

QUANTUM YIELD MEASUREMENTS OF $\text{Cl}(3^2\text{P}_{1/2})$ AND $\text{Cl}(3^2\text{P}_{3/2})$ IN THE PHOTOLYSIS OF C_1 CHLOROFLUOROCARBONS DETERMINED BY ATOMIC RESONANCE ABSORPTION SPECTROSCOPY IN THE VACUUM UV

RICHARD H. CLARK and DAVID HUSAIN

Department of Physical Chemistry, The University of Cambridge, Lensfield Road, Cambridge CB2 1EP (Gt. Britain)

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Summary

We describe measurements of the relative quantum yields of electronically excited and ground state chlorine atoms generated following the broad band pulsed irradiation of the C_1 chlorofluorocarbons CF_3Cl , CF_2Cl_2 , CFCl_3 and CCl_4 . $\text{Cl}((3\text{p})^5, ^2\text{P}_{1/2})$ and $\text{Cl}((3\text{p})^5, ^2\text{P}_{3/2})$ produced by the pulsed irradiation of these Freons in the presence of excess helium buffer gas were monitored photoelectrically by time-resolved atomic resonance absorption spectroscopy in the vacuum UV using signal averaging. The two atomic resonance transitions employed to construct concentration-time profiles for $\text{Cl}(3^2\text{P}_{3/2})$ and $\text{Cl}(3^2\text{P}_{1/2})$ were those at $\lambda = 134.72 \text{ nm}$ ($\text{Cl}((3\text{p})^4(4\text{s})^1, ^2\text{P}_{3/2}) \leftarrow \text{Cl}((3\text{p})^5, ^2\text{P}_{3/2})$) and $\lambda = 136.34 \text{ nm}$ ($\text{Cl}((3\text{p})^4(4\text{s})^1, ^2\text{P}_{3/2}) \leftarrow \text{Cl}((3\text{p})^5, ^2\text{P}_{1/2})$) respectively and hence involved a common upper state which was specifically required for the analysis. The higher energized spin-orbit state $\text{Cl}(3^2\text{P}_{1/2})$, which is 882 cm^{-1} above the $\text{Cl}(3^2\text{P}_{3/2})$ ground state, decayed on a short time scale (about 0 - 500 μs) before the onset of Boltzmann equilibrium. This can be contrasted with the longer-lived decay of $\text{Cl}(3^2\text{P}_{3/2})$ (about 0 - 10 ms) which was monitored in a regime where both spin-orbit states were Boltzmann equilibrated. Computerized extrapolation of the decay traces of I_{tr} at these two wavelengths for the resonance transitions to $t = 0$ yielded the following relative quantum yields ($\phi = [\text{Cl}(3^2\text{P}_{1/2})]_{t=0} / [\text{Cl}(3^2\text{P}_{3/2})]_{t=0}$) which were found to be sensibly independent of the initial Freon concentration: CF_3Cl , 6.2 ± 2.3 ; CF_2Cl_2 , 3.0 ± 1.1 ; CFCl_3 , 3.8 ± 1.3 ; CCl_4 , 3.7 ± 1.3 . Whilst these results indicate population inversions in all cases, it is considered highly unlikely that these molecules could form the basis of atomic photodissociation lasers operating on the transition $\text{Cl}(3^2\text{P}_{1/2}) \rightarrow \text{Cl}(3^2\text{P}_{3/2}) + h\nu$ (882 cm^{-1}) on account of the very low Einstein coefficient ($A_{nm} = 0.012 \text{ s}^{-1}$) and the highly efficient collisional quenching of the $^2\text{P}_{1/2}$ state by the Freons themselves. The present results are compared with analogous results for bromides and iodides reported previously.

1. Introduction

Quantum yield measurements of electronically excited $\text{I}((5p)^5, {}^2P_{1/2})$ and $\text{Br}((4p)^5, {}^2P_{1/2})$, which are 7603 cm^{-1} and 3685 cm^{-1} respectively above the $(np)^5, {}^2P_{1/2}$ ground state [1] and are normally determined in the fractional form $[X {}^2P_{1/2}]/([X {}^2P_{1/2}] + [X {}^2P_{3/2}])$ when generated from the photolysis of various halides, have been the subject of a large number of investigations [2] on account of the roles played by these two ${}^2P_{1/2}$ states in stimulated emission [3]. More emphasis has been directed towards quantum yield measurements of the states of atomic iodine where both broad band [4 - 8] and laser [9 - 15] photolysis have been employed. In the case of atomic bromine, such measurements on $\text{Br}(4 {}^2P_{1/2})$ and $\text{Br}(4 {}^2P_{3/2})$ have primarily resulted from laser photolysis rather than broad band photolysis [15, 16]. A wide range of techniques for direct monitoring of the spin-orbit states has included time-resolved atomic resonance absorption spectroscopy [5 - 7, 17, 18], photographic kinetic absorption spectroscopy [4] and time-resolved forbidden emission (${}^2P_{1/2} \rightarrow {}^2P_{3/2} + h\nu$) [10 - 13] including correction for exciplex emission [14] and laser gain [8]. Indirect or marker methods include the photoacoustic effect [9] and molecular IR emission following electronic to vibrational energy transfer [16]. In contrast, and to the best of our knowledge, quantum yield measurements on the specific spin-orbit states $\text{Cl}(3 {}^2P_{1/2})$ and $\text{Cl}(3 {}^2P_{3/2})$ (ΔE for $\text{Cl}(3 {}^2P_{1/2}) - \text{Cl}(3 {}^2P_{3/2}) = 882 \text{ cm}^{-1}$ [19]) following the photolysis of chlorides have not been reported. This is primarily due to technical difficulty rather than lack of fundamental interest.

