On the energy dependence of the steric effect for atom–molecule reactive scattering. II. The reaction Ca(1D)+CH3F(JKM=111)→CaF(2II)+CH3

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The observed increase in the steric effect of the reaction Ca(1D)+CH3F(JKM=111)→CaF(2II)+CH3 with increasing energy has been tentatively ascribed to a reorientation of the initially oriented CH3F axis, due to anisotropic long-range forces [M. H. M. Janssen, D. H. Parker, and S. Stolte, J. Phys. Chem. 95, 8142 (1991)]. Here we present ab initio calculations and use these to construct a long-range potential. To this potential we fit an isotropic model potential and two anisotropic model potentials. On the long-range potential and on the model potentials we perform classical trajectory calculations, and we compare the two methods presented in the preceding paper [G. C. Groenenboom and A. J. H. M. Meijer, J. Chem. Phys. 101, 7592 (1994)] for the extraction of the steric effect. We conclude that already the attractive isotropic model presented in this paper can account for the observed energy dependence of the steric effect for this reaction via a “trapping” mechanism. We show that although reorientation is possible, it contributes little to the positive energy dependence of the steric effect.

I. INTRODUCTION

In the last two decades there have been numerous investigations into the role of reagent orientation for reactive collisions in crossed-beam experiments. Most of these experiments were done using symmetric top (like) molecules and (earth) alkali atoms, in which the molecules were in a specific rotational state (JKM), selected by using a hexapole field, where J, K, and M denote the symmetric top rotational quantum numbers. With a beam of state selected molecules it is possible to give the (presumed) reactive end of the molecule a specific average orientation with respect to the relative velocity of the reactants. This results in a "favorable" or "unfavorable" orientation of the reactants, corresponding to an orientation with the reactive end of the molecule first or an orientation with the nonreactive end of the molecule first, respectively. Examples of reactions, studied in this way, are (Rb,K)+CH3I3-11 NO+O3,12 Ba+N2O,13-16 Ca(1D)+CH3X(X=F,Cl,Br).17,18

One reaction, studied extensively both experimentally and theoretically, is the Rb+CH3I→Rbi+CH3 reaction. It was found that the total cross section for this reaction is higher in the case of a favorable orientation of the reactants (I-first) than in the case of an unfavorable orientation of the reactants (CH3-first), thus confirming very basic chemical intuition.4-6 This difference in the total reactive cross section, relative to the total reactive cross section for a beam of unoriented molecules, is called the "steric effect." In the case of Rb+CH3I no investigations were made into the dependence of the steric effect on the average translational energy, E, of the reactants. However, these investigations were made in the cases of the Ba+N2O→BaO*+N2 and Ca(1D)+CH3X(X=F,Cl,Br)→CaX(A 2Π,B 2Σ)+CH3 reactions.

For the Ba+N2O reaction a negative dependence of the steric effect on E was found. This was explained in terms of the angle dependent line of centers (ADLC) model.19-22 This is a classical model, in which the molecule is surrounded by an energy barrier, pictured as an imaginary shell. Reaction is assumed to occur only if the atom has sufficient radial kinetic energy to surmount the barrier. This barrier is often chosen to depend on the angle-of-attack γ, i.e., the angle between the symmetry axis of the molecule and the line of centers (the line connecting the center of mass of the molecule and the atom). Usually γ=0° is chosen to correspond to a favorable orientation of the reactants. Furthermore, this barrier is often taken to be infinite between a certain cutoff angle γc and γ=180°, the so-called "cone of nonreaction." Evidence for the existence of such cones of nonreaction has been found experimentally.5,6

From this model one obtains, as might be expected, a negative energy dependence of the steric effect, since at higher energy the reactants are able to surmount the barrier for a larger range of angles γ, thus lowering the steric effect. This agrees with the results observed for the Ba+N2O reaction. For the total reactive cross section for a beam of unoriented molecules this model predicts a positive energy dependence at low energy and a negative energy dependence at energies well above the barrier.23,24 Also this behavior is exactly what was found for the Ba+N2O reaction.13-16 A positive dependence of the steric effect on E was found in the case of the Ca(1D)+CH3F(JKM=111)→CaF(A 2Π)+CH3 reaction, together with a negative energy dependence of the total cross section for the unoriented beam.17,18 No measurements were made for the other possible reaction products: CaF(X 2Σ), CaF(B 2Σ), or CaF(A 2Δ), due to experimental difficulties.17,18 The result for the CaF(A 2Π) product channel points to a barrierless reaction, which is in agreement with the "harpooning mechanism," proposed for this reaction.17,18 The results for the steric effect could not be explained using the ADLC model. They were tentatively ascribed to a reorientation of the CH3F molecule during the approach of the Ca atom due to anisotropic terms in the long range interactions between
the $^1D$ state of Ca and CH$_3$F. Supposedly, these anisotropic forces would turn the C–F axis towards the approaching Ca atom, thus scrambling the initially prepared orientation and subsequently lowering the steric effect. At higher energies there would not be enough time for this reorientation to occur and the steric effect should increase.

In paper I\textsuperscript{26} we presented an alternative mechanism which does not rely on reorientation, which we called the “trapping model.” The key to understanding this model and the reaction under scrutiny lies in the fundamental difference between the Euler angle $\vartheta$, which describes the orientation of the molecular symmetry axis, and the angle-of-attack $\gamma$. The probability distribution of the angle $\vartheta$ is prepared experimentally by selecting the rotational state of the molecule and is dependent on the rotational quantum numbers $J$, $K$, and $M$.\textsuperscript{27} However, even in the case of a vanishing interaction potential, the angle $\gamma$ will differ from $\vartheta$ for purely geometrical reasons, if the impact parameter is nonzero. The presence of an attractive potential may considerably enlarge this difference.

In paper I we placed the barrier to reaction at the harpooning radius ($R_f$) and assumed that it was zero between $\gamma=0^\circ$ and $\gamma=\gamma_c$, thus obtaining agreement with the notions of a harpooning mechanism and a barrierless reaction. For an attractive isotropic potential we showed that at low energies atoms with impact parameters $b$, large relative to $R_f$, are able to “fly around” the molecule and hit it at the back, thus washing out the effect of the initial orientation and lowering the steric effect. We call this trapping. This happens less at higher energies, since high impact parameter atoms will fly past the molecule in that case and be nonreactive. Hence, at higher energies the steric effect will increase.

In paper I we only presented results for isotropic model potentials, but we described two methods for the computation of the steric effect for anisotropic potentials. Both methods assume the existence of an orientation dependent reactive cross section, which can be used to compute the steric effect and to make the correspondence between the classical mechanics in the trajectory calculations and the quantum mechanics in the experiment. The first method is the standard quasiclassical trajectory (QCT) method. Its basic assumption is that the reaction is a barrierless classical reaction, which can be used to compute the steric effect and to make the correspondence between the classical mechanics in the trajectory calculations and the quantum mechanics in the experiment. The second method was called in paper I the modified quasiclassical trajectory (MQCT) method. Its basic assumption is that initially all classically allowed $M$ values should be included in the trajectory calculations. It amounts to the calculation of an $M$-dependent reactive cross section, which is transformed to the orientation dependent cross section, from which the steric effect is calculated. We will return to this in Sec. II D.

In the present paper, we describe ab initio calculations and use these to construct a long-range potential, which we will call the “full long-range potential” (FLRP). To this FLRP we fit an isotropic model potential (IMP), which we use to compute and estimate values for the parameters in the trapping model. Those parameters are the strength of the potential, the harpooning radius ($R_f$), and the cutoff angle $\gamma_c$. We will show that it is possible to fit the experimental observations of the energy dependent steric effect with a reasonable choice of those parameters. Furthermore, we analyze the effect of the anisotropy in the potential by performing trajectory calculations on the FLRP, as well as on two anisotropic model potentials (AMP1 and AMP2) fitted to the FLRP. These model potentials enable us to distinguish the pure reorientation effects from other possible effects, caused by the complex topology of the FLRP.

In Sec. II we outline the theory needed for the computation of the FLRP and for the trajectory calculations. We summarize the method for extracting the steric information from the trajectory calculations. In Sec. III we discuss the computational details and the results from the calculation of the FLRP. We also discuss the results of the trajectory calculations on the model potentials, as well as on the FLRP. Finally, in Sec. IV we summarize our conclusions and suggest possible improvements of both the FLRP and the trajectory calculations.

