**DETERMINATION OF BRANCHING
RATIOS IN A KINETIC INVESTIGATION
OF THE ATOMIC RESONANCE
FLUORESCENCE AND MOLECULAR
CHEMILUMINESCENCE,
 $\text{CaCl}(A^2\Pi_{1/2,3/2}, B^2\Sigma^+ \rightarrow X^2\Sigma^+)$, RESULTING
FROM THE REACTION
OF $\text{Ca}[4s4p(^3P_J)]$ WITH CH_3Cl FOLLOWING
PULSED DYE LASER EXCITATION
OF ATOMIC CALCIUM**

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Measurements in the time-domain of molecular chemiluminescence from $\text{CaCl}(A^2\Pi_{1/2}, A^2\Pi_{3/2}, B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ and atomic resonance fluorescence from $\text{Ca}(4^3P_1 \rightarrow 4^1S_0)$ have been made in order to determine electronic branching ratios to yield $\text{CaCl}(A_{1/2}, A_{3/2}, B)$ following the Cl-atom abstraction reaction of electronically excited calcium atoms, $\text{Ca}[4s4p(^3P_J)]$, 1.888 eV above the $4s^2(^1S_0)$ ground state, with CH_3Cl . $\text{Ca}[4s4p(^3P_1)]$ was generated by the pulsed dye-laser excitation of ground state calcium atoms at $\lambda = 657.3 \text{ nm}$ $\{\text{Ca}[4s4p(^3P_1)] \leftarrow \text{Ca}[4s^2(^1S_0)]\}$ at elevated temperatures in the presence of CH_3Cl and excess helium buffer gas in a slow flow system, kinetically equivalent to a static system. Atomic and molecular emissions were recorded following rapid Boltzmann equilibration within the $\text{Ca}(4^3P_{0,1,2})$ spin-orbit manifold, atomic emission being restricted to the 3P_1 state as the 3P_0 and 3P_2 states are long-lived, being so called 'reservoir states'. Atomic fluorescence emission profiles at the resonance wavelength together with the molecular chemiluminescence emissions $\text{CaCl}(A^2\Pi_{1/2} \rightarrow X^2\Sigma^+, \Delta v = 0, \lambda = 621 \text{ nm})$,

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$\text{CaCl}(A^2\Pi_{3/2} \rightarrow X^2\Sigma^+, \Delta\nu=0, \lambda=618\text{ nm})$ and $\text{CaCl}(B^2\Sigma^+ \rightarrow X^2\Sigma^+, \Delta\nu=0, \lambda=593\text{ nm})$ were recorded. The atomic and molecular emissions demonstrated exponential decays characterised by decay coefficients which were equal under identical chemical conditions thus demonstrating the production of $\text{CaCl}(A^2\Pi_{1/2,3/2}, B^2\Sigma^+)$ by direct reaction of $\text{Ca}(^3P_1)$ with CH_3Cl . The combination of the time-dependences of the atomic and molecular profiles as a function of the concentration of CH_3Cl together with the integrated atomic and molecular intensities, placed on a common intensity scale by calibration of the optical system against a spectral radiometer, yielded branching ratios into the $A^2\Pi_{1/2}$, $A^2\Pi_{3/2}$ and $B^2\Sigma^+$ states of CaCl . These were found to be as follows: $A_{1/2} (2.6 \pm 1.1) \times 10^{-3}$; $A_{3/2} (1.9 \pm 0.8) \times 10^{-3}$ and $B (3.6 \pm 2.0) \times 10^{-4}$. To the best of our knowledge, these data represent the first measurements of electronic branching ratios of calcium chlorides into specific molecular states for reactions of $\text{Ca}(4^3P_1)$ determined in the time-domain. The results are compared with various related data for total branching ratios into electronic states studied in the single collision condition for this atomic state with CH_3Cl using molecular beams. These are also compared with branching ratios of $\text{SrCl}(A^2\Pi_{1/2}, A^2\Pi_{3/2}, B^2\Sigma^+)$ following the reaction of $\text{Sr}[5s5p(^3P_1)] + \text{CH}_2\text{Cl}_2$ investigated following pulsed dye-laser excitation where the yields of $\text{SrCl}(A_{1/2}, A_{3/2}, B)$ were of similar low magnitudes.