We have stressed in previous publications [20 - 22] that the large body of rate data reported in the literature for atomic chlorine [23] generally describes the collisional behaviour of a system where the two spin-orbit states are in Boltzmann equilibrium. Under such circumstances, a reported effective second-order rate constant for $\text{Cl}(3 {}^2P_J)$ will, in fact, be given by

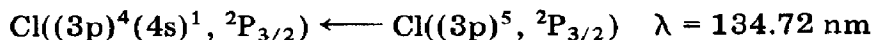
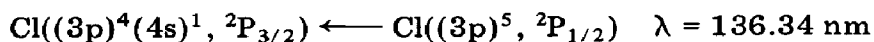
$$k_2 = \frac{k_a + k_b K}{1 + K}$$

where k_a and k_b are the specific rate constants for $\text{Cl}(3 {}^2P_{1/2})$ and $\text{Cl}(3 {}^2P_{3/2})$ respectively. K is the equilibrium constant connecting these two spin-orbit states which will show identical kinetics under equilibrium conditions. Thus the measured chemistry of $\text{Cl}(3 {}^2P_J)$ could be dominated by the collisional behaviour of the ${}^2P_{1/2}$ state. A further fundamental objective is the study of the quenching of $\text{Cl}(3 {}^2P_{1/2})$ which has been the subject of recent investigations [22]. In this latter connection, we have also emphasized that time-resolved atomic resonance absorption in the vacuum UV on $\text{Cl}(3 {}^2P_{1/2})$ out of Boltzmann equilibrium remains, at present, the only practical method of determining absolute rate data for this specific spin-orbit state. This contrasts with a technique that would depend on either the weak spontaneous emission ${}^2P_{1/2} \rightarrow {}^2P_{3/2} + h\nu$ (882 cm^{-1}) ($A_{nm} = 0.012 \text{ s}^{-1}$ [2, 24 - 26]) or a resonance fluorescence technique which would involve optical excitation

to an upper state connecting with both $\text{Cl}(3^2\text{P}_{1/2})$ and $\text{Cl}(3^2\text{P}_{3/2})$ [22]. Thus the atomic absorption technique permits kinetic measurements to be made at short times before the onset of Boltzmann equilibrium resulting from the rapid transfer of the small spin-orbit energy [21, 22]. In the present study, effectively two sets of kinetic measurements are carried out following the pulsed irradiation of the molecules CF_3Cl , CF_2Cl_2 , CFCl_3 and CCl_4 : (i) $\text{Cl}(3^2\text{P}_{1/2})$ was monitored in the "short-time" domain to yield a linear measure of $[\text{Cl}(3^2\text{P}_{1/2})]_{t=0}$; (ii) $[\text{Cl}(3^2\text{P}_{3/2})]$ was then monitored in the "long-time" domain after Boltzmann equilibrium had been established between all the atomic chlorine present. Extrapolation to $t = 0$ then yields $[\text{Cl}(3^2\text{P}_{3/2})]_{t=0}$, the Boltzmann fraction in the $^2\text{P}_{1/2}$ state being negligible (0.7%). Hence the relative quantum yields of the $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ states of atomic chlorine are determined. Rebert and Ausloos [27] have reported overall quantum yields for atomic chlorine derived from the photolysis of CF_2Cl_2 and CFCl_3 at specific wavelengths using the competitive techniques of classical photochemistry. To the best of our knowledge, the present measurements constitute the first determination of quantum yields of atomic chlorine by direct monitoring of the transient atoms and the first measurements for the specific spin-orbit states.

2. Experimental details

The experimental arrangement for monitoring $\text{Cl}(3^2\text{P}_{1/2})$ in the short-time domain and $\text{Cl}(3^2\text{P}_{3/2})$ on the longer time scale during which Boltzmann equilibrium between the spin-orbit states is established has essentially been described in previous publications [20 - 22, 28]. However, there are some modifications regarding the atomic resonance transitions, which are employed for reasons fundamental to the analysis, and in the data-handling procedure. In general terms, for measurements on both $\text{Cl}(3^2\text{P}_{1/2})$ and $\text{Cl}(3^2\text{P}_{3/2})$, the atoms were generated from the repetitive pulsed irradiation of chlorofluorocarbons (RCl) in the presence of excess helium buffer gas ($p_{\text{He}}/p_{\text{RCl}} \approx 10^4$) in a flow system kinetically equivalent to a static system ($E = 180 \text{ J}$; repetition rate, 0.2 Hz) through the Spectrosil wall of a coaxial lamp and vessel assembly [22] ($\lambda \gtrsim 165 \text{ nm}$). These two spin-orbit states were then both monitored photoelectrically (Gencom G-26E315 photomultiplier tube; CsI photocathode; MgF_2 window; photomultiplier voltage, 2.2 - 2.4 kV; Wallis power supply) by resonance absorption following optical isolation (Hilger and Watts 1 m concave grating vacuum UV monochromator) of the following atomic transitions:



