**THE COLLISIONAL BEHAVIOUR
OF Ba[6s5d(³D₁)] WITH CH₃Cl
INVESTIGATED BY TIME-RESOLVED
ATOMIC EMISSION AND MOLECULAR
CHEMILUMINESCENCE
BaCl (A²Π_{1/2, 3/2}, B²Σ⁺ → X²Σ⁺)
FOLLOWING THE PULSED DYE-LASER
EXCITATION OF ATOMIC BARIUM**

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The collisional behaviour of Ba[6s5d(³D₁)], 1.151 eV above the 6s²(¹S₀) ground state, is investigated in the presence of CH₃Cl at elevated temperature (900 K) following the initial pulsed dye-laser excitation of atomic barium via the allowed transition at λ = 553.5 nm {Ba[6s6p(¹P₁)] ← Ba[6s²(¹S₀)]} in excess helium buffer gas. The optically metastable Ba(³D₁) is then subsequently generated in the 'long-time domain' by a combination of radiative and collisional processes and may then be monitored by the spectroscopic marker atomic emission transition at λ = 791.1 nm {Ba[6s6p(³P₁)] → Ba[6s²(¹S₀)]} described previously. Following the collision of Ba[6s5d(³D₁)] with CH₃Cl, the following molecular chemiluminescence transitions of BaCl are also monitored as a function of time: BaCl (A²Π_{1/2} → X²Σ⁺, λ = 966 nm, Δv = 0), BaCl (A²Π_{3/2} → X²Σ⁺, λ = 910 nm, Δv = 0) and BaCl (B²Σ⁺ → X²Σ⁺, λ = 843 nm, Δv = 0), the atomic and molecular profiles all demonstrating exponential decays characterised by decay coefficients which are equal in given reactant mixtures. It may thus be readily seen from the kinetic analysis that the three molecule states, BaCl (A²Π_{1/2, 3/2}, B²Σ⁺), are generated directly on collision of Ba(³D₁) with CH₃Cl via exothermic reactions. A detailed kinetic analysis employing both the integrated intensities of the atomic emission and these long wavelength molecular emissions, coupled with optical sensitivity

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calibrations, yields branching ratios in the $\text{BaCl}(\text{A}^2\Pi_{1/2,3/2}, \text{B}^2\Sigma^+)$ states. These are found to be as follows: $\text{BaCl}(\text{A}^2\Pi_{1/2})$ 4.68%, $\text{BaCl}(\text{A}^2\Pi_{3/2})$ 1.29%, $\text{BaCl}(\text{B}^2\Sigma^+)$ 0.24%. The logarithmic variation of these branching ratios with the energies of the states is essentially Boltzmann in character, with an effective temperature close to the ambient temperature of the measurements. This is consistent with the absence of propensity in the yields of these excited molecular states on collision, reflecting the role of late barriers in the potential surfaces involved.

Keywords: BaCl molecular chemiluminescence; electronically excited Ba; atomic emission; electronic branching ratios

INTRODUCTION

The collisional behaviour of chemical reactions of low lying, optically metastable states of Mg, Ca and Sr involving atom abstraction have been widely investigated in the time-domain as the atomic states are directly accessible on pulsed dye-laser excitation [1–4]. By contrast, such studies on the low lying metastable states of atomic barium, namely, $\text{Ba}[6s5d(^3D_{1,2,3})]$ (1.120, 1.143 and 1.190 eV, respectively [5]) and $\text{Ba}[6s5d(^1D_2)]$ (1.413 eV [5]) have normally involved the use of strong atomic transitions with laser excitation into higher lying short-lived states followed by a range of collisional and radiative processes eventually leading to the metastable species. Typical initial excitation has involved transitions to $\text{Ba}[6s6p(^1P_1)]$ ($\tau_e = 8.37 \pm 0.38$ ns [6]) and $\text{Ba}[6s6p(^3P_1)]$ ($\tau_e = 1.2 \pm 0.1$ μ s [7–9]). The metastable states are, of course, characterised by long mean radiative lifetimes ($\tau_e\{\text{Ba}[6s5d(^3D_J)]\} = \text{ca.} 100$ μ s ≥ 1 ms [10, 11]; $\tau_e\text{Ba}[6s5d(^1D_2)] \leq 31.3$ μ s [12, 13]) and may readily be investigated on time scales far greater than the short-lived states of atomic barium initially excited by the pulsed laser methods. The generation of these metastable species of this electronically excited alkaline earth atom in molecular beams, especially by low voltage discharge, coupled with atomic emission and molecular chemiluminescence studies on reaction has been extensively employed for investigating a range of fundamental collisional processes [14–16].