Keywords: CaCl molecular chemiluminescence; Electronically excited Ca ; Atomic resonance fluorescence; Laser excitation; Molecular electronic branching ratios

1. INTRODUCTION

Measurements of the collisional behaviour of electronically excited alkaline earth atoms in low lying, optically metastable states using molecular beams in the single-collision condition [1–9] and in the time-domain following pulsed dye-laser excitation [10–13] is an area that has been reviewed in some detail from both the experimental and theoretical viewpoints [10–13]. In particular, the collisional behaviour of electronically excited calcium atoms in their low lying $\text{Ca}[4s4p(^3P_1)]$ state, 1.888 eV above the $4s^2(^1S_0)$ ground state [14], with alkyl halides, has been investigated in the time-domain in order to study the electronic energy distribution in the diatomic products following halogen atom abstraction [15–18]. These studies were limited to comparisons of the time-resolved atomic fluorescence from $\text{Ca}(4^3P_1)$ and time-resolved molecular chemiluminescence from $\text{CaX}(A^2\Pi, B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ following the pulsed dye-laser generation of the atomic state for mechanistic interpretation of the collisional processes. Measurements of branching ratios on collision into specific molecular product quantum states for this type of chemical system for reactions of $\text{Ca}(4^3P_1)$ in particular, whether from investigations in the time-domain or using single collision conditions, are limited. Dagdigian and co-workers [8] have studied the reactions of $\text{Ca}(4^3P_1)$ with Cl_2 , CH_3Cl ,

CH_3Br , CH_2Br_2 , $\text{CH}_2 = \text{CHCH}_2\text{Br}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ using molecular beams. Chemiluminescence cross sections were used to characterise the total electronic branching ratios into all the accessible excited states, $\text{CaX}(A^2\Pi_{1/2, 3/2}, B^2\Sigma^+)$, by these authors [8]. Gonzalez Ureña *et al.* [19] have studied the reactions $\text{Ca}(^1\text{D}_2, ^3\text{P}_J) + \text{CH}_3\text{I} \rightarrow \text{CaI}(A, B) + \text{CH}_3$ under beam-gas conditions and report an electronic branching ratio of $r = \text{CaI}(A^2\Pi)/\text{CaI}(B^2\Sigma^+) = 1.35$ for $\text{Ca}(^1\text{D}_2)$ and $\text{Ca}(^3\text{P}_J)$ in both cases.

Measurements of the time-resolved atomic fluorescence and molecular chemiluminescence following the reaction of $\text{Ca}(4^3\text{P}_J) + \text{CH}_3\text{X}$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) [15–18] indicated that $\text{CaX}(A^2\Pi_{1/2, 3/2}, B^2\Sigma^+)$ arise from direct reaction rather than secondary processes involving electronic energy transfer and can thus be related to analogous studies on energy distribution in molecular beams. These studies, in some cases, are in contrast to analogous later measurements in the time-domain on the reactions $\text{Sr}(5^3\text{P}_J)$ [20–24], 1.807 eV above the $5s^2(^1\text{S}_0)$ ground state, following pulsed dye-laser excitation of atomic strontium in the presence of various halides which did yield molecular electronic product branching ratios. This arose from improvements in data capture and optical calibrations [20–24]. This type of experimental development is now employed in this paper to characterise molecular electronic branching ratios yielding $\text{CaCl}(A^2\Pi_{1/2, 3/2}, B^2\Sigma^+)$ following the reactions of $\text{Ca}(4^3\text{P}_J)$ with CH_3Cl . The results are compared with related results for reactions of $\text{Ca}(4^3\text{P}_J)$ in molecular beams and branching ratio measurements for $\text{Sr}(5^3\text{P}_J)$ with halides in the time-domain [20–24], particularly the production of $\text{SrCl}(A^2\Pi_{1/2, 3/2}, B^2\Sigma^+)$ from the reactions of $\text{Sr}(5^3\text{P}_J)$ with CH_2Cl_2 [21].

2. EXPERIMENTAL

Measurements of molecular electronic branching ratios in the present system require a combination of the comparisons of time-dependences for atomic and molecular emissions together with determinations of the integrated intensities using an optically calibrated system. Thus, the general experimental arrangement for monitoring atomic resonance fluorescence and molecular chemiluminescence in the time-domain following the reaction of $\text{Ca}(4^3\text{P}_J)$ with CH_3Cl is a combination of that described hitherto for this atomic state [15–18]

