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Cite as: J. Chem. Phys. 122, 194103 (2005); https://doi.org/10.1063/1.1899603
Submitted: 08 February 2005 . Accepted: 10 March 2005 . Published Online: 16 May 2005

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Long-range transition state theory

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(Received 8 February 2005; accepted 10 March 2005; published online 16 May 2005)

The implementation of variational transition state theory (VTST) for long-range asymptotic potential forms is considered, with particular emphasis on the energy and total angular momentum resolved (μJ-VTST) implementation. A long-range transition state approximation yields a remarkably simple and universal description of the kinetics of reactions governed by long-range interactions. The resulting (μJ-VTST) implementation is shown to yield capture-rate coefficients that compare favorably with those from trajectory simulations (deviating by less than 10%) for a wide variety of neutral and ionic long-range potential forms. Simple analytic results are derived for many of these cases. A brief comparison with a variety of low-temperature experimental studies illustrates the power of this approach as an analysis tool. The present VTST approach allows for a simple analysis of the applicability conditions for some related theoretical approaches. It also provides an estimate of the temperature or energy at which the “long-range transition state” moves to such short separations that short-range effects, such as chemical bonding, steric repulsion, and electronic state selectivity, must be considered. © 2005 American Institute of Physics. [DOI: 10.1063/1.1899603]

I. INTRODUCTION

Due to their large rate coefficients, barrierless reactions are of key importance in a variety of chemical environments including the combustion, atmospheric, and interstellar environments. For such reactions there are generally two reasonably distinct transition state regions.1,2 These two transition state regions correlate with two different aspects of the potential-energy surface. The “outer” transition state correlates qualitatively with the location of the centrifugal barriers on the long-range potential-energy surface. An “inner” transition state generally arises in the region where chemical interactions (e.g., covalent bonding and steric repulsions) are of similar, or somewhat greater, strength than the long-range interactions (i.e., multipole, dispersion, and induced interactions).

At the high temperatures typical of the combustion environment only the inner transition state region is important. In contrast, in the low-temperature limit of importance in interstellar chemistry only the outer transition state region is of importance. The transition from a dominant outer transition state to a dominant inner transition state generally takes place quite gradually at temperatures of the order of 100 K.2,3 As a result, both transition states generally play a significant role at the temperatures of importance in atmospheric chemistry.

In prior and continuing work we have developed accurate and efficient methods for treating the inner transition-state region of importance in combustion chemistry.4–8 These approaches have focused on the details of the potential-energy surface and their effect on the optimal transition-state dividing surfaces. In the present study we instead focus on the outer transition state with the goal of enhancing our understanding of the low-temperature kinetics. This analysis also allows for improved treatments of the transition regime of importance in atmospheric chemistry, as is illustrated in a related study of the reaction of C2H4 with OH.3

When the interaction potential does not depend on the orientation of the reacting species the reactive scattering problem is easily solved.9–12 In general, however, the long-range forces are anisotropic, and the problem is considerably more complicated. Two different classical-based approaches for calculating the capture rate have been promulgated. In the effective potential method13,14 the real anisotropic potential is mapped onto an effective isotropic one, which is later used for the standard rate constant calculation. Various different versions of the effective potential method have been used,13–18 differing primarily in the procedures employed in the generation of the effective potentials. The effective potential methods, while physically appealing due to their simplicity, are difficult to justify rigorously. Furthermore, it is difficult to generalize them to include the treatment of angular momentum conservation and so they are not considered further in this paper.

Classical variational transition state theory (VTST)19–22 provides an alternative, more rigorous approach. The applications of VTST to barrierless reactions have traditionally involved canonical (C-VTST) and microcanonical (μ-VTST) forms, in part due to an erroneous but apparently common belief that the conservation of angular momentum is of little relevance.13,28 As will be demonstrated here, the proper inclusion of the conservation of total angular momentum resolves many of the observed discrepancies between VTST and trajectory simulations. Thus, the present study will focus on the implementation of an energy E and total angular momentum J resolved VTST (μJ-VTST). Prior flexible transition state theory31 and variable reaction coordinate
transition state theory\textsuperscript{32–35} treatments have also properly incorporated the conservation of total angular momentum (and duly noted its importance), as have a few other treatments for ionic reactions.\textsuperscript{36,37} However, these treatments have largely ignored the low-temperature limit/large-separation behavior and have made no effort to obtain simple analytic forms for this limit.

When considering the inner transition state region it is important to consider various forms for the reaction coordinate, with simple variations in the form often providing variationally lower rate constants by factors of two or more.\textsuperscript{33,34,38} In contrast, the dependence on the form of the reaction coordinate is expected to be very weak at the large separations of the outer transition state. Thus, for simplicity we consider only the reaction coordinate defined by the separation between the centers of mass of the two reacting fragments. The good agreement between the resulting $\mu$-$J$-VTST predictions and trajectory simulations verifies that the dependence on the reaction coordinate is indeed very weak.

For temperatures at which the quantum and classical rotational partition functions differ significantly, one might expect there to be significant quantum effects on the capture rate. In reality, quantum effects likely become significant only at even lower temperatures, since there is a significant cancellation of error in taking the ratio of the partition function for the transition state to that for the reactants. Thus, one expects the present classical predictions to generally be appropriate down to temperatures of a few kelvins or less.

Nevertheless, we note that for the “center-of-mass” reaction coordinate, quantum effects can be partially incorporated into the transition state theory by treating the nonreactive degrees of freedom, i.e., the rotations of both fragments and the orbital rotation, quantum mechanically. Two essentially equivalent approaches to doing so were developed by Clary\textsuperscript{39} under the name of adiabatic capture centrifugal sudden approximation (ACCSA) and by Troe\textsuperscript{40} as the statistical adiabatic channel model (SACM). These adiabatic theories are in principle completely equivalent to variational transition state theory for the center-of-mass reaction coordinate. In both approaches the Hamiltonian is diagonalized for fixed values of the distance between the fragments’ centers-of-mass in a certain range. The computed energies are then treated as effective one-dimensional potentials, upon which the reaction dynamics is assumed to proceed adiabatically. Considerable numerical work is required in the classical range of temperatures, where many quantum-rotational wave functions are involved in the formation of the adiabatic states. Furthermore, each reactive system with different kinetic (the masses and inertia moments of the fragments) and potential parameters must be treated separately.

In this paper, $E$, $J$-resolved classical variational transition state theory is applied to the treatment of reactions controlled by long-range interactions. It is shown that at moderately low temperatures, where the classical description is still applicable, $\mu$-$J$-VTST provides a surprisingly simple and reasonably accurate procedure for calculating the capture rate. For example, for the ion-linear dipole capture the so-derived analytic rate expression coincides with the classical trajectory results to within 1% accuracy. For other types of interactions the $\mu$-$J$-VTST rate constant is found to be within 10% of the results from classical trajectory simulations.

The present analysis is based on a long-range transition state approximation that is valid at large separations. The final result of the analysis is a universal description of the capture rate valid for a long-range interaction potential with a power-law dependence on the distance between the fragments, $V \approx 1/R^n$ [cf. Eq. (32)]:

\begin{equation}
    k = C_1 \mu^{-1/2} V_0^{2n/3} T^{1/2-2/n},
\end{equation}

where $\mu$ is the reduced mass of the system, $V_0$ is the strength of interaction between the fragments, and $T$ is the temperature (in energy units). The dimensionless proportionality constant $C_1$ is specific for each type of interaction, but is independent of $T$, $V_0$, $\mu$, and of the fragments’ moments of inertia. For the reader’s convenience we summarized our main results for $C_1$ in Tables I and II.\textsuperscript{41} Generalizations to other long-range potentials, although not specifically considered here, can be straightforwardly obtained from the formalism described here.

An advantage of Eq. (1) is that it is independent of most of the parameters characterizing the reactants, such as the moments of inertia of the fragments and the orientation of the multipole moments in the fragments’ molecular frames. Its simple dependence on only the magnitude of the multipole moments makes it readily implemented for real experimental situations. We illustrate this utility with sample calculations and comparison with experiment for a variety of reactions.

The long-range transition state approximation implies certain limits of applicability for the present approach. Notably, the maximum temperature at which this approximation is valid is much greater than the temperature at which the long-range potential expansion [cf. Eq. (31) below] becomes practically inapplicable due to the contraction of the transition state. These applicability limits are discussed in some detail along with the related limits inherent in the adiabatic channel approaches.

<table>
<thead>
<tr>
<th>$A$</th>
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<td>$L$</td>
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<td>$N$</td>
<td>2.68</td>
<td>2.03</td>
<td>2.24</td>
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\textsuperscript{3}Charge-dipole interaction, $V_0=q\cdot d$, Eq. (60).
\textsuperscript{4}Charge-quadrupole interaction, $V_0=q\cdot Q > 0$, Eq. (68).
\textsuperscript{5}Charge-quadrupole interaction, $V_0=q\cdot Q < 0$, Eq. (68).

\textsuperscript{a}Dipole-dipole interaction, $V_0=d_i\cdot d_j$, Eq. (71).
\textsuperscript{b}Dipole-quadrupole interaction, $V_0=d_i\cdot Q_j$, Eq. (73).
\textsuperscript{c}Dipole-induced-dipole interaction, $V_0=d_i\cdot \alpha_j$, Eq. (75).
\textsuperscript{d}Dispersion interaction, $V_0=1.5\alpha_i\alpha_j E_i E_j/(E_i+E_j)$, Eq. (57).
The outline of the paper is as follows. In Sec. II the long-range transition state approximation is introduced and general \( \mu J \)-VTST, \( \mu \)-VTST, and C-VTST rate expressions are derived. Also, the classical trajectory method we use is briefly described in this section. Then, in Sec. III, specific results are obtained for several practically important types of long-range interaction and the results are compared with those from classical trajectory simulations. In Sec. IV comparisons are made with a variety of experimental studies. A summary of the results is provided in Sec. V, along with a discussion of the various applicability conditions. Some concluding remarks are made in Sec. VI.