Following this procedure of initial excitation of atomic barium via a strong atomic transition, we have reported a range of detailed kinetic studies in the ‘long time-domain’ of $\text{Ba}(^3D_J)$ in noble gases following the laser generation $\text{Ba}[6s6p(^1P_1)]$ from $\text{Ba}[6s^2(^1S_0)]$ [17–19]. $\text{Ba}(^3D_J)$ was monitored using the spectroscopic transition at $\lambda = 791.1$ nm $\text{Ba}[6s6p(^3P_1)] \rightarrow \text{Ba}[6s^2(^1S_0)]$ where the 3P_1 state was derived from collisional excitation of $\text{Ba}(^3D_J)$ and also at $\lambda = 553.5$ nm $\{\text{Ba}[6s6p-$

(1P_1)]} $\rightarrow$ Ba[$6s^2(^1S_0)$]} where the 1P_1 state resulted from $^3D_J + ^3D_J$ energy pooling [17–19]. We have recently reported the extension of this method to the study of the reaction between Ba(3D_J) + CH₃F, including chemiluminescence monitoring of BaF($A^2\Pi_{1/2,3/2}$, $B^2\Sigma^+ - X^2\Sigma^+$) in the time-domain following F-atom abstraction [20]. This approach involves monitoring chemiluminescence from electronically excited barium fluoride in the time-regime at long wavelength and was necessarily limited in the form of the kinetic analysis that could be employed as a result of the relatively weak molecular BaF($A_{1/2,3/2}$, B – X) emission. In this paper, we describe the reaction of Ba(3D_J) in the time-domain where, as a result of the magnitude of the molecular BaCl($A_{1/2,3/2}$, B – X) chemiluminescence signals, it has become possible to employ a fuller kinetic analysis. Chemiluminescence methods have been employed by Campbell and Dagdigan [21] to study halogen atom abstraction reactions of Ba(3D_J), generated by electric discharge, with Cl and Br-halogenated species in beam-gas scattering measurements. Solarz and Johnson [10] report measurements on Ba(3D_J) + halogenated methanes, in a molecular beam apparatus, where the atomic barium was initially excited by a pulsed dye-laser to Ba[$6s6p(^1P_1)$] and the electronic ground state diatomic barium halide products were then monitored by laser-induced fluorescence. Engelke [22] has presented a particularly detailed set of chemiluminescence studies of the reactions of metastable alkaline earth atoms, generated in a molecular beam system by arc discharge, with molecular halogens, including the reaction between Ba(3D_J) + Cl₂. In this paper we present an investigation of the time-resolved chemiluminescence molecular emission BaCl($A^2\Pi_{1/2,3/2}$, $B^2\Sigma^+ \rightarrow X^2\Sigma^+$), together with the spectroscopic atomic marker transition at 791.1 nm, following the reaction of Ba(3D_J) with CH₃Cl. The measurements are analogous to those described for the investigations in the time-domain for Ca[$4s4p(^3P_J)$] + CH₃Cl [23] and Sr[$5s5p(^3P_J)$] + CH₃Cl [24]. As we have stressed in the time-resolved chemiluminescence measurements on BaF [20], these new chemiluminescence measurements on BaCl, whilst necessarily limited in terms of sensitivity, have become feasible on account of the use of a long wavelength response photomultiplier tube whose application we have previously described [25]. Branching ratios for the production of the $A^2\Pi_{1/2}$, $A^2\Pi_{3/2}$ and $B^2\Sigma^+$ states of BaCl resulting from the direct reaction of Ba(3D_J) + CH₃Cl are reported. These are seen to be Boltzmann in character in the distribution of the production of the molecular electronic states on collision, with no electronic propensity

in the product states, and indicating late barriers in the appropriate potential surfaces for reaction.

EXPERIMENTAL

The experimental arrangement for studying atomic emission and molecular chemiluminescence at long wavelength was similar to that reported hitherto for the investigation of $\text{Ba}[6s5d(^3D_J)]$ in noble gases [17–19] and $\text{Ba}(^3D_J) + \text{CH}_3\text{F}$ [20]. Initial excitation of ground state atomic barium to $\text{Ba}[6s6p(^1P_1)]$ employed a dye-laser (Rhodamine chloride 590) operating at $\lambda = 553.5 \text{ nm}$ ($\text{Ba}[6s6p(^1P_1)] \leftarrow \text{Ba}[6s^2(^1S_0)]$) and pumped by the second harmonic (532 nm) of a Nd:YAG primary laser (10 Hz) (J.K. Lasers, System 2000). We have previously established that atomic emission directly from $\text{Ba}[6s5d(^3D_1)] \rightarrow \text{Ba}[6s^2(^1S_0)]$ at $\lambda = 1106.9 \text{ nm}$ using the long wavelength p.m. tube could not be detected directly, even using an interference filter for greater light gathering power [17–19]. Thus, $\text{Ba}(^3D_J)$ was monitored using the atomic spectroscopic marker at $\lambda = 791.1 \text{ nm}$ ($\text{Ba}[6s6p(^3P_1)] \rightarrow \text{Ba}[6s^2(^1S_0)]$) following collisional activation of $\text{Ba}(^3D_J)$ to the 3P_1 state. The product molecular electronic states resulting from the reaction of $\text{Ba}(^3D_J) + \text{CH}_3\text{Cl}$ were monitored by time-resolved molecular chemiluminescence at long wavelength from $\text{BaCl}(A^2\Pi_{1/2} \rightarrow X^2\Sigma^+, \lambda = 966 \text{ nm}, \Delta v = 0)$, $\text{BaCl}(A^2\Pi_{3/2} \rightarrow X^2\Sigma^+, \lambda = 910 \text{ nm}, \Delta v = 0)$ and $\text{BaCl}(B^2\Sigma^+ \rightarrow X^2\Sigma^+, \lambda = 843 \text{ nm}, \Delta v = 0)$.

