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THE INFLUENCE OF HINDERED ROTATIONS/ON
RECOMBINATION/DISSOCIATION KINETICS

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Abstract. The variational canonical flexible transition state theory expressions for the thermal reaction rate constant are reviewed and then applied to the barrier-less recombination reactions $\text{H}+\text{CCH}$, $\text{H}+\text{CF}_3$, and $\text{CH}+\text{H}_2$. The rate constant expressions can classically accommodate any description of the hindering potential governing relative orientation changes between the reactants at a given distance. The distance held fixed during the relative orientation changes can be fully optimized. The three applications display comparable and large variations between the harmonic oscillator and free rotor limits of the hindering potential. The actual hindering potentials are all derived from similar ab initio electronic structure calculations. With these potentials, the rate constant for $\text{H}+\text{CF}_3$ is somewhat free-rotor like, the rate constant for $\text{CH}+\text{H}_2$ is mostly harmonic-oscillator like, and the rate constant for $\text{H}+\text{CCH}$ is largely in between these two limits.

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1. Introduction

Barrier-less reactions are commonplace in chemistry and are particularly important in combustion, atmospheric, and interstellar processes. Such reactions typically characterize the recombination of molecular radicals or the reverse dissociative process of single bond fission. The transition states or "bottlenecks" for barrier-less reactions often exhibit large amplitude motion. A reliable description of the degree and complexity of this motion is a challenge for statistical theories of reaction kinetics and has generated considerable theoretical attention, as exemplified by two other articles in this issue^{1,2}. Despite ongoing advances in classical trajectories and quantum dynamics, statistical theories remain the most widely used theories for modeling reaction rates. Thus the incorporation of large-amplitude motion into these theories is an important area of development.

This paper will be exclusively concerned with flexible transition state theory (FTST)^{2,3,4}, one class of statistical theories specifically designed to address large amplitude motion. Like all modern theories for barrier-less reactions, FTST is a variational theory that minimizes the rate constant by varying the transition state location along the reaction path, thus optimizing bottleneck location. In FTST, the large amplitude modes of the transition state are treated as fully coupled to each other and to overall rotation of the molecular system. These modes are called transitional modes and correspond to free rotations of the separated reactants that evolve into vibrational motions of the parent molecule. In FTST, these modes are treated by classical mechanics which makes feasible the inclusion of the full transitional mode hindering potential as well as all the coupling of these modes with the overall rotations. While classical mechanics is not as accurate as quantum mechanics, the unimportance of tunneling in barrier-less reactions and the insignificance of zero-point energy in large amplitude, and hence low-frequency, oscillations suggests that a classical treatment will be quite reliable. The conserved degrees of freedom, namely those found in

both the reactants and the products, are treated quantally, as in other statistical theories, because their high frequencies make zero-point effects important.

The consequences of a *classical* treatment of large amplitude motion go beyond the specifics of the transitional modes. FTST must strictly eliminate coupling between conserved and transitional modes because of the contrasting quantal/classical treatments. Furthermore, in FTST, the minimization process for the rate constant can in principle be carried out only for each collective conserved vibrational state, not for each full vibrational-rotational state. The Statistical Adiabatic Channel Model^{1,5} (SACM), another class of statistical theories for large amplitude motion, incorporates a full quantal treatment (at the price of a full description of the transitional mode potential). (Recent developments in SACM are reported in this issue by Troe¹.) In many SACM applications, considerable change in transition state location occurs with variation in the transitional-rotational mode quantum numbers. The kinetics implications of the approximations in FTST versus those in SACM and other theories remains an issue for further theoretical and experimental study. However, as discussed in the article by Klippenstein² in this issue, there are now some examples of exquisitely detailed agreement between measurements and FTST calculations.

As originally developed, intensive numerical calculations of phase space integrals were required to incorporate complex potentials into the FTST calculation of the rate constant. Recently, Smith⁶, Klippenstein et. al.^{7,8}, Aubanel, Robertson, and Wardlaw⁹ and others have developed versions or approximations to the original FTST which are easier to implement and are physically more transparent. In four recent papers by the authors¹⁰⁻¹³, a particularly simple but exact *canonical* version of FTST was developed. In canonical, as opposed to a microcanonical, applications of FTST, the minimization of the rate constant to obtain the optimum transition state location is directly applied to an integral expression for the rate constant, rather than to each component of the integrand characterized by a

conserved total energy and total angular momentum. This approximation can produce significant errors but for many chemically interesting systems, e.g. $\text{H}+\text{CH}_3$, the errors are in the range of 10%¹⁴. Because of these errors, this paper, which will concentrate on canonical FTST, is the most approximate of the three papers on statistical theories of kinetics in this issue (see Refs. 1 and 2). However, the advantage of a canonical FTST is ready accessibility to the full complexity of transitional mode hindering potentials which produce variations in the rate constant much larger than 10%. In the next section, canonical FTST theory will be reviewed. In the following section, applications to three different recombination reactions, $\text{H}+\text{CCH}$, $\text{H}+\text{CF}_3$, and H_2+CH , will be presented. The final section is a discussion of the results and a summary.

