Semiclassical calculations on the energy dependence of the steric effect for the reaction Ca(1D)+CH$_3$F($jkm=111$)→CaF+CH$_3$

Anthony J. H. M. Meijer, Gerrit C. Groenenboom, and Ad van der Avoird
Institute of Theoretical Chemistry, NSR Center, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

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In a previous article [A. J. H. M. Meijer, G. C. Groenenboom, and A. van der Avoird, J. Chem. Phys. 101, 7603 (1994)] we investigated the energy dependence of the steric effect of the reaction Ca (1D)+CH$_3$F ($jkm=111$)→CaF (A $^2\Pi$)+CH$_3$ using a quasiclassical trajectory method. It was found that we could not reproduce the experimental results for this reaction [M. H. M. Janssen, D. H. Parker, and S. Stolte, J. Phys. Chem. 95, 8142 (1991)]. In this article, we re-investigate this reaction using a semiclassical method, in which the rotation of the molecule and the electronic states of the interacting atom and molecule are treated quantum mechanically. For the chemical reaction we use a model which correlates the projection of the electronic orbital angular momentum of the Ca atom on the intermolecular axis with the projection of the electronic orbital angular momentum of the CaF product on the diatomic axis [M. Menzinger, Polon. Phys. Acta A 73, 85 (1988)]. This model is applied to examine the CaF (A $^2\Pi$, $^2\Sigma^-$, A $^2\Delta$) exit channels separately. We conclude that we can reproduce the experimental results for the steric effect using this model. The improvement with respect to the classical trajectory results is shown to be due primarily to the extended reaction model rather than to the semiclassical description of the dynamics. We find trapping and reorientation in the semiclassical calculations, as in the previous classical trajectory results, but also non-adiabatic effects are present. The latter do not affect the reactive cross sections very much. © 1996 American Institute of Physics. [S0021-9606(96)01427-4]

I. INTRODUCTION

There have been a number of investigations into the role of reagent orientation in reactions. A widely used technique for orienting symmetric top (like) molecules in crossed beam experiments is the hexapole technique, in which a hexapole field is used to select a certain rotational state (labeled by the symmetric top quantum numbers $j$, $k$, and $m$) of the molecule. This allows control of the (average) orientation (angle $\beta$) of the symmetry axis of the molecule with respect to the initial relative velocity of the reagents. Other techniques to obtain a certain degree of orientation have been reported as well, see, e.g., Refs. 15–18.

In this article we will focus on the experiments by Janssen, Parker, and Stolte for the reaction Ca (1D)+CH$_3$F ($jkm$)→CaF (A $^2\Pi$, $^2\Sigma^-$, A $^2\Delta$)+CH$_3$. They report the steric effect, i.e., the difference between the reactive cross section for favorably oriented molecules (which means in this case that the F atom comes first) and unfavorably oriented molecules (CH$_3$ side first), relative to the total reactive cross section for unoriented molecules. Note, that they were only able to measure the A $^2\Pi$ exit channel, because of experimental limitations.

Most theoretical studies on orientational effects employ some version of the angle dependent line of centers (ADLC) model to model the reaction probability. The ADLC model is a classical model in which the molecule is surrounded by an energy barrier, visualized by an imaginary shell. Reaction is assumed to occur only if the atom arriving at this shell has enough radial kinetic energy to surmount the barrier. Often this barrier is taken to be dependent on the angle ($\beta_R$) between the symmetry axis of the molecule and the line connecting the centers-of-mass of the molecule and the atom. From this model one predicts a decrease of the steric effect with increasing relative translational energy of the colliding particles, because at higher energies the atom is able to react at a wider range of angles $\beta_R$, which lowers the steric effect. This behavior has been found experimentally, e.g., for the Ba+N$_2$O reaction.

For the Ca (1D)+CH$_3$F ($jkm=111$)→CaF (A $^2\Pi$)+CH$_3$, an increase of the steric effect with the relative translational energy was found, which could not be explained using the ADLC model outlined above. This result was tentatively explained in terms of reorientation of the CH$_3$F molecule during the approach of the Ca atom due to anisotropic terms in the long range interaction. Supposedly, these anisotropic forces reorient the CH$_3$F molecule towards the Ca atom, especially at low energies, thus washing out the initially prepared orientation and lowering the steric effect. At higher energies there would not be sufficient time for this reorientation to occur, which would lead to an increase in the steric effect. These anisotropic terms were assumed to be primarily due to the interaction between a quadrupole moment on the Ca atom and the permanent multipole moments of the CH$_3$F molecule. Although an isolated atom cannot have a multipole moment, the presence of the electric field of the molecule lifts the fivefold degeneracy of the 1D state, giving rise to five substates, each of which has a quadrupole moment.

In paper II, we investigated this reaction using the standard quasiclassical trajectory (QCT) method with a long...
range potential based on the above mentioned interaction between atom and molecule. We used a slightly modified version of the ADLC model to account for the harpooning mechanism proposed for this reaction. These calculations show that reorientation cannot solely be responsible for the observed energy dependence of the steric effect, since it was impossible to reproduce the experimental results. A possible explanation could be that the initial probability distribution function for the angle $\beta$ in the QCT approach is sharply peaked, unlike the quantum mechanical distribution (see paper II, Fig. 1). Thus, to sample the initial distribution of $\beta$ more quantum-like, we also did the calculations with the modified quasiclassical trajectory (MQCT) approach, defined in paper I.\textsuperscript{24} This improved the results slightly, but did not lead to qualitative or quantitative agreement with experiment.

An alternative explanation for the observed energy dependence of the steric effect was proposed in paper I. It was based on calculations using an attractive isotropic model potential, for which reorientation is impossible. We showed in paper I that for such a potential, at low energies, atoms with a large impact parameter will fly around the molecule and hit it at the back. This washes out the effect of the initial preparation and lowers the steric effect. We called this “trapping.” At higher energies, these atoms will simply fly by the molecule and be non-reactive, thus raising the steric effect. Careful analysis of the MQCT results shows that this mechanism also plays a role in the trajectory calculations. However, initially favorably oriented molecules tend to follow the approaching atom; this reorientation effect partly cancels the effect of trapping. This results in a steric effect that does not reproduce the experimental data.

We assumed in paper II that the branching ratio to the different exit channels ($A$ $^3\Pi$, $B$ $^2\Sigma^+$, $A$ $^2\Delta$) was independent of the translational energy. Furthermore, we assumed that the entire reaction proceeds on the adiabatic potential energy surfaces. In the present paper we avoid the latter assumption and investigate the former using a semiclassical (SC) method.\textsuperscript{25–37} The main characteristic of a SC (or classical path) approach is that some coordinates are treated quantum mechanically and others classically. In our calculations we simultaneously propagate a quantum mechanical wave function using the time-dependent Schroedinger equation and a classical particle using the Hamilton formalism from a separation of 30 bohr to the harpooning radius. Up to this point the scattering is assumed to be (in)elastic. The harpooning event and the subsequent reaction are modeled by the ADLC model, as defined above, and by a second model that correlates the electronic angular momentum of the atom at the harpooning radius with the electronic angular momentum of the CaF product. These models for the reactive part of the process are crude, obviously, but a full \textit{ab initio} calculation of the potential energy surfaces in the reactive region, and the associated full-dimensional reactive scattering calculations, are not feasible at the moment. From the experiment we would need, e.g., inelastic cross sections, cross sections for reaction to the ground state channel, or energy dependent branching ratios, to extend the model beyond the current level (see also Sec. II G).

In Sec. II we outline the semiclassical theory needed for the calculation and the analysis of the trajectories. In Sec. III we present some computational details including the algorithm that we used to evaluate the matrix elements of the potential operator. In Sec. IV we discuss the results for the Ca+$+$CH$_3$F $\rightarrow$ CaF ($A$ $^3\Pi$)+CH$_3$F reaction and compare them to the previous MQCT results and the experimental results. Furthermore, we will make some predictions regarding the CaF ($B$ $^2\Sigma^+$) and CaF ($A$ $^2\Delta$) exit channels, although these were not measured in the experiment. Finally, in Sec. V we will draw conclusions regarding the validity and accuracy of the SC method and we will point out where we see room for improvement of the theory and our calculations.

II. THEORY

For the SC calculations, we separate the coordinates into two different groups. The first of these groups, consisting of the electronic coordinates of Ca and CH$_3$F and the rotational coordinates of CH$_3$F, is treated quantum mechanically. The evolution of the wave function in these coordinates is given by the time-dependent Schrödinger equation. The other group, consisting of the translational coordinates of the Ca atom with respect to the CH$_3$F molecule, is treated using classical mechanics in the Hamilton formalism. The coupling from the classical coordinates to the quantum mechanical ones is obtained through the interaction potential, which depends on the classical coordinates. The back coupling is obtained by letting the classical coordinates move in the Ehrenfest averaged potential $\langle \Psi|V|\Psi \rangle$, where $V$ is the interaction operator and $\Psi$ the quantum mechanical wave function, which will be expanded in a basis set. The SC method gives us a number of coupled first order differential equations, which are used to propagate the quantum mechanical wave function and the classical particle simultaneously in time.

This approach for the coupling between quantum mechanical and classical coordinates provides us with trajectories that conserve energy.\textsuperscript{25–27,29,31,32,37} However, microscopic reversibility is not obeyed, i.e., the probability of an excitation from state $n$ to state $m$ is not equal to the probability of the reverse process. Methods have been published to circumvent this problem (see, e.g., Refs. 32 and 37). However, since the rotational energy is approximately 200 times smaller than the relative kinetic energy, the violation of microscopic reversibility will be small\textsuperscript{37} and therefore we have not implemented these methods.