II. THEORY

A. Coordinates and Hamiltonian

We distinguish three coordinate systems. The first is the center-of-mass (c.o.m.) frame of the colliding species. The second coordinate system, called the space-fixed (SF) system, is parallel to this c.o.m. frame. Its origin is located at the center of mass of the molecule. The third frame, called the body-fixed (BF) frame, is the inertial frame of the molecule.

The Cartesian coordinates of the Ca atom in the SF frame are given by a vector $\mathbf{x}=(x,y,z)$. The orientation of the CH$_3$F molecule is given by a rotation over $\phi=(\phi,\theta,\psi)$ of the BF frame with respect to the SF frame, where the domain of the angles is $[0,2\pi]$ for $\phi$ and $\psi$ and $[0,\pi]$ for $\theta$. $\phi$ denotes the Euler angles for this rotation in the $(z,y,z)$ parameterization. Throughout this article we use the active conventions for rotations.\textsuperscript{28–30}

If we assume that no external force is present in the experiment, the total momentum of the complex will be constant of the motion. It is zero in the c.o.m. frame.\textsuperscript{14,17} Note that this relies on the assumption that the harpoon field, used in the experiment,\textsuperscript{14,17} is homogeneous. The interaction potential will be expressed in the spherical polar coordinates $R=(R,\gamma,\zeta)$ of the Ca atom in the BF frame of the CH$_3$F molecule. Note that $\mathbf{R}$ depends on the SF-coordinates $x$ and $\phi$.

Our trajectory calculations are made in the Hamiltonian formalism of classical mechanics. The Hamiltonian in SF coordinates has the following form:

$$H(x,\phi,p_x,p_\phi) = H_{tr}(p_x) + H_{rot}(\phi,p_\phi) + V[R(x,\phi)],$$

where $H_{tr}(p_x)$ denotes the translational part of the Hamiltonian, which is given by

$$H_{tr}(p_x) = \frac{(p_x \cdot p_x)}{2 \mu}.$$ 

In this equation $p_x=(p_x,p_y,p_z)$ denotes the linear momentum of the Ca atom in the SF frame and $\mu$ is the reduced
mass of the colliding system. $H_{\text{rot}}(\phi, p_{\phi})$ in Eq. (1) denotes the rotational part of the Hamiltonian and is given by

$$H_{\text{rot}}(\phi, p_{\phi}) = \left( \frac{p_{\phi} - p_{\phi} \cos \vartheta}{\sin \vartheta} \right)^2 + A p_{\phi}^2 + C p_{\phi}^2,$$

where $p_{\phi} = (p_\theta, p_{\phi}, p_\psi)$ denotes the momentum conjugate to the Euler angles; $A$ and $C$ are the rotational constants of the prolate symmetric top molecule $\text{CH}_3\text{F}$.

### B. Reaction model

To describe the reaction between the Ca atom and the $\text{CH}_3\text{F}$ molecule we use the modified ADLC model, introduced in paper I. This means that we assume that the barrier to reaction is zero between $\gamma = 0^\circ$ and a certain cutoff angle $\gamma_c$. Between $\gamma = \gamma_c$ and $\gamma = 180^\circ$ the barrier is infinitely high. This results in the reaction probability

$$W(\gamma) = \begin{cases} 1 & 0 \leq \gamma \leq \gamma_c \\ 0 & \gamma_c < \gamma \leq \pi \end{cases}$$

This modified ADLC model is consistent with the harpooning model, proposed for this reaction. In the harpooning model the reaction is initiated by an electron jump at a certain harpooning radius ($R_h$) which is thought to correspond to the crossing of an ionic and a covalent potential energy surface. The harpooning radius is an unknown quantity for this reaction. Therefore, we will choose two harpooning radii in this article, for two reasons. First, we want to investigate the influence of the harpooning radius on the steric effect. Second, the ionic and covalent potential energy surfaces of importance to this reaction show two avoided crossings at which an electron jump can occur. The outer avoided crossing corresponds to a crossing of the covalent $\text{CaF}(^1D) + \text{CH}_3\text{F}^-$ surface with the ionic $\text{CaF}(^1S^+) + \text{CH}_3\text{F}^-$ surface. The inner avoided crossing is the crossing of the covalent $\text{CaF}(^1D) + \text{CH}_3\text{F}^-$ surface with the ionic $\text{Ca}^+(^2S^+) + \text{CH}_3\text{F}^-$ surface. We take the outer harpooning radius at 8.5 bohr, which is comparable to the value of 4.8 Å (=9.07 bohr), suggested by Janssen et al. For the calculation of the inner harpooning radius we used the model of Ref. 24. The outer harpooning radius of 8.5 bohr corresponds within this model to an electron affinity of 0.2 eV for $\text{CH}_3\text{F}$. This electron affinity would lead to an inner harpooning radius of 5.6 bohr. However, a recent article by Brooks et al. suggested a value for the electron affinity of $\text{CH}_3\text{F}$ of 0.75 eV, which would result in an inner harpooning radius of 6.24 bohr. In view of these estimates we decided to take a value of 6.0 bohr for the inner harpooning radius. Most calculations were done with this harpooning radius, since it is at the inner avoided crossing that the reaction to the electronically excited products presumably occurs. (See Refs. 17, 25, and 35.)

Note, incidentally, that the ADLC model has no electrons, which can help us to determine which of the reaction products $[\text{CaF}(^2\Sigma), \text{CaF}(^2\Pi), \text{CaF}(^2\Sigma)]$ or $\text{CaF}(^4\Delta)]$ formed at a certain angle of attack on a certain potential energy surface (PES). In the experiment by Janssen et al. the branching ratio was not measured. Thus throughout this article we assume that the branching ratio for this reaction is energy independent, so that we can use the ADLC model in order to get a measure for the steric effect. Furthermore, we assume that the reacting species proceed to the harpooning radius on the adiabatic PESs, i.e., no surface hops are included in our model.

### C. The full long-range potential

We have developed a long-range potential FLRP, using first-order degenerate perturbation theory and a multipole expansion of the interaction operator. This results in five asymptotically degenerate potential energy surfaces, because of the fivefold degeneracy of the $^1D$ state of the Ca atom. All five surfaces are used in the scattering calculations.

The first-order contribution to the interaction potential, the electrostatic part, is the interaction between the permanent multipoles of the monomers. Although an isolated atom cannot have a permanent multipole moment, the presence of an electric field from $\text{CH}_3\text{F}$ will split the $^1D$ state of Ca into a number of substates, each having a "permanent" multipole moment. Because this effect already occurs in first order perturbation theory, even the presence of a weak field will result in a considerable splitting.

We do not include the second-order contributions of induction and dispersion in the FLRP. To compute these terms one must compute the (frequency dependent) polarizabilities, which correspond to the degenerate $^1D$ state of Ca. This is still an unresolved problem.

In first-order degenerate perturbation theory one diagonalizes the interaction matrix. The elements of this matrix are defined as

$$V_{\mu\mu'}(R) = \langle 0\text{CH}_3\text{F}(\lambda, \mu')\text{Ca} \mid V_{\text{int}}(R) \mid 0\text{CH}_3\text{F}(\lambda, \mu')\text{Ca} \rangle.$$  \hspace{1cm} (5)

Here, $0\text{CH}_3\text{F}$ denotes the unperturbed ground state of the $\text{CH}_3\text{F}$ molecule; $\lambda$ and $\mu$ (or $\mu'$) denote the orbital angular momentum number and magnetic quantum number.

![FIG. 1. Quantum mechanical (dashed line) and classical PDFs (solid line) for the cosine of the Euler angle $\theta$ for the $(\text{JKM})=(1,1,1)$ rotational state.](image)
of the substates of Ca. For the \(^1D\) state of Ca, \(\lambda=2\) and \(\mu\) or \(\mu'\) run from \(-2\) to \(2\). Finally, \(V^{\text{int}}(R)\) denotes the electrostatic interaction operator.

