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Molecular electronic branching ratios of CaI($A^2\Pi_{1/2,3/2}$,$B^2\Sigma^+$) resulting from the reaction of Ca[4s4p(^3P_J)] with CH_3I following the pulsed dye-laser excitation of atomic calcium.

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Molecular electronic branching ratios to yield CaI($A^2\Pi_{1/2}$), CaI($A^2\Pi_{3/2}$) and CaI($B^2\Sigma^+$) have been determined following the reaction of Ca[4s4p(^3P_J)], 1.888 eV above the 4s^2($^1S_0$) ground state, with CH_3I. These were determined from the combination of time-dependence and calibrated integrated intensity measurements of the atomic resonance fluorescence from Ca($4^3P_1 \rightarrow 4^1S_0$) and the molecular chemiluminescence from CaI($A^2\Pi_{1/2}$,$A^2\Pi_{3/2}$,$B^2\Sigma$+ $\rightarrow X^2\Sigma^+$) following pulsed dye-laser generation of Ca(4^3P_1). The results were found to be as follows: $A_{1/2}$ (2.7 ± 1.1) × 10^{-3}, $A_{3/2}$ (2.6 ± 1.3) × 10^{-3} and B, (2.0 ± 0.8) x 10^{-3}.

Measurements of branching ratios into specific molecular halide product states for reactions of electronically excited calcium atoms in its low lying Ca[4s4p(^3P_J)] state, 1.888 eV above the 4s^2($^1S_0$) ground state,[1] whether from investigations in the time-domain or using single collision conditions, are limited. Branching ratios for reactions of this atomic state with CH_3F, CH_3Cl and CH_3Br have recently been reported using the time-domain.[2–4] Dagdigian and co-workers[5] have studied the reactions of Ca(4^3P_J) with Cl_2, CH_3Cl, CH_3Br, CH_2Br_2, CH_2=$CHCH_2Br$ and $C_6H_5CH_2Br$ using molecular beams and report total electronic branching ratios into all the accessible excited states, CaX($A^2\Pi_{1/2,3/2}$, $B^2\Sigma^+$).[5] Gonzalez Ureña *et al.*[6] have studied the reactions Ca($^1D_2$, ^3P_J) + $CH_3I \rightarrow$ CaI(A,B) + CH_3 under beam-gas conditions and report electronic branching ratios for CaI($A^2\Pi$)/CaI($B^2\Sigma^+$). In this paper, molecular electronic branching ratios yielding CaI($A^2\Pi_{1/2,3/2}$, $B^2\Sigma^+$) following the reactions of Ca(4^3P_J) with CH_3I are reported following earlier experimental developments originally designed for the study in the time-domain of Sr(5^3P_J),[7–11] 1.807 eV above the 5s^2($^1S_0$) ground state.[1]

The experimental arrangement employed in this system is essentially described in earlier recent time-resolved measurements on Ca(4^3PJ)[2–4] with minor modifications. Ca[4s4p($^3P_1$)] was generated by the pulsed dye-laser excitation (10 Hz) of calcium vapour at elevated temperature (T = 940 K) at λ = 657.3 nm {Ca[4s4p($^3P_1$)] ← Ca[4s^2($^1S_0$)]} in the presence of methyl iodide and excess helium buffer gas. Atomic emission at the resonance wavelength from Ca(4^3P_1) was recorded on time-scales by which Boltzmann equilibration within the spin-orbit components of Ca(4^3P_J) had been established.[12,13] Molecular chemiluminescence from the states CaI [($A^2\Pi_{1/2,3/2}$, $B^2\Sigma^+ \rightarrow X^2\Sigma^+$) was also monitored. As in previous measurements,[2–4] the gain of the photomutiplier tube (E.M.I., 9797B) was taken from the commercial characteristic[4] and the combined optical and detection system was calibrated against a spectral radiometer. The procedure for data capture and computerised analysis has been given previously.[2–4]

Figure 1(a) gives an example of the intensity profile of the atomic resonance fluorescence emission from atomic calcium at λ = 657.3 nm following pulsed dye-laser excitation in the presence of CH_3I and excess helium buffer gas. Figure 1(b)–(d) gives examples of the accompanying digitised output for the molecular chemiluminescence emissions from CaI($A^2\Pi_{1/2} \rightarrow X^2\Sigma^+$, Δv = 0, 641 nm), CaI($A^2\Pi_{3/2} \rightarrow X^2\Sigma^+$, Δv = 0, 639 nm) and CaI($B^2\Sigma^+ \rightarrow X^2\Sigma^+$, Δv = 0, 636 nm), respectively, recorded under identical chemical conditions to those given for the atomic emission. Both logarithmic plots and computerised fitting of the raw data to the exponential profiles indicate the first-order nature of the removal of Ca(^3P_J) and CaI($A_{1/2,3/2}$,B). A quantitative comparison of the first-order decay coefficients for the atomic and molecular decays demonstrates a 1:1 relationship between the atomic fluorescence and molecular chemiluminescence and indicates that CaI($A^2\Pi$ $_{1/2,3/2}$,$B^2\Sigma^+$) arise from direct reaction between Ca(4^3P_J) + CH_3I. The $^3P_0$ and $^3P_2$ states are called 'reservoir states' and emission from them can be neglected[15] and thus atomic emission is given by the form: [2–4]

