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Steric Effects on Electronically Excited Product Channels in Reactions between $\text{Ca}(^1\text{D}_2)$ and $\text{CH}_3\text{X}(\text{JKM})$ ($\text{X} = \text{Cl}, \text{Br}$)[†]

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Steric effects are reported for the chemiluminescent $\text{CaCl}(\text{B } ^2\Sigma)$ and $\text{CaBr}(\text{A } ^2\Pi)$ exit channels of the reaction of $\text{Ca}(^1\text{D}_2)$ with oriented CH_3Cl ($\text{JKM} = 111$) and CH_3Br ($\text{JKM} = 111$), respectively. The translational energy dependence of the total chemiluminescence and the steric effect of the $\text{CaCl}(\text{B } ^2\Sigma)$ channel was measured. An enhanced $\text{CaCl}(\text{B})$ chemiluminescence is observed for a tails (methyl end) approach and an enhanced $\text{CaBr}(\text{A})$ production for a heads (Br end) approach geometry. The observed energy dependence of the steric effect is attributed mainly to a correlation between the projection of the electronic angular momentum of the $\text{Ca}(^1\text{D}_2)$ on the intermolecular axis and the projection of the electronic angular momentum of the diatomic product on the diatomic axis. A full report of semiclassical trajectory calculations on a long-range potential is presented in the accompanying paper by Meijer *et al.* (Meijer, A. J. H. M.; Groenenboom, G. C.; van der Avoird, A. *J. Phys. Chem.* **1996**, *100*, 16072).

1. Introduction

The study of elementary gas phase reactive collisions has developed more and more toward the investigation of correlations between various vectorial quantities of the reactants and products.¹ Relatively new or strongly improved experimental techniques have given the ability to control to a high extent the initial spatial orientation of the reactants.^{2–5} Polarized laser-induced fluorescence⁶ and resonance-enhanced multiphoton ionization⁷ offer a very sensitive way of detecting the anisotropy of the angular momentum distribution of reaction products. From the observed vector correlations detailed information about the reaction dynamics can be obtained.⁸

The rich but spectroscopically well characterized excited states of the alkali earth monohalides make these systems both experimentally and theoretically interesting to investigate in oriented beam scattering experiments. Experimental results on the steric effect of the reaction $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{F}$ ($\text{JKM} = 111$) have been reported.⁹ A positive steric effect was measured for the $\text{CaF}(\text{A } ^2\Pi)$ chemiluminescent channel and this steric effect was found to increase with increasing translational energy. This dependence with translational energy is at first sight contrary to what is usually anticipated and in fact observed experimentally for the chemiluminescent reaction $\text{Ba} + \text{N}_2\text{O} \rightarrow \text{BaO}^* + \text{N}_2$ reaction by Jalink *et al.*^{10,11} In the latter system the steric effect was found to decrease with increasing translational energy. This decrease could be explained using a hard sphere line-of-

centers model where increasing the translational energy helps to overcome the steric barrier at more unfavorable approach angles which reduces the steric effect of the reaction.

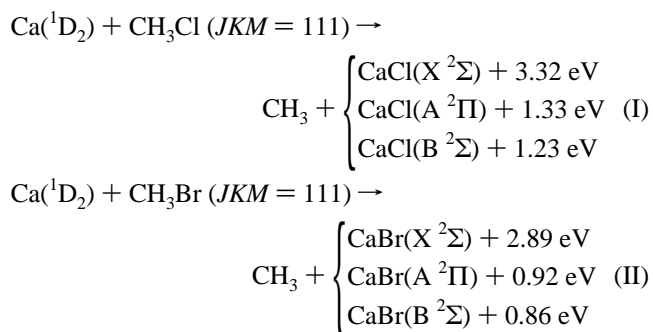
For the $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{F}$ ($\text{JKM} = 111$) system it was suggested⁹ that long-range anisotropic interactions could be responsible for the reduced steric effect at low collision energy. These interactions would reorient the incoming CH_3F and, thereby, reduce the effect of the initially prepared orientation. Subsequent quasiclassical trajectory calculations on this system by Meijer *et al.*^{12,13} showed that the positive energy dependence of the steric effect for the $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{F}$ ($\text{JKM} = 111$) system could not be fully explained by the trapping and reorientation effects which are caused by the long-range interaction. In a following study they reported semiclassical calculations where the reaction model was extended by correlating the projection of the electronic angular momentum of the incoming Ca atom with the symmetry of the final electronic angular momentum of the diatomic product.¹⁴

