Microcanonical Transition State Theory Rate Coefficients from Thermal Rate Constants via Inverse Laplace Transformation

Prasana K. Venkatesh,[†,‡,§] **Robert W. Carr,**[†] **Morrel H. Cohen,***[,‡] **and Anthony M. Dean**[‡]

University of Minnesota, Minneapolis, Minnesota, 55455, and Exxon Research and Engineering Co., Annandale, New Jersey, 08801

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On the basis of concepts from the mathematical theory of approximation of functions, we propose a method of deriving microcanonical transition state theory rate coefficients, both as a function of the total energy and the total angular momentum, from thermal data, namely, the limiting high-pressure rate coefficients. The method does not require the knowledge of the frequencies and degeneracies of the transition state and is general in that it allows for non-Arrhenius forms of thermal data, but it only applies to reactions possessing an intrinsic energy barrier. It is shown that the derived microcanonical rate coefficient is almost identical to the computed Rice−Ramsperger−Kassel−Marcus (RRKM) microcanonical rate coefficient using explicit frequencies and degeneracies of the transition state, and furthermore, that the difference between the two is uniformly distributed over the entire range of total energy and the entire range of the total angular momentum. Comparison of the microcanonical coefficients from the proposed method with those from a standard nonvariational RRKM calculation is presented for the unimolecular decomposition of the ethyl radical and the unimolecular isomerization of methyl isocyanide. The agreement is shown to be excellent. A theoretical analysis of the fine structure of the microcanonical rate coefficient near the threshold of the reaction is enunicated and the difficulty of extending the method to obtain variational microcanonical rate coefficients is described. We also, briefly, speculate on the possible merits of certain theoretical methods of analysis for coping with the representation of thermal data, whose argument is the temperature which is of semiinfinite range.

1. Introduction

The Rice−Ramsperger−Kassel−Marcus (RRKM) method,[1] a version of microcanonical transition state theory, derived as an approximate statistical theory for generating microscopic rate coefficients and promulgated[2] as a predictive tool for unimolecular and bimolecular kinetics, is now commonly used by chemical kineticists[3] to estimate the absolute temperature- and pressure-dependent rate constants of elementary dissociation, radical recombination, ion−molecule, and chemically-activated reactions. Its exercise requires knowledge of the transition-state properties, in particular the barrier heights for dissociation, degeneracies, frequencies, rotational constants, separation of fragments, equilibrium bond lengths, and the interfragment potential parameters. The estimation of such properties of the transition state is nontrivial and is made from a combination of heuristics,[4] ab initio calculations,[5] and highly state-resolved experiments near the threshold of reaction.[6] Such esimation is not always practicable for large molecules due to the computational complexity of quantum-dynamics calculations and for reactions which possess no intrinsic barrier. Reactions without an intrinsic barrier are those which have no barrier in the exoergic direction and whose barrier equals the endoergicity of the reverse diection; for such reactions it is necessary to perform a variational analysis.[7−9] Furthermore, not only is the computation of activation barriers from ab initio methods possible for simple reactions alone, and that too with only moderate accuracy, but careful examination of the potential energy surface is required for systems exhibiting large tunneling effects or other dynamical characteristics.

Without abandoning the concept of the transition state, we propose here a method of generating the microcanonical rate coefficient $k(E,J)$ for the dissociation of a molecule, where E is the energy of the molecule and J is the total angular momentum quantum number, solely from the knowledge of the limiting high-pressure rate coefficient, which may be obtained from experimental observations augmented by extrapolation, and the interfragment parameters of the transition state. Our method does not require the knowledge of the transition state frequencies and degeneracies. These are implicit in the knowledge of the limiting high-pressure rate coefficient, because one can always compute the limiting high-pressure rate coefficient from elementary transition state thermodynamics given the transition state frequencies and degeneracies. The microcanonical rate coefficient $k(E,J)$ is given in microcanonical transition state theory[1] by

$$k(E,J) = \frac{\alpha G^*(E - E_J)}{hN(E)} \tag{1.1}$$

Here $G^*(E - E_J)$ is the integrated density of states for the transition state with E_J being the effective critical energy for

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[†] Department of Chemical Engineering and Materials Science.

[‡] Corporate Research Science Laboratories.

[§] Current Address: Schlumberger-Doll Research, Old Quarry Road, Ridgefield, CT 06877.

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the dissociation. The effects due to J are subsumed in E_J. $N(E)$ is the density of states of all of the chemically active modes of the dissocating molecule at the same E. The chemically active modes encompass all vibrational and internal rotational modes and for nonlinear molecules their relevant one- and two-dimensional external rotational degrees of freedom, α is the reaction path degeneracy. h is Planck's constant. Our method obviates the need to know the transition state frequencies and degeneracies for the computation of the accessible quantum states of the transition state. This is achieved by the use of an inverse Laplace transformation to estimate the microcanonical rate coefficient $k(E,0)$ from the equilibrium average of $k(E,J)$. During the course of our calculation of $k(E,0)$ we explicitly take into account Forst's centrifugal correction factor,[1] which represents averages over the angular momenta. Then, making the observation that the number of accessible quantum states is a univariate function in the total energy, the knowledge of $k(E,0)$ and the density of states of the chemically active modes $N(E)$ of the molecule yields the microcanonical rate coefficient $k(E,J)$ for any specified E and J by means of a simple interpolation technique. The only transition-state properties required in our prescription are the rotational constants such as the moments of inertia and the interfragment potential. These particular transition state properties are easier to estimate than the frequencies and degeneracies of the transition state. The position of the transition state is located at the centrifugal maximum of the effective interfragment potential. We make the semiclassical approximation in summing over the total angular momentum quantum numbers. Within the limitations of this approximation, the microcanonical rate coefficients thus generated by our method show excellent agreement with those obtained from methods of generating nonvariational RRKM rate coefficients[10] which require explicit knowledge of the frequencies and degeneracies of the transition state in their concomitant calculations.

The use of inverse Laplace transforms in unimolecular reaction-rate theory is very well documented. Originally proposed by Bauer[11] and Slater[12] and later introduced[1,9] as a means of obtaining the density of states from the knowledge of the partition function, it has been suggested as an alternative means of evaluating the microcanonical rate coefficient without any knowledge of the transition state properties.[13−15] In such treatments, rotational effects are treated simply by setting the angular momentum to zero. When a strict Arrhenius form for the limiting high-pressure rate coefficient $k_\infty(T)$ is presumed,

$$k_\infty(T) = A_\infty e^{-E_\infty/k_B T} \tag{1.2}$$

where k_B is the Boltzmann constant and T is the temperature, one obtains for the microcanonical rate coefficient $k_{RRK}(E)$,

$$k_{RRK}(E) = A_\infty \frac{N(E - E_\infty)}{N(E)} \tag{1.3}$$

where A_∞ is the preexponential factor independent of temperature and E_∞ is the high-pressure activation energy in the Arrhenius expression for the limiting high-pressure rate coefficient. $N(E)$ is the density of states for all internal degrees of freedom and vanishes for all $E \leq 0$. Equation 1.3 implies that only modes with $E > E_\infty$ are chemically active. $k_{RRK}(E)$ represents the microcanonical rate coefficient generated by the Rice−Ramsperger−Kassel (RRK) theory; apart from E_∞, no transition state properties are required. As is well-known, in a classical mechanical treatment with harmonic oscillators and with the total angular-momentum quantum number set to zero, the microcanonical transition state theory rate coefficient is identical with this RRK expression (eq 1.3). Two principal objections have been raised in connection with the expression 1.3: (a) Equation 1.3 breaks down if the limiting high-pressure rate coefficient does not follow a strict Arrhenius rate law. Objective arguments against this objection have been raised by Pritchard; see page 39 of ref 15. (b) When tunneling phenomena occur, the first reactive state may occur at an energy substantially below E_∞. Equation 1.3 will then be invalid, particularly for weak collision systems near their low-pressure limit.