A. Coordinates

Three coordinate systems will be defined in this section. First, we define a space-fixed (SF) frame, located at the center-of-mass of the colliding particles. Its $z$-axis is defined to be parallel to the initial relative velocity vector of the colliding particles. The coordinates of the atom with respect to the molecule are given by $R=(R, \Theta, \Phi)$, where $R$ is the length of the vector connecting the centers-of-mass of the
molecule and the atom. The angles $\Theta$ and $\Phi$ are the polar angles of this vector in the SF frame. The orientation of the molecule in the SF frame is given by $\alpha=(\alpha, \beta, \gamma)$, which are the Euler angles of the molecule in the $xyz$-parameterization. The coordinates of the electrons of the Ca atom are given schematically by $r$, which has its origin on the Ca atom.

Second, we define a dimer-fixed (DF) frame. The DF frame is obtained from the SF frame by rotation over $(\Phi, \Theta, 0)$, which means that Ca has coordinates $(R, 0, 0)$ in this frame. Hence, the $z$-axis of the DF frame lies parallel to $R$. Therefore, the orientation of the molecule $\alpha_r=(\alpha_R, \beta_R, \gamma_R)$ and the electronic coordinates of the Ca atom $r_R$ in the DF frame are labeled by a subscript $R$.

Finally, we define a molecule-fixed (MF) frame. This is the inertial frame of the molecule and it is equal to the BF frame we used before. In this frame the electronic coordinates of the CH$_3$F molecule are schematically designated by $\rho$, which has its origin at the center-of-mass of the CH$_3$F molecule.

**B. Basis functions**

The basis set used in the expansion of the wave function is a direct product of three bases for the three sets of coordinates, i.e., the electronic coordinates of both CH$_3$F and Ca and the rotational coordinates of the CH$_3$F molecule.

$$\psi_{\lambda\mu jkm}(\rho, r, \alpha) = \phi_{\text{CH}_3\text{F}}(\rho) \phi_{\text{Ca}}(r) \chi_{jkm}(\alpha), \quad (1)$$

where $\psi_{\lambda\mu jkm}(\rho, r, \alpha)$ is the resulting basis function, labeled by the rotational symmetric top quantum numbers $j, k, l$, and $m$, and by the electronic orbital angular momentum quantum number $\lambda$ and the magnetic quantum number $\mu$ of the Ca atom. Since we will restrict our basis to the functions of the $^1D$ state of the Ca atom, $\lambda$ will be 2 throughout this article and therefore we will drop this label wherever possible. The factor $\phi_{\text{CH}_3\text{F}}(\rho)$ in Eq. (1) designates the electronic wave function of the CH$_3$F molecule. It is defined with respect to the MF frame. The electronic wave function for Ca is designated by $\phi_{\text{Ca}}(r)$ and it is defined with respect to the SF frame. This wave function has five components, labeled by $\mu$ ranging from $-2$ to $2$. Lastly, the functions $\chi_{jkm}(\alpha)$ in Eq. (1) are the symmetric top wave functions of the CH$_3$F molecule, defined as

$$\chi_{jkm}(\alpha) = \sqrt{\frac{2j+1}{8\pi}} D_{mk}^{(j)}(\alpha), \quad (2)$$

where $D_{mk}^{(j)}(\alpha)$ denotes a Wigner D-matrix (see Refs. 38 and 39). It is defined with respect to the SF frame.

**C. Hamiltonian**

The classical part of the SC calculations contains the following kinetic energy

$$T_e(P_R) = \frac{1}{2\mu_e} \left( \frac{P_R^2}{R^2} + \frac{P_\theta^2}{R^2 \sin^2 \Theta} + \frac{P_\Phi^2}{R^2 \sin^2 \Theta} \right), \quad (3)$$

where $P_R = (P_R, P_\theta, P_\Phi)$ denotes the momentum conjugate to $R$ and $\mu_e$ is the reduced mass of the colliding particles.

The Hamilton operator for the quantum mechanical part is defined as follows

$$\hat{H}_q(p, r, \alpha, R) = \hat{H}_0(p, r, \alpha) + \hat{V}(p, r, \alpha, R) = \hat{H}_e^{\text{CH}_3\text{F}}(p) + \hat{H}_e(r) + \hat{H}_e(\alpha) + \hat{V}(p, r, \alpha, R). \quad (4)$$

In Eq. (4) the term $\hat{H}_e^{\text{Ca}}(r)$ is the Hamiltonian for the electronic coordinates of the Ca atom. The five basis functions $\phi_{\mu}(r)$ are its degenerate eigenfunctions with eigenvalue $\epsilon_{\mu}^{\text{Ca}}$. The term $\hat{H}_e^{\text{CH}_3\text{F}}(p)$ in Eq. (4) is the Hamiltonian for the electronic coordinates of the CH$_3$F molecule. The basis function $\phi_{\mu}^{\text{CH}_3\text{F}}(p)$ is its ground state eigenfunction with eigenvalue $\epsilon_{\mu}^{\text{CH}_3\text{F}}$. $\hat{H}_e(\alpha)$ is the symmetric top Hamiltonian that describes the rotation of the CH$_3$F molecule. Hence,

$$\hat{H}_e(\alpha) \chi_{jkm}(\alpha) = \epsilon_{jkm} \chi_{jkm}(\alpha) = [A(j+1) + (C-A)k^2] \chi_{jkm}(\alpha), \quad (5)$$

where $\epsilon_{jkm}$ is the eigenvalue for the state $\chi_{jkm}(\alpha)$, while $A$ and $C$ are the rotational constants for the symmetric top molecule CH$_3$F. Throughout this article, we will use $\epsilon_{\text{Ca}} + \epsilon_{\text{CH}_3\text{F}}$ as the reference energy.

Lastly, the term $\hat{V}(p, r, \alpha, R)$ in Eq. (4) is the electrostatic interaction operator. If this operator is expanded in a multipole series, we get the following general expression:\cite{40,41}

$$\hat{V}(p, r, \alpha, R) = \sum_{l_a, l_b=0}^{\infty} \left[ \frac{(2l_a+2l_b+1)!}{(2l_a)!(2l_b)!} \right] (-1)^{l_a} r^{-l_a-l_b-1} \times \sum_{m_a=-l_a}^{l_a} \sum_{m_b=-l_b}^{l_b} C^{(l_a+l_b)}_{-m_a-m_b}(\Theta, \Phi) \times \left( \begin{array}{c} l_a \; l_b \; l_a+l_b \\ m_a \; m_b \; -m_a-m_b \end{array} \right) \times \sum_{m_{l_a}=m_{l_a}}^{l_a} \hat{Q}^{(l_a)}_{m_{l_a}}(\rho) D_{m_a}^{(l_a)}(\alpha) \hat{Q}_{m_{l_a}}^{(l_a)}(r). \quad (6)$$

Here, $A$ labels the molecule and $B$ the atom. The operator $\hat{Q}^{(l_a)}_{m_{l_a}}(\rho)$ in Eq. (6) is defined as the $m_a$ component of a $2l_a$ multipole operator on CH$_3$F with respect to the MF frame. Transformation with the functions $D_{m_a}^{(l_a)}(\alpha)$ rotates $\hat{Q}^{(l_a)}_{m_{l_a}}(\rho)$ to the SF frame. The operator $\hat{Q}_{m_{l_a}}^{(l_a)}(r)$ is defined in an analogous way on the Ca atom, but directly with respect to the SF frame. The factor ($\hat{\cdot}$) in Eq. (6) is a $3jm$ symbol. Lastly, the function $C^{(l_a+l_b)}_{-m_a-m_b}(\Theta, \Phi)$ is a spherical harmonic in the Racah normalization and the phase convention of Condon and Shortley.\cite{39} We wish to emphasize here that by restricting the electronic basis to only one (degenerate) state on
Ca and one state on CH$_3$F we only include the electrostatic interactions. Interactions like dispersion or polarization would be included if the basis set were extended to other electronic states of Ca or CH$_3$F, but this is not done in the present article.

D. Equations of motion

The total wave function is expanded in the basis defined in Sec. II B as follows:

$$
\Psi^{(\kappa)}(\rho, r, \alpha, t) = \sum_{\mu = -2}^{2} \sum_{j=0}^{j_{\text{max}}} \sum_{k, m=-j}^{j} \psi_{\mu jkm}^{(\kappa)}[R(t)] \times \exp(-i e_{\mu j} t / h).
$$

(7)

The variable $j_{\text{max}}$ in Eq. (7) denotes the highest $j$ quantum number in the basis set. The superscript $\kappa = (N_i, j_i, k_i, m_i, b)$ denotes the initial state, where $(j_i, k_i, m_i)$ are the initial rotational quantum numbers of the CH$_3$F molecule, $N_i$ is the initial electronic state of the Ca atom, and $b$ is the impact parameter. The dependence of the wave function on the initial state and the definition of $N_i$ will be discussed in Sec. II F.