In the present study we report on experiments investigating how the spatial orientation of methyl halide molecules, CH_3Cl and CH_3Br , reacting with electronically excited $\text{Ca}(^1\text{D}_2)$ affects the branching into the chemiluminescent product channels $\text{CaCl}(\text{B } ^2\Sigma)$ and $\text{CaBr}(\text{A } ^2\Pi)$. A hexapole state selector focuses a beam of CH_3X ($\text{X} = \text{Cl}, \text{Br}$) in the ($\text{JKM} = 111$) rotational state into the scattering zone, where it crosses a beam of metastable $\text{Ca}(^1\text{D}_2)$ atoms. A homogeneous electric field in the reaction zone orients the molecular axis of the methyl halide parallel or antiparallel to the relative velocity and the chemiluminescence of the CaX product is detected for a “favorable”, an “unfavorable” and a random approach.

[†] The experimental results reported here were obtained as part of the thesis work of M.H.M.J. in Nijmegen.

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The energetics of the reactions studied are^{15,16}



The $\text{C}^2\Pi$ chemiluminescent channel is essentially thermo-neutral for reaction with CH_3Cl and endothermic for reaction with CH_3Br (0.2 eV). Chemiionization is not energetically possible for either of the reactions.

Absolute chemiluminescent cross sections (both A and B channels) for beam-gas reaction of $\text{Ca}(^1\text{D}_2)$ with CH_3Cl and CH_3Br have been reported as 4.7 ± 1.0 and $5.6 \pm 1.2 \text{ \AA}^2$, respectively.¹⁷ The total chemiluminescent branching ratio $\sigma(\text{A} \rightarrow \text{X})/\sigma(\text{B} \rightarrow \text{X}) = 1.5$ was measured for the beam-gas reaction $\text{Ca}(^3\text{P}, ^1\text{D}_2) + \text{CH}_3\text{Cl}$ ¹⁸ (chemiluminescence mainly from the $\text{Ca}(^1\text{D}_2)$ reactant) and $\sigma(\text{A} \rightarrow \text{X})/\sigma(\text{B} \rightarrow \text{X}) = 3\text{--}5$ for the reaction of $\text{Ca}(^3\text{P}, ^1\text{D}_2) + \text{CH}_3\text{Br}$.¹⁷

Reactions between alkali earth atoms and halogen containing molecules have been studied quite extensively.¹⁹ Dagdigian and co-workers^{20,21} studied the influence of the spin-orbit state of the electronically excited alkali earth atom on ground state and chemiluminescent channels and observed an enhanced chemiluminescence with increasing spin-orbit level. Menzinger *et al.*^{22,23} measured chemiluminescent and chemiionizing product channels of the reactions $\text{Ca}, \text{Ba} + \text{Cl}_2, \text{F}_2$ and developed a multipotential energy surface model explaining the observed selectivity effects.²⁴ Rettner and Zare²⁵ studied the effect of the alignment of laser excited $\text{Ca}(^1\text{P})$ with respect to the collision plane on the CaCl product yield from reaction with HCl and Cl_2 and observed an enhanced $\text{CaCl}(\text{A } ^2\Pi)$ chemiluminescence when the p orbital was aligned perpendicular to the reaction plane. Soep and co-workers²⁶ observed a strong dependence of the chemiluminescent branching ratio into the $\text{CaBr}(\text{A } ^2\Pi, \text{B } ^2\Sigma)$ channels on the electronic excited state of the $\text{Ca}\text{--HBr}$ dimer. Lee and co-workers²⁷ studied the alignment dependence of ion pair production in the reaction of $\text{Ba}(^1\text{P})$ with Br_2 . Steric effects on the total reaction cross section and the product state distribution in the reaction of Sr with laser aligned and vibrationally excited HF have been reported by Loesch and co-workers.²⁸ Recently, the group of A. González Ureña obtained absolute reaction cross sections and product polarization of the chemiluminescent product channels $\text{CaCl}(\text{A}, \text{B})$, $\text{CaBr}(\text{A}, \text{B})$ of the reactions $\text{Ca}(^1\text{D}_2) + \text{HCl}, \text{HBr}$.²⁹

Orientation effects, i.e., a difference in reactive yield between a heads and a tails approach of the reactants, have been reported for several chemiluminescent systems. Van den Ende and Stolte³⁰ measured an increase in NO_2^* chemiluminescence from oriented $\text{NO} + \text{bulk O}_3$ for heads and broadside-tails approach, which was explained by a bimodal angular scattering reaction mechanism. Kuwata and co-workers³¹ found an enhanced CF_3^* chemiluminescence for F-end and sideways approaches in the reaction of metastable $\text{Ar}^* + \text{oriented CF}_3\text{H}$.

