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Reactions of ground state atomic calcium, Ca[$4s^2(^1S_0)$], investigated by time-resolved atomic resonance absorption spectroscopy at elevated temperature

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Abstract

Absolute second-order rate data at elevated temperature are reported for reactions of ground state calcium atoms, Ca[$4s^2(^1S_0)$], generated by broad band pulsed photodissociation of CaI_2 vapour in the presence of various reactants and excess helium buffer gas and monitored by time-resolved atomic resonance absorption spectroscopy at $\lambda = 422.673$ nm (Ca[$4p(^1P_1)$] $\leftarrow$ Ca[$4s^2(^1S_0)$]). Unlike most previous time-resolved atomic resonance absorption measurements on ground state atomic calcium at this wavelength, complete decay profiles were recorded digitally in the 'single-shot mode' in the time-domain using resonance radiation from a highly intense microwave-powered sealed atomic emission source. The following second-order rate constants for the reactions of Ca(^1S) are reported: k_R ($cm^3\,s^{-1}$ per molecule) (873 K), 1-C_3H_7Cl $(3.5 \pm 0.1) \times 10^{-12}$; 1-$C_4H_9Cl$ $(2.5 \pm 0.2) \times 10^{-12}$; 1-$C_5H_{11}Cl$ $(2.2 \pm 0.4) \times 10^{-12}$; 1-$C_6H_{13}Cl$ $(2.8 \pm 0.3) \times 10^{-12}$; CHF_2Cl $(4.8 \pm 0.2) \times 10^{-12}$; and CH_3I $(16.3 \pm 3.0) \times 10^{-12}$ (errors 1σ). These data are compared with analogous rate data for reactions of atomic calcium with other halides. Estimates are also reported for diffusion coefficients for Ca($^1S_0$) in various buffer gases, D_{12} ($cm^2\,s^{-1}$) (STP): He, 0.47 ± 0.05; Kr, 0.14 ± 0.02; Xe, 0.09 ± 0.02; and N_2, 0.26 ± 0.02. These are found to be in sensible accord with analogous values of D_{12} (Ba($^1S_0$) + He, Kr and Xe) derived hitherto by laser methods. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Calcium; Ca[$4s^2(^1S_0)$]; Photolysis; Abstraction

1. Introduction

Whilst absolute rate data of reactions of ground state alkaline earth atoms are of current interest [1–3], including their role in flame chemistry [4], direct rate measurements of atomic calcium, Ca[$4s^2(^1S_0)$], in particular, by direct spectroscopic monitoring in bulk investigations are limited in scope. Vinckier and coworkers [5,6] have studied the reactions of atomic calcium with N_2O and O_2 in a fast flow reactor where the metal vapour was carried in the flow and monitored by atomic resonance absorption spectroscopy. Plane and coworkers have described detailed measurements carried out in the time-domain on the reactions of Ca(^1S) with O_2, O_3 and N_2O using pulsed laser photolysis for the generation of atomic calcium with monitoring of this atomic state by laser-induced fluorescence [2,7–9], with particular emphasis of the role of such reactions in atmospheric chemistry. Clay and Husain [10,11] have reported absolute rate data at elevated temperatures for the reactions of Ca(^1S) with a range of molecules, including CH_3Cl and C_2H_5Cl, by time-resolved atomic resonance absorption spectroscopy following the generation of atomic calcium by broad band pulsed photolysis of a halide precursor. Such measurements were considered within the context of flame chemistry [4,11]. Rate data for reactions of atomic calcium with molecules such as O_2, N_2O and NO_2 have also been reported by Kashireninov and coworkers [12–14] using the 'temperature variation of the diffusion flame method'. This followed the earlier development of this method for the study of the reaction of BF_3 + amines by Garvin et al. [15]. The various complexities and limitations of this method when applied to reactions of metal atoms have been emphasised in some detail [3].

In this manuscript, we describe absolute rate data for reactions of Ca(^1S), generated by pulsed irradiation of a calcium halide precursor and monitored by time-resolved atomic resonance at elevated temperature with higher alkyl chlorides and methyl iodide following earlier rate measurements on atomic calcium [10,11]. Measurements are described using 'single-shot' decay profiles in the time-domain. Modifications of the experimental technique from those employed hitherto [10,11] include variations in the data

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capture method and the use of an intense atomic emission spectroscopic source for atomic resonance measurements on Ca($^1S_0$). Measurements of diffusion coefficients for Ca(^1S) in He, Kr, Xe and N_2 are reported and compared with analogous data for atomic barium, Ba($^1S_0$), in these buffer gases.