The photomultiplier-monochromator system employed the new infrared sensitive photomultiplier tube (Hamamatsu R632–S1 response) that we have described previously in our investigations on atomic strontium at $\lambda = 1124.1 \text{ nm}$ ($\text{Sr}[5s6s(^1S_0)] \rightarrow \text{Sr}[5s5p(^1P_1)]$) [25] and on $\text{Ba}(^3D_J) + \text{CH}_3\text{F}$ [20] at long wavelength with a photocathode material of Ag-O-Cs and a sensitivity range of ca. 400–1200 nm. The gain of this tube can sensibly be described by the form $\ln(G) = 8.48 \ln(V/\text{Volt}) - 47.28$ from the commercial gain characteristic [25]. This was combined with a further high throughput compact monochromator operating in the range 350–1100 nm and marginally beyond [20, 25]. The optical detection system was gated electronically against the scattered light from the laser and the wavelength response calibrated against a spectral radiometer [20, 25]. The combination of the wavelength response of the p.m. – grating system together with the gain characteristic of the p.m. tube are

employed in determining integrated atomic and molecular intensities from the decay profiles used in the determination of branching ratios. Characterisation of the time-dependencies alone of both the atomic and molecular decay profiles themselves are, of course, independent of these calibrations. Digitised data for complete atomic and molecular emission profiles were captured using a double-channel transient digitiser interfaced to a computer. 255 decay profiles were captured and averaged as were 255 background profiles before transfer and subtraction for computerised analysis [17–20, 25]. The materials (Ba (Aldrich Chemicals), He, CH₃Cl) were employed essentially as described in the previous time-resolved investigations [17–19, 23, 24].

RESULTS AND DISCUSSION

Atomic and Molecular Decay Profiles

Figure 1 shows examples of the time variation of the digitized output indicating the exponential decay profiles for Ba(³D_J) in the ‘long-time domain’ and the associated first-order decay plots using the time-resolved atomic emission at $\lambda = 791.1$ nm following the pulsed dye-laser excitation of barium vapour at 900K [26] at $\lambda = 553.5$ nm {Ba[6s6p(¹P₁)] $\leftarrow$ Ba[6s²(¹S₀)]} in the presence of CH₃Cl and excess helium buffer gas. The use of this spectroscopic marker methods for monitoring the time-variation of Ba(³D_J) following the initial pulsed dye-laser excitation of atomic barium to Ba[6s6p(¹P₁)] has been established in earlier investigations on studies in noble gases [17–20]. The rate constants for the processes of collisional activation:

may be calculated employing the rate data reported for the reverse of processes (1) and (2) for collisional relaxation of Ba(³P_J) by He and Ba(¹S₀) to Ba(³D_J) given by Kallenbach and Koch [27, 28] using the principle of detailed balance. This yields $k_1^{\text{He}}(900\text{K}) = 1.2 \times 10^{-16} \text{ cm}^3 \text{ atom}^{-1} \text{ s}^{-1}$ and $k_2^{\text{Ba}}(900\text{K}) = 1.0 \times 10^{-11} \text{ cm}^3 \text{ atom}^{-1} \text{ s}^{-1}$ [17–19] and provides the basis of employing emission from Ba(³P₁) at $\lambda = 791.1$ nm {Ba[6s6p(³P₁)] $\rightarrow$ Ba[6s²(¹S₀)]} as a direct spectroscopic marker for the ³D_J state. The decay of Ba(³D_J) may then be expressed

FIGURE 1 Examples of the time variation of the digitized output indicating the exponential decay profiles [(a),(b)] and the associated computerised fitting indicating the first-order decay plots [(c),(d)] for the time-resolved atomic emission at $\lambda = 791.1$ nm{Ba[6s6p(3P_1)] $\rightarrow$ Ba[6s 2 (1S_0)]} following the pulsed dye-laser excitation of barium vapour at $\lambda = 553.5$ nm{Ba[6s6p(1P_1)] $\leftarrow$ Ba[6s 2 (1S_0)]} in the presence of CH₃Cl and excess helium buffer gas mixture gas ($p_{\text{total with He}} = 80$ Torr) at elevated temperature ($T = 900$ K). [CH₃Cl]/10¹⁵ molecules cm⁻³: (a), (c) 7.0; (b), (d) 10.3.

in the form:

$$\text{Ba}[6s5d(^3D_J)]_t = \text{Ba}[6s5d(^3D_J)]_{t=0} \exp(-k't) \quad (\text{i})$$

where the first-order decay coefficients, k' , are derived from slopes of plots of the type given Figures 1(c) and 1(d) and include collisional removal by CH₃Cl. The first-order decay coefficient for Ba(3D_J) can thus be written as

$$k' = k'_{\text{em}} + \beta/p_{\text{He}} + \Sigma k_Q[Q] + k_R[\text{CH}_3\text{Cl}] \quad (\text{ii})$$

where the symbols have their usual significance [17–20]. Removal of Ba(3D_J) is assumed to be dominated by chemical reaction to yield