In this paper, orientation effects on the $\text{CaCl}(\text{B } ^2\Sigma)$ channel from reaction I and the $\text{CaBr}(\text{A } ^2\Pi)$ channel from reaction II are presented. Section 2 contains a brief description of the experimental setup. In section 3, experimental results are given,

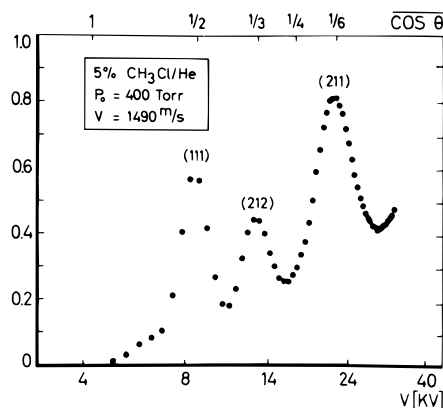


Figure 1. Focusing curve for CH_3Cl . The beam intensity (in arbitrary units) measured by the mass detector is plotted as a function of the hexapole voltage V between neighboring rods of the hexapole. The numbers at the peaks indicate the quantum numbers of the rotational level (JKM) focused. The values $\cos \theta$ along the upper horizontal axis denote the corresponding average cosine of the angle between the molecular axis and the electric field, $\cos \theta = MK/J(J+1)$. The beam intensity at the (111) peak is 10 times the intensity of the nonfocused beam, i.e., with no voltage on the hexapole.

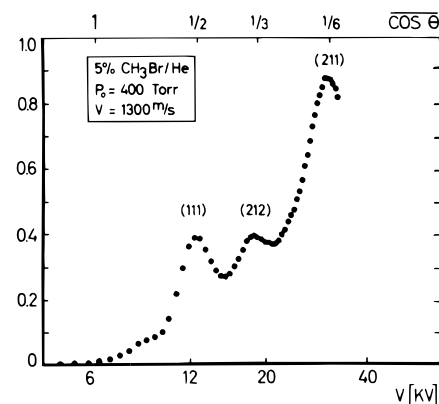


Figure 2. Focusing curve for CH_3Br . The intensity at the (111) peak is 5.2 times the intensity of the nonfocused beam; see also the caption of Figure 1.

which are discussed in section 4. A full report on the theoretical calculations is presented in the accompanying paper.³²

2. Experimental Section

The experimental setup has been described in detail previously⁹ and will be discussed only briefly. A hexapole state selector is used to state select and focus a (seeded) beam of CH_3X ($\text{X} = \text{Cl}, \text{Br}$) into the scattering zone where an orientation field orients the CH_3X molecule with respect to a metastable atomic Ca^* beam. The collision energy is varied by using different seeding mixtures and nozzle temperatures. The total flux of CH_3X molecules is determined by a quadrupole mass detector behind the scattering chamber. Focusing curves at room temperature for 5% $\text{CH}_3\text{Cl}/\text{He}$ and 5% $\text{CH}_3\text{Br}/\text{He}$ mixtures at 400 Torr backing pressure (nozzle diameter 110 μm) are shown in Figures 1 and 2, respectively. Rotational temperatures estimated from the focused peak intensities for the (JKM) = (111) and (JKM) = (212) states are about 7–8 K. A more detailed analysis of the rotational state distribution of the focused beams can be obtained from a theoretical simulation of the focusing curves.³³

The metastable Ca^* beam is produced in a dc discharge (typically 50–70 V, 300–400 mA) between a molybdenum electrode and the oven orifice. The fluorescence from the

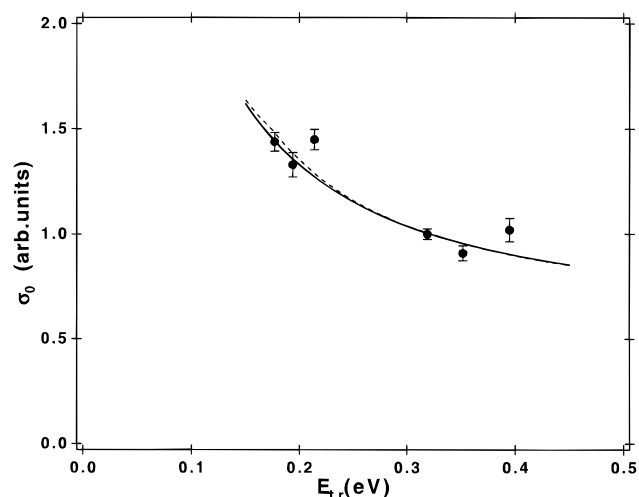


Figure 3. Translational energy dependence of the cross section of the CaCl(B) channel of the reaction of $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{Cl}$ ($JKM = 111$). The dashed curve is the best fit to the data points (plotted with error bar) resulting from a convolution of an excitation function of the Eu type (see eq 1) with the velocity distribution of the Ca beam. The solid curve represents the fitted Eu type cross section without convolution (see text).

