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

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Steric effects are reported for the chemiluminescent CaCl(B \(^{2} \Sigma\)) and CaBr(A \(^{2} \Pi\)) exit channels of the reaction of Ca(\(^{1} \text{D}_2\)) with oriented CH\(_3\text{Cl}\) (\(\text{JKM} = 111\)) and CH\(_3\text{Br}\) (\(\text{JKM} = 111\)), respectively. The translational energy dependence of the total chemiluminescence and the steric effect of the CaCl(B \(^{2} \Sigma\)) channel was measured. An enhanced CaCl(B) chemiluminescence is observed for a tails (methyl end) approach and an enhanced CaBr(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 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.\(^2\) Polarized laser-induced fluorescence\(^2\) and resonance-enhanced multiphoton ionization\(^2\) 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.\(^3\)

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 Ca(\(^{1} \text{D}_2\)) + CH\(_3\text{F}\) (\(\text{JKM} = 111\)) have been reported.\(^4\) A positive steric effect was measured for the CaF(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 Ba + N\(_2\text{O}\) → BaO\(^{+}\) + N\(_2\) reaction by Jalink et al.\(^5\) 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 Ca(\(^{1} \text{D}_2\)) + CH\(_3\text{F}\) (\(\text{JKM} = 111\)) system it was suggested\(^2\) that long-range anisotropic interactions could be responsible for the reduced steric effect at low collision energy. These interactions would reorient the incoming CH\(_3\text{F}\) and, thereby, reduce the effect of the initially prepared orientation. Subsequent quasiclassical trajectory calculations on this system by Meijer et al.\(^12\) showed that the positive energy dependence of the steric effect for the Ca(\(^{1} \text{D}_2\)) + 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.\(^13\)

In the present study we report on experiments investigating how the spatial orientation of methyl halide molecules, CH\(_3\text{Cl}\) and CH\(_3\text{Br}\), reacting with electronically excited Ca(\(^{1} \text{D}_2\)) affects the branching into the chemiluminescent product channels CaCl(B \(^{2} \Sigma\)) and CaBr(A \(^{2} \Pi\)). A hexapole state selector focuses a beam of CH\(_3\text{X}\) (\(X = \text{Cl, Br}\)) in the \(\text{JKM} = 111\) rotational state into the scattering zone, where it crosses a beam of metastable 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 energetics of the reactions studied are

\[
\begin{align*}
\text{Ca}(^{3}D_2) + \text{CH}_3\text{Cl} (J_{KM} = 111) & \rightarrow \\
\text{CaCl} (X) + \text{CH}_3 + \text{Cl} & + 3.32 \text{ eV} \\
\text{CaCl} (A) + \text{HCl} & + 1.33 \text{ eV} \quad (I) \\
\text{CaCl} (B) & + 1.23 \text{ eV} \quad (II)
\end{align*}
\]

\[
\begin{align*}
\text{Ca}(^{3}D_2) + \text{CH}_3\text{Br} (J_{KM} = 111) & \rightarrow \\
\text{CaBr} (X) + \text{CH}_3 + \text{Br} & + 2.89 \text{ eV} \\
\text{CaBr} (A) & + 0.92 \text{ eV} \quad (II) \\
\text{CaBr} (B) & + 0.86 \text{ eV} \\
\end{align*}
\]

The \( ^{3}II \) chemiluminescent channel is essentially thermo- 

dynamic for reaction with \( \text{CH}_3\text{Cl} \) and endothermic for reaction 

with \( \text{CH}_3\text{Br} \) \((0.2 \text{ eV})\). Chemionization is not energetically 

possible for either of the reactions.