2. Procedure

In this section, the basic components of a canonical FTST theory are reviewed. More detailed discussions can be found in References 10 - 13. The canonical variational transition state theory expression for the rate constant is (with $\beta = 1/kT$)

$$k(T) = [g_e/\beta h] [\sigma/\sigma^\ddagger] [Q^\ddagger_{\text{TS}}(T)/Q_{\text{react}}(T)] \exp[-\beta V^\ddagger] \quad (1)$$

The quantity $Q^\ddagger_{\text{TS}} = Q_{\text{TS}}(R^\ddagger, T)$ is the pseudo-partition function of the system at the transition state, the transition state location $R^\ddagger$ being that value of the reaction coordinate R which, at a given T , minimizes $Q_{\text{TS}}(R, T)$. This partition function has its zero of energy on the minimum energy path (MEP) where the potential is $V^\ddagger = V_{\text{MEP}}(R^\ddagger)$. The form of Q_{TS} will be described in detail below. Q_{react} is the partition function of the reactants; $\sigma/\sigma^\ddagger$ is the ratio of reactant and transition state symmetry factors, g_e is the ratio of electronic

degeneracy factors for the reactants and transition state and h is Planck's constant. The incorporation of large amplitude transition state motion is through Q_{TS} .

FTST assumes that the transitional and rotational modes of the system are separable from the conserved modes:

$$Q_{TS}(R,T) = Q_c(R,T)Q_{tr}(R,T) \quad (2)$$

where Q_c and Q_{tr} are the conserved mode and transitional/external-rotational mode partition functions, respectively. As in all transition state theories, Q_c is treated quantum mechanically, but in FTST, Q_{tr} is treated classically:

$$Q_{tr} = 1/h^n \int \exp[-\beta H] dp dq \quad (3)$$

where H is the classical Hamiltonian for the n transitional/external-rotation modes and $\mathbf{q}$ and $\mathbf{p}$ are generalized coordinates and their conjugate momenta. H can be written as the sum of a transitional/rotational mode kinetic energy T_{tr} and a potential energy V_{tr} . Because of the separation of conserved and transitional degrees of freedom, H describes the motion of reactants which are *rigid* bodies. The shapes of these rigid reactants are those they assume on the MEP. At any point on the MEP, each reactant adjusts its optimized internal geometry in response to the presence of the other reactant. When either reactant departs from the MEP in transitional mode directions or when both reactants take part in an external rotation, their internal geometries remain fixed in the Hamiltonian H and only the relative orientation of each reactant to the other changes under the constraint that the value of R is held constant.

Rigid reactants means that the atomic constituents of each reactant are fixed to the principal axes, the latter determined by a moment of inertia analysis at a given value of R . As far as T_{tr} is concerned, the details of the atomic arrangement are irrelevant. The only thing that is important is whether the arrangement makes the reactant an atomic, linear, or (a)symmetric top. The effective masses used in T_{tr} are the principal moments of inertia; the angles needed to describe the relative orientation of the reactants are those that govern the orientation of the principal axes of each top. As far as V_{tr} is concerned, the decomposition of the full potential energy surface (PES) to V_{tr} can similarly be formulated as a function of only those orientation angles of the principal axes of each top and also of R . Because the number of angles specifying orientation change with the nature of the top, in canonical FTST, all kinetics becomes one of five cases: linear top + atom (1 angle), (a)symmetric top + atom (2 angles), linear top + linear top (3 angles), (a)symmetric top + linear top (4 angles), and (a)symmetric top + (a)symmetric top (5 angles).

