

THE DIFFUSION COEFFICIENT OF CHLORINE ATOMS $\text{Cl}(3p^5(^2P_J))$ IN THE GAS PHASE

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Summary

We describe a kinetic study of chlorine atoms in the $3p^5(^2P_J)$ ground state using time-resolved resonance line absorption in the vacuum UV. $\text{Cl}(3^2P_J)$ was generated by the repetitive pulsed irradiation of molecular chlorine in a flow system kinetically equivalent to a static system and monitored photoelectrically at $\lambda = 138.79 \text{ nm}$ ($3p^4 4s(^4P_{5/2}) \leftarrow 3p^5(^2P_{3/2})$) using signal-averaging techniques. A kinetic regime was employed in which first order diffusion of chlorine atoms to the walls completely dominated the competing effect of atomic recombination. The variation of this decay process in helium, coupled with the use of the "long-time solution" of the diffusion equation for a cylinder, was used to measure the diffusion coefficient $D_{1,2}$ of $\text{Cl}(3^2P_J)$ in helium which was found to be $0.43 \pm 0.01 \text{ cm}^2 \text{ s}^{-1}$ at 1 atm ($T = 300 \text{ K}$). The result is compared with that for the diffusion of argon in helium.

1. Introduction

A large body of absolute rate data for reactions of atomic chlorine in the $3p^5$ ground state configuration has been reported in recent years [1] as a result both of fundamental kinetic interest in this species and of the role of chlorine atoms in stratospheric pollution by chlorofluorocarbons (freons) [2, 3]. The atomic diffusion coefficient is clearly of basic concern to the consideration of such gas phase kinetic processes. In this work the measurement of the diffusion coefficient of $\text{Cl}(3^2P_J)$ by resonance line absorption in the vacuum UV in the time-resolved mode is described. Two general considerations of this technique will clarify the nature of the measurement.

(1) Decay rate measurements in which the atom is monitored directly in "real time", as opposed to the use of a mechanistic assumption of a balance between, say, the production of chlorine atoms by a combination of photochemical and kinetic processes and the loss of chlorine atoms by diffusion, ensures that it is the diffusion process that is being studied. In the simplest terms, the decay rate in real time should be inversely proportional to the total pressure. This condition should be satisfied when diffusional decay followed by efficient wall removal dominates gas phase kinetic removal. This is achieved in the present measurements by the low energy photochemical generation of chlorine atoms from Cl_2 under conditions in which the rate of atomic recombination is small.

(2) The rate measurements described here were made on a time scale and in a pressure regime such that spin-orbit relaxation of any photochemically generated chlorine atoms in the $^2\text{P}_{1/2}$ state, 881 cm^{-1} above the $^2\text{P}_{3/2}$ ground state [4], had been completed. This can be seen by reference to the collisional quenching rate data for $\text{Cl}(3\text{p}^5(^2\text{P}_{1/2}))$ [5, 6]. Hence, the two states are in Boltzmann equilibrium in this investigation and it can be shown readily that monitoring of either the $J = \frac{1}{2}$ level or the $J = \frac{3}{2}$ level will lead to identical kinetics. Thus, the resulting rate measurement, in the present case a diffusional rate, describes the behaviour of a Boltzmann averaged system for these two close-lying electronic states. In contrast, rate measurements specific to the $J = \frac{1}{2}$ level can be made provided that a short time scale is employed following the pulsed generation of $\text{Cl}(3^2\text{P}_{1/2})$ before a Boltzmann equilibrium is established [5, 6].

