A Search for Isotope Effects in Chemiluminescent Reactions of Metastable Ca*(^3P_J, $^1D_2$) Atoms with CH_3I and CD_3I Molecules

B. Pranszke, P. Kierzkowski, and A. Kowalski
Institute of Experimental Physics, University of Gdańsk,
ul. Wita Stwosza 57, PL-80-952 Gdańsk, Poland

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Chemiluminescent reactions of calcium atoms in the metastable ^3P_J and $^1D_2$ states with CH_3I and CD_3I were studied in a beam-gas arrangement. Calcium monoiodide spectra associated with transitions from the electronic A $^2\Pi$, B $^2\Sigma^+$ and C $^2\Pi$ states to the X $^2\Sigma^+$ ground state were recorded. Total collision and chemiluminescence cross sections were measured. It was found that isotopic substitution in the methyl group does not change the reaction cross sections and the chemiluminescence spectra.

Key words: Chemiluminescence; Energy Transfer; Atomic Collisions; Molecular Collisions; Isotopic Effect.

Introduction

In the past attempts were made to observe isotope effects in reactions of alkaline earth atoms, M, with RI molecules (where R stands for CH_3 or CD_3 and I for iodine). Reactive collisions of ground state barium and strontium atoms with these molecules were studied by laser-induced fluorescence [1] and single photon ionization [2] techniques, and no effect of isotopic substitution was found. In the present paper we apply the method of chemiluminescence to search for isotope effects in the same family of reactions.

It is known that chemiluminescence spectra and photon yields of electronically excited alkaline earth monohalide products, MX*, depend on the size and identity of the R' group departing after MX* is formed. This is due to the fact that different R' groups consume different parts of available reaction energy in form of internal excitation, as these groups contain different numbers of atoms (influencing the number of vibrational modes) or are built of unlike atoms. In this context we want to consider isotopic substitution CH_3I / CD_3I in the Ca*(^3P_J, $^1D_2$) + methyl iodide reaction. As the vibrational and rotational frequencies of CH_3 and CD_3 are quite different, it appeared interesting to look if the influence of the methyl group can be seen from chemiluminescence spectra or from the electronic branching ratio of the CaI product.

The reaction of metastable Ca*(^3P_J, $^1D_2$) with CH_3I was studied previously by the method of chemiluminesence [3, 4] and in time-resolved mode [5]. The former studies report on chemiluminescence spectra from the first two excited electronic states of CaI and give cross sections for formation of these states. In this paper we extend the studies to the CaI(C $^2\Pi$) state and further compare reactions of Ca* with iodomethane and iodomethane-d_3:

$$\begin{aligned}&Ca^*(^3P_J,{}^1D_2) + CH_3I\,/\,CD_3I\\ &\quad\rightarrow CaI(X\,^2\Sigma^+) + CH_3\,/\,CD_3, &(1)\\ &\quad\rightarrow CaI^*(A\,^2\Pi,\,B\,^2\Sigma^+,\,C\,^2\Pi) + CH_3\,/\,CD_3, &(2)\end{aligned}$$

where channel (1) describes formation of ground state calcium monoiodide and channel (2) corresponds to electronic chemiluminescence. We try to find an isotope effect in either the chemiluminescence spectra or the total collision cross sections (these are the upper limits of overall reactivity), or in chemiluminescence cross sections. The latter are determined using the experimental method of [6, 7].

Experimental

The experiment was performed in a stainless steel cylindrical vacuum chamber, 80 cm in diameter and 70 cm in height. The chamber was pumped by a 7 l/s

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Reprint requests to Dr. A. Kowalski; Fax: (00-48) (58) 341-3175.