together with that used for the study of $\text{Sr}(5^3\text{P}_j)$ and leading to molecular electronic branching ratios [20–24]. $\text{Ca}[4s4p(^3\text{P}_1)]$ was generated by the pulsed dye-laser excitation (10 Hz) of calcium vapour at elevated temperature ($T = 940\text{ K}$) at $\lambda = 657.3\text{ nm}$ $\{\text{Ca}[4s4p(^3\text{P}_1)] \leftarrow \text{Ca}[4s^2(^1\text{S}_0)]\}$ in the presence of methyl chloride and excess helium buffer gas in a slow flow system, kinetically equivalent to a static system. Atomic emission at the resonance wavelength and molecular chemiluminescence from the states $\text{CaCl}[(A^2\Pi_{1/2, 3/2}, B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ were then monitored using the standard combination of a small monochromator and a photomultiplier under identical chemical conditions. The atomic and molecular emission profiles were recorded by data capture of the complete profiles for each individual decay using a two-channel transient digitiser (Digital Storage Adapter, Thurlby DSA 524) in contrast with earlier studies on $\text{Ca}(^3\text{P}_j)$ using boxcar integration [15–18]. 256 decay profiles were averaged as were 256 background profiles before subtraction and interfaced into a computer for data analysis. The materials (Ca, 99%; He, 99.999%; CH_3Cl Aldrich) were employed essentially as described in a previous investigations [16].

Whilst comparison of the time dependences of the atomic and molecular emission profiles could be made using arbitrary intensity scales for each, measurements of the integrated molecular and atomic intensities for the purpose of determining branching ratios required that these be placed on a common intensity scale. Thus the optical and detection system was calibrated both with respect to electronic gain and wavelength sensitivity for measurements of the integrated molecular and atomic intensities derived from the recorded decay profiles. Measurements were made using significantly different photomultiplier voltages for the atomic and molecular profiles especially on account of the relatively small branching ratios into the excited molecular states and the resulting weak emission compared with that of the atomic fluorescence. The molecular profiles were thus recorded at p.m. voltages considerably higher than those of the atomic emission. The gain (G) for the p.m. tube (E.M.I., 9797B) as a function of voltage was taken from the commercial calibration expressed in the form $\ln(G/\text{arb. units}) = 8.7 \ln(V/\text{Volts}) - 54.4$ [25]. The wavelength response of the photomultiplier-grating combination ('Minichrom' monochromator, MC1-02-10288, Fastie-Ebert mounting) was calibrated

against a 'xenophot' lamp that had, in turn, been calibrated against a spectral radiometer (International Light Inc., USA IL 783). This yielded two peaks in the sensitivity response curve, one at ca. 460 nm and the other at ca. 540 nm [20–24], representing the expected combination of the grating response for the monochromator and the maximum response for the p.m. tube. In contrast to the previous time-resolved investigation on $\text{Ca}(^3\text{P}_1) + \text{CH}_3\text{Cl}$ using the largest pair of slits (600 μm) for the monochromator [16], a smaller pair of slits (300 μm) were employed in these measurements in order to increase the wavelength resolution for the recorded chemiluminescence profiles, particularly for two close-lying spin-orbit components of $\text{CaCl}(A^2\Pi)$. The data capture system using the transient digitiser indicated above was more efficient than boxcar integration in the previous time-dependent studies on $\text{Ca}(4^3\text{P}_J) + \text{CH}_3\text{X}$ with recording of the complete emission profiles and the use of smaller slits necessary for optical isolation of the chemiluminescence of the molecular spin-orbit states.

3. RESULTS AND DISCUSSION

3.1. Time-dependence of the Atomic Resonance Fluorescence,

$\text{Ca}[4s4p(^3\text{P}_1) \rightarrow 4s^2(^1\text{S}_0)]$ and the Molecular

Chemiluminescence, $\text{CaCl}(A^2\Pi_{1/2}, A^2\Pi_{3/2}, B^2\Sigma^+ \rightarrow X^2\Sigma^+)$

Figure 1(a) gives an example of the digitised output showing the time-resolved variation of intensity of the atomic resonance fluorescence emission from atomic calcium $\{\text{Ca}[4s4p(^3\text{P}_1)] \rightarrow \text{Ca}[4s^2(^1\text{S}_0)]\}$ at $\lambda = 657.3 \text{ nm}$ following the pulsed dye-laser excitation of calcium vapour at $T = 940 \text{ K}$ in the presence of CH_3Cl and excess helium buffer gas. Figures 1(b)–(d) gives examples of the accompanying digitised output for the molecular chemiluminescence emissions from $\text{CaCl}(A^2\Pi_{1/2} \rightarrow X^2\Sigma^+, \Delta v = 0, \lambda = 621 \text{ nm})$, $\text{CaCl}(A^2\Pi_{3/2} \rightarrow X^2\Sigma^+, \Delta v = 0, \lambda = 618 \text{ nm})$ and $\text{CaCl}(B^2\Sigma^+ \rightarrow X^2\Sigma^+, \Delta v = 0, \lambda = 593 \text{ nm})$, respectively, recorded under identical chemical conditions to that given for the atomic emission. Figures 2(a)–(d) show the logarithmic plots as a function of time, constructed from the raw data given in Figure 1, indicating their first-order nature of the removal of

