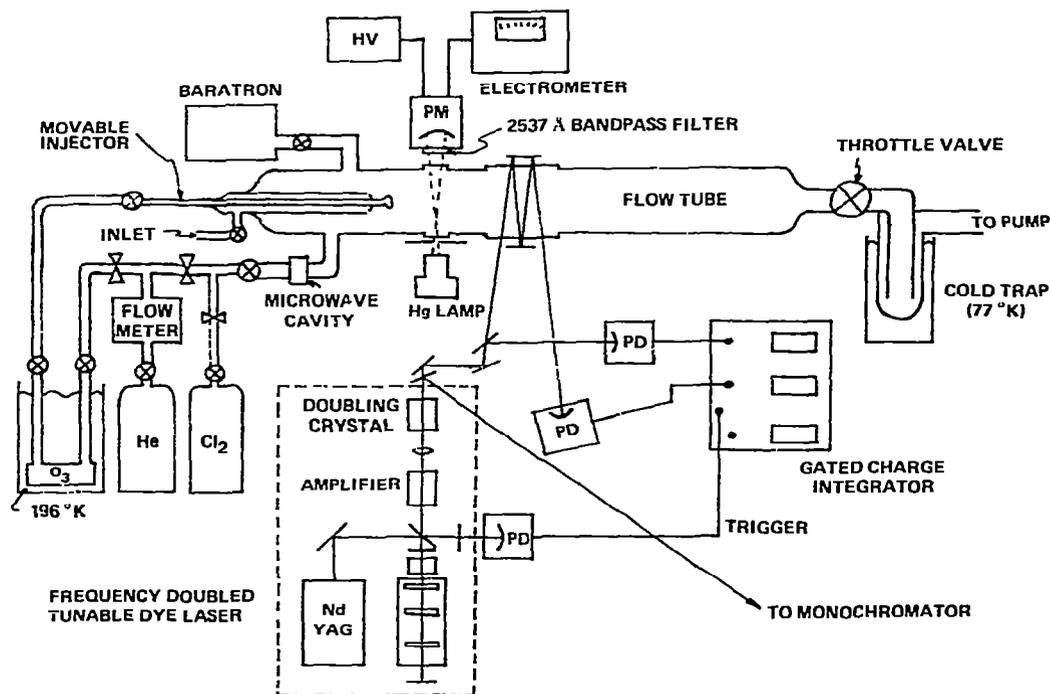

Fig. 1. Schematic of experimental apparatus.

2 cm upstream from the monitoring region to ensure complete mixing of gases. The O_3 concentration in the absence of Cl atoms was monitored by absorption of the 2537 Å line from a mercury pen-ray lamp. In the presence of an excess of Cl atoms, reaction (1) proceeds very quickly to completion ($k \approx 10^{-11}$ cm^3/ molecule s), resulting in a ClO concentration equal to the initial O_3 concentration. Experiments were always performed with Cl atoms in excess to avoid overlapping absorption by O_3 and ClOO. The ClOO molecule is formed in secondary reactions but itself reacts so quickly with Cl that, if Cl is in excess, the steady state concentration of ClOO is negligible. Two criteria were satisfied simultaneously to prove that Cl atoms were in excess: (1) absorption at 2537 Å falls by a factor of 2.7 when Cl atoms are added to the O_3 (2.7 is the ratio of the absorption cross sections at 2537 Å for O_3 and ClO [13–15]) and (2) the chlorine afterglow, which results from atom–atom radiative recombination, is observed downstream from the observation region. To ensure that the ClO concentration remained constant during an experiment, absorption at 2537 Å was monitored continuously. The typical operating pressure in the flow tube was 1.2 torr.