BaCl (vide infra) and will be the basis of estimating an upper limit for the branching ratio into the electronic ground state ground state, BaCl($X^2\Sigma^+$). It must be stressed, as hitherto [20], however, that this is the only consequence of this assumption, recognising that there could be a contribution from collisional quenching of Ba(3D_J) to Ba(1S_0). It does not affect the time-dependencies in the kinetic analyses of either the atomic or molecular decays nor the determination of the branching ratios into BaCl($A^2\Pi_{1/2,3/2}$, $B^2\Sigma^+$).

k'_{em} will be dominated by electric dipole-allowed emission from Ba[6s5d(3D_1)] in (j,j) coupling for which we may write [17–19]:

$$k'_{em} = A_{nm}/(1 + K_1 + K_1K_2) \quad (\text{iii})$$

as rapid Boltzmann equilibration between the 3D_J levels will have taken place in the long-time-regime [29]. A_{nm} is the Einstein coefficient for the electric dipole-allowed transition $^3D_1 \rightarrow ^1S_0$. The equilibrium constants connecting these spin-orbit states, are written as $^3D_1 \rightleftharpoons ^3D_2$ ($\Delta\epsilon = 182 \text{ cm}^{-1}$) [5,29] K_1 , and $^3D_2 \rightleftharpoons ^3D_3$ ($\Delta\epsilon = 381 \text{ cm}^{-1}$) [5,29] K_2 and may readily be calculated by statistical thermodynamics. The function $F = (1 + K_1 + K_1K_2)$ does not vary largely over the range of measurements typically used in the study of Ba(3D_J) at elevated temperatures, taking, for example, the values of 3.05 at 800 K and 3.32 at 1000 K, and 3.18 in the present measurements (900 K). This function reaches the value of 5 at infinite temperature where it is solely dependent on the statistical weights of the spin-orbit components. The term β/p_{He} describes diffusional loss of Ba(3D_J) and is negligible in relation to other kinetic loss processes in this type of system above pressures of helium greater than ca. 30 Torr [17–19]. More important in the present system where measurements are taken at $p_{He} = 80$ Torr is that its contribution is constant. The term $\Sigma k_Q[Q]$ includes collisional removal of Ba(3D_J) by He which is small [17] and by ground state Ba(1S_0)($k_{Ba}[Ba]$) itself. k_{Ba} has been characterised in this type of system [17–19] and in other measurements [30–32] and, again, the term $k_{Ba}[Ba]$ is constant in this system where measurements are carried out at constant temperature (900 K). The term in k_R includes all collisional removal of Ba(3D_J) by CH_3Cl and is taken to be described by various exothermic chemical reactions to yield BaCl in the various accessible electronic states, including the ground state. The intensity of the atomic emission arising from collisional excitation from Ba(3D_J) to Ba[6s6p(3P_1)], as well as its time-dependence, will take the form [17–20]:

$$I_{\text{em}}(791.1\text{nm}) = GS\{k_1^{\text{He}}[\text{He}] + k_2^{\text{Ba}}[\text{Ba}]\}\text{Ba}[6s5d(^3\text{D}_J)]_{t=0} \exp(-k't) \quad (\text{iv})$$

where G is the gain of the photomultiplier tube which is a function of the voltage and S is the sensitivity of the optical system. All emission intensities can, of course, be normalised to a common relative scale (see experimental). In the kinetic analysis presented later, the symbols involving G and S are not given in the presentation for simplicity but are, of course, included in the analysis involving integrated intensity measurements.

Figures 2 and 3 give examples of the time-variation of the digitized output showing the exponential decay profiles and the associated computerised fitting indicating the first-order decays for the time-resolved molecular chemiluminescence from $\text{BaCl}(A^2\Pi_{1/2} \rightarrow X^2\Sigma^+, \lambda = 966\text{ nm}, \Delta v = 0)$ and from $\text{BaCl}(A^2\Pi_{3/2} \rightarrow X^2\Sigma^+, \lambda = 910\text{ nm}, \Delta v = 0)$ following the pulsed dye-laser excitation of barium vapour at the resonance wavelength of $\lambda = 553.5\text{ nm}$ in the presence of CH_3Cl and excess helium buffer gas under conditions identical to those indicated in Figure 1 for the atomic profiles. At these longer wavelengths, the molecular emission signals are weak due both to the relatively low sensitivity of the photomultiplier tube (R632), compensated in magnitude by increasing the gain by an increased voltage but also, of course, increasing the noise, and the low branching ratios into the electronically excited molecular states on reaction. This is seen particularly in the quality of the first-order decay profiles which are presented. It must, however, be emphasised strongly that first-order profiles are constructed from exponential fitting to the raw profiles in Figures 2 and 3 as are the integrated molecular intensities. Figure 4 shows analogous plots to those in Figures 2 and 3 for the time-resolved molecular chemiluminescence from $\text{BaCl}(B^2\Sigma^+ \rightarrow X^2\Sigma^+, \lambda = 843\text{ nm}, \Delta v = 0)$ following the pulsed dye-laser excitation of barium vapour at $\lambda = 553.5\text{ nm}$ again under identical conditions to those given in Figure 1.

