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The collisional quenching of Ca[4s4p(^{3}P$_J$)] by Ca[4s^2(^{1}S$_0$)] following pulsed dye-laser excitation of atomic calcium

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Abstract

The collisional quenching of electronically excited calcium atoms, Ca[4s4p(^{3}P$_J$), 1.888 eV above the 4s^2(^{1}S$_0$) ground state by ground state calcium atoms, Ca[4s^2(^{1}S$_0$)], has been investigated. Ca[4s4p(^{3}P$_1$)] was generated by the pulsed dye-laser excitation of ground state calcium atoms at λ=657.3 nm {Ca[4s4p(^{3}P$_1$)] ← Ca[4s^2(^{1}S$_0$)]} over a range of elevated temperatures in the presence of excess helium buffer gas. Measurements were then made of the atomic resonance fluorescence from Ca(4^3P$_1$ → 4^1S$_0$) after Boltzmann equilibration within Ca(4^3P$_{0,1,2}$). First-order decay coefficients for the atomic emission profiles were quantified both as a function of temperature and hence, atomic density of Ca(4^1S$_0$) and of helium density itself. Consideration of the terms contributing to the measured decay coefficients, viz. emission, diffusion, and collisional quenching of Ca(4^3P$_J$) by Ca(4^1S$_0$) and He yields the collisional rate data. The absolute second-order rate constant for quenching of Ca(^{3}P) by Ca(^{1}S) is found to be $k_{\mathrm{Ca}}=(2.4\pm0.3)\times10^{-12}$ cm^3 per atom s^{-1} (810–997 K) marginally lower than obtained by phase angle modulation following dye-laser excitation for a similar temperature range. It is significantly larger than that obtained from earlier estimates derived from the departure of a $T^{1.5}$ dependence of the temperature variation of the diffusion coefficient, D_{12}(Ca^{3}P-He), measured in the time-domain. A related analysis of the first-order decay coefficients for Ca(4^3P$_J$) yielded the rate constant for the collisional quenching of Ca(^{3}P) by He, viz. $k_{\mathrm{He}}=(2.3\pm0.3)\times10^{-16}$ cm^3 per atom s^{-1} (T=940 K). This is in agreement with the upper limit obtained earlier in the time-domain but significantly lower than that resulting from phase angle modulation measurements across a temperature range in this region.

Keywords: Ca[4s4p(^{3}P$_J$)]; Collisional quenching by Ca[4s^2(^{1}S$_0$)] and He; Pulsed dye-laser excitation

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1. Introduction

The collisional behaviour of electronically excited alkaline earth atoms in low lying, optically metastable states in the time-domain has been widely studied following pulsed dye-laser excitation [1–4]. This has, of course, included a wide range of physical and chemical processes undergone by electronically excited calcium atoms in its low lying Ca[4s4p(^{3}P$_J$)] state, 1.888 eV above the 4s^2(^{1}S$_0$) ground state [5]. Molecular beam studies of electronically excited alkaline earth atoms, including Ca(4^3P$_J$), have normally employed electric discharges coupled with atomic emission and chemiluminescence monitoring [6–15]. Most studies in the time-domain involving the generation of Ca(4^3P$_J$) by direct pulsed dye-laser generation of Ca(4^3P$_1$) at the resonance wavelength (λ=657.3 nm, Ca[4s4p(^{3}P$_1$)] ← Ca[4s^2(^{1}S$_0$)]) [1–4] have involved optical excitation of significant vapour densities of calcium vapour in equilibrium with its solid at elevated temperature. Characterisation of the rate data of Ca(4^3P$_J$) is normally carried out at a constant temperature and pressure of a noble gas with varied added reactant concentration so that contributions to kinetic decay by processes such as diffusion, emission and collisional quenching of Ca(4^3P$_J$) by the noble gas and ground state Ca(4^1S$_0$) are held constant. Such a procedure may then be repeated, for example, at different temperatures. Thus, knowledge of the quenching rate constant for Ca(4^3P$_J$) by ground state atomic calcium is not required in those investigations.