Absolute chemiluminescent cross sections (both \( \text{A} \) and \( \text{B} \) 

channels) for beam-gas reaction of \( \text{Ca}(^{3}D_2) \) with \( \text{CH}_3\text{Cl} \) and 

\( \text{CH}_3\text{Br} \) have been reported as \( 4.7 \pm 1.0 \) and \( 5.6 \pm 1.2 \) \( \AA^2 \), 

respectively.\(^\text{17} \)

The total chemiluminescence branching ratio \( \sigma \) 

\((A-X)/\sigma(B-X) = 1.5 \) was measured for the beam-gas reaction 

\( \text{Ca}(^{3}P, ^{3}D_2) + \text{CH}_3\text{Cl} \) (chemiluminescence mainly from the \( \text{Ca} 

(^{3}D_2) \) reactant) and \( \sigma(A-X)/\sigma(B-X) = 3 - 5 \) for the reaction 

\( \text{Ca}(^{3}P, ^{3}D_2) + \text{CH}_3\text{Br} \).\(^\text{17} \)

Reactions between alkali earth atoms and halogen containing 

molecules have been studied quite extensively.\(^\text{19} \) Dagdijian and 

coworkers\(^\text{20,21} \) 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 chemi- 

luminescence with increasing spin—orbit level. Menzinger \textit{et al.}\(^\text{22,23} \) 

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.\(^\text{24} \) Rettnner and Zare\(^\text{25} \) studied the effect of 

the alignment of laser excited \( \text{Ca}(^3P) \) with respect to the collision 

plane on the \( \text{CaCl} \) product yield from reaction with \( \text{HCl} \) and 

\( \text{HBr} \) and observed an enhanced \( \text{CaCl}(A^3II) \) chemiluminescence 

when the \( p \) orbital was aligned perpendicular to the reaction 

plane. Soep and coworkers\(^\text{26} \) observed a strong dependence 

of the chemiluminescent branching ratio into the \( \text{CaBr}(A^3II, 

B^3Σ) \) channels on the electronic excited state of the \( \text{Ca}-\text{HBr} \) 

dimer. Lee and coworkers\(^\text{27} \) studied the alignment dependence 

of ion pair production in the reaction of \( \text{Ba}(^1P) \) with \( \text{Br}_2 \). 

Steric 

effects on the total reaction cross section and the product state 

distribution in the reaction of \( \text{Sr} \) with laser aligned and 

vibrationally excited \( \text{HF} \) have been reported by Loesch and 

coworkers.\(^\text{28} \) Recently, the group of A. González Ureña 

obtained absolute reaction cross sections and product polarization of 

the chemiluminescent product channels \( \text{CaCl}(A,B), \text{CaBr}(A,B) \) of 

the reactions \( \text{Ca}(^3D_2) + \text{HCl, HBr} \).\(^\text{29} \)

Orientation effects, i.e., a difference in reactive yield between 

two heads and a tails approach of the reactants, have been reported 

for several chemiluminescent systems. Van den Ende and 

Sotile\(^\text{30} \) measured an increase in \( \text{NO}_2* \) chemiluminescence from 

oriented \( \text{NO} + \text{bulk} \text{O}_2 \) for heads and broadside-tails approach, 

which was explained by a bimodal angular scattering reaction 

mechanism. Kuwata and co-workers\(^\text{31} \) found an enhanced \( \text{CF}_2* 

chemiluminescence for \( F \)-end and sideways approaches in the 

reaction of metastable \( \text{Ar}^* \) and oriented \( \text{CF}_2\text{H} \).

In this paper, orientation effects on the \( \text{CaCl}(B^3Σ) \) channel from 

reaction I and the \( \text{CaBr}(A^3II) \) channel from reaction II 

are presented. Section 2 contains a brief description of the 

experimental setup. In section 3, experimental results are given, 

which are discussed in section 4. A full report on the theoretical 
calculations is presented in the accompanying paper.\(^\text{32} \)

2. Experimental Section

The experimental setup has been described in detail previ- 

ously\(^\text{9} \) and will be discussed only briefly. A hexapole state 

selector is used to state select and focus a (seeded) beam of 

\( \text{CH}_3\text{X} (X = \text{Cl}, \text{Br}) \) into the scattering zone where an orientation 

field orients the \( \text{CH}_3\text{X} \) molecule with respect to a metastable 

atomic \( \text{Ca}^* \) beam. The collision energy is varied by using 

different seeding mixtures and nozzle temperatures. The total 

flux of \( \text{CH}_3\text{X} \) 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 \( \mu \text{m} \)) are 

shown in Figures 1 and 2, respectively. Rotational temperatures 

estimated from the focused peak intensities for the \( \text{JKM} = 

(111) \) and \( \text{JKM} = (212) \) 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.\(^\text{33} \)

The metastable \( \text{Ca}^* \) 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
The dashed curve is the best fit to the data points (plotted with error bars) 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).