FIGURE 1 Examples of the digitised output indicating the exponential decay profiles for the time-resolved atomic fluorescence emission and the molecular chemiluminescence following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength $\{\text{Ca}[4s4p(^3P_1)] \leftarrow \text{Ca}[4s^2(^1S_0)], \lambda = 657.3 \text{ nm}\}$ in the presence of CH_3Cl and excess helium buffer gas at elevated temperature. $T = 940 \text{ K}$. $[\text{CH}_3\text{Cl}] = 1.7 \times 10^{16} \text{ molecules cm}^{-3}$, $p_{\text{Total with He}} = 60 \text{ Torr}$. (a) $\text{Ca}[4s4p(^3P_1)] \rightarrow \text{Ca}[4s^2(^1S_0)]$, $\lambda = 657.3 \text{ nm}$. (b) $\text{CaCl}(A^2\Pi_{1/2} \rightarrow X^2\Sigma^+, \Delta v = 0, 621 \text{ nm})$. (c) $\text{CaCl}(A^2\Pi_{1/2} \rightarrow X^2\Sigma^+, \Delta v = 0, 618 \text{ nm})$. (d) $\text{CaCl}(B^2\Sigma^+ \rightarrow X^2\Sigma^+, \Delta v = 0, 593 \text{ nm})$.

$\text{Ca}(^3P_J)$ and $\text{CaCl}(A_{1/2, 3/2}, B)$. A quantitative comparison of the first-order decay coefficients for the atomic and molecular decays taken from slopes of plots of the type given in Figure 2 are presented for the study overall in Figure 3. The slope of the resulting plot, placed through the origin, which is a physically realistic point, is unity within experimental error ($\pm 10\%$), indicating that the first-order decay coefficients for the atomic and molecular decays are equal.

Boltzmann equilibrium within the three spin-orbit levels of $\text{Ca}(^3P_{0,1,2})$ is rapidly established on the time scales of the present measurements by collisions with helium gas [26, 27] and is further facilitated by molecular collisions with the presence of the molecular reactant, CH_3Cl . The first-order atomic decay coefficient, k' , may

FIGURE 2 Examples of the computerised fitting indicating the first-order decay profiles of the time-resolved atomic fluorescence emission and the molecular chemiluminescence following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength $\{Ca[4s4p(^3P_1)] \leftarrow Ca[4s^2(^1S_0)], \lambda = 657.3 \text{ nm}\}$ in the presence of CH_3Cl and excess helium buffer gas at elevated temperature. $T = 940 \text{ K}$. $[CH_3Cl] = 1.7 \times 10^{16} \text{ molecules cm}^{-3}$, $p_{\text{Total with He}} = 60 \text{ Torr}$. (a) $Ca[4s4p(^3P_1)] \rightarrow Ca[4s^2(^1S_0)]$, $\lambda = 657.3 \text{ nm}$. (b) $CaCl(A^2\Pi_{1/2} \rightarrow X^2\Sigma^+, \Delta v = 0, 621 \text{ nm})$. (c) $CaCl(A^2\Pi_{3/2} \rightarrow X^2\Sigma^+, \Delta v = 0, 618 \text{ nm})$. (d) $CaCl(B^2\Sigma^+ \rightarrow X^2\Sigma^+, \Delta v = 0, 593 \text{ nm})$.

be given by the standard expression:

$$k' = A_{nm} / (1 + 1/K_1 + K_2) + \beta/p_{\text{He}} + \Sigma k_Q[Ca(^1S_0), \text{He}] + k_R \varepsilon[CH_3Cl] \quad (1)$$

$A_{nm}(=1/\tau_e)$ is the Einstein coefficient for emission from $Ca(^3P_1)$, K_1 and K_2 represent equilibrium constants connecting the 3P_0 and 3P_1 states, and the 3P_1 and 3P_2 states, readily calculated by statistical thermodynamics at a given temperature. The 3P_0 and 3P_2 states are called 'reservoir states' and emission from them can be neglected [28]. The term in β describes diffusional loss out of the region of optical observation. k_R is the absolute second-order rate constant for the total collisional removal of $Ca(^3P_J)$ by CH_3Cl . The term involving