Using the multipole expansion for \(V^{\text{int}}(R)\) and the fact that the expectation values of the multipole operators for the \(^1D\) substates of Ca are related through the Wigner–Eckart theorem, we find that a general matrix element has the following form:

\[
V_{\mu\mu'}(R,\gamma,\zeta) = \sum_{l_a=0}^{\infty} \sum_{l_b=0}^{\infty} \left( 2l_a + 2l_b + 1 \right)!^{1/2} \left( 2l_a \right)! \left( 2l_b \right)! R^{-l_a-l_b-1} (-1)^l_a (-1)^l_b (-\mu\lambda\mu'\lambda') \\
\times \sum_{m_a=-l_a}^{l_a} \sum_{m_b=-l_b}^{l_b} C_{l_a+l_b-m_a-m_b}(\gamma,\zeta) \langle Q_{m_a}^{l_a} \rangle \langle Q_{m_b}^{l_b} \rangle \left( \begin{array}{ccc} l_a & l_b & l_a+l_b \\ m_a & m_b & m_a+m_b \end{array} \right) \left( \begin{array}{ccc} \lambda & \mu & \lambda' \\ m_b & m_b & \mu' \end{array} \right). \tag{6}
\]

Here, \(\mu\) labels the molecule and \(\lambda\) the atom. \(\langle \lambda \| Q^{l_b} \| \lambda' \rangle\) is the reduced matrix element of a \(2^l_b\)-pole operator for the \(^1D\) state according to the Wigner–Eckart theorem. It is defined from the \(m_b\) component of a \(2^l_b\) pole on Ca as

\[
\langle (\lambda, \mu) \| Q_{m_b}^{l_b} \| (\lambda', \mu') \rangle = (-1)^{l_b} \left( \begin{array}{ccc} \lambda & \mu & \lambda' \\ m_b & \mu & -\mu' \end{array} \right) \langle \lambda \| Q^{l_b} \| \lambda' \rangle. \tag{7}
\]

\(C_{l_a+l_b-m_a-m_b}(\gamma,\zeta)\) denotes a spherical harmonic function in the Racah normalization and the phase convention of Condon and Shortley. The symbols \(\cdots\) denote \(3jm\) symbols.

Last, \(\langle Q_{m_a}^{l_a} \rangle\) is the \(m_a\) component of a \(2^{l_a}\) pole on CH\(_3\)F. The adiabatic potential energy surfaces are obtained by diagonalizing the interaction matrix for each value of \(R\). In order to obtain the gradient of the PES with respect to the components of \(R\), we employ the Hellmann–Feynman theorem, which implies

\[
\frac{\partial V_{\lambda}(R)}{\partial R} = \sum_{\mu, \mu'} c_{\mu \lambda}^{\mu'} \left( 0^{\text{CH}_3\text{F}}(\lambda, \mu) \right) c_{\mu' \lambda}, \tag{8}
\]

in which \(V_{\lambda}\) is the \(k\)th eigenvalue of the interaction matrix and \(c_{\mu \lambda}\) denotes the \(\mu\)th component of its \(k\)th eigenvector.

From the FLRP we develop model potentials to be able to investigate the role of reorientation during the approach of the reagents. Inspection of Eq. (6) shows that at \(\gamma=0\) and at \(\gamma=\pi\) the contributions from the different \(2^l\) poles of CH\(_3\)F to the FLRP decouple and the interaction matrix becomes diagonal. We remind the reader that we are dealing with an adiabatic PES, obtained by taking the lowest eigenvalue of the interaction matrix [Eqs. (5) and (6)]. Inspection of this PES in these points shows that the leading (dipole–quadrupole) term in the expansion, which has an \(R^{-4}\) dependence, has the same coefficient in both points. The coefficient for the second (quadrupole–quadrupole) term in the expansion, which has an \(R^{-5}\) dependence, switches sign when going from \(\gamma=0\) to \(\gamma=\pi\). Therefore, we approximate the FLRP by model potentials of the following form:

\[
V(R, \gamma) = \frac{C_0}{R^4} + \frac{C_1 \cos \gamma}{R^5}, \tag{8}
\]

in which \(C_0=0.717 14(2\|Q^2\|2)\langle Q_0^1 \rangle\) a.u. and \(C_1=1.434 27(2\|Q^2\|2)\langle Q_0^2 \rangle\) a.u.

**D. Dynamics**

1. Preparation and propagation

The phase space in our calculations is 12 dimensional and consists of the coordinates \(x\) and \(\phi\) and their conjugate momenta \(p_x\) and \(p_\phi\), as defined in Sec. II A. All trajectories start in the SF \(xz\) plane at \(|x|=30\) bohr with the \(y\) coordinate equal to the impact parameter. The impact parameters \(b\) are distributed uniformly in \(b^2\) (Refs. 32 and 38) between 0 and \(b_{\text{max}}=15\) bohr (which is sufficiently large not to miss any reactive trajectory). \(p_x\) is initially parallel to the \(z\) axis and \(p_\phi\) is determined by the translational energy \(E\), which is taken from the experiment.

The Euler angles \(\phi\) and \(\psi\) are uniformly distributed between 0 and \(2\pi\). For \(\theta\) we take the classical probability density function (PDF) given by Eq. (60) in paper I. The function is well known and can be derived from geometrical arguments and from classical mechanics. We cannot state from the quantum mechanical PDF in classical calculations since it is not a stationary distribution even in the absence of an interaction potential. Furthermore, the quantum mechanical PDF contains areas, which are classically forbidden. The quantum mechanical and classical PDFs are plotted in Fig. Note that these are strongly different.

The classical PDF depends on \(j, k,\) and \(m\), which are the classical analogs of the rotational quantum numbers \(I, L,\) and \(M\), for which we make the usual quasiclassical approximations

\[
j = \hbar \sqrt{j(j+1)}, \tag{10}
\]
\[
j_z^\text{SF} = p_\phi = m = \hbar M, \tag{11}
\]
\[
j_z^\text{BF} = p_\phi = k = \hbar K, \tag{12}
\]

in which \(j_z^\text{SF}\) and \(j_z^\text{BF}\) are the length of the classical rotational angular momentum, its projection on the SF \(z\) axis, and its projection on the BF \(z\) axis, respectively. It can be shown that \(p_\phi\) and \(p_\phi\) are equal to \(j_z^\text{SF}\) and \(j_z^\text{BF}\), respectively.
Note that Eq. (10b) no longer holds when \( m \) is allowed to take all classically allowed values (in the MQCT method, see Sec. II D 2). With all initial values specified we propagate the trajectories using the classical equations of motion

\[
\begin{align*}
\frac{\partial H}{\partial q_i} &= \dot{q}_i, \\
\frac{\partial H}{\partial \dot{q}_i} &= -\dot{p}_i,
\end{align*}
\]

in which \( q_i \) is a general coordinate and \( p_i \) its conjugate momentum.

A numerical problem arises because of the singularities in Eq. (5) at \( \theta = 0 \) or \( \pi \). Following Kroes et al.,\textsuperscript{42} we solve this problem by switching back and forth between the \((xyz)\) parametrization (with singularities at \( \theta = 0 \) and \( \pi \)) and the \((xyz)\) parametrization, which has singularities at \( \theta' = \pm \pi \). The Hamiltonian in the \((xyz)\) parametrization is

\[
H_{\text{coll}}(\phi',p_{\phi'}) = A \left( \frac{p_{\phi'} p_{\phi'} \sin \theta'}{\cos \theta'} \right)^2 + A p_\theta^2 + C p_\phi^2,
\]

in which \( \phi' = (\phi, \theta', \psi') \) and \( p_{\phi'} = (p_{\phi'}, p_\theta, p_\phi) \) are the transformed Euler angles and their conjugate momenta, respectively. As was shown by Kroes et al.,\textsuperscript{42} this solves the numerical problems, since the rotational Hamiltonian cannot be singular in both sin \( \theta \) and \( \cos \theta' \) at the same time, because this would require the SF \( z \) axis and the SF \( x \) axis to be both parallel to the BF \( z \) axis. Note, incidentally, that Kroes et al. use the \((xyz)\) parametrization for the Euler angles and the passive convention for rotations, instead of the \((xyz)\) parametrization and the active convention for the Euler angles used throughout this article.

After propagation of a number of trajectories we compute the total reactive cross section, which is the ratio of the number of reactive trajectories, as determined by the ADLC procedure, to the total number of trajectories, multiplied by the maximum total reactive cross section possible \( (= \pi b_{\text{max}}^2) \).

### 2. Analysis

We wish to compare the results of our classical trajectory calculations with the experimental data. Thus since the experiment starts from prepared quantum states \((JKM)\), we have to use the correspondence principle. For this purpose, we defined an orientation dependent reactive cross section \( \sigma_{JKM}(p,E) \) in paper I. In this section we will first give \( \sigma_{JKM}(p,E) \) in a quantum mechanical framework. Then, we present the corresponding classical expressions, which can be obtained in two different ways. The first method corresponds to the standard QCT method. In this method calculations are only performed for a discrete set of \( m \) values, corresponding to the quantum mechanical \( M \) values through Eq. (10b). The second method is called the modified quasiclassical trajectory (MQCT) method. In this method all classically allowed \( m \) values between \(-j\) and \( j \) are used. This results in \( m \)-dependent reactive cross sections which can be transformed into the orientation dependent cross section, which is subsequently used to calculate the steric effect.