2. Experimental details

The main features of the technique for time-resolved atomic resonance absorption measurements on Ca(4^1S_0) in the 'single-shot mode' following pulsed irradiation in a high temperature quartz reactor have been described hitherto [10,11] and will only be summarised here with a description of modifications where appropriate. Ca(^1S) was generated by the pulsed irradiation of CaI_2 vapour in equilibrium with its solid at elevated temperatures [16,17] in the presence of reactant gases and excess buffer gas. Following irradiation, atomic calcium was monitored at the resonance transition at $\lambda = 422.673$ nm (Ca[4p($^1P_1$)] ← Ca[4s^2($^1S_0$)], $gA = 2.18 \times 10^8\,s^{-1}$ [18–20]). Unlike previous time-resolved measurements on Ca($^1S_0$) using a high current atomic resonance source [10,11], in these measurements, an intensely strong microwave-induced plasma lamp was employed for use with calcium using a resonance cavity following the earlier design of Beenakker [21] and Beenakker and Boumans [22]. A similar configuration has been described previously by Bell and Husain [23,24] for kinetic studies of ground state bismuth and lead atoms. The critical component for calcium in particular, is a quartz tube, 14 cm in length and 0.8 cm in diameter, with a sealed tap, and in which 5–10 pellets of the alkaline earth metal sample with new-cut shinning surfaces are loaded and in which krypton gas is filled to a low pressure of ca. 5 Torr. Although alkaline earth metals at elevated temperatures attack quartz, it is found that this process is acceptably slow here, and given careful handling, the calcium lamps have an operating emission lifetime of the order of 30 h. From the kinetic viewpoint, the principal requirement is that the atomic emission output at $\lambda = 422.7$ nm is constant over the decay profile of the calcium atom that is photochemically generated and that the lamp output is intense for monitoring in the 'single-shot mode'. The lamps were tuned as described previously [23,24] and powered by a standard microwave generator (E.M.S. Greenham Ltd., Microtron MK2, 50 W, 2450 MHz).

The atomic resonance transition was optically isolated with a grating monochromator (Monospec 1000, focal length = 1000 mm, grating 1200 lines mm^{-1}) and detected with a standard photomultiplier tube (E.M.I. 9783B, Wallis R53/6R power supply, 500–1000 V) mounted on the exit slit. This transition at $\lambda = 422.7$ nm lies close to the maximum of optical sensitivity of the p.m.-grating combination at ca. $\lambda = 500$ nm characterised by means of a spectral radiometer (International Light Inc., USA, IL 783). Thus, relatively narrow slit widths (ca. 0.1 mm) yielding an optical resolution of ca. 0.1 nm could be employed in the time-domain on account of the high intensity of the atomic resonance source limiting, in turn, the magnitude of the scattered light on photolysis which, nevertheless, was still significant (see later). The photoelectric signals representing atomic resonance absorption at $\lambda = 422.7$ nm were amplified without distortion using a current-to-voltage converter containing a fast-settling operational amplifier [10,11,25]. In contrast to most of the previous kinetic measurements on Ca(^1S) following pulsed irradiation [10,11], where decay profiles were captured in a transient recorder and transferred to an XY-recorder in analogue form, the signals for the total decay profiles were captured here in digital form in the 'single-shot mode' using a digital storage adapter (Thurlby DSA 524, two channels, 1024 data points) and subsequently transferred into a computer (486 PC) for analysis. The resonance absorption decay profiles were also displayed on the computer screen. Computerised analysis of the digitised decay profiles was carried out using a computer programme, initially written by Carl [26], but with limited modifications for the present study. Most materials (Ca, He, Kr, Xe, N_2, CH_3I) were used essentially as described in previous publications [10,11,27–29]. The alklyl chlorides (1-C_3H_7Cl, 1-C_4H_9Cl, 1-$C_5H_{11}Cl$ and 1-$C_6H_{13}Cl$ and CHF_2Cl (Aldrich)) were used following purification by various freeze-pump-thaw cycles.

3. Results and discussion

Fig. 1 gives examples of the digitised time-variation of the transmitted light intensity (I_{tr}) at $\lambda = 422.7$ nm (Ca(4p($^1P_1$)) → Ca(4s^2($^1S_0$)) + $h\nu$) indicating the decay of resonance absorption by ground state calcium atoms following the pulsed irradiation of CaI_2 vapour at elevated temperature ($T = 873$ K) in the presence of C_3H_7Cl, in this instance, and excess helium at different total pressures. It may be seen that the atomic profiles, in this instance, exhibit line saturation and decays are analysed once this saturation has passed. Of course, experimental conditions may be chosen where such line saturation is not evident (see later). The nature of the kinetic analysis has been given in previous measurements on reactions of Ca($^1S_0$) in the time-domain [10,11] and is only summarised here. First-order decay profiles for Ca($^1S_0$) after line saturation derived from the computerised plots of the transmitted light intensity (I_{tr}) at $\lambda = 422.7$ nm are shown in Fig. 2. These are presented in the form $\ln(\ln(I_0/I_{tr}))$ versus time from the combination of the Beer–Lambert law ($I_{tr}(t) = I_0 \exp(-\varepsilon c_t l)$) in its standard form and where $c_t = [\mathrm{Ca}(^1S_0)]_0 \exp(-k't)$ describing first-order decay of Ca(^1S), where k' is the first-order decay coefficient, the immediate object of kinetic interest. The ordinate is presented in arbitrary units, typically increased by 4 units to present the magnitudes of $\ln(\ln(I_0/I_{tr}(t))$ as positive quantities as only the slope of the resulting plot, $-k'$, is required for kinetic purposes. The values of k' are, in fact, obtained from