Kinetic Analysis

The reaction of $\text{Ba}(^3\text{D}_J)$ with CH_3Cl is highly exothermic and the $A^2\Pi_{1/2}$, $A^2\Pi_{3/2}$ and $B^2\Sigma^+$ states are thermodynamically accessible on collision [5, 33–35]:

FIGURE 2 Examples of the time-variation of the digitized output indicating the exponential decay profiles [(a), (b)] and the associated computerised fitting indicating the first-order decays [(c), (d)] for the time-resolved molecular chemiluminescence from BaCl($A^2\Pi_{1/2} \rightarrow X^2\Sigma^+$, $\lambda = 966$ nm, $\Delta v = 0$) following the pulsed dye-laser excitation of barium vapour at $\lambda = 553.5$ nm {Ba[$6s6p(^1P_1) \leftarrow Ba[6s^2(^1S_0)]$] in the presence of CH₃Cl and excess helium buffer gas ($p_{\text{total with He}} = 80$ Torr) at elevated temperature ($T = 900$ K). [CH₃Cl]/ 10^{15} molecules cm⁻³: (a), (c) 7.0 ; (b), (d) 10.3.

$$\Delta H / \text{kJmol}^{-1}$$

The low lying $A^2\Delta$ state ($T_e = 9361.42$ cm⁻¹) of BaCl is optically metastable and the $C^2\Pi_{1/2,3/2}$ state is not energetically accessible

FIGURE 3 Examples of the time-variation of the digitized output indicating the exponential decay profiles [(a), (b)] and the associated computerised fitting indicating the first-order decays [(c), (d)] for the time-resolved molecular chemiluminescence from $\text{BaCl}(\text{A}^2\Pi_{3/2} \rightarrow \text{X}^2\Sigma^+, \lambda = 910 \text{ nm}, \Delta v = 0)$ following the pulsed dye-laser excitation of barium vapour at $\lambda = 553.5 \text{ nm}$ $\{\text{Ba}[6s6p(^1\Pi_1)] \leftarrow \text{Ba}[6s^2(^1\text{S}_0)]\}$ in the presence of CH_3Cl and excess helium buffer gas ($p_{\text{total with He}} = 80 \text{ Torr}$) at elevated temperature ($T = 900 \text{ K}$). $[\text{CH}_3\text{Cl}]/10^{15} \text{ molecules cm}^{-3}$: (a), (c) 7.0; (b), (d) 10.3.

[33, 34]. For the electronically excited states which are observed in chemiluminescence, the following vibrational levels are accessible: $\text{A}^2\Pi_{1/2}(v' \leq 39)$, $\text{A}^2\Pi_{3/2}(v' \leq 35)$, $\text{B}^2\Sigma^+(v' \leq 20)$. This can be seen from the spectroscopic data for these states. The data for the electronic ground state are also listed for the purpose of Franck-Condon calculations: $\text{X}^2\Sigma^+$, $\omega_e = 279.3$ and $\omega_e x_e = 0.89 \text{ cm}^{-1}$, $r_e = 0.2683 \text{ nm}$; $\text{A}^2\Pi_{1/2}$, $\omega'_e = 256.35$ and $\omega'_e x'_e = 0.73 \text{ cm}^{-1}$, $r_e = 0.2732 \text{ nm}$; $\text{A}^2\Pi_{3/2}$, $\omega'_e = 256.35$ and $\omega'_e x'_e = 0.73 \text{ cm}^{-1}$, $r_e = 0.2732 \text{ nm}$; $\text{B}^2\Sigma^+$, $\omega'_e = 255.25$ and $\omega'_e x'_e = 0.83 \text{ cm}^{-1}$, $r_e = 0.2730 \text{ nm}$. The inter-atomic distances in the $\text{A}^2\Pi_{1/2,3/2}$ states are estimated following the measurements of Gustafsson *et al.* [36]. Franck-Condon factors were calculated using a

FIGURE 4 Examples of the time-variation of the digitized output indicating the exponential decay profiles [(a), (b)] and the associated computerised fitting indicating the first-order decays [(c), (d)] for the time-resolved molecular chemiluminescence from BaCl($B^2\Sigma^+ \rightarrow X^2\Sigma^+$, $\lambda = 843$ nm, $\Delta v = 0$) following the pulsed dye-laser excitation of barium vapour at $\lambda = 553.5$ nm {Ba[6s6p(1P_1)] $\leftarrow$ Ba[6s 2 (1S_0)]} in the presence of CH₃Cl and excess helium buffer gas ($p_{\text{total with He}} = 80$ Torr) at elevated temperature ($T = 900$ K). [CH₃Cl]/10¹⁵ molecules cm⁻³: (a), (c) 7.0; (b), (d) 10.3.

simplified Morse oscillator model following Tuckett [37], yielding the following examples: A – X, (0,0) 0.7918, (1,0) 0.1867, (1,1) 0.4634, (0,1) 0.1824; B – X, (0,0) 0.7615, (1,0) 0.2095, (1,1) 0.3990, (0,1) 0.2050. The main emission arises from the $\Delta v = 0$ transitions, at least from the lower vibrational levels, and these were monitored here.