metastable beam is dispersed by a monochromator. From the fluorescence intensities at $\lambda = 457.5$ nm ($^1\text{D}_2 \rightarrow ^1\text{S}_0$) and $\lambda = 657.3$ nm ($^3\text{P}_1 \rightarrow ^1\text{S}_0$) the metastable state population ratio $n(^1\text{D}_2)/n(^3\text{P}) \sim 90\text{--}120$ is determined, depending somewhat on the discharge conditions. In our previous study⁹ more details about the dc discharge producing this dramatically strong $n(^1\text{D}_2)/n(^3\text{P})$ population inversion and the high yield of $\text{Ca}(^1\text{D}_2)$ can be found. Moreover, in this paper⁹ a comparison with the yields of other experiments using discharges is given.

The chemiluminescence from the reaction zone is collected with a lens system containing a narrow interference filter (10 nm fwhm bandwidth) to block the discharge light and imaged onto a photomultiplier. Because of accidental overlap of relative strong Ca^* discharge lines with the $\text{CaBr}(\text{B} \rightarrow \text{X})$ and the $\text{CaCl}(\text{A} \rightarrow \text{X})$ band only the $\text{CaBr}(\text{A} \rightarrow \text{X})$ and the $\text{CaCl}(\text{B} \rightarrow \text{X})$ chemiluminescence from beam-beam reaction could be studied. For the $\text{CaCl}(\text{B} \rightarrow \text{X})$ $\Delta\nu = 0$ system, centered around 593.5 nm, an interference filter with a center wavelength of 604 nm was slightly tilted ($\approx 29^\circ$) to shift the transmittance window of the filter 10 nm to the blue. The tilt angle was optimized by maximizing the collected chemiluminescence signal from the reaction with bulk CH_3Cl . For the $\text{CaBr}(\text{A} \rightarrow \text{X})$ $\Delta\nu = 0$ band around 626 nm a filter with a center wavelength of 626 nm was used. In both cases two filters with the same center wavelength were used in tandem.

A microcomputer (Apple 2C) controls the data acquisition and switching of the orientation voltages. All data at a single collision energy are transferred to a mainframe computer for statistical analysis. Data points outside 2.5 times the standard deviation are rejected and average chemiluminescent intensities for approach with X (X = Cl, Br) in front, I_- , random approach (orientation fields grounded), I_0 , and approach with CH_3 in front I_+ , are calculated.

3. Results

The total cross section for the $\text{CaCl}(\text{B} \rightarrow \text{X})$ chemiluminescent channel from the reaction $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{Cl}$ ($JKM = 111$) has been measured as a function of the translational energy, E_{tr} , and is shown in Figure 3. Within the energy range measured, $0.18 \text{ eV} < E_{\text{tr}} < 0.4 \text{ eV}$, the cross section decreases by about 40%. The solid curve in Figure 3 is an excitation function of

the type^{34,35}

$$\sigma_0(E_{\text{tr}}) = C_0 E_{\text{tr}} \left(1 + \frac{Q_m}{E_{\text{tr}}} \right)^n \quad (1)$$

This excitation curve was convoluted with the velocity distribution of the Ca beam, which was assumed to be a Maxwellian distribution with a temperature $T = 1133 \text{ K}$ and fitted to the experimental data points. The dashed curve in Figure 3 is the convoluted cross section which is very close to the deconvoluted excitation function. The maximum exoergicity of the reaction, $Q_m = 1.23 \text{ eV}$, was fixed in the least-squares fitting, and the scaling parameter C_0 and the exponent n were fitted to the experimental data giving $C_0 = 0.150 \pm 0.014 \text{ arb units/eV}$ and $n = 1.927 \pm 0.049$. Using the measured cross section of the beam-gas experiment at an average collision energy of 0.15 eV ,¹⁷ we can relate one arbitrary unit to 2.9 \AA^2 .

Eu³⁴ has derived a theoretical value of $n = 5/2$ in case of atom plus diatomic products and Menzinger and Wren²³ found values of $n = 1.6$ to 1.8 for the $\text{Ba} + \text{Cl}_2$ and $\text{Ba} + \text{F}_2$ system, respectively. In our case the excitation function appears to be nicely represented by an excitation function of the Eu type, eq 1, where the exponent turns out to be somewhat less than $5/2$.