In early time-resolved emission studies of Ca(4^3P$_J$) following pulsed dye-laser excitation of atomic calcium [16,17], the collisional quenching of the excited atom by Ca(4^1S$_0$) was neglected. This is, of course, dependent on the vapour density of atomic calcium employed. In subsequent time-resolved studies on Ca(4^3P$_J$), Husain and Roberts [18,19] employed the temperature dependence of the diffusion coefficient D_{12} of Ca(4^3P$_J$) in He, in particular, the departure from the simplified gas kinetic dependence — $D_{12}\propto T^{1.5}$ — to estimate an average rate constant,

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k_{Ca}, for the collision quenching of Ca(4^3P_J) by Ca(4^1S_0) at elevated temperatures. In their study of the collisional quenching of Ca(4^3P_J) with noble gases employing modulated dye-laser excitation coupled with phase-sensitive detection and Stern–Volmer analyses, Malins and Benard [20] have reported rate data for the quenching of Ca(4^3P_J) by Ca(4^1S_0). In this paper, we describe the characterisation of this rate constant directly by time-resolved emission at λ=657.3 nm [Ca($4^3P_1 \rightarrow 4^1S_0$)] following pulsed dye-laser excitation at elevated temperatures by measuring the decay constant for the removal of Ca(4^3P_J) across a wide concentration range for Ca(4^1S_0). The result is compared with the earlier data as indicated. The rate constant for quenching of Ca(4^3P_J) by helium buffer gas is also characterised and compared with previous data reported using phase-sensitive detection.

2. Experimental

The experimental arrangement was essentially that employed in previous investigations followed by pulsed dye-laser excitation of electronically excited Ca and Sr with emission measurements in the time-resolved mode [21,22]. Ca[4s4p($^3P_1$)] was generated by the pulsed dye-laser excitation (10 Hz) of calcium vapour at elevated temperatures (T=810–1013 K) at λ=657.3 nm {Ca[4s4p($^3P_1$)] ← Ca[4s^2($^1S_0$)]} in the presence of excess helium buffer gas in a slow flow system, kinetically equivalent to a static system. This yielded vapour densities across the range of 1.83×10^{13} to 2.42×10^{15} atom cm^{-3} [23]. In practice, the upper limit employed for rate measurements was 997 K above which data were very scattered. 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 [24,25] on a photomultiplier tube (E.M.I. 9797B) mounted on the exit slit of a small monochromator (‘Minichrom’ monochromator, MC1-02-10288, Fastie–Ebert mounting). The atomic 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). 256 decay profiles were averaged as were 256 background profiles and interfaced into a computer for data analysis. The materials (Ca, He) were employed essentially as described in previous investigations on chemical reactions of Ca(4^3P_J) [26].

3. Results and discussion

3.1. Collisional quenching of Ca[4s4p(^3P_J)] by Ca[4s^2($^1S_0$)]

Fig. 1 gives examples of the digitised output for the time-resolved atomic fluorescence emission at λ=657.3 nm following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength {Ca[4s4p($^3P_1$)] ← Ca[4s^2($^1S_0$)]} at different temperatures and a fixed pressure of helium gas. Computerised fitting of these profile intensities (I_F) indicating the first-order decay of Ca(4^3P_J) are given in Fig. 2 in the form of ln(I_F-B) versus time where B is the intensity of the basal light signal which mainly arises from the photomultiplier dark current. Thus, the decay of

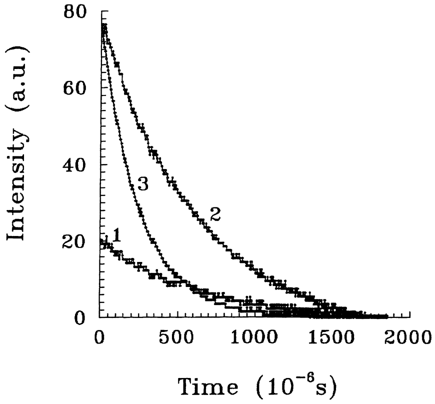

Fig. 1. Examples of the digitised output indicating the exponential decay profiles for the time-resolved atomic fluorescence emission following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength {Ca[4s4p($^3P_1$)] ← Ca[4s^2($^1S_0$)], λ=657.3 nm} in the presence of varying concentrations of excess helium buffer gas at different temperatures. p_{He}=80 Torr. T/K: (1) 810; (2) 882; (3) 972.