In our inverse Laplace transform method for generating the microcanonical rate coefficients, we represent the limiting high-pressure coefficient as

$$k_\infty(T) = A_\infty(T)\, e^{-E_\infty/k_B T} \tag{1.4}$$

where $A_\infty(T)$ *is a function of temperature and can be nonmonotonic.* We express $\tilde{k}_\infty(T)$

$$\tilde{k}_\infty(T) = \frac{k_\infty(T)}{f_\infty(T)} = \frac{A_\infty(T)}{f_\infty(T)} \exp\left(-\frac{E_\infty}{k_B T}\right) \tag{1.5}$$

where $f_\infty(T)$ is a centrifugal factor,[1] as a finite sum of Laguerre basis functions[16] in temperature. An advantage of such a representation is that any arbitrary nonArrhenius form for the limiting high-pressure rate coefficient can be approximated accurately. The Laguerre basis set is orthonormal and complete over $[0, \infty]$. They are eigenfunctions of the Sturm−Liouville operator and, indeed, form the optimal basis[16] for any function over the semi-infinite interval $[0, \infty]$. In addition, equation 1.5 is analytic over the entire complex plane apart from poles, and hence, it is amenable to the application of the Laplace transform. We have thus surmounted criticism (a) of the previous paragraph. It is instructive to note that when the centrifugal factor is unity and $A_\infty(T)$ is independent of temperature we recover the RRK result of equation 1.3.

In general, tunneling makes only a minor contribution to the microcanonical rate coefficient. When the effects of tunneling are important, the rate law for the limiting high-pressure rate coefficient will be pronounced non-Arrhenius at low temperatures. Under such circumstances, we expect our Laguerre-function representation of eq 1.4 to approximate the rate law well, as they form an optimal basis set for approximating any arbitrary temperature dependence of the rate coefficient. We have thus also surmounted criticism (b).

Thus we propose in this paper a method, founded on the knowledge of the experimentally observed limiting high-pressure rate coefficient, for generating microcanonical transition state theory rate coefficients from a set of minimal transition state parameters which are easily estimated. Our method does not neglect any of the rotational degrees of freedom and is exact for all temperatures above which the semiclassical approximation holds true. We expect our method to be very useful for multiple-well systems where knowledge of the frequencies and degeneracies of isomerization transition states is not easily obtainable.

The remainder of the paper is organized as follows. Section 2 provides a complete description of our inverse Laplace transform method. We describe the interpolation strategy to obtain the integrated density of states of the transition state and the consequent derivation of the microcanonical transition state theory rate coefficient. All of this is illustrated within the context of the Laguerre basis representation of the ratio of the limiting high-pressure rate coefficient to the centrifugal factor. Limitation of the method for situations where variational microcanonical rate coefficients are desired is described. Section 3 describes a pathological behavior of the inverse Laplace rate coefficients when a modified Arrhenius form is used to represent the limiting high-pressure rate coefficient. The microscopic rate coefficients exhibit negative curvature at large energies due to a mathematical artifact of a modified Arrhenius formalism. Section 4 compares the microcanonical rate coefficients generated by our method for two reactions. The first is the unimolecular decomposition of the ethyl radical. The computations for this reaction, from our nonvariational inverse Laplace scheme, are compared with those from Gilbert's RRKM code[10] which requires explicit knowledge of the transition state frequencies and degeneracies. This is done for a range of angular momentum quantum numbers. We show that excellent agreement is obtained. The second reaction is the isomerization of methyl isocyanide. The computations for this reaction, performed over a wide range of angular momentum quantum numbers, from our nonvariational inverse Laplace scheme are compared with those from Gilbert's RRKM code. We show that, once again, excellent agreement is obtained. The inverse Laplace microcanonical rate coefficients reproduce the fine structure of the microcanonical transition state theory rate coefficients. Section 5 discusses the implications of coping with the knowledge of the limiting high pressure coefficient obtained from experimental measurements over a finite temperature range. Section 6 describes our conclusions. Throughout this paper we adhere to the notations set forth by Forst.[1]

2. The Inverse Laplace Transform Method

Under the assumption holding at high pressures that collisions are much more rapid than chemical reaction, the reacting system can be represented by the Gibbsian canonical ensemble wherein an equilibrium population of the molecules is maintained over all energies and angular momenta. Thus the limiting high-pressure rate coefficient may be interpreted as the average of the microcanonical rate coefficient over the Maxwell−Boltzmann distribution,

$$k_\infty(T) = \langle k(E,J)\rangle_{\text{equilibrium}} = \sum_{J=0}^{\infty}\int_0^\infty k(E,J)P(E,J)_{\text{equilibrium}}\,\mathrm{d}E \tag{2.1}$$

$P(E,J)_{\text{equilibrium}}$ is the equilibrium probability density function for a specific E and J. It has been pointed out by Forst[1] that at the high-pressure limit, within the context of a steady state analysis, the averaged microcanonical rate coefficient is identical with the microcanonical rate coefficient represented by equation 2.1. Making the assumptions that rotations may be treated semiclassically and that the overall rotations are completely decoupled from E, i.e., the moments of inertia are independent of E, the averaged microcanonical rate coefficient may be expressed as

$$\langle k(E,J)\rangle_{\text{equilibrium}} = \frac{1}{Q(T)Q_{\text{rot}}(T)}\int_0^\infty\int_{E_J}^\infty (2J+1)N(E)k(E,J)\exp\left(-\frac{E+E_{\text{r}}(J)}{k_{\text{B}}T}\right)\mathrm{d}E\,\mathrm{d}J \tag{2.2}$$

Here $Q(T)$ is the partition function for the pertinent degrees of freedom involved in the density of states $N(E)$. $Q_{\text{rot}}(T)$ is the partition function for the two-dimensional rotor of energy $E_{\text{r}}(J)$. All other symbols retain their previous meanings. It follows from eqs 2.1 and 2.2 that

$$L^{-1}\left\{\int_0^\infty\int_{E_J}^\infty(2J+1)N(E)k(E,J)\exp(-s(E+E_{\text{r}}(J)))\mathrm{d}E\,\mathrm{d}J\right\} = L^{-1}[k_\infty(s)Q(s)Q_{\text{rot}}(s)] \tag{2.3}$$

where $L^{-1}\{\ \}$ is the inverse Laplace transform operator with respect to the variable E and the parameter s is given by

$$s = \frac{1}{k_{\text{B}}T} \tag{2.4}$$

From the Fourier−Mellin integration theorem,[16] equation 2.3 may be written down as

$$\int_0^\infty(2J+1)N(E-E_{\text{r}}(J))k(E-E_{\text{r}}(J),J)\mathrm{d}J = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}k_\infty(s)Q(s)Q_{\text{rot}}(s)\exp(sE)\mathrm{d}s \tag{2.5}$$

where c is the abscissa of integration in the complex plane. Although the right-hand side of eq 2.5 can be evaluated upon the provision of the limiting high-pressure rate coefficient, the integrand on the left-hand side cannot be deconvoluted to obtain the microcanonical rate coefficient $k(E,J)$ explicitly. It is thus necessary to postulate a model for the microcanonical rate coefficient.

2.1. A Model for $k(E,J)$: Microcanonical Transition State Theory. The microcanonical rate coefficient is given in general by

$$k(E,J) = \frac{\Gamma(E,J)}{hN(E)} \tag{2.6}$$

where $\Gamma(E,J)$ is the cumulative reaction probability at total energy E and total angular momentum J. In the framework of transition state theory, the cumulative reaction probability is approximated by the product of the reaction-path degeneracy and the number of accessible quantum states $G^*(E - E_J)$ for the modes orthogonal to the reaction coordinate and thus the microcanonical transition state theory rate coefficient is given by

$$k(E,J) = \frac{\alpha G^*(E-E_J)}{hN(E)} \tag{2.7}$$

The statistically important modes making effective contributions to the reactive flux are the transitional modes and the number of accessible quantum states is evaluated at the position of the transition state. The position of the transition state depends on the total energy, total angular momentum, and the structure of the interfragment potential, and it may be located at the centrifugal maximum of the effective interfragment potential. This is a simple and nonvariational calculation. Under these circumstances we may write

$$E_J = E_0 - E_r(J) + \phi(J) \tag{2.8}$$

where $\phi(J)$ is the maximum value of the effective interfragment potential. Description of forms of the interfragment potentials is to be found in ref 1 and a recapitulation in ref 17.

For reactions without a chemical barrier, such as radical recombinations and ion−molecule associations or their reverse counterparts, it has been demonstrated[7−9] that it is necessary to perform a variational calculation to locate the position of the transition state at the local minimum of $G^*(E - E_J(t))$, the number of accessible quantum states of the transition state along the reaction coordinate,

$$\frac{\mathrm{d}}{\mathrm{d}t}G^*(E - E_J(t)) = 0 \tag{2.9}$$

where t is the distance along the reaction coordinate. The rest of the presentation of the concepts underlying our inverse Laplace formalism will be based on the nonvariational microcanonical transition state theory. Finally in Section 2.6 the difficulties in adapting the inverse Laplace formalism for the estimation of variational microcanonical rate coefficient will be discussed.