FIGURE 3 Comparison of the first-order rate coefficients for the time-resolved molecular chemiluminescence from $\text{CaCl}(A^2\Pi_{1/2,3/2}, B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ and the time-resolved atomic fluorescence emission from $\text{Ca}(4^3P_1)$ at $\lambda = 657.3 \text{ nm}$ following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength $\{\text{Ca}[4s4p(^3P_1)] \leftarrow \text{Ca}[4s^2(^1S_0)], \lambda = 657.3 \text{ nm}\}$ in the presence of varying concentrations of CH_3Cl and excess helium buffer gas at elevated temperature. $T = 940 \text{ K}$. p_{Total} with $\text{He} = 60 \text{ Torr}$.

Σk_Q describes collisional quenching of $\text{Ca}(^3P_J)$ principally by ground state calcium atoms. The exact concentration of CH_3Cl in the excitation region of the reactor is unknown due to the loss of this species by reaction with gaseous ground state $\text{Ca}(^1S_0)$ atoms [29] before entry into the region of optical laser excitation. However, the determination of the mechanism of this reaction system firstly relies on comparisons between the first-order decay coefficients of the atomic and molecular emission profiles under identical conditions. The absolute concentration of CH_3Cl is not required. One procedure for characterisation of the branching ratios depends on a monotonic variation of k' and $[\text{CH}_3\text{Cl}]$. This is parameterised using ε , the fraction of the initial $[\text{CH}_3\text{Cl}]$ entering the excitation zone which, within experimental error, is a constant in these measurements. At constant total pressure, fixed temperature and fixed laser pulse output, Eq. (1) may be simplified as

$$k' = K + k_R \varepsilon [\text{CH}_3\text{Cl}] \quad (2)$$

where K is a constant. Figure 4 shows the variation of k' with $[\text{CH}_3\text{Cl}]$ (initial) but this cannot be used to determine an accurate value of the

FIGURE 4 Variation of the pseudo first-order rate coefficient, k'_{657} , for the decay of $\text{Ca}(4^3\text{P}_J)$ in the presence of CH_3Cl at elevated temperature following pulsed dye-laser excitation of calcium vapour at the resonance wavelength $\{\text{Ca}[4s4p(^3\text{P}_J)] \leftarrow \text{Ca}[4s^2(^1\text{S}_0)]$, $\lambda = 657.3 \text{ nm}$ at elevated temperature. $T = 940 \text{ K}$. $p_{\text{Total with He}} = 60 \text{ Torr}$.

rate constant for the reaction of $\text{Ca}(^3\text{P}_J)$ with CH_3Cl for the reasons given.

The first-order decay of $\text{Ca}(4^3\text{P}_J)$ in the presence of CH_3Cl (Fig. 2(a)) can be expressed as

$$[\text{Ca}(^3\text{P}_J)]_t = [\text{Ca}(^3\text{P}_J)]_{t=0} \exp(-k't) \quad (3)$$

where the first-order decay coefficient for $[\text{Ca}(^3\text{P}_J)]$, k' , is given by Eq. (2). Atomic emission only arises essentially from one spin-orbit level, $^3\text{P}_1$, in the $\text{Ca}(^3\text{P}_J)$ manifold [28] and hence the atomic emission intensity is given by the form [15–18]:

$$I_{em}(^3\text{P}) = \{A_{nm}/F\}[\text{Ca}(^3\text{P}_J)]_{t=0} \exp(-k't) \quad (4)$$

where $A_{nm} = 1/\tau_e$ for $\text{Ca}(^3\text{P}_1 - ^1\text{S}_0)$ and $F = (1 + 1/K_1 + K_2)$ [15–18]. A_{nm} has been characterised separately in this work from measurements of atomic decay profiles similar to that in Figure 1(a) at different temperatures yielding $\tau_e = 1/A_{nm} = 0.36 \text{ ms}$, a value in very close accord with a wide range of measurements obtained in

the time-domain [10]. $F = 1 + 1/K_1 + K_2 = 2.778$ at $T = 940$ K, calculated by statistical thermodynamics.