Following paper I, we define this orientation dependent reactive cross section in a quantum mechanical framework implicitly as

\[
\sigma^{JKM}_{JKM}(p,E) = \int_{-1}^{1} \sigma^{JK}_{JK}(p,E) \mathcal{P}^{JKM}(p) d\rho,
\]

in which \( \sigma^{JKM}_{JKM}(E) \) is the total reactive scattering cross section for a molecule in the initial state \((JKM)\) and \( \mathcal{P}^{JKM}(p) \) is the quantum mechanical PDF for \( p = \cos \theta \) for a rotational state with quantum numbers \( J, K, \) and \( M \). The latter is known analytically as a finite sum over unnormalized Legendre polynomials\textsuperscript{27}

\[
\mathcal{P}^{JKM}(p) = \sum_{l=0}^{2J} c^{JKM}_{l} P_{l}(p).
\]

The orientation dependent reactive cross section is defined by Eq. (13), together with the requirement that \( \sigma^{JK}_{JK}(p,E) \) is expanded in a finite sum of Legendre polynomials,

\[
\sigma^{JK}_{JK}(p,E) = \sum_{l=0}^{2J} \sigma^{JK}_{l}(E) P_{l}(p).
\]

Substituting Eqs. (14) and (15) into Eq. (13), we obtain a set of \( 2J+1 \) equations for the Legendre moments \( \sigma^{JK}_{l}(E) \)

\[
\sigma^{JKM}_{JKM}(E) = \sum_{l=0}^{2J} \sigma^{JK}_{l}(E) c^{JKM}_{l} \frac{2}{2l+1}.
\]

For reasons of convenience we replace the equation for \( M=0 \) by the equation for unoriented molecules. In that case the PDF equals

\[
\mathcal{P}^{JKM}_{JKM}(p) = \frac{1}{2J+1} \sum_{M=-J}^{J} \mathcal{P}^{JKM}(p) = \frac{1}{2}.
\]

Thus the total reactive cross section for unoriented molecules equals

\[
\sigma^{JK}_{JK}(E) = \int_{-1}^{1} \sigma^{JK}_{l}(p,E) \mathcal{P}^{JKM}_{JKM}(p) d\rho = \frac{1}{2} \int_{-1}^{1} \sigma^{JK}_{l}(p,E) d\rho = \sigma^{JK}_{0}(E),
\]

which shows that the reactive cross section for the unoriented molecules is equal to the zeroth Legendre moment of the orientation dependent reactive cross section.

If we were to use the quantum mechanical PDFs \( \mathcal{P}^{JKM}(p) \), we could derive familiar expressions for the Legendre moments for \( J=K=1 \) (Refs. 15 and 18)

\[
\sigma^{110}_{110}(E) = \sigma^{111}_{111}(E),
\]

\[
\sigma^{111}_{111}(E) = \sigma^{111}_{111}(E) - \sigma^{111-1}_{111}(E),
\]

\[
\sigma^{11-1}_{11-1}(E) = \frac{1}{2} \left[ \sigma^{111}_{111}(E) - \sigma^{11-1}_{11-1}(E) - \sigma^{111}_{111}(E) \right],
\]

in which \( \sigma^{111}_{111}(E)/\sigma^{110}_{110}(E) \) is called the steric effect and \( \sigma^{111}_{111}(E)/\sigma^{110}_{110}(E) \) the alignment effect for the \((JK)=(1,1)\) states.
The above holds for the calculation of the orientation dependent cross section on an arbitrary potential, using a quantum mechanical description of the symmetric top. The classical orientation dependent cross section \( \tilde{\sigma}^{(E)}(p, E) \) is then defined by analogy to Eq. (13) as

\[
\tilde{\sigma}^{(E)}_{jk}(E) = \int_{-1}^{1} \tilde{\sigma}^{(E)}(p, E) \tilde{\sigma}^{(E)}_{jk}(p) dp,
\]

(23)

where \( \tilde{\sigma}^{(E)}_{jk}(E) \), \( \tilde{\sigma}^{(E)}(p, E) \), and \( \tilde{\sigma}^{(E)}(p) \) are the classical counterparts of \( \sigma^{K_{j}M_{j}}(E) \), \( \sigma^{K_{j}}(p, E) \), and \( \sigma^{K_{j}M_{j}}(p) \), respectively.

As was shown in paper I, there are two ways to proceed. The first is to make the standard QCT assumption that the reactants are initially in quantum states. This means that the only \( m \) values allowed are those corresponding to the quantum mechanical \( M \) values through Eq. (10b). This implies that the assumption is made that the classical total reactive cross sections \( \tilde{\sigma}^{(E)}_{jk}(E) \) are good approximations to the quantum mechanical total reactive cross sections \( \sigma^{K_{j}M_{j}}(E) \).

This approach will be referred to as the QCT approach. An alternative way to proceed from Eq. (23) is to use all \( \tilde{\sigma}^{(E)}_{jk}(E) \) [With the notation \( \tilde{\sigma}^{11}_{01}(E) \) we mean \( \tilde{\sigma}^{11}_{01}(E), \) where \( j = 1, \sqrt{J(J+1)} \hbar \) and \( k = 0, \hbar \) and \( \tilde{\sigma}^{21}_{01}(E) \) (see paper I for a derivation)]

\[
\tilde{\sigma}^{11}_{01}(E) = \tilde{\sigma}^{11}_{01}(E),
\]

(24)

\[
\tilde{\sigma}^{11}_{01}(E) = \frac{\tilde{\sigma}^{11}_{11}(E) - \tilde{\sigma}^{11}_{11}(E)}{\tilde{\sigma}^{11}_{11}(E)},
\]

(25)

\[
\tilde{\sigma}^{11}_{01}(E) = 8 \left( \frac{\tilde{\sigma}^{11}_{11}(E) + \tilde{\sigma}^{11}_{11}(E)}{\tilde{\sigma}^{11}_{11}(E)} - 2 \right).
\]

(26)

This approach will be referred to as the QCT approach.

An alternative way to proceed from Eq. (23) is to use all classically allowed \( m \) values. This means, that the assumption is made that all values of \( m \) between \(-j\) and \( j \) are possible. The total reactive cross section can consequently be conceived as a function of \( m \), which can be expanded in a series of Legendre polynomials, which themselves are functions of the reduced variable \( m \), as

\[
\tilde{\sigma}^{(E)}_{jk}(E) = \sum_{l=0}^{\infty} \tilde{c}^{(E)}_{jk}(E) P_{l}(m) P_{l}(j).
\]

(27)

Thus using Eqs. (27) and (23) and the classical analogue of Eq. (15), the coefficients \( \tilde{c}^{(E)}_{jk}(E) \) are found to be

\[
\tilde{c}^{(E)}_{jk}(E) = \int_{-1}^{1} \tilde{\sigma}^{(E)}_{jk}(E) P_{l}(m) P_{l}(j) d(m) d(j),
\]

(28a)

\[
= \sum_{l'=0}^{2l+1} \frac{2}{2} \tilde{\sigma}^{(E)}_{jk}(E) \int_{-1}^{1} d\rho d(m) d(j)
\]

\[
\times P_{l}(m) P_{l'}(j) P_{l'}(j).
\]

(28b)

This equation can be simplified as follows:

\[
\tilde{c}^{(E)}_{jk}(E) = \tilde{\sigma}^{(E)}_{jk}(E) \sum_{i=0}^{N_{l}} P_{i}(m) P_{i}(j).
\]

(29)

This is a direct relation between the Legendre moments of the \( m \)-dependent reactive cross section and the Legendre moments of the orientation dependent reactive cross section (see paper I).

The Legendre moments of the \( m \)-dependent reactive scattering cross section are obtained from a calculation with a finite number of trajectories. Thus, we approximate the numerator of Eq. (28a) by its Monte Carlo equivalent, in general the Monte Carlo equivalent of an integral over a function \( f(x) \) is given by

\[
\int_{x_{1}}^{x_{2}} f(x) dx = \frac{N_{f}}{N_{t}} \sum_{i=1}^{N_{f}} f(x_{i}),
\]

(30)

where \( N_{f} \) is the number of points in the integration.