Because of the simplicity of rigid body Hamiltonians, all of the integration over $\mathbf{p}$ and all of the integrations over the Euler angles describing rotation can be done analytically. What remains is the dependence of V_{tr} in an integral over the angles that describe the relative orientations of the tops. In the case that R , which is held fixed during the angular integration, describes the separation of the centers of mass or the reactants, the final form of the rate constant is exceedingly simple and physically transparent:

$$k(T) = \{ [g_e/\beta h] [\sigma/\sigma^\ddagger] [Q_{pd}^\ddagger \exp[-\beta V^\ddagger]/ Q_{trans}(T)] \} \\ [Q_c^\ddagger(T)/\prod_i Q_{vib,i}(T)] [\prod_i Q_{rot,i}^\ddagger(T)/\prod_i Q_{rot,i}(T)] \Gamma^\ddagger(T) \quad (4)$$

where

$$Q_{pd}(R,T) = 2\mu R^2/\beta\hbar^2 \quad (5)$$

$$\Gamma(R,T) = C_{norm} \int \exp[-\beta V_{tr}(\mathbf{q}_{tops};R)] \prod_i \sin\theta_i d\mathbf{q}_{tops} \quad (6)$$

where the indexed products $\prod_i$ are over both reactants if necessary (e.g., an atomic reactant has no vibrational or rotational partition function), where $Q_{pd}(R,T)$ is the partition function for the pseudo-diatomic of bond length R and reduced collisional mass μ , where $\Gamma(R,T)$ is a steric hindrance function with a normalization constant C_{norm} that makes the function unity if the hindrance potential is zero, where $\mathbf{q}_{tops}$ is the internal coordinates of $\mathbf{q}$ that orient the tops (i.e., no Euler angles for overall rotation), where θ_i is an element of $\mathbf{q}_{tops}$ which describes the orientation of the i^{th} linear or nonlinear top with the vector connecting the centers of mass of the reactants, where $Q_{react}(T)$ of Eq. (1) has been decomposed into vibrational, rotational, and translational components:

$$Q_{react}(T) = \prod_i Q_{vib,i}(T) \prod_i Q_{rot,i}(T) Q_{trans}(T) \quad (7)$$

and where the “ $\ddagger$ ” symbol indicates, as in Eq. (1), that all R -dependent quantities are evaluated at $R^\ddagger$, the value that minimizes $k(T)$. Equation (4) has in effect rigorously decomposed $Q_{tr}(R,T)$ of Eq. (2) into:

$$Q_{tr}(R^\ddagger,T) = Q_{pd}^\ddagger \Gamma^\ddagger(T) \prod_i Q_{rot,i}^\ddagger(T) \quad (8)$$

where the final product corresponds to the rotational partition function of each reactant but for the shape it has at $R^\ddagger$, where Q_{pd} is closely related to the overall rotational partition

function, and where all information concerning the hindering potential is contained in $\Gamma(R,T)$ evaluated at $R^\ddagger$. The only numerical integrals required in the rate constant expression are those defining $\Gamma(R,T)$ and the dimensionality of the integration varies with the five different combinations of tops the reactants represent. The hindrance potential in the integration, i.e., $V_{tr}(\mathbf{q}_{tops};R)$, is by definition zero when $\mathbf{q}_{tops}$ assumes the values it has on the MEP when the separation of the reactants is R . The integration in $\Gamma(R,T)$ samples all of V_{tr} under the constraint that R is fixed.

The rate constant expression in Eq. (4) is readily interpretable. It contains a "core" rate constant in $\{ \}$ modified by three trailing factors. The core rate constant contains all the dependency on the MEP potential, the reduced collision mass, the reaction path multiplicities (through $\sigma/\sigma^\ddagger$), and the electronic degeneracy factors. The first of the trailing factors contains a ratio of vibrational partition functions that is unity if the conserved frequencies at $R^\ddagger$ are little different from their values in the isolated reactants. The second factor is a ratio of rotational partition functions which is also unity if the shape of the reactants have not changed much from that of the isolated reactants. The final factor is that for steric hindrance. It is unity in the free rotor case where there can be no steric hindrance by definition. For any positive hindrance potential, the steric hindrance is a positive fraction whose value is exclusively controlled by the potential. Any potential can be accommodated. That includes a harmonic potential, in which case $\Gamma(R,T)$ becomes the equivalent of a classical version of a vibrational partition function. Typically, $V_{tr}(\mathbf{q}_{tops};R)$ is free-rotor like at large R , harmonic like at small R , and hindered-rotor like in between. At the price of being canonical, this FTST expression will accommodate any potential and let the variation with respect to R determine what the nature of V_{tr} is at the reaction bottleneck.