We emphasize the use of the common upper state for the two transitions. This is necessary for the analysis leading to the quantum yields. The $\lambda = 136.34 \text{ nm}$ transition has been employed for monitoring $\text{Cl}(3^2\text{P}_{1/2})$ as

previously [21, 22]. Measurements on $\text{Cl}(3^2\text{P}_{3/2})$ have hitherto used the $\lambda = 138.97$ nm transition $\text{Cl}((3\text{p})^4(4\text{s})^1, 4^2\text{P}_{5/2}) \leftarrow \text{Cl}((3\text{p})^5, 2^2\text{P}_{3/2})$ [20, 28] on account of its greater intensity when derived from a microwave-powered flow lamp of the type described by Davis and Braun [29] employing a Fehsenfeld cavity [30] ($p_{\text{Cl}_2} = 2.0 \text{ N m}^{-2}$; $p_{\text{He}} = 130 \text{ N m}^{-2}$; incident power, 25 W; EMI microwave generator type T1001). The vacuum UV atomic emission spectrum of chlorine obtained using this type of system has been reported by Fletcher and Husain [31] and a similar set of atomic spectral intensities was observed in these studies. The weaker resonance source at $\lambda = 134.72$ nm (compared with that at $\lambda = 138.97$ nm [31]) does give rise to greater noise, but this is at least partly offset by the use of the long-time domain for the ground state atom, permitting larger RC components in the amplification of the decay profiles. In contrast with earlier measurements on the quenching of $\text{Cl}(3^2\text{P}_{1/2})$ by the C_1 chlorofluorocarbons [21] which employed a 200-point signal averager (Data Laboratories DL 102A; Biomation transient recorder type 610), all the present decay profiles for both $\text{Cl}(3^2\text{P}_{1/2})$ and $\text{Cl}(3^2\text{P}_{3/2})$ derived from these Freons involved a transient recorder (Data Laboratories DL 920 with 2048 data points) coupled to a signal averager with a 1024-point memory (Data Laboratories DL 4000). Hence, following pulsed photolysis, the photoelectric signals representing transmittance at $\lambda = 136.34$ nm and $\lambda = 134.72$ nm were amplified without distortion using a current-to-voltage converter [32]. The signals were then captured and digitized in a transient recorder and were transferred to the signal averager for summation and averaging before transfer to a paper tape punch (Data Dynamics 1183) in ASCII code for direct input into the University of Cambridge IBM 3081 computer. Decay traces of $I_{\text{tr}}(\lambda = 136.34 \text{ nm})$ and $I_{\text{tr}}(\lambda = 134.72 \text{ nm})$ against time were derived by averaging the results of 32 individual experiments. Each profile of the transmitted light intensity at the two wavelengths indicated, which described the decays of the two spin-orbit states generated on photolysis, was measured on a given flow and hence on a mixture of identical composition. All materials were prepared as described previously [21, 22].

3. Results and discussion

Figures 1(a) - 1(d) show examples of the digitized time variation of the transmitted light intensity at $\lambda = 136.34$ nm indicating the decay of resonance absorption by $\text{Cl}(3^2\text{P}_{1/2})$ following the pulsed irradiation of CF_3Cl , CF_2Cl_2 , CFCl_3 and CCl_4 respectively. Figure 2 shows the time variation of I_{tr} at $\lambda = 134.72$ nm indicating the decay of $\text{Cl}(3^2\text{P}_{3/2})$ on a much longer time scale for the same mixtures as listed in Fig. 1. The quantum yields of $\text{Cl}(3^2\text{P}_{1/2})$ and $\text{Cl}(3^2\text{P}_{3/2})$ are derived from decay measurements on the two spin-orbit states for a range of concentrations of the chlorinated photochemical precursors at approximately constant total pressures of helium buffer gas. The results of interest arising from the analyses of the digitized