The $A^2\Pi$ and $B^2\Sigma^+$ states of BaCl are short-lived and have recently been characterised by Berg and coworkers for these long wavelength transitions [38] (τ_e/ns : $A^2\Pi_{3/2}$ 109.8, $B^2\Sigma^+$ 98.9). The mean radiative life-time of BaCl($A^2\Pi_{1/2}$) has not been characterised to the best of our knowledge but it should clearly be close to that reported for the

$A^2\Pi_{3/2}$ state [38]. Considering $BaCl(A^2\Pi_{1/2})$ as an example, its concentration may readily be placed in steady state, namely,

$$d[BaCl(A_{1/2})]/dt = k_4[Ba^3D]_t[CH_3Cl] - A_{nm'}[BaCl(A_{1/2})] = 0 \quad (v)$$

where $A_{nm'} = 1/\tau_e$ for $BaCl(A_{1/2})$. Combining equation (v) with equation (i), we readily see that, on this basis, the $A_{1/2} - X$ emission intensity follows the form:

$$I(A - X) = k_4[CH_3Cl][Ba[6s5d(^3D_J)]]_{t=0} \exp(-k't) \quad (vi)$$

where the appropriate values of G and S are included later in the integrated intensity calculations. Thus, following equations (iv) and (vi), the molecular and atomic ($\lambda = 791.1$ nm) intensities should both follow the same exponential form for the production of the $A_{1/2}$, $A_{3/2}$ and B states of $BaCl$ resulting from direct reaction as indicated in processes (4–6).

Figure 5 gives examples of the comparison of the first-order rate coefficients (k') for the atomic fluorescence derived from the intensity profiles at $\lambda = 791.1$ nm with those of the molecular chemiluminescence for the $BaCl(A^2\Pi_{1/2} \rightarrow X^2\Sigma^+)$ emissions at $\lambda = 966$ nm and of the $BaCl(A^2\Pi_{3/2} \rightarrow X^2\Sigma^+)$ emissions at $\lambda = 910$ nm. These decay coefficients are equal within 10%, the error arising from the scatter in the molecular profiles. Similar results are obtained from the $B-X$ profiles (Fig. 6). Thus the production of $BaCl(A_{1/2}, A_{3/2}, B)$ occur by the direct reactions (4–6).

Branching Ratios

Branching ratios into the specific electronic states of $BaCl$, $A_{1/2}$, $A_{3/2}$ and B , may be calculated and constitute a fundamental objective of the present investigation. This describes the rate of production of a given electronic state of $BaCl$ on reaction with CH_3Cl relative to the total removal of $Ba(^3D_J)$ on collision with this molecule. This has been attributed to chemical reaction, namely, for $BaCl(A_{1/2})$, k_4/k_R or $k_{A_{1/2}}/k_R$. We have emphasised that this could include collisional quenching of $Ba(^3D_J)$ to the 1S_0 ground state where the assumption of total chemical removal only affects the estimate of the branching ratio in the $X^2\Sigma^+$ ground state. We may first consider the atomic intensity at $\lambda = 791.1$ nm (eqn. (iv)), appropriately normalised via the relevant values of G and S from the intensity calibration which are not included

FIGURE 5 Comparison of the first-order rate coefficients (k') for the atomic emission derived from the intensity profiles for the Ba[6s6p(³P₁)] $\rightarrow$ Ba[(6s²(¹S₀)] emission at $\lambda = 791.1$ nm with those of the molecular chemiluminescence for the BaCl(A² $\Pi_{1/2} \rightarrow X^2\Sigma^+$) emissions at $\lambda = 966$ nm [(a), (b)] and of the BaCl(A² $\Pi_{3/2} \rightarrow X^2\Sigma^+$) emissions at $\lambda = 910$ nm [(c), (d)] following the pulsed dye-laser excitation of barium vapour at $\lambda = 553.5$ nm {Ba[6s6p(¹P₁)] $\leftarrow$ Ba[6s²(¹S₀)]} in the presence of CH₃Cl and excess helium buffer gas ($p_{\text{total with He}} = 80$ Torr) at elevated temperature ($T = 900$ K) (Upper line, atomic emission; lower line, molecular emission). [CH₃Cl]/10¹⁵ molecules cm⁻³: (a), (c) 7.0; (b), (d) 14.1 (a) $k'_{966}/k'_{791} = 1.06$ (b) $k'_{966}/k'_{791} = 1.1$ (c) $k'_{910}/k'_{791} = 1.03$ (d) $k'_{910}/k'_{791} = 1.05$.

in the presentation but are, of course, employed in the analysis. Writing $k_1^{\text{He}}[\text{He}] + k_2^{\text{Ba}}[\text{Ba}] = k'_{\text{tr}}$, we may integrate equation (iv) (not including G and S) and obtain

$$I_{3p} = \int_0^{\infty} I_{\text{em}}(791.1 \text{ nm}) = k'_{\text{tr}}[\text{Ba}^3\text{D}_J]_{t=0}/k' \quad (\text{vii})$$