The time evolution of the wave function is given by the time-dependent Schrödinger equation

$$
i \hbar \frac{\partial \Psi^{(\kappa)}}{\partial t} = \hat{H}_{q} \Psi^{(\kappa)}.
$$

(8)

Substituting the definitions for $\hat{H}_{q}$ and $\Psi^{(\kappa)}$ into Eq. (8) yields the following equations of motion for the expansion coefficients:

$$
i \hbar \frac{\partial \psi_{\mu jkm}^{(\kappa)}[R(t)]}{\partial t} = \sum_{\mu' j' k' m'} V_{\mu jkm, \mu' j' k' m'}(R(t)) \times \exp[(i e_{\mu j} - i e_{\mu' j'}) t / h].
$$

(9)

The elements $V_{\mu jkm, \mu' j' k' m'}(R)$ of the interaction matrix $V$ are given by

$$
V_{\mu jkm, \mu' j' k' m'}(R) = \langle \psi_{\mu jkm} | \hat{V}(\rho, r, \alpha, \tau) | \psi_{\mu' j' k' m'} \rangle.
$$

(10)

Following the Ehrenfest theorem, a total classical Hamiltonian can be defined for this system as

$$
H_{\text{tot}} = T_{\text{cl}} + V_{\text{av}} = T_{\text{cl}} + \langle \Psi^{(\kappa)} | \hat{H}_{q} | \Psi^{(\kappa)} \rangle.
$$

(11)

From this equation, the equations of motion for the classical coordinates can be derived as

$$
\frac{\partial R}{\partial t} = \frac{\partial H_{\text{tot}}}{\partial P_{R}} = \frac{\partial T_{\text{cl}}}{\partial P_{R}},
$$

(12a)

$$
\frac{\partial P_{R}}{\partial t} = -\frac{\partial (\Psi^{(\kappa)} \hat{H}_{q} \Psi^{(\kappa)})}{\partial R} = -\langle \Psi^{(\kappa)} | \frac{\partial \hat{V}}{\partial R} | \Psi^{(\kappa)} \rangle,
$$

(12b)

where by differentiation with respect to a vector, we mean differentiation with respect to the components of that vector. The last step in Eq. (12b) can be easily proven using Eq. (9) and the fact that the basis functions are orthonormal eigenfunctions of $\hat{H}^{0}$.

With the definition for $H_{\text{tot}}$, Eq. (9), and the proof of Eq. (12b) it can be demonstrated quite straightforwardly that this approach leads to trajectories along which the total energy of the system is always conserved. Furthermore, the above expressions for the Hamiltonians show clearly that the classical and quantum mechanical degrees of freedom are coupled exclusively through the intermolecular interaction operator.

E. The interaction matrix

The interaction matrix $V$ is defined by Eq. (10). In its evaluation we use the fact that the matrix elements of the multipole operators are related through the Wigner–Eckart theorem.

$$
\langle \phi_{\mu}^{C_{\alpha}} | Q_{\mu b}^{(l b)} | \phi_{\mu'}^{C_{\alpha}} \rangle = (-1)^{2-\mu} \begin{pmatrix} 2 & l_b & 2 \\ -\mu & m_b & \mu' \end{pmatrix} (2 | Q_{\mu b}^{(l b)} | 2),
$$

(13)

where the factor $2 | Q_{\mu b}^{(l b)} | 2$ denotes the reduced matrix element of a $2^{l b}$ operator for the $1D$ state of Ca.

We substitute Eqs. (1) and (6) into Eq. (10). Using the Wigner–Eckart theorem and the analytical form for the integration of a product of three Wigner $D$-matrices, we get the following expression for $V_{\mu jkm, \mu' j' k' m'}(R)$:

$$
V_{\mu jkm, \mu' j' k' m'}(R) = (-1)^{k-m}(1)^{-2-\mu} \sqrt{(2j+1)(2j'+1)} \sum_{l_{a}=0}^{\infty} \sum_{l_{b}=0}^{\infty} \left( \frac{2l_{a}+2l_{b}+1}{(2l_{a})!(2l_{b})!} \right)^{1/2} (-1)^{l_{a}} (2 | Q_{\mu b}^{(l b)} | 2) \times (Q_{k-k}^{(l a)}) R^{-l_{a}+l_{b}-1} C_{m'-m+\mu-\mu'}^{l_{a}+l_{b}}(\Theta, \Phi) \begin{pmatrix} l_{a} & l_{b} & l_{a}+l_{b} \\ m-m' & \mu-\mu' & m'-m+\mu' \end{pmatrix} \times \begin{pmatrix} l_{a} & j' & j \\ m'-m & -m & -\mu-\mu' \end{pmatrix} \begin{pmatrix} 2 & l_{b} & 2 \\ -\mu & \mu & j' \end{pmatrix} \begin{pmatrix} l_{a} & j' & j \\ (k'-k) & -k & k \end{pmatrix}.
$$

(14)
The factor $Q_{k-k'}^{(l_a)}$ denotes a $k-k'$ component of a $2l_a$ pole on CH$_3$F. In theory, we would need all multipole moments on CH$_3$F. In practice, the multipole moments on CH$_3$F are included up to the octupole moment ($l_a=1, 2, \text{ and } 3$). The Ca atom has a quadrupole and a hexadecupole moment, of which only the quadrupole moment is taken into account ($l_b=2$).

**F. Sampling of initial states**

The initial conditions for the wave function and for the classical coordinates and momenta are indicated by the experiment. For the initial translational energy and the initial rotational state the sampling is straightforward, since the experimental values can be used directly. The sampling of the initial state of the Ca atom is less trivial. In the experiment the Ca atom is not prepared in a specific component of the $^1D$ state and the Ca atom must therefore be treated as a statistical mixture with equal weights for the five components (see Ref. 42, p. 204 ff.). Therefore, the correct quantum mechanical procedure is clear cut. One has to start a calculation with each of the five substates of the $^1D$ state, calculate the observables and average over the substates with equal weights. Furthermore, since in a quantum mechanical calculation the equations of motion are linear in the expansion coefficients for the wave function [see Eq. (9)], each orthonormal basis in the fivefold degenerate space of the $^1D$ state will lead to the same result after statistical averaging.

In a semiclassical method the same procedure can be used in principle. However, from Eq. (12b) it is clear that the classical equations of motion are quadratic in the expansion coefficients and therefore the choice of the initial states will not be arbitrary. Each basis will lead to a different result after statistical averaging. Thus, we have devised the following procedure to define the initial states on Ca. Bearing in mind that the SC approximation will be most reliable when the number of non-adiabatic transitions is small, since in that case the average potential $V_{\text{av}}$ [see Eq. (11)] will be most similar to the true potential,$^{32,37}$ the initial states are taken to be adiabatic states at the initial separation of atom and molecule. These states are defined to be the eigenstates of the average interaction matrix, because the CH$_3$F molecule is described quantum mechanically. Its elements are defined as

$$\langle j^i k^i m_i | V | j^f k^f m_f \rangle,$$

where we assume that we start in a pure rotational state $(j^i k^i m_i)$. Since the eigenvectors of this matrix are calculated at a finite separation of atom and molecule (in this case 30 bohr), they will be a function of the impact parameter $b$. However, this dependence on $b$ is very weak at this separation, so in practice for all trajectories the same $b$ ($b=1$ bohr) for the calculation of the initial states is chosen. We cannot use a zero impact parameter, because in that case the eigenvectors of the averaged interaction matrix would not be completely defined.

**G. Reaction model**

To describe the chemical reaction between Ca and CH$_3$F the angle dependent line-of-centers (ADLC) model is used, as in paper II. In this model the reaction probability, expressed in the DF frame, is defined as follows

$$W(\beta_R) = \begin{cases} 1; & 0 < \beta_R < \beta_c \\ 0; & \beta_c < \beta_R \leq \pi. \end{cases}$$

where the angle $\beta_c$ is the "cut-off angle," used to model the "cone of non-reaction," the part of the molecule, that is assumed to be non-reactive during the collision. Evidence for the existence of such a cone of non-reaction was reported in the literature for the Rb$^+ +$CH$_3$I reactive collision.$^{5,6}$

The barrierless form of the ADLC model used in these calculations is consistent with the harpooning mechanism, proposed for this reaction. In the harpooning mechanism, the reaction is initiated by an electron jump from Ca to CH$_3$F at a certain distance, the harpooning distance $R_h$. This harpooning radius, which is also taken to be the final radius of the SC trajectories, is not precisely known experimentally. Therefore, we have used the same harpooning radius as in paper II, i.e., 6.0 bohr. This fixed harpooning radius gives, in combination with the ADLC model, a crude description of the reaction. If we define the harpooning radius as the distance where the covalent and the ionic surfaces cross, then this radius depends on the orientation of the reactants. Furthermore, it depends on the electronic state of the reactants, because the repulsive covalent adiabatic surfaces cross the ionic surfaces at different radii than the attractive covalent surfaces. Actually, there are many crossings of electronic states in this region, because the ionic surface which corresponds to Ca$^+$ ($^2D$) + CH$_3$F$^-$ asymptotically, also consists of asymptotically degenerate surfaces. Last, in the ADLC model we do not account for the occurrence of recrossing in the entrance channels, nor in the exit channels. However, for all three problems mentioned, there are no experimental data or ab initio calculations, from which the information needed to improve the reaction model can be extracted. Therefore, we were forced to keep the model simple, and to use it especially to gain more understanding of the influence of the long range dynamics on the steric effect and its energy dependence.