II. THEORY

The \( \mu J \)-VTST expression for the high-pressure recombination rate constant \( k(T) \) at temperature \( T \) can be written as,

\[
k(T) = \sigma g_e \frac{T}{2\pi \mu T} \left( \frac{2\pi}{\mu T} \right)^{3/2} \frac{Q_1(T)}{Q_2(T)},
\]

for the purpose of this paper, we assume \( \sigma = g_e = 1 \), \( \mu = m_1 m_2 / (m_1 + m_2) \) is the reduced mass, and \( Q_1 \) and \( Q_2 \) are the partition functions of the fragments, which are treated classically with respect to rotational degrees of freedom. \( N'(E,J) \) is the transition state number of states, which corresponds to the minimum in the \( E \)- and \( J \)-resolved number of states \( N(E,J) \) for the motion of the reactive complex on a given dividing surface separating reactants from products. Here and further we use atomic units in which \( \hbar = 1 \) and measure the temperature in energy units, \( k_B = 1 \).

In the low-temperature range of interest here the vibrational degrees of freedom of the fragments are decoupled from the rotational ones and their contributions to the fragment and transition state partition functions cancel. Considering then only the rotational degrees of freedom, the partition function of the \( k \)th polyatomic fragment \( Q_k \) can be written as

\[
Q_k = \pi^{-1/2} T^{\nu_k^2/2} \prod_{i=1}^{v_k} \sqrt{2\pi \hbar_i^{(k)}},
\]

where \( v_k \) is the number of rotational degrees of freedom of the fragment and \( \hbar_i^{(k)} \) are its principal moments of inertia.

The classical expression for \( N(E,J) \) can be written as

\[
N(E,J) = (2\pi)^{3/2} \int \cdots \int dQ dP \delta(R(Q) - R') \delta(H(Q,P) - E)] \delta(\hat{J}(Q,P) - J(\hat{R})) \delta(\hat{R}(\hat{R})),
\]

where \( \nu = \nu_1 + \nu_2 + 3 \) is the total number of degrees of freedom, \( Q \) and \( P \) are the \( \nu \)-dimensional generalized coordinates and momenta, the dividing surface is defined in terms of a fixed value \( R' \) for the “reaction coordinate” \( R(Q) \), the dynamical variable for the total angular momentum is denoted as \( \hat{J} \), while its numerical value is denoted as \( J \), \( \Theta \) is the Heaviside step function, and the dot denotes the time derivative, \( \dot{R} = dR/dt \).

A. Long-range transition state approximation

We start from an expression for the number of states \( N(E,J|R) \) of two reacting fragments with total energy \( E \) and total angular momentum \( J \), the centers of mass of which are separated by the distance \( R \),

\[
N(E,J|R) = \langle N(E,J|R,O) \rangle_O
\]

where \( \langle \ldots \rangle_O \) denotes the averaging over all possible orientations \( O \) of each of the fragments and of the vector which connects their centers of mass. In Eq. \( (7) \langle \ldots \rangle_O \) denotes the averaging over all possible orientations \( O_j \) of the vector \( J \), while its length is fixed. \( \{x\} = x \) if \( x > 0 \) and 0 otherwise, \( V(O,R) \) is the interfragment interaction potential, \( I_i^{(tot)} \), \( i = 1, 2, 3 \) are the principal moments of inertia for the system as a whole, \( \mu \) is the reduced mass, \( k_B = 0, 1 \) is the number of monoatomic fragments, and \( \Gamma(x) \) is the gamma function.

The transition state number of states \( N'(E,J) \) corresponds to the minimum of \( N(E,J|R) \) as a function of \( R \),

\[
N'(E,J) = \min_R N(E,J|R),
\]

while the transition state separation \( R' \) corresponds to the value of \( R \) at that minimum. For a given \( J \) the transition state separation generally increases with decreasing energy. Furthermore, the energies of importance to the integral in Eq. \( (3) \) decrease with decreasing temperature. Thus, the relevant transition state separation increases with decreasing temperature. At low enough temperatures (which are still higher than the rotational constants of the fragments so that the classical treatment is applicable) the following condition is satisfied:

\[
\mu R^2 \gg I_i^{(k)}, \quad k = 1, 2.
\]

In this long-range transition state situation, it is easy to show that the system as a whole has one small principal moment of inertia \( I_i^{(tot)} \),

\[
I_i^{(tot)} \approx I_n^{(1)} + I_n^{(2)} + I_3^{(tot)} \approx \mu R^2,
\]

and two large ones, which are approximately equal

\[
I_2^{(tot)} \approx I_3^{(tot)} \approx \mu R^2
\]

The axis which is associated with the small principal moment of inertia is directed along the unit vector \( n \) between
the centers of mass of the fragments. In Eq. (10) $\mathcal{I}^{(k)}_n$ denotes
the moment of inertia for the $k$th fragment relative to the axis $n$ (which is not the principal one and depends on the con-
figuration $\mathcal{O}$ of the reactive complex).

Using Eqs. (10) and (11) the average $\langle \cdots \rangle_{\mathcal{O}}$ in Eq. (7) can be rewritten as
\[
\int_0^{\pi/2} \left[ E - V(\mathcal{O}, R) - J^2 \cos^2 \theta / 2 \mathcal{I}_{1,1}^{(tot)} \right. \\
- \frac{1}{2} \left( 1 - \cos^2 \theta / 2 \mu R^2 \right)^{1/2} \sin \theta d\theta.
\]
As we will see the main contribution to the rate constant comes from a large $J$, in particular,
\[
J^2 / \mu R^2 \sim E.
\]

Then, because of the condition $\mathcal{I}_{1,1}^{(tot)} \ll \mu R^2$ [cf. Eq. (9)], the main contribution to the integral in Eq. (12) comes from a small range of $\theta$ around $\pi/2$, and the integral over $\theta$ reduces to
\[
\sqrt{\frac{\pi}{2} \Gamma(n/2 - 1/2)} \mathcal{I}_{1,1}^{(tot)} J [E - V(\mathcal{O}, R) - J^2 / 2 \mu R^2]^{(n-3)/2}.
\]
Substituting Eqs. (10), (11), and (13) back into Eq. (7), one obtains
\[
N(E,J|R,\mathcal{O}) = \frac{2 \prod_{k=1}^{v} \sqrt{2 \mathcal{I}_{1,1}^{(k)}}}{\pi^{2-n} \Gamma(n/2 - 1/2)} J [E - V(\mathcal{O}, R) - J^2 / 2 \mu R^2]^{(n-3)/2}.
\]

**B. Rate expressions**

We introduce a new parameter $X$ and a new auxiliary function $N_s(E,X|R)$, which, up to a constant, coincides with the number of states per unit $X$,
\[
X = \frac{J^2}{2\mu},
\]
where
\[
N_s(E,X) = \{ E - V(\mathcal{O}, R) - X/R^2 \}^{(n-3)/2}_{\mathcal{O}}.
\]

Then, the expression for the rate Eq. (2) can be rewritten in the long-range transition state approximation as
\[
k(T) = \frac{\sqrt{8 \pi \mu^{-1/2} T^{-v/2}}}{\Gamma(n/2 - 1/2)} \int_0^{\infty} dE e^{-E/T} \int_0^{\infty} dX N_s(E,X),
\]
where we have made use of Eq. (4).

Equations (16) and (18) provide a simple and reasonably accurate (we will see that the accuracy of the method is better than 10%) means to calculate rate constants for reactions that have a loose transition state. One notes that this $\mu J$-VTST expression for the rate, Eq. (18), does not depend on the moments of inertia of the fragments but depends only on the dimensionality of the whole system, $v$.

The function $N_s(E,X)$, Eq. (17), monotonically decreases with $X$ at a fixed energy $E$, reaching zero at some $X=X_0(E)$. At $X_0$ the function $E-V(\mathcal{O},R)-X/R^2$ becomes completely negative for the first time at some $R=R_0(E)$. Thus, both the function $E-V_{\min}(R)-X/R^2$, where $V_{\min}(R) = \min_{X} V(\mathcal{O},R)$, and its derivative are equal to zero at this point:
\[
E - V_{\min}(R_0) = X_0/R_0^2 = 0,
\]
\[
dV_{\min} / dR \bigg|_{R=R_0} = -2X_0 / R_0^3 = 0,
\]
which can be rewritten as
\[
E - V_{\min}(R_0) = \frac{R_0^2}{2} \frac{dV_{\min}}{dR} \bigg|_{R=R_0} = 0,
\]
\[
X_0 = \frac{R_0^2}{2} \frac{dV_{\min}}{dR} \bigg|_{R=R_0}.
\]
Thus, the integral over $X$ in Eq. (18) is actually taken from 0 to $X_0(E)$, Eq. (22). The transition state distance $R(E,X)$ typically decreases with $X$ at a given energy $E$, being at infinity at $X=0$ and reaching $R_0$, as specified by Eq. (21), at $X=X_0$.