2.2. Computation of $k(E,0)$. Upon substituting the transition state theory expression for the microcanonical rate coefficient into equation 2.2, the following relationship

$$\langle k(E,J)\rangle_{\mathrm{equilibrium}} = k_\infty(T) = \frac{\alpha}{hQ(T)Q_{\mathrm{rot}}(T)}\int_0^\infty\int_{E_J}^\infty(2J+1)G^*(E-E_J)\exp\left(-\frac{E+E_r(J)}{k_{\mathrm{B}}T}\right)\mathrm{d}E\,\mathrm{d}J \tag{2.10}$$

results. Following Forst,[1] the angular momentum portion of the integrand in eq 2.10 may be separated out by utilizing eq 2.8, and a temperature-dependent centrifugal factor, $f_\infty(T)$, representing the average over the angular momenta,

$$f_\infty(T) = \frac{1}{Q_{\mathrm{tot}}(T)}\int_0^\infty(2J+1)\exp\left(-\frac{\phi(J)}{k_{\mathrm{B}}T}\right)\mathrm{d}J \tag{2.11}$$

can be obtained. It is then observed that the averaged microcanonical rate coefficient may be written as

$$\langle k(E,J)\rangle_{\mathrm{equilibrium}} = k_\infty(T) = \frac{f_\infty(T)}{Q(T)}\int_0^\infty k(E,0)N(E)\exp\left(-\frac{E}{k_{\mathrm{B}}T}\right)\mathrm{d}E \tag{2.12}$$

where $k(E,0)$ is identically zero when $E < E_0$, and

$$k(E,0) = \frac{\alpha G^*(E-E_0)}{hN(E)} \tag{2.13}$$

when $E \geq E_0$. Now that the preliminaries are completed, our next step is to obtain $k(E,0)$ via the inverse Laplace transform of eq 2.12. It follows from 2.4, 2.12, and 2.13 that

$$\frac{k_\infty(s)Q(s)}{f_\infty(s)} = \frac{\alpha}{h}L\{G^*(E-E_0)\} = L\{k(E,0)N(E)\} \tag{2.14}$$

where L{ } is the Laplace transform with respect to the parameter s and the variable E. The inverse Laplace transform of eq 2.14 may be written down as

$$k(E,0)N(E) = L^{-1}\left\{\frac{k_\infty(s)Q(s)}{f_\infty(s)}\right\} \tag{2.15}$$

Each of $k_\infty(s)$, $Q(s)$, and $f_\infty(s)$ are individually inverse Laplace transformable, and hence, using the convolution theorem[16] for Laplace transforms we may write

$$k(E,0)N(E) = L^{-1}\left\{\frac{k_\infty(s)}{f_\infty(s)}\right\}\otimes \mathrm{L}^{-1}\{Q(s)\} \tag{2.16}$$

Here ⊗ is the Faltung operator.[16] Equation 2.16 is exact and is easily evaluated upon the provision of a functional form for $k_\infty(s)$, the limiting high-pressure rate coefficient and the centrifugal factor $k_\infty(s)$, since $L^{-1}\{Q(s)\}$ is simply $N(E)$ itself.

2.2.1. Computing the Centrifugal Factor. Equation 2.16 could have been written down explicitly as

$$k(E,0)N(E) = L^{-1}\{k_\infty(s)\}\otimes L^{-1}\{Q(s)\}\otimes L^{-1}\left\{\frac{1}{f_\infty(s)}\right\} \tag{2.17}$$

Even though all of the individual terms in the convolution (eq 2.17) possess inverse Laplace transforms, in general, explicit analytical forms exist only for $L^{-1}\{Q(s)\}$. The coefficient $k_\infty(s)$ is an arbitrary function of temperature, and hence, its inverse Laplace transform can be evaluated only numerically. $L^{-1}\{1/f_\infty(s)\}$ can also be evaluated only via numerical means or by the method of steepest descents[18] by computing the location of a saddle point. The method of steepest descents, although widely used, is not necessarily the method of utmost accuracy.[19−22] Numerical evaluation of contour integrals, such as in eq 2.5, is cumbersome. Among the numerical inversion methods, the Stehfest algorithm[20] requires only a few function evaluations along the real axis and its convergence is therefore rapid although the test for the convergence of this algorithm is not straightforward. Alternatively, one may use the Dubner and Abate method;[19] its convergence properties, albeit not as attractive as the Stehfest algorithm's are easy to test and the convergence itself may be accelerated using Pade's approximants as set forth by Crump.[21]

For reasons of accuracy, we compute numerically the ratio

$$\tilde{k}_\infty(s) = \frac{k_\infty(s)}{f_\infty(s)} \tag{2.18}$$

and fit it to a Laguerre basis sum, the description of which follows in the next section. Analytical forms for the inverse Laplace transform of Laguerre basis functions are readily written down. The evaluation of the ratio in eq 2.18 requires the computation of the centrifugal factor

$$f_\infty(s) = \frac{1}{Q_{\mathrm{rot}}(s)}\int_0^\infty(2J+1)\exp(-s\phi(J))\mathrm{d}J \tag{2.19}$$

The partition function $Q_{\mathrm{rot}}(s)$ is given by the integral

$$Q_{\mathrm{rot}}(s) = \int_0^\infty(2J+1)\exp(-s\{E_0-E_J+\phi(J)\})\mathrm{d}J \tag{2.20}$$

The next step is the computation of the integral

$$\int_0^\infty(2J+1)\exp(-s\phi(J))\mathrm{d}J \tag{2.21}$$

This can be done analytically for some forms of the interfragment potential as shown in Forst,[1] but in general, for other forms of the interfragment potential, it is done most effectively via the Gauss−Chebyshev quadrature[23] adapted for the semiinfinite interval, [0, ∞] by the introduction of a scale parameter L. The quadrature formula is then given by

$$\int_0^\infty(2J+1)\exp(-s\phi(J))\mathrm{d}J \approx \frac{\pi}{N}\sum_{i=0}^{N-1}\sqrt{\frac{J_i}{L}}(J_i+L)(2J_i+1)\exp(-s\phi(J_i)) \tag{2.22}$$

Here the quadrature points are the roots of the Nth order Chebyshev polynomial in $(J-L)/(J+L)$. These quadrature points may be written down analytically[23] as

$$J_{i-1} = L\frac{\left(1 + \cos\left[\frac{(2i-1)}{2N}\pi\right]\right)}{\left(1 - \cos\left[\frac{(2i-1)}{2N}\pi\right]\right)} \tag{2.23}$$

The scale parameter L is empirically chosen, and its choice should ensure that the absolute value of $\exp(-s\phi(J_{N-1}))$ is negligible. This determines the number of quadrature points, N for the accurate transcription of the integral to a discrete sum. For the various choices described in ref 1 and recapitulated in ref 17, $\phi(J)$ decays rather rapidly. In our computations it was found that a choice of N taken to be 250 gave rise to an inaccuracy of no more than 0.02% in the quadrature sum. The use of Gaussian points to approximate definite and improper integrals is well-known in approximation theory, and little is to be gained by repeating the details here. The reader will find good expositions in treatises such as Cheney's.[24] The partition function given by eq 2.20 may be similarly computed using this quadrature.