We bear in mind that \( \tilde{c}^{(E)}_{jk}(E) \) can be written as follows:

\[
\tilde{c}^{(E)}_{jk}(E) = 2 \pi \int_{0}^{h_{\text{max}}} \tilde{g}^{(E)}_{jk}(b) b \, db
\]

\[
= \pi \int_{0}^{\sqrt{r_{\text{max}}} \tilde{g}^{(E)}_{jk}(\sqrt{y}) y \, dy,
\]

(31)

(32)

where \( \tilde{g}^{(E)}_{jk}(b) \) is the usual opacity function, which can be conceived as the reaction probability as a function of the impact parameter, and \( y \) is defined as \( b^{2} \). Then, we combine Eqs. (28a), (30), and (32) to get the following expression for the Legendre moments of the \( m \)-dependent reactive scattering cross section

\[
\tilde{c}^{(E)}_{jk}(E) = \frac{2l+1}{2} \pi b_{\text{max}}^{2} \sum_{i}^{N_{l}} P_{i}(m) P_{i}(j).
\]

(33)

where the summation is carried out over the reactive trajectories only. The factor \((2l+1)/2\) is a result of the integration in the denominator of Eq. (28a). This approach will be called the modified quasiclassical trajectory (MQCT) approach.

One of the differences between the QCT and the MQCT methods is that, because the MQCT method uses all \( m \) values between \(-j\) and \( j \) it works effectively with a “beam” of randomly oriented molecules, which can be expected to probe the potential more realistically than the strongly peaked \( \tilde{\sigma}^{(E)}_{jk}(E) \) used in the QCT method.

### III. RESULTS AND DISCUSSION

#### A. The full long-range potential

For our potential we need the permanent multipole moments of the CH\(_{3}\)F molecule. For the Ca atom we need the expectation values of the quadrupole operator over the first substates of the \( ^{1}D \) state. However, if we use the Wigner-Eckart theorem, the expectation value of one component of the quadrupole operator over one \( ^{1}D \) substate will suffice.

We calculated the permanent multipole moments for the CH\(_{3}\)F molecule at the self-consistent field (SCF) level as well as at the MP2 level, using the ATOMOL program.
The geometry of the \( \text{CH}_3\text{F} \) molecule in our calculations, together with the masses of the atoms is given in Table I. Note that the origin for this calculation lies at the center of mass of the molecule. The principal moments of inertia are 127 585, 127 585, and 21 242 a.u. Data regarding bond lengths and bond angles was taken from Refs. 44 and 45.

The basis set for fluorine in the \( \text{CH}_3\text{F} \) molecule consists of a \((16s,11p)/[8s,6p]\) basis set of contracted Gaussian-type orbitals (CGTOs) due to Partridge,\(^{6,47}\) augmented by a diffuse \( s \) function \((\alpha_s=0.088 607)\), a diffuse \( p \) function \((\alpha_p=0.053 605)\) and three \( d \) functions \((\alpha_d=1.0, 0.369, \text{and} 0.136 163 46)\). The basis set for the carbon atom consists of a \((16s,11p)/[8s,6p]\) basis set due to Partridge,\(^{46,47}\) extended by a diffuse \( s \) function \((\alpha_s=0.038)\), a diffuse \( p \) function \((\alpha_p=0.026)\) and three \( d \) functions \((\alpha_d=0.7, 0.22, \text{and} 0.099)\).\(^{48}\) Last, the basis set for the hydrogen atoms consists of a \((6s)/[4s]\) basis set from Ref. 49, augmented by a diffuse \( s \) function \((\alpha_s=0.0313)\) (Ref. 48), and three \( p \) functions \((\alpha_p=0.5, 0.194 164 6, \text{and} 0.075 399 8)\).

The results for the multipole moments of the \( \text{CH}_3\text{F} \) molecule up to the octupole moment are given in Table II. Comparing our results for the dipole moment and the quadrupole moment with the available experimental data, we conclude that we have reasonable agreement with experiment for both properties. In the case of the quadrupole moment we even agree within the experimental accuracy. Comparing with another calculation of the dipole moment and the quadrupole moment\(^{50}\) there is a good agreement at the SCF level, although the older calculations were done in a smaller basis set (71 atomic orbitals vs 132 atomic orbitals). For the octupole moment no experimental data or other computational data were available.

### Table I. Geometry of the \( \text{CH}_3\text{F} \) molecule, atom masses, and principal moments of inertia.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Mass (amu)</th>
<th>( x ) (a.u.)</th>
<th>( y ) (a.u.)</th>
<th>( z ) (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>18.998 4</td>
<td>0.000 0</td>
<td>0.000 0</td>
<td>1.211 4</td>
</tr>
<tr>
<td>C</td>
<td>12.000 0</td>
<td>0.000 0</td>
<td>0.000 0</td>
<td>-1.400 3</td>
</tr>
<tr>
<td>H1</td>
<td>1.007 825</td>
<td>-0.981 6</td>
<td>-1.700 2</td>
<td>-2.054 2</td>
</tr>
<tr>
<td>H2</td>
<td>1.007 825</td>
<td>-0.981 6</td>
<td>1.700 2</td>
<td>-2.054 2</td>
</tr>
<tr>
<td>H3</td>
<td>1.007 825</td>
<td>-0.981 6</td>
<td>1.700 2</td>
<td>-2.054 2</td>
</tr>
</tbody>
</table>

For the \( \text{Ca} \) atom, the calculations become less trivial, because there are low lying perturber states, which mix strongly with the \((3d4s)/D\) state.\(^{51,52}\) Because of the five-fold degeneracy of the \(^1D\) state, a multiconfiguration SCF (MCSCF) approach, which included a symmetry averaging procedure,\(^{53}\) was used to optimize the electronic wave function. To calculate the expectation values for one component of the multipole operators over one component of the wave function, we used a linear response method. Both the optimization and the calculation of the expectation values were done using the SIRIUS program package.\(^{54}\) In all calculations we took the \( m_h=0 \) component of the multipole operator and the \( \mu=-2 \) component of the wave function.

The basis set used in the calculations on the \( \text{Ca} \) atom consists of a \((14s,9p)/[10s,5p]\) basis set due to Wachters.\(^{55}\) It was extended by adding a diffuse \( s \) function \((\alpha_s=0.01)\)\(^{56}\) and four \( p \) functions from Refs. 55 and 56. From Ref. 47, page 115, nine \( d \) functions were added. Furthermore, four diffuse \( d \) functions \((\alpha_d=0.033 484, 0.014 439, 0.006 226, \text{and} 0.002 685)\) were used, whose exponents were optimized with respect to the energy at the complete active space SCF (CASSCF) level with an active space consisting of the five \( 3d \) orbitals, containing only one electron. We also did calculations with an extended basis set, which included 2 \( f \) functions \((\alpha_f=1.4 \text{ and} 0.3)\).\(^{56}\)

We expected to find a large dependence of the wave function and of the properties of the \( \text{Ca} \) atom on the level of electron correlation, because of the large polarizability of the \( \text{Ca} \) atom and the low-lying perturber states for the \((4s3d)/D\) state.\(^{51,52}\) Indeed, we found that the expectation value of the \( Q_0^2 \) operator for the \( \mu=-2 \) substate varied between 2.7 and 5.4 a.u. at different levels of electron correlation.

In Table III we show the results for a number of characteristic calculations including those that we used in our potential. In all our calculations the \( 1s, 2s, \text{and} 2p \) orbitals remain doubly occupied. However, those orbitals were optimized during the calculation. The configurations, used in the MCSCF calculations, are denoted as follows: /Restricted Active Space #1 (RAS1) [minimum number of electrons, maximum number of electrons] /RAS2/RAS3 [minimum number of electrons, maximum number of electrons]/. The total number of active electrons in all calculations was ten. In case there is only a RAS2 specified, the calculation was a CASSCF calculation with only two electrons in the active space. The following results are given in Table III. First, the energy of the \(^1D\) state in hartree, denoted by \( E(\text{\footnotesize{1D}}) \). Second, the energy gap between the \(^1D\) state and the \(^1S\) ground state in hartree, denoted by \( \Delta E(\footnotesize{1D}-\footnotesize{1S}) \). Third, the expectation value of the \( Q_0^2 \) operator for the \( \mu=-2 \) substate in atomic units. Fourth, the number of configuration state functions in the calculation of the \(^1D\) state, denoted by \#CSF. Last, the number of orbital rotations in the calculation of the \(^1D\) state, denoted by \#orb. Looking at the energy gap between the \(^1D\) state and the \(^1S\) ground state, we see, that in our most extensive calculation it deviates with respect to the experiment by 0.010 837 hartree, which is about 10%. We think that the reason for this lies in an insufficient description of the correlation of the core electrons of the \( \text{Ca} \) atom in the calculation of the \(^1D\) state, which is very important in this case.\(^{57}\)
TABLE III. MCSCF results for different reference wave functions for the Ca atom.