We have seen earlier that the activation rate data, $k_1^{\text{He}}(900\text{K}) = 1.2 \times 10^{-16} \text{ cm}^3 \text{ atom}^{-1} \text{ s}^{-1}$ and $k_2^{\text{Ba}}(900\text{K}) = 1.0 \times 10^{-11} \text{ cm}^3 \text{ atom}^{-1} \text{ s}^{-1}$ [17–19], may be characterised using the principle of detailed balance and the collisional relaxation rate data for Ba(³P_J) of Kallen-

FIGURE 6 Comparison of the first-order rate coefficients (k') for the atomic emission derived from the intensity profiles for the $\text{Ba}[6s6p(^3P_1)] \rightarrow \text{Ba}[(6s^2(^1S_0))]$ emission at $\lambda = 791.1$ nm with those of the molecular chemiluminescence for the $\text{BaCl}(\text{B}^2\Sigma^+ \rightarrow \text{X}^2\Sigma^+, \lambda = 843 \text{ nm}, \Delta v = 0)$ emission following the pulsed dye-laser excitation of barium vapour at $\lambda = 553.5$ nm $\{\text{Ba}[6s6p(^1P_1)] \leftarrow \text{Ba}[6s^2(^1S_0)]\}$ in the presence of CH_3Cl and excess helium buffer gas (p_{total} with He = 80 Torr) at elevated temperature ($T = 900$ K) (Upper line, atomic emission; lower line, molecular emission). $[\text{CH}_3\text{Cl}]/10^{15}$ molecules cm^{-3} : (a), (c) 7.0 (b), (d) 14.1 (a) $k'_{843}/k'_{791} = 1.06$ (b) $k'_{843}/k'_{791} = 1.08$.

bach and Koch [27, 28]. Thus for $p_{\text{He}} = 80$ Torr and a temperature of 900 K where $[\text{Ba}] = 6.15 \times 10^{13}$ atoms cm^{-3} from vapour pressure data [26], k'_{tr} may be calculated and takes the value of 722 s^{-1} for this temperature and pressure of helium.

For the example of $\text{BaCl}(\text{A}^2\Pi_{1/2})$, we may integrate equation (vi), namely,

$$I_{\text{A}_{1/2}} = \int_0^\infty I_{\text{em}}(966 \text{ nm}) = k_4[\text{CH}_3\text{Cl}][\text{Ba}^3\text{D}_J]_{t=0}/k' \quad (\text{viii})$$

where $I_{\text{em}}(966 \text{ nm}) = I(\text{A} - \text{X})$. The branching ratio may then be determined as follows. Following equations (ii) and (iv), we may plot k' for $\text{Ba}(^3\text{D}_J)$ versus $[\text{CH}_3\text{Cl}]$ using the emission at $\lambda = 791.1$ nm (Fig. 7) and obtain the value of k_{R} from the slope (S(I)). Further, combining equations (vii) and (viii) we see that

$$I_{\text{A}_{1/2}}/I_{3\text{P}} = k_4[\text{CH}_3\text{Cl}]/k'_{\text{tr}} \quad (\text{ix})$$

Thus, a plot of $I_{\text{A}_{1/2}}/I_{3\text{P}}$ from the calibrated molecular and atomic integrated intensities versus $[\text{CH}_3\text{Cl}]$ is of slope (S(II)) k_4/k'_{tr} . Hence, $\text{S(II)}/\text{S(I)} = k_4/k_{\text{R}}k'_{\text{tr}}$ or $k_{\text{A}_{1/2}}/k_{\text{R}}k'_{\text{tr}}$, yielding the branching ratio into $\text{BaCl}(\text{A}^2\Pi_{1/2})$. Relevant plots of $I_{\text{A}_{1/2}}/I_{3\text{P}}$, $I_{\text{A}_{3/2}}/I_{3\text{P}}$ and $I_{\text{B}}/I_{3\text{P}}$ versus

[CH₃Cl] are given in Figures 8(A), 8(B) and 8(C), respectively. These plots are scattered as the intensities of the molecular emissions are weak, arising from the use of the photomultiplier tube at long wavelength where its sensitivity is relatively low, coupled with the low overall sensitivity of the tube and the low branching ratios into the electronic states. This then involves the use of increased gain in the photomultiplier tube with an accompanying increase in noise. The plots are, nevertheless, usable. We may also note that the inclusion of a factor, f , in equations (ii) and (ix) to allow for the removal of some proportion of the CH₃Cl before reaching the centre of the reactor prior to laser excitation, and thus, writing the effective reactant concentration as f [CH₃Cl], will cancel. Indeed, the present method only depends on the use identical concentrations of CH₃Cl when recording the atomic and molecular decay profiles in a given

FIGURE 7. Variation of the pseudo first-order rate coefficient $k'_{791}(^3P_1)$ for the decay of Ba[6s6p(3P_1)] generated by energy transfer from Ba[6s5p(3D_1)] in the presence of varying concentrations of CH₃Cl and excess helium buffer gas ($p_{\text{total with He}} = 80$ Torr) at elevated temperature ($T = 900$ K) following the pulsed dye-laser excitation of barium vapour at = 553.5 nm {Ba[6s6p(1P_1)] $\leftarrow$ Ba[6s $^2(^1S_0)$]}.