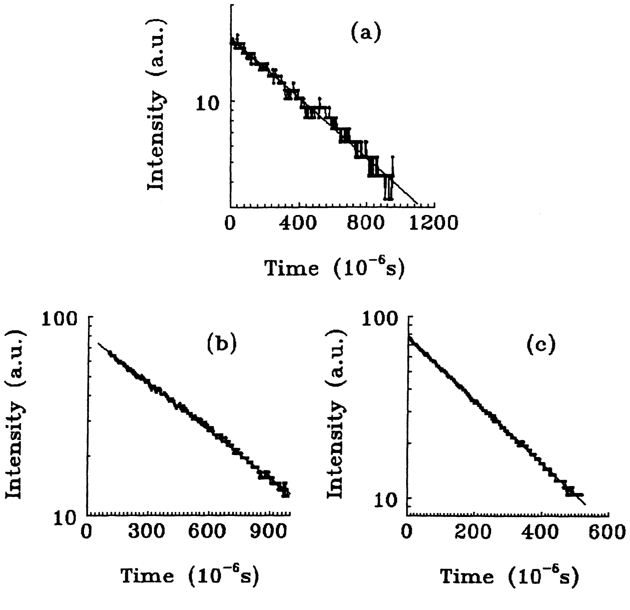

Fig. 2. Examples of the computerised fitting indicating the first-order decay profiles of the time-resolved atomic fluorescence emission following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength {Ca[4s4p($^3P_1$)] ← Ca[4s^2($^1S_0$)], λ=657.3 nm} in the presence of excess helium buffer gas at different temperatures. p_{He}=80 Torr. T/K: (a) 810; (b) 882; (c) 972.

$Ca(4^3P_J)$ may be written in the form [21]

$$[Ca(4^3P_J)]_t = [Ca(4^3P_J)]_{t=0}\exp(-k't) \quad (1)$$

where k' is the overall first-order decay coefficient of $Ca(4^3P_J)$ and obtained from the slopes of plots of the type given in Fig. 1. It has been demonstrated by direct measurement that, subsequent to the generation of $Ca(4^3P_1)$ by laser excitation, rapid collisional Boltzmann equilibration within the ^3P_J multiplet (4^3P_0, E=15158 cm^{-1}; 4^3P_1, E=15210 cm^{-1}; 4^3P_2, E=15316 cm^{-1}) [5] is established on the time-scales of all the present measurement [24,25]. $Ca(4^3P_0)$ and $Ca(4^3P_2)$ are so-called 'reservoir states' and emission from them can be neglected [27].

The first-order decay coefficient, k', may thus be written in the standard form [21]

$$k' = \frac{A_{nm}}{1+(1/K_1)+K_2} + \frac{\beta}{p} + k_{Ca}[Ca(^1S_0)] + k_{He}[He] \quad (2)$$

where A_{nm} is the Einstein coefficient describing the spontaneous emission from $Ca(4^3P_1)$ and K_1 and K_2 are the equilibrium constants connecting the $^3P_0$ and $^3P_1$ states, and the $^3P_1$ and $^3P_2$ states, respectively, readily calculated by statistical thermodynamics. The function $F = 1/(1+1/K_1+K_2)$ takes the value of 2.746 at 810 K and 2.789 at 997 K, increasing monotonically to 3 at infinite temperature. The variation of F over the temperature range of interest here is small (<2%) permitting the use of the average value F=2.768 (904 K) without a major loss in accuracy. β/p represents the first-order diffusional loss of $Ca(4^3P_J)$ out of the observation region and arises from the solution of the standard diffusion equation with appropriate boundary conditions [28,29]. k_{ca} and k_{He} are the absolute second-order quenching rate constants for the collisional removal of $Ca(4^3P_J)$ by ground state calcium atoms, the prime object of investigation here and by helium buffer gas which is also studied here. It must be stressed that, whilst energy pooling into various higher lying states of atomic calcium arise from $Ca(4^3P_J)+Ca(4^3P_J)$ self-annihilation under present conditions [19], the yield into such individual states is typically 1 ppm of the initial concentration of $Ca(4^3P_J)$. Thus, there is no measurable departure from first-order kinetics for $Ca(4^3P_J)$ as energy pooling only constitutes a small 'bleed off' from the concentration of the optically metastable calcium atom.