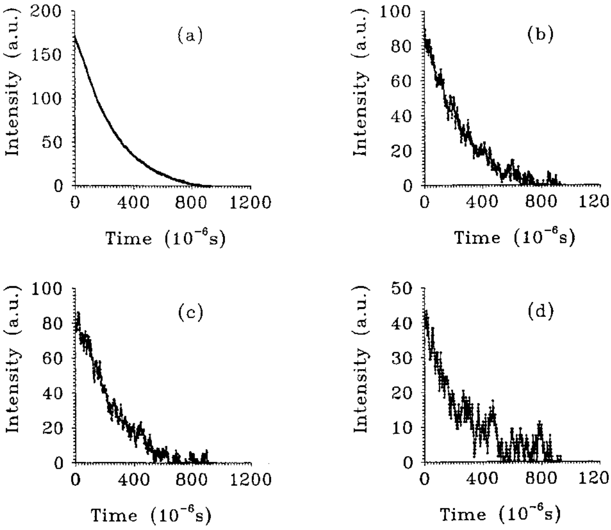

Fig. 1 Examples of the digitised output indicating the exponential decay profiles for the time-resolved atomic fluorescence emission and the molecular chemiluminescence following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength {Ca[4s4p($^3P_1$)] ← Ca[4s^2($^1S_0$)], λ = 657.3 nm} in the presence of CH_3I and excess helium buffer gas at elevated temperature. T = 940 K. [CH_3I] = 1.7 × 10^{16} molecules cm^{-3}, $p_{\text{Total with He}}$ = 60 torr.

(a) Ca[4s4p(^{3}P1)] → Ca[4s^2($^1S_0$)], λ = 657.3 nm
(b) CaI($A^2\Pi_{1/2} \rightarrow X^2\Sigma^+$, Δv = 0, 641 nm).
(c) CaI($A^2\Pi_{3/2} \rightarrow X^2\Sigma^+$, Δv = 0, 639 nm).
(d) CaI($B^2\Sigma^+ \rightarrow X^2\Sigma^+$, Δv = 0, 636 nm).

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

where $A_{nm} = 1/\tau_e$ for Ca($^3P_1 - {}^1S_0$) and $F = \{1 + (1/K_1) + K_2\}$. τ_e has been characterised separately in this work (360 µs) following earlier measurements.[16] 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. At constant total pressure, fixed temperature and fixed laser pulse output, k' may be expressed as

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$$k' = K + k_R \varepsilon[CH_3I] \qquad (ii)$$

where ε is the fraction of $[CH_3I]$ (initial) reaching the excitation region of the reactor.

Only the $A^2\Pi$ and $B^2\Sigma+$ electronicallly states of CaI are energetically accessible on direct I-atom abstraction by $Ca(4^3P_J)$ with CH_3I:

$$\Delta H/\mathrm{kJ\ mol^{-1}}$$

$$Ca(_3P_J) + CH_3I \rightarrow CaI(X^2\Sigma+) + CH_3 \qquad -203.1 \qquad (k_1)$$
$$Ca(_3P_J) + CH_3I \rightarrow CaI(A^2\Pi) + CH_3 \qquad -16.2 \qquad (k_2)$$
$$Ca(_3P_J) + CH_3I \rightarrow CaI(B^2\Sigma+) + CH_3 \qquad -15.3 \qquad (k_3)$$

As the mean radiative lifetime for $CaI(A^2\Pi_{1/2})$, for example, is very short compared to that of $Ca(4^3P_1)$, the molecular emission intensity from $CaI(A_{1/2} - X)$ is thus given by

$$I_{em}(A_{1/2} - X) = k_1\varepsilon[CH_3I]\,[Ca(^3P_J)]t{=}0\,\exp(-k't) \qquad (iii)$$

indicating equal decay coefficients for atomic and molecular emission.