We have also derived related microcanonical (E-resolved) and canonical expressions, since they are commonly used and do provide some conceptual simplifications. The microcanonical number of states $N_{\mu,VTST}(E|R)$ is given by
\[
N_{\mu,VTST}(E|R) = \mu R^2 2^{v/2-2} \prod_{k=1}^{v} \sqrt{2 \mathcal{I}_{1,1}^{(k)}}
\]
\[
\frac{\Gamma(n/2 + 1/2)}{\lim_{n \to \infty} \Gamma(n/2 - 1/2)} \times [E - V(\mathcal{O},R)]^{(n-1)/2}_{\mathcal{O}}.
\]
Substituting Eqs. (4) and (23) into Eq. (2), one obtains the following expression for the $\mu$-VTST rate constant
\[
k_{\mu,VTST}(T) = \sqrt{8 \pi \mu^{-1/2} T^{-v/2}} \int_0^{\infty} N_s(E)e^{-E/T} dE,
\]
where $N_s(E)$ is, up to a constant, the microcanonical number of states:
\[
N_s(E|R) = R^2 [E - V(\mathcal{O},R)]^{(n-1)/2}_{\mathcal{O}},
\]
\[
N_s(E) = \min_{R} N_s(E|R).
\]

The canonical partition function $Q_{\mathcal{C},VTST}(T,R)$ is given by
\[
Q_{\mathcal{C},VTST}(T,R) = 2 \pi^{v/2-2} T^{-v/2} \mu R^2 \prod_{k=1}^{v} \sqrt{2 \mathcal{I}_{1,1}^{(k)}}
\]
\[
\times \langle e^{-V(\mathcal{O},R)/T} \rangle_{\mathcal{O}}.
\]
Substituting Eqs. (4) and (27) into Eq. (2) one obtains the following expression for the canonical rate constant
\[ k_{\text{C-VTST}}(T) = \sqrt{8\pi \mu}^{-1/2} T^{1/2} N^0_T, \]  \hspace{1cm} (28)

where \( N^0_T \) is, up to a constant, the canonical number of states:
\[ N_f(R) = R^3 \left( e^{-V(O,R)/T} \right)_O, \]  \hspace{1cm} (29)
\[ N^0_f = \min N_f(R). \]  \hspace{1cm} (30)

\section*{C. Long-range potentials and the low-temperature regime}

The long-range potential consists of several terms, which represent multipole, induced-dipole, and dispersion interactions,\textsuperscript{44} and have a power-law dependence on the interfragment separation \( R \):
\[ V(O,R) = \sum_n \frac{U^{(n)}(O)}{R^n}. \]  \hspace{1cm} (31)

At low temperatures the transition state distances are large (see the discussion above). The most slowly decaying term then makes the main contribution to the potential and the other terms may be neglected:
\[ V(O,R) = \frac{V_0 f(O)}{R^n}, \]  \hspace{1cm} (32)

where the dimensionless function \( f(O) \) characterizes the angular dependence of the potential and \( V_0 \) is a dimensional constant, which characterizes the strength of the potential.

To find the dependence of \( N^0_f(E,X) \) on \( E \) for the potential given by Eq. (32) it is convenient to introduce the dimensionless variables
\[ \tilde{R} = R(E/V_0)^{1/n}, \quad \tilde{X} = X E^{2n-1} V_0^{-2/n}. \]  \hspace{1cm} (33)

It is easy to see then that
\[ N^0_f(X) = E^{(n-3)/2} \tilde{N}^0_f(\tilde{X}), \]  \hspace{1cm} (34)

where \( \tilde{N}^0_f(\tilde{X}) \) corresponds to a reference system with energy \( E=1 \) and \( V_0=1 \):
\[ \tilde{N}_f(\tilde{X}) = \langle 1 - f(O)/\tilde{R}^n - \tilde{X}/\tilde{R}^2 \rangle_{\tilde{X}}, \]  \hspace{1cm} (35)
\[ \tilde{N}^0_f(\tilde{X}) = \min_{\tilde{R}} \tilde{N}_f(\tilde{X}/\tilde{R}). \]  \hspace{1cm} (36)

Substituting Eqs. (33) and (34) into Eq. (18) one obtains the following expression for the \( \mu J \)-VTST rate at low temperatures:
\[ k(T) = C_1 \mu^{-1/2} V_0^{2/n} T^{1/2-2/n}, \]  \hspace{1cm} (37)
\[ C_1 = \frac{\Gamma(\nu/2 + 1/2 - 2/n)}{(8\pi)^{-1/2} \Gamma(\nu/2 - 1/2)} \int_{0}^{\infty} \tilde{N}^0_f(\tilde{X})d\tilde{X}. \]  \hspace{1cm} (38)

Similarly, the microcanonical number of states \( N^0_f(E) \), Eq. (26), can be represented as
\[ N^0_f(E) = \tilde{N}^0_f(E^{(1-n)/2-2/n} V_0^{2/n}). \]  \hspace{1cm} (39)

Then, the \( \mu \)-VTST expression for the rate constant, Eq. (24), can be written as
\[ k_{\mu \text{-VTST}}(T) = C_2 \mu^{-1/2} V_0^{2/n} T^{1/2-2/n}. \]  \hspace{1cm} (40)
\[ C_2 = \frac{\Gamma(\nu/2 + 1/2 - 2/n)}{(8\pi)^{-1/2} \Gamma(\nu/2 + 1/2)} \tilde{N}_E. \]  \hspace{1cm} (41)

The canonical number of states \( N^0_T \), Eq. (30), can be expressed as
\[ N^0_f = \tilde{N}^0_f T^{-2/n} V_0^{2/n}. \]  \hspace{1cm} (42)

where \( \tilde{N}^0_f \) corresponds to a reference system with temperature \( T=1 \) and \( V_0=1 \):
\[ \tilde{N}_f(\tilde{R}) = \tilde{R}^2 \langle 1 - f(O)/\tilde{R}^n - \tilde{X}/\tilde{R}^2 \rangle_{\tilde{X}}, \quad \tilde{R} = R/E^{1/n}, \]  \hspace{1cm} (43)
\[ \tilde{N}^0_f = \min_{\tilde{R}} \tilde{N}_f(\tilde{R}). \]  \hspace{1cm} (44)

Then, the canonical expression for the rate constant, Eq. (28), can be rewritten as
\[ k_{\text{C-VTST}}(T) = C_3 \mu^{-1/2} V_0^{2/n} T^{1/2-2/n}. \]  \hspace{1cm} (45)
\[ C_3 = \sqrt{8\pi \tilde{N}^0_f}. \]  \hspace{1cm} (46)

It is worth noting that the canonical expression for the rate constant does not depend on the dimensionality of the reactive complex.

The applicability conditions of Eqs. (37), (42), and (47) are given by Eq. (9) and by the condition that in the transition state the first term in the long-range interaction, Eq. (32), dominates over the remaining ones, including the chemical one. The distances which satisfy the latter condition are relatively large, so Eq. (9) is usually automatically satisfied.\textsuperscript{45} The specific value of the interfragment distance \( R_{lr} \) at which the chemical bonding becomes similar in magnitude to the long-range interaction is different for different systems. Nevertheless, we consider the value \( R_{lr} = 10 \) bohr to be fairly representative of this distance and use this value in making estimates of the range of applicability. The transition state distance can be estimated as \( R^* = R^*(V_0/T)^{1/n} \) [cf. Eq. (45)], where the numerical value of \( R^* \) is of the order of unity (see below for the estimates of \( \tilde{R}^* \) for the specific interaction potentials). Thus, the applicability condition of the considered approach can be simply expressed as
\[ T \leq V_0/R_{traj}^2 \leq V_0/10^s, \]  
(49)

with \( V_0 \) generally being on the order of unity in atomic units. From this equation one can see that the range of temperatures at which the derived expressions are applicable is generally largest for the charge-dipole interaction and it decreases by a factor of ten with each successive order.

**D. Classical trajectory method**

Classical trajectory calculations of the capture rate constant were performed for charge-dipole, charge-quadrupole, dipole-dipole, and dipole-quadrupole interaction potentials for some exemplary systems. These simulations were used to explore the accuracy of the transition state theory expressions, Eqs. (37), (42), and (47), for the capture process governed by long-range interactions. The classical trajectory method we use was briefly described earlier in Refs. 4, 5, and 46. The reaction rate constant \( k_{\text{traj}} \) is represented as

\[ k_{\text{traj}} = \kappa \cdot k_T, \]  
(50)

where \( k_T \) is the transition state theory rate expression for a predefined dividing surface for a given temperature and \( \kappa \) is the recrossing factor, which is defined as the ratio of the reactive trajectories initiated on the chosen dividing surface to the total number of the trajectories. The initial conditions for the trajectories are statistically weighted, with the reactive flux used as a weighting factor. The method of Keck of initiating trajectories at an approximate C-VTST dividing surface for a given temperature is employed,20 which allows one to decrease the fraction of nonreactive trajectories and, consequently, increase the accuracy of the recrossing factor calculation.

Each trajectory is propagated first forward in time (the initial generalized velocities of the reactive complex are chosen so that at the first moment the fragments propagate inward from the dividing surface). The trajectory is deemed to be reactive if the potential energy of the complex drops below a predefined level \( E_{\text{min}} \), and nonreactive if the trajectory recrosses the dividing surface. Any trajectory found reactive by the forward propagation is then propagated backward in time. It is then deemed to be fully reactive if the interfragment distance exceeds a certain value, and nonreactive if the potential energy drops below \( E_{\text{min}} \). A set of \( E_{\text{min}} \) values is considered, and the recrossing factor is calculated as a function of \( E_{\text{min}} \). When this function reaches a plateau value at low enough energies, the no-return condition is deemed to be satisfied, and the value of the recrossing factor is accepted.