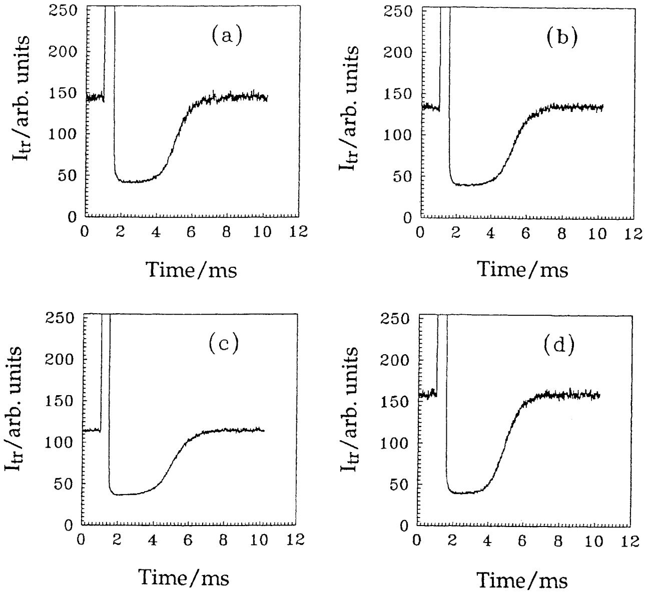

Fig. 1. Examples of the digitised time-variation of the transmitted light intensity (I_{tr}) at $\lambda = 422.7\,\mathrm{nm}$ ($\mathrm{Ca(4p(^1P_1))} \rightarrow \mathrm{Ca(4s^2(^1S_0))} + h\nu$) indicating the decay of resonance absorption by ground state calcium atoms following the pulsed irradiation of $\mathrm{CaI_2}$ vapour at elevated temperature ($T = 873\,\mathrm{K}$) in the presence of $\mathrm{C_3H_7Cl}$ and excess helium at different total pressures (p_{T}). Here, $f = [\mathrm{C_3H_7Cl}]/([\mathrm{He}] + [\mathrm{C_3H_7Cl}]) = 5.2 \times 10^{-4}$ and p_{T} (Torr): (a) 15.4; (b) 33.4; (c) 41.8; (d) 50.4.

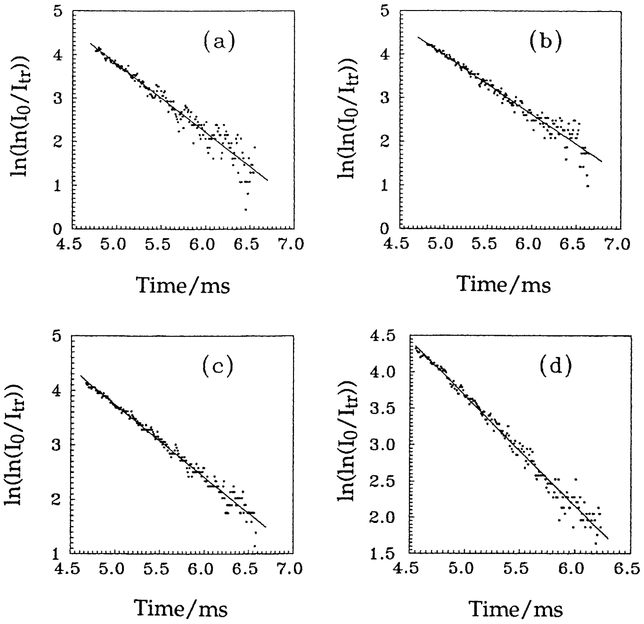

Fig. 2. Examples of the computerised plots derived from the digitised time-variation of the transmitted light intensity (I_{tr}) at $\lambda = 422.7\,\mathrm{nm}$ ($\mathrm{Ca(4p(^1P_1))} \rightarrow \mathrm{Ca(4s^2(^1}S_0))} + h\nu$) indicating the first-order decay of ground state calcium atoms following the pulsed irradiation of $\mathrm{CaI_2}$ vapour at elevated temperature ($T = 873\,\mathrm{K}$) in the presence of $\mathrm{C_3H_7Cl}$ and excess helium at different total pressures (p_{T}). Here, $f = [\mathrm{C_3H_7Cl}]/([\mathrm{He}] + [\mathrm{C_3H_7Cl}] = 5.2 \times 10^{-4}$ and p_{T} (Torr): (a) 15.4; (b) 33.4; (c) 41.8; (d) 50.4.

computerised fitting of the raw data to the form $I_{\mathrm{tr}}(t)(\lambda = 422.7\,\mathrm{nm}) = I_0 \exp(-A \exp(-k't))$, the first-order forms being presented to indicate the kinetic order of the decay of $\mathrm{Ca(^1S_0)}$.

