Steric Effects on Electronically Excited Product Channels in Reactions between Ca(1D2) and CH3X(JKM) (X = Cl, Br)

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Steric effects are reported for the chemiluminescent CaCl(B 2Σ) and CaBr(A 2Π) exit channels of the reaction of Ca(1D2) with oriented CH3Cl (JKM = 111) and CH3Br (JKM = 111), respectively. The translational energy dependence of the total chemiluminescence and the steric effect of the CaCl(B 2Σ) 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(1D2) 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 Ca(1D2) + CH3F (JKM = 111) have been reported.9 A positive steric effect was measured for the CaF(A 2Π) 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 + N2O → BaO* + N2 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-center 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(1D2) + CH3F (JKM = 111) system it was suggested2 that long-range anisotropic interactions could be responsible for the reduced steric effect at low collision energy. These interactions would reorient the incoming CH3F 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 Ca(1D2) + CH3F (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, CH3Cl and CH3Br, reacting with electronically excited Ca(1D2) affects the branching into the chemiluminescent product channels CaCl(B 2Σ) and CaBr(A 2Π). A hexapole state selector focuses a beam of CH3X (X = Cl, Br) in the (JKM) = (111) rotational state into the scattering zone, where it crosses a beam of metastable Ca(1D2) 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.
Reactions between Ca(D\textsubscript{2}) and CH\textsubscript{3}X(JKM) (X = Cl, Br)

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

\[
\begin{align*}
\text{Ca}(\text{D}_2) + \text{CH}_3\text{Cl} & \rightarrow \\
\text{CH}_3 + \left\{ \begin{array}{l}
\text{CaCl}(X=^2\Sigma) + 3.32 \text{ eV} \\
\text{CaCl}(A^2\Pi) + 1.33 \text{ eV} \\
\text{CaCl}(B^2\Sigma) + 1.23 \text{ eV}
\end{array} \right. \\
\text{Ca}(\text{D}_2) + \text{CH}_3\text{Br} & \rightarrow \\
\text{CH}_3 + \left\{ \begin{array}{l}
\text{CaBr}(X=^2\Sigma) + 2.89 \text{ eV} \\
\text{CaBr}(A^2\Pi) + 0.92 \text{ eV} \\
\text{CaBr}(B^2\Sigma) + 0.86 \text{ eV}
\end{array} \right.
\end{align*}
\]

The C\textsubscript{II} chemiluminescent channel is essentially thermo-

Absolute chemiluminescent cross sections (both A and B channels) for beam-gas reaction of Ca(D\textsubscript{2}) with CH\textsubscript{3}Cl and CH\textsubscript{3}Br have been reported as 4.7 \pm 1.0 and 5.6 \pm 1.2 Å\textsuperscript{2}, respectively.\textsuperscript{17} The total chemiluminescent branching ratio \(\sigma(\lambda=\text{X})/\sigma(\lambda=\text{X}) = 1.5\) was measured for the beam-gas reaction Ca(P\textsubscript{3},D\textsubscript{2}) + CH\textsubscript{3}Cl\textsuperscript{18} (chemiluminescence mainly from the Ca-

Reactions between alkali earth atoms and halogen containing molecules have been studied quite extensively.\textsuperscript{19} Dalgarno and co-workers\textsuperscript{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. Menninger \textit{et al.}\textsuperscript{22} measured chemiluminescent and chemionizing product channels of the reactions Ca, Ba + Cl\textsubscript{2}, F\textsubscript{2} and developed a multiprocess energy surface model explaining the observed selectivity effects.\textsuperscript{24} Rettner and Zare\textsuperscript{25} studied the effect of the alignment of laser excited Ca(P\textsubscript{3}) with respect to the collision plane on the CaCl product yield from reaction with HCl and Cl\textsubscript{2} and observed an enhanced CaCl(A\textsuperscript{2}\Pi) chemiluminescence when the p orbital was aligned perpendicular to the reaction plane. Soep and co-workers\textsuperscript{26} observed a strong dependence of the chemiluminescent branching ratio into the CaBr(A\textsuperscript{2}T\textsubscript{1}, B\textsuperscript{2}Σ) channels on the electronic excited state of the Ca-HBr dimer. Lee and co-workers\textsuperscript{27} studied the alignment dependence of ion pair production in the reaction of Ba(P\textsubscript{3}) with Br\textsubscript{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.\textsuperscript{28} Recently, the group of A. González Ureña obtained a detailed analysis of the rotational state distribution of the focused (JKM) peak. 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 1. Focusing curve for CH\textsubscript{3}Cl. 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, \(\cos \theta = MKJ/J + 1\). 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\textsubscript{3}Br. 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.\textsuperscript{32}

2. Experimental Section

The experimental setup has been described in detail previously\textsuperscript{9} and will be discussed only briefly. A hexapole state selector is used to state select and focus a (seeded) beam of CH\textsubscript{3}X (X = Cl, Br) into the scattering zone where an orientation field orientation of the CH\textsubscript{3}X 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\textsubscript{3}X molecules is determined by a quadrupole mass detector behind the scattering chamber. Focusing curves at room temperature for 5% CH\textsubscript{3}Cl/He and 5% CH\textsubscript{3}Br/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.\textsuperscript{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
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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).