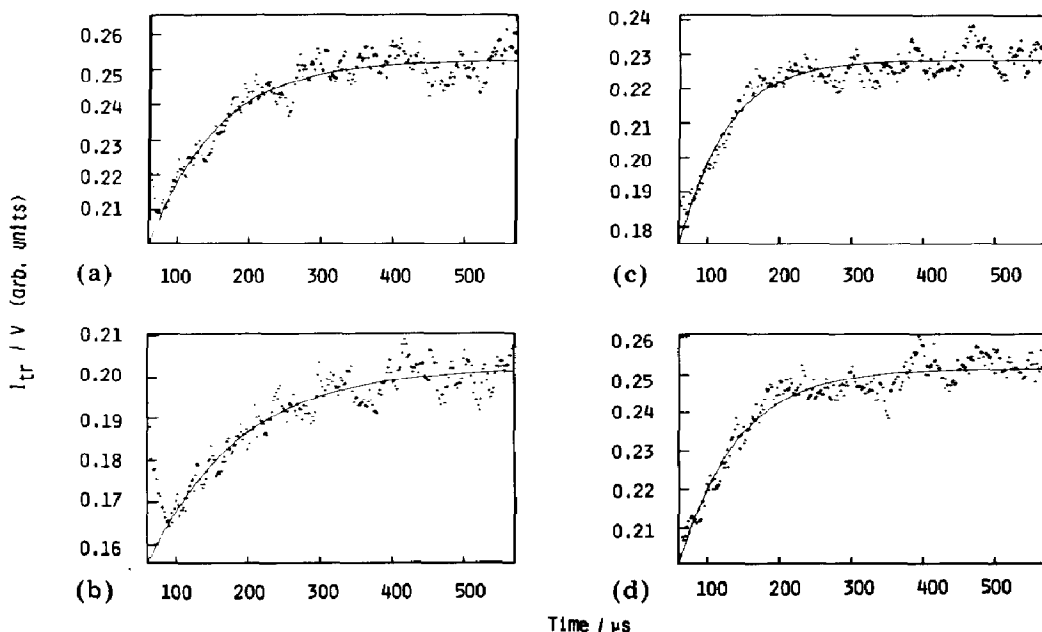


Fig. 1. Examples of the digitized time variation of the transmitted light intensity I_{tr} at $\lambda = 136.34$ nm ($\text{Cl}((3p)^4(4s)^1, ^2P_{3/2}) \rightarrow \text{Cl}((3p)^5, ^2P_{1/2})$) showing the decay of resonance absorption by $\text{Cl}(3^2P_{1/2})$ following the pulsed irradiation of CF_3Cl , CF_2Cl_2 , CFCl_3 and CCl_4 in the presence of excess helium buffer gas ($p_{\text{total with He}} \approx 2.2$ kN m $^{-2}$; $E = 180$ J; repetition rate, 0.2 Hz; +25% density of 1024 digitized data points; —, computerized fitting of raw data to the form $I_{tr} = I_0' \exp\{-A \exp(-k't)\}$; average of 32 individual experiments): (a) CF_3Cl (7.7×10^{13} molecules cm $^{-3}$); (b) CF_2Cl_2 (7.3×10^{13} molecules cm $^{-3}$); (c) CFCl_3 (7.4×10^{13} molecules cm $^{-3}$); (d) CCl_4 (7.3×10^{13} molecules cm $^{-3}$).

traces of the types indicated in Figs. 1 and 2 are the photochemical yields $[\text{Cl}(3^2P_{1/2})]_{t=0}$ and $[\text{Cl}(3^2P_{3/2})]_{t=0}$. In principle, the first-order coefficients k' for the decay of either spin-orbit state are simply parameters for curve fitting in these measurements and are not reported here. Their magnitudes are employed, for example, to determine the second-order collisional quenching constants of $\text{Cl}(3^2P_{1/2})$ by these Freons [22] in the case of the $\lambda = 136.34$ nm resonance transition; the quenching constant for the buffer gas helium is negligible in its effect on the decay of the excited atom [31, 33]. Decay measurements in the long-time domain (which in fact previously employed the $\lambda = 138.97$ nm transition) yield kinetic data for the "Boltzmannized" $\text{Cl}(3^2P_J)$ [20, 28]. The extrapolation of the signals to $t = 0$ (Figs. 1 and 2) and the extraction of the quantum yields of $\text{Cl}(3^2P_{1/2})$ and $\text{Cl}(3^2P_{3/2})$ require some further consideration.

From the general viewpoint of the analysis, we note the following.

(a) $\text{Cl}(3^2P_{1/2})$ decays on a much more rapid time scale than does $\text{Cl}(3^2P_{3/2})$ prior to the onset of Boltzmann equilibrium between the spin-orbit states, as is clearly shown by the present work and by previous work [20, 21], and decays of the two spin-orbit states can be considered as kinetically separate processes.