The first-order decay coefficients may be expressed in the form [10,11]

$$k' = \frac{\beta}{p_{\mathrm{T}}} + k_{\mathrm{R}} f p_{\mathrm{T}} \tag{i}$$

comprising the loss of $\mathrm{Ca(^1S_0)}$ by diffusion to the walls of the reaction vessel at given total pressure, p_{T}, principally determined by the excess buffer gas, He in this instance and removal by chemical reaction of the type

$$\mathrm{Ca(4^1S_0)} + \mathrm{RCl} \rightarrow \mathrm{CaCl(X^2\Sigma^+)} + \mathrm{R} \tag{ii}$$

where p_{T} represents the partial pressure of the reactant, p_{RCl}, f the fractional composition of the reactant ($f = [\mathrm{RCl}]/([\mathrm{He}] + [\mathrm{RCl}])$ and k_{R} in this form describes collisional loss using the appropriate units of pressure and time. The diffusional loss term, β/p_{T}, may be approximated to the form

$$\beta = \left(\frac{\pi^2}{l^2} + \frac{2.41^2}{r^2}\right) D_{12} \tag{iii}$$

using the "long-time solution" of the diffusion equation for a cylinder (length l, radius r) [30,31] assuming removal of Ca at the walls of the reactor on every collision where D_{12} is the diffusion coefficient of Ca in He at a given pressure and temperature. This type of treatment has been extended using a simplified 1D random walk model via a Monte–Carlo simulation employing different "sticking coefficients" as described in the removal of $\mathrm{K(4^2S_{1/2})}$ by diffusion loss in $\mathrm{N_2}$ [32]. Further, the temperature dependence of D_{12} can be considered in terms of the relevant transport integrals requiring the use of the standard term, kT/ε_{12} [33]. Such an approach has been used when considering the temperature dependence of diffusion coefficients of alkali atoms in flames at different temperatures [34–36]. The present measurements on diffusional removal (see later), coupled with the above approximation on wall removal, do not merit this level of analysis in our view. Hence, estimates of D_{12} of Ca at STP have been made assuming an inverse pressure dependence of the form $D_{12} = D_{12}^0(p_0/p)$ and $D_{12} \propto T^{3/2}$ in accord with simple gas kinetic theory.

Eq. (iii) may be recast in the form

$$k' p_{\mathrm{T}} = \beta + k_{\mathrm{R}} f p_{\mathrm{T}}^2 \tag{iv}$$

Fig. 3 shows the variation of the measured pseudo first-order rate coefficients (k') for the decay of $\mathrm{Ca(4^1S_0)}$ in the presence of varying pressures ($P = p_{\mathrm{T}}$) in the form $k'P$ versus P^2 for mixtures of fixed relative composition of $\mathrm{C_3H_7Cl}$, $\mathrm{C_4H_9Cl}$, $\mathrm{C_5H_{11}Cl}$ and $\mathrm{C_6H_{13}Cl}$ with He derived from plots of the type presented in Figs. 1 and 2. The slopes of these plots, coupled with the values of f employed (Fig. 3), yield the absolute rate constants for the reactions