In the present measurements on k_{Ca}, the pressure of helium gas is held constant (p_{He}=80 Torr). The small contribution to k' from the highly inefficient collisional removal of $Ca(4^3P_J)$ with the helium buffer gas, which will be demonstrated later, can be neglected in a series of kinetic runs in which the concentration of calcium atoms is varied notwithstanding the change in the concentration of He with temperature. Any variation with diffusional loss arises from the variation of the diffusion coefficient with temperature, ideally of the simple gas kinetic form $D_{12}[Ca(4^3P_J)\text{-}He]\propto T^{1.5}$. Inspection of the appropriate plot of ln(β) versus ln(T/K) reported by Husain and Roberts [19] with this experimental system indicates that the diffusional contribution constitutes ca. 18% of the total first-order loss of $Ca(4^3P_J)$ at the low temperature end (810 K) of the measurements and ca. 6% at 1013 K. Over this range, k' increases by a factor of approximately 5. Hence, from the foregoing conditions, Eq. (2) may therefore be written as

$$k' = K + K_{Ca}[Ca(^1S_0)] \quad (3)$$

where K is a constant within the limitations described.

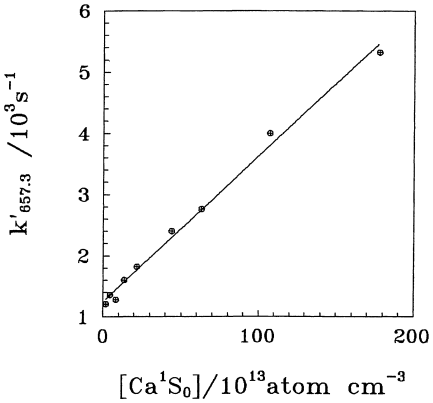

Fig. 3. Variation of the pseudo first-order rate coefficient, k', for the decay of $Ca(4^3P_J)$ at varying elevated temperatures and concentrations of $Ca(4^1S_0)$ following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength {$Ca[4s4p(^3P_1)] \leftarrow Ca[4s^2(^1S_0)]$, λ=657.3 nm} in the presence of excess helium buffer gas.

Fig. 3 shows the plot of k' against $[Ca(^1S_0)]$ constructed from the negative of slopes of the plots of the type given in Fig. 2 and yielding the absolute second-order rate constant for collisional quenching of $Ca(4^3P_J)$ by its ground state atoms of $k_{Ca}=(2.4\pm0.3)\times10^{-12}$ cm^3 per atom s^{-1}. The quoted error principally reflects the variation of diffusional loss with temperature. This result is in sensible agreement with the value of $k_{Ca}=5.1\times10^{-12}$ cm^3 per atom s^{-1} derived from the measurements of phase angle modulation following dye-laser excitation [20]. The difference may possibly arise from the different temperature ranges used in the present study (810–997 K) and that employed by Malins and Benard (923–1173 K) [20]. In contrast to the present measurements, the value of k_{Ca} derived by Malins and Benard [20] from the intercept of a modified Stern–Volmer plot, the diffusional loss term there, β/p, was neglected. The present value of k_{Ca} reported here is significantly higher than the earlier estimates made from the observed variation in the diffusion coefficient, D_{12}, with temperature and, in particular, its departure from a $T^{1.5}$ dependence ($k_{Ca}=4\times10^{-14}$ cm^3 per atom s^{-1} [18], $(1.4\pm1.1)\times10^{-14}$ cm^3 per atom s^{-1} [19]). An estimate based on a similar procedure has been made of the collisional quenching of $Mg[3s3p(^3P_J)]$, 2.712 eV above its $3s^2(^1S_0)$ ground state [5] by ground state Mg atoms. This was found to be $k_{Mg}\approx2\times10^{-15}$ cm^3 per atom s^{-1} (800–1100 K) derived from the temperature dependence of the diffusion coefficient, $D_{12}[Mg(3^3P_J)\text{-}He]$, measured in the time-domain following pulsed dye-laser excitation [30]. Whilst the electronic states arising from $Ca(4^3P_{0,1,2}) + Ca(4^1S_0)$ have not been assigned, we may note that Ca_2 is a species of limited stability in its ground state and in higher lying states [31], clearly indicating an attractive interaction on collision and facilitating the transfer of 1.888 eV electronic energy to translational energy.