2. Experimental

The experimental arrangement for studying $\text{Cl}(3^2\text{P}_J)$ was similar to that described by Fletcher and Husain [5, 6] for the study of $\text{Cl}(3^2\text{P}_{1/2})$ with some modifications. In contrast with these earlier spin-orbit relaxation studies, which employed CCl_4 as the photochemical precursor [5, 6], atomic chlorine was generated in these experiments by the repetitive pulsed irradiation ($E = 63\text{ J}$, 0.2 Hz) of Cl_2 in the presence of excess helium in a standard coaxial lamp and vessel assembly using a flow system kinetically equivalent to a static system [5, 6]. $\text{Cl}(3^2\text{P}_J)$ was monitored via the resonance transition in the vacuum UV at $\lambda = 138.79\text{ nm}$ ($3\text{p}^44\text{s}(^4\text{P}_{5/2}) \leftarrow 3\text{p}^5(^2\text{P}_{3/2})$) [4] using a microwave-powered atomic emission spectroscopic flow lamp [7, 8] ($p_{\text{Cl}_2} = 2.0\text{ N m}^{-2}$, $p_{\text{He}} = 130\text{ N m}^{-2}$ typically; EMI microwave generator type T 1001; EMI cavity C 111; incident power, 35 W) and was detected photoelectrically by means of a "solar blind" photomultiplier (EMR 541G-08-18) mounted on the exit slit of a 1 m concave grating monochromator (Hilger and Watts E 760). The resulting photoelectric signals, representing transient resonance absorption by $\text{Cl}(3^2\text{P}_{3/2})$, were amplified without distortion [9], were transferred and were stored in a transient recorder (Biomation 610 B) which was interfaced to a 200-point signal averager (Data Laborato-