The metastable beam is dispersed by a monochromator. From the fluorescence intensities at \( \lambda = 457.5 \text{ nm} \) (\( \text{D}_2 \rightarrow \text{S}_0 \)) and \( \lambda = 657.3 \text{ nm} \) (\( \text{P}_1 \rightarrow \text{S}_0 \)) the metastable state population ratio \( n(\text{D}_2)/n(\text{P}) \approx 90-120 \) is determined, depending somewhat on the discharge conditions. In our previous study\(^2\) more details about the dc discharge producing this dramatically strong \( n(\text{D}_2)/n(\text{P}) \) population inversion and the high yield of \( \text{Ca}^{1+} \) can be found. Moreover, in this paper\(^3\) 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 \( \text{Ca}^* \) discharge lines with the \( \text{CaBr}(\text{A}→\text{X}) \) and the \( \text{CaCl}(\text{A}→\text{X}) \) band only the \( \text{CaBr}(\text{A}→\text{X}) \) and the \( \text{CaCl}(\text{B}→\text{X}) \) chemiluminescence from beam-gas reaction could be studied. For the \( \text{CaCl}(\text{B}→\text{X}) \) \( \Delta v = 0 \) 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 transmission 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 \( \text{CH}_3\text{Cl} \). For the \( \text{CaBr}(\text{A}→\text{X}) \) \( \Delta v = 0 \) 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 \( \text{X} (= \text{Cl}, \text{Br}) \) in front, \( I_\text{f} \), random approach (orientation fields grounded), \( I_\text{r} \), and approach with \( \text{CH}_3\text{Cl} \) in front \( I_\text{t} \), are calculated.

The total cross section for the \( \text{CaCl}(\text{B}→\text{X}) \) chemiluminescent channel from the reaction \( \text{Ca}^{1+}(\text{D}_2) + \text{CH}_3\text{Cl}(\text{JKM} = 111) \) has been measured as a function of the translational energy, \( E_\text{t} \), and is shown in Figure 3. Within the energy range measured, \( 0.18 \text{ eV} < E_\text{t} < 0.4 \text{ eV} \), the cross section decreases by about 40%. The solid curve in Figure 3 is an excitation function of the type\(^{34,35}\)

\[
\sigma_0(E_\text{t}) = C_0 E_\text{t} \left( 1 + \frac{E_\text{t}}{E_\text{t}^0} \right)^n
\]  

(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, \( Q_\text{m} = 1.23 \text{ eV} \), 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,\(^7\) we can relate one arbitrary unit to 2.9 \( \text{A}^2 \).

\( \text{Eu}^{1+} \) has derived a theoretical value of \( n = 5/2 \) in case of atom plus diatomic products and Menzinger and Wren\(^23\) found values of \( n = 1.6 \) to 1.8 for the \( \text{Ba} + \text{Cl} \) and \( \text{Ba} + \text{F} \) 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 \( I_\text{f} - I_\text{f} \), the ratio of the difference in chemiluminescent yield of the two approach geometries (methyl halide with halide in front, \( I_\text{f} \), versus methyl halide with methyl in front, \( I_\text{t} \)) and the yield for random approach \( I_\text{r} \), is dependent on the electric field strength, \( E_\text{g} \), used to orient the molecule in the scattering zone. Hyperfine interaction in the \( \text{CH}_3\text{Cl} \) 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, \( E_{\text{guide}} \), is applied in the region inbetween.