measurement. An alternative approach has been employed hitherto [20] for calculating branching ratios of BaF in the $A_{1/2,3/2}$ and B states from $Ba(^3D_J) + CH_3F$ [20] using a given concentration of $[CH_3F]$ with the analogue of equation (ix) coupled with S(I), point by point, where plots such as those in Figure 8 could not be constructed as a result of scatter in the plots. In the present case, equation (ix) and Figure 8 was used to determine the branching ratios which were found to be as follows: $BaCl(A^2\Pi_{1/2})$, 4.68%; $BaCl(A^2\Pi_{3/2})$, 1.29%; $BaCl(B^2\Sigma^+)$, 0.24%. These may be compared with the branching ratios for the production of the analogous electronic states resulting from the reaction of $Ba(^3D_J)$ with CH_3F [20]: $BaF(A^2\Pi_{1/2})$, 0.86%; $BaF(A^2\Pi_{3/2})$, 0.42%; $BaF(B^2\Sigma^+)$, 0.05%.

FIGURE 8 Variation of integrated intensity ratios for the molecular chemiluminescence emission to the atomic emission at $\lambda = 791$ nm $\{Ba[6s6p(^3P_1)] \rightarrow Ba[(6s^2(^1S_0))]\}$ for (A) $BaCl(A^2\Pi_{1/2} \rightarrow X^2\Sigma^+, \lambda = 966$ nm, $\Delta v = 0$), (B) $BaCl(A^2\Pi_{3/2} \rightarrow X^2\Sigma^+, \lambda = 910$ nm, $\Delta v = 0$) and (C) $BaCl(B^2\Sigma^+ \rightarrow X^2\Sigma^+, \lambda = 843$ nm, $\Delta v = 0$) as a function of the concentration of CH_3Cl following the pulsed dye-laser excitation of barium vapour at $\lambda = 553.5$ nm $\{Ba[6s6p(^1P_1)] \leftarrow Ba[6s^2(^1S_0)]\}$ in the presence of excess helium buffer gas (p_{total} with He = 80 Torr) at elevated temperature ($T = 900$ K).

These branching ratios are of comparable magnitude with those reported hitherto for the production of various diatomic strontium halides in the $\text{A}^2\Pi_{1/2,3/2}$, $\text{B}^2\Sigma^+$ states following reactions of $\text{Sr}(5^3\text{P}_J)$ with halogenated species [39–42] in pulsed dye-laser measurements where $\text{Sr}(5^3\text{P}_1)$ was directly populated on laser excitation. Similarly, from the above data for the branching ratios into BaCl , $\text{F}(\text{A}^2\Pi_{1/2,3/2}, \text{B}^2\Sigma^+)$ from the reactions of $\text{Ba}(^3\text{D}_J) + \text{CH}_3\text{Cl}$ and CH_3F , plots of the logarithm of the branching ratios versus the energy of the states of BaCl and BaF are sensibly linear (Fig. 9). The slope of the plot for CH_3Cl yields an effective temperature of ca. 730 K and that for CH_3F , ca. 1200 K, comparable with the ambient temperature employed (900 K). It must be stressed that measurements are made over a limited range of electronic energies for the states of both BaCl and BaF . Assuming that removal of $\text{Ba}(^3\text{D}_J)$ by CH_3Cl results only in reaction to yield BaCl and not to physical quenching to yield $\text{Ba}(^1\text{S}_0)$ (see

FIGURE 9 Variation of the branching ratios into electronically excited BaCl and BaF (BaX : $\text{A}^2\Pi_{1/2}$, $\text{A}^2\Pi_{3/2}$, $\text{B}^2\Sigma^+$) observed by time-resolved chemiluminescence following halogen atom abstraction reactions of $\text{Ba}[6s5d(^3\text{D}_J)]$ with (a) CH_3Cl and (b) CH_3F following the pulsed dye-laser excitation of barium vapour at elevated temperature as a function of the electronic energy of the state, $E(\text{BaX})$.

earlier), this yields an upper limit for the branching ratio into $\text{BaCl}(X^2\Sigma^+)$ of ca. 94%. The analogous upper limit for $\text{BaF}(X^2\Sigma^+)$ was found to be ca. 99% [20]. The absolute values for the branching ratios are influenced by the magnitude of k'_{tr} , namely, by the collisional activation rates of $\text{Ba}(^3\text{D}_J)$ into $\text{Ba}(^3\text{P}_J)$ by Ba and He [27, 28] described earlier. The relative branching ratios are not, neither is the sensible linearity of the effective Boltzmann plot of the logarithm of the branching ratio versus the energy of the state of BaCl and the resulting effective temperature. As hitherto [39–42], this yields the important fundamental conclusion that there is no propensity in the production of the electronically excited states of BaCl on collision of $\text{Ba}(^3\text{D}_J)$ with CH_3Cl , nor of those of BaF on the collision of $\text{Ba}(^3\text{D}_J)$ with CH_3F , as seen via the branching ratios, rather that the yields of these molecular states are statistical in nature, presumably reflecting late barriers in the appropriate potential surfaces describing reaction in each case.

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