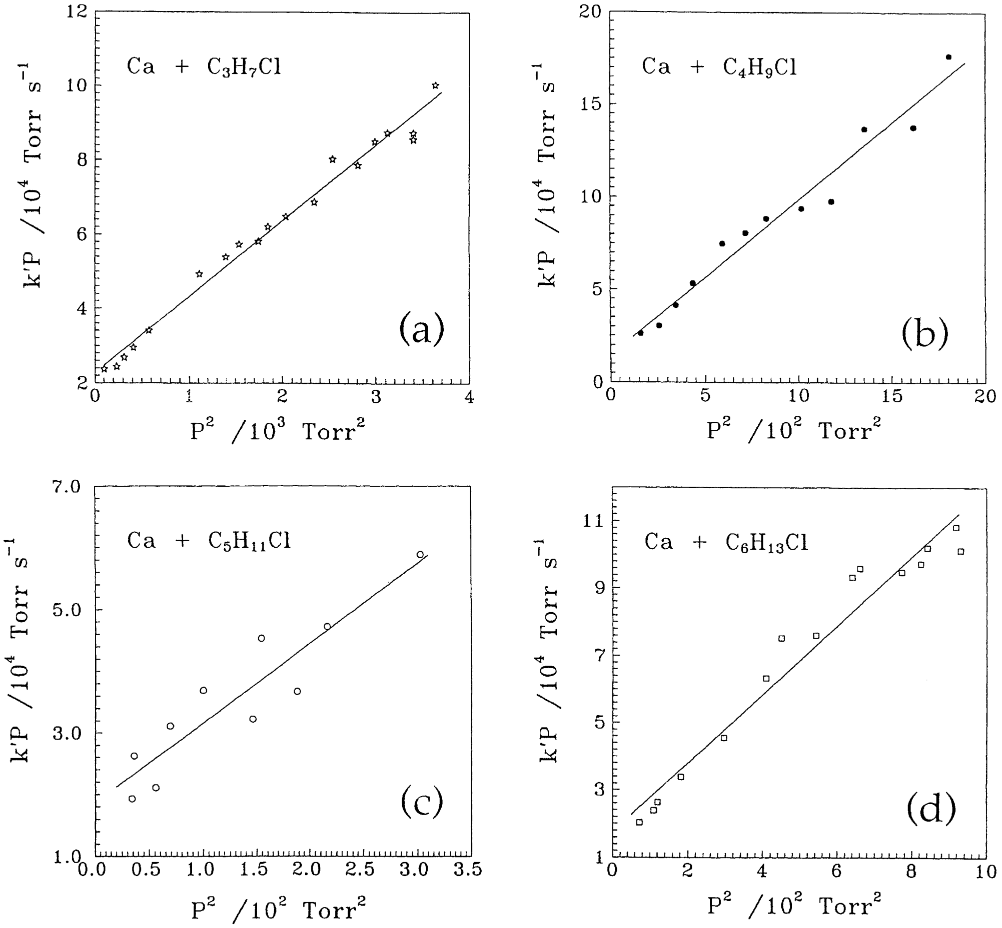

Fig. 3. Variation of the pseudo first-order rate coefficient (k') for the decay of Ca(4^1S_0) following the pulsed irradiation of CaI_2 vapour at elevated temperature (873 K) in the presence of varying pressures ($P = p_T$) of mixtures of fixed relative composition of C_3H_7Cl, C_4H_9Cl, $C_5H_{11}Cl$ and C_6H_{13} with He (f = [C_3H_7Cl, C_4H_9Cl, $C_5H_{11}Cl$ and $C_6H_{13}Cl$]/([He] + [C_3H_7Cl, C_4H_9Cl, $C_5H_{11}Cl$ and $C_6H_{13}Cl$]). $k'P$ vs. P^2: (a) C_3H_7Cl ($f = 5.2 \times 10^{-4}$); (b) C_4H_9Cl ($f = 3.0 \times 10^{-3}$); (c) $C_5H_{11}Cl$ ($f = 5.3 \times 10^{-3}$); (d) $C_6H_{13}Cl$ ($f = 3.2 \times 10^{-3}$).

$$\mathrm{Ca(^1S) + C_3H_7Cl \rightarrow CaCl + C_3H_7} \quad (1)$$

$$\mathrm{Ca(^1S) + C_4H_9Cl \rightarrow CaCl + C_4H_9} \quad (2)$$

$$\mathrm{Ca(^1S) + C_5H_{11}Cl \rightarrow CaCl + C_5H_{11}} \quad (3)$$

$$\mathrm{Ca(^1S) + C_6H_{13}Cl \rightarrow CaCl + C_6H_{13}} \quad (4)$$

Thus, the following absolute second-order rate constants for reactions with Ca(^{1}S) are found at a single elevated temperature: k_R (cm^3 s^{-1} per molecule (873 K), 1-C_3H_7Cl (3.5 ± 0.1) × 10^{-12}; 1-C_4H_9Cl (2.5 ± 0.2) × 10^{-12}; 1-$C_5H_{11}Cl$ (2.2 ± 0.4) × 10^{-12}; and 1-$C_6H_{13}Cl$ (2.8 ± 0.3) × 10^{-12}, respectively (errors 1σ). Fig. 4(a) shows the analogous plot of $k'P$ versus P^2 for the reaction of Ca(^{1}S) with CHF_2Cl

$$\mathrm{Ca(^1S) + CHF_2Cl \rightarrow CaCl + CHF_2} \quad (5)$$

to yield $k(\mathrm{Ca(^1S)} + \mathrm{CHF_2Cl})(T = 873\,\mathrm{K}) = (4.8 \pm 0.2) \times 10^{-12}\,\mathrm{cm^3\,s^{-1}}$ per molecule (1σ). The thermochemistry of reactions (1)–(5) are of approximate magnitude $\Delta H = -50\,\mathrm{kJ\,mol^{-1}}$ (D_0^0(CaCl($X^2\Sigma^+$)) = 395 kJ mol^{-1} [37]; D_0^{298}(C_3H_7Cl) = 339 kJ mol^{-1}; D_0^{298}(CHF_2Cl) = 347 kJ mol^{-1} [38]).