metastable beam is dispersed by a monochromator. From the fluorescence intensities at \( \lambda = 457.5 \text{ nm} \) \((\text{D}_2 \rightarrow ^3\text{S}_0)\) and \( \lambda = 657.3 \text{ nm} \) \((\text{P}_1 \rightarrow ^3\text{S}_0)\) the metastable state population ratio \( n(\text{D}_2)/n(\text{P}) \sim 90-120\) is determined, depending somewhat on the discharge conditions. In our previous study\(^ 6\) more details about the dc discharge producing this dramatically strong \( n(\text{D}_2)/n(\text{P}) \) population inversion and the high yield of \( \text{Ca}(\text{D}_2) \) can be found. Moreover, in this paper\(^ 2\) 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 the strong \( \text{Ca}^* \) 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 (\( \sim 29^\circ \)) 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 \( \text{CH}_2\text{Cl} \). 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 \((\text{n(}\text{P}) \sim 90-120\) is determined, depending somewhat on the discharge conditions. In our previous study\(^ 6\) more details about the dc discharge producing this dramatically strong \( n(\text{D}_2)/n(\text{P}) \) population inversion and the high yield of \( \text{Ca}(\text{D}_2) \) can be found. Moreover, in this paper\(^ 2\) a comparison with the yields of other experiments using discharges is given.

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, \(E_{\text{g}}\), used to orient the molecule in the scattering zone. Hyperfine interaction in the \( \text{CH}_2\text{Cl} \) 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.\(^ 35\) To maintain the state selection from the exit of the hexapole state selector to the scattering zone a guiding field, \(E_{\text{guid}}\), 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 \(E_t = 31 \text{ V/cm}\). 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 \( \text{CaCl}(\text{B} \rightarrow \text{X}) \), \((I_+ - I_-)/I_0\) (which essentially equals \( \sigma(E_{\text{tr}}) \) 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 \( \gamma_0 = \arccos(P_{\text{h}}/P) \) the angle between the relative velocity, \( \nu_0 \) and the orientation of the molecular axis, \( \beta \), the cross section is commonly expanded in Legendre polynomials \( P_n \) with coefficients \( \sigma_n \).\(^ 37\) 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 \( \sigma(0)/\sigma_0 \). To characterize the deconvoluted energy dependence of \( \sigma(0)/\sigma_0 \) the energy dependence of \( \sigma(E_{\text{tr}}) \) is represented by a smooth curve \( \sigma(E_{\text{tr}}) = \sigma_0 + a_1 E_{\text{tr}} + a_2 E_{\text{tr}}^2 \) and \( \sigma_0, a_1, a_2 \) 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 the

\[
\sigma(E_{\text{tr}}, \cos \gamma_0) = \sigma_0(E_{\text{tr}}) + \sigma(E_{\text{tr}})P_1(\cos \gamma_0) + \sigma_2(E_{\text{tr}})P_2(\cos \gamma_0) + \ldots \]
Surfaces involved in the chemiluminescent channels. The reactions of the CaCl (B) channel. The clashed curve represents the convoluted fit to the measured data of the steric asymmetry. The energy dependence of $\sigma(E_0)$ was represented by a smooth curve (see text) and $\sigma_0$ and $\sigma_0(E_0)$ by the solid curve of Figure 3. The solid curve shows the "true" deconvoluted steric effect $\sigma(E_0)/\sigma_0(E_0)$.

The best fit (deconvoluted) $\sigma_0/E_0$ curve shows the solid line in Figure 4, with the fit parameters $\sigma_0 = -0.365$ arb units and $a_1 = 0.544$ arb units/eV and the deconvoluted excitation function $\sigma_0(E_0)$ 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 higher Legendre moments are set to zero in the convolution. A few measurements of the steric effect for the CaBr(A $^2\Sigma^+$) channel from the reaction with CH$_3$Br ($J=K=7/2, 9/2$) 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 + CH$_3$F and CH$_3$Cl, we obtain from the measurements $\sigma_0(E_0) = 0.319$ eV$^{-1}$ or $a_1 = 0.026$ and $\sigma_0(E_0) = 0.352$ eV$^{-1}$ or $a_1 = 0.033$. No significant $\sigma_0/E_0$ was extracted from the measured 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 CH$_3$Br ($J=K=7/2, 9/2$) is limited, it can be concluded that the CaBr-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 CaCl-B channel and the positive steric effect of the CaBr(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 $\lambda = 617$ nm, assigned to the $5p4s^2P^0 \rightarrow 3d4s^1D$ 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($^1D_2$) + 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 reactants Ca($^1D_2$) and CH$_3$X 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'). Menzinger$^{24}$ 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, Cl$_2$, and CCl$_4$. For Ca(P) + HCl $\rightarrow$ CaCl(A $^2\Pi$, B $^2\Sigma$) $+$ H an enhanced production of CaCl(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 CaCl(B $^2\Sigma$) channel. This result was explained by a harpooning of the 4s Ca electron at the (inner) crossing with the Ca$^+(2D)$ + 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 CaCl(A $^2\Pi$) production and a parallel p orbital to CaCl(B $^2\Sigma$), which qualitatively accounts for the observed alignment effect on the chemiluminescent yield.