The ClO concentration was expected to decay down the flow tube as a result of the reaction

$$ClO + ClO \xrightarrow[k_2]{k_1} \begin{array}{l} Cl_2 + O_2 \\ ClOO + Cl , \end{array} \qquad (2)$$
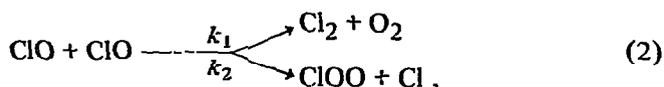
whose total rate constant ($k_1 + k_2$) is 2.5×10^{-14} cm^3/molecule s [2]. Experiments in which ClO absorption was measured at varying distances from the formation region confirmed that reaction (2) controls the ClO gradient. For most experiments, the laser probe was positioned 4 cm downstream from the pen-ray lamp. With our linear flow rate of ≈ 400 cm/s and an initial ClO concentration of 1×10^{15} molecule/ cm^3, reaction (2) resulted in a 25% decay over 4 cm. Since ClO was probed more than 0.01 s after its formation, total relaxation was virtually ensured and absorption due to "hot" bands should have been negligible. Absorption measurements were carried out at ClO concentrations which varied from 3.8×10^{14} to 1.2×10^{15} molecule/cm^3. The amount of absorption was found to scale linearly with concentration, thus indicating that no product of ClO + ClO chemistry could be an interfering absorber. To further test the possibility that an impurity or product of secondary

chemistry could absorb radiation in the same wavelength region as ClO, an experiment was performed where NO was added to the flow through the secondary inlet. NO consumes ClO very quickly via the reaction

$$NO + ClO \rightarrow NO_2 + Cl, \qquad (3)$$

so in the presence of excess NO, no ClO absorption should have been observed downstream at the laser probe. In fact, when ClO was titrated with NO, no absorption was observed. Even though this result is not completely definitive (i.e., it is possible that some species which also reacts quickly with NO could still be an interfering absorber), it strongly suggests that interfering absorptions were not a problem.

The frequency doubled tunable dye laser is described in detail elsewhere [16,17]. The tuning elements were three air-gap Fabry–Pérot etalons. Laser wavelengths and line profiles were measured with a SPEX 3/4 meter monochromator in fourth order. The monochromator was calibrated using several iron lines in the spectral region 2800–2850 Å; the wavelength measurements are estimated to be accurate to ±0.1 Å. The laser spectral profiles showed a strong line containing > 95% of the total intensity with a weak satellite 0.2 Å on one side of the main line. The linewidth was too narrow to measure with the monochromator, but was estimated by pressure tuning through an OH absorption line (Doppler width = 0.012 Å) and observing the fluorescence signal as a function of pressure. The laser linewidth was found to ≈ 0.015 Å.

To obtain peak absorptions of 10–15% at ClO concentrations of 1×10^{15} molecule/cm^3, a four pass absorption path was employed. The path length was determined to be 20.6 cm by measuring the absorption resulting from known amounts of added Cl_2 and O_3. The incident laser intensity was measured by deflecting a few percent of the incoming beam to a photodiode while the transmitted intensity was measured by a second photodiode. The photodiode signals were fed into different channels of a gated charge integrator for signal averaging. A single data point was obtained by measuring the ratio of incident to transmitted laser power with ozone turned off (I_0), then with ozone turned on (I), then again with ozone off (to check for drift in I_0). About 3000 laser pulses (pulse rate = 10 s^{-1}) were averaged to obtain each data point. Both photodiodes were carefully tested

for saturation by measuring the absorption resulting from known amounts of Cl_2 in a cell of known path length; no evidence for saturation was found. Laser power and beam spatial profile measurements were carried out to assess the importance of bleaching — a phenomenon which occurs when the population of absorbers is significantly depleted due to absorption from an intense laser beam. It was concluded from these measurements that the reduction in measured absorption resulting from bleaching was negligible.

4. Results and discussion

Absolute apparent absorption cross sections are plotted versus wavelength in fig. 2. The solid line in the 2829—2831 Å region represents a "visual" average of all the experimental data in that spectral region. The 2σ error in the reported cross sections is typically ±20%, with the ClO concentration measurement and (particularly in the case of weaker absorptions) the uncertainty in I/I_0 being the principal sources of error.