20 000 trajectories were run for each temperature, which yields a statistical error in the recrossing factor of less than 0.7%, assuming, as was generally the case, that \( \kappa > 0.5 \). The transition state theory calculations of \( k_T \) in Eq. (50) were performed with an accuracy of 0.5%, so that the total error of \( k_{\text{traj}} \) was less than 1%. It was found that within the accuracy of the classical trajectory calculation the dependence of the rate constant on the temperature follows the power law,

\[ k_{\text{traj}} = C_{\text{traj}} \mu^{-1/2} V_0^{2/n} T^{1/2-2/n}, \]  
(51)

for all considered potentials and temperature intervals. Therefore, only the value of the proportionality constant \( C_{\text{traj}} \) will be reported.

**III. SPECIFIC LONG-RANGE INTERACTIONS**

In this section Eqs. (37), (42), and (47) are applied to several important multipole interaction potentials, and the resultant expressions are compared with the results of classical trajectory calculations.

**A. Isotropic interactions**

The reactive event in this situation is effectively reduced to an atom-atom collision and is analytically solvable. The application of the present VTST methodology to this system demonstrates its simplicity as well as the effect of angular momentum conservation within transition state theory. The potential \( V(O,R) \) is orientationally independent,

\[ V(R) = -\frac{V_0}{R^n}. \]  
(52)

Using Eqs. (35) and (36) one arrives at the following expression for \( \tilde{N}_s(X) \):

\[ \tilde{N}_s(X) = (1 - A \cdot \tilde{X}^{n(-2)})(r-3/2), \quad A = (2/n)^{2(n-2)}(1 - 2/n). \]  
(53)

The transition state distance \( \tilde{R}_s \) as a function of \( \tilde{X} \) is given by

\[ \tilde{R}_s(\tilde{X}) = (2\tilde{X}/n)^{-1/(n-2)}. \]  
(54)

Substituting Eq. (53) into Eq. (38) one obtains the following expression for the capture rate constant,

\[ k(T) = (8\pi)^{1/2} \left( \frac{n-2}{2} \right)^{2n} \Gamma(1 - 2/n) \mu^{-1/2} V_0^{2/n} T^{1/2-2/n}. \]  
(55)

It is interesting to note that even though the function \( \tilde{N}_s(X) \) depends on the dimensionality \( n \) of the system, the final result does not. The explanation for this fact is that with isotropic potentials the inclusion of additional degrees of freedom, while changing the \( E, J \)-resolved number of states, cf. Eq. (53), does not change the transition state separation, cf. Eq. (54). As a result, the new transition state partition function, Eq. (3), becomes a simple product of the original transition state partition function with the partition function of the additional modes, which cancels with the corresponding partition function for the reactants.

Two important specific cases are the charge-induced-dipole interaction and the dispersion interaction. For the charge-induced-dipole interaction, substituting \( V_0 = \alpha q^2/2 \) (\( q \) is the charge of the ionic fragment and \( \alpha \) is a polarizability of the other fragment, which is assumed to be isotropic) and \( n=4 \) into Eq. (55) one arrives at the famous Langevin expression.9
Similarly, for the case of the dispersion interaction, substituting result of a \( m \) approximation will be made here. 

\[
k(T) = k_L = 2 \pi q \sqrt{\alpha/m}. \tag{56}
\]

Similarly, for the case of the dispersion interaction, substituting \( V_0 = C_6 \) and \( n = 6 \) one obtains

\[
k(T) = 8.55 \mu^{-1/2} C_6^{1/3} T^{1/6}. \tag{57}
\]

This result bears some relation to earlier Gorin model results.\(^{48,49}\) For practical purposes the dispersion coefficient \( C_6 \) is often approximated as 1.5 \( \alpha_1 \alpha_2 E_1 E_2 / (E_1 + E_2) \), where \( \alpha_i \) are the polarizabilities of the fragments and \( E_i \) are approximated as the ionization energies of the fragments.\(^{50}\) This approximation will be made here.

It is instructive to compare Eq. (55) with the corresponding result of a \( \mu \)-VTST calculation. Substituting Eq. (52) into Eqs. (40) and (41) one obtains the following expression for \( \tilde{N}_E \):

\[
\tilde{N}_E = [n(n - 1)/4]^{(v - 1)/2} [n(n - 1)/4 - 1]^{(2/n - (v - 1)/2}. \tag{58}
\]

For the charge-induced-dipole interaction, \( n = 4 \), substituting Eq. (58) into Eq. (42) and assuming that \( \nu = 5 \) (atom + linear molecule) one obtains\(^{28}\)

\[
k_{\mu\text{-VTST}} = \frac{2}{\sqrt{3}} k_L. \tag{59}
\]

Thus, the \( \mu \)-VTST rate constant differs from the \( \mu J \)-VTST one by ca. 15% in this case. If, instead, the polarizable fragment is nonlinear with \( \nu = 6 \), then the \( \mu \)-VTST rate constant is 1.19 times the \( \mu J \)-VTST one.

The difference between Eq. (59) and the Langevin rate constant, Eq. (56), was explained by the presence of the uncoupled modes (the internal rotational modes of the linear fragment in this case) that are included in the VTST treatment.\(^{28}\) We believe that this explanation is incorrect. As was discussed earlier, for isotropic potentials the inclusion of additional uncoupled modes does not change the rate constant. Rather, the difference between the microcanonical and \( E \), \( J \)-resolved treatments is related to the transition state dependence on the angular momentum, cf. Eq. (54). The \( \mu \)-VTST treatment, which does not take this dependence into account, does not fully minimize the reactive flux and, as a consequence, gives an approximate result. One also notes that for isotropic potentials the microcanonical transition state \( \tilde{R}_E \) and, as a consequence, the rate constant \( k_{\mu\text{-VTST}} \) depends on the dimensionality of the system \( \nu \) in contrast with \( \mu J \)-VTST. These effects should be considered as artifacts of the microcanonical implementation of the transition state theory.

Our results show that the \( \mu J \)-VTST calculation provides a considerable improvement over the \( \mu \)-VTST estimate of the rate [cf. Eq. (56) versus Eq. (59)] for the charge-induced-dipole interaction. This result differs from the conclusion from Ref. 28, where it was stated that taking into account the conservation of angular momentum gives little improvement over the \( \mu \)-VTST result.\(^{51}\)

Implementation of the present methodology at the canonical level again yields a rate constant that is independent of \( \nu \), but which is now 1.32 times the Langevin rate. The further increase in this estimate is due to the additional neglect of the dependence of the transition state separation on \( E \).

### B. Charge-dipole interaction

This is the simplest reactive system with an anisotropic interaction potential. The interaction potential is given by\(^{52}\)

\[
V(\theta, R) = - \frac{V_0 \cos \theta}{R^2}, \quad V_0 = qd, \tag{60}
\]

where \( q \) is the charge of the first fragment and \( d \) is the permanent dipole moment of the second fragment. First, we consider the atom + linear molecule reactive complex. Using Eqs. (35) and (36) the following expression for \( \tilde{N}_E' (\tilde{X}) \) is obtained

\[
\tilde{N}_E' (\tilde{X}) = 1 - \tilde{X}, \quad \tilde{X} < 1. \tag{61}
\]

The transition state distance \( \tilde{R}^* \) is given by
The rate constant is obtained

$$k(T) = \sqrt{2\pi q d\mu^{-1/2}} T^{-1/2}.$$  \hspace{1cm} (63)

This expression coincides, within numerical accuracy, to the results of the classical trajectory calculations summarized below.

The \(\mu\)-VTST calculation is performed using Eqs. (40)–(42). Substituting the potential, Eq. (60), into Eq. (40) one obtains

$$N^\prime = 1.125,$$

$$\vec{R}^\prime = 1/\sqrt{2}.$$  \hspace{1cm} (65)

Substituting these equations into Eq. (42) one obtains

$$k_{\mu-VTST}(T) = 1.125\sqrt{2\pi q d\mu^{-1/2}} T^{-1/2}.$$  \hspace{1cm} (66)

Comparing Eqs. (63) and (66) one sees that, again, the \(\mu\)-VTST rate constant is ca. 12% higher than its \(\muJ\)-VTST analog.

The effects of the dimensionality of the reactive complex\(^{47}\) as well as the results of the different levels of transition state theory calculation for the charge-dipole interaction are summarized in Table III, where the proportionality constants from Eqs. (37), (42), and (47) are shown together with the dimensionless microcanonical and canonical transition state distances. The \(\mu\)-VTST expression is seen to also differ from the \(\muJ\)-VTST one by ca. 12% for the nonlinear dipole. The \(\muJ\)-VTST rate constant for a linear dipole differs from the one for a nonlinear dipole by ca. 7%.

The dependence of the transition state distance on the angular momentum is shown in Fig. 1 for both linear and nonlinear polar fragments. From Fig. 1 one can see that the dimensionality of the reactive complex affects the position of the transition state. This conclusion is consistent with the earlier notion that it is only for isotropic potentials that the presence of additional modes leaves the transition state position and, therefore, the rate constant unchanged. As was shown earlier for a linear dipole, at large values of the angular momentum the transition state collapses, which means that higher-order terms in the potential expansion, Eq. (31), should be used. However, the contribution from this region to the integral number of states is negligibly small, cf. Fig. 2.