2.2.2. The Laguerre Representation. Once the centrifugal factor is computed as prescribed in the previous section, the next task is to approximate the ratio $\tilde{k}_\infty(s)$ by a finite Laguerre basis set,

$$\tilde{k}_\infty(s) \approx \sum_{n=0}^{M-1} B_n \exp(-E_\infty s) L_n(s^{-1}) \tag{2.24}$$

where $L_n(s^{-1})$ is the Laguerre polynomial[16] of order n. The coefficients $\{B_n;\ 0 \le n \le M-1\}$ are determined by a least-squares fit to the numerically tabulated values of the ratio of the limiting high-pressure rate coefficient to the centrifugal factor. The integer parameter M is chosen to provide as accurate a representation as desired. This form possesses the property that the ratio $k_\infty(s)/f_\infty(s)$ is infinite when the temperature goes to infinity because $f_\infty(s)$ goes to unity (see eq 2.19) and $k_\infty(s)$ diverges. This property prevents pathological behavior in the computed microcanonical rate coefficient which might otherwise arise and will be the subject of discussion in section 3. The Laguerre basis set $\{L_n(s^{-1})\}$ is orthonormal in $[0, \infty)$ with respect to the weight function $\exp(-1/2s)$, and the Laguerre polynomials are evaluated via the following recursion relations.

$$L_0(s^{-1}) = 1 \tag{2.25}$$

$$L_1(s^{-1}) = 1 - s^{-1} \tag{2.26}$$

$$(n+1)L_{n+1}(s^{-1}) = [(2n+1) - s^{-1}]L_n(s^{-1}) - nL_{n-1}(s^{-1}) \tag{2.27}$$

The Laguerre basis functions are straightforwardly Laplace transformable.[25] Noticing the correspondence between eqs 1.4 and 2.24, what has been essentially done here is that the ratio of the preexponential in the limiting high-pressure rate coefficient to the centrifugal factor has been approximated by a sum of Laguerre polynomials in k_BT,

$$\frac{A_\infty(s)}{f_\infty(s)} \approx \sum_{n=0}^{M-1} B_n L_n(s^{-1}) \tag{2.28}$$

Just as the Fourier basis is the optimal approximating basis for a periodic function in $[-1, 1]$ and a Chebyshev basis is the optimal approximating basis for a nonperiodic function in $[-1, 1]$ the Laguerre basis $\{L_n(s^{-1})\}$ is the optimal approximating basis[24] for a general function which is defined over the support $[0, \infty]$ and is dominated by the exponential weight function as $k_BT \to 0$. The highest exponent of k_BT in eq 2.24 is $M - 1$.

$$\lim_{T\to\infty} A_\infty(T) \propto (k_BT)^{M-1} \tag{2.29}$$

which has been used on empirical grounds for the high-temperature behaviour of $A_\infty(T)$. However, as we discussed in section 1, because of tunneling such behavior cannot be extended to low temperatures for some systems despite the fact that it follows from simplified applications of transition state theory.

2.2.3. Final Analytical Expression for k(E,0). It is convenient to reexpress eq 2.24 in the following form,

$$\tilde{k}_\infty(s) \approx \sum_{n=0}^{M-1} \beta_n \frac{\exp(-sE_\infty)}{s^n} \tag{2.30}$$

where the coefficients $\{\beta_n;\ 0 \le n \le M-1\}$ possess a simple linear algebraic relationship to the coefficients $\{B_n;\ 0 \le n \le M-1\}$. Equation 2.16 may now be written down as

$$k(E,0)N(E) = \int_0^E \Bigg\{ \delta(E' - E_\infty)\beta_0 + \sum_{n=1}^{M-1} \frac{(E' - E_\infty)^{n-1}}{(n-1)!} u(E' - E_\infty)\beta_n \Bigg\} N(E - E')\,\mathrm{d}E' \tag{2.31}$$

Here $\delta(E' - E_\infty)$ is the Dirac delta function and $u(E' - E_\infty)$ is the Heaviside function. We may write eq 2.31 as

$$k(E,0) = \beta_0 \frac{N(E' - E_\infty)}{N(E)} + \sum_{n=1}^{M-1} \beta_n \int_0^E \frac{(E' - E_\infty)^{n-1}}{(n-1)!} u(E' - E_\infty) \frac{N(E - E')}{N(E)}\,\mathrm{d}E' \tag{2.32}$$

The first term on the right-hand side of eq 2.32 is the standard RRK expression for the microcanonical rate coefficient. We may now note from eq 2.13 that the integrated density of the transition state may be written as

$$G^*(E - E_0) = \frac{h}{\alpha}\Bigg(\beta_0 N(E - E_\infty) + \sum_{n=1}^{M-1} \beta_n \int_0^E \frac{(E' - E_\infty)^{n-1}}{(n-1)!} u(E' - E_\infty) N(E - E')\,\mathrm{d}E' \Bigg) \tag{2.33}$$

It should be noted that in eq 2.33 E_0 is not strictly identical to E_∞, although kineticists usually estimate E_0 to be the E_∞ obtained from high-pressure thermal experimental observations.

2.2.4. Comments on the Laguerre Representation: Uniform Approximation. We have approximated the ratio of the limiting high-pressure rate coefficient to the centrifugal factor by a sum of Laguerre basis functions; this set of basis functions can be shown to be the optimal basis set for such an approximation and minimizes approximation errors due to the classically well-known Runge phenomenon—a characteristic of nonuniform approximation.[24] The inverse Laplace transform of the Laguerre sum is analytically written down and the microcanonical rate coefficient for zero angular momentum is then obtained.

Schoenenberger and Forst[26] have considered the Gauss−Laguerre discretization of the semiinfinite integral in eq 2.12 and this is quite different from the method we have presented. Their procedure amounts to a discrete Laplace transform over a *finite* range of the total energy E. They have shown that in using such an inversion strategy to calculate the microcanonical rate coefficients, large errors can result with high oscillations as a function of the total energy. They have also shown that approximating the ratio of the limiting high-pressure rate coefficient to the centrifugal factor by a sum of simple polynomials in s and analytically inverting the resulting expression results in substantially lower errors for the calculated microcanonical rate coefficient than that obtained from the Gauss−Laguerre discretization of the Laplace transform.

Approximation theory tells us that approximating the ratio of the limiting high-pressure rate coefficient to the centrifugal factor by a sum of Laguerre basis functions, as we have done, is vastly superior to approximation by a sum of simple polynomial functions. The choice of a Laguerre basis serves to overcome the Runge phenomenon. This means that the Laguerre approximant obtained via the least-squares minimization will converge uniformly[24] to the function over the entire interval of approximation $s \in [0, \infty)$ *or equivalently* $T \in [0, \infty)$, most importantly, this means that the errors in the microcanonical rate coefficients computed via the inverse Laplace methodology are *uniformly distributed over the entire semifinite range*, $[0, \infty)$, of the total energy E. If one were to fit a function to a sum of arbitrary polynomials or non-linear functions the resulting approximant, besides being numerically ill-conditioned, will capture the function well only in the middle of the interval while exhibiting highly oscillatory behavior toward the ends of the interval; this pathology is known as the Runge phenomenon. The Laguerre basis set is able to overcome this precisely because the Sturm−Liouville weight function for the Laguerre basis is a damping exponential.

2.3. Computing $k(E,J)$ by Interpolating for the Integrated Density. In order to compute $k(E,J)$ for a nonzero angular momentum, we must know the integrated density of states $G^*(E - E_J)$ of the transition state. Knowledge of $G^*(E - E_0)$ is sufficient to determine $G^*(E - E_J)$ through the relation

$$G^*(E - E_J) = G^*(E'_J - E_0),\ E'_J = E + (E_0 - E_J) \tag{2.34}$$

In other words, the knowledge of $k(E,0)$ from the inverse Laplace step in eq 2.32 and the density of states of all chemically active modes of the dissociating molecule $N(E)$ provides us with the integrated density of states $G^*(E - E_J)$ for any E_J. We suggest here a smooth radial basis function (RBF) approximant[27] to the integrated density of states. In the RBF approch we fit

$$\frac{h}{\alpha} k(E,0) N(E) \tag{2.35}$$

to the special form

$$\frac{h}{\alpha} k(E,0) N(E) = \lambda_0 + \sum_{i=1}^{d} \lambda_i \phi(||E - E_i||) \tag{2.36}$$

with the constraint

$$\sum_{i=1}^{\mathrm{d}} \lambda_i = 0 \tag{2.37}$$

Here the norm $||E - E_i||$ denotes the absolute value of $E - E_i$. The d parametrs λ_i, $i = 1, ..., d$, are to be determined by matrix inversion such that eqs 2.36 and 2.37 hold. The E_i, $i = 1, ..., d$ (called the centers of the radial bases) are distinct and are the points at which $k(E_i,0)$ is obtained from the inverse Laplace transform procedure. It has been shown that systems such as those described by eqs 2.36 and 2.37 will be nonsingular for many choices[28] of the radial basis $\phi(||E - E_i||)$, including the thin-plate splines recommended by us. Thin-plate splines are given by

$$\phi(||E - E_i||) = ||E - E_i||^2 \log||E - E_i|| \tag{2.38}$$

RBF approximants consisting of thin-plate splines may be evaluated rapidly through a truncated Laurent-expansion technique.[29] The numerically stable and well-conditioned inversion of eqs 2.36 and 2.37 is best done by normalizing the norms onto the interval $[-1, 1]$ and by applying a sequence of Householder transformations[30] to the resultant equations. Once the effective critical energy for the dissociation E_J is computed, the interpolated integrated density of the transition state may be used to obtain $k(E,J)$ from eq 2.7 for any total energy E and any nonzero angular momentum quantum number J.