Naturally, the electronic state of the Ca atom will evolve during the propagation of the wave function and to investigate the effect of the electronic state at impact on the branching ratio we use a second model. This model, proposed in 1988 by Menzinger,$^{33,44}$ which we call the "correlation model," assumes that during the reaction the projection of the electronic orbital angular momentum of the atom on the intermolecular axis, designated by the quantum number $\Lambda$, is conserved and becomes the electronic orbital angular momentum quantum number of the product molecule. Note, that it is tacitly assumed in this model that the intermolecular axis and the symmetry axis of the product CaF molecule coincide, which is usually not the case. However, the angle between these axes at the harpooning radius is 10 degrees at worst, when the C–F axis and the Ca–F axis are perpendicu-
lar to each other, which makes this assumption less severe. Evidence for the existence of the correlations assumed in this model have been found experimentally for Ca+Cl2 and Ca+HCl reactive scattering by Rettner and Zare.45,46 In order to apply this correlation model the basis functions for the rotation of the CH3F molecule and the electrons of the Ca atom need to be transformed to the DF frame. This transformation is given by

$$
\phi^C_{\mu}(r) = \sum_{m=\pm 2} \phi^C_{\mu}(r) D^2_{\mu\lambda}(\Phi, \Theta, 0),
$$

(17a)

$$
\chi_{\lambda\Omega}(\alpha) = \sum_{m=-j}^{j} \chi_{\lambda\Omega}(\alpha) D^{j\lambda}_m(\Phi, \Theta, 0).
$$

(17b)

Here \( \Omega \) is the projection of the rotational angular momentum of the CH3F molecule on the intermolecular axis, i.e., the vector \( R \) and \( \Lambda \) is the projection of the Ca angular momentum on the same axis. The wave function can then be written as

$$
\Psi^{(k)}(\rho, r, \alpha, t) = \sum_{\lambda \Omega} d^{(k)}_{\lambda\Omega}[R(t)] \Psi_{\lambda\Omega}(\rho, r, \alpha)
\times \exp(-i \epsilon \cdot t / \hbar),
$$

(18)

where \( \Psi_{\lambda\Omega}(\rho, r, \alpha) \) is defined analogously to \( \psi_{\mu j k m}(\rho, r, \alpha) \). Using the equivalence between Eqs. (7) and (18), we can easily prove that

$$
d^{(k)}_{\lambda\Omega}[R(t)] = \sum_{m \mu} e^{(k)}_{m \mu j k m}[R(t)] D^{(2)\mu\lambda}(\Phi, \Theta, 0) \times D^{j\lambda}_m(\Phi, \Theta, 0).
$$

(19)

H. Analysis

We want to compare our results with the experimental results obtained by Janssen et al.14 and with the results from the modified quasiclassical trajectory (MQCT) calculations in paper II. Furthermore, we wish to examine the evolution of the electronic state of Ca during the approach of the re-agents in three different representations of the electronic basis set of Ca.

1. Comparison to experiment and MQCT results

The wave function at the end of a trajectory is given by

$$
\Psi^{(k)}(\rho, r, \alpha, t = t_c).
$$

In order to use the correlation model, we need the wave function in the DF frame per \( \lambda \) state, \( \Psi^{(k)}(\alpha, r, t = t_c) \), which is defined by projecting the wave function in the DF frame, \( \Psi^{(k)}(\rho, r, \alpha, t) \) with \( \phi^C_{\mu}(r) \phi^{CHF}(\rho) \), i.e., by multiplication with \( \phi^C_{\mu}(r) \phi^{CHF}(\rho) \) and integration over the coordinates \( r \) and \( \rho \).

$$
\Psi^{(k)}_{\lambda}(\alpha, r, t = t_c) = \langle \phi^C_{\mu}(r) \phi^{CHF}(\rho) | \Psi^{(k)}(\rho, r, \alpha, t) \rangle_{r, \rho}
$$

(20a)

$$
= \sum_{j \Omega} d^{(k)}_{\lambda\Omega}[R(t_c)] \chi_{j\Omega}(\alpha) \exp(-i \epsilon \cdot t_c / \hbar).
$$

(20b)

From \( \Psi_{\lambda}(\alpha, r, t = t_c) \) the probability distribution function, \( \mathcal{S}_{\lambda}(\beta) \), for the orientation of the CH3F molecule in the DF frame is obtained by integrating the square modulus of \( \Psi^{(k)}(\alpha, r, t = t_c) \) over all coordinates, except \( \beta \).

$$
\mathcal{S}_{\lambda}(\beta) = \int |\Psi^{(k)}(\alpha, r, t = t_c)|^2 d\alpha d\gamma.
$$

(21)

Using this probability function we can calculate the reactive cross section for each \( ^1D \) state \( \Lambda \) in the DF frame by multiplying \( \mathcal{S}_{\lambda}(\beta) \) by \( W(\beta) \), defined by Eq. (16), and by subsequent integration over \( \beta \) and \( b \) and averaging over \( N_i \) as

$$
\sigma_{\lambda}(j, k, m) = \frac{1}{5} \sum_{N_i=1}^5 \int \mathcal{S}_{\lambda}(\beta) W(\beta) \sin \beta d\beta db,
$$

(22)

where the factor 1/5 in Eq. (22) arises from averaging over the initial electronic states \( N_i \).

Subsequently, two approaches can be followed to obtain the total reactive cross section \( \sigma_{j, k, m} \). The first is to assume that the branching ratio to the different exit channels is independent of the relative translational energy, as we did in paper II. In that case, \( \sigma_{j, k, m} \) is simply defined as

$$
\sigma_{j, k, m} = \sum_{\lambda} \sigma_{\lambda}(j, k, m).
$$

(23)

From this we can define the total cross section for an unoriented beam of molecules, \( \sigma_0^{(1,1)}(E) \), the steric effect, \( \sigma_1^{(1,1)}(E) \), and the alignment effect, \( \sigma_2^{(1,1)}(E) \), for a initial rotational energy \( \varepsilon_{1,1} \) as

$$
\sigma_0^{(1,1)}(E) = \frac{1}{5} \sum_{m=-1}^1 \sigma_{1,1}(m),
$$

(24a)

$$
\sigma_1^{(1,1)}(E) = \frac{\sigma_{1,1}^{(1,1)} - \sigma_{1,1}^{(1,1,-1)}}{\sigma_{0,1}^{(1,1)}(E)},
$$

(24b)

$$
\sigma_2^{(1,1)}(E) = \frac{5 \sigma_{1,1}(E) + \sigma_{1,1}^{(1,1,-1)}}{\sigma_{0,1}^{(1,1)}(E) - 2}.
$$

(24c)

The second approach is to assume that the projection of the electronic angular momentum of the Ca atom on the intermolecular axis, i.e., the quantum number \( \Lambda \), correlates with the electronic orbital angular momentum quantum number of the CaF product. Thus, the total reactive cross section for the \( A^2\Pi \), \( B^2\Sigma^+ \), and \( A^2\Sigma^+ \) states is defined as

$$
\sigma_{\lambda}(j, k, m) = \sigma_{\lambda=-2}(j, k, m) + \sigma_{\lambda=-1}(j, k, m),
$$

(25a)

$$
\sigma_{\lambda}(j, k, m) = \sigma_{\lambda=-1}(j, k, m) + \sigma_{\lambda=0}(j, k, m),
$$

(25b)

$$
\sigma_{\lambda}(j, k, m) = \sigma_{\lambda=0}(j, k, m).
$$

(25c)

From these cross sections we calculate for each state \( \Gamma = \Sigma, \Pi, \Delta \), \( \sigma_{0,1}^{(1,1)}(E), \sigma_{1,1}^{(1,1)}(E) / \sigma_{0,1}^{(1,1)}(E), \) and \( \sigma_{2,1}^{(1,1)}(E) / \sigma_{0,1}^{(1,1)}(E) \), analogously to Eqs. (24).

The MQCT calculations have shown that two dynamical effects are important for the Ca + CH3F collision: trapping
and reorientation. The occurrence of trapping is easy to check by examining the trajectories. In order to check the occurrence of reorientation the \((\alpha, \beta)\) probability distribution for the orientation of the CH\(_3\)F molecule in the SF frame is needed. It is calculated by integrating the square modulus of the wave function at \(t = t_r\) in the SF frame over all electronic coordinates and over \(\gamma\)

\[
\zeta^{(k)}(\alpha, \beta) = \int |\Psi^{(k)}(\mathbf{p}, r, \alpha, t = t_r)|^2 d\mathbf{p} dr d\gamma.
\]

(26)

The change in \(\zeta^{(k)}(\alpha, \beta)\) as a function of the impact parameter and along the classical path is a measure of the amount of reorientation during the collision.

2. The evolution of the electronic state of Ca

The difference between the MQCT calculations in paper II and the present SC calculations lies partly in the description of the electronic states of Ca. In the SC method nonadiabatic transitions between Ca states are possible, which is not the case in the MQCT calculations. To examine the evolution of the electronic state of Ca during the collision we want to monitor the population of each of the five substates in three different representations.

In representation 1 we use the (diabatic) basis in the SF frame, \(\psi_{\mu j k m}(\mathbf{p}, r, \alpha)\). To calculate the population of a \(1^D\) state we need the wave function per \(\mu\) state at a certain time \(t\), \(\Psi^{(k)}(\alpha, t)\), which is defined by projecting \(\langle \phi^{\text{CH}_3\text{F}}(\mathbf{p}) | \Psi^{(k)}(\mathbf{p}, r, \alpha, t) \rangle\) onto the wave function

\[
\Psi^{(k)}(\alpha, t) = \langle \phi^{\text{Ca}}(r) | \phi^{\text{CH}_3\text{F}}(\mathbf{p}) | \Psi^{(k)}(\mathbf{p}, r, \alpha, t) \rangle_{r, \mathbf{p}}
\]

(27a)

\[
= \sum_{jkm} c^{(k)}_{\mu j k m}(R(t)) \chi_{j k m}(\alpha) \exp(-iE_{j k m} t / \hbar).
\]

(27b)

The population of a certain \(1^D\) state \(\mu\) in the SF frame is then given by taking the square modulus of \(\Psi^{(k)}(\alpha, t)\) and integrating over \(\alpha\)

\[
\zeta^{(k)}(\mu) = \int |\Psi^{(k)}(\mu, \alpha, t)|^2 d\alpha.
\]

(28a)

\[
= \sum_{jkm} |c^{(k)}_{\mu j k m}(R(t))|^2,
\]

(28b)