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double stage rotary pump and a 2000 l/s diffusion pump. The vacuum system gave a background pressure of 0.13 mPa in the chamber; the pressure increased to 1 mPa when iodomethane gas was admitted. An atomic beam of Ca was obtained from a resistively heated oven mounted vertically and operated at 1080 K. A hot-cathode discharge (8 V, 0.8 A) along the beam just above the oven produced an estimated fraction of 20% of Ca atoms in the metastable ^3P_J states, as was measured in [8] for a similar source. The beam contained also a small fraction of $^1D_2$ states: the $N(^1D_2) / N(^3P_J)$ number density ratio was 0.05 ÷ 0.06, as determined by comparison of the intensities of the $Ca(^3P_1\text{-}^1S_0)$ and $Ca(^1D_2\text{-}^1S_0)$ atomic lines. In the recorded spectra the $Ca(^1P_1\text{-}^1S_0)$ line is also present. Its intensity, considering the transition probability $A(^1P_1\text{-}^1S_0) = 2.18 \times 10^8\ s^{-1}$ [9], indicates that the number density of $Ca^*(^1P_1)$ atoms amounts to a fraction 10^{-4} of that of $Ca^*(^1D_2)$, and therefore the contribution of the former atoms to the observed chemiluminescence spectra can be neglected. The scattering cell with a quartz window was mounted above the beam source. The window was masked for the cross section measurements to make the scattering path length equal to $x = (28 \pm 2)$ mm. Assuming statistical population of metastable states in the discharge, from the radiative lifetime of the $^3P_1$ state we estimate that the radiating $Ca^*(^3P_1)$ fraction of the $Ca^*(^3P_J)$ atoms in the window was 0.26. The target gases were admitted to the scattering cell ($T = 330$ K) through a manometer-controlled valve (Granville-Phillips, model 245) at pressures up to 0.2 Pa, as measured with a capacitance differential manometer (MKS Baratron type 120AD-00001RAU), using the background vacuum in the chamber as a reference. The chemiluminescence spectra were recorded with a Carl Zeiss Jena SPM-2 monochromator (focal length 0.4 m, grating 651 l/mm, blazed at $\lambda_B = 570$ nm) and a photon counting system (SR-400 with a preamplifier) equipped with a Burle C31034 cooled photomultiplier. To determine the chemiluminescence cross sections, the monohalide spectra and Ca* lines were corrected for the spectral response of the detecting system. This callibration was done with an Osram Wi 17/G tungsten band lamp. Transition probabilities used were: $A(^3P_1\text{-}^1S_0) = 2460\ s^{-1}$ (average of literature values collected in [10]), $A(^1D_2\text{-}^1S_0) = 40\ s^{-1}$ (average of data in [10]). The target compounds CH_3I (purity 99%) and CD_3I (99,5+ atom %D) were obtained from Aldrich and used after several pump-freeze cycles.

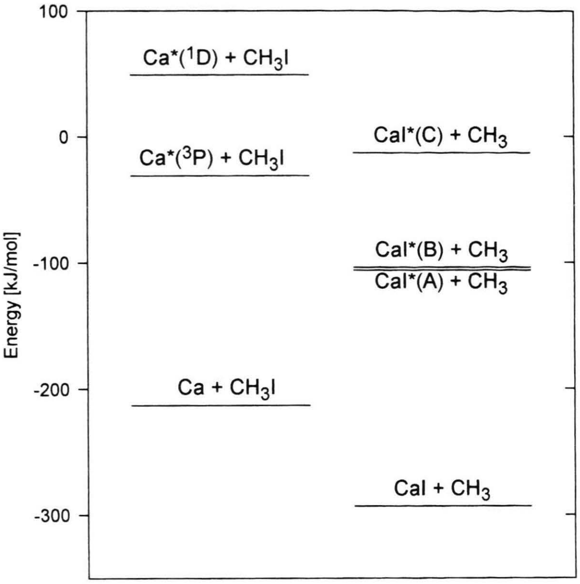

Fig. 1. Energy levels for the system studied. Reactants are given in the left, products in the right column. Zero on the energy scale corresponds to dissociation into Ca atom, I atom and CH_3 / CD_3 group. Average translational and internal energies of reactants are included; accessible product channels are those located below corresponding reactant states. Since the dissociation energies of normal and deuterated iodomethane are almost identical, the levels for CH_3I represent also those for CD_3I.

Energetics

The energy levels of the system studied are given in Figure 1. Atomic energy levels were taken from [11], molecular levels from [12]. The bond strength used was $D_0(CH_3\text{-}I) = 233$ kJ/mol [1], while this value for deuterated iodomethane is 1 kJ/mol less [13]. The dissociation energy of CaI is 293 kJ/mol [14]. The sums of the average translational and internal energies of the reactants were estimated as in [15] and found to be 20 kJ/mol for both reactions.