All of the above expressions have been developed under the requirement that R is the separation between the centers of mass of the reactants. As has been developed in a series of papers by Klippenstein^{2,8c,e,f}, such a restriction is unnecessary. R can be more generally thought of as a separation between a "spot" on each reactant where the "spot" is located by a vector $\mathbf{d}$ in the principal axis system of each reactant. Since the origin of the principal axis system is the reactant's center of mass, when $\mathbf{d}$ is zero for each reactant, this generalized definition of R reduces to the separation of the centers of mass. However, when $\mathbf{d}$ is not zero, the separation held fixed in the evaluation of $\Gamma(R,T)$ is *not* the center of mass separation. This means that the rate constant can not only be lowered by optimizing the length of R but also by optimizing the definition of R through $\mathbf{d}_1$ and $\mathbf{d}_2$. Klippenstein has applied this approach in both the canonical and microcanonical version of FTST to systems where symmetry constraints allow $\mathbf{d}$ to only vary along bond axes. Recently the authors have developed a completely general but canonical formulation¹³ which leaves the rate constant expression of Eq. (4) unchanged but redefines the steric hindrance function:

$$\Gamma(R,T) = C_{\text{norm}} \int J(\mathbf{q}_{\text{tops}}; \mathbf{d}_i, I_i, R) \exp[-\beta V_{\text{tr}}(\mathbf{q}_{\text{tops}}; R)] \prod_i \sin\theta_i d\mathbf{q}_{\text{tops}} \quad (9)$$

where the new Jacobean-like factor $J(\mathbf{q}_{\text{tops}}; \mathbf{d}_i, I_i, R)$ in the integrand depends on the definition and value of R and on the moments of inertia, collectively represented by I_i , of the i^{th} reactant. This factor goes to unity when $\mathbf{d}_i$ for either value of i goes to zero. The form of Eq. (9) means that kinematic factors (which depend on moments) and potential factors can not be strictly separated. Although $J(\mathbf{q}_{\text{tops}}; \mathbf{d}_i, I_i, R)$ can be tedious for the more complicated cases, it is still completely analytic and trigonometric in form. In one of the

applications of the next section, this generalization of R will be illustrated for a linear top + atom case. For this case, $\Gamma(R,T)$ assumes the form^{11,13}:

$$\Gamma(R,T) = \int_0^\pi \{ (F/R)^2 (1 + [\mu F^2/I] d_s^2 \sin^2 \theta)^{1/2} (1 - d_s^2 \sin^2 \theta)^{-1/2} \} \exp[-\beta V_{tr}(\theta; R)] \sin \theta d\theta / 2 \quad (10)$$

where

$$F = \pm d \cos \theta + (R^2 - d^2 \sin^2 \theta)^{1/2} \quad (11)$$

where there is only one d measured from the center of mass of the linear top and $d_s = |d|/R$. For symmetry reasons, d is compelled to lie along the axis of the linear top and the sign option in Eq. (11) indicates in which direction along the axis it lies. In Eq. (10), the factor in $\{ \}$ is $J(\mathbf{q}_{\text{tops}}; \mathbf{d}_i, I_i, R)$ for the linear top + atom case.

If it is assumed that the reactants do not significantly alter their shape or frequencies in the kinetically important region, then Eq. (4) simplifies to

$$k(T) = [g_e/\beta h][\sigma/\sigma^\ddagger] Q_{pd}^\ddagger \Gamma^\ddagger(T) \exp[-\beta V^\ddagger]/Q_{\text{trans}}(T) \quad (12)$$

This assumption is often quite good for barrier-less reactions and this form of the rate constant will be used in the applications of the next section.

3. Results

In this section, the above canonical rate constant theory will be applied to three reactions. These three reactions are representatives of first three of five possible cases: linear top + atom ($\text{H}+\text{CCH}$), symmetric top + atom (CF_3+H), and linear top + linear top (H_2+CH). All three applications will use an ab initio V_{MEP} and V_{tr} derived from multi-reference singles and doubles configuration interaction (MRSDCI) calculations with the COLUMBUS program system¹⁵. The calculations used dzp basis sets¹⁶ that are reliable for V_{tr} but somewhat underestimates the attractiveness of V_{MEP} . The three applications below will emphasize the sensitivity of the rate constant to V_{tr} . Consequently the kinetics implications of the accuracy of V_{MEP} and of the variation of the conserved frequencies and reactant shapes with R will not be pursued. These effects are of quantitative, though not qualitative, importance and for each application will be developed in full elsewhere. Similarly, experimental results, where available, will be compared to the calculations (in the next section), but not in detail.