The classical trajectory calculations were performed for both the linear and nonlinear polar fragments. For the linear polar fragment it was found that \(C_{\text{traj}}=2.48\), in agreement with the results of Ref. 53. If the polar fragment is nonlinear, \(C_{\text{traj}}\) was found to depend weakly on the moments of inertia of the fragment as well as on the orientations of the dipole moment in the fragment molecular frame. Some examples are shown in Table IV.\(^{54}\) The difference between the classical trajectory calculation and the \(\muJ\)-VTST rate constant is seen to be 1%–2% for the linear polar fragment and about 6% for the nonlinear polar fragment.

### C. Charge-quadrupole interaction

For linear molecules the permanent quadrupole tensor can be represented as

$$Q_{ij} = \frac{Q}{2}(3n_i n_j - \delta_{ij}),$$  \hspace{1cm} (67)

where \(n_i\) are the components of the unit vector directed along the molecular axis. In this case the charge-quadrupole interaction potential is given by\(^{52}\)

$$V(\theta,R) = \frac{V_0}{4R^2}(3\cos^2 \theta - 1), \hspace{0.5cm} V_0 = qQ.$$  \hspace{1cm} (68)

The rate constant for the reaction controlled by the charge-quadrupole interaction can be written as [cf. Eqs. (37), (42), (47), and (51)].

### Table V. VTST parameters for charge-linear quadrupole interaction.

<table>
<thead>
<tr>
<th>(V_0)</th>
<th>(C_1)</th>
<th>(C_2)</th>
<th>(C_3)</th>
<th>(\vec{R}_{1}^d)</th>
<th>(\vec{R}_{1}^i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;0</td>
<td>1.97</td>
<td>2.05</td>
<td>2.71</td>
<td>0.66</td>
<td>0.60</td>
</tr>
<tr>
<td>&lt;0</td>
<td>2.07</td>
<td>2.08</td>
<td>3.04</td>
<td>0.68</td>
<td>0.66</td>
</tr>
</tbody>
</table>

### Table VI. VTST parameters for dipole-dipole interaction.

<table>
<thead>
<tr>
<th>(\nu)</th>
<th>(C_1)</th>
<th>(C_2)</th>
<th>(C_3)</th>
<th>(\vec{R}_{1}^d)</th>
<th>(\vec{R}_{1}^i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>5.27</td>
<td>5.51</td>
<td>6.88</td>
<td>1.26</td>
<td>0.99</td>
</tr>
<tr>
<td>8</td>
<td>5.36</td>
<td>5.73</td>
<td>6.88</td>
<td>1.35</td>
<td>0.99</td>
</tr>
<tr>
<td>9</td>
<td>5.42</td>
<td>5.87</td>
<td>6.88</td>
<td>1.43</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Different signs of $V_0=qQ$ correspond to different reaction kinetics and should be considered separately. The coefficients in the $\mu$J-VTST, $\mu$-VTST, and canonical rate expressions, Eqs. (38), (43), and (48), are shown in Table V for a linear fragment with a quadrupole moment.

The dependence of the transition state separation and the number of states on the angular momentum is shown in Figs. 3 and 4, respectively. The difference between the $\mu$J-VTST rate constant and that of the $\mu$-VTST comes from the dependence of the transition state on the angular momentum. It is interesting to note that for the charge-quadrupole interaction with $V_0<0$ the transition state position is almost independent of the angular momentum, cf. Fig. 3. As a result, the $\mu$-VTST rate constant and that of the $\mu$J-VTST differ by less than 1% for such a system, cf. Table V and Fig. 5. In general, with increasing order of multipole interaction the transition state becomes less sensitive to the angular momentum and, as a result, the difference between the $\mu$J-VTST and $\mu$-VTST rate constants decreases.

For nonlinear molecules Eqs. (67) and (68) are valid if the molecule has a rotational symmetry axis of order three or higher. In the general situation the interaction cannot be completely described by a single parameter. The rate constant, however, can still be represented by Eq. (69) where one should equate $Q$ with $Q_{zz}$, the largest principal quadrupole moment of the molecule. The proportionality constant $C^{(\omega)}$ in Eq. (69) then depends on the asymmetry parameter $\Delta$, which is defined as

$$\Delta = \frac{Q_{xx} - Q_{zz}}{Q_{zz}}, \quad 0 < \Delta < 1,$$

where $|Q_{zz}| < |Q_{xx}| < |Q_{yy}|$ are the principal quadrupole moments of the molecule. In Fig. 5 the dependence of $C^{(\omega)}$ on $\Delta$ is shown for the $\mu$J-VTST, $\mu$-VTST, and C-VTST levels of theory. One can see that the effect of the quadrupole asymmetry is more pronounced for the positive interaction, $qQ > 0$, and can increase the rate constant by at most ca. 18%.

### D. Dipole-dipole interaction

The dipole-dipole interaction potential can be written as

$$V(\theta_1, \theta_2, \phi, R) = \frac{V_0}{R^3} (\sin \theta_1 \sin \theta_2 \cos \phi - 2 \cos \theta_1 \cos \theta_2), \quad V_0 = d_id_j,$$

where $d_i$, $i=1, 2$, is the permanent dipole moment of the $i$th fragment.

The rate constant for the reaction controlled by the dipole-dipole interaction, Eq. (71), can be written as [cf. Eqs. (37), (42), (47), and (51)]
The proportionality constants for the $\mu J$-VTST [$C_1$, Eq. (38)], $\mu$-VTST [$C_2$, Eq. (43)], and canonical [$C_3$, Eq. (48)] expressions are shown in Table VI for all possible dimensions of the fragments. The important feature of the VTST rate expressions, Eqs. (37), (42), and (47), for the dipole-dipole interaction is that they depend on a single parameter $d_1d_2$, characterizing the strength of the dipole-dipole interaction, and do not depend on the orientation of the dipole moments in the fragment molecular frames. From Table VI one can see that for the dipole-dipole interaction the dimensionality effects are small: The difference between the $\mu J$-VTST rate constants for two linear versus two nonlinear fragments is less than 3%.

The dependence of the transition state distance and the number of states on the angular momentum parameter is shown in Figs. 6 and 7, respectively. The transition state distance decreases slowly with increasing angular momentum, except in a narrow region of small angular momenta where it rapidly contracts from infinity at $J = 0$ (no barrier) to $\tilde{R} \approx 1.5$.

The classical trajectory calculations were performed for both linear and nonlinear fragments. For two linear fragments the proportionality constant was found to be $C_{\text{traj}} = 4.77$, which agrees with the results of Ref. 55. For nonlinear fragments the proportionality constant $C_{\text{traj}}$ in Eq. (51) was found to weakly depend on the moments of inertia of the fragments as well as on the orientations of the dipole moments in the molecular frames of the fragments. Some examples are shown in Table VII.\(^{54}\)

---

**TABLE VII.** Classical trajectory calculation results for some reactive systems with dipole-dipole interaction.

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$C_{\text{traj}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$O</td>
<td>CH</td>
<td>4.89</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>NaO</td>
<td>5.02</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>CH</td>
<td>4.85</td>
</tr>
</tbody>
</table>

$^a$Equation (51).

$$k = C\mu^{-1/2}(d_1d_2)^{2/3}T^{-1/6}. \quad (72)$$

E. Dipole-quadrupole interaction

The dipole-quadrupole interaction is so weak that the present approach is only applicable to temperatures of the order of 30 K or lower [cf. Eq. (49)]. Nevertheless, even at higher temperatures the result should still be qualitatively useful.

The dipole-quadrupole interaction potential can be written as\(^{52}\)

$$V(\theta_d, \theta_Q, \phi, R) = \frac{3V_0}{4R^4}(3 \cos \theta_d \cos^2 \theta_Q - \cos \theta_d$$

$$- \sin \theta_d \sin 2\theta_Q \cos \phi), \quad V_0 = dQ, \quad (73)$$

where $d$ and $Q$ are the permanent dipole and quadrupole moments of the fragments, assuming that the quadrupole tensor has the form given by Eq. (67).

The rate constant for the reaction controlled by the dipole-quadrupole interaction does not depend on the temperature and can be written as [cf. Eqs. (37), (42), (47), and (51)]

$$k = C\mu^{-1/2}|dQ|^{1/2}. \quad (74)$$

The proportionality constants for the $\mu J$-VTST [$C_1$, Eq. (38)], $\mu$-VTST [$C_2$, Eq. (43)], and canonical [$C_3$, Eq. (48)] expressions are shown in Table VIII for all possible dimensions of the fragments.

The dependence of the transition state separation and the number of states on the angular momentum parameter is shown in Figs. 8 and 9, respectively. One can see from Fig. 8 that the dependence of the transition state separation on the angular momentum for the dipole-quadrupole interaction is weak and, as a result, the $\mu J$-VTST and $\mu$-VTST rate constants differ by no more than 3%, cf. Table VIII.

As with the charge-quadrupole interaction, Eq. (73) should be generalized for molecules which do not have a symmetry axis of order three or higher. The proportionality

---

**TABLE VIII.** VTST parameters for dipole-quadrupole interaction.

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$\tilde{R}_0^2$</th>
<th>$\tilde{R}_0^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>4.43</td>
<td>4.53</td>
<td>5.38</td>
<td>1.11</td>
<td>0.91</td>
</tr>
<tr>
<td>8</td>
<td>4.49</td>
<td>4.65</td>
<td>5.38</td>
<td>1.17</td>
<td>0.91</td>
</tr>
<tr>
<td>9</td>
<td>4.53</td>
<td>4.74</td>
<td>5.38</td>
<td>1.22</td>
<td>0.91</td>
</tr>
</tbody>
</table>
constant $C$ in Eq. (74) then becomes a function of the quadrupole asymmetry parameter $\Delta$, Eq. (70), and $Q$ must be understood as the biggest principal quadrupole moment of the molecule. In Fig. 10 the dependence of $C$ on $\Delta$ is shown for the $\mu$J-VTST, $\mu$-VTST, and $C$-VTST levels of the theory. The dependence of the rate constant on the quadrupole asymmetry is again quite weak, being less than 9% in this case.