<table>
<thead>
<tr>
<th>Active space</th>
<th>(E^{(1)}(D))</th>
<th>(\Delta E^{(1)}(D - 1.5))</th>
<th>((Q_0^2))</th>
<th>#CSF</th>
<th>#orb</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1s^3,3d^{10})</td>
<td>-676.749 687</td>
<td>0.107 326</td>
<td>2.72</td>
<td>1</td>
<td>133</td>
</tr>
<tr>
<td>(1s^3,3d^{10})</td>
<td>-676.777 507</td>
<td>0.110 210</td>
<td>5.17</td>
<td>5</td>
<td>133</td>
</tr>
<tr>
<td>(1s^3,5s,3d,4d,4p,5p^{11})</td>
<td>-676.778 507</td>
<td>0.110 210</td>
<td>5.17</td>
<td>5</td>
<td>133</td>
</tr>
<tr>
<td>(1s^3,5s,3d,4d,4p,5p^{11})</td>
<td>-676.920 599</td>
<td>0.110 210</td>
<td>5.17</td>
<td>5</td>
<td>133</td>
</tr>
<tr>
<td>(1s^3,5s,3d,4d,4p,5p^{11})</td>
<td>-676.929 929</td>
<td>0.110 210</td>
<td>5.17</td>
<td>5</td>
<td>133</td>
</tr>
</tbody>
</table>

8ROHF calculation.
9Calculation with extended basis set.

This could be improved by including excitations from the 2s,2p shell in the MCSCF calculation. However, this leads to such an increase in the number of CSFs, that it is not feasible at the moment.

The best value we find for \((Q_0^2)\) is 3.77 a.u. No experimental results are available for the value of \((Q_0^2)\) to compare our results with. In a recent study, Sundholm et al. calculated a value for \((Q_0^2)\) of 4.164 a.u. (4.267 including some relativistic effects).

This result was obtained from a series of numerical multiconfiguration Hartree–Fock (N-MCHF) calculations, in which only a few outer orbitals were optimized. The inner orbitals up to the 4p orbitals were always kept frozen at a level of electron correlation comparable to our \(1s^3,5s,3d,4d,4p,5p^{11}\) calculation. When we compare our calculations with those of Sundholm et al., there seems to be reasonable agreement. If anything, we expect to find a lower value for \((Q_0^2)\), if we improve on our calculations by adding more configurations, thus making the agreement between our results and the results of Sundholm et al. worse. This conclusion can be drawn in view of the calculations of Sundholm et al., because the configuration space of our best calculation is equal to their T3#4 calculation, for which they found a value of 5.112 for \((Q_0^2)\). The difference between their T3#4 calculation and ours is that we optimized all orbitals with respect to the energy. Adding more configurations, which can be viewed as a correction for the nonoptimized orbitals, made the value for \((Q_0^2)\) go down in their case.

Using the values for the multipole moments of the CH₃F molecule from Table II and the value for the quadrupole moment of the \(\mu = -2\) substate of the Ca atom of 3.77 a.u. we constructed the FLRP. A representative cut through the five surfaces of the FLRP at \(R = (6.0, \cos \gamma, 30^\circ)\) is given in Fig. 2.

From the FLRP we derive three model potentials according to Eq. (9). For the isotropic model potential (IMP) we take \(C_0 = -8.253\) 87 a.u. and \(C_1 = 0\). For the purely anisotropic model potential #1 (AMPI) we take \(C_0 = 0\) and \(C_1 = -8.323\) 19 a.u. The coefficients \(C_0\) and \(C_1\) for the anisotropic model potential #2 (AMP2), are \(-8.253\) 87 and \(-8.323\) 19 a.u.

B. Dynamics

A Fortran computer program was written to perform classical trajectory calculations. The initial conditions were generated with the use of the random number generator "G05CAF" from the NAG library. The propagation of the trajectories was performed using a variable order, variable step Adams integrator from the NAG library (subroutine "D02CJF").

We performed calculations for a number of relative translational energies. They were chosen to coincide with energies used in the experiment by Janssen et al. The experimental values for the properties \(c_\beta q(E)/c_\beta \bar{q}(E)\) are given in Table IV. Per energy and per potential surface our calculation consisted of a batch of 100 000 trajectories. The threefold symmetry of the CH₃F molecule was exploited in our calculations. We used an IBM RS6000/370 workstation. The calculation of 100 000 trajectories on one PES took approximately 3 h, of which the calculation of the potential and its derivatives formed the major part.

In this section we will present the results of the trajectory calculations for the different potentials used. Unless stated otherwise we use a harpooning radius of 6.0 bohr.10

FIG. 2. Cut through PESs of the FLRP at \(R = 6.0\) bohr and \(\gamma = 30^\circ\)
The calculations on the model potentials we only give the results obtained by the MQCT approach since the quasiclassical approach turns out to give practically the same answers.

For the calculations on the FLRP we use both the MQCT approach and the QCT approach since the answers appear to be quite different in that case. We use three values for \( \gamma \) to determine the influence of the cutoff angle on the steric effect and on its energy dependence. The angles we used are 60°, 90°, and 120°, which will be called "model 60," "model 90," and "model 120" calculations, respectively. First we will discuss the calculations on the three model potentials, defined through Eq. (9) and the parameters \( C_0 \) and \( \gamma \) given in the last paragraph of Sec. III A. Finally, the FLRP will be discussed.

1. Isotropic model potential (IMP)

The model potential IMP is an isotropic potential. This implies that the relative motion of the center of mass of the reactants and the rotation of the \( \text{CH}_3\text{F} \) molecule are decoupled. Reorientation is not possible when using this potential and the PDFs for the variables associated with the rotation of the molecule will remain stationary during the approach of the atom.

The results for the total reactive cross section for unoriented molecules \( \bar{\sigma}_0^{11}(E) \) for the three ADLC models used with this potential are given in Fig. 3, where all values are normalized to \( \bar{\sigma}_0^{11}(E) \) at \( E=0.286 \) eV, as was done in the experimental paper by Janssen et al.,\textsuperscript{18} who give only relative cross sections. A fit to the experimental data, as presented by Janssen et al.,\textsuperscript{18} in which they corrected for the velocity distribution of the Ca beam, is shown also. The results for \( \bar{\sigma}_0^{11}(E)/\bar{\sigma}_0^{01}(E) \) for these models are given in Fig. 4. In this figure also a fit to the experimental data as presented by Janssen et al.\textsuperscript{18} is plotted.

When looking at the results for \( \bar{\sigma}_0^{11}(E) \), it is immediately clear that the slope of the experimental line is much higher than that of the calculated lines. If we look at the ratio between \( \bar{\sigma}_0^{11}(E) \) at 0.068 eV and \( \bar{\sigma}_0^{01}(E) \) at 0.451 eV, the experimental ratio is 11.4, whereas the model calculations give a ratio of 2.3. This behavior was expected, however. For an attractive isotropic potential with an \( R^{-4} \) dependence in a calculation without any barrier to reaction, the cross section will be proportional to \( E^{1/2} \). This will lead to a ratio between \( \bar{\sigma}_0^{11}(E) \) at 0.068 eV and \( \bar{\sigma}_0^{01}(E) \) at 0.451 eV of 2.6.

To obtain the same energy dependence of \( \bar{\sigma}_0^{11}(E) \) as in the experiment one would need to use an \( R^{-2/3} \) potential, which is unrealistic for the interaction between a neutral atom and a neutral molecule. Hence, we must conclude that some elements necessary to reproduce the experimental results for \( \bar{\sigma}_0^{11}(E) \) are still missing from our calculations. Most likely these elements are of quantum mechanical nature. Of course the above arguments apply for all our model potentials. Thus we will restrict the discussion of \( \bar{\sigma}_0^{11}(E) \) to this paragraph and only return to it in Sec. III B 4, where we discuss the calculations on the FLRP.

Looking at the curves for \( \bar{\sigma}_0^{11}(E)/\bar{\sigma}_0^{01}(E) \) we see that the experimental curve for the steric effect for this reaction as a function of \( E \) can be reproduced. The model parameter \( \gamma \) would have to be approximately 110°. With this potential, the reduced energy \( a \), as defined in paper I, ranges from 0.392 to 2.602.