2.4. Transition State. Our motive in this section is to show the relation between the frequencies and degeneracies of the transition-state and the inverse Laplace expression for the integrated density. The RRKM expression for the integrated density at zero angular momentum is given by

$$G^*(E - E_0) = \int_0^{E-E_0} N^*(E')\, \mathrm{d}E' \tag{2.39}$$

where $N^*(E')$ is the density of states of the transition state at energy E'. The inverse Laplace expression for the integrated density at zero angular momentum is given by

$$G^*(E - E_0) = \frac{h}{\alpha}\left(\beta_0 N(E - E_\infty) + \sum_{n=1}^{M-1} \beta_n \int_0^E \frac{(E' - E_\infty)^{n-1}}{(n-1)!} u(E' - E_\infty) N(E - E')\mathrm{d}E'\right) \tag{2.40}$$

In the limit of $M \rightarrow \infty$ eqs 2.39 and 2.40 are identical. Because the Laguerre basis is orthonormal and complete over $[0, \infty]$, β_M decays rapidly as a function of M. In the cases examined by us β_M is negligibly small for $M > 10$. We note that the forms of eqs 2.39 and 2.40 are identical, in the sense that both of them are convolutions in energy. $N^*(E')$ is a function of the frequencies and degeneracies of the transition state. Similarly $\{\beta_n;\ 0 \le n \le M - 1\}$ are functions of the frequencies and degeneracies of the transition state, except that they have been determined numerically from the knowledge of the limiting high-pressure rate coefficient alone. The smooth function approximation to the density of states of the transition state is then given by

$$N^*(E) = \beta_0 \frac{h}{\alpha} \frac{\mathrm{d}}{\mathrm{d}E} N(E + E_0 - E_\infty) + \sum_{n=1}^{M-1} \beta_n \frac{h}{\alpha} \frac{(E + E_0 - E_\infty)^{n-1}}{(n-1)!} u(E + E_0 - E_\infty) N(E_0) + \sum_{n=1}^{M-1} \beta_n \frac{h}{\alpha} \int_0^{E+E_0} \frac{(E' - E_\infty)^{n-1}}{(n-1)!} u(E' - E_\infty) \frac{\mathrm{d}}{\mathrm{d}E} N(E + E_0 - E')\mathrm{d}E' \tag{2.41}$$

Equation 2.41 is obtained by differentiating eq 2.40; an application of the Newton−Leibniz formula. We may note that eq 2.40 is of utility in determining the critical energy for dissociation E_0 from the knowledge of the high-pressure activation energy E_∞ and the coefficients $\{\beta_n;\ 0 \leq n \leq M - 1\}$.

2.5. Threshold Behavior of the Inverse Laplace $k(E,J)$. It has been shown by Rice[31] and Forst[13] that the threshold behavior of the microcanonical transition state theory rate coefficient obeys

$$\lim_{E \to E_0} k(E,0) = \frac{1}{hN(E_0)} \tag{2.42}$$

where E_0 is the effective critical energy for the dissociation of the molecule when the angular momentum quantum number is set to zero. For very low energies $N(E)$ can be viewed as a linear combination of discrete delta functions which are widely spaced. This gives rise to the fine structure or jaggedness of the microcanonical transition state theory rate coefficients which is pronounced at very low energies, but present in principle at higher energies.

At the threshold, the inverse Laplace microcanonical rate coefficient obeys

$$\lim_{E \to E_0} k(E,0) = \beta_0 \frac{N(E_0 - E_\infty)}{N(E_0)} + O(k_B T) \tag{2.43}$$

where we have taken the appropriate limit of eq 2.32. For consistency with microcanonical transition state theory, it is necessary that

$$h\beta_0 N(E_0 - E_\infty) = 1 \tag{2.44}$$

where we have neglected the $O(k_B T)$ term in eq 2.43. The lack of experimental information often leads kineticists to set E_0 to E_∞. However, a semiclassical model of the density of states will lead to zero density of states at zero energy. Equation 2.44 would then imply that $\beta_0 = \infty$. Our examination of specific cases leads us to observe that β_0 is finitely large and $N(E_0 - E_\infty)$ is thus small but nonzero. This implies that E_0 exceeds E_∞ by a few $k_B T$ conforming the analysis presented by Forst in ref 13. As a consequence, $E_J < E_0$ for any J, which is physically plausible. E_0 can be numerically estimated from E_∞ by applying the Newton−Raphson technique to equation 2.40.

2.6. Variational Microcanonical Rate Coefficients and the Inverse Laplace Method. A principal advantage of the inverse Laplace procedure described here is that there are no adjustable parameters and that guessing the frequencies and degeneracies of the transition state is obviated. A drawback of the method is that the position of the transition state is not located variationally, and hence, the microcanonical rate coefficients thus generated will not be descriptive of the kinetics of simple bond-fission unimolecular reactions, particularly at low temperatures. Extension of the inverse Laplace procedure to incorporate a variational treatment presents difficulties. Consider eq 2.14 within a variational framework,

$$G^*(E - E_0(t_{\min})) = \frac{h}{\alpha} L^{-1}\left\{\frac{k_\infty(s)Q(s)}{f_\infty^{\mathrm{var}}(s)}\right\} \tag{2.45}$$

where $t_{\min}$ is the reaction coordinate (for zero angular momentum) at which $G^*(E - E_0(t))$ possess a local minimum. The centrifugal factor $f_\infty^{\mathrm{var}}(s)$ is now given by

$$f_\infty^{\mathrm{var}}(T) = \frac{1}{Q^{\mathrm{var}}{}_{\mathrm{rot}}(T)} \int_0^\infty (2J + 1) \exp\left(-\frac{\phi(J)|_{t_{\min}(J)}}{k_B T}\right) \mathrm{d}J \tag{2.46}$$

where $Q^{\mathrm{var}}{}_{\mathrm{rot}}(T)$ is the associated partition function. $\phi(J)$ is now evaluated at $t_{\min}(J)$, which is a function of E_J and is the reaction coordinate at which $G^*(E - E_J(t))$ possesses a local minimum. Evaluation of the centrifugal factor cannot be accomplished unless $t_{\min}(J)$ is known for all J. Without any knowledge of the transition state frequencies and degeneracies, which will be dependent on the reaction coordinate, it is not possible to obtain $t_{\min}(J)$ for each J.

This seems to render the inverse Laplace framework self-defeating because the essential appeal in the non-variational treatment has been that the knowledge of the limiting high-pressure rate coefficient circumvents the need to know the transition state frequencies and degeneracies. Because the limiting high-pressure rate coefficient represents the equilibrium average over the total energy E and total angular momentum J, recovering the $t_{\min}(J)$ at which the integrated density achieves a minimum at a given J from $k_\infty(T)$ seems implausible if not downright impossible.

Rigorous Monte-Carlo calculation[7,8] of the variational microcanonical transition state theory rate coefficients is complicated. It is computationally expensive and requires the knowledge of many parameters pertinent to the potential energy surface but not any knowledge of the limiting high-pressure rate coefficient. Forst[9] has proposed a variational theory wherein a simple interpolation strategy, which switches between the reactant and product frequencies as a function of the reaction coordinate, is used. His method is computationally undemanding but does require the knowledge of the limiting high-pressure rate coefficient to adjust his switching function.

In conclusion the inverse Laplace transform method of calculating microcanonical transition state theory rate coefficients proposed here should be used for cases where it is legitimate to locate the position of the transition state at the centrifugal maximum of the effective interfragment potential. It requires the knowledge of the limiting high-pressure rate coefficient and does not embed any adjustable parameters.

2.7. Summary of the Underlying Assumptions. We now recapitulate the assumptions invoked in the derivation of the inverse Laplace method described here.

It has been assumed throughout that the limiting high-pressure rate coefficient is known exactly. In reality, there will exist systematic experimental errors in these measured coefficients. Furthermore, they are usually measured accurately only over selected temperature ranges and this can introduce an artificial skewness; notable exceptions include the reactions of methyl isocyanide, ethyl isocyanide, cyclopropane, cyclobutane, hydrazine, nitrous oxide, and carbon dioxide for which comprehensive measurements are available.[15] This artifical skewness of data, when it occurs, is the major source of objections to the inverse Laplace method. However, the objection in fact applies to all methods drawing information from $k_\infty(T)$; such as those that guess the frequencies and degeneracies of the transition state from $k_\infty(T)$. In section 5 below, we propose a method of reducing the error from this source. A second source of error will be due to the finite truncation of the Laguerre series in eq 2.24. Equation 2.24 is an exact equality when $M \to \infty$. One can prove[32] that the coefficients of the Laguerre expansion of a smooth function, such as $\tilde{k}_\infty(s)$, decay faster than algebraically.