3.1 $\text{H} + \text{CCH} \rightarrow \text{HCCH}$.

A recent theoretical study¹⁷ of the low pressure dissociation rate constant for acetylene has indicated the importance of hindered rotations through the vinylidene structure ($\text{H}_2\text{CC}:$). This study involved the ab initio calculation of large parts of the potential energy surface. One of the parts that was calculated is the approach of H to CCH in its equilibrium configuration. Although this is not important in the low pressure dissociation of acetylene, it provides both the V_{MEP} and V_{tr} needed for the canonical high pressure limiting rate constant for recombination. The $\text{H} + \text{CCH}$ system is one of the few linear top + atom systems studied to this level of detail where the linear top is not a diatomic molecule.

For a linear top + atom, V_{tr} can be fully represented as a function of the center of mass separation R_{cm} and the angle of approach θ with respect to the linear top axis. A

topographical plot of $V_{tr}(\theta, R_{cm})$ determined from the ab initio calculations described in Ref. 17 is found in Fig. 1. Each band in the surface corresponds to a 0.25 kcal/mol increment. θ is defined so that the minimum energy path occurs at $\theta = 0^\circ$ where by definition $V_{tr} = 0$. The figure clearly shows that the potential increases at each R_{cm} as θ deviates from its minimum energy value and that the degree of the increase dramatically increases as R_{cm} decreases.

Although a plot of V_{MEP} will not be shown, it is everywhere attractive. However, over the range of values of R_{cm} shown in the figure, V_{MEP} is not attractive enough to prevent the whole interaction potential from becoming positive for the least favorable angles of approach in Fig. 1. As discussed in Ref. 17, the total potential is such that H can not only attractively attack the end carbon atom but the inner carbon atom as well. Only attack of the H atom on the H atom of CCH is completely unfavorable. The small range of angles that are favorable to inner carbon atom attack can best be thought of as forming a highly distorted vinylidene. The flattening out of V_{tr} at intermediate angles clearly seen for the smallest values of R_{cm} in Fig. 1 is a signature of the vinylidene-dominated region of the angles of approach.

It is also visually clear from the figure that V_{tr} has a limiting harmonic dependence on θ in the region of the MEP configuration. A MEP analysis of the frequencies perpendicular to the reaction path have a doubly degenerate low frequency that vanishes as R_{cm} increases. To the degree that the conserved and transitional degrees of freedom can be rigorously uncoupled, this low frequency is a consequence of the harmonic limit of the potential displayed in Fig. 1. On the other hand, Fig. 1 clearly shows that as R_{cm} increases, V_{tr} becomes less and less significant, suggesting a free rotor model of $V_{tr} = 0$ at large values of R . Thus, the actual V_{tr} of Fig. 1 or its limiting harmonic or zeroed forms can define three

rate constants corresponding to the hindered rotor (HR), harmonic oscillator (HO) limit, and free rotor (FR) limit, respectively.

In Fig. 2, these three rate constants as calculated from Eq. (12) and Eq. (6) are displayed as a function of inverse temperature. As the figure shows, the difference between the HO and FR limits is about a factor of 6 with the best estimate HR value lying closer, but still about 50% smaller, than the FR limit. Although unshown, the reaction transition state location at all temperatures falls within the range of R_{cm} values seen in Fig. 1.

For this example alone, the optimization of the definition of R , the distance held constant during the calculations of $\Gamma(R,T)$, was explored using the applicable Eq. (10) and optimizing d to minimize the rate constant. The final rate constant for the exact potential is also displayed in Fig. 2. The effect is significant, about a factor of two lowering of the rate constant at low temperatures. The displacement is also very large, about .5 Å *beyond* the radical Carbon atom. Such large effects are surprising but have been seen before in other systems (e.g., see Ref. 8f). The same optimization can also in principle be applied in the FR and HO limits. However, analysis¹³ shows that it can have no effect in the FR limit. Calculations show a similar but smaller lowering of the HO rate constant in Fig. 2. This implies that optimization of the reaction path definition produces rate constants with hindered rotor effects that are intermediate between the FR and HO limits.

3.2 $H + CF_3 \rightarrow CHF_3$.

An electronic structure study of the part of the PES that governs the recombination of $H + CF_nH_{3-n}$ has been carried out by Harding and reported in this issue¹⁸ for all three values of n . The recombination/dissociation of this series will permit a characterization of the importance of the degree of asymmetry for reactants that are tops. Here the kinetic

implications of the electronic structure study is reported for the most symmetric member of that series, $\text{H} + \text{CF}_3$. This reaction represents a typical case of a symmetric top + atom.