The electric field strengths used in the energy dependence measurements of the steric effect are \( E_{\text{guide}} = 70 \text{ V/cm} \) and \( E_\text{t} = 31 \text{ V/cm} \). 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 \( \text{CaCl}(\text{B}^2\Sigma), I_{\text{f}} - I_{\text{t}} \) (which essentially equals \( \sigma(\text{E}_\text{t}, \text{cos } \gamma_0) \) 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 \( \sigma(\text{E}_\text{t}, \text{cos } \gamma_0) \), with \( \gamma_0 = \arccos(\vec{b} \cdot \hat{b}) \) the angle between the relative velocity, \( \vec{b} \), and the orientation of the molecular axis, \( \hat{b} \), the cross section is commonly expanded in Legendre polynomials \( P_\ell \) with coefficients \( \sigma_{\ell} \).\(^{37} \) It should be noted that this angle is denoted by \( \beta \) in the theoretical calculations by Meijer et al.\(^{14,32} \) For the \( \text{JKM} = 111 \) state the steric effect equals the ratio \( \sigma_0/\sigma_1 \). To characterize the deconvoluted energy dependence of \( \sigma(\text{E}_\text{t}, \text{cos } \gamma_0) \) is represented by a smooth curve \( \sigma(\text{E}_\text{t}) = \sigma_0 + \sigma_1 E_\text{t} + \sigma_\ell E_\text{t}^\ell \) with \( \sigma_0 \) and \( \sigma_1 \) as fit parameters.

The total convoluted yield for a favorably or unfavorably oriented (111) state was calculated convoluting the cross section with the velocity distribution of the Ca beam.\(^9\) Because of the

\[
\sigma(\text{E}_\text{t}, \text{cos } \gamma_0) = \sigma_0(\text{E}_\text{t}) + \sigma_1(\text{E}_\text{t}) P_1(\text{cos } \gamma_0) + \sigma_\ell(\text{E}_\text{t}) P_\ell(\text{cos } \gamma_0) + \ldots \tag{2}
\]
Reactions between Ca(1D2) and CH3X(JKM) (X = Cl, Br)

significant $\sigma/E_0$ was extracted from the measured data, $\sigma(E_0)$ and higher Legendre moments are set to zero in the convolution. The best fit (deconvoluted) $\sigma/E_0$ curve to the data points is shown by the solid line in Figure 4, with the fit parameters $E_0 = -0.365$ arb units and $\sigma = 0.544$ arb units/eV and the deconvoluted excitation function $\sigma(E_0)$ 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 CaBr(A 2II) channel from the reaction with CH3Br (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 Ca + CH3Br and CH3Cl, we obtain from the measurements $\sigma_0(E_0) = 0.319$ eV$^2$ and $\sigma_0(E_0) = 0.352$ eV$^2$ = 0.168 ± 0.033. No significant $\sigma_0(E_0)$ 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 CH3Br (JKM = 111) is limited, it can be concluded that the CaBr(A 2II) 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 CaCl(B 2Σ) channel and the positive steric effect of the CaBr(A 2II) 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 $\lambda = 617$ nm, assigned to the Sp4s 1P$^2$ - 3d4s 3P transition, produced a large amount of background light in the spectral region of the CaCl (A) and CaBr (B) fluorescence and overwhelmed the observation of beam-beam chemiluminescence from these channels. The reaction between Ca(1D2) + 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 reactants Ca(1D2) and CH3X 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']. Menninger 28 has discussed in detail the effect of the geometry and symmetry of the collision on the propensity for the various chemiluminescent, chemionization 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 Zare 25 investigated the effect of atomic orbital alignment on the chemiluminescent branching of reactions of Ca*(P) with HCl, CH3, and Cl2. For Ca*(P) + HCl → CaCl(A 2II, B 2Σ) + H an enhanced production of CaCl(A 2II) was observed when the p orbital was prepared perpendicular to the reaction plane, whereas a parallel aligned p orbital was found to enhance the CaCl(B 2Σ) channel. This result was explained by a harpooning of the 4s Ca electron at the (inner) crossing with the Ca+(2D) + HCl(2Σ) surface leaving the aligned orbital positioned at the Ca atom. The aligned Ca orbital is subsequently transformed to a CaCl molecular orbital. A perpendicular aligned p orbital correlates to CaCl(A 2II) production and a parallel p orbital to CaCl(B 2Σ), which qualitatively accounts for the observed alignment effect on the chemiluminescence yield.