The experimentally observable steric effect, i.e., the measured steric asymmetry $(I_- - I_+)/I_0$, the ratio of the difference in chemiluminescent yield of the two approach geometries (methyl halide with halide in front, I_- , versus methyl halide with methyl in front, I_+) and the yield for random approach (I_0), is dependent on the electric field strength, E_{or} , used to orient the molecule in the scattering zone. Hyperfine interaction in the CH_3Cl molecules dilutes the spatial orientation of the molecular frame and is most deleterious at low field strengths. Detailed calculations on the electric field dependence of the steric effect were reported by Bulthuis *et al.*³⁶ To maintain the state selection from the exit of the hexapole state selector to the scattering zone a guiding field, E_{guid} , is applied in the region inbetween. The electric field strengths used in the energy dependence measurements of the steric effect are $E_{\text{guid}} = 70 \text{ V/cm}$ and $E_{\text{or}} = 31 \text{ V/cm}$. These fields saturate the measured steric effect and no correction of the steric data for incomplete spatial orientation is necessary.³⁶

The translational energy dependence of the steric asymmetry for $\text{CaCl}(\text{B } ^2\Sigma)$, $(I_- - I_+)/I_0$ (which essentially equals σ_1/σ_0 for a deconvoluted steric effect,⁹ see eq 2 below), is shown in Figure 4. Due to the relatively large scatter of the data it is difficult to make definite conclusions about the energy dependence. Within the energy range measured the steric effect seems to be nearly independent of the collision energy. To obtain the orientation dependence of the cross section $\sigma(E_{\text{tr}}, \cos \gamma_0)$, with $\gamma_0 = \arccos(\hat{r} \cdot \hat{v}_{\text{tr}})$ the angle between the relative velocity, \hat{v}_{tr} , and the orientation of the molecular axis, \hat{r} , the cross section is commonly expanded in Legendre polynomials P_n with coefficients σ_n .³⁷ It should be noted that this angle is denoted by β in the theoretical calculations by Meijer *et al.*^{14,32} For the (JKM) = (111) state the steric effect equals the ratio σ_1/σ_0 . To characterize the deconvoluted energy dependence of σ_1/σ_0 the energy dependence of $\sigma_1(E_{\text{tr}})$ is represented by a smooth curve $\sigma_1(E_{\text{tr}}) = a_0 + a_1 E_{\text{tr}}$, with a_0 and a_1 as fit parameters.

The total convoluted yield for a favorably or unfavorably oriented (111) state was calculated convoluting the cross section

$$\sigma(E_{\text{tr}}, \cos \gamma_0) = \sigma_0(E_{\text{tr}}) + \sigma_1(E_{\text{tr}})P_1(\cos \gamma_0) + \sigma_2(E_{\text{tr}})P_2(\cos \gamma_0) + \dots \quad (2)$$

with the velocity distribution of the Ca beam.⁹ Because no

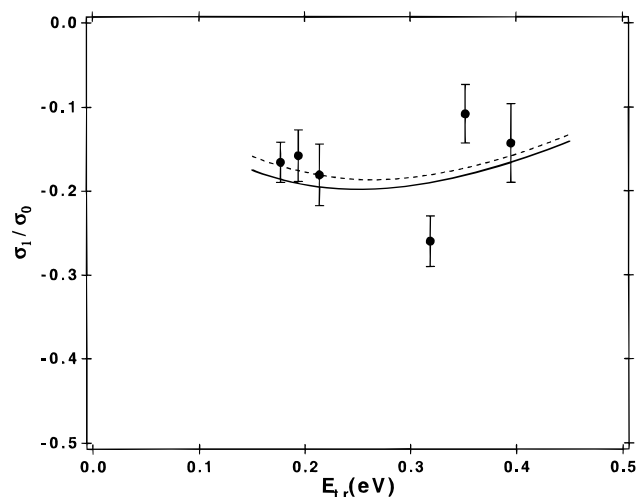


Figure 4. Translational energy dependence of the steric effect σ_1/σ_0 of the $\text{CaCl}(\text{B})$ channel. The dashed curve represents the convoluted fit to the measured data of the steric asymmetry. The energy dependence of $\sigma_1(E_{\text{tr}})$ was represented by a smooth curve (see text) and σ_0 and $\sigma_0(E_{\text{tr}})$ by the solid curve of Figure 3. The solid curve shows the “true” deconvoluted steric effect $\sigma_1(E_{\text{tr}})/\sigma_0(E_{\text{tr}})$.

significant σ_2/σ_0 was extracted from the measured data, $\sigma_2(E_{\text{tr}})$ and higher Legendre moments are set to zero in the convolution.