Two interesting aspects of the data in the 2829—2831 Å region are the appearance of an unassigned peak at 2830.6 Å and the overall lack of resolution. Neither of these features was expected based on the reported ^{35}ClO spectrum [10]. No rotational analysis of ^{37}ClO has been carried out, but positions of the ^{37}ClO bandheads relative to the corresponding ^{35}ClO bandheads have been reported by Briggs [18]. Using Briggs' isotope shifts and an approximate ^{37}ClO rotational constant calculated from the reported ^{35}ClO rotational constant and the ratio of reduced masses, we have calculated ^{37}ClO line positions. Considering the isotopic abundances (24.5% ^{37}ClO, 75.5% ^{35}ClO) and assuming a thermal population distribution (300 K) of ground state rotational levels, it is estimated that ≈ 35% of the total absorption intensity in the 2829—2831 Å region is due to ^{37}ClO. The exact appearance of the spectrum depends not only upon line positions and relative intensities, but also upon linewidths. Estimates for ^{35}ClO linewidths are available but ^{37}ClO linewidths are unknown. For the purpose of simulating the spectrum, we have assumed that the ^{37}ClO linewidths are equal to those for ^{35}ClO. In fig. 3, spectra which were calculated assuming lorentzian lineshapes and linewidths of 0.20 Å and 0.32 Å respectively (the
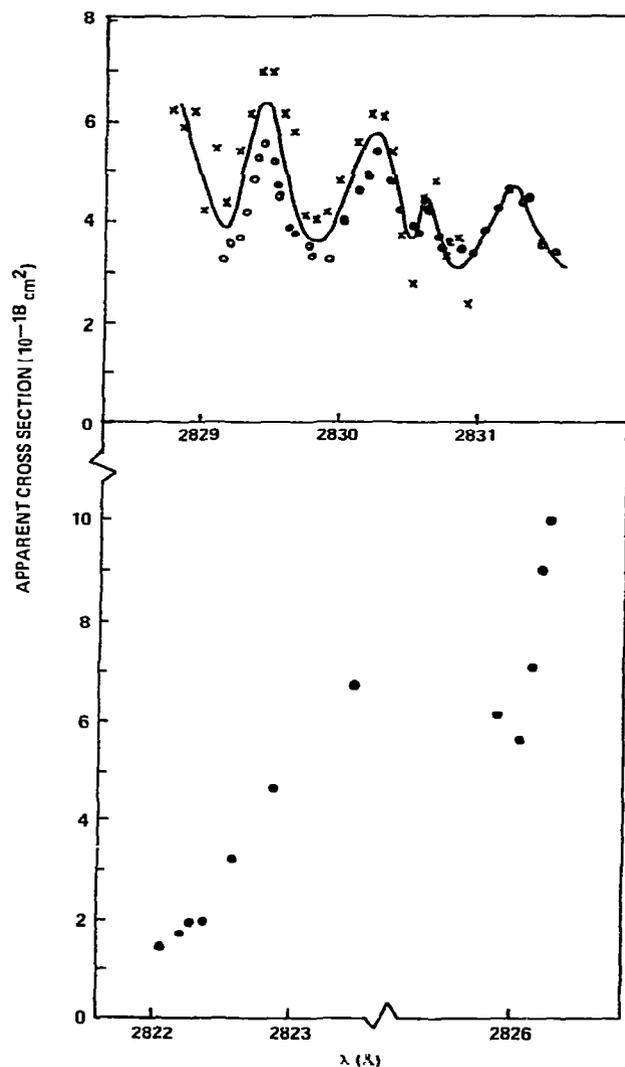

Fig. 2. Experimental apparent absorption cross sections for the ClO $A^2\Pi_{3/2}-X^2\Pi_{3/2}$ 9—0 band. o: (ClO) = 1.2 × 10^{15} molecule/cm^3; •: (ClO) = 1.0 × 10^{15} molecule/cm^3; ×: (ClO) = 3.8 × 10^{14} molecule/cm^3; ——: "visual average" spectrum.