For the reactions between Ca(1D2) + 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 alignment 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 reactions 38 and have been discussed for neutral–neutral systems like Rb + CH3I. 39

As was remarked before, 3D the reaction between Ca(1D2) + 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 Ca(1D2) give rise to a long-range, 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 \( \text{Ca}(^2\text{D}_2) + \text{CH}_3\text{F} \). 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 CaF(A' 2II) channel.

The semiclassical correlated model has been recently applied by Meijer et al.\(^{25}\) to calculate the steric effect of the chemiluminescent channels for the reaction of \( \text{Ca}(^2\text{D}_2) + \text{CH}_3\text{Cl} \) and \( \text{CH}_3\text{Br} \). 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 \( \text{Ca}(^2\text{D}_2) + \text{CH}_3\text{F}, \text{CH}_3\text{Cl} \) and \( \text{CH}_3\text{Br} \) are globally quite similar. The quadrupole moments of \( \text{CH}_3\text{Cl} \) and \( \text{CH}_3\text{Br} \) are, however, larger and of different sign than for \( \text{CH}_3\text{F} \). 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 Ca + CH3Cl 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 \( \Delta \). If it is assumed that this symmetry determines the symmetry of the CaCl product channel, most trajectories produce CaCl(A' 2\( \Delta \)) and few trajectories produce CaCl(B 2\( \Sigma \)). For an initially unfavorable approach the dominant symmetry character correlates with \( \Sigma \) and most reactive trajectories will produce CaCl(B 2\( \Sigma \)). This means that the reactivity into the CaCl(B 2\( \Sigma \)) exit channel will be larger for initially unfavorable oriented CH3Cl (with the methyl in front) relative to initially favorable oriented CH3Cl (with the Cl in front) and this results in a negative steric effect for the \( \Sigma \) product channel. The negative steric effect observed experimentally for the CaCl(B 2\( \Sigma \)) channel can be reproduced by assuming a somewhat larger cutoff angle of 150° compared to 105° for the CaF(A' 2II) channel from reaction with \( \text{CH}_3\text{F} \). 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 \( \text{CH}_3\text{Br} \) only limited data is available and the calculations suggest a cutoff angle of about 140°, also larger than the \( \text{CH}_3\text{F} \) value.

The calculations also predict the steric effect of the other chemiluminescent channels and it turns out that for the A 2II and B 2\( \Sigma \) channels all reactions show the similar increasing trend with translational energy this in contrast to the A' 2\( \Delta \) channel. The calculations show that over the studied collision energy range for the \( \text{Ca}(^2\text{D}_2) + \text{CH}_3\text{Cl} \) reaction reorientation plays an important role as was found for the \( \text{Ca}(^2\text{D}_2) + \text{CH}_3\text{F} \) 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 \( \text{Ca}(^2\text{D}_2) + \text{CH}_3\text{Cl} \) reaction the symmetry of the observed (B 2\( \Sigma \)) product channel differs from the symmetry of the observed (A' 2II) channel for the \( \text{Ca}(^2\text{D}_2) + \text{CH}_3\text{F} \) reaction. The main difference, as suggested by Meijer et al.,\(^{23}\) 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 \( \text{Ca}(^2\text{D}_2) + \text{CH}_3\text{Cl} \) reaction.

For the \( \text{Ca}(^2\text{D}_2) + \text{CH}_3\text{Br} \) reaction only limited experimental data on the CaBr(A' 2II) 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 CaBr(A' 2II) 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.\(^{22}\)

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 \( \text{Ca}(^2\text{D}_2) + \text{CH}_3\text{X} \) surface labeled \( (2) \) with the ionic \( \text{Ca}^+(^2\text{D}) + \text{CH}_3\text{X}^- \) 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 \( \text{Ca}(^2\text{D}_2) + \text{methyl halides} \).

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Reactions between Ca(D2) and CH3X(JKM) (X = Cl, Br)

References and Notes


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