Based on a steepest descent analysis it can be shown[32,33] that the truncation error in eq 2.24 is given by the following asymptotic order of magnitude relationship

$$\text{truncation error} \approx 0\ (a_{M-1}) \tag{2.47}$$

where M is the total number of retained basis functions in the Laguerre expansion. In our calculations, it was found that a choice of $M = 10$ was sufficient to obtain negligibly small truncation errors. For a critical appraisal of the convergence properties of Laguerre spectral expansions, the reader is referred to ref 32.

(i) Rotations may be treated semiclassically and that overall rotations can be decoupled from the total energy E. This assumption will be invalid for very low temperatures.

(ii) In the treatment of the intramolecular energy transfer, simplifications inherent in the quasidiatomic model of energized complexes may be relied upon; the analysis can be extended to include the effect of asymmetric rotors.[34]

(iii) The microcanonical rate coefficients $k(E,J)$ may be modeled using microcanonical transition state theory. This is a safe assumption provided the barrier heights for the reaction are higher than a certain low threshold limit.

(iv) The integrated density of the transition state may be obtained from a smooth radial basis approximant. The integrated density is a monotonically increasing function but is best described as a linear combination of Heaviside functions. The radial basis approximant will provide very accurate approximations to the integrated density provided the number of centers for the radial bases is taken to be suitably large.

3. A Pathology in Using van't Hoff's Modification of Arrhenius' Form

Non-Arrhenius forms for the limiting high-pressure rate coefficient have been considered before for the generation of microcanonical rate coefficients by the use of the inverse Laplace transform procedure. In particular, Pritchard[15] and Forst and Turrell[35] have investigated the forms

$$k_\infty(T) = A_\infty T^n \exp\left(-\frac{E_\infty}{k_B T}\right) \tag{3.1}$$

with $n > 0$, and

$$k_\infty(T) = A_\infty \exp(\lambda T) \exp\left(-\frac{E_\infty}{k_B T}\right) \tag{3.2}$$

with $\lambda > 0$. However these forms do not allow for nonmonotonicity in the limiting high-pressure rate coefficient. An approach[36] might be to use the modification of *van't Hoff* to Arrhenius' form,

$$k_\infty(T) = A_\infty T^n \exp(-\alpha T) \exp\left(-\frac{E_\infty}{k_B T}\right) \tag{3.3}$$

with $n > 0$ and $\alpha > 0$. This form allows for decay at high temperatures while exhibiting increasing behavior at low temperatures. For simplicity of exposition, we neglect the centrifugal factor in eq 2.16

$$k(E,0)N(E) = L^{-1}\{k_\infty(s)\} \otimes \mathrm{L}^{-1}\{Q(s)\} \tag{3.4}$$

and upon substituting eq 3.3 we obtain

$$k(E,0)N(E) = \frac{A_\infty}{k_B^n}\int_0^E \left(\frac{E' - E_\infty}{\alpha/k_B}\right)^{n-1/2} J_{n-1}\left(2\sqrt{\frac{\alpha}{k_B}(E' - E_\infty)}\right) u(E' - E_\infty) N(E - E')\,\mathrm{d}E' \tag{3.5}$$

Here $u(E' - E_\infty)$ is the Heaviside function and J_{n-1} is the Bessel function of continuous order $n - 1$ and is given by[37]

$$J_{n-1}\left(2\sqrt{\frac{\alpha}{k_B}(E' - E_\infty)}\right) = \frac{1}{\pi}\int_0^\pi \cos\left[(n-1)\theta - 2\sqrt{\frac{\alpha}{k_B}(E' - E_\infty)}\sin\theta\right]\mathrm{d}\theta - \frac{\sin[(n-1)\pi]}{\pi}\int_0^\infty \exp\left[-(n-1)\theta - 2\sqrt{\frac{\alpha}{k_\mathrm{B}}(E' - E_\infty)}\sinh\theta\right]\mathrm{d}\theta \tag{3.6}$$

Equation 3.6 is valid for $E' \geq E_\infty$. As for the case of the evaluation of the centrifugal factor, equation 3.6 is easily and accurately evaluated by quadrature.[23,24]

One may note that the integrand of the first integral in the right-hand side of eq 3.6 is an oscillatory function of $E' - E_\infty$. In particular for large values of $E' - E_\infty$, $k(E,0)$, as given by eq 3.5 will not only exhibit negative curvature but will also assume rapidly oscillating negative values, because T and E are Laplace transform pairs and it is necessary that

$$\lim_{T\to\infty} k_\infty(T) = \lim_{E\to\infty} k(E,0) \tag{3.7}$$

holds. The pathological behavior in using the modified Arrhenius formalism arises because in the high-temperature limit the $k_\infty(T)$ given by eq 3.3 asymptotes to zero, when in fact it should approach infinity or asymptote to a finitely large value. Such pathology does not arise in our generic Laguerre representation given by eq 2.24.

4. A Comparison of the Inverse Laplace and RRKM Rate Coefficients

In this section we present the comparison of the microcanonical rate coefficients obtained from the inverse Laplace and RRKM methodologies for two well studied reactions; the RRKM methodology requires explicit knowledge of the frequencies and degeneracies of the transition state while the inverse Laplace methodology does not. Our paramount objective is to compare the microcanonical rate coefficients obtained from these methods rather than elucidating the chemical dynamics of the reactions considered. Accordingly, the calculations have been performed at selected temperatures for each system. Defining the relative error between the inverse Laplace and the RRKM microcanonical rate coefficient as

$$R(E,J) = 1 - \frac{k(E,J)|_{\mathrm{Laplace}}}{k(E,J)|_{\mathrm{RRKM}}} \tag{4.1}$$

the results are presented here for specific total angular momenta J with respect to two norms. The first is the infinity norm $\xi_{L_\infty}(J)$ which we define as

$$\xi_{L_\infty}(J) = [|R(E,J)|]_{\mathrm{maximum}} \tag{4.2}$$

and represents the maximum deviation, over the total energy

TABLE 1: Comparison of the Inverse Laplace and RRKM Microcanonical Rate Coefficients for the Decomposition of the Ethyl Radical for 10- and 15-Term Laguerre Expansion

total angular momentum	$\xi_{L_\infty}(J) = \left[\left\|1 - \frac{k(E,J)\|_{\text{Laplace}}}{k(E,J)\|_{\text{RRKM}}}\right\|\right]_{\text{maximum}}$	$\xi_{L_2}(J) = \left[\frac{\int_E \left(1 - \frac{k(E,J)\|_{\text{Laplace}}}{k(E,J)\|_{\text{RRKM}}}\right)^2 \mathrm{d}E}{\int_E \mathrm{d}E}\right]^{1/2}$
	(a) 10 Term	
0	3.4e-05	1.2e-05
20	4.1e-06	1.0e-06
40	3.7e-06	1.6e-06
60	3.3e-06	1.6e-06
80	3.3e-06	1.4e-06
100	1.9e-07	1.1e-07
200	2.3e-08	1.7e-08
	(b) 15 Term	
0	1.0e-6	1.0e-06
20	7.3e-07	1.7e-07
40	6.3e-07	1.7e-07
60	9.8e-08	9.2e-08
80	7.0e-08	6.5e-08
100	3.2e-08	2.3e-08
200	2.6e-08	2.1e-08

E, of the inverse-Laplace microcanonical rate coefficient from the RRKM microcanonical rate coefficient relative to the latter. The second is the Euclidean norm $\xi_{L_2}(J)$ which we define as

$$\xi_{L_2}(J) = \left[\frac{\int_E R(E,J)^2 \, \mathrm{d}E}{\int_E \mathrm{d}E}\right]^{1/2} \tag{4.3}$$

and represents the averaged Euclidean norm of the deviation of the inverse Laplace microcanonical rate coefficient from the RRKM microcanonical rate coefficient relative to the latter over the total energy E. Additionally, the relative errors $R(E,J)$ are graphically displayed for chosen fixed total energies and fixed total angular momenta.

