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Density of States of One-Dimensional Hindered Internal Rotors and Separability of Rotational Degrees of Freedom

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Analytical formulas for the density-of-states and sum-of-states functions of internal one-dimensional hindered rotors are developed and analyzed. Quantum effects are taken into account via the inverse Laplace transform of the classical rotational partition function corrected for quantum effects by the method of Pitzer and Gwinn. Density-of-states and partition functions of *i*-C_3H_7, *n*-C_4H_{10}, *n*-C_5H_{12}, and *sec*-C_4H_9 are calculated under a separability assumption with internal hindered rotors treated either classically or classically with corrections for quantum effects. Results are compared with those obtained in a full treatment with explicit accounting for interaction between internal and external (overall) rotations. It is demonstrated that separability of the rotational degrees of freedom can be assumed in most cases with reasonable accuracy, the main source of disagreement between the two approaches being not the separability assumption but the approximation of a complex torsional potential with a simpler sinusoidal function.

I. Introduction

Modeling of many classes of chemical reactions requires a knowledge of the density-of-states and sum-of-states functions of the involved molecules. The established common approach is to assume separability of vibrational and rotational degrees of freedom, as well as separability of the external and internal rotations of the molecule.[1,2] Thus, a model of the molecule consisting of a collection of harmonic oscillators and free one- and two-dimensional rotors is created. The density-of-states and sum-of-states functions of such an idealized molecule are easily calculated using, for example, the modified Beyer−Swinehart algorithm.[3] Anharmonicity of constituent oscillators can be accounted for via the Stein−Rabinovitch approach.[4]

Two drawbacks to such analysis are related to (1) the presence of one-dimensional hindered internal rotors and (2) the potential interference of coupling between internal and external (overall) rotations of the molecule. One approach to the treatment of hindered internal rotors is to solve the corresponding quantum-mechanical problem. This was done by Pitzer and Gwinn,[5] who tabulated the contributions of hindered internal rotations to thermodynamic functions for a variety of combinations of rotational constants and hindering barriers. Applying the method of Pitzer and Gwinn to calculating density of states would involve a time-consuming determination of individual energy levels and their inclusion in the total density-of-states function of the molecule by direct count. An alternative method was suggested by Knyazev et al.,[6] who developed analytical formulas for the density-of-states and sum-of-states functions of a sinusoidally hindered one-dimensional rotor based on the inverse Laplace transform (ILT) of the classical partition function.

While the classical treatment is applicable with a good degree of accuracy to many internal rotors encountered in real molecules, quantum effects may become important at room temperature and below. Forst[7] developed an algorithm for calculating the density-of-states function of a system consisting of independent oscillators, free rotors, and one-dimensional hindered rotors via a numerical inversion of the overall partition function. In its quantum form, the algorithm uses the approximation of Truhlar[8] to the quantum partition function of a one-dimensional hindered rotor. This approach requires performing a numerical inverse Laplace transform of the overall partition function, a procedure unique to each molecule. However, there exists a demand for universal analytical formulas that can be applied to any molecule possessing one or several different one-dimensional hindered rotors. In section II of the current article, new formulas for the density-of-states and sum-of-states functions of internal one-dimensional hindered rotors are developed via ILT of the classical partition function corrected for quantum effects. The quantum correction is based on the method of Pitzer and Gwinn,[5] which, generally, provides significantly higher accuracy than the approximation of Truhlar[8] (section II).

The problem of coupling between the external and internal rotational degrees of freedom was addressed by Robertson and Wardlaw[9] and Gang et al.,[10.11] who calculated densities of states of a variety of molecules using the inverse Laplace transform of the partition function. In these calculations, no separability of the rotational degrees of freedom was assumed, and rotational partition functions were derived from the exact kinetic energy expressions (which included all coupling between internal and external rotations) and potential energy functions describing the hindrances of the internal rotations.

The rigorous approach exercised by Robertson and Wardlaw[9] and Gang et al.[10,11] results in more accurate densities of states than those obtained by a traditional method based on the assumed separability of the rotational degrees of freedom. However, it is necessary to assume this separability in many cases. In particular, such a necessity arises in statistical theories of unimolecular reactions where it is frequently essential to calculate density-of-states and sum-of-states functions of only active[1,2,12,13] degrees of freedom (which excludes some or all of the external rotations). Furthermore, full treatment of rotational coupling requires cumbersome algebraic manipulations and numerical integrations unique to each molecule, while

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assumed separability of the degrees of freedom enables the use of significantly simpler procedures which can be easily automated and universally applied to a variety of different molecules. It is, therefore, essential to fully understand the influence of the separability assumption on the calculated density-of-states and sum-of-states functions and partition functions.

In section III of this article, the results of Robertson and Wardlaw[9] and Gang et al.[10,11] on the density-of-states functions and appropriate partition functions of a variety of molecules are compared with those obtained under a separability assumption with internal hindered rotors treated either classically by the method of Knyazev et al.[6] or classically with corrections for quantum effects, as described in section II. It is demonstrated that separability of the rotational degrees of freedom can be assumed in most cases with reasonable accuracy and that the main inaccuracy in the density-of-states function arises not from the separability assumption but from the approximation of a complex torsional potential with a simpler sinusoidal function.