The combination of equations (i) – (iii) and their integrated forms yield the result:

$$r_{A1/2} = (A_{nm}/F)\ \text{slope (1)/slope (2)} \qquad (iv)$$

where $r_{A1/2} = k_1/k_R$, the rate of production of $CaI(A^2\Pi_{1/2})$ from the reaction of $Ca(^3P_J)$ by CH_3I relative to the total removal rate of $Ca(^3P_J)$ by this molecule, namely, the molecular electronic branching ratio. Slope (1) is that of the plot of the ratio of the integrated molecular to atomic intensities, $I(A_{1/2} - X)/I\ (^3P_J)$ versus $[CH_3I]$ (initial) (Fig. 2), and slope (2), that of k' for $Ca(4^3P_J)$ versus $[CH_3I]$ (initial), presented in the full manuscript of this paper. The factor ε cancels. The results of this work and analogous studies in the time-domain on measurements of the branching ratios into the $A^2\Pi_{1/2}$, $A^2\Pi_{3/2}$ and $B^2\Sigma^+$ states following the reactions of $Ca(4^3P_J)$ with CH_3F, CH_3Cl and CH_3Br[2–4] are given in Table 1. The present results may be compared with analogous data from studies of the reactions of $Ca(^1D_2, {}^3P_J) + CH_3I$ derived from molecular beams,[6] yielding sensible agreement. The results are also compared with analogous measurements determined in the time-domain for branching ratios into the states $SrI(A^2\Pi_{1/2}, A^2\Pi_{3/2}, B^2\Sigma^+)$ following the reaction of $Sr[5s5p(^3P_J)]$, 1.807 eV above the $5s^2(^1S_0)$ ground state,[1] and generated by pulsed dye-laser excitation, with CH_3I [10] and CF_3I, [11] again yielding ratios similar to those observed here.

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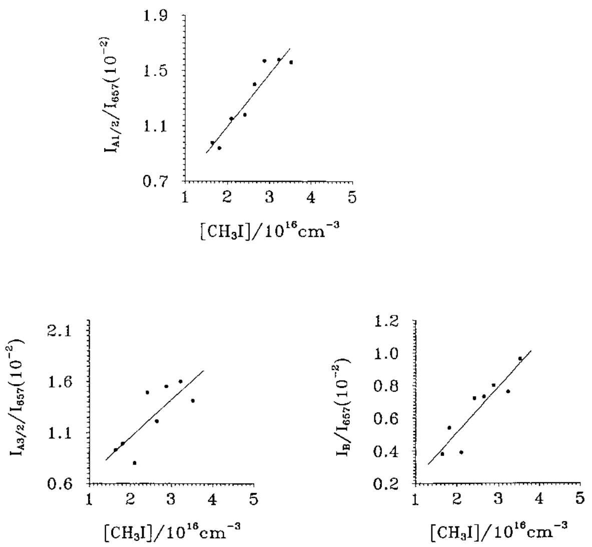

Fig. 2 Variation of the integrated intensity ratios of the molecular chemiluminescence emissions to the atomic fluorescence emission $Ca(4^3P1 \rightarrow 4^1S_0)$ (λ = 657.3 nm) for (a) $CaI(A^2\Pi_{1/2} \rightarrow X^2\Sigma+, \Delta v = 0$, 641 nm), (b) $CaI(A^2\Pi_{3/2} \rightarrow X^2\Sigma^+, \Delta v = 0$, 639 nm) and (c) $CaI(B^2\Sigma^+ \rightarrow X^2\Sigma^+, \Delta v = 0$, 636 nm) as a function of the concentration of CH_3I following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength (λ = 657.3 nm) in the presence of excess helium buffer gas at elevated temperature. (T = 940 K, $p_{\text{Total with He}}$ = 60 torr).

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Table 1 Molecular Electronic Branching ratios into $CaX^*(A^2\Pi_{1/2}, A^2\Pi_{3/2}, B^2\Sigma^+)$ from the halogen atom abstraction reactions of $Ca(4^3P_J)$ with the halogenated methanes, CH_3X, at T = 940 K determined by time-resolved measurements of atomic resonance fluorescence $(4^3P_1 - 4^1S_0)$ and molecular chemiluminescence $CaX^*(A_{1/2}, A_{3/2}, B - X)$ following pulsed dye-laser excitation.

CH_3X	$A_{1/2}$	$A_{3/2}$	B	$\Sigma(A_{1/2} + A_{3/2} + B)$
CH_3F_2	$(1.4\pm0.6) \times 10^{-3}$	$(1.2\pm0.5) \times 10^{-3}$	–	$(2.6\pm1.0)\mathrm{x}10^{-3}$
CH_3Cl_3	$(2.6\pm1.1) \times 10^{-3}$	$(1.9\pm0.8) \times 10^{-3}$	$(3.6\pm2.0) \times 10^{-4}$	$(4.9\pm2.3) \times 10^{-3}$
CH_3Br^4	$(9.8\pm3.9) \times 10^{-4}$	$(8.5\pm3.4) \times 10^{-4}$	$(3.4\pm1.7) \times 10^{-4}$	$(2.2\pm1.0) \times 10^{-3}$
CH_3I^a	$(2.7\pm1.1) \times 10^{-3}$	$(2.6\pm1.3) \times 10^{-3}$	$(2.0\pm0.8) \times 10^{-3}$	$(7.3\pm2.3) \times 10^{-3}$

[a] This work.