3.2. Collisional quenching of $Ca[4s4p(^3P_J)]$ *by He*

The collisional quenching of $Ca[4s4p(^3P_J)]$ by He and the subsequent transfer of 1.888 eV of electronic energy to translational energy following a collision on a dominantly repulsive potential would necessarily be expected to be of low efficiency, indeed, earlier measurements indicate that this is the case [16,20]. In fact, from the experimental viewpoint, the term describing this, $k_{He}[He]$, in Eq. (2) is normally the smallest term by far. Such low quenching efficiencies are difficult to extract from the background of more dominant removal processes as indicated in Eq. (2) and lower measured values are to be preferred. Of course, this measurement is sensitive to quenching by O_2 impurity which is assumed to proceed with close to unit collisional efficiency. In contrast to a flow method [20], the present procedure employed a sealed system where any impurity in the helium gas (99.999%, Gas & Equipment Ltd.) was presumed to have been removed by reaction with hot calcium in the 30 s residence in the reactor prior to laser excitation. As far as the role of helium buffer gas is concerned, for lower pressures, the diffusional loss term β/p_{He} dominates. At higher pressures, typically above 30 Torr, collisional quenching by He dominates diffusional loss and collisional quenching can be characterised at a given temperature as described here.

Fig. 4 gives examples of the digitised output for the time-resolved atomic fluorescence emission following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength $(Ca[4s4p(^3P_J)] \leftarrow Ca[4s^2(^1S_0)])$ at $\lambda = 657.3$ nm at $T = 940$ K and varying concentrations of helium gas. As described in the previous section, computerised fitting of plots of $\ln(I_F - B)$ versus time are given in Fig. 5 yielding the overall first-order decay coefficients (k') for $Ca(4^3P_J)$. Thus, assuming collisional quenching of $Ca(4^3P_J)$ dominates diffusional loss in the pressure range indicated ($p_{He} = 30$–115 Torr), equation (2) can be simplified to the form

$$k' = C + k_{He}[He] \qquad (4)$$

for a fixed temperature. Fig. 6 shows the plot of k' versus [He] for helium gas pressures greater than 38.5 Torr. The linear nature of this plot supports the simplification implicit in Eq. (4) as does the earlier estimate of diffusional loss of $Ca(4^3P_J)$ described in the previous section. This plot thus yields the collisional quenching rate coefficient of $k_{He} = (2.3 \pm 0.3) \times 10^{-16}$ cm^3 per atom s^{-1} ($T = 940$ K) in agreement with the upper limit ever reported by Husain and Schifino [16] of $k_{He} \leq 4 \times 10^{-15}$ cm^3 per atom s^{-1} ($T = 1000$ K) but lower than that resulting from the phase angle modulation measurements of Malins and Benard [20] of $k_{He} = 2.13 \times 10^{-15}$ cm^3 per atom s^{-1} ($923\,K < T < 1173\,K$).