In representation 2 we use the (diabatic) basis in the DF frame, \(\psi_{\Lambda j k l}(\mathbf{r}, \mathbf{R}, \alpha_R)\). To calculate the population of a \(1^D\) state we need the wave function per \(\Lambda\) state at a certain time \(t\), \(\Psi^{(k)}(\alpha_R, t)\), which is defined by Eq. (20). The population of a certain \(1^D\) state \(\Lambda\) in the DF frame is the integral over \(\alpha_R\) of the square modulus of \(\Psi^{(k)}(\alpha_R, t)\)

\[
\zeta^{(k)}(\Lambda) = \int |\Psi^{(k)}(\Lambda, \alpha_R, t)|^2 d\alpha_R.
\]

(29a)

\[
= \sum_{jkl} |a^{(k)}_{\Lambda j k l}(R(t))|^2.
\]

(29b)

If \(\Lambda\) is conserved in this frame, this is known as "orbital following."\(^{43,46,47}\)

In representation 3, we use an adiabatic basis on Ca and the DF basis for CH\(_3\)F. The adiabatic basis functions are defined as

\[
G_N(\mathbf{r}_R; \alpha_R) = \sum_{\Lambda = 1}^{2} \phi^{\Lambda}_{\alpha_R}(\mathbf{r}_R) U_{\Lambda \ell}(\alpha_R),
\]

(30)

where \(U_{\Lambda \ell}(\alpha_R)\) is the coefficient of the \(\ell\)th basis function of the \(\Lambda\)th eigenvector of the \(5 \times 5\) interaction matrix \(V\), where 

\[
V_{\Lambda \ell} = \langle \phi^{\Lambda}_{\alpha_R} | \phi^{\ell}_{\alpha_R} \rangle.
\]

Note that this definition does not completely fix the (complex) phase of \(U_{\Lambda \ell}(\alpha_R)\). It is not possible to choose \(U_{\Lambda \ell}(\alpha_R)\) real and at the same time continuous for all \(\alpha_R\), because of the geometrical phase problem (see e.g., Refs. 48–50). Fortunately, for the computation of the population of a given adiabatic state, we only need the square modulus of \(U_{\Lambda \ell}(\alpha_R)\), as will be shown below, and so we do not need to worry about this subtlety. The wave function for each adiabatic state \(N\) is defined by projecting \(\langle G_N(\mathbf{r}_R; \alpha_R) | \phi^{\text{CH}_3\text{F}}(\mathbf{p}) \rangle\) onto the wave function, i.e.,

\[
\Psi^{(k)}(\alpha_R, t) = \langle G_N(\mathbf{r}_R; \alpha_R) | \phi^{\text{CH}_3\text{F}}(\mathbf{p}) | \Psi^{(k)}(\mathbf{p}, r, \alpha_R, t) \rangle_{r, \mathbf{p}}
\]

(31)

The populations of the adiabatic states are then defined as

\[
\zeta^{(k)}(N) = \int |\Psi^{(k)}(\alpha_R, t)|^2 d\alpha_R.
\]

(32)

Now we could proceed in the same manner as in the definition of \(\zeta^{(k)}(\mu)\) and \(\zeta^{(k)}(\Lambda)\) and calculate \(\zeta^{(k)}(N)\) as the sum over the squares of the coefficients of the expansion of the wave function in the adiabatic states \(G_N(\mathbf{r}_R; \alpha_R)\). However, the transformation of the wave function is very awkward, because of the geometric phase effect mentioned above. Hence, we use Eq. (32) directly and calculate \(\zeta^{(k)}(N)\) as

\[
\zeta^{(k)}(N) = \int |\Psi^{(k)}(\alpha_R, t)|^2 d\alpha_R.
\]

(33)

Thus, we can derive a form for \(\zeta^{(k)}(N)\), which only contains the coefficients obtained from the SC calculation. There is no need to transform the wave function to the adiabatic basis to get the expansion coefficients and from there on \(\zeta^{(k)}(N)\).

III. COMPUTATIONAL DETAILS AND IMPLEMENTATION

A Fortran program was written to perform the propagation of the SC trajectories and the evolution of the wave functions, according to the equations of motion Eqs. (9) and (12). For the propagation we used a variable order, variable step Adams integrator from the NAG library\(^{51}\) (subroutine ‘‘D02JCF’’). The tolerance of the integration was set to \(10^{-6}\) using absolute error checking. This means that energy and the norm of the wave function are both conserved to four to six significant figures. Calculations were performed for six
different energies, chosen to coincide with experimental energies of Janssen et al.,14 they are the same as those in paper II. The experimental values for $\sigma_0(E)$, $\sigma_1(E)/\sigma_0(E)$, and $\sigma_2(E)/\sigma_0(E)$ for these energies are given in Table I. For each translational energy, each initial electronic state for the Ca atom and for each $m_1$ state for the rigid rotor 17 trajectories with different impact parameters were calculated. These impact parameters were distributed equidistantly in $b^2$ between 0.0 and 9.0 bohr in such a way as to make an integration over the impact parameter possible with the trapezoidal rule. The maximum value of $b$ of 9.0 bohr turned out to be sufficient to not to miss any reactive trajectories, except at a relative translational energy of 0.068 eV with $m_1=1$ and $N_i=1,2$ where one more trajectory had to be added. All trajectories started at $R=30$ bohr. The harpooning radius was taken to be 6.0 bohr, as in paper II. For the calculations an IBM RS6000/370 and an IBM RS6000/390 were used. Trajectories typically took one hour on the 370 or half an hour on the 390. Per trajectory the number of coupled equations was 27283 and the number of function evaluations in the order of 300.

The bottleneck in these calculations was the evaluation of the matrix elements of the interaction matrix $V$, defined through Eq. (14). Evaluation of these matrix elements at each integration step would make the propagation computationally too expensive for basis sets with maximum $j$-values over six. In practice, $j_{\text{max}}$ has to be around 15 in order to converge the wave function. Advantage can be taken from the structure of $V$, which will make the evaluation of the matrix elements of $V$ less costly.

Inspection of the definition of the matrix elements $V_{l_a,m_l,k}^{\lambda,k,m_l}(R)$ of $V$ in Eq. (14) shows that the dependence on $R$ arises solely through the irregular solid harmonic $R^{-l_a-l_b-1}C_{m_l}^{l_a+l_b,m_l}e^{i(m_l+\mu)}(\Theta,\Phi)$. This means that before any propagation a matrix $A^{(l_a-l_b)}$ can be calculated, which is implicitly defined as

$$V_{l_a,m_l,k}^{\lambda,k,m_l}(R) = \sum_{l_a=0}^{\infty} \sum_{l_b=0}^{\infty} R^{-l_a-l_b-1} \times C_{l_a+l_b,m_l}^{l_a+l_b,m_l} \times A^{(l_a-l_b)}_{\lambda,k,m_l} e^{i(m_l+\mu)}(\Theta,\Phi) \times A^{(l_a-l_b)}_{\lambda,k,m_l}.$$  

Thus, the calculation will be sped up considerably. Furthermore, given the restrictions on the indices in Eq. (14) and given the fact that only a small number of multipoles is used and that of those multipoles only a few components are non-zero, the matrix $A^{(l_a-l_b)}$ will be very sparse. In fact, for a value of $j_{\text{max}}$ of 15 less than 1% of $A^{(l_a-l_b)}$ is actually non-zero. Much memory can be saved by storing only these non-zero elements. We want to emphasize here that the sparsity of $A^{(l_a-l_b)}$ is what makes these calculations possible, because even when only the non-zero elements of $A^{(l_a-l_b)}$ are stored, the amount of memory needed for a calculation with $j_{\text{max}}=15$, $l_a=1,2,3,$ and $l_b=2$ is about 30 Mb, compared to 11 Gb for storing the entire matrix.

The multipole moments used for CH$_3$F are given in paper II. For Ca the same quadrupole moment is used as in paper II. Its reduced matrix element, cf. Eq. (13), is 15.7664 a.u.23 The rotational constants of CH$_3$F used in the calculation of the rotational energies $v_{jk}$ are the experimental values, see paper II.

After the propagation the trajectories are analyzed according to the strategies outlined in Sec. II H. The integrals over the angles $\gamma$ and $\gamma_a$ are performed analytically, except for Eq. (33), where an equidistant grid of 100 points is used.

The integrations over $\alpha$ and $\alpha_R$ can be performed analytically, except for the integration over $\alpha_R$ in Eq. (33). Examination of the eigenvectors $V_{\lambda,k}^{A,N}$ of $A_R$ and the symmetric top functions $\lambda_{jk\Omega}(\alpha_k)$ appearing in Eq. (33) shows that the dependence on $\alpha_R$ of the integrand is a linear combination of functions of the form $\cos(\lambda+\Omega)\alpha_R$. Therefore, $2(2+j_{\text{max}}+1)$ equidistant points are sufficient to integrate Eq. (33) exactly over $\alpha_R$.

The integration over $\beta_R$ was done numerically using a Gauss–Legendre quadrature in $\cos(\beta_R)$ with 50 Gauss–Legendre points, using the routine "D01BCF" from the NAG-library.51 Lastly, the integration over the impact parameter $b$ in Eq. (22) was done using the trapezoidal rule.

For all propagations the same criterion of $R = 6.0$ bohr was used to end the propagation. Four cutoff angles were used to examine the influence of the cutoff angle, $\beta_c$, on the steric effect and its energy dependence. The angles used were 60°, 90°, 120°, and 180° and therefore the calculations will be called "model 60," "model 90," "model 120," and "model 180" calculations, respectively.