For the reactions between Ca($^1D_2$) + 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 reactions$^{38}$ and have been discussed for neutral-neutral systems like Rb$^+$ + CH$_4$.$^{29}$

As was remarked before$^{5,12}$ the reaction between Ca($^1D_2$) + 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 Ca($^1D_2$) 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 Ca(\textsuperscript{1}D\textsubscript{2}) + CH\textsubscript{3}F. It was found\textsuperscript{2,12} 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,\textsuperscript{14} they extended the reaction model along ideas originally introduced by Menzing.\textsuperscript{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\textsuperscript{\textsuperscript{2}}\Sigma) channel.

The semiclassical correlated model has been recently applied by Meijer et al.\textsuperscript{25} to calculate the steric effect of the chemiluminescent channels for the reaction of Ca(\textsuperscript{1}D\textsubscript{2}) + CH\textsubscript{3}Cl and CH\textsubscript{3}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 Ca(\textsuperscript{1}D\textsubscript{2}) + CH\textsubscript{3}F, CH\textsubscript{3}Cl and CH\textsubscript{3}Br are globally quite similar. The quadrupole moments of CH\textsubscript{3}Cl and CH\textsubscript{3}Br are, however, larger and of different sign than for CH\textsubscript{3}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 crossing) 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 + CH\textsubscript{3}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 \(\Delta\). If it is assumed that this symmetry determines the symmetry of the CaCl product channel, most trajectories produce CaCl(\(\textsuperscript{2}\Sigma\)) and few trajectories produce CaCl(B\textsuperscript{\textsuperscript{2}}\Sigma). For an initially unfavorable approach the dominant symmetry character correlates with \(\Sigma\) and most reactive trajectories will produce CaCl(B\textsuperscript{\textsuperscript{2}}\Sigma). This means that the reactivity into the CaCl(B\textsuperscript{\textsuperscript{2}}\Sigma) exit channel will be larger for initially unfavorable oriented CH\textsubscript{3}Cl (with the methyl in front) relative to initially favorable oriented CH\textsubscript{3}Cl (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\textsuperscript{\textsuperscript{2}}\Sigma) channel can be reproduced by assuming a somewhat larger cutoff angle of 150\(^\circ\) compared to 105\(^\circ\) for the CaF(A\textsuperscript{\textsuperscript{2}}\Sigma) channel from reaction with CH\textsubscript{3}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 CH\textsubscript{3}Br, only limited data is available and the calculations suggest a cutoff angle of about 140\(^\circ\), also larger than the CH\textsubscript{3}F value.

The calculations also predict the steric effect of the other chemiluminescent channels and it turns out that for the A\textsuperscript{\textsuperscript{2}}\Sigma and B\textsuperscript{\textsuperscript{2}}\Sigma channels all reactions show the similar increasing trend with translational energy thus in contrast to the A\textsuperscript{\textsuperscript{2}}\Delta channel. The calculations show that over the studied collision energy range for the Ca(\textsuperscript{1}D\textsubscript{2}) + CH\textsubscript{3}Cl reaction reorientation plays an important role as was found for the Ca(\textsuperscript{1}D\textsubscript{2}) + CH\textsubscript{3}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 Ca(\textsuperscript{1}D\textsubscript{2}) + CH\textsubscript{3}Cl reaction the symmetry of the observed (B\textsuperscript{\textsuperscript{2}}\Sigma) product channel differs from the symmetry of the observed (A\textsuperscript{\textsuperscript{2}}\Sigma) channel for the Ca(\textsuperscript{1}D\textsubscript{2}) + CH\textsubscript{3}F reaction. The main difference, as suggested by Meijer et al.,\textsuperscript{25} 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 Ca(\textsuperscript{1}D\textsubscript{2}) + CH\textsubscript{3}Cl reaction.

For the Ca(\textsuperscript{1}D\textsubscript{2}) + CH\textsubscript{3}Br reaction only limited experimental data on the CaBr(A\textsuperscript{\textsuperscript{2}}\Sigma) 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\textsuperscript{\textsuperscript{2}}\Sigma) 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.\textsuperscript{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 Ca(\textsuperscript{1}D\textsubscript{2}) + CH\textsubscript{3}X surface labeled [2] with the ionic Ca\textsuperscript{+}(\textsuperscript{2}D\textsubscript{2}) + CH\textsubscript{3}X\textsuperscript{-} 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 Menzing,\textsuperscript{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 Ca(\textsuperscript{1}D\textsubscript{2}) + methyl halides.

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Reactions between Ca($^{13}$D$_2$) and CH$_3$X($^{1}$JM) (X = Cl, Br)

References and Notes


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