4.1. The Decomposition of the Ethyl Radical. The β-scission of the ethyl radical

$$C_2H_5 \rightarrow C_2H_4 + H \tag{4.4}$$

is a well-studied reaction. Estimates of the transition state parameters are available from an ab initio calculation[38] which shows good agreement with experimental data.[39] Recently, Feng and co-workers[40] have studied the weak-collision effects in this reaction in a helium bath. We have chosen the transition state frequencies and degeneracies, rotational constants, and the limiting high-pressure data from their study. The limiting high-pressure Arrhenius parameters A_∞ and E_∞ were obtained as a function of temperature for the range 200−1100 K. These were then used to generate the limiting high-pressure rate coefficient over a dense set of points covering the said temperature range. The ratio of the limiting high-pressure rate coefficient to the centrifugal factor was computed at each of these points and was fitted to a Laguerre expansion of the form given by equation 2.24. The E_∞ in eq 2.24 is taken to be the best fit for E_∞ over the temperature range 200−1100 K. The inverse Laplace microcanonical rate coefficients were generated separately for Laguerre expansions with 10, 15, and 20 terms; in carrying out the inversions, the Laguerre expansions were inverted over the entire temperature range $[0, \infty)$. The microcanonical RRKM rate coefficients were generated using Gilbert's UNIMOL code.[10] The methods for computing the density of states and the energy spacings were taken to be identical in both of these calculations. Table 1 displays the relative errors in the inverse Laplace coefficients with respect to the RRKM coefficients for Laguerre expansions with certain specific number of terms and Figure 1 depicts the same errors for certain fixed total energies and certain fixed total angular momenta. The equidistant energy spacing taken in these calculations was 0.1 kcal/mol. All of the plots display the results for the case of the ten-term Laguerre expansion. It can be seen that the relative errors with respect to the infinity- and Euclidean-norms are so small that the microcanonical rate coefficients delivered by these two methods are virtually identical over the entire range of total angular momenta $J \in [0, 200]$ and the entire range of total energy $E \in [0, 200]$ Kcal/Mole. Additional comparisons and a full compendium of results for this reaction are available in [17].

4.2. Isomerization of Methyl Isocyanide. The isomerization of methyl isocyanide

$$CH_3NC \leftrightarrow CH_3CN \tag{4.5}$$

has proven to be of great importance[1,3,15] in the development of unimolecular reaction rate theories. In 1987, Roenigk and co-workers[41] theoretically estimated the high-pressure parameters for this reaction by non-linear regression of RRKM predictions on published experimental data.[42,43] We performed inverse-Laplace and RRKM calculations based on the limiting high-pressure and transition state parameters described in their work. The ratio of the limiting high-pressure rate coefficient to the centrifugal factor was computed over a densely spaced temperature grid of the range 400−600 K. This was then fitted to a Laguerre representation of the form eq 2.24 with E_∞ taken to be the mean of the values recommended in ref 41. The inverse Laplace microcanonical rate coefficients were generated separately for Laguerre expansions with 10, 15, and 20 terms; in carrying out the inversions, the Laguerre expansions were inverted over the entire temperature range $[0, \infty)$. The microcanonical RRKM rate coefficients were generated using Gilbert's UNIMOL code[10] with identical manner of computations of the density of states. Table 2 displays the relative errors in the inverse Laplace coefficients with respect to the RRKM coefficients for Laguerre expansions with certain specific number of terms and Figure 2 depicts the same errors for certain fixed total energies and certain fixed total angular

TABLE 2: Comparison of the Inverse Laplace and RRKM Microcanonical Rate Coefficients for the Isomerization of the Methyl Isocyanide for 10- and 15-Term Laguerre Expansion

total angular momentum	$\xi_{L_\infty}(J) = \left[\left\|1 - \frac{k(E,J)\|_{\text{Laplace}}}{k(E,J)\|_{\text{RRKM}}}\right\|\right]_{\text{maximum}}$	$\xi_{L_2}(J) = \left[\frac{\int_E \left(1 - \frac{k(E,J)\|_{\text{Laplace}}}{k(E,J)\|_{\text{RRKM}}}\right)^2 \mathrm{d}E}{\int_E \mathrm{d}E}\right]^{1/2}$
	(a) 10 Term	
0	2.4e-06	2.2e-06
20	2.5e-06	2.2e-06
40	1.04e-06	1.0e-06
60	1.04e-06	1.1e-06
80	8.1e-07	8.0e-07
100	3.0e-07	2.6e-07
200	1.12e-07	1.09e-07
	(b) 15 Term	
0	2.2e-6	2.1e-06
20	9.3e-07	8.9e-07
40	8.2e-07	7.6e-07
60	7.4e-07	7.3e-07
80	4.9e-07	3.4e-07
100	1.07e-07	9.7e-08
200	1.07e-07	9.9e-08

momenta. The equidistant energy spacing taken in these calculations was 0.1 kcal/mol. All of the plots display the results for the case of 10-term Laguerre expansion. As for the case of the decomposition of the ethyl radical, the relative errors with respect to the infinity and Euclidean norms are so small that the microcanonical rate coeffients delivered by these two methods are virtually identical over the entire range of total angular momenta $J \in [0, 200]$ Kcal/mol. As with the case of the decomposition of the ethyl radical, additional comparisons and conspectus of results for this reaction are available in ref 17.

The full data set for each of the aforementioned examples and the computer programs for the computation of the microcanonical rate coefficients from thermal data are available from the authors.

5. Coping with a Finite Temperature Range

A criticism leveled on the inverse Laplace methodology for deriving microcanonical rate coefficients has been that the limiting high-pressure rate coefficient is experimentally measurable only over a finite range of temperature while the Laplace transform is taken over the semiinfinite temperature range $[0,\infty)$. Such criticism is equally applicable to using the RRKM formalism for computing microcanonical rate coefficients when the transition state frequencies and degeneracies are obtained via regression from identities relating them to the limiting high-pressure rate coefficient. For small molecules, the transition state frequencies for gas phase dissociation reactions can be accurately computed using ab initio methods; for such molecules RRKM is the method of choice. In general, for larger molecules, there will be errors in the frequencies computed by ab initio methods which will be tightly correlated with the computed barrier heights and it is a well-known fact that ab initio estimates of the barrier heights of gas phase dissociation reactions are often overestimates.

It has been argued[44,45] that while experimental values of the limiting high-pressure rate coefficient for gas phase dissociation reactions cannot in general be determined accurately over a wide temperature range, precise experimental techniques are available for measuring rate constants for gas phase recombination reactions and that the limiting high-pressure rate coefficients for such reactions are only weak functions of temperature thus allowing experimental measurements over a wide range of temperature. Hence, in computing the E and J dependent microcanonical rate coefficients for gas phase dissociation reactions via the method described in this paper, the employment of the experimental limiting high-pressure rate coefficients of the associated recombination reaction through the relation with the equilibrium constant will result in more accurate microcanonical rate coefficients for the dissociation process than with those obtained from the knowledge of the limiting high-pressure dissociation rate coefficients.

Superb agreement between the inverse Laplace and the RRKM microcanonical rate coefficients has been obtained here for the two cases studied because of the excellent correlation between the transition state parameters and the best available thermal data for each of these cases; in the case studied, the best available thermal data are really very good representations of the exact thermal data and the Laguerre approximants accurately capture the asymptotic behavior of the thermal data at the boundaries of zero and infinite temperature. The method proposed herein is an excellent technique to deduce microcanonical coefficients. *But, great progress in the utility of the inverse Laplace method as an instrument for modeling unimolecular reactions cannot be made unless the issue of coping with a finitie temperature range is addressed in a rigorously mathematical fashion.* The mathematical problem is one of simultaneous interpolation, extrapolation, and approximation of a univariate function over semi-infinite support. The full analytical features of this function over a semi-infinite support need to be estimated from those of another function over a finite support. The tools of the mathematical theory of sampling of functions[46,47] which have been maturely developed in the fields of information and communications theories are perhaps best suited for such a purpose and may form the starting point for further research in this area.