Results and Discussion

Chemiluminescence spectra of CaI(A-X,B-X) observed for $Ca^*(^3P_J, {}^1D_2)$ colliding with CH_3I and CD_3I are given in Figure 2. The spectra for CH_3I were presented before in [3 - 5], but with lower resolution. The chemiluminescence spectra of CaI(C-X) recorded for the same reactions were obtained here for the first time and are shown in Figure 3. The spectra in both, the red and the blue region are independent of the CH_3 / CD_3 isotopic substitution.

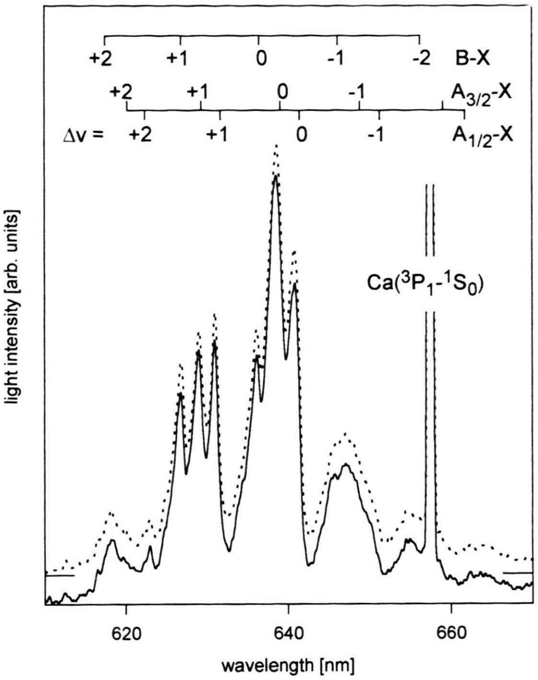

Fig. 2. Chemiluminescence spectra of Ca(A-X,B-X) observed in collisions of Ca* with CH_3I (dotted line) and CD_3I (continuous line). The spectra are corrected for spectral response of the detecting system. Spectral resolution is 1.0 nm in both cases. For better comparison, the baseline of the former spectrum is shifted upwards as indicated.

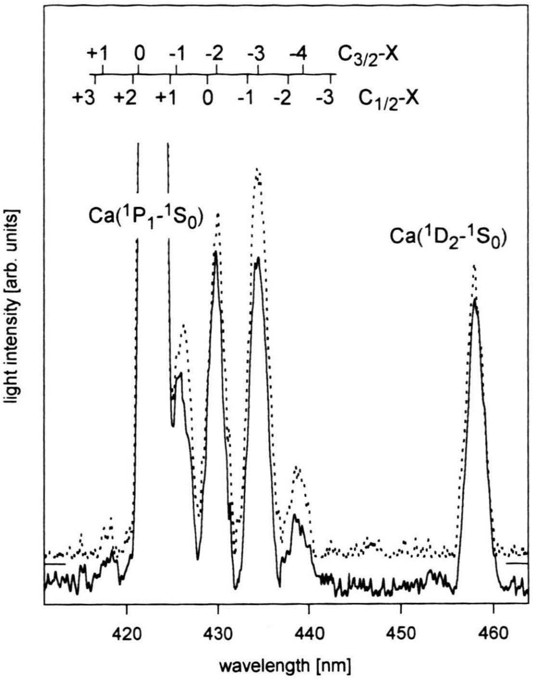

Fig. 3. Chemiluminescence spectra of Ca(C-X) observed in collisions of Ca* with CH_3I (dotted line) and CD_3I (continuous line). The spectra are corrected for spectral response of the detecting system. Spectral resolution is 4.0 nm in both cases. For better comparison, the baseline of the former spectrum is shifted upwards as indicated.