Quadrupole-quadrupole and higher-order interactions are dominated in the transition state region by short-range interactions already at very low temperatures. Thus, such interactions are not considered here.

F. Dipole-induced-dipole interaction

The polarizability of some, especially bigger, molecules can be of the order of 100 bohr$^3$. As a result, the dipole-induced-dipole interaction may provide a comparable contribution to the leading order term in the expansion (31), or even dominate when the temperature is not too low.

The dipole-induced-dipole interaction potential can be written as

$$V(\theta, R) = -\frac{V_0}{2R^6} (1 + 3 \cos^2 \theta), \quad V_0 = d^2 \alpha,$$  \hspace{1cm} (75)

where $d$ is the permanent dipole moment of the first fragment and $\alpha$ is the polarizability of the second fragment, which is assumed isotropic.

The rate constant for the reaction controlled by the dipole-induced-dipole interaction, Eq. (75), can be written as [cf. Eqs. (37), (42), (47), and (51)]

$$k = C \mu^{-1/2} (d^2 \alpha)^{1/3} T^{1/6}. \hspace{1cm} (76)$$

The proportionality constants for the $\mu$J-VTST [$C_1$, Eq. (38)], $\mu$-VTST [$C_2$, Eq. (43)], and canonical [$C_3$, Eq. (48)] expressions are shown in Table IX for all possible dimensions of the fragments.

The dependence of the transition state distance and the number of states on the angular momentum parameter is shown in Figs. 11 and 12, respectively.

IV. EXPERIMENTAL DATA ANALYSIS

Long-range transition state theory predictions for the rate coefficient should be most meaningful in the temperature range from about 10 to 100 K. That is, at temperatures that are not too low for quantum statistical effects to be important and not too high for shorter-range potential interactions to be important. Smith has recently observed the reaction rate for a wide variety of reactions down to temperatures of 10 to 25 K. A comparison of the present theoretical predictions with these experimental observations, which are primarily for radical molecule reactions, is provided in Table X. This comparison serves to illustrate the utility of the present theoretical analysis in obtaining a qualitative understanding of the factors affecting the kinetics.

In the theoretical analysis we have considered four separate long-range potential forms: the dipole-dipole interaction, the dipole-quadrupole interaction, the dipole-induced-dipole interaction, and the dispersion interaction. We have also considered a sum term consisting of these four terms (including both pairs of dipole-quadrupole and dipole-dipole interactions when both fragments have a permanent dipole moment), as well as the quadrupole-quadrupole interaction. The parameters for the first three terms were obtained from the three-parameter Becke–Lee–Yang–Parr (B3LYP) density-functional theory employing Dunning’s augmented correlation-consistent polarized valence triple-zeta basis set. The ionization potentials for the estimate of the dispersion coefficient were taken from the National Institute of Standards and Technology (NIST) database.

When both reactants have a permanent dipole moment, the dipole-dipole interaction is the longest-ranged term in the potential expansion ($\propto 1/R^6$) and should determine the low-temperature capture rate. In the absence of a permanent dipole-moment for one of the molecules, the dipole-quadrupole interaction is the longest-ranged term in the potential ($\propto 1/R^3$). The dipole-induced-dipole and dispersion interactions are not considered here.
interactions, although of shorter range \((\propto 1/R^6)\), might still be of importance in the 10–100-K range due to their different form and particularly their larger potential constants \(V_0\). The dipole-dipole interaction yields a rate coefficient proportional to \(T^{−1/6}\), while the dipole-quadrupole interaction yields a temperature-independent rate coefficient, and both the dipole-induced-dipole and dispersion terms yield a rate coefficient proportional to \(T^{1/6}\).

Focusing initially on the different theoretical predictions, we note that the four separate terms are of remarkably similar magnitude. The maximum and minimum of the four terms for a given reaction generally differ by only about a factor of two to three (or at least when they are not identically zero). The capture rate for the dispersion interaction generally dominates at the lowest temperature studied experimentally. At even lower temperatures, the dipole-dipole (or dipole-quadrupole when one of the fragments does not have a permanent dipole moment) rate gradually becomes the dominant one, typically before 1 K. Meanwhile, the dipole-induced-dipole interaction generally yields the lowest rate estimate. The dominance of the dispersion interaction, as well as the quite large contribution from the dipole-induced-dipole term, are due to the relatively large magnitude of the polarizabilities (~10–50 bohr³) compared with the permanent moments of the molecules studied here (i.e., dipole moments of less than 1 a.u. and quadrupole moments between 1 and 10 a.u.). The somewhat larger size for the quadrupole moment as compared to the dipole moment is responsible for the similarity in the dipole-dipole and dipole-quadrupole capture rates.

The similar magnitude of the four capture rates considered here suggests that quantitative \(a\ priori\) predictions for the rate in the 10–100-K range should consider potentials incorporating at least these four potential terms. Importantly, the predicted rate for such a potential is not just the sum of the four individual predictions, because the rates are not linearly related to the potential values and because the transition state location for different interactions is different. One might also ponder whether terms involving the octapole (such as the dipole-octapole) or the quadrupole-quadrupole term are also important. The former seems very unlikely, given that the octapole moments have a similar magnitude to the dipole moments, which are typically less than 1 a.u. The quadrupole-quadrupole term may be of more importance, but is still probably dominated by the dipolar terms.

Unfortunately, the present analysis does not directly yield simple analytic results for a potential which is a sum of different long-range forms. Thus, we have simply calculated the rate from Eq. (18) for a potential consisting of the sum of the dipole-dipole interaction, the two dipole-quadrupole interactions, the two dipole-induced-dipole interactions, the quadrupole-quadrupole interaction, and the dispersion interaction. The rates calculated with this cumulative potential, as reported in Table X, range from 1.02 to 1.35 times greater than that calculated for the dominant interaction alone. Perhaps most remarkable is how little variation there is in the predicted rate from system to system when all of the terms are considered together. A simple system-independent prediction of \((4.0 \pm 1.0) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) for the capture rate at 25 K encompasses all but three of the predictions. This invariance is even more striking when considering solely the dispersion term.

We turn now to a comparison of the predicted rates with the experimental results. The ratio of the theoretical capture rate for the full potential to the experimentally observed rate coefficient is always equal to or greater than unity. The greatest discrepancy from unity occurs for the reactions of OH with propene and with isoprene. In a detailed study of the related reaction of OH with C\(_2\)H\(_4\) we have recently observed that an inner saddle point, at negative energies on the addition pathway, yields a reduction in the predicted capture rate that persists down to temperatures as low as 20 K. At 58 K, the temperature of the OH + propene and OH + isoprene studies, the inner transition state reduces the C\(_2\)H\(_4\)+OH rate by a factor of three. Furthermore, it is quite possible that the observations are not in the high-pressure limit. The sharply decreasing nature of the OH + HBr rate coefficient with increasing temperature suggests that short-range interactions are likely important in that reaction as well. Similar, short-range effects may also explain a number of the more minor overestimates.

The best agreement between theory and experiment occurs for the CN reactions, with significant discrepancies arising for only the reactions with C\(_2\)H\(_6\) and O\(_2\). For the CN + C\(_2\)H\(_6\) reaction we have chosen to explore the adequacy of the long-range expansion via comparison with direct \(ab\ initio\) evaluations of the potential. The results plotted in Fig. 13 indicate reasonably good agreement between the present long-range predictions for the full potential and for spin-restricted second-order Møller–Plesset augmented correlation-consistent polarized valence triple-zeta (MP2/aug-cc-PVTZ) direct evaluations of the potentials. The minor discrepancy between these two rate predictions, which amounts to about 20% at 10 K, may simply be an indication of the limited accuracy of the crude estimate for the dispersion coefficient in terms of the ionization potentials and polarizabilities. Alternatively, it may be indicative of some inaccuracy in the \(ab\ initio\) simulations of the interaction energies or of the contribution of some additional long-range terms in the potential.