Determination of the branching ratios into the $A^2\Pi_{1/2}$, $A^2\Pi_{3/2}$ and $B^2\Sigma^+$ states of CaCl, and also an upper limit for the $X^2\Sigma^+$ ground state, requires characterisation of the first-order atomic and molecular decay profiles under identical conditions with CH_3Cl concentration. Clay and Husain [27] have studied the reaction of $\text{Ca}[4s^2(^1S_0)] + \text{CH}_3\text{Cl}$ using time-resolved atomic resonance absorption measurements on $\text{Ca}(4^1P_1 \leftarrow 4^1S_0, \lambda = 422.7 \text{ nm})$ following generation of ground state atomic calcium by flash photodissociation of a calcium halide. From the absolute rate constant for reaction reported by those authors [27], $k_R[\text{Ca}(^1S_0) + \text{CH}_3\text{Cl}] = (3.7 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $T = 900$ K, it is clear that, under the present experimental conditions (Fig. 4), a significant reduction in the initial CH_3Cl concentration from a typical initial value of ca. $10^{16} \text{ molecules cm}^3$ takes place on reaction with ground state atomic calcium. This results in part from the high equilibrium vapour pressure of atomic calcium above the calcium samples in these measurements (ca. 52 mTorr at 940 K, $6 \times 10^{14} \text{ atoms cm}^{-3}$ [30]). Hence, absolute rate data for the collisional removal of $\text{Ca}(^3P_J)$ with CH_3Cl cannot be quantified in the present measurements, however, the slope of the plot Figure 4 can be employed to estimate branching ratios into the $A^2\Pi_{1/2}$, $A^2\Pi_{3/2}$ and $B^2\Sigma^+$ ground states of CaCl and also used to obtain an upper limit for the branching ratio into the $X^2\Sigma^+$ ground state.

Only the $A^2\Pi$ and $B^2\Sigma^+$ states of CaCl are energetically accessible on direct Cl abstraction by $\text{Ca}(4^3P_J)$ with CH_3Cl . Marginal differences in the thermochemistry and the accessible vibrational states within $\text{CaCl}(A^2\Pi_{1/2, 3/2}, B^2\Sigma^+)$ naturally arise from the value used for the bond dissociation energy of CaCl. Here the recent value adopted by Furio *et al.* [8] of $D_0^\circ[\text{CaCl}(X^2\Sigma^+)] = 4.18 \pm 0.13 \text{ eV}$ ($403.3 \pm 12.5 \text{ kJ mol}^{-1}$) will be used. This, together with the value for the bond dissociation energy of CH_3Cl ($D(\text{CH}_3\text{-Cl}) = 3.625 \text{ eV}$, $349.8 \text{ kJ mol}^{-1}$ [31]) yields the thermochemistry for the reaction

Significant levels of vibrational excitation within the $A^2\Pi$ and $B^2\Sigma^+$ states of CaCl are accessible on reaction (T_e/cm^{-1} : $X^2\Sigma^+, 0$;

$A^2\Pi_{1/2}$, 16,093.7; $A^2\Pi_{3/2}$, 16,163.2; $B^2\Sigma^+$, 16,849.4 [31])

CaCl($A^2\Pi$) and CaCl($B^2\Sigma^+$) cannot be generated by electronic energy transfer between Ca($^3\text{P}_J$) (1.888 eV, 182.2 kJ mol⁻¹) and ground state CaCl($X^2\Sigma^+$, $v'' = 0$) resulting from the overall reaction.

Relative intensities of the vibronic bands within the *A-X* and *B-X* systems may be estimated from calculations of Franck–Condon factors. Möller *et al.* [33] have characterised the spectroscopic constants for the ground state using microwave spectroscopy from which one may extract some of the data required for the Franck–Condon calculations ($X^2\Sigma^+$: $\omega_e'' = 370.1\text{ cm}^{-1}$, $\omega_e''x_e'' = 1.3732\text{ cm}^{-1}$, $r_e'' = 0.24353\text{ nm}$) [33, 34]. Berg *et al.* [35, 36] have characterised the spectroscopic constants for CaCl($A^2\Pi$, $B^2\Sigma^+$) from laser spectroscopic investigations of the *A-X* and *B-X* systems ($A^2\Pi$: $\omega_e' = 373.16\text{ cm}^{-1}$, $\omega_e'x_e' = 1.4972\text{ cm}^{-1}$, $r_e' = 0.2405\text{ nm}$; $B^2\Sigma^+$: $\omega_e' = 367.196\text{ cm}^{-1}$, $\omega_e'x_e' = 1.524\text{ cm}^{-1}$, $r_e' = 0.24157\text{ nm}$). Franck–Condon factors (f) have been calculated using these data for transitions within the *A-X* and *B-X* systems on the basis of a Morse potential [37]. Some examples of these are given as follows: CaCl(*A-X*), $f(0, 0) = 0.9105$, $f(1, 1) = 0.7512$, $f(2, 2) = 0.6184$, $f(1, 0) = 8.201 \times 10^{-2}$, $f(2, 0) = 6.835 \times 10^{-3}$, $f(3, 0) = 5.566 \times 10^{-4}$, $f(0, 1) = 8.778 \times 10^{-2}$; CaCl(*B-X*), $f(0, 0) = 0.9625$, $f(1, 1) = 0.8933$, $f(0, 1) = 3.753 \times 10^{-2}$, $f(0, 2) = 3.898 \times 10^{-5}$. Thus the intensity of any molecular chemiluminescence should be concentrated in the $\Delta v = 0$ sequences, with those for $\Delta v = 1$ and 2 being significantly weaker.