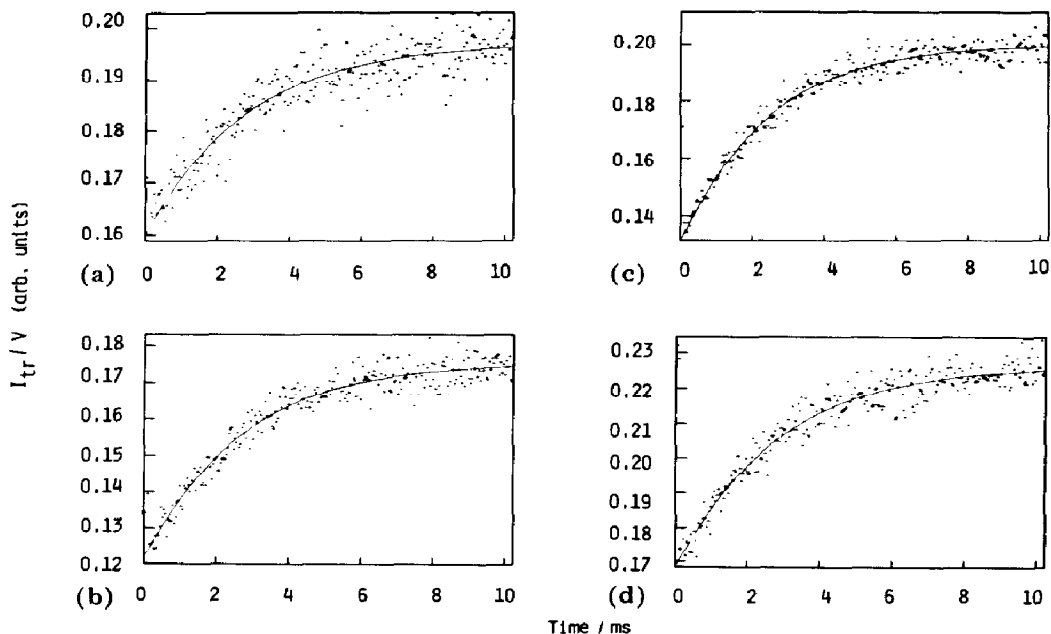


Fig. 2. Examples of the digitized time variation of the transmitted light intensity I_{tr} at $\lambda = 134.72$ nm ($\text{Cl}((3p)^4(4s)^1, {}^2P_{3/2}) \rightarrow \text{Cl}((3p)^5, {}^2P_{3/2})$) indicating the decay of resonance absorption by $\text{Cl}(3^2P_{3/2})$ following the pulsed irradiation of CF_3Cl , CF_2Cl_2 , CFCl_3 and CCl_4 in the presence of excess helium buffer gas ($p_{\text{total with He}} \approx 2.2$ kN m $^{-2}$; $E = 180$ J; repetition rate, 0.2 Hz; +25% density of 1024 digitized data points; —, computerized fitting of raw data to the form $I_{tr} = I_0 \exp\{-A \exp(-k't)\}$; average of 32 individual experiments): (a) CF_3Cl (7.7×10^{13} molecules cm $^{-3}$); (b) CF_2Cl_2 (7.3×10^{13} molecules cm $^{-3}$); (c) CFCl_3 (7.4×10^{13} molecules cm $^{-3}$); (d) CCl_4 (7.3×10^{13} molecules cm $^{-3}$).

(b) In mixtures of C_1 chlorofluorocarbons and helium, quenching of the ${}^2P_{1/2}$ state by the Freons proceeds at rates of the order of the collision number [21]. On the simplest considerations, $\text{Cl}(3^2P_{1/2})$ might be expected to decay totally by spin-orbit relaxation to the ${}^2P_{3/2}$ ground state. The high endothermicity of the chlorine abstraction reactions of the type



($D_0^0\{\text{Cl}_2(X^1\Sigma_g^+)\} = 2.479$ eV [34]; $\Delta H \approx +1$ eV [35, 36]) should also be noted. Kinetic extrapolation of the observed decays of $\text{Cl}(3^2P_{1/2})$ to $t = 0$ yields a direct measurement of the initial photochemical yield $[\text{Cl}(3^2P_{1/2})]_{t=0}$ regardless of whether the mode of removal is physical or chemical or both.

(c) Extrapolation of the observed decays of $\text{Cl}(3^2P_{3/2})$ to $t = 0$ yields $[\text{Cl}(3^2P_{3/2})]_{t=0}$ despite the fact that the observed decay coefficient k' for $\text{Cl}(3^2P_{3/2})$ in the long-time domain is determined by the kinetic behaviour of the Boltzmannized system of $\text{Cl}(3^2P_J)$. Hence with a given gas R

$$k' \{\text{Cl}(3^2P_{3/2})\} = \frac{(k_a + k_b K)[R]}{1 + K}$$

(see earlier) and is, in this context, one of the parameters involved in the extrapolation. Nevertheless the magnitude of k' is employed in the interpretation of the data and hence the quantum yields. Typical values of k' for $\text{Cl}(3^2\text{P}_{3/2})$ are found to be of the order of 400 s^{-1} ($1/k' \approx 25 \text{ ms}$). This is about three times faster than the calculated diffusion rate following our measurements [28].