^{35}ClO linewidth reported by Coxon and Ramsay is 0.17 Å [10]), are compared with the experimental spectrum. Due to the uncertainties in ClO line positions and linewidths, the simulated spectra are very approximate in nature. Nonetheless, some useful qualitative conclusions can be drawn: (1) a baseline resolved spectrum is not feasible, (2) the unassigned spectral feature *could* be a ^{37}ClO line, and (3) when compared with experimental data, the simulated spectra suggest that the ^{35}ClO linewidth could be some-
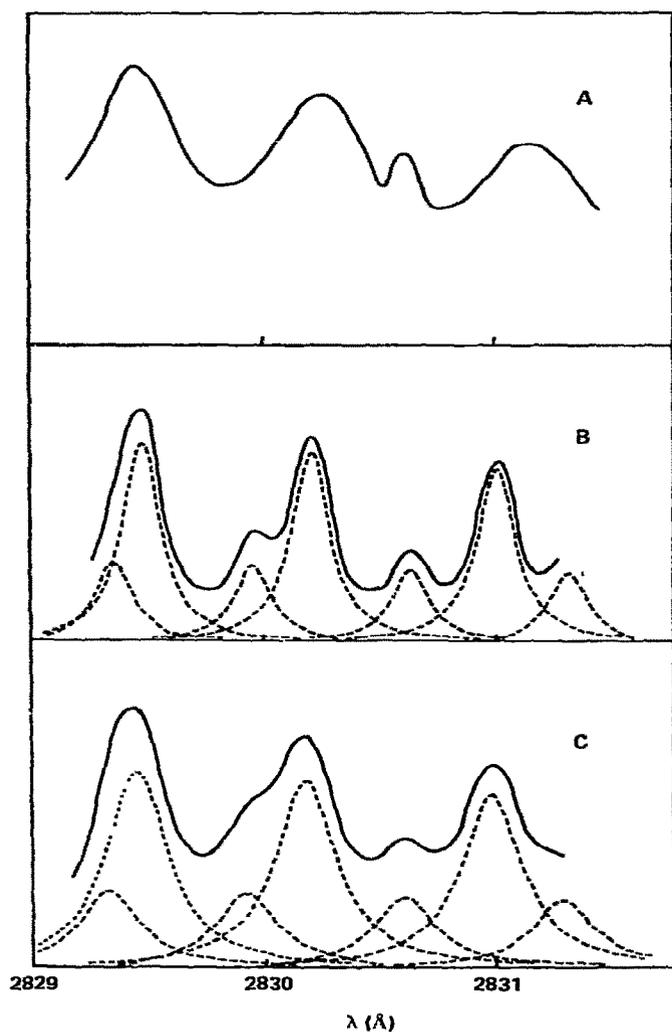
Fig. 3. Comparison of simulated ClO spectra with the experimental spectrum. The more intense sequence of lines in the simulated spectra represent ^{35}ClO; the weaker sequence of lines represent ^{37}ClO. A: experimental spectrum; B: all (pairs of) lines assumed to have 0.20 Å linewidth; C: all (pairs of) lines assumed to have 0.32 Å linewidth.

what wider than estimated by Coxon and Ramsay [10].