To clarify the origin of the positive energy dependence of the steric effect, we plot the distribution of \( \cos \gamma \), the

---

<table>
<thead>
<tr>
<th>( E_i ) (eV)</th>
<th>( \sigma_0^{11}(E) )</th>
<th>( \sigma_0^{01}(E) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.068 \textsuperscript{a}</td>
<td>4.41</td>
<td>0.174</td>
</tr>
<tr>
<td>0.119</td>
<td>2.67</td>
<td>0.252</td>
</tr>
<tr>
<td>0.182</td>
<td>1.281</td>
<td>0.324</td>
</tr>
<tr>
<td>0.286 \textsuperscript{b}</td>
<td>1.000</td>
<td>0.414</td>
</tr>
<tr>
<td>0.358</td>
<td>0.556</td>
<td>0.491</td>
</tr>
<tr>
<td>0.451</td>
<td>0.387</td>
<td>0.592</td>
</tr>
</tbody>
</table>

\( \textsuperscript{a} \) Values extrapolated from fit to experimental data (Ref. 18).

\( \textsuperscript{b} \) Reference point.
cosine of the SF angle at which the Ca atom hits the sphere at which harpooning takes place (the “sphere of harpooning”). The distributions of cos $\chi_f$ for an average relative translational energy of 0.068 and 0.451 eV are shown in Fig. 5. From this figure it is clear that for $E=0.068$ eV a number of trajectories will hit the back of the sphere of harpooning. This leads to a lowering of the steric effect. The trajectories which hit the back of the sphere are those with a large impact parameter. Those trajectories will not be reactive at higher values of $E$. Therefore, the curve of the distribution of cos $\chi_f$ will not extend far beyond cos $\chi_f=0$ for $E$ of 0.451 eV, as can be seen in Fig. 5. This effect we call “trapping.”

Regarding $\sigma^0_{2,1}(E)/\sigma^0_{0,1}(E)$, we can say that the number of trajectories is too low to get an accurate result. However, $\sigma^0_{2,1}(E)/\sigma^0_{0,1}(E)$ scatters around zero for all cutoff angles and energies and is in the order of magnitude of $-0.2$. This compares reasonably well with experiment taking into account the noisy character of both the theoretical and the experimental data.

The results for different model potentials are comparable. Therefore, we will resume the discussion of $\sigma^0_{2,1}(E)/\sigma^0_{0,1}(E)$ in Sec. III B 4, where we discuss the calculations on the FLRP.

2. Anisotropic model potential (AMP1)

This model potential is antisymmetric in cos $\gamma$. Furthermore, it has an $R^{-5}$ dependence instead of an $R^{-4}$ dependence. It allows reorientation. A consequence of this is that the motion of the center of mass of the reacting system and the rotation of the molecule are no longer decoupled, thus their equations of motion have to be solved simultaneously. The PDFs of the variables associated with the rotation of the molecule are no longer stationary.

The results for $\sigma^1_{2,1}(E)/\sigma^0_{0,1}(E)$ together with the fit to the experimental data are shown in Fig. 6. With regard to the results for $\sigma^1_{0,1}(E)$ and $\sigma^1_{2,1}(E)/\sigma^0_{0,1}(E)$ we refer to Sec. III B 1.

The results for $\sigma^1_{1,1}(E)/\sigma^0_{0,1}(E)$ show that in the model 60 case the energy dependence of the steric effect is comparable to the experimentally found energy dependence. However, the magnitude of the steric effect is much too high. Increasing the cutoff angle to 90 or 120 degrees lowers the steric effect, but at the same time weakens the energy dependence.

As it turns out, it is only possible with this potential to model either the energy dependence of the steric effect or the magnitude of the steric effect. So, it is not possible to reproduce the experimental results with this potential. This suggests that reorientation cannot primarily be responsible for the results found by Janssen et al. 18

3. Anisotropic model potential (AMP2)

This model potential is the sum of the purely isotropic model potential IMP and the purely anisotropic model potential AMP1. We use this potential to study the combined effect of trapping and reorientation on the steric effect.

The results for $\sigma^1_{1,1}(E)/\sigma^0_{0,1}(E)$ for the IMP and AMP2 potentials are given in Fig. 7. From this figure, the conclusion can be drawn that reorientation indeed lowers the steric effect, but only slightly. When looking at $\sigma^1_{0,1}(E)$ and $\sigma^1_{2,1}(E)$ separately (see Figs. 8 and 9, respectively), it becomes clear that the lowering of the steric effect is almost entirely due to an increase in $\sigma^1_{0,1}(E)$ [note that $\sigma^1_{0,1}(E)$ and $\sigma^1_{1,1}(E)$ in Figs. 8 and 9 are unnormalized]. Thus the AMP2 potential gives a better result for $\sigma^1_{0,1}(E)$ than the IMP potential. The reason why $\sigma^1_{0,1}(E)$ does not change when going from the IMP to the AMP2 potential becomes clear when comparing the distributions in cos $\gamma$, both for favorable and unfavorable orientation of the reactants (see Fig. 10). A favorable orientation means that the molecule is in the classical equivalent of the $(JMK)=(1,1,1)$ state, an unfavorable orientation means that the molecule is in the classical equivalent of the $(JMK)=(1,1,-1)$ state. Figure 10 shows that reorientation increases the cross section for both favorable and unfavorable orientations of the reactants. Thus the overall effect of reorientation on $\sigma^1_{1,1}(E)$ is small whereas it increases $\sigma^1_{0,1}(E)$. In fact, when we increase the anisotropy...
the potential the steric effect goes slightly up, instead of down, although \( \tilde{\sigma}_0^{-1}(E) \) increases significantly. The results for the model 60 and model 120 calculations are similar.

4. The full long-range potential (FLRP)

The full long range potential (FLRP) is defined in Sec. II.C. It consists of five surfaces, which are asymptotically degenerate. Hence, in the asymptotic region, the trajectories will have to be equally distributed among the five PESs. During the approach of the reactants, however, it is possible that some of the trajectories drop to a lower surface. Our model does not include such surface hops, but we consider two extreme cases: approach (I), where all trajectories drop to the lowest surface and approach (II), where no surface hops take place at all.

The MQCT results for \( \tilde{\sigma}_0^{-1}(E) \) using approach (II) are shown in Fig. 11. The energy dependence of \( \tilde{\sigma}_0^{-1}(E) \) for model 90 and model 120 calculations is quite weak. In fact, the ratio between \( \tilde{\sigma}_0^{-1}(E) \) at \( E=0.068 \) eV and \( E=0.451 \) eV is 1.47 for model 90 and 1.28 for model 120. When approach (I) is used these ratios are much higher (2.36 and 2.20, respectively). The reason for this becomes clear when looking at the forms of the PESs as a function of \( \cos \gamma \) at \( R=6.0 \) bohr and \( \xi=30^\circ \) that are shown in Fig. 2. The repulsive PESs 4 and 5 will only be reactive at higher energies thus lowering the energy dependence in approach (II). In approach (I) only the lowest, attractive, PES contributes, resulting in a stronger energy dependence. In approach (II) PES 1 contributes for approximately 43% to \( \tilde{\sigma}_0^{-1}(E) \) at 0.068 eV and for approximately 27% at 0.451 eV.

The energy dependence for the model 60 calculations is much higher than for the model 90 or model 120 calculations for both approaches. In fact, the ratio between \( \tilde{\sigma}_0^{-1}(E) \) at \( E=0.068 \) eV and \( \tilde{\sigma}_0^{-1}(E) \) at \( E=0.451 \) eV is 3.49 for approach (I) and 2.35 for approach (II). The reason for this becomes clear when looking at the distributions for \( \cos \gamma \).

FIG. 7. The energy dependence of the steric effect \( \tilde{\sigma}_0^{-1}(E)/\tilde{\sigma}_0^{-1}(E) \) for model 90 for the IMP and AMP2 potentials.

FIG. 9. The energy dependence of \( \tilde{\sigma}_0^{-1}(E) \) for model 90 for the IMP and AMP2 model potentials.

FIG. 8. The energy dependence of \( \tilde{\sigma}_0^{-1}(E) \) for model 90 for the IMP and AMP2 model potentials.

FIG. 10. The distribution of \( \cos \gamma \) at \( E=0.119 \) eV for the IMP and AMP2 potentials for unfavorable and favorable approaches of the reactants.
resulting from approach (I) and approach (II) calculations in Fig. 12. Since, at $E=0.451$ eV the distributions are practically independent of $\cos \gamma$, $\bar{\sigma}_0^{1,1}(E)$ will approximately double when going from a model 60 to a model 90 calculation and that it will triple when going from a model 60 to a model 120 calculation, as might be expected for high energies. However, at an energy of 0.068 eV a large number of trajectories will end up between $\gamma=0^\circ$ and $\gamma=60^\circ$ for both approaches. This means, that $\bar{\sigma}_0^{1,1}(E)$ for a model 60 calculation will be practically the same as for a model 90 or model 120 calculation, which results in a stronger energy dependence for the model 60 calculations for both approaches.