The best fit (deconvoluted) σ_1/σ_0 curve to the data points is shown by the solid line in Figure 4, with the fit parameters $a_0 = -0.365$ arb units and $a_1 = 0.544$ arb units/eV and the deconvoluted excitation function $\sigma_0(E_{\text{tr}})$ from eq 1. The convoluted steric effect is given by the dashed curve in Figure 4 and is only slightly shifted with respect to the deconvoluted curve. As can be concluded from the deconvolution analysis, the convolution of the cross section and the steric effect with the velocity distribution of the Ca beam has no significant effect on the data.

A few measurements of the steric effect for the $\text{CaBr}(\text{A } ^2\Pi)$ channel from the reaction with CH_3Br ($\text{JKM} = 111$) were made. At two translational energies the steric effect was measured. Assuming little influence of the convolution from the Ca velocity distribution, as was observed for $\text{Ca} + \text{CH}_3\text{F}^9$ and CH_3Cl , we obtain from the measurements $\sigma_1/\sigma_0(E_{\text{tr}} = 0.319 \text{ eV}) = 0.106 \pm 0.026$ and $\sigma_1/\sigma_0(E_{\text{tr}} = 0.352 \text{ eV}) = 0.168 \pm 0.033$. No significant σ_2/σ_0 was extracted from the data. The orientation field used in the scattering zone was 94 V/cm and the guiding field strength was 70 V/cm. No saturation curve was measured. Although the data on the steric effect for the reaction with $\text{CH}_3\text{-Br}$ ($\text{JKM} = 111$) is limited, it can be concluded that the $\text{CaBr}(\text{A})$ channel shows a small positive steric effect.

4. Discussion

One of the main observations from the measurements described in section 3 is the negative steric effect of the $\text{CaCl}(\text{B } ^2\Sigma)$ channel and the positive steric effect of the $\text{CaBr}(\text{A } ^2\Pi)$ channel. It would be desirable to obtain the steric effect of both the A and B channels for the same reactive system. Experimental conditions have prevented these observations. A strong Ca^* line at $\lambda = 617 \text{ nm}$, assigned to the $5p4s \text{ } ^3\text{P} \rightarrow 3d4s \text{ } ^3\text{D}$ transition, produced a large amount of background light in the spectral region of the $\text{CaCl}(\text{A})$ and $\text{CaBr}(\text{B})$ fluorescence and overwhelmed the observation of beam-beam chemiluminescence from these channels.

The reaction between $\text{Ca}(^1\text{D}_2)$ + methyl halides is believed to be initiated by a harpooning mechanism. In Figure 5 we show schematically the most important covalent and ionic surfaces involved in the chemiluminescent channels. The

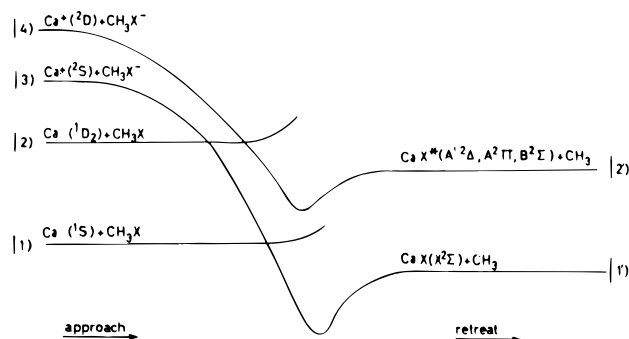


Figure 5. Schematic drawing of the covalent and ionic potential surfaces involved in the reaction between $\text{Ca} + \text{CH}_3\text{X}$. The crossing of the covalent $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{X}$ surface (labeled [2]) and the ionic $\text{Ca}^+(^2\text{S}) + \text{CH}_3\text{X}^-$ surface (labeled [3]) defines the outer crossing point, and a harpooning electron jump at this outer point will produce ground state $\text{CaX}(\text{X } ^2\Sigma) + \text{CH}_3$ (channel [1']). The crossing of the covalent surface [2] with the excited ionic surface $\text{Ca}^+(^2\text{S}) + \text{CH}_3\text{X}^-$ (labeled [4]) defines the inner crossing point, and an electron jump at this inner point will produce electronically excited $\text{CaX}(\text{A } ^2\Delta, \text{A } ^2\Pi, \text{B } ^2\Sigma) + \text{CH}_3$ (channel [2']) (adapted from Menzinger, ref 24).

reactants $\text{Ca}(^1\text{D}_2)$ and CH_3X approach along the surface labeled [2] where at the crossing with the ionic surface [4] (estimated around 3 Å) an electron jump initiates the reaction to produce the chemiluminescent product channels retreating along the surface [2']. Menzinger²⁴ has discussed in detail the effect of the geometry and symmetry of the collision on the propensity for the various chemiluminescent, chemiionization and ground state channels for alkaline earth + halogen reactions. A global multipotential energy surface (MPES) model based on group theoretical arguments and adiabatic/diabatic behaviour at the crossing of the ionic and covalent surfaces were proposed to explain the specificity and selectivity effects observed experimentally for the alkaline earth + halogen reactions.