Whilst the reaction of Ca ($^1S_0$) with CH_3I

$$\mathrm{Ca(^1S) + CH_3I \rightarrow CaI + CH_3} \quad (6)$$

is less exothermic ($\Delta H = -33\,\mathrm{kJ\,mol^{-1}}$; D_0^0(CaI($X^2\Sigma^+$) = 267 kJ mol^{-1} [37]; D_0^{298}(CH_3I) = 234 kJ mol^{-1} [38]), this reaction is significantly more rapid with greater scatter in the rate measurements. Fig. 5 gives examples of the digitised variation of the transmitted light intensity (I_{tr}) at λ = 422.7 nm indicating the decay of resonance absorption by ground state calcium atoms at elevated temperature (T = 873 K) in the presence of CH_3I and excess helium at different total pressures. Computerised plots derived from these profiles indicating the first-order decay of Ca($^1S_0$) are given in Fig. 6. The resulting plot of $k'P$ versus P^2 is given in Fig. 4(b). This is seen to be scattered with a significant error in the intercept, presumably arising from some decomposition of the alklyl iodide. The slope of this plot, yielding $k(\mathrm{Ca(^1S)} + \mathrm{CH_3I}, T = 873\,\mathrm{K})$ =

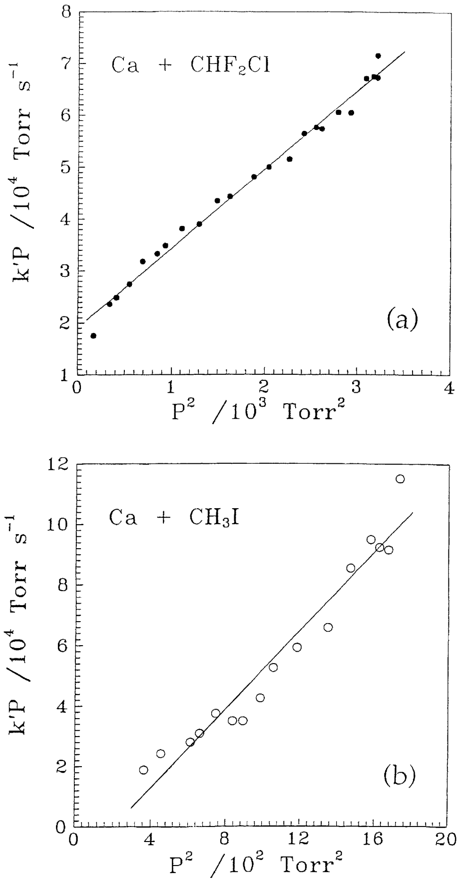

Fig. 4. Variation of the pseudo first-order rate coefficient (k') for the decay of Ca(4^1S_0) following the pulsed irradiation of CaI_2 vapour at elevated temperature (873 K) in the presence of varying pressures ($P = p_T$) of mixtures of fixed relative composition of CHF_2Cl and CH_3I with He (f = [CHF_2Cl, CH_3I]/([He] + [CHF_2Cl and CH_3I]). $k'P$ vs. P^2: (a) CHF_2Cl ($f = 2.8 \times 10^{-4}$) and (b) CH_3I ($f = 2.7 \times 10^{-3}$).

$(16.3 \pm 3.0) \times 10^{-12}\,cm^3\,s^{-1}$ per molecule (1σ), nevertheless indicates significantly more rapid reaction than with Cl containing molecules.

The reactions of Ca(4^1S_0) with C_3H_7Cl, C_4H_9Cl, $C_5H_{11}Cl$ and $C_6H_{13}Cl$ are not significantly more rapid than found from time-resolved atomic resonance absorption measurements with the lighter chlorides, namely, k_R ($cm^3\,s^{-1}$ per molecule): CH_3Cl ((3.7 ± 0.4) × 10^{-12}, 900 K) and C_2H_5Cl ((4.6 ± 0.4) × 10^{-12}, 897 K) [10,11]. The reaction of Ca(4^1S_0) with CHF_2Cl is slower than that observed with the dichloride using the analogous technique to that employed here, namely, k_R ($CHFCl_2$, $T = 898$ K) = $(1.1 \pm 0.1) \times 10^{-11}\,cm^3\,s^{-1}$ per molecule [10,11]. Finally, in this context, the reactions of Ca($^1S_0$) with CH_3F (k_R (901 K) = $(3.4 \pm 0.2) \times 10^{-12}\,cm^3\,s^{-1}$ per molecule) and CH_3Cl (k_R (900 K) = $(3.7 \pm 0.4) \times 10^{-12}\,cm^3\,s^{-1}$ per molecule) [10,11] are slower than that with the heavier molecule, CH_3I, not withstanding the thermochemistry for reaction which is still exothermic in all cases.