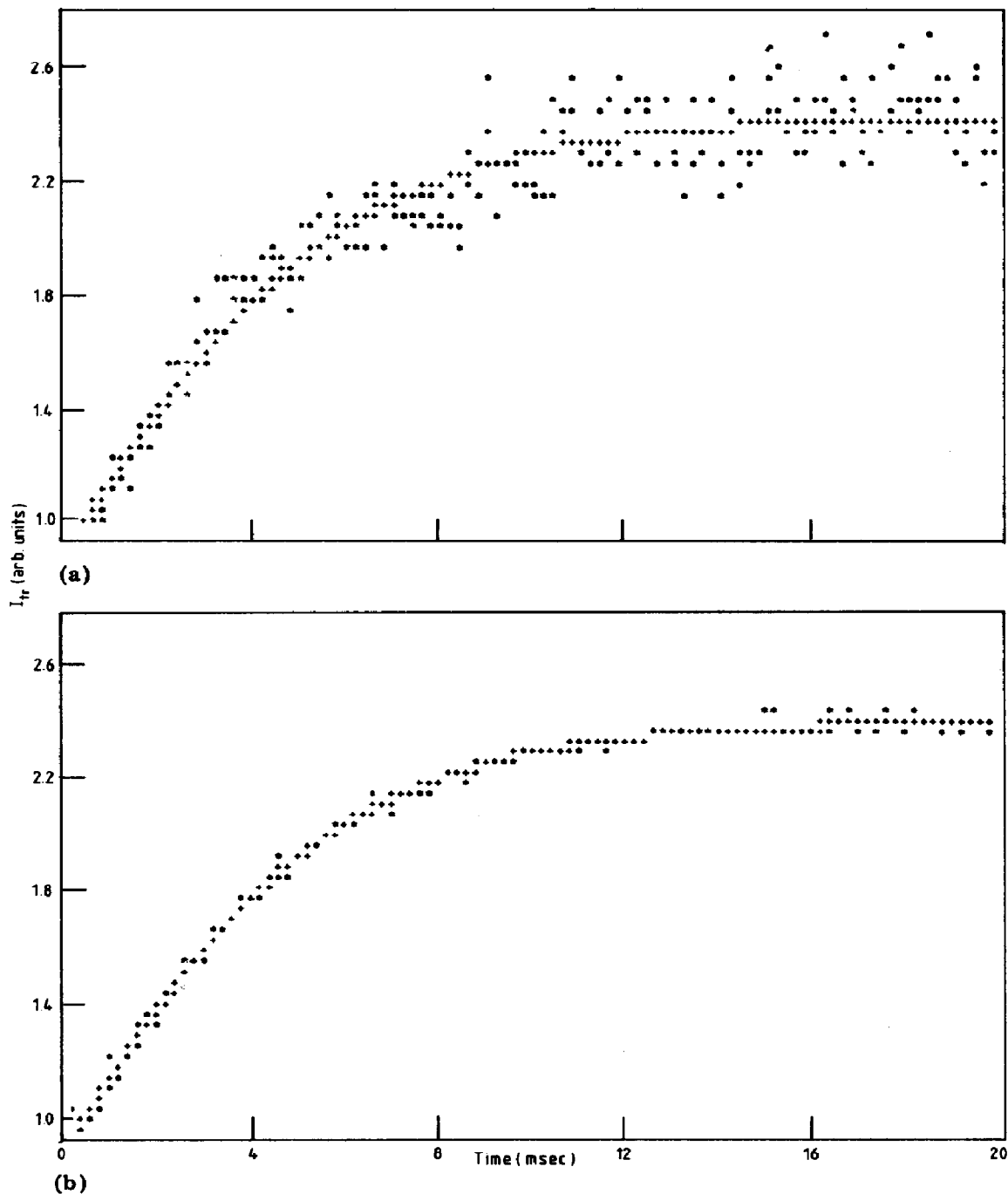


Fig. 1. Digitized time variation of the transmitted light intensity I_{tr} at $\lambda = 138.79$ nm ($\text{Cl}(3p^4 4s(^4P_{5/2})) \rightarrow \text{Cl}(3p^5(^2P_{3/2}))$) indicating the decay of $\text{Cl}(3^2P_J)$ following the pulsed irradiation of molecular chlorine in the presence of helium ($E = 63$ J; repetition rate, 0.2 Hz; $p_{\text{Cl}_2} = 17$ N m $^{-2}$, $p_{\text{total with He}} = 1.05$ kN m $^{-2}$; sweep rate, 100 $\mu\text{s channel}^{-1}$; average of 16 individual experiments): *, experimental data points; +, computerized fitted points; (a) raw data; (b) smoothed data.

ries DL 102A). The contents of the signal averager, representing the results of typically 16 individual experiments on a given flowing reactant mixture, were transferred onto paper tape (Data Dynamics Punch 1133) in binary code for analysis using the University of Cambridge IBM 370/165 computer.

3. Results and discussion

Figure 1(a) shows the result of a typical photoelectric signal at $\lambda = 138.79$ nm indicating the decay of $\text{Cl}(3^2\text{P}_{3/2})$ following the pulsed irradiation of Cl_2 in helium. The data were analysed using the standard Beer-Lambert law directly ($I_{\text{tr}} = I_0 \exp(-\epsilon cl)$) rather than a modified law ($I_{\text{tr}} = I_0 \exp\{-\epsilon(\epsilon l)^\gamma\}$ [10]). γ was found to be extremely difficult to calibrate in these experiments in view of the large scatter in the intercepts of first order kinetic plots derived from decays such as that given in Fig. 1(a); this calibration depends on the reproducibility of *absolute* atomic chlorine concentrations at $t = 0$ in contrast, of course, with the slopes of first order decays which only depend on the time variation of *relative* atomic chlorine concentrations. From an empirical viewpoint the photoelectric signals (e.g. Fig. 1(a)) can be readily fitted by means of the Beer-Lambert law to a first order kinetic decay, *i.e.*

$$[\text{Cl}(3^2\text{P}_{3/2})]_t = [\text{Cl}(3^2\text{P}_{3/2})]_{t=0} \exp(-k't)$$

or

$$\ln\{\ln(I_0/I_{\text{tr}})\}_t = -k't + \text{constant}$$

where k' is the overall first order decay coefficient for $\text{Cl}(3^2\text{P}_j)$ in a given experiment. This can be seen by the inclusion of both the experimental data points and the points resulting from computerized curve fitting in Fig. 1(a) and, more satisfactorily, from the smoothed curve (Fig. 1(b)) which was obtained using the data-smoothing procedure of Patterson [11]. Thus, k' may be derived from the decay of atomic chlorine in the various reaction mixtures investigated using the computerized curve-fitting procedure. We may also note the collisional spin-orbit relaxation time τ_e' for the low excess population of $\text{Cl}(3^2\text{P}_{1/2})$ above the Boltzmann distribution that would be photochemically generated, for example, with the reaction mixture indicated in Fig. 1. Employing the spin-orbit relaxation quenching rate constant for $\text{Cl}(3^2\text{P}_{1/2})$ by Cl_2 obtained by Fletcher and Husain [5] ($k = (4.5 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (300 K)), we see that, for $[\text{Cl}_2] = 17 \text{ N m}^{-2}$, $\tau_e' = 18 \pm 2 \mu\text{s}$ which is negligible compared with the time scale indicated in Fig. 1. The collisional relaxation time is, of course, very rapid compared with the mean radiative lifetime τ_e for spontaneous emission for $\text{Cl}(3^2\text{P}_{1/2}) \rightarrow \text{Cl}(3^2\text{P}_{3/2}) + h\nu$ (881 cm^{-1}), calculated by Husain and Donovan [12] to be 83 s using the standard equations for magnetic dipole emission [13 - 15]. Thus, we are clearly monitoring the kinetic decay of a Boltzmann distribution for $\text{Cl}(3^2\text{P}_j)$ using the resonance transition connected with $\text{Cl}(3^2\text{P}_{3/2})$.