Rettner and Zare²⁵ investigated the effect of atomic orbital alignment on the chemiluminescent branching of reactions of $\text{Ca}(^1\text{P})$ with HCl , Cl_2 , and CCl_4 . For $\text{Ca}(^1\text{P}) + \text{HCl} \rightarrow \text{CaCl}(\text{A } ^2\Pi, \text{B } ^2\Sigma) + \text{H}$ an enhanced production of $\text{CaCl}(\text{A } ^2\Pi)$ was observed when the p orbital was prepared perpendicular to the reaction plane, whereas a parallel aligned p orbital was found to enhance the $\text{CaCl}(\text{B } ^2\Sigma)$ channel. This result was explained by a harpooning of the 4s Ca electron at the (inner) crossing with the $\text{Ca}^+(^2\text{D}) + \text{HCl}-(^2\Sigma)$ surface leaving the aligned orbital positioned at the Ca ion. The aligned Ca orbital is subsequently transformed to a CaCl molecular orbital. A perpendicular aligned p orbital correlates to $\text{CaCl}(\text{A } ^2\Pi)$ production and a parallel p orbital to $\text{CaCl}(\text{B } ^2\Sigma)$, which qualitatively accounts for the observed alignment effect on the chemiluminescent yield.

For the reactions between $\text{Ca}(^1\text{D}_2)$ + oriented methyl halides studied here an important ingredient in the explanation of the energy dependence of the observed steric effects is reorientation of the initially prepared orientation during the approach of the reactants. Reorientation and realignment effects, i.e., the change in the initial mutual orientation of the reactants due to long-range (electrostatic) forces during the approach, are known to be important in ion-molecule reactions³⁸ and have been discussed for neutral-neutral systems like $\text{Rb} + \text{CH}_3\text{I}$.³⁹

As was remarked before^{9,12} the reaction between $\text{Ca}(^1\text{D}_2)$ + methyl halides involves an electronically excited Ca atom, which has a quadrupole moment associated with it, colliding with a polar (dipole, quadrupole, octupole) molecule. The permanent electric moments of the methyl halide and the excited $\text{Ca}(^1\text{D}_2)$ give rise to a long-range, $\alpha(R^{-4} + R^{-5} + R^{-6})$, anisotropic potential,⁴⁰ with R the interparticle distance. Meijer *et al.*¹²⁻¹⁴ have studied theoretically the effect of this long-range interaction

on the total cross section and the steric effect for the reaction $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{F}$. It was found^{12,13} that the effect of the long-range interaction alone results in trapping and reorientation effects which partially cancel each other and could not account for the observed energy dependence of the steric effect. In a subsequent study,¹⁴ they extended the reaction model along ideas originally introduced by Menzinger.²⁴ Meijer *et al.* described the electronic states of the interacting atom and molecule quantum mechanically and correlated the projection of the electronic angular momentum of the Ca atom on the intermolecular axis with the projection of the electronic angular momentum of the CaF product on the diatomic axis. This correlation thus assumes that in the reaction the projection of the electronic angular momentum of the Ca is conserved as the electronic angular momentum of the diatomic product. Using this correlation model they could reproduce the translational energy dependence of the observed steric effect for the $\text{CaF}(\text{A } ^2\Pi)$ channel.

The semiclassical correlated model has been recently applied by Meijer *et al.*³² to calculate the steric effect of the chemiluminescent channels for the reaction of $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{Cl}$ and CH_3Br . At this place we would only like to state the main conclusion from this study and refer to the accompanying paper for a full account of the calculations.

The long-range potential surfaces for the three reactive systems $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{F}$, CH_3Cl and CH_3Br are globally quite similar. The quadrupole moments of CH_3Cl and CH_3Br are, however, larger and of different sign than for CH_3F . This affects the order of the symmetry of the surfaces around angles where the Ca atom approaches the halogen atom. As reaction model, a simple hard-sphere line-of-centers model is assumed. The reaction probability of all trajectories arriving at a certain distance (the hard-sphere radius is taken as the inner harpooning radius) is determined by the angle between the figure axis of the methyl halide and the interparticle distance. If this angle is smaller than a certain cutoff angle the reaction probability is assumed to be 1, otherwise the trajectory is non-reactive.