The agreement between the two long-range theoretical predictions for the CN+C\(_2\)H\(_6\) reaction strongly suggests that the deviation between theory and experiment for this reac-

FIG. 12. The number of states \(N_s\) as a function of the angular momentum parameter \(X\) for the dipole-induced-dipole interaction. \(v\) is the dimensionality of the reactive complex.
TABLE X. Long-range transition state theory predictions for the rate constants (10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) of experimentally studied low-temperature systems.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T °</th>
<th>Expt</th>
<th>D-D</th>
<th>D-Q</th>
<th>D-iD</th>
<th>Disp</th>
<th>Sum</th>
<th>Sum/Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH + HBr</td>
<td>23</td>
<td>1.07±0.04(^a)</td>
<td>6.00,3.56</td>
<td>3.39</td>
<td>0.89,1.50</td>
<td>1.58,2.66</td>
<td>4.8</td>
<td>4.49</td>
</tr>
<tr>
<td>OH + Propene</td>
<td>58</td>
<td>0.57±0.09(^j)</td>
<td>4.20,2.13</td>
<td>2.97</td>
<td>1.13,2.23</td>
<td>1.95,3.84</td>
<td>4.8</td>
<td>8.42</td>
</tr>
<tr>
<td>OH + 1-Butene</td>
<td>23</td>
<td>4.27±0.56(^k)</td>
<td>4.58,2.71</td>
<td>2.63</td>
<td>1.19,0.00</td>
<td>2.04,3.44</td>
<td>4.55</td>
<td>1.07</td>
</tr>
<tr>
<td>OH + 2-2-Butene</td>
<td>23</td>
<td>3.89±0.23(^k)</td>
<td>2.92,1.73</td>
<td>2.77</td>
<td>1.20,0.02</td>
<td>2.03,3.43</td>
<td>4.24</td>
<td>1.09</td>
</tr>
<tr>
<td>OH + E-2-Butene</td>
<td>23</td>
<td>4.52±0.32(^k)</td>
<td>0.0</td>
<td>2.76</td>
<td>1.20,0.03</td>
<td>2.04,3.44</td>
<td>4.18</td>
<td>0.92</td>
</tr>
<tr>
<td>OH + isoprene</td>
<td>58</td>
<td>0.78±0.12(^j)</td>
<td>2.86,1.45</td>
<td>3.85</td>
<td>1.27,2.50</td>
<td>2.15,4.23</td>
<td>5.54</td>
<td>7.10</td>
</tr>
<tr>
<td>CCH+O</td>
<td>15</td>
<td>1.05±0.02(^l)</td>
<td>0.0</td>
<td>0.76</td>
<td>0.40,0.64</td>
<td>1.77,2.78</td>
<td>2.83</td>
<td>2.70</td>
</tr>
<tr>
<td>CCH+C(_2)H(_2)</td>
<td>15</td>
<td>2.27±0.29(^j)</td>
<td>3.09</td>
<td>0.56,0.87</td>
<td>2.41,3.78</td>
<td>4.74</td>
<td>2.09</td>
<td></td>
</tr>
<tr>
<td>CCH+C(_2)H(_4)</td>
<td>15</td>
<td>2.17±0.17(^j)</td>
<td>2.17</td>
<td>0.82,0.91</td>
<td>2.47,3.88</td>
<td>4.24</td>
<td>1.95</td>
<td></td>
</tr>
<tr>
<td>CCH+C(_2)H(_6)</td>
<td>15</td>
<td>1.14±0.32(^j)</td>
<td>2.23,1.42</td>
<td>1.79</td>
<td>0.60,0.95</td>
<td>2.54,3.99</td>
<td>4.31</td>
<td>3.78</td>
</tr>
<tr>
<td>CCH+CH(_2)C(_2)H(_2)</td>
<td>63</td>
<td>2.9±0.3(^m)</td>
<td>3.52,1.77</td>
<td>2.60</td>
<td>0.59,1.17</td>
<td>2.51,5.01</td>
<td>5.66</td>
<td>1.95</td>
</tr>
<tr>
<td>CCH+CH(_2)C(_2)H(_2)</td>
<td>63</td>
<td>3.5±0.4(^m)</td>
<td>2.15</td>
<td>0.61,1.22</td>
<td>2.57,5.12</td>
<td>5.53</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>CN+O(_2)</td>
<td>10</td>
<td>1.34±0.07(^a)</td>
<td>0.0</td>
<td>1.00</td>
<td>0.59,0.90</td>
<td>1.69,2.59</td>
<td>2.64</td>
<td>1.97</td>
</tr>
<tr>
<td>CN+NH(_3)</td>
<td>25</td>
<td>4.09±0.20(^n)</td>
<td>9.32,5.45</td>
<td>3.21</td>
<td>0.93,1.59</td>
<td>2.16,3.70</td>
<td>6.33</td>
<td>1.55</td>
</tr>
<tr>
<td>CN+C(_2)H(_2)</td>
<td>25</td>
<td>4.60±0.25(^o)</td>
<td>0.0</td>
<td>4.08</td>
<td>0.81,1.38</td>
<td>2.30,3.94</td>
<td>4.98</td>
<td>1.08</td>
</tr>
<tr>
<td>CN+C(_2)H(_4)</td>
<td>25</td>
<td>4.35±0.22(^o)</td>
<td>2.87</td>
<td>0.84,1.44</td>
<td>2.36,4.04</td>
<td>4.49</td>
<td>1.03</td>
<td></td>
</tr>
<tr>
<td>CN+C(_2)H(_6)</td>
<td>25</td>
<td>1.13±0.21(^o)</td>
<td>1.34</td>
<td>0.84,1.43</td>
<td>2.39,4.09</td>
<td>4.24</td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td>CN+CH(_2)C(_2)H(_2)</td>
<td>15</td>
<td>3.8±0.7(^o)</td>
<td>5.13,3.26</td>
<td>3.43</td>
<td>0.85,1.34</td>
<td>2.39,3.76</td>
<td>5.04</td>
<td>1.33</td>
</tr>
<tr>
<td>CN+CH(_2)C(_2)H(_2)</td>
<td>15</td>
<td>4.4±1.1(^o)</td>
<td>2.84</td>
<td>0.89,1.39</td>
<td>2.45,3.84</td>
<td>4.3</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>CH+H(_2)</td>
<td>23</td>
<td>1.87±0.20(^p)</td>
<td>0.0</td>
<td>3.48</td>
<td>1.42,2.39</td>
<td>3.49,5.89</td>
<td>6.33</td>
<td>3.39</td>
</tr>
<tr>
<td>CH+D(_2)</td>
<td>13</td>
<td>1.43±0.05(^p)</td>
<td>2.62</td>
<td>1.07,1.64</td>
<td>2.63,4.03</td>
<td>4.37</td>
<td>3.06</td>
<td></td>
</tr>
<tr>
<td>CH+O(_2)</td>
<td>13</td>
<td>1.54±0.13(^p)</td>
<td>0.0</td>
<td>1.29</td>
<td>0.76,1.17</td>
<td>1.81,2.77</td>
<td>2.89</td>
<td>1.88</td>
</tr>
<tr>
<td>CH + NO</td>
<td>13</td>
<td>2.34±0.16(^q)</td>
<td>2.09,1.36</td>
<td>2.45</td>
<td>0.79,1.22</td>
<td>1.80,2.76</td>
<td>3.44</td>
<td>1.47</td>
</tr>
<tr>
<td>CH+NH(_3)</td>
<td>23</td>
<td>2.21±0.17(^q)</td>
<td>11.4,6.76</td>
<td>3.90</td>
<td>0.98,1.65</td>
<td>2.19,3.70</td>
<td>7.75</td>
<td>3.51</td>
</tr>
<tr>
<td>CH+N(_2)</td>
<td>23</td>
<td>1.11±0.17(^q)</td>
<td>0.0</td>
<td>2.23</td>
<td>0.74,1.25</td>
<td>1.83,3.09</td>
<td>3.81</td>
<td>3.43</td>
</tr>
<tr>
<td>CH + CO</td>
<td>23</td>
<td>1.55±0.13(^q)</td>
<td>1.49,0.38</td>
<td>2.60</td>
<td>0.77,1.29</td>
<td>1.86,3.14</td>
<td>4.06</td>
<td>2.62</td>
</tr>
</tbody>
</table>

\(^a\) Lowest temperature (K) examined experimentally.
\(^b\) Experimentally observed rate coefficient for the lowest temperature studied.
\(^c\) The first entry is the long-range transition state prediction for the parameter A in the expression A/T\(^6\) (T in K) for the capture rate with a dipole-dipole potential, i.e., the rate at 1 K. The second entry (the one in bold) is the value of this expression for the lowest temperature examined experimentally.
\(^d\) The long-range transition state prediction for the capture rate with the dominant dipole-quadrupole potential.
\(^e\) The first entry is the long-range transition state prediction for the parameter C in the expression CT\(^6\) (T in K) for the capture rate with the dominant dipole-induced-dipole potential, i.e., the rate at 1 K. The second entry (the one in bold) is the value of this expression for the temperature examined experimentally.
\(^f\) The first entry is the long-range transition state prediction for the parameter C in the expression CT\(^6\) (T in K) for the capture rate with the dispersion interaction, i.e., the rate at 1 K. The second entry (the one in bold) is the value of this expression for the temperature examined experimentally.
\(^g\) VTST capture rate for a potential represented by the sum of the dipole-dipole, dipole-quadrupole, dipole-induced-dipole, quadrupole-quadrupole, and the dispersion terms.
\(^h\) Ratio of the predicted capture rate to the experimental rate.

\(^1\) Reference 69.
\(^2\) Reference 70.
\(^3\) Reference 71.
\(^4\) Reference 72.
\(^5\) Reference 73.
\(^6\) Reference 74.
\(^7\) Reference 75.
\(^8\) Reference 76.
\(^9\) Reference 77.

The deviations between theory and experiment are often more readily understood when considering the full temperature dependence. For brevity we provide only two illustrative figures demonstrating the predicted and observed temperature dependence of the CN+O\(_2\) and the CH+NH\(_3\) reactions.
more detailed ab initio-based simulations covering the full range of experimentally studied temperatures.

The long-range TST predictions for the CH reactions are the most inadequate, generally being a factor of two to three too high. The temperature dependence for the CH+NH$_3$ reaction, illustrated in Fig. 15, is representative of this class of reactions where the predictions appear to be significantly too high even at the lower temperatures. These deviations are not fully understood and should provide interesting fodder for theoretical analysis in the future. It is possible that the experimental observations do not correspond to the high pressure limit. Alternatively, it may be that one of the dipolar orientations does not lead to overall reaction. A nonreactive dipolar orientation might lead to a reduction in the rate by a factor of 2. Third, it may be that the assumption of a contribution at low temperatures from both spin–orbit states of CH is incorrect. Such an electronic state selectivity may also be responsible for the overestimates for CH+H$_2$ and CH+D$_2$. However, for the latter two cases the large rotational constants suggest that the discrepancies may also be due to quantum effects.