### IV. RESULTS AND DISCUSSION

The SC results obtained by using the correlation model for the $\Delta^2\Sigma$ state, the $B^2\Sigma^+$ state, and the $\Delta^2\Delta$ state will be designated by SC–$\Sigma$, SC–$\Pi$, and SC–$\Delta$, respectively. The results will be compared to the experimental results by Janssen et al.14 and to the MQCT results, using approach (II) in paper II. Since all our calculations refer to the reaction of the Ca with CH$_3$F, prepared in its $(j,k)=(1,1)$ state, we will omit the label $(1,1)$ from the cross sections from this point on.
A. Steric effect: \( \sigma_1(E)/\sigma_0(E) \)

The results for \( \sigma_1(E)/\sigma_0(E) \) using the standard SC method (see Fig. 1) are in slightly better agreement with experiment than the MQCT results in paper II, Fig. 13. However, for different cut-off angles either the magnitude of \( \sigma_1(E)/\sigma_0(E) \) or the energy dependence of \( \sigma_1(E)/\sigma_0(E) \) is in agreement with experiment. This was also concluded after the MQCT calculations in paper II. This SC result shows that the quantum mechanical description of CH\(_3\) F and Ca has a weak, but positive, influence on this result.

The use of the correlation model for the \( A^2\Pi \) state yields the SC-II results in Fig. 2. The results fit the experimental data rather well. A cut-off angle of approximately 105° would fit the experiment almost perfectly within error bars. Thus, while the SC method alone does not lead to better results, it enables us to use a model that correlates electronic states at the harpooning radius with the final electronic states, which does lead to better agreement for \( \sigma_{1\Pi}(E)/\sigma_{0\Pi}(E) \) with experiment.

In order to understand these results it is useful to consider the five adiabatic potential energy surfaces (PESs) at \( R=6.0 \) bohr. These PESs are plotted in Fig. 3 as a function of \( \beta_R \) at \( \alpha_R=0 \) and \( \gamma_R=60° \). The labels \( \Sigma, \Pi, \) and \( \Delta \) are the symmetry assignments of the PESs at \( \beta_R=0 \) and \( \beta_R=\pi \). Note that for \( \beta_R=0 \) the lowest surface has \( \Delta \) symmetry, whereas for \( \beta_R=\pi \) it has \( \Sigma \) symmetry. Since the \( \Pi \) surfaces lie between the \( \Sigma \) and \( \Delta \) surfaces at \( \beta_R=0 \) and \( \beta_R=\pi \), we first discuss and explain the results for the \( \Sigma \) and \( \Delta \) exit channels. We then use these results to explain the results for the \( \Pi \) exit channel.

The SC–\( \Sigma \) results are plotted in Fig. 4(a). The curve for a model 180 calculation shows a negative steric effect for all energies used. This negative steric effect can be explained qualitatively from the symmetry of the five PESs (see Fig. 3). At low energies for an unfavorable collision geometry \([j,k,m]=(1,1,-1)\] most reactive trajectories are on the lowest surface, since this is the most attractive one. Most of these trajectories arrive at the harpooning radius around \( \beta_R=\pi \). This surface at that side of the molecule corresponds to a \( \Sigma \) (exit) channel. For a favorable collision geometry \([j,k,m]=(1,1,1)\] very few reactive trajectories are on the \( \Sigma \) surface, since it is repulsive. Therefore, it seems plausible to find a negative steric effect for a model 180 calculation for the \( B^2\Sigma^+ \) exit channel. In the MQCT calculations no negative steric effect was found, except in the calculations using the isotropic model potential. However, in that case the steric effect became negative only at extremely low translational energies or for unphysically strong potentials. Here, the steric effect is negative for a “normal” long range potential over a range of translational energies. This result suggests that the negative steric effect, measured in the experiments on the reaction Ca (\( ^1D \))+CH\(_3\)Cl \((jkm=111)\)→CaCl (\( B^2\Sigma^+ \))+CH\(_3\) (Ref. 13) will be reproduced by our calculations. Furthermore, this result suggests that the
negative steric effect found for the $B\ ^2\Sigma^+$ exit channel in the Ca+CH$_3$Cl reaction might be a feature of the final electronic state rather than an effect of the interaction potential in the entrance channel.

Decreasing the cut-off angle will mainly affect the reactive cross section for unfavorably oriented molecules, $\sigma^{(1,1,-1)}_\Sigma(E)$. Thus, the steric effect becomes less negative and even positive at smaller cut-off angles, as is evident from Fig. 4(a).

The SC–Δ results are plotted in Fig. 4(b). For model 180 calculations, the panel shows a decreasing (positive) steric effect with increasing energy. This can be understood qualitatively using the same reasoning as for the negative steric effect for the model 180 SC–Σ calculations. At low energies for a favorable collision geometry most reactive trajectories are on the lowest two surfaces, since these surfaces are attractive (final angle $\beta_R$ around 0). At this side of the molecule they correspond to a Δ (exit) channel. For an unfavorable collision geometry very few trajectories are reactive on the Δ surfaces, because they are repulsive. Therefore, the steric effect will be positive at low energies for model 180 calculations. At higher energies the cross section for the $A'\ ^2\Delta$ state in the favorable collision geometry will decrease, because more trajectories end up on the surfaces which correspond to the $A'\ ^2\Pi$ and $B\ ^2\Sigma^+$ exit channels. The cross section for the $A'\ ^2\Delta$ exit channel in the unfavorable reaction geometry will increase for the same reason. Therefore, the steric effect will decrease at higher energies.

Decreasing the cut-off angle for the SC–Δ calculations will (again) mainly affect the reactive cross section for unfavorably oriented molecules, $\sigma^{(1,1,-1)}_\Delta(E)$. At low energies $\sigma^{(1,1,-1)}_\Delta(E)$ is small compared to $\sigma^{(1,1,1)}_\Delta(E)$, which means that the increase of the steric effect with decreasing cut-off angle will be small as well. At higher energies $\sigma^{(1,1,-1)}_\Delta(E)$ becomes larger compared to $\sigma^{(1,1,1)}_\Delta(E)$, which results in a larger increase in the steric effect with decreasing cut-off angle.

Comparing Fig. 2 and Fig. 4 we conclude that the SC–Π results are more like the SC–Σ results than like the SC–Δ results. This is not surprising, since the Π-surfaces are, like the Σ-surfaces, repulsive at $\beta_R = 0$ and attractive at $\beta_R = \pi$. Therefore, the explanations given for the SC–Σ results will hold also to a large extent for the SC–Π results.

Given this strong dependence of the steric effect and of the total cross section for unoriented molecules on the exit channel predicted by this correlation model, it will be very interesting to repeat the experiment, but now using Ca atoms that have been state selected by a polarized laser beam. Experiments on the effect of the polarization of the electronic state of the atom on the cross sections for the different products have been performed for Ca ($^1P$)+HCl, Cl$_2$, and CCl$_4$ by Rettner and Zare. In their experiment they used unoriented molecules and they polarized the $^1P$ state of the atom with respect to the relative velocity of the colliding particles. This setup was used to show that certain exit channels were enhanced by the polarization. It will also be very interesting to measure the other energetically allowed exit channels in the Ca+CH$_3$F reaction, i.e., the $X^2\Sigma^+$, $B\ ^2\Sigma^+$, and $A'\ ^2\Delta$ states of CaF, to see whether our theoretical predictions are correct.

### B. Total cross section for unoriented molecules:

$\sigma_\alpha(E)$

In Fig. 5, we give the experimental results by Janssen et al. together with their fit to the experimental data in which they corrected for the velocity distribution of the Ca beam. Furthermore, we give the MQCT results for model 90 calculations from paper II and the SC and SC–Π results also for model 90 calculations, using the procedure outlined in...
Sec. II H. Model 90 calculations were arbitrarily chosen for this figure, since the other cut-off angles give comparable results. For all our calculated curves and for the experimental curve in Fig. 5 $\sigma_0(E)$ at $E=0.451$ eV was set to 1 for a more clear presentation. Note, that in paper II and Ref. 14, all data was plotted relative to $\sigma_0(E)$ at $E=0.286$ eV.

Figure 5 shows that the energy dependence of $\sigma_0(E)$ in the SC calculations and the SC–II calculations is much weaker than in the experiment. The energy dependence of $\sigma_0(E)$ in the SC calculations is slightly better than in the MQCT calculations. This shows again that a more elaborate description of the dynamics of the reaction using the SC method has a weak, but positive effect. We have assumed that all trajectories that reach the harpooning radius, within the cone of acceptance, are reactive. Perhaps a better modeling of the harpooning mechanism using Landau–Zener type transition probabilities around the harpooning radii at $R=6.0$ and at $R=8.5$ bohr will yield better results for $\sigma_0(E)$. Another way to try to get more accurate results for the total reactive cross sections would be to improve the potential by including more Ca and/or CH$_3$F states to introduce polarization and dispersion forces or by including Ca$^+$ and/or CH$_3$F$^-$ states. However, from paper II we know that an $R^{-2/3}$ model potential was needed to get $\sigma_0(E)$ within experimental error bars. Since the SC calculations do not improve very much upon the MQCT results, it seems reasonable to assume that an $R^{-2/3}$ potential is needed here as well to get agreement with experiment. Such a potential would be unphysical. Therefore, we conclude that probably more can be gained by a better description of the harpooning mechanism.

The correlation model allows us to calculate $\sigma_0(E)$ not only for the $A^2\Pi$ exit channel measured in the experiment, but also for other exit channels. We will only use these results to compare the three exit channels and to calculate the branching ratios. Assuming that comparable errors are made for all three exit channels, the branching ratio is still meaningful. The results for $\sigma_0(E)$ at $E=0.068$ eV for the three exit channels for different cut-off angles are shown in Table II. They are given relative to $\sigma_0(E)$ at $E=0.451$ eV, which was set to 1, as stated previously. We only give the ratio between $\sigma_0(E)$ at $E=0.068$ eV and $\sigma_0(E)$ at $E=0.451$ eV here, since all curves are monotonously decreasing or increasing with energy. If we examine the model 60 calculations in Table II, we see that the $B^2\Sigma^+$ exit channel has an increasing $\sigma_0(E)$ with energy. This seems surprising at first, but it can be understood qualitatively from the adiabatic

<table>
<thead>
<tr>
<th>Model</th>
<th>$\sigma_{0,60}(0.068)$</th>
<th>$\sigma_{0,60}(0.451)$</th>
<th>$\sigma_{0,60}(0.451)$</th>
<th>$\sigma_{0,60}(0.451)$</th>
<th>$\sigma_{0,60}(0.451)$</th>
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<td>1.52</td>
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<td>1.82</td>
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</table>

Table II. $\sigma_0(0.068)/\sigma_0(0.451)$ for different exit channels and different cut-off angles.