Collision cross sections determined in this work are collected in Table 1. The attenuation cross sections for removal of Ca*($^3P_1$) and Ca*($^1D_2$) reactants from the beam, as well as for attenuation of CaI(A,B-X) chemiluminescence (the latter cross section describes a weighted removal of Ca*(^3P_J) and Ca*($^1D_2$) reaction precursors) are almost identical for both target gases. The total cross sections can be compared with literature values [3, 4]. The agreement is satisfactory. The CaI(A+B) chemiluminescence is produced in reactions of both, Ca*(^3P_J) and Ca*($^1D_2$) atoms [3, 4]. The contributions of these reactants can be obtained for example by laser depletion of a given reactant [3] or by changing the discharge conditions and influencing in this way the number density ratio of the metastables [4]. We do not have access to a laser nor a cathode emission stabiliser (this type of power supply was not necessary in [4] because the CL spectra there were recorded with an optical multichannel analyser) therefore we have run the discharge at the voltage corresponding to minimum production of Ca*($^1D_2$) while maintaining stable conditions of the excited beam. The chemiluminescence cross sections σ_{CL}(A+B) are derived here by comparison of the chemiluminescence intensity with the intensity of the Ca($^3P_1$-$^1S_0$) atomic line only – in this way we completely neglect the contribution of Ca*($^1D_2$) and obtain upper limits of chemiluminescence cross sections for Ca*(^3P_J) reactants. Knowing that the concentration of Ca*($^1D_2$) in the observed reaction zone is in our experiment about 16 times lower than that of Ca*(^3P_J) (see Experimental section) and using the literature data of [3, 4], which indicate that in the chemiluminescence channel Ca*($^1D_2$) is 4 times more reactive than Ca*(^3P_J), one finds that our upper limit overestimates the true values of σ_{CL}(A+B) by about 25% for the latter reactant. With this correction, our value of σ_{CL}(A+B) is still twice as high as that obtained by other authors [3, 4]. One possible source of this discrepancy could stem from the fact that we have a lower average collision energy (substantially lower beam source temperature: 1080 K vs. 1250 - 1400 K in [4]; the other

Table 1. Total collision cross sections, σ_t, derived from the attenuation of the Ca*($^3P_1$), Ca*($^1D_2$) atoms or from the pressure dependence of CaI(A,B-X) chemiluminescence, and chemiluminescence cross sections σ_{CL} (all values in 10^{-20} m^2).

Cross section	Ca* + CH_3I	Ca* + CD_3I
$\sigma_t(^3P_1)$	105 ± 7[a]	104 ± 7
$\sigma_t(^1D_2)$	110 ± 10[b]	111 ± 10
σ_t(CL(A+B))	116 ± 7	114 ± 7
σ_{CL}(A+B) [c]	4.6 ± 0.9[d,e]	5.0 ± 0.9
σ_{CL}(C) [f]	6 ± 2	6 ± 2

[a] [3] gives $(155 \pm 5)\times 10^{-20}$ m^2, [4] gives $(84 \pm 6)\times 10^{-20}$ m^2; [b] [4] gives $(124 \pm 8)\times 10^{-20}$ m^2; [c] the chemiluminescence cross section is obtained as if all observed CaI(A+B) chemiluminescence were due to reactions of Ca*(^3P_J) atoms only, therefore it is an upper limit for this atomic reactant; [d] [3] gives σ_{CL}(A+B) = $(1.34 \pm 0.24)\times 10^{-20}$ m^2 for Ca*(^3P_J) reactant and σ_{CL}(A+B) = $(7.46 \pm 1.71)\times 10^{-20}$ m^2 for Ca*($^1D_2$) reactant; [e] [4] gives σ_{CL}(A+B) = $(1.8 \pm 0.9)\times 10^{-20}$ m^2 for Ca*(^3P_J) reactant and σ_{CL}(A+B) = $(8.0 \pm 3.2)\times 10^{-20}$ m^2 for Ca*($^1D_2$) reactant; [f] the energy balance indicates that the CaI*(C $^2\Pi$) state can be formed exclusively in collisions of the Ca*($^1D_2$) reactant.

reference does not give this parameter). It is also possible that we have a lower level of the Ca*($^3P_1$-$^1S_0$) light scattered from the beam source discharge, and comparing the corresponding line intensity with the chemiluminescence spectrum we arrive at higher values of σ_{CL}(A+B). All these problems are absent in the derivation of the σ_{CL}(C) because from the energy balance given in Fig. 1 it is clear that CaI*(C) can be formed only in collisions of Ca*($^1D_2$) with both target molecules. We find that all the chemiluminescence cross sections are independent of the isotopic substitution CH_3I / CD_3I.

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