The characterisation of diffusion coefficients from intercepts of plots, such as those in Figs. 3, 4 and 6 based on

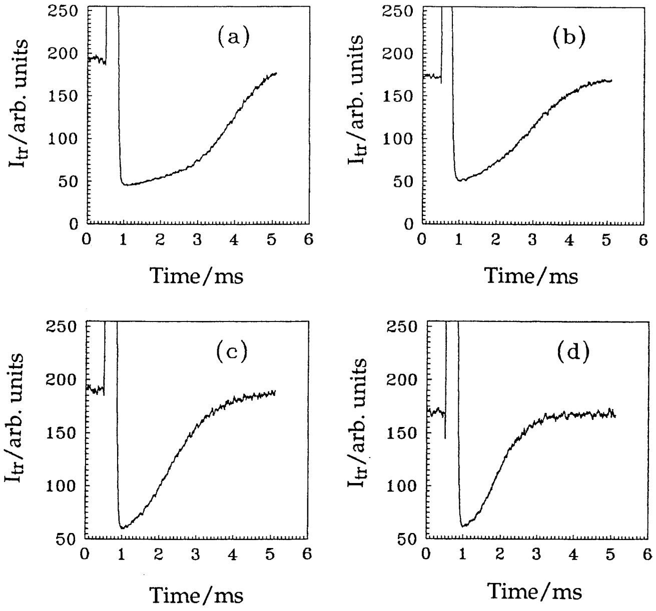

Fig. 5. Examples of the digitised time-variation of the transmitted light intensity (I_{tr}) at λ = 422.7 nm (Ca(4p($^1P_1$)) → Ca(4s^2($^1S_0$)) + $h\nu$) indicating the decay of resonance absorption by ground state calcium atoms following the pulsed irradiation of CaI_2 vapour at elevated temperature ($T = 873$ K) in the presence of CH_3I and excess helium at different total pressures (p_T). Here, $f = [CH_3I]/([He] + [CH_3I]) = 3.2 \times 10^{-4}$ and p_T (Torr): (a) 14.5; (b) 24.7; (c) 29.8; (d) 34.4.

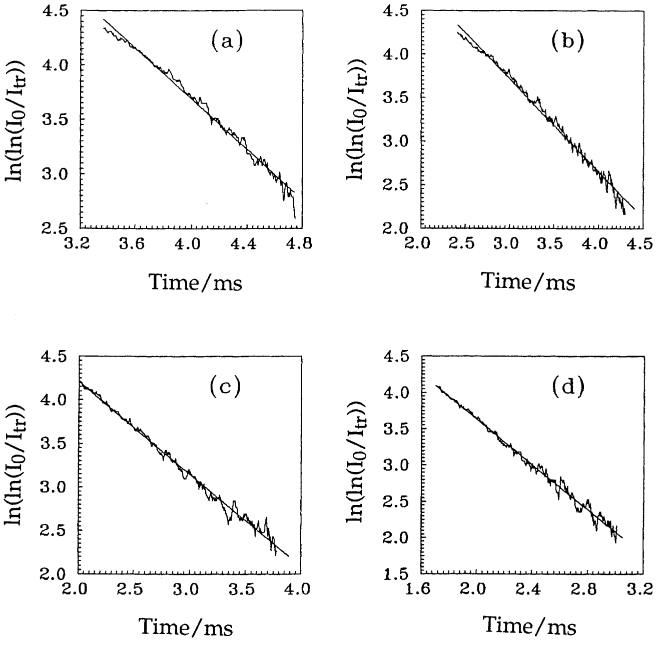

Fig. 6. Examples of the computerised plots derived from the digitised time-variation of the transmitted light intensity (I_{tr}) at λ = 422.7 nm (Ca(4p($^1P_1$)) → Ca(4s^2($^1S_0$)) + $h\nu$) indicating the first-order decay of ground state calcium atoms following the pulsed irradiation of CaI_2 vapour at elevated temperature ($T = 873$ K) in the presence of CH_3I and excess helium at different total pressures (p_T). Here, $f = [CH_3I]/([He] + [CH_3I]) = 3.2 \times 10^{-4}$ and p_T (Torr): (a) 14.5; (b) 24.7; (c) 29.8; (d) 34.4.