As discussed by Harding¹⁸, the kinetically important region of the PES was sampled at four values of the C-H distance (5, 6, 7, and 8 a_0). The variation in the PES as a function of the angles of approach for a rigid CF_3 (fixed at its asymptotic geometry) was determined for all angles of approach. The results were then accurately fit to a sinusoidal expansion in the angles of approach. For this application, an interpolation of these expansions as a function of the C-H distance is needed. Because of the large variation in the potential with C-H distance, a simple polynomial or spline interpolation produced undesired ringing of the fit. Instead the following procedure was used. The V_{MEP} part of the PES was fitted with an exponential dependence. At each C-H distance, that fit was subtracted from the total interaction potential. At any desired angles of approach, the absolute value of the resulting difference at the extremes of the C-H distance (i.e., 5 a_0 and 8 a_0) was fit to an exponential. When that fit is factored out of the differences at each C-H distance, a slowly varying function of R results that can be smoothly fit with a spline. The whole interaction potential is thus fit by a sum of an exponential for V_{MEP} and an exponential/spline product for the rest that is a function of the desired angles of approach. This fit exactly reproduces the Harding fit¹⁸ at the four fixed values of C-H distance and interpolates in between with no apparent ringing. This fit must be converted into angles of approach and separation distances measured from an origin at the center of mass of CF_3 , but standard geometric relationships allow this to be done straightforwardly.

Given a fit to the PES, V_{tr} can be extracted which assumes the form $V_{\text{tr}}(\theta, \phi; R_{\text{cm}})$ where the spherical angle θ and the azimuthal angle ϕ locate the H with respect to the C_{3v} axis of CF_3 at an origin at the center of mass of CF_3 . The trifluoromethyl radical is noticeably non-planar with the C-F bond bent 17° off the plane perpendicular to the C_{3v} axis that

contains the C atom. Consequently, the origin of the spherical coordinate system is not centered on the carbon atom. More importantly, there is a front-side and back-side approach to the CF_3 along the C_{3v} axis that are not energetically equivalent. The back-side approach is always more repulsive because the F atoms lean toward the attacking H atom.

A perspective contour plot of V_{tr} is displayed in Fig. 3 at $R_{\text{cm}} = 3.3\text{\AA}$. In the figure, each band represents a 0.25 kcal/mol increment. The value of R_{cm} turns out to be the transition state location at about 600 K for the canonical FTST rate constant. Thus Fig. 3 is a typical representation of the hindering potential in the kinetically important region. In the figure, the spherical angle θ is varied from 0° to 180° and the azimuthal angle ϕ varies from 0° to 120° (the potential has a periodicity in this coordinate of 120°). The reaction path corresponds to $\theta = 180^\circ$ and at that value V_{tr} in the figure is zero for all values of ϕ . This corresponds to the front-side approach. The back-side approach is also clearly visible in the figure at $\theta = 0^\circ$ and it is higher in energy but independent of ϕ , as it must be.

In the figure, V_{tr} clearly has a plane of symmetry about $\phi = 60^\circ$, as is required. At a fixed value of ϕ , V_{tr} peaks at $\theta < 90^\circ$ because of the splayed nature of CF_3 . For any value of θ , V_{tr} is highest at $\phi = 0^\circ$ or 120° , where H passes right over a C-F bond. Correspondingly, V_{tr} is lowest for $\phi = 60^\circ$ where F passes exactly between two C-F bonds.

The HO version of V_{tr} is the limiting quadratic form of the θ dependence at $\theta = 180^\circ$ which is also independent of ϕ . This kind of harmonic potential supports a doubly degenerate rocking degree of freedom that would appear as two low frequencies in the typical analysis of frequencies perpendicular to the MEP. However, as is clear from the figure, a similar

expansion can be made about $\theta = 0^\circ$ for the back-side approach (see Ref. 18 for more details on the back-side approach). The closest HO approximation to the true V_{tr} is to use both expansions but take the lowest of the two at any angle of θ . That is what will be used here. The FR version of V_{tr} is also of interest but that has the trivial form of $V_{tr} = 0$ for all angles of approach.

In Fig.4, the HR (i.e., exact V_{tr}), HO, and FR rate constants as calculated from Eq. (12) and Eq. (6) are displayed as a function of inverse temperature. As the figure shows, the difference between the HO and FR limits is again about a factor of 6 or 7 with the best estimate HR value lying approximately midway between the two limits at high temperature but closer to the FR limit at low temperatures. The transition state locations at all temperatures fall within the range of C-H bond distances at which all the PES calculations by Harding¹⁸ were carried out, indicating that the kinetically important region of the PES was correctly sampled.