TABLE 1

First order rate coefficients k' for the decay of $\text{Cl}(3^2P_J)$ at various pressures with helium

p_{total} (Torr)	k' (s^{-1})	p_{total} (Torr)	k' (s^{-1})
1.42	1490	7.83	258
1.71	1250	8.50	268
2.29	875	9.74	233
2.39	924	10.90	150
2.92	853	11.50	237
3.39	601	12.30	197
4.29	619	13.00	206
5.87	397	14.90	161
6.70	382	19.40	146
7.79	319		

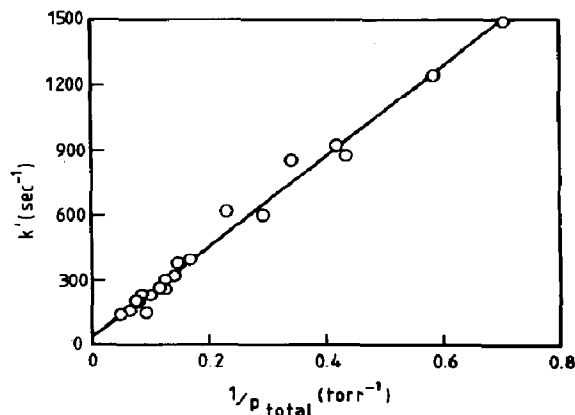
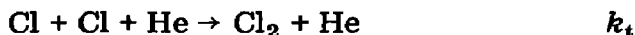


Fig. 2. Variation of the pseudo first order rate coefficient k' for the decay of $\text{Cl}(3p^5(^2P_J))$ in the presence of excess helium, obtained by time-resolved line absorption at $\lambda = 138.79$ nm ($3p^44s(^4P_{5/2}) \leftarrow 3p^5(^2P_{3/2})$) following the pulsed irradiation of Cl_2 .

The resulting measured first order rate coefficients for the decay of $\text{Cl}(3^2P_J)$ in the presence of excess helium are listed in Table 1. Before deriving the diffusion coefficient for atomic chlorine from these data, we stress that the good first order decays that may be fitted to plots of the type given in Fig. 1 are further substantiated both by order-of-magnitude calculations, including the effect of atomic recombination, and (see later) by the plot itself (Fig. 2) from which the diffusion coefficient is derived. Dealing first with the effect of atomic recombination, the removal of atomic chlorine both by first order kinetic decay (k') and by atomic recombination according to the overall processes



yields an integrated rate expression of the form

$$[\text{Cl}]_t = \frac{[\text{Cl}]_{t=0} e^{-k't}}{1 + 2k_t [\text{Cl}]_{t=0} [\text{He}] (1 - e^{-k't}) / k'}$$

An experimentally observed first order decay for atomic chlorine will clearly result if the ratio $R = 2k_t [\text{Cl}]_{t=0} [\text{He}] / k'$ is much less than unity. Taking the most unfavourable case of the last datum point in Table 1 ($p_{\text{He}} = 19.40$ Torr (1 Torr = 133 N m^{-2}), $k' = 146 \text{ s}^{-1}$), an estimate of 1% photolysis of molecular chlorine ($p_{\text{Cl}_2} = 0.05$ Torr) at the energy of 63 J employed here (compared with a previously observed value of 10% for a flash energy of 1500 J [16]) and $k_t = 6 \times 10^{-33} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1}$ [16], we see that $R \approx 8 \times 10^{-4}$.

On the basis of the foregoing, given that the removal of atomic chlorine is governed by diffusion to the walls of the reaction vessel, then the "long-time solution" of the diffusion equation for a cylinder (length $l = 30$ cm, radius $r = 0.95$ cm) yields [17, 18]

$$k' = (\pi^2/l^2 + 2.41^2/r^2)D_{1,2} \approx 5.81 D_{1,2}/r^2$$

as $l^2 \gg r^2$. Since the diffusion coefficient $D_{1,2}$ is inversely proportional to the pressure p , a plot of k' versus $1/p$ should yield a straight line as shown in Fig. 2. Furthermore, the intercept of the plot passes through the origin within experimental error and the slope yields $D_{1,2}(\text{Cl}(3^2\text{P}_j)$ in helium) = $0.43 \pm 0.01 \text{ cm}^2 \text{ s}^{-1}$ at 1 atm.