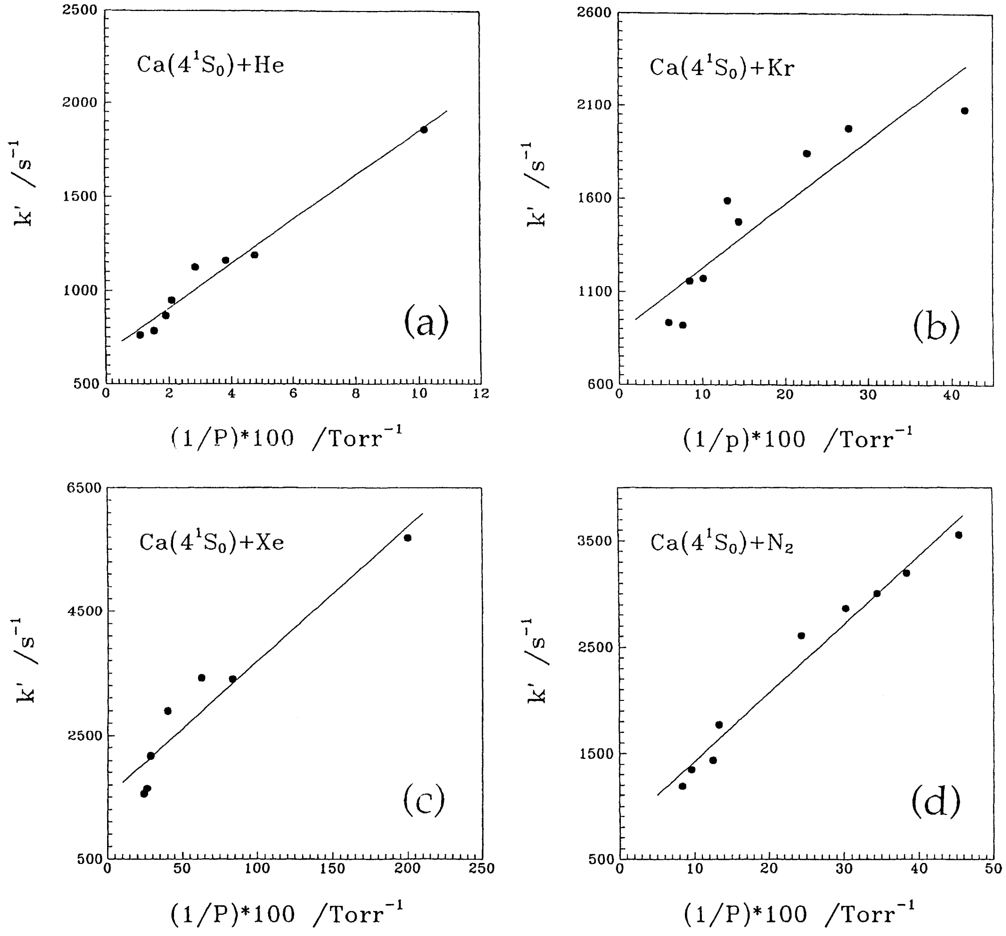

Fig. 7. Variation of the overall first-order rate coefficient (k') for the decay of Ca(4^1S_0) generated from the pulsed irradiation of CaI_2 vapour at $T = 873$ K and monitored by time-resolved atomic resonance absorption spectroscopy at $\lambda = 422.7$ nm in the presence of varying pressures (P) of different buffer gas, indicating diffusional loss. k' vs. $1/P$: (a) He; (b) Kr; (c) Xe; (d) N_2.

Eq. (iv), namely, β, cannot be made with accuracy as diffusion represent a small component of the overall decay when competing with chemical removal of Ca(4^1S_0) and, indeed, these intercepts are subject to significant scatter. In principle, the values of β from such plots and the long-time solution of the diffusion equation for a cylinder, where $l \gg r (r = 1$ cm) would enable an estimate of D_{12} (Ca–He) (cm^2 s^{-1}) to be made as $\beta \approx (5.81/l^2)D^0_{12}(\mathrm{STP}) \times 760 \times (873/273)^{3/2}$ as implied earlier. Better estimates of D_{12} can be made from plots of k' versus $1/p$ (Torr) for the decay of Ca(4^1S_0) in the presence of buffer gases alone though these plots are still subject to the kinetic effects of small levels of impurities of halogens, e.g. I_2 from the CaI_2 precursor at elevated temperatures. This will be manifest in the intercepts of such plots. Fig. 7 shows plots of k' versus $1/P$ for the buffer gases He, Kr, Xe and N_2 at $T = 873$ K. An earlier measurement for D^0_{12} (Ca–He) has been reported as (0.19 ± 0.01) cm^2 s^{-1} [10]. The slopes of these plots combined with the long-time solution of the diffusion Eq. (iii), the geometry of the present reactor, the assumption of unit efficiency in the loss of Ca(^{1}S) at the walls and the pressure and temperature dependences of D_{12} described above yields the following estimates for the diffusion coefficients, D^0_{12}(cm^2 s^{-1}): He, 0.47±0.05; Kr, 0.14 ± 0.02; Xe, 0.09 ± 0.02; and N_2,0.26 ± 0.02. These results may be compared with analogous data for the diffusion coefficients for ground state atomic barium Ba(6^1S_0) in the noble gases, D^0_{12} (Ba–gas) determined from the detailed laser measurements of Namiotka et al. [39]: He, 0.364 ± 0.031; Kr, 0.0839 ± 0.0078; and Xe, 0.0593 ± 0.0077 indicating a sensible monotonic variation across the noble gases for both alkaline earth atoms consistent with a monotonic variation in collision cross-sections.

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