3.3 $\text{CH} + \text{H}_2 \rightarrow \text{CH}_3$.

This reaction has been the subject of several theoretical studies¹⁹ and a variety of experimental studies of which the two most relevant to this work are discussed in this issue^{20,21}. The published theoretical work discussed calculations of the hindered rotation barriers for different values of $R_{\text{C-H}_2}$, the distance of C from the center of mass of H_2 . This work has now been supplemented by a much more extensive mapping of the hindered rotational potential reported here. As previously discussed, these calculations are at the dzp basis set level¹⁶ with MRSDCI wavefunctions¹⁵. Values on the PES were obtained at approximately 600 different geometries on a grid of values for $R_{\text{C-H}_2}$, two spherical angles orienting CH and H_2 with respect to $R_{\text{C-H}_2}$, and the dihedral angle between the between the

two planes defined by (R_{C-H_2} , the C-H bond) and (R_{C-H_2} , the H-H bond). The C-H and H-H bond lengths were frozen at their equilibrium values for these calculations. The SURVIB program system²² was used to generate a fit of this portion of the PES with sinusoidal expansions in the three angles and inverse power expansions of the distance. Ultimately, standard geometrical relationships converted this fit to one in terms of R_{cm} , θ_{CH} , θ_{HH} , and χ where the spherical angles θ_i orient the diatomic molecule with respect to the R_{cm} vector (not the R_{C-H_2} vector) and where χ is the dihedral angle for the two planes that encompass a diatomic molecule and R_{cm} .

This system is a linear top + linear top case where V_{tr} assumes the form $V_{tr}(\theta_{CH}, \theta_{HH}, \chi; R_{cm})$. As a function of 3 independent variables for a fixed R_{cm} , V_{tr} can not be readily plotted for this case. However, it is possible to imagine a 3D cube with the axes labeled by θ_{CH} , θ_{HH} , and χ where the gray shading at any point in the cube is related to the value of the potential. Then if the cube is largely cut away leaving 3 planes perpendicular to the three axes, the shading on the now visible planes take the form seen in Fig. 5 for $R_{cm} = 2.7 \text{ \AA}$ (where in the figure $\theta_1 = \theta_{CH}$ and $\theta_2 = \theta_{HH}$). In the figure, each band represents a 0.5 kcal/mol increment. These bands are concentric about two dark spots that are energetically equivalent and symmetrically related. The MEP passes through the center of these spots where V_{tr} is therefore zero. The symmetry-related versions of the MEP involve simultaneous changes in θ_{HH} and χ with θ_{CH} unchanged that act to permute the interatomic distances of each identical atom in H_2 with the atoms in CH.

As suggested by the concentric nature of the bands in Fig. 5, the limiting behavior of V_{tr} about the minimum energy path is harmonic in the three angles. At any given R_{cm} , the minimum of the two harmonic expansions about both symmetrically equivalent minimum

energy points defines a HO version of V_{tr} . This potential would support three low frequency rock or torsional frequencies in the typical analysis of frequencies perpendicular to the minimum energy path. The FR version of V_{tr} remains $V_{tr} = 0$.

In Fig.6, the HR (i.e., exact V_{tr}), HO, and FR rate constants as calculated from Eq. (12) and Eq. (6) are displayed as a function of inverse temperature. As the figure shows, the difference between the HO and FR limits is about a factor of 3 to 5 with the best estimate HR value lying quite close to the HO result over the whole range of temperatures. The transition state locations at all temperatures fall within the range of C-H bond distances at which all the PES calculations were carried out, indicating that the kinetically important region of the PES was correctly sampled.

4. Discussion

The calculated rate constants of the preceding section all display significant sensitivity to the nature of V_{tr} . In all three examples, the difference between the free rotor and the harmonic oscillator treatment of V_{tr} is at least a factor of 3 over a temperature range from about 300 K to 2000 K. Within that range inclusion of the exact V_{tr} produces rate constants that are somewhat free rotor like in $H + CF_3$, somewhat harmonic oscillator like in $CH + H_2$, and somewhere in between these two extremes for $H+CCH$. Although the rate constant expressions used have a canonical approximation, the sensitivity displayed in these examples is noticeably larger than the error found in a number of other systems due to this approximation.