From the foregoing, the overall removal of $\text{Cl}(3^2\text{P}_{3/2})$ and hence $\text{Cl}(3^2\text{P}_{1/2})$ is considered to be chemical, and presumably proceeds via the reaction with photolytic fragments in view of the endothermicity of the chlorine abstraction reaction with RCl (see earlier). On this basis the measured yields $[\text{Cl}(3^2\text{P}_{3/2})]_{t=0}$ do not reflect cascading from $\text{Cl}(3^2\text{P}_{1/2})$ and, indeed, the measured ratios of the $^2\text{P}_{1/2}$ to $^2\text{P}_{3/2}$ concentrations do not support this (see later). In fact, $[\text{Cl}(3^2\text{P}_{1/2})]_{t=0}$ will decay to its equilibrium value $[\text{Cl}(3^2\text{P}_{1/2})]_{\text{eq}}$ whatever the overall decay mechanism for this atomic state. This is not actually 0.7% ($K = g_2/\{g_1 \exp(-\Delta E/kT)\}$ where the symbols have their usual meaning) of $[\text{Cl}(3^2\text{P}_{1/2})]_{t=0}$, but 0.7% of the total atomic chlorine concentration. However, it can clearly be neglected in considering these atomic yields, although account must be taken of this equilibrium yield in the analysis of the observed traces for $I_{\text{tr}}(\lambda = 136.34 \text{ nm}) = I_0'$ at the end of the decay of $\text{Cl}(3^2\text{P}_{1/2})$. This is not the completely unattenuated signal from the resonance source at this wavelength. In contrast, $I_{\text{tr}}(\lambda = 134.72 \text{ nm})$ at infinite time following the total removal of $\text{Cl}(3^2\text{P}_J)$ is the completely unattenuated signal I_0 at that particular wavelength.

The analysis of the decays of $I_{\text{tr}}(\lambda = 136.34 \text{ nm})$ describing $\text{Cl}(3^2\text{P}_{1/2})$ requires further approximations but these are comparably very small effects and have been considered previously [22]. Briefly, the first-order kinetic equations for $\text{Cl}(3^2\text{P}_{1/2})$ and $\text{Cl}(3^2\text{P}_{3/2})$ out of Boltzmann equilibrium yield a decay of the $^2\text{P}_{1/2}$ state determined by the sum of two exponential terms. However, this is readily reduced to a single exponential term by the omission of the diffusional loss of $\text{Cl}(3^2\text{P}_{1/2})$ which has been shown to be negligible compared with the collisional removal of $\text{Cl}(3^2\text{P}_{1/2})$ by the Freons [21, 28]. Employment of the Beer-Lambert law [21] then yields

$$I_{\text{tr}}(\lambda = 136.34 \text{ nm}) = I_0' \exp\{-A \exp(-k't)\} \quad (2)$$

I_0' can be seen by inspection of traces of the type given in Fig. 1, but it is in fact computed from the traces over the complete decay measurement as are the quantities A and k' . A is the object of experimental interest in these observations and is given by

$$A = \epsilon(\lambda = 136.34 \text{ nm})l([\text{Cl}(3^2\text{P}_{1/2})]_{t=0} - [\text{Cl}(3^2\text{P}_{1/2})]_{\text{eq}}) \\ \approx \epsilon(\lambda = 136.34 \text{ nm})l[\text{Cl}(3^2\text{P}_{1/2})]_{t=0} \quad (3)$$

where the symbols have their usual meanings. The decay of I_{tr} at $\lambda = 134.72 \text{ nm}$ (e.g. Fig. 2) is computed in a similar manner to yield

$$A = \ln\left(\frac{I_0}{I_{\text{tr}}}\right)_{t=0} \approx \epsilon(\lambda = 134.72 \text{ nm})l[\text{Cl}(3^2\text{P}_{3/2})]_{t=0} \quad (4)$$

Whilst the assumption of the Beer-Lambert law in each case has not been established for these experimental conditions from the construction of curves of growth [37], the line shapes for the two transitions should be very similar given the deliberate choice of the common upper state $(3p)^4(4s)^1, {}^2P_{3/2}$ and the small spin-orbit coupling in $\text{Cl}((3p)^5, {}^2P_J)$.

The relative quantum yields are then determined (in effect via A for both states) through computation of the ratio α from eqns. (3) and (4):

$$\alpha = \frac{\ln(I_0'/I_{tr})_{t=0}(\lambda = 136.34 \text{ nm})}{\ln(I_0/I_{tr})_{t=0}(\lambda = 134.72 \text{ nm})} \approx \frac{\epsilon(\lambda = 136.34 \text{ nm})[\text{Cl}(3 {}^2P_{1/2})]_{t=0}}{\epsilon(\lambda = 134.72 \text{ nm})[\text{Cl}(3 {}^2P_{3/2})]_{t=0}} \quad (5)$$

Attention must now be directed to the ratio of the two extinction coefficients.

The term in the exponent relating the property I_{tr} to I_0 involves a standard line shape integral $\int k_\nu d\nu$ [37], and for atomic chlorine should include the summation of Voigt profiles over the nuclear hyperfine components on account of the nuclear spin $I = 3/2$ in both ${}^{35}\text{Cl}$ (75.4%) and ${}^{37}\text{Cl}$ (24.6%) [38] for the two resonance transitions employed here. The construction of such profiles for radiation trapping calculations has been described in some detail for a range of atomic transitions by Husain and coworkers [39 - 42]. Similar profiles for atomic bromine, but not for chlorine, have been described by Tellinghuisen and Clyne [43]. The deliberate choice of a common upper state connecting with two close-lying spin-orbit components of the overall ground state configuration enables the approximation to be made that the ratio of the extinction coefficients for the experiments is equal to the ratio of the appropriate f values. Clyne and Nip [44, 45] have measured curves of growth for atomic chlorine generated in titrations involving atomic hydrogen and chlorine in a flow discharge system and have reported the following results:

$$\lambda = 136.34 \text{ nm} \quad \text{Cl}((3p)^4(4s)^1, {}^2P_{3/2}) - \text{Cl}((3p)^5, {}^2P_{1/2}) \quad f = (3.8 \pm 0.6) \times 10^{-2}$$

$$\lambda = 134.72 \text{ nm} \quad \text{Cl}((3p)^4(4s)^1, {}^2P_{3/2}) - \text{Cl}((3p)^5, {}^2P_{3/2}) \quad f = (1.0 \pm 0.3) \times 10^{-1}$$