6. Conclusions

In this paper we have proposed an extension of the inverse Laplace methodology originally developed by Forst in the late sixties and early seventies. The original formalism treated rotations by assuming a temperature-independent centrifugal

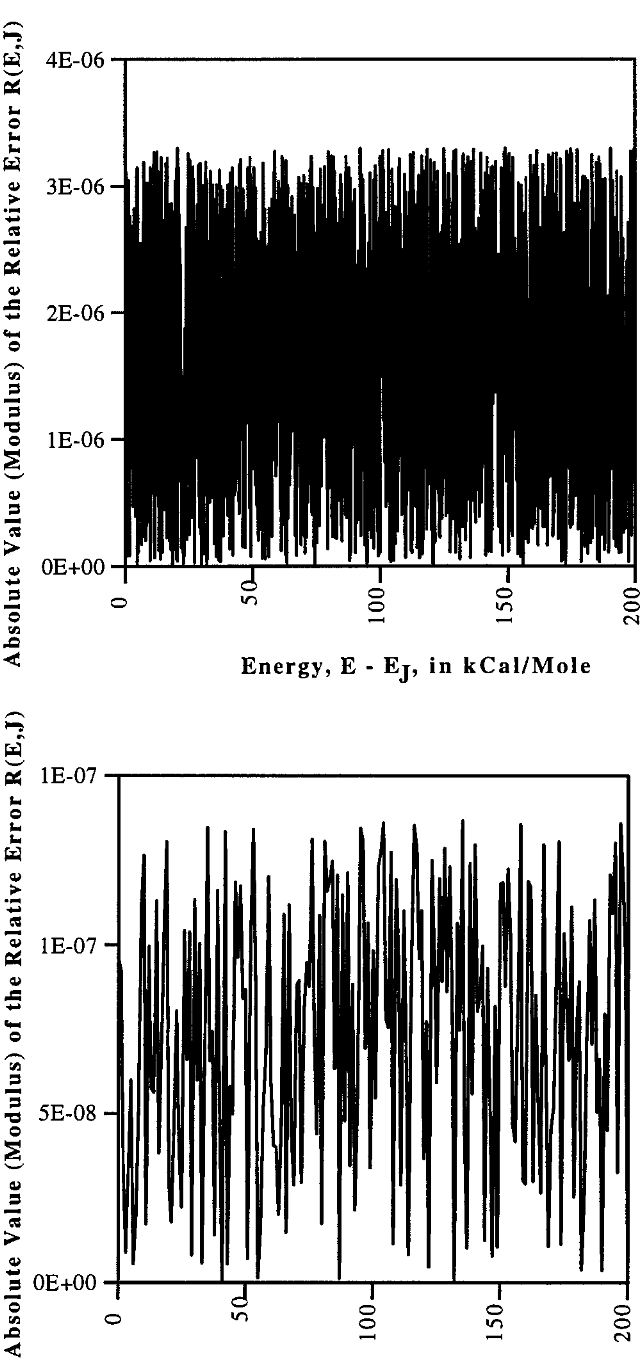

Figure 1. (a) Decomposition of the ethyl radical. Comparison of the inverse laplace and RRKM microcanonical rate coefficients for $J = 60$. (b) Decomposition of the ethyl radical. Comparison of the inverse Laplace and RRKM microcanonical rate coefficients for $E - E_J = 75$ kCal/mol.

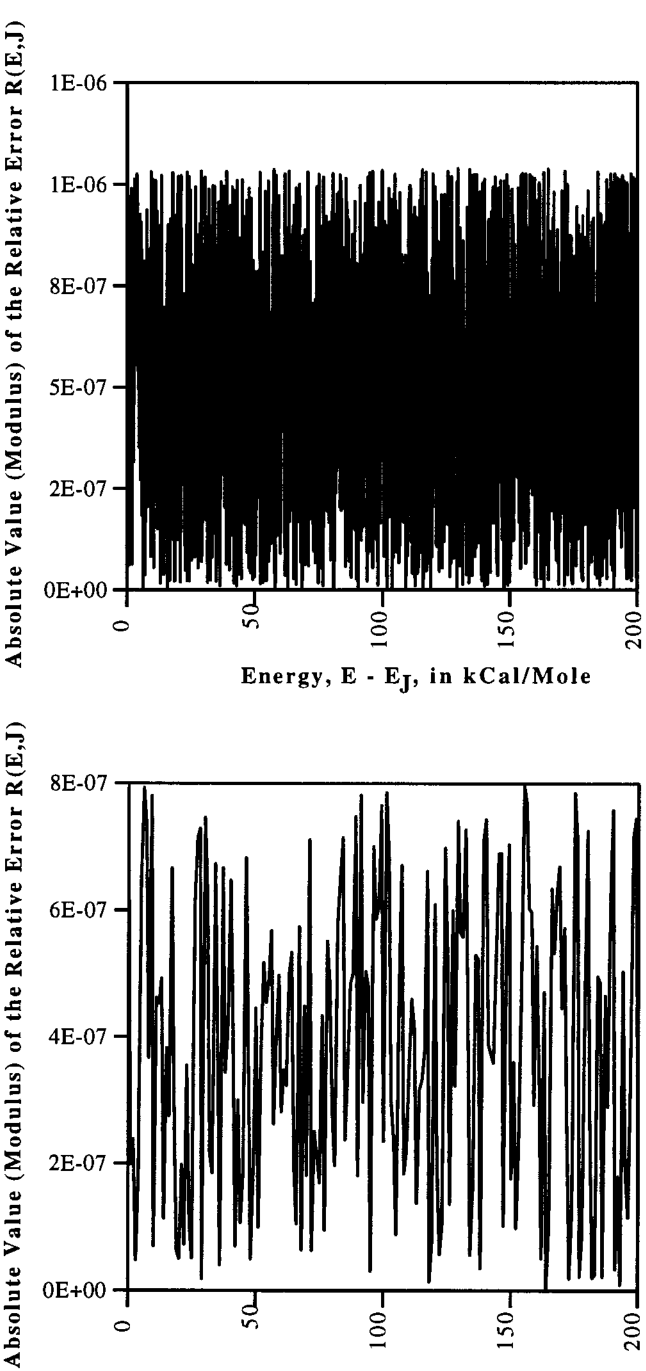

Figure 2. (a) Isomerization of methyl isocyanide. Comparison of the inverse Laplace and RRKM microcanonical rate coefficients for $J = 60$. (b) Isomerization of methyl isocyanide. Comparison of the inverse Laplace and RRKM microcanonical rate coefficients for $E - E_J = 75$ kCal/mol.

factor. The limiting high-pressure rate coefficient was assumed to be of Arrhenius or monotonic non-Arrhenius forms. This gave rise to certain limitations[15] in the method as discussed in sections 1 and 3. Our principal contribution here has been to provide a more general framework for the inverse Laplace methodology. A spectral Laguerre expansion is used to accurately approximate the ratio of any arbitrary limiting high-pressure rate coefficient to a temperature-dependent centrifugal factor. Assuming separability from the total energy, overall rotations are treated explicitly within the boundaries of the semiclassical approximation. We have shown that the microcanonical transition state theory rate coefficients derived from our method, which obviates the need to know the frequencies and degeneracies of the transition state, are identical to those obtained from direct RRKM calculations which require explicit knowledge of such frequencies and degeneracies. This has been demonstrated on the unimolecular decomposition of the ethyl radical and the isomerization of methyl isocyanide. The advantage of our method is that it possesses no adjustable parameters and requires only the knowledge of the limiting high-pressure rate coefficient and rotational constants. It does not require the frequencies and degeneracies of the transition state. The position of the transition state is located at the centrifugal maximum of the effective interfragment potential. The method, of course, requires knowledge of thermal data over a reliably wide temperature range.

As is well recognized, there are substantial difficulties associated in calculating the microcanonical transition state theory rate coefficients for reactions without a chemical barrier where it is necessary to locate the position of the transition state at the variational minimum of the cumulative reaction probability along the reaction coordinate. Unfortunately, this variational calculation cannot be performed with the knowledge of the thermally averaged limiting high-pressure rate coefficient $\langle k(E,J)\rangle_{\text{equilibrium}}$ alone. In order to extend the inverse Laplace formalism to obtain variational microcanonical coefficients without the knowledge of the frequencies and degeneracies of the transition state, it is necessary, at the very least, to know from experiment or otherwise the vlue of $k_\infty(T,J)$, the limiting high-pressure rate coefficient as a function of temperature, T, and the total angular momentum J, for each J. Since this is not practicable, it appears that the inverse Laplace formalism is limited for reactions possessing no chemical barrier.

In conclusion, the inverse Laplace formalism presented here should be viewed as an alternative means of obtaining microcanonical transition state theory rate coefficients for certain classes of elementary unimolecular or bimolecular reactions *for which high-pressure experimental data are available over a reliably wide temperature range*. In particular the method could prove to be a useful means of obtaining such microcanonical rate coefficients for multiple-well reactions where data for the isomerization transition states' frequencies and degeneracies are scarce and not well-known.

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