For the $\text{Ca} + \text{CH}_3\text{Cl}$ reaction it turns out that for an initially favorable orientation reorientation takes place toward angles where for most of the reactive trajectories the dominant symmetry character correlates with Δ . If it is assumed that this symmetry determines the symmetry of the $\text{CaCl}(\text{A}' ^2\Delta)$ and few trajectories produce $\text{CaCl}(\text{B } ^2\Sigma)$. For an initially unfavorable approach the dominant symmetry character correlates with Σ and most reactive trajectories will produce $\text{CaCl}(\text{B } ^2\Sigma)$. This means that the reactivity into the $\text{CaCl}(\text{B } ^2\Sigma)$ exit channel will be larger for initially unfavorable oriented CH_3Cl (with the methyl in front) relative to initially favorable oriented CH_3Cl (with the Cl in front) and this results in a negative steric effect for the Σ product channel. The negative steric effect observed experimentally for the $\text{CaCl}(\text{B } ^2\Sigma)$ channel can be reproduced by assuming a somewhat larger cutoff angle of 150° compared to 105° for the $\text{CaF}(\text{A } ^2\Pi)$ channel from reaction with CH_3F . The larger cutoff angle for methyl chloride may be attributed to a smaller shielding of the Cl atom by the methyl group compared to the shielding of the F atom in methyl fluoride resulting in a larger cone of reaction. For CH_3Br , only limited data is available and the calculations suggest a cutoff angle of about 140° , also larger than the CH_3F value.

The calculations also predict the steric effect of the other chemiluminescent channels and it turns out that for the $\text{A } ^2\Pi$ and $\text{B } ^2\Sigma$ channels all reactions show the similar increasing trend with translational energy this in contrast to the $\text{A}' ^2\Delta$ channel. The calculations show that over the studied collision energy

range for the $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{Cl}$ reaction reorientation plays an important role as was found for the $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{F}$ reaction. However, due to differences in the long-range potential between the two systems, there are differences in the detailed localization of the C–X axis between the two reactions. Furthermore, for the $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{Cl}$ reaction the symmetry of the observed ($\text{B } ^2\Sigma$) product channel differs from the symmetry of the observed ($\text{A } ^2\Pi$) channel for the $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{F}$ reaction. The main difference, as suggested by Meijer *et al.*,³² between the two systems to explain the sign and energy dependence of the steric effect, is attributed to the different cutoff angle for the two reactions. The combination of these effects leads to a rather weak energy dependence of the steric effect for the $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{Cl}$ reaction.

For the $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{Br}$ reaction only limited experimental data on the $\text{CaBr}(\text{A } ^2\Pi)$ channel over a small range of relatively high collision energy is available. Because of the relatively high collision energy, reorientation is expected to be less important. The calculations do reproduce the experimental data for the $\text{CaBr}(\text{A } ^2\Pi)$ channel using the semiclassical correlated reaction model, although the accuracy of the optimal cutoff angle is much smaller.

For a more comprehensive discussion of the results of the calculations we refer to the paper by Meijer *et al.*³²

The model discussed above of course has its limitations. The reaction model is based on a harpooning mechanism and the reactants have to proceed towards the inner harpooning crossing region (see Figure 5) of the covalent $\text{Ca}(^1\text{D}_2) + \text{CH}_3\text{X}$ surface labeled |2) with the ionic $\text{Ca}^+(^1\text{D}) + \text{CH}_3\text{X}^-$ surface labeled |4) to produce the chemiluminescent channels. Figure 5 elucidates also the competing possibility of harpooning at the outer crossing of the incoming reactants on the surface labeled |2) with the ionic surface |3). Harpooning at this outer crossing leads, as argued by Menzinger,²⁴ to electronic ground state products retreating along the surface labeled |1'). CaX product molecules can only be born in electronically excited states when the electron jump at the outer crossing is avoided. The crossing at the outer harpooning region may well be dependent on the orientation as well as the translational energy of the reactants and this may affect the cross section and the steric effect. A Landau–Zener type of crossing probabilities may improve the modeling of the harpooning mechanism. Furthermore, the hard-sphere line-of-centers model with a sharp cutoff angle is certainly a simplification of the real angle-dependent reaction probability.

Nevertheless, taking into account these limitations, it is very encouraging that the semiclassical calculations are able to reproduce the general trend of the steric effect for these type of reactions and have given much insight in the importance of long-range effects and electronic correlation in the reactions between $\text{Ca}(^1\text{D}_2) +$ methyl halides.

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