PESs in Fig. 3. At low translational energies for model 60 calculations (in which $\beta_R\approx60^\circ$ is reactive) most reactive trajectories are on the lowest two, attractive, surfaces and will therefore end up in a $\Delta$ (exit) channel. At higher energies, more trajectories on the highest surfaces are reactive. Therefore, the percentage of the $A^2\Pi$ state in the product drops at higher relative translational energies and the percentage of the $B^2\Sigma^+$ state rises. The $A^2\Pi$ state lies in between the two other states and turns out to have a small negative dependence of $\sigma_0(E)$ on the relative translational energy, see Table II. At larger cut-off angles $\beta$, the direct correspondence between the adiabatic surfaces and the exit channels diminishes. Thus, at larger cut-off angles the $B^2\Sigma^+$ curves show a less positive dependence on the relative translational energy and the $A^2\Delta$ curves a less negative energy dependence. The weak negative dependence of $A^2\Pi$ becomes slightly more negative. For a model 180 calculation one obtains three curves that are alike, as can be concluded from Table II, fourth row, because the ordering of the adiabatic surfaces at large angles $\beta_R$ is exactly opposite to the situation at small angles $\beta_R$.

If one assumes that the effect of the different adiabatic surfaces averages out at large cut-off angles, one expects the branching ratio $[\sigma_{0,60}(E)/\sigma_{0,70}(E)]$ between the $B^2\Sigma^+$ and the $A^2\Pi$ exit channels to be around 0.5 for high energies and large cut-off angles, because the $A^2\Pi$ exit channel is doubly degenerate. The branching ratio $[\sigma_{0,50}(E)/\sigma_{0,11}(E)]$ between the $A^2\Delta$ and the $A^2\Pi$ exit channels is expected to be around 1, because both the $A^2\Pi$ and the $A^2\Delta$ exit channels are doubly degenerate. This is indeed the case (see Tables III and IV). Based on our calculations, we predict a branching ratio between the $B^2\Sigma^+$ and the $A^2\Pi$ exit channels $[\sigma_{0,60}(E)/\sigma_{0,70}(E)]$ of approximately 0.5, relatively independent of the translational energy. This branching ratio

<table>
<thead>
<tr>
<th>$E$ (eV)</th>
<th>Model 60</th>
<th>Model 90</th>
<th>Model 120</th>
<th>Model 180</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.068</td>
<td>0.23</td>
<td>0.37</td>
<td>0.54</td>
<td>0.60</td>
</tr>
<tr>
<td>0.119</td>
<td>0.32</td>
<td>0.40</td>
<td>0.49</td>
<td>0.55</td>
</tr>
<tr>
<td>0.182</td>
<td>0.39</td>
<td>0.44</td>
<td>0.48</td>
<td>0.52</td>
</tr>
<tr>
<td>0.286</td>
<td>0.43</td>
<td>0.49</td>
<td>0.48</td>
<td>0.51</td>
</tr>
<tr>
<td>0.358</td>
<td>0.44</td>
<td>0.49</td>
<td>0.49</td>
<td>0.51</td>
</tr>
<tr>
<td>0.451</td>
<td>0.44</td>
<td>0.49</td>
<td>0.48</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Table III. Branching ratio $[\sigma_{0,60}(E)/\sigma_{0,70}(E)]$ between the $B^2\Sigma^+$ and the $A^2\Pi$ exit channels for different relative translational energies and different cut-off angles.

<table>
<thead>
<tr>
<th>$E$ (eV)</th>
<th>Model 60</th>
<th>Model 90</th>
<th>Model 120</th>
<th>Model 180</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.068</td>
<td>4.50</td>
<td>2.73</td>
<td>1.83</td>
<td>1.21</td>
</tr>
<tr>
<td>0.119</td>
<td>3.20</td>
<td>2.15</td>
<td>1.53</td>
<td>1.11</td>
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<tr>
<td>0.182</td>
<td>2.40</td>
<td>1.78</td>
<td>1.32</td>
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</tr>
<tr>
<td>0.286</td>
<td>1.84</td>
<td>1.54</td>
<td>1.19</td>
<td>1.02</td>
</tr>
<tr>
<td>0.358</td>
<td>1.69</td>
<td>1.44</td>
<td>1.16</td>
<td>1.03</td>
</tr>
<tr>
<td>0.451</td>
<td>1.52</td>
<td>1.34</td>
<td>1.11</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Table IV. Branching ratio $[\sigma_{0,50}(E)/\sigma_{0,11}(E)]$ between the $A^2\Delta$ and the $A^2\Pi$ exit channels for different relative translational energies and different cut-off angles.
lies between the branching ratio of 0.67 for the Ca+CH₃Cl reaction and the branching ratio of 0.2–0.3 found for the Ca+CH₃Br reaction. In a gas cell experiment Janssen et al. measured branching ratios of 5.6 and 1 for the Ca+CH₃F reaction, depending on the experimental setup. The branching ratio between the \( A^2\Sigma \) calculation and the \( A^2\Pi \) exit channels \([\sigma_{0\Delta}(E)/\sigma_{0\Pi}(E)]\) is predicted by us to be around 2.3 at \( E = 0.068 \) eV and around 1.2 at \( E = 0.451 \) eV. For these predictions we use a cut-off angle of 105 degrees, which appears to give the most accurate results in the calculation of \( \sigma_{1\Pi}(E)/\sigma_{0\Pi}(E) \) (see Sec. IV A).

C. Alignment effect: \( \sigma_2(E)/\sigma_0(E) \)

As shown in Fig. 6 the alignment effect \( \sigma_2(E)/\sigma_0(E) \) is reproduced within experimental scatter by model 60, model 90, and model 120 calculations using the SC approach without using the correlation model. As it turns out the results for \( \sigma_2(E)/\sigma_0(E) \) are very insensitive to the cut-off angle used. The result for the SC–II calculation resemble those for the SC calculation and are therefore not shown here.

The results for the \( B^2\Sigma^+ \) and the \( A^2\Delta \) exit channel do not differ very much from the results for the \( A^2\Pi \) exit channel. Apparently, the alignment effect is more or less the same for the three exit channels. Therefore, the results for the \( B^2\Sigma^+ \) and the \( A^2\Delta \) exit channels are not shown here.

D. Trapping and reorientation

We wish to examine the role of trapping and reorientation in the dynamics of the Ca+CH₃F reaction. Classical trajectory calculations on model potentials and on the long range potential have shown earlier that both the effect of trapping and of reorientation on the steric effect can be quite significant. The effect of trapping seemed to be dominant.

Trapping and reorientation are expected to be strongest on the lowest adiabatic surface for a “favorable” orientation, because the PES is strongest and most anisotropic in that situation. Therefore, we examine both trapping and reorientation in calculations, starting with initial conditions \( N_i = 1 \) (i.e., using the eigenvector of \( \vec{r}^{(\kappa)} \) with the lowest eigenvalue [see Eq. (15)] as startup vector for Ca) and \( m_i = 1 \) (i.e., the projection of the initial rotational angular momentum \( j_i = 1 \) on the SF \( z \)-axis equals 1). The SC trajectories are plotted in Fig. 7. They are run at 0.119 eV for 14 different impact parameters evenly distributed in \( b^2 \) between \( b = 0 \) and \( b = 8.11 \) bohr (larger impact parameters were not reactive). As is evident from this figure, there is a considerable amount of trapping on this surface. The trajectory with the largest impact parameter even flies around the molecule to end up at the “bottom-side” of the “sphere of harpooning,” the sphere with the harpooning distance as radius.

We also find a considerable amount of reorientation on this surface at all impact parameters. In Fig. 8 we plotted the initial distribution function \( \zeta^{(\kappa)}(\alpha, \beta) \) [see Eq. (26)] for the C–F axis in the SF frame [panel (a)] and the final distribution function \( \zeta^{(\kappa)}(\alpha, \beta) \) for impact parameters \( b = 6.36 \) bohr [panel (a)] and \( b = 7.79 \) bohr [panel (b)]. Note that for both final distribution functions the initial distribution function is the same! As is clear from these pictures, there is reorientation not only in the \( \beta \)-angle, but also, and more pronounced, in the \( \alpha \)-angle. The arrows in Figs. 8(b) and 8(c) show where the atom hits the sphere of harpooning. This gives a possible explanation why the energy dependence of the steric effect for the reaction model without correlation is too weak for \( \beta_c \) between 90 and 120 degrees. Because the molecule reorients to follow the atom, it partly cancels the influence that the trapping of the trajectories with the higher impact parameters has on the steric effect. At higher energies the influence of both trapping and reorientation will diminish, resulting in a weak energy dependence of the steric effect.

The orientational localization of the wave function, which is evident in Fig. 8, has an interesting implication. It shows that CH₃F in this calculation behaves more or less as a classical rotor and explains why our rotational basis set had to include basis functions up to \( j_{\text{max}} = 15 \) to converge. This also implies that a classical approach should be able to produce results with a similar accuracy as the SC approach, provided that a quantum-like way of sampling the orientation of CH₃F in the initial rotational state is used, as in the
MQCT calculations in paper II. That this is the case was shown in Secs. IV B and IV A.