3.2. Molecular Electronic Branching Ratios for CaCl($A^2\Pi_{1/2}$, $A^2\Pi_{3/2}$, $B^2\Sigma^+$)

Molecular electronic branching ratios into CaCl($A_{1/2}$, $A_{3/2}$, *B*) from the reaction Ca($^3\text{P}_J$) + CH₃Cl are determined using measurements of the integrated atomic and molecular intensities derived from the recorded decay profiles. As in related investigations on branching ratios for reactions of Sr[5s5p($^3\text{P}_J$)] with halides in the time-domain [20–24], the integration of the appropriate rate equations leading to the intensities

of atomic and molecular states are presented here without immediate correction for the response of the optical system at different wavelengths and the electronic gain of the photomultiplier at different operating voltages but these corrections are included in obtaining the final values of the integrated intensities. The mean radiative lifetimes (τ'_e) of the molecular states $\text{CaCl}(A^2\Pi_{1/2}, A^2\Pi_{3/2}, B^2\Sigma^+)$ have been characterised (τ'_e/ns : $A^2\Pi_{1/2}$ 29.5 [38], 29.4 [39]; $A^2\Pi_{3/2}$ 28.4 [39]; $B^2\Sigma^+$ 44.8 [40], 38.2 [39]). The short radiative lifetimes of these species permits the densities of these emitting states to be placed in steady state within the time-scales employed in the present investigations, namely, short relative to the mean radiative lifetime, τ_e , of $\text{Ca}[4s4p(^3P_1)]$ and its overall first-order decay coefficient (Eq. (1)). Thus, taking $\text{CaCl}(A^2\Pi_{1/2})$ as an example,

$$-d[\text{CaCl}(A_{1/2})]/dt = k_1[\text{Ca}(^3P_J)]\varepsilon[\text{CH}_3\text{Cl}] - A'_{nm}[\text{CaCl}(A_{1/2})] = 0 \quad (5)$$

where $A'_{nm} = 1/\tau'_e$ for $\text{CaCl}(A^2\Pi_{1/2})$. The molecular emission intensity from $\text{CaCl}(A_{1/2} - X)$ is thus given by

$$I_{em}(A_{1/2} - X) = k_1\varepsilon[\text{CH}_3\text{Cl}][\text{Ca}(^3P_J)]_{t=0} \exp(-k't) \quad (6)$$

where k_1 is the rate constant for the production of $\text{CaCl}(A^2\Pi_{1/2})$. The integrated molecular intensity from Eq. (6) is then given by

$$I(A_{1/2} - X) = k_1\varepsilon[\text{CH}_3\text{Cl}][\text{Ca}(^3P_J)]_{t=0}/k' \quad (7)$$

The atomic integrated intensity from Eq. (4) is given by

$$I(^3P_J) = A_{nm}[\text{Ca}(^3P_J)]_{t=0}/k'F \quad (8)$$

From Eqs. (7) and (8), the ratio of the integrated molecular intensity for $\text{CaCl}(A_{1/2} - X)$ to that of the ($^3P_1 - ^1S_0$) atomic fluorescence emission is then given by

$$I(A_{1/2} - X)/I(^3P_J) = k_1\varepsilon(F/A_{nm})[\text{CH}_3\text{Cl}] \quad (9)$$

Hence, it may further be seen that the ratio of the slopes of the plots of (1): $I(A_{1/2} - X)/I(^3P_J)$ versus $[\text{CH}_3\text{Cl}]$ (Fig. 5(a)) (Eqs. (8) and (9)) and (2) k' versus $[\text{CH}_3\text{Cl}]$ (Fig. 4) (Eq. (2)), yields the branching ratio for