Hence $\epsilon(\lambda = 134.72 \text{ nm})/\epsilon(\lambda = 136.34 \text{ nm}) \approx 2.63 \pm 0.89$. The effect of λ_0^2 [37] on the ratio of the extinction coefficients is negligible (about 2%). Thus from the foregoing and the definition of α

$$\frac{[\text{Cl}(3 {}^2P_{1/2})]_{t=0}}{[\text{Cl}(3 {}^2P_{3/2})]_{t=0}} = 2.63\alpha$$

Table 1 lists all the data for this ratio obtained in the present investigation for the range of concentrations of CF_3Cl , CF_2Cl_2 , CFCl_3 and CCl_4 indicated together with the fraction of $\text{Cl}(3 {}^2P_{1/2})$ of the total atomic

TABLE 1

Relative quantum yields for the broad band photolysis of CF_3Cl , CF_2Cl_2 , CFCl_3 and CCl_4

Freon concentration ($\times 10^{13}$ molecules cm^{-3})	α^a	ϕ^b	F^c
<i>CF₃Cl</i>			
3.6	1.9	5.0 ± 1.7	0.83 ± 0.28
4.8	1.9	5.0 ± 1.7	0.83 ± 0.28
6.3	2.8	7.4 ± 2.5	0.88 ± 0.30
7.7	2.1	5.5 ± 1.9	0.85 ± 0.29
10.6	2.6	6.9 ± 2.3	0.87 ± 0.29
12.1	2.7	7.1 ± 2.4	0.88 ± 0.30
$\phi_{\text{av}} = 6.2 \pm 2.3$			
<i>CF₂Cl₂</i>			
2.8	1.5	3.9 ± 1.3	0.80 ± 0.27
3.6	1.2	3.2 ± 1.1	0.76 ± 0.26
4.6	0.9	2.4 ± 0.8	0.71 ± 0.24
6.2	1.0	2.6 ± 0.9	0.72 ± 0.25
7.3	1.2	3.2 ± 1.1	0.76 ± 0.26
10.3	1.2	3.2 ± 1.1	0.76 ± 0.26
$\phi_{\text{av}} = 3.0 \pm 1.1$			
<i>CFCl₃</i>			
2.6	1.3	3.4 ± 1.1	0.77 ± 0.25
3.7	1.3	3.5 ± 1.2	0.78 ± 0.27
5.1	1.5	3.9 ± 1.3	0.80 ± 0.27
7.4	1.6	4.3 ± 1.5	0.81 ± 0.28
9.2	1.4	3.4 ± 1.4	0.79 ± 0.26
$\phi_{\text{av}} = 3.8 \pm 1.3$			
<i>CCl₄</i>			
4.6	1.3	3.4 ± 1.2	0.77 ± 0.26
6.1	1.3	3.5 ± 1.2	0.78 ± 0.26
7.3	1.7	4.4 ± 1.5	0.81 ± 0.28
8.8	1.3	3.3 ± 1.1	0.77 ± 0.26
10.2	1.4	3.8 ± 1.3	0.79 ± 0.27
12.0	1.5	3.9 ± 1.3	0.80 ± 0.27
$\phi_{\text{av}} = 3.7 \pm 1.3$			

$${}^a\alpha = \frac{\ln(I_0'/I_{\text{tr}})_{t=0} (\lambda = 136.34 \text{ nm})}{\ln(I_0/I_{\text{tr}})_{t=0} (\lambda = 134.72 \text{ nm})}$$

$${}^b\phi = 2.63\alpha = \frac{[\text{Cl}(3^2\text{P}_{1/2})]_{t=0}}{[\text{Cl}(3^2\text{P}_{3/2})]_{t=0}}$$

$${}^cF = \frac{[\text{Cl}(3^2\text{P}_{1/2})]_{t=0}}{[\text{Cl}(3^2\text{P}_{1/2})]_{t=0} + [\text{Cl}(3^2\text{P}_{3/2})]_{t=0}} = \frac{\phi}{1 + \phi}$$

chlorine concentrations generated photochemically. The quoted errors were obtained from the values of 1σ determined from the scatter in the measured ratio of α and the error in the ratio of the f values given above which is

dominant. The data are scattered primarily on account of the low concentrations of $\text{Cl}(3^2\text{P}_{1/2})$ that have to be monitored, but the quantum yields are found, within experimental error, to be sensibly independent of Freon concentration.