In only one example, the simplest one of $H + CCH$, was the optimization of the definition of the reaction path separation distance explored. In this example, the effect was a surprisingly large reduction in both the harmonic oscillator limit of V_{tr} and its exact hindered rotor form. As discussed elsewhere¹³, the optimization of the separation

definition can not effect the free rotor limit of V_{tr} . Further work is needed to determine if the other two examples will display a similar large effect for this optimization.

All the rate constants displayed are for recombination reactions. As such, they can only be compared to experiments in the high pressure limit where frequent collisions with a thermalized third body prevent the "product" of recombination, e.g. a chemically activated molecule, from unimolecularly dissociating. Furthermore, as discussed above, the calculations have focused on the qualitative changes in the rate constant induced by the description of V_{tr} . They have ignored more quantitative effects such as the accuracy of ab initio values of V_{MEP} and the variations in the shape and conserved frequencies of the reactants as they progress along the reaction path. With these considerations in mind, some guarded comparisons to experiment can be given.

For only one of the three examples, namely $CH + H_2$, there are direct measurements of the high pressure limit, as reported elsewhere in this issue^{20,21}. These measurements at 300 K, including error bars, encompass both the recommended (HR) and HO calculated rate constants of Fig. 6. For a second example, $H + CF_3$, there is a highly exoergic molecular elimination channel of $HF + CF_2$ that is thought to be accessible to the chemically activated CF_3H "product" of the recombination. This might imply that the recombination product will essentially never unimolecularly decay back to $H + CF_3$ reactants even at low pressures of a third body buffer gas. With this assumption, low pressure measurements of reactant loss have been reported^{23,24} at 300 K that are consistent only with the HO calculated rate constants in Fig. 4. By this measure, the recommended HR rate constant is too large. For the last example of $H + CCH$, there are no recombination measurements of any kind available and all reverse dissociation measurements are near the low pressure limit¹⁷. This brief review of the experimental comparison suggests that the calculations

characterization of the agreement will require more thorough theoretical and experimental studies.

To summarize, this paper has reviewed a simple variational canonical rate constant theory and applied it to three different recombination reactions. The theory classically accommodates any interaction potential that governs motion in transitional degrees of freedom, namely those bound degrees of freedom in the products that arise from free rotations in the reactants. The theory also allows an optimization of the definition of the reaction path by an optimization of that separation between reactants which is held fixed as the full range of transitional degrees of freedom are varied. The three applications are $\text{H}+\text{CCH}$, $\text{H}+\text{CF}_3$, and $\text{CH}+\text{H}_2$. In all cases, published ab initio electronic structure calculations were used to characterize the kinetically relevant portions of the potential energy surface. In one case, $\text{CH}+\text{H}_2$, published results were augmented by additional electronic structure calculations reported here. In all cases, the rate constant showed significant sensitivity to the nature of the hindering potential for the transitional degrees of freedom. More detailed theoretical studies of the three reactions discussed here are in progress to more quantitatively describe the effect of anharmonic hindering potentials on the rate constant.

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Figure 1. Contour plot of $V_{tr}(\theta, R_{cm})$ for $H + CCH$. Each band is a 0.25 kcal/mole increment.

Figure 2. Three different calculated canonical rate constant $k(T)$ vs. $1000/T$ for $H + CCH$: HO version (••••), HR version (—), HR version with optimization of reaction path definition (—•—), and FR version (— ... —) (see text).

Figure 3. Contour plot of $V_{tr}(\theta, \phi)$ at $R_{cm} = 3.15 \text{ \AA}$ for $H+CF_3$. Each band is 0.25 kcal/mole.

Figure 4. Calculated canonical rate constant $k(T)$ vs. $1000/T$ for $H+CF_3$: HO version (••••), HR version (—), and FR version (— ... —) (see text).

Figure 5. Contour plot slices of $V_{tr}(\theta_{CH}, \theta_{HH}, \chi)$ at $R_{cm} = 3.44 \text{ \AA}$ for $CH+H_2$ (see text). Each band is 0.5 kcal/mole.

Figure 6. Calculated rate constant $k(T)$ vs. $1000/T$ for $CH+H_2$: HO version (••••), HR version (—), and FR version (— ... —) (see text).

Fig. 1

Wagner et al.

Fig. 2 Wagner et al.

$$R(\text{H-CF}_3) = 3.3 \text{ \AA}$$

Fig. 3 Wagner et al.

Fig. 4 Wagner et al.

Fig. 5 Wagner et al.

Fig. 6 Wagner et al.