The results for $\bar{\sigma}_0^{1,1}(E)/\bar{\sigma}_0^{1,1}(E)$ following approach (II) are shown in Fig. 13. The results for energies of 0.068 and 0.451 eV following approach (I) are given in Table V. Figure 13, together with Table V shows that for all models approach (I) leads to a steric effect that is higher and has a much weaker energy dependence than for approach (II). The reason for this lies in the topology of the PESs in the FLRP. The local maximum near $\cos \gamma=0$ in the lowest PES (see Fig. 2) prevents trajectories from reorienting towards $\cos \gamma=1$, which makes the steric effect large. In the case of approach (II), this is compensated at lower energies by the trajectories on PES 2 which does not have the maximum, thus resulting in a lower steric effect for the approach (II) calculations.

We now turn to the discussion of the difference between the MQCT and QCT methods. We do this for calculations following approach (II). The MQCT and QCT results for $\bar{\sigma}_0^{1,1}(E)/\bar{\sigma}_0^{1,1}(E)$ are shown in Figs. 13 and 14, respectively. $\bar{\sigma}_0^{1,1}(E)$ is computed in the same way in both methods. There is a large difference between the MQCT and QCT results for the steric effect. The QCT results are much too high compared to the experiment, and in some regions even the sign of the energy dependence is wrong. The MQCT results are much better agreement. Since the calculation of $\bar{\sigma}_0^{1,1}(E)$ is the same for the MQCT and QCT calculations, this implies that $\bar{\sigma}_0^{1,1}(E)$ is too large in the QCT method. This can be understood from Figs. 1 and 2. In a QCT calculation $\bar{\sigma}_0^{1,1}(E)$ is calculated from a calculation with $m=1$ and a calculation with $m=-1$. The PDFs of these states have sharp peaks at $\delta=0^\circ$ and $90^\circ$ and at $\delta=90^\circ$ and $180^\circ$, respectively. This means that the PESs are probed very unevenly in this calculation in contrast with the quantum mechanical PDF. In the MQCT approach a "beam" of randomly oriented molecules is used, thus resulting in a better (more like the quantum mechanical) probing of the configuration space with respect to $\gamma$, giving much better results for $\bar{\sigma}_0^{1,1}(E)/\bar{\sigma}_0^{1,1}(E)$.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Model 60</th>
<th>Model 90</th>
<th>Model 120</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.068</td>
<td>1.28</td>
<td>1.09</td>
<td>0.48</td>
</tr>
<tr>
<td>0.451</td>
<td>1.37</td>
<td>0.99</td>
<td>0.50</td>
</tr>
</tbody>
</table>
ever, even in the case of a MQCT calculation the steric effect is higher than with the model potentials. This is probably due to the maxima in some of the PESs (see Fig. 2), which hinder the rotation of the molecule. This difference between the MQCT approach and the QCT approach is even more evident when looking at the results for the calculation of $\sigma_0^{1/1}(E)/\sigma_0^{1/1}(E)$. In the MQCT case, the values for $\sigma_0^{1/1}(E)/\sigma_0^{1/1}(E)$ still scatter around zero and are in the order of magnitude of $-0.2$, just like the experimentally found values for $\sigma_0^{1/1}(E)/\sigma_0^{1/1}(E)$ and the values found for the model potentials. However, in the QCT case these values become all positive and are in the order of magnitude of $10$.

Summarizing it can be said that because of the unrealistic probing of the PESs in the QCT approach in comparison with the MQCT approach, the steric effect and the alignment effect in the QCT case will be unrealistically higher than in the MQCT case. Therefore, it has to be concluded that the QCT approach in this case is not very good.

Of course, it is possible to vary the size of the steric effect by varying the harpooning radius. However, if we make the harpooning radius larger the steric effect increases, as can be seen from Fig. 15 for a calculation following the MQCT approach. Furthermore, this results in a weaker energy dependence for the steric effect. Thus in order to reproduce the experimental results, the harpooning radius would have to be decreased making it less than 6.0 bohr. In that case the harpooning radius lies in a range where the validity of the harpooning model becomes highly questionable. Furthermore, our potentials are no longer valid since at such short separations exchange and penetration effects can no longer be excluded.

**IV. SUMMARY AND CONCLUSIONS**

Molecular and atomic multipole moments have been calculated for the CH3F molecule and for the Ca atom, respectively, using ab initio methods. The results agree quite well with existing experimental and theoretical data, as far as these were available. From these multipole moments a long range potential (actually, a set of five adiabatic potentials which are asymptotically degenerate) has been constructed by diagonalization of the interaction matrix which describes the interaction between the CH3F molecule and the exited fivefold degenerate Ca($^1D$) atom. From this long range potential three model potentials were constructed to investigate certain features of the full long-range potential.

Using these potentials, we investigated, by a classical trajectory method, the energy dependence of the total cross section and the magnitude and energy dependence of the steric effect for the Ca+CH3F($JKM=111$)$→$CaF($^2\Pi$)+CH3 reaction. For all potentials, we find the observed negative energy dependence of the total cross section $\sigma_0^{1/1}(E)$, but considerably weaker than in the experiment. A reason for this might be that our classical description for the motion of the reactants and of the reaction is not sufficient. In order to obtain the correct $\sigma_0^{1/1}(E)$, it will probably be necessary to describe elements of this reaction quantum mechanically. Another reason for the difference between theory and experiment is that the measured $\sigma_0^{1/1}(E)$ is the reactive cross section for only one exit channel, whereas the calculated $\sigma_0^{1/1}(E)$ is the reactive cross section for all exit channels. The measured value might not be proportional to the total reactive cross section, because the branching ratio to the different products might be energy dependent. Thus the measured exit channel might exhibit a much stronger energy dependence than the other exit channels. To check this hypothesis it is necessary that also the reactive cross sections for other exit channels than the CaF ($A^2\Sigma^+$) channel are measured.

Although surface hops between the five adiabatic PESs were not explicitly included in our model, we looked at two extreme cases: (I) all trajectories drop to the lowest surface during the approach of the reactants and (II) no surface hops take place at all. Regarding $\sigma_0^{1/1}(E)$, the energy dependence is more in agreement with experiment for the calculations.
following approach (I) than for the calculations following approach (II). However, for the steric effect, the opposite situation occurs. In view of the results for the steric effect, we favor approach (II).

Regarding the steric effect, $\Delta \alpha_{11}(E)/\Delta \alpha_{00}(E)$, we get good agreement between theory and experiment for the IMP and AMP2 model potentials. The IMP potential is isotropic and no reorientation is possible for this potential. This makes reorientation a less likely explanation for the positive energy dependence of the steric effect. We rather think of trapping as the primary source of the positive energy dependence of the steric effect. On the other hand, from the results for the FLRP, it becomes clear that the steric effect is quite sensitive to the topology of the potential. Maxima in some of the PESs of the FLRP, can cause a considerable increase in the steric effect compared to the calculations on the model potentials. Therefore, we conclude that although reorientation is not required to explain the energy dependence of the steric effect, it may still have some influence. We conclude that the MQCT method is to be preferred over the QCT method because the former probes the PESs more realistically.

From literature it is known that there are two avoided crossings for this system at which harpooning could take place. Our calculations show that in order to account for the observed steric effect harpooning has to take place at close range (6.0 bohr) rather than at large separation (8.5 bohr). This implies that the steric effect for the ground state channel of this reaction will probably exhibit a weaker energy dependence than the reaction to the $^2\Pi$ excited state channel.

Of course, our FLRP potential is quite crude and does not include any possibly important contributions, such as induction or dispersion. The inclusion of these interactions might cause the maximum, which is present in some surfaces of the FLRP, to disappear, resulting in a better agreement between theory and experiment for this potential. Furthermore, it is only a long range potential, which means that no chemical and short range interactions resulting from exchange and penetration are included. Thus, more definite conclusions must await the calculation of more accurate PESs.

To obtain a better insight into the mechanism of this reaction, we plan to perform more calculations in the near future. These calculations will include a quantum mechanical description of the rotating molecule and a better description of the FLRP by the inclusion of induction and dispersion interactions. Alternatively, the model could be improved if more experimental data were available, in particular the energy dependence of the branching ratio between the different exit channels.

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33. Note that Janssen et al. (Ref. 18) mistakenly mention the harpooning radius corresponding to the outer crossing as the harpooning radius for the reaction to the $^2\Pi$ excited state (private communication).
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