In all cases the quantum yields indicate population inversions for the $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ states. These results are comparable with the relative yields for the broad band photolysis of CF_3Br and CF_3I where Wiesenfeld and co-workers report

$$\frac{[\text{Br}(4^2\text{P}_{1/2})]_{t=0}}{[\text{Br}(4^2\text{P}_{3/2})]_{t=0}} = 2$$

for the former [18] and

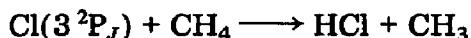
$$\frac{[\text{I}(5^2\text{P}_{1/2})]_{t=0}}{[\text{I}(5^2\text{P}_{3/2})]_{t=0}} = 9$$

for the latter [5, 6]. However, the possibility of constructing an atomic chlorine photochemical dissociation laser operating on the $(3p)^5, ^2\text{P}_{1/2}$ and $(3p)^5, ^2\text{P}_{3/2}$ states based on this type of system is extremely remote on account of collisional removal by the photochemical precursor and presumably photolytic fragments. It is instructive to compare the quenching rate constants of $\text{X}(^2\text{P}_{1/2})$ by CF_3X in this context: $k\{\text{Cl}(^2\text{P}_{1/2}) + \text{CF}_3\text{Cl}\} = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (300 K) [21]; $k\{\text{Br}(^2\text{P}_{1/2}) + \text{CF}_3\text{Br}\} = 1.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (300 K) [18]; $k\{\text{Br}(^2\text{P}_{1/2}) + \text{CF}_3\text{Br}\} = 5.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (300 K) [46]; $k\{\text{I}(^2\text{P}_{1/2}) + \text{CF}_3\text{I}\} = 3.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (300 K) [47]. A high radiation density would require extremely high absolute concentrations of $\text{Cl}(3^2\text{P}_{1/2})$ in order to offset the very low Einstein A coefficient (0.012 s^{-1} [2, 24 - 26]) and this could only be achieved by almost complete photolysis of the chlorinated Freon in view of the high collisional removal efficiencies exhibited by these molecules towards $\text{Cl}(3^2\text{P}_{1/2})$, namely of the order of unity [21]. Indeed, it is the extremely low quenching efficiency of $\text{I}(5^2\text{P}_{1/2})$ by CF_3I [47] that permits the construction of high gain photodissociation atomic lasers using this molecule [48].

The present results bear a close relationship to the photochemical decomposition of chlorinated fluorocarbons, particularly Freons 11 and 12 (CFCl_3 and CF_2Cl_2), in a polluted stratosphere [49 - 52]. Solar emission on the stratosphere can be approximated to a black body of temperature about 5900 K [53]. Christie and Porter [54] have shown that a classical flash-lamp can be approximated to a black body of temperature about 6500 °C. Thus the present results describe overall quantum yields for $[\text{Cl}(3^2\text{P}_{1/2})]/[\text{Cl}(3^2\text{P}_{3/2})]$ effectively integrated over the combination of the light output from a black body of temperature approximately 6500 °C and the UV absorption spectra of the C_1 chlorinated Freons. They are therefore the analogues of similar measurements that have been reported for the heavier halides using broad band flash photolysis (see Section 1). Unfortunately, there are no spectroscopic data available indicating the production of the

specific spin-orbit states of $\text{Cl}(3^2P_J)$ for light absorption of these chlorides either at particular wavelengths in the UV or in defined wavelength regions. Hence we cannot deconvolute the overall measured quantum yields into contributions at various wavelengths. However, as we have indicated above, the overall quantum yields measured in the laboratory approximate to stratospheric conditions.

Atmospheric modelling of the radiative input poses similar difficulties to those normally encountered with the photodissociation of ozone in the UV [49 - 52]. Hudson and Reed [51] have compiled the UV absorption cross sections of the Freons and in particular those for CFCl_3 and CF_2Cl_2 which rise in value from $\lambda \approx 230$ nm into the far UV. Hence the photolytic yields of atomic chlorine depend critically on the solar fluxes on the short wavelength side of the black body emission maximum in a region where such fluxes are decreasing rapidly with decreasing wavelength and therefore need to be determined accurately. Atmospheric modelling at the chemical level, as far as the reactions of the specific spin-orbit states of chlorine are concerned, will be most aided by the present results for abstraction processes by atomic chlorine which are close to thermoneutral and hence in which the spin-orbit energy is significant with respect to the reaction thermochemistry. For example, the activation energy for the process



reported in the compilation by Baulch *et al.* [55] corresponds to a value of 938 cm^{-1} . A recent highly detailed investigation of this reaction by Ravishankara and Wine [56], which is prominent in the compilation by Baulch *et al.* [55], yields an activation energy of $739 \pm 24 \text{ cm}^{-1}$. These activation energies are comparable with a spin-orbit energy of 882 cm^{-1} . Hence, measured reactivities in this type of case may in fact be reflecting the specific reactivity of $\text{Cl}(3^2P_{1/2})$ through k_b (see Section 1). Clearly, atmospheric modelling for $\text{Cl}(3^2P_{3/2})$ and $\text{Cl}(3^2P_{1/2})$ requires both kinetic data on the collisional behaviour of these spin-orbit states [22] and quantum yield measurements of them for which the present results provide an initial basis.

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