This type of kinetic method has been used to determine diffusion coefficients of electronically excited iodine atoms $\text{I}(5p^5(^2\text{P}_{1/2}))$ in noble gases [12, 19, 20]. The most sensible quantitative comparison is perhaps that with the result for the diffusion coefficient of the nearest noble gas (argon) in helium where $D_{1,2} = 0.641 \text{ cm}^2 \text{ s}^{-1}$ at 1 atm [21]. The larger intermolecular forces that would be expected between chlorine and helium would, in the simplest terms [21], lead to a lower value for $D_{1,2}$. A quantitative estimate of this, however, such as that arising from the use of the "first approximation Chapman-Enskog equation" [21], would require more fundamental data than at present available in order to calculate the collision diameter $\sigma_{1,2}$ and the appropriate transport integrals $\Omega^{(1,s)*}$ via the interaction energy $\epsilon_{1,2}$ and thus the resulting effect on $D_{1,2}$. Significant differences in $D_{1,2}$ for $\text{Cl}(3^2\text{P}_{3/2})$ and $\text{Cl}(3^2\text{P}_{1/2})$ in helium would not be expected in view of the small energy difference between these two electronic states.

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References

- 1 R. T. Watson, *J. Phys. Chem. Ref. Data*, **6** (3) (1977) 621.
- 2 Halocarbons: effects on stratospheric ozone, *Natl. Acad. Sci. Rep. (U.S.)*, 1976, available from National Academy of Sciences (U.S.), Washington, D.C.
- 3 R. D. Hudson and E. I. Reed (eds.), *The stratosphere: present and future*, *NASA Ref. Publ.*, 1049, 1980, available from NASA Goddard Space Flight Centre.
- 4 C. E. Moore (ed.), *Atomic energy levels*, *Natl. Bur. Stand. (U.S.), Circ. 467*, Vols. I - III, 1958, available from U.S. Government Printing Office, Washington, D.C.
- 5 I. S. Fletcher and D. Husain, *Chem. Phys. Lett.*, **49** (1977) 516.
- 6 I. S. Fletcher and D. Husain, *J. Chem. Soc., Faraday Trans. II*, **76** (1978) 203.
- 7 D. D. Davis and W. Braun, *Appl. Opt.*, **7** (1968) 2071.
- 8 F. C. Fehsenfeld, K. M. Evenson and H. P. Broida, *Rev. Sci. Instrum.*, **36** (1965) 294.
- 9 W. H. Wing and T. M. Sanders, Jr., *Rev. Sci. Instrum.*, **38** (1967) 1341.
- 10 R. J. Donovan, D. Husain and L. J. Kirsch, *Trans. Faraday Soc.*, **66** (1970) 2551.
- 11 T. N. L. Patterson, *Math. Comput.*, **22** (1968) 847.
- 12 D. Husain and R. J. Donovan, *Adv. Photochem.*, **8** (1970) 1.
- 13 G. H. Shortley, *Phys. Rev.*, **57** (1940) 225.
- 14 R. H. Garstang, in D. R. Bates (ed.), *Forbidden Transitions in Atomic and Molecular Processes*, Academic Press, New York, 1962, p. 1.
- 15 R. H. Garstang, *J. Res. Natl. Bur. Stand., Sect. A*, **68** (1964) 61.
- 16 R. P. Widman and B. A. DeGraaff, *J. Phys. Chem.*, **77** (1973) 1325.
- 17 A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms*, Cambridge University Press, London, 1934, p. 24.
- 18 M. W. Zemansky, *Phys. Rev.*, **34** (1929) 213.
- 19 J. J. Deakin, D. Husain and J. R. Wiesenfeld, *Chem. Phys. Lett.*, **10** (1971) 146.
- 20 E. W. Abrahamson, L. J. Andrews, D. Husain and J. R. Wiesenfeld, *J. Chem. Soc., Faraday Trans. II*, **68** (1972) 48.
- 21 J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.