Examination of the simulated spectra suggests that, at each of the three main peaks, a good estimate for the fraction of intensity which is attributable to ^{35}ClO is 85 ± 5%. This fraction of the total cross section is partitioned between the R($J'' + 3$) and P(J'') lines. The ratio of apparent cross sections for the two overlapped lines is given by

Table 1

Absolute peak absorption cross sections for individual lines of the ^{35}ClO A $^2\Pi_{3/2}-$X $^2\Pi_{3/2}$ 9—0 band ($T = 300$ K). Accuracy is ±25%. Precision is ±10%

Line	σ_{app} (10^{-18} cm^2)	σ (10^{-17} cm^2)
R(19.5)	2.5$_5$	10.6
R(20.5)	2.3	10.3
R(21.5)	1.9	9.2
P(16.5)	2.8$_5$	10.0
P(17.5)	2.6	9.6
P(18.5)	2.2	8.6

$$\sigma^R_{J''+3_{app}} / \sigma^P_{J''_{app}} = (S^R_{J''+3}/S^P_{J''})\, e^{-\Delta E/KT} \qquad (4)$$

where $S^P_{J''}$ is the line strength of the P(J'') line [19] and $\Delta E \equiv E_{J''+3} - E_{J''}$. The real cross section is the apparent cross section divided by the fraction of the total X $^2\Pi_i$ population found in the level from which absorption occurs. Isotopic abundances, spin—orbit splitting ($A = 318$ cm^{-1} [20]), and the rotational and vibrational state population distributions have been considered in computing this fraction. Apparent and real cross sections for the R(19.5—21.5) and P(16.5—18.5) lines are given in table 1.

It has been observed that the optimum wavelength region for stratospheric measurements of ClO by absorption is ≈ 3000 Å (3—0 and 4—0 bands), even though the absorption cross sections in this wavelength region are rather small [6]. This is because Rayleigh scattering and interfering absorption by ozone become progressively more important at shorter wavelengths. Thus, our future efforts at measuring ClO absorption cross sections will be focussed on the 3—0 and 4—0 bands; a more complete set of measurements on the 9—0 band is also anticipated.

References

[1] M.J. Molina and F.S. Rowland, Nature 249 (1974) 810.
[2] R.T. Watson, Rate Constants of ClO$_x$ of Atmospheric Interest, Chemical Kinetics Data Survey, NBSIR 74-516 (1974).
[3] P. Hogan, R.T. Watson and D.D. Davis, unpublished results.
[4] M.A.A. Clyne, I.S. McDermid and A.H. Curran, J. Photochem. 5 (1976) 201.
[5] M.A.A. Clyne and J.A. Coxon, Proc. Roy. Soc. A 303 (1968) 207.

[6] P. Rigaud, B. Leroy, G. LeBras, G. Poulet, J.L. Jourdain and J. Combourieu, Chem. Phys. Letters 46 (1977) 161.

[7] G. Pannetier and A.G. Gaydon, Nature 161 (1948) 241.

[8] G. Porter, Discussions Faraday Soc. 9 (1950) 60.

[9] R.A. Durie and D.A. Ramsay, Can. J. Phys. 36 (1958) 35.

[10] J.A. Coxon and D.A. Ramsay, Can. J. Phys. 54 (1976) 1034.

[11] J.A. Coxon, J. Photochem. 5 (1976) 337.

[12] J.A. Coxon, to be published.

[13] W.B. DeMore and O. Raper, J. Phys. Chem. 68 (1964) 412.

[14] M. Griggs, J. Chem. Phys. 49 (1968) 857.

[15] H.S. Johnston, E.D. Morris Jr. and J.van der Bogaerde, J. Am. Chem. Soc. 91 (1969) 7712.

[16] A. Moriarty, W. Heaps and D.D. Davis, Opt. Commun. 16 (1976) 324.

[17] D.D. Davis, W. Heaps, D.L. Philen, T. McGee, A.C. Nelson and P.H. Wine, Appl. Opt., to be published.

[18] A.G. Briggs, Nature Phys. Sci. 239 (1972) 13.

[19] G. Herzberg, Spectra of diatomic molecules, 2nd Ed. (Van Nostrand, Princeton, 1950).

[20] N. Basco and R.D. Morse, J. Mol. Spectry. 45 (1973) 35.