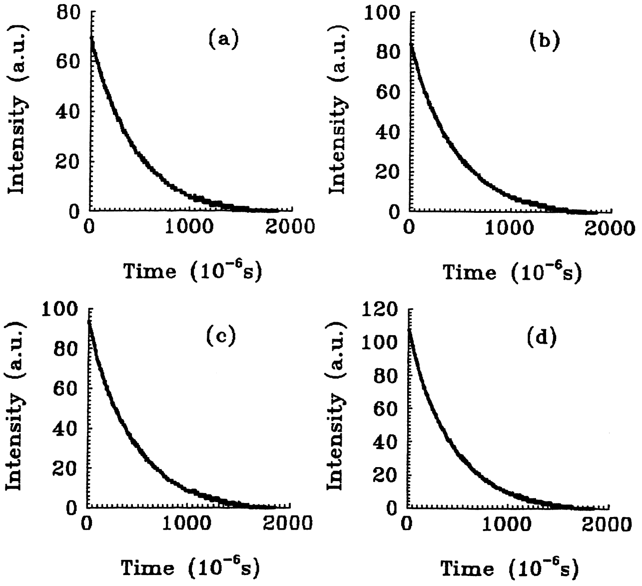

Fig. 4. Examples of the digitised output indicating the exponential decay profiles for the time-resolved atomic fluorescence emission following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength $\{Ca[4s4p(^3P_1)] \leftarrow Ca[4s^2(^1S_0)], \lambda = 657.3\,nm\}$ in the presence of varying concentrations of excess helium buffer gas at elevated temperature. $T = 940$ K. $[He]/10^{17}$ atoms cm^{-3}: (a) 3.1; (b) 6.6; (c) 8.7; (d) 11.9.

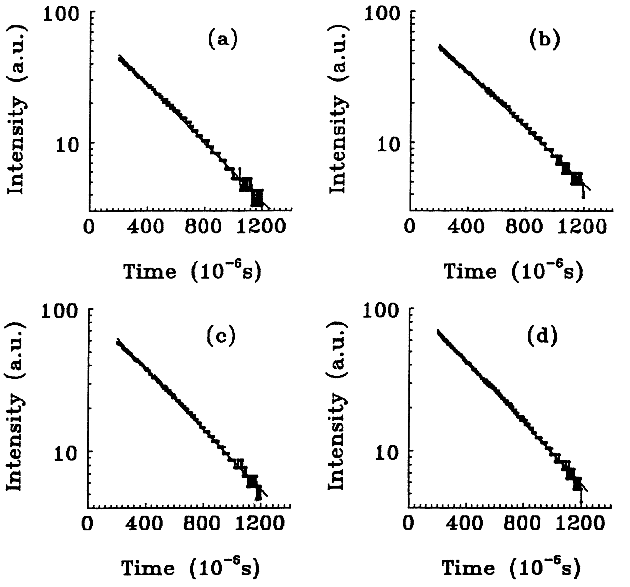

Fig. 5. Examples of the computerised fitting indicating the first-order decay profiles of the time-resolved atomic fluorescence emission following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength $\{Ca[4s4p(^3P_1)] \leftarrow Ca[4s^2(^1S_0)], \lambda = 657.3\,nm\}$ in the presence of varying concentrations of excess helium buffer gas at elevated temperature. $T = 940$ K. $[He]/10^{17}$ atoms cm^{-3}: (a) 3.1; (b) 6.6; (c) 8.7; (d) 11.9.

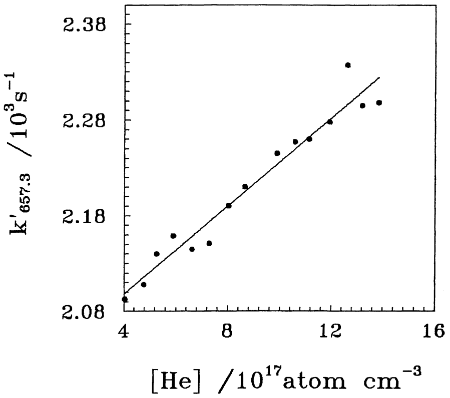

Fig. 6. Variation of the pseudo first-order rate coefficient, k', for the decay of Ca(4^3P_J) at elevated temperature following the pulsed dye-laser excitation of calcium vapour at the resonance wavelength {Ca[4s4p($^3P_1$)] ← Ca[4s^2($^1S_0$)], λ=657.3 nm} in the presence of varying concentrations of excess helium buffer gas at elevated temperature. T=940 K.

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