FIGURE 5 Variation of the integrated intensity ratios of the molecular chemiluminescence emissions to the atomic fluorescence emission $\text{Ca}(4^3\text{P}_1 \rightarrow 4^1\text{S}_0)$ ($\lambda = 657.3 \text{ nm}$) for (a) $\text{CaCl}(A^2\Pi_{1/2} \rightarrow X^2\Sigma^+, \Delta\nu = 0, \lambda = 621 \text{ nm})$, (b) $\text{CaCl}(A^2\Pi_{3/2} \rightarrow X^2\Sigma^+, \Delta\nu = 0, \lambda = 618 \text{ nm})$ and (c) $\text{CaCl}(B^2\Sigma^+ \rightarrow X^2\Sigma^+, \Delta\nu = 0, \lambda = 593 \text{ nm})$ as a function of the concentration of CH_3Cl following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength ($\lambda = 657.3 \text{ nm}$) in the presence of excess helium buffer gas at elevated temperature. ($T = 940 \text{ K}$, $p_{\text{Total with He}} = 60 \text{ Torr}$).

the, formation of $\text{CaCl}(A^2\Pi_{1/2})$, namely,

$$r_{A_{1/2}} = (A_{nm}/F) \text{ slope (1)}/\text{slope (2)} \quad (10)$$

where $r_{A_{1/2}} = k_1/k_R$, the rate of production of $\text{CaCl}(A^2\Pi_{1/2})$ from the reaction of $\text{Ca}(^3\text{P}_J)$ by CH_3Cl relative to the total removal rate of $\text{Ca}(^3\text{P}_J)$ by this molecule.

Considering now all three states, $\text{CaCl}(A_{1/2}, A_{3/2}, B)$, Figure 5 shows the variation of the integrated intensity ratios of the molecular chemiluminescence emissions to that of the atomic fluorescence emission $\text{Ca}(4^3\text{P}_1 \rightarrow 4^1\text{S}_0)$ ($\lambda = 657.3 \text{ nm}$) as a function of the concentration of CH_3Cl following the pulsed dye-laser excitation of

calcium vapour in the presence of excess helium buffer gas at $T = 940\text{ K}$. The plots yield slopes of 4.3×10^{-19} , 3.1×10^{-19} and $6.0 \times 10^{-20}\text{ cm}^3\text{ molecule}^{-1}$ for the emissions $\text{CaCl}(A^2\Pi_{1/2} \rightarrow X^2\Sigma^+)$, $\text{CaCl}(A^2\Pi_{3/2} \rightarrow X^2\Sigma^+)$ and $\text{CaCl}(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ respectively. These data, together with the value of the slope of $1.646 \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ derived from plot of k' against $[\text{CH}_3\text{Cl}]$ (Fig. 4), yield the following branching ratios into the electronically excited states of CaCl : $A_{1/2}(2.6 \pm 1.1) \times 10^{-3}$; $A_{3/2}(1.9 \pm 0.8) \times 10^{-3}$ and $B(3.6 \pm 2.0) \times 10^{-4}$. The errors quoted here mainly arise from the errors of the slopes of the plots (Figs. 5(a)–(c)). This overall yield for reaction into the three excited states of $\Sigma(\text{CaCl}(A_{1/2}, A_{3/2}, B)) = 4.9 \times 10^{-3}$ can be compared with analogous molecular beam data [8] where only the total yield into analogous excited states are reported and found to be 1.52×10^{-3} for $\text{Ca}(4^3\text{P}_J) + \text{CH}_3\text{Cl}$. Assuming that the collisional removal of $\text{Ca}(^3\text{P}_J)$ with CH_3Cl is entirely dominated by Cl-atom abstraction reaction and that physical quenching of $\text{Ca}(4^3\text{P}_J)$ by CH_3Cl to the $\text{Ca}(4^1\text{S}_0)$ ground state can be neglected, an upper limit for the branching ratio of the reaction into the $\text{CaCl}(X^2\Sigma^+)$ ground state of ca. 99.5% can be estimated. We may also compare the present results with analogous data determined in the time-domain for branching ratios into the states $\text{SrCl}(A^2\Pi_{1/2}, A^2\Pi_{3/2}, B^2\Sigma^+)$ following the reaction $\text{Sr}[5s5p(^3\text{P}_J)]$, 1.807 eV above the $5s^2(^1\text{S}_0)$ ground state, and generated by pulsed dye-laser excitation, with CH_2Cl_2 . These were found to be $A_{1/2}(3.0 \times 10^{-3})$, $A_{3/2}(1.7 \times 10^{-3})$ and $B(4.4 \times 10^{-4})$ [21].

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