In summary, the theoretically predicted capture rates provide a useful reference frame from which to consider the experimental results. In some cases the agreement between the two is quite good suggesting that the kinetics is reasonably well understood. In other cases, the discrepancies are quite significant and the deviations point toward interesting possible explanations.

V. DISCUSSION

Equation (18) provides a general expression for the $\mu J$-VTST rate constant in the long-range transition state approximation. The applicability condition of this expression is given by Eq. (9) and by the condition that the quantum effects are not important. It is interesting to note that the atomic masses of the fragments come into Eq. (18) in the form of the only parameter: the reduced mass of the system. Thus, Eq. (18) predicts a very simple isotopic dependence of the capture rate constant as being the same as the collision frequency of the fragments. This kind of dependence was known for C-VTST and $m_J$-VTST expressions, but, to the best of our knowledge, it is the first time it is proven for the most accurate $m_J$-VTST expression. It provides a solid theoretical footing for the recent low temperature measurements of the rates of the CH+H$_2$ and D$_2$ reactions.

In the literature it is fairly common to consider models which include the induced-dipole term in addition to the main multipole term in Eq. (31). Such multiple term potentials have provided a useful test bed for different theoretical approaches and approximations and so we briefly consider the application of the present model to this potential. In Fig. 16 the $\mu J$-VTST rate constant is compared with the results of the classical trajectory calculation from Ref. 53 in the dynamically adiabatic regime (see below) for the sum of the ion-linear dipole and ion-induced-dipole terms,

$$V(\theta, r) = -\frac{qd \cos \theta}{r^2} - \frac{a q^2}{2r^4}.$$  

(77)

At low temperatures the transition state distances are large, and the ion-dipole interaction dominates. As a result, the rate
constant is given by Eq. (63). At large temperatures the transition state is contracted and the ion-induced-dipole interaction prevails. In this region the rate constant is well represented by Eq. (56). The difference between the $\mu$J-VTST and classical trajectory calculations was found to be about 2% at low temperatures and effectively reduces to zero at high temperatures.

In the application of the transition state theory to barrierless reactions it is fairly commonplace to use either canonical or microcanonical implementations of the theory. One of the reasons why $\mu$J-VTST has not been more widely used is due to the rather cumbersome nature of the expressions [cf. Eq. (7)]. Moreover, it is fairly widely believed that taking into account the angular momentum conservation gives little improvement in the estimate for the rate constant. The present approach greatly simplifies the incorporation of angular momentum conservation into the theory for reactions on a long-range potential. Furthermore, we have shown that in many instances the $E$, $J$-resolved version of VTST considerably improves the rate constant estimates obtained with its microcanonical and canonical versions.

The appealing feature of the long-range VTST rate expressions is that they do not depend on the individual properties of the reactive species, such as the inertia moments of the fragments and the orientation of the multipole moments in the molecular frames of the corresponding fragments, but only on the type of interaction and the overall dimensionality of the reactive complex. As a result, the obtained expressions are ready for use with real systems. Such universality comes at the expense of some accuracy in the rate estimate. The cost is very modest, however. The comparison of the VTST and classical trajectory calculations reveals that for all potentials considered here, $\mu$J-VTST provides the reaction rate constant to within 10% of its trajectory value. The difference between $E$, $J$-resolved and microcanonical levels of VTST decreases with the increase of the interaction order from ca. 12% for the charge-dipole interaction to ca. 3% for the dipole-quadrupole interaction.

The applicability condition for the long-range transition state approximation is given by Eq. (9). The distance which should be substituted into this equation is a typical transition state distance, and for the potential given by Eq. (32) is of the order of

$$R \sim \left(V_0/T\right)^{1/n}.$$  

Substituting Eq. (78) into Eq. (9), one comes to the following condition for the temperature at which the obtained expressions are valid

$$T \ll V_0\left(\frac{\mu}{I}\right)^{n/2}.$$  

Comparing Eq. (79) with the results of Maergoiz et al., one notes that this condition coincides with the dynamical adiabatic limit, which is defined in terms of the Massey parameter $\xi$.

$$\xi = t_{\text{col}}/t_{\text{rot}},$$

where $t_{\text{col}}$ is a characteristic time of the reactive collision and $t_{\text{rot}}$ is a characteristic rotational time of the fragments. The adiabatic approximation is expected to be valid if $\xi \gg 1$ and breaks down for $\xi \ll 1$. Thus, the adiabatic limit is valid precisely when the long-range transition state approximation is appropriate.

The opposite limit,

$$T \gg V_0\left(\frac{\mu}{I}\right)^{n/2},$$

corresponds to the situation when the so-called sudden approximation is applicable. In this approximation the fragments are assumed to be so heavy that they have no time to change their orientation during the reactive collision, and are treated as orientationally fixed. A similar approximation was also considered in which only one of the fragments was treated in the sudden approximation. The sudden approximation together with the multipole expansion of the potential, Eq. (31), was frequently used to calculate the rate constants for barrierless reactions of small molecules and radicals. Our results show, however, that for all but very exotic situations at temperatures high enough for Eq. (81) to be satisfied, the transition state becomes so contracted [cf. Eq. (78)] that chemical bonding dominates the interaction between the fragments and the multipole expansion of the potential, Eq. (31), is not valid. At such temperatures more realistic potential forms (e.g., $ab$ initio potential calculations on the fly) should be used to obtain a reasonable estimate for the reaction constant. Also, the distance between the centers of mass of the fragments may not be a good choice for the reaction coordinate at such temperatures, and a more elaborate transition state theory approach should be used to obtain accurate rate constant estimates. Note that the use of an alternative form for the reaction coordinate can correct the failure of the adiabatic approximation in the center-of-mass reaction coordinate system.

VI. CONCLUSION

Variational transition state theory with a long-range transition state approximation provides a simple and accurate way to estimate the rate constants of reactions controlled by long-range forces. When the interfragment interaction potential can be reasonably represented by a single term in the long-range expansion (31) the rate constant is expressed in a
universal way in terms of the basic parameters characterizing the potential and the reduced mass of the reactive complex. The general expression for the rate, Eq. (18), predicts a very simple dependence of the capture rate constant on the isotopic composition of the fragments, being the same as the collision frequency of the fragments. The validity criterion for the long-range transition state approximation is found to be equivalent to the adiabaticity criteria of Troe and co-workers. The implementation of limited long-range expansions for the potential within the present long-range transition state approach is most meaningful at moderately low temperatures, e.g., 10–100 K. In this temperature range it provides a useful reference frame for considering experimental observations. Within this range the agreement with the experimental observations of Smith is often quite satisfactory. However, there are a number of cases where the deviations are large enough to suggest the presence of interesting short-range effects.

At slightly higher temperatures, as the transition state separation decreases with increasing temperatures, it becomes important to include additional terms in the potential. In this case, it is probably most effective to evaluate the potential with \( \text{ab initio} \) calculations on the fly. Notably, the long-range transition state approximation will only break down at much higher temperatures [cf. Eq. (79)] than those at which the long-range potential expansion (31) becomes practically inapplicable. However, in most situations, before such a temperature is reached a separate inner transition state becomes dominant. The long-range transition state approach is not applicable to this region, because it is then typically necessary to consider more general forms for the reaction coordinate. Nevertheless, with microcanonical implementations the long-range transition state result continues to have an important effect on the rate constant at temperatures beyond that at which the inner transition state is dominant.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94-AL85000.

13. In Tables I and II \( A \) stands for atom, \( L \) for linear molecule, and \( N \) for nonlinear molecule. Any ionic fragment should be treated as an atom. The quadrupole tensor of the fragment is assumed to have the form of Eq. (67).
17. The hypothetical system in which the potential can be represented by Eq. (32) while Eq. (9) is not satisfied, may consist of one very light fragment, e.g., the hydrogen atom or ion, and a very heavy one, with large inertia moments. The chemical interaction in such a system should be weak and the long-range interaction should be strong.
19. If the higher order terms in the potential expansion, Eq. (31), are neglected for reactions in which one of the fragments is ionic, only the rotational degrees of freedom of the nonionic fragment should be considered, because the rotational degrees of freedom of the ionic fragment are then totally uncoupled from the reaction dynamics. It is then best to simply neglect these degrees of freedom in the calculation of the rate constant.
22. Reference 44, p. 963.
23. The conclusion made in Ref. 28 strongly influenced subsequent theoretical development, see, e.g., Refs. 13, 62, and 67.
24. Reference 44, p. 27.
from the NIST Computational Chemistry Comparison and Benchmark Database, http://srdata.nist.gov/cccbdb/.


58 The interfragment interaction potential effectively depends on the isotopic composition of the fragments due to the isotopic displacement of the fragments’ centers of mass. We assume here that the effect of this dependence on the rate constant is negligible.


61 The only exception we are aware about is Ref. 36, where it was shown that taking into account the conservation of the angular momentum for the ion-linear dipole reactive system explains the differences with the trajectory simulation.


63 Equations (2.7), (2.4), and (2.5) in Refs. 53, 68, and 55, correspondingly.

64 E. E. Nikitin, Theory of Elementary Atomic and Molecular Processes in Gases (Clarendon, Oxford, 1974).