Figure 9 shows $Q^{(k)}(\alpha, \beta)$ at $b = 7.79$ bohr (c). The arrow designates the position of the atom. Note that for both final probability distributions the initial probability distribution is the same.

Figure 9. SF probability distribution $Q^{(k)}(\alpha, \beta)$ for the C–F axis at $b = 8.11$ bohr. (a): $R = 10.0$ bohr. (b): $R = 8.0$ bohr. (c): $R = 6.0$ bohr. The arrow designates the position of the atom.

E. Evolution of the electronic state of Ca

As explained in Sec. II H, we have chosen three representations in which to study the evolution of the electronic state of Ca in the SC calculations. For the first representation, the populations of the $^1D$ substates $Q^{(k)}(t)$ in the SF frame are monitored. Since the populations depend on the initial conditions, we have chosen a few characteristic examples. The impact parameter $b$ is 6.0 bohr and $m_i = 1$ in all cases discussed. The trajectories at $E = 0.119$ eV for $N_i = 5$ are not reactive. Therefore, we have chosen to plot the probability functions up to $R = 7.5$ bohr to get the same lower limit for $R$ in all plots.

Figure 10 shows the change in the populations as a func-
tion of \( R \) at \( E = 0.119 \text{ eV} \) for initial states \( N_i = 1 \) (i.e., using the eigenvector of \( \mathcal{F}(\mathbf{k}) \) with the lowest eigenvalue [see Eq. (15)] as startup vector for Ca) and \( N_i = 5 \) (i.e., using the eigenvector of \( \mathcal{F}(\mathbf{k}) \) with the highest eigenvalue as startup vector). Figure 10 contains cumulative plots, i.e., the area between two curves is the population of a certain state as indicated by the double-headed arrow in the figure. The curves look rather jagged, since we chose to print out the wave function only at intervals of 2.5 bohr, because of limitations in disk space. The propagation itself was of course performed with a much smaller step size for \( R \). It is evident from these figures that \( \mu \) is not a conserved quantum number, i.e., that the evolution of the electronic state of Ca is far from diabatic. The scrambling of \( \mu \) starts already at relatively large separations (\( R \approx 20 \text{ bohr} \)). Note that at this radius the energy splitting between the five electronic surfaces is comparable to the rotational excitation energies of the \( \text{CH}_3\text{F} \) molecule. For all \( N_i \) the wave function at \( R = 7.5 \text{ bohr} \) is almost evenly distributed among the five (diabatic) \( \mu \) substates. In Fig. 11, we plotted the populations for the \( ^1D \) substates for the \( N_i = 1 \) initial state at a relative translational energy of 0.451 eV. Clearly, the \( \mu \)-scrambling starts at a shorter distance than in Fig. 10(a). This shows very nicely that a higher translational energy is equivalent to an effectively weaker potential.

In the second representation, the \( ^1D \) populations in the DF frame, \( \mathcal{F}_N^\Lambda(t) \) [see Eq. (29a)], are monitored. For \( N_i = 1 \) and \( N_i = 5 \) at 0.119 eV these are plotted in Fig. 12 as a function of \( R \). It is clear from the panels in this figure, that also \( \Lambda \) is not a conserved quantity. This implies that the “orbital following” model in terms of the “pure” \( ^1D \) states in the DF frame provides a poor description of the evolution of the electronic state of Ca for this system. However, if one compares Fig. 12 to Fig. 10, it is clear that the evolution of the electronic state of Ca is represented better in representation 2 than in representation 1, i.e., that \( \Lambda \) is better conserved than \( \mu \). The results at \( E = 0.451 \text{ eV} \) do not provide any additional insight and will not be discussed here.

In the third representation, the populations of the eigenstates of the interaction matrix in the DF frame \( \mathcal{F}_N^\Lambda(t) \) [see Eq. (32)] are monitored. For \( N_i = 1 \) and \( N_i = 5 \) at 0.119 eV these are plotted in Fig. 13. The curves in Fig. 13(a) are relatively flat, which means that the adiabatic description fits
the evolution of the electronic state of Ca for this initial state ($N_f = 1$) rather well. Only at relatively short distances, is there a substantial deviation from pure adiabatic behavior. For $N_f = 5$ in Fig. 13(b), the situation is somewhat different. Here, the evolution of the electronic state of Ca is apparently more non-adiabatic than in the calculation for $N_f = 1$. This results in more deviation from a flat curve than in Fig. 13(a). To be more precise, the population of the higher adiabatic curves drops during the collision, whereas the lower two states become more populated. In this way electronic energy is released during the collision.

Concluding, we find that the collision of Ca + CH$_3$F follows an almost adiabatic pathway for the lowest initial state (i.e., $N_f = 1$). For higher initial states (i.e., $N_f > 1$) non-adiabatic effects start to play a larger role. This explains the observation that the difference between the SC calculation of $\sigma_{0}(E)$, $\sigma_{1}(E)/\sigma_{0}(E)$, and $\sigma_{2}(E)/\sigma_{0}(E)$ and the MQCT calculation is rather small. Namely, if the reaction is largely adiabatic, then the MQCT description should yield the same results as the SC calculations, provided that the motion of the particles is represented well by a classical description. We have argued in Sec. IV D that this is the case.

We checked whether we could get a different amount of adiabatic behavior by using a different method of generating initial states. Starting in the (complex) $^1D$ substates with $\mu = -2, \ldots, 2$ yielded practically the same results as our method with regard to the amount of non-adiabatic transitions. Any other definition of the starting Ca wave function that we tried yields more non-adiabatic transitions.

V. CONCLUSIONS

We have performed semiclassical calculations on the Ca ($^1D$) CH$_3$F reactive system. The potential for this reaction consists of five, asymptotically degenerate PESs. In the calculations the relative motion of Ca with respect to CH$_3$F was treated classically. The rotation of the CH$_3$F molecule and the five electronic states of the Ca atom were treated quantum mechanically. To calculate the cross sections we used two different reaction models, which we referred to as the correlated model and the uncorrelated model. In the correlated model it is assumed that the projection of the electronic orbital angular momentum on the intermolecular axis is conserved as the electronic orbital angular momentum quantum number of the CaF product. This gives us the possibility to examine the three CaF products ($A^2\Pi$, $B^2\Sigma^+$, and $A^2\Delta$) separately. In the uncorrelated model we assume that the branching ratio for the different exit channels is energy independent, which means that the three exit channels can not be distinguished from each other.

The results for $\sigma_{1\Pi}(E)/\sigma_{0\Pi}(E)$ calculated with the correlated model reproduce the experimental results very well. It is possible to choose a cut-off angle such that they almost match ($\beta_c = 105^\circ$). Using the uncorrelated model we could not get agreement with experiment. In this case the steric effect is either too large (for small cut-off angles) or its energy dependence is too weak (for large cut-off angles). Comparison with the MQCT results from paper II shows that the SC results calculated with the uncorrelated model are in slightly better agreement with experiment. Thus, it is apparent that the semiclassical description of the dynamics has a small positive influence on the results. However, the reaction model has a larger influence. This adds credence to the validity of the MQCT approach for this problem. Furthermore, we think that if a similar correlation approach is implemented in the MQCT framework, already the MQCT calculations will reproduce the experimental results for $\sigma_{1\Pi}(E)/\sigma_{0\Pi}(E)$.

For the alignment effect, $\sigma_{2\Pi}(E)/\sigma_{0\Pi}(E)$, reproduce the experimental data for both the correlated and the uncorrelated approach. Apparently, the alignment effect is not as sensitive to the reaction model as the steric effect.

Using the correlated approach, we were also able to predict the results for the CaF ($B^2\Sigma^+$) and CaF ($A^2\Delta$) product channels. These were not measured by Janssen et al. due to experimental limitations. With regard to the steric effect, $\sigma_{1\Pi}(E)/\sigma_{0\Pi}(E)$ will be slightly higher than $\sigma_{1\Pi}(E)/\sigma_{0\Pi}(E)$ with approximately the same energy dependence. For the $A^2\Delta$ state, $\sigma_{1\Delta}(E)/\sigma_{0\Delta}(E)$ will be higher than $\sigma_{1\Pi}(E)/\sigma_{0\Pi}(E)$. Furthermore, its energy dependence will be negative. This might seem an unexpected result, but it can be understood from the symmetry of the adiabatic surfaces in the Ca + CH$_3$F system. The results for $\sigma_{0\Delta}(E)$ and $\sigma_{0\Pi}(E)$ are used to calculate the branching ratios for the three exit channels. For the branching ratio $B^2\Sigma^+/A^2\Pi$ we predict a value of approximately 0.5, which will be relatively independent of energy. For the branching ratio $A^2\Delta/A^2\Pi$ we predict a value of 2.3 at $E = 0.068$ eV and 1.2 at $E = 0.451$ eV.
Lastly, we examined the evolution of the electronic state of Ca in three different representations. We have shown in Sec. IV E that the evolution is best represented in an adiabatic basis set. This means that the amount of non-adiabatic transitions for this system is low, especially if one starts on the lowest potential energy surface. From the other representations we conclude that the “orbital following” model in terms of “pure” Ca states cannot completely describe the evolution of the electronic state of Ca. Still, the projection $\Lambda$ of the electronic angular momentum of Ca on the dimer axis $R$ is partly conserved, whereas its projection $\mu$ on the direction of the relative initial velocity vector is completely scattered.

Concluding, it can be said that the SC method in itself does not strongly improve the MQCT results for the steric effect. However, using the SC method, we have included the electronic state of the atom in the reaction model, which leads to much better agreement with experiment for $\sigma_{11}(E)/\sigma_{11}(E)$. Furthermore, we now have introduced a way to calculate the branching ratio to the different exit channels for the Ca+CH$_3$F reaction.

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