II. Density of States of One-Dimensional Hindered Rotor via an Inverse Laplace Transform of a Classical Partition Function with Quantum Correction

The partition function of any system can be considered as a Laplace transform of the corresponding density-of-states function $\rho(E)$ by definition:

$$Q(\beta) = \int_0^\infty \rho(E) \exp(-\beta E)\, \mathrm{d}E = L[\rho(E)]$$

where $\beta = (k_B T)^{-1}$ is an inverse reduced temperature and E is the energy. Thus, provided that the dependence of the partition function on temperature is known, one can obtain the density-of-states function by inverse Laplace transform (ILT):

$$\rho(E) = L^{-1}[\mathrm{Q}(\beta)]$$

The classical partition function of a one-dimensional sinusoidally hindered rotor is given by[5]

$$Q_{\mathrm{class}}(\beta) = Q_{\mathrm{f}}(\beta) \exp\left(-\frac{V_0\beta}{2}\right) I_0\left(\frac{V_0\beta}{2}\right) = \frac{1}{\sigma}\left(\frac{\pi}{B\beta}\right)^{1/2} \exp\left(-\frac{V_0\beta}{2}\right) I_0\left(\frac{V_0\beta}{2}\right) \quad \text{(I)}$$

where Q_{f} is a partition function of the corresponding free rotor, V_0 is the amplitude of the hindering potential ($V = (1/2)V_0(1 - \cos(n\phi)$, n is the symmetry number of the potential), $\beta = (k_B T)^{-1}$ is the inverse reduced temperature, I_0 is the modified Bessel function, σ is the symmetry number, and B is a rotational constant. It was shown by Knyazev et al.[6] that the corresponding density of states $\rho_{\mathrm{h}}(E)$ determined by ILT of $Q_{\mathrm{class}}(\beta)$ is described by the equations

$$\rho_{\mathrm{h}}(E) = \begin{cases} \dfrac{2\boldsymbol{K}\left(\sqrt{\dfrac{E}{V_0}}\right)}{\pi\sigma\sqrt{BV_0}}, & 0 < E < V_0 \\[2ex] \dfrac{2\boldsymbol{K}\left(\sqrt{\dfrac{V_0}{E}}\right)}{\pi\sigma\sqrt{BE}}, & E > V_0 \end{cases} \quad \text{(II)}$$

where $\boldsymbol{K}$ is a complete elliptic integral of the first kind. The corresponding sum-of-states function is given by[6]

$$W_{\mathrm{h}}(E) = \begin{cases} \dfrac{4}{\pi\sigma}\sqrt{\dfrac{V_0}{B}}\left[\boldsymbol{E}\left(\sqrt{\dfrac{E}{V_0}}\right) - \left(1 - \dfrac{E}{V_0}\right)\boldsymbol{K}\left(\sqrt{\dfrac{E}{V_0}}\right)\right], & 0 < E < V_0 \\[2ex] \dfrac{4}{\pi\sigma}\sqrt{\dfrac{E}{B}}\boldsymbol{E}\left(\sqrt{\dfrac{V_0}{E}}\right), & E > V_0 \end{cases}$$

where $\boldsymbol{E}$ is a complete elliptic integral of the second kind.

Pitzer and Gwinn[5] suggested that equation I for the classical partition function can be corrected to account for quantum effects via a multiplication by the ratio of quantum ($Q_{\mathrm{quant}}^{\mathrm{HO}}$) and classical ($Q_{\mathrm{class}}^{\mathrm{HO}}$) partition functions of a corresponding harmonic oscillator (i.e., oscillator with a frequency derived from the curvature at the bottom of the rotor's hindering potential):

$$Q_{\mathrm{quant}}^{\mathrm{approx}} = Q_{\mathrm{class}} \frac{Q_{\mathrm{quant}}^{\mathrm{HO}}}{Q_{\mathrm{class}}^{\mathrm{HO}}} \quad \text{(III)}$$

Isaacson and Truhlar[14] have demonstrated that such a correction for quantum effects can be applied with good accuracy to a variety of potentials with different functional forms. Gang et al.[10,11] applied the approximation of formula III to obtain the density-of-states function of *sec*-butyl radical via the ILT of the total rotational partition function $Q_{\mathrm{quant}}^{\mathrm{approx}}(\beta)$, with the vibrational densities of states included by the Beyer−Swinehart algorithm.

Such an approach to determining the density-of-states function should be used with caution, since the approximation of expression III, while describing the temperature dependence of the quantum partition function with reasonable accuracy for a variety of systems, is not derived from any fundamental principles and, therefore, does not have a physical meaning. It is only a phenomenological expression providing for a smooth transition from the low-temperature region on one side, where the ratio $Q_{\mathrm{class}}/Q_{\mathrm{class}}^{\mathrm{HO}}$ is equal to 1 and the partition function of a system can be described by $Q_{\mathrm{quant}}^{\mathrm{HO}}$, to the high-temperature region on the other side, where $Q_{\mathrm{quant}}^{\mathrm{HO}}$ approaches $Q_{\mathrm{class}}^{\mathrm{HO}}$ and the partition function is well approximated by Q_{class}.

Forst[7] applied a numerical ILT of the overall rovibrational partition function of a molecule to obtain the density-of-states function using a different approximation to the quantum partition function of a hindered rotor, the one proposed by Truhlar.[8] While the formula of Truhlar is convenient to use (it contains only exponential and hyperbolic functions), its accuracy, generally, is significantly lower than that of formula III. Comparison of the partition functions calculated using the method of ref 8 and formula III with the exact values of Pitzer and Gwinn[5] (calculations performed for rotors with $0.15 < B < 15$ cm^{-1} and $0.5 < V_0 < 50$ kJ mol^{-1} at $T = 100-6000$ K) demonstrates that while formula III yields an accuracy not worse than 3% (usually, better than 1%) for all chemically meaningful cases ($3 \leq V_0 \leq 50$ kJ mol^{-1}), that of ref 8 exhibits deviations up to 18%, yielding, in many cases, accuracy poorer than that of a purely classical formula I. Thus, the approximation of formula III is used in further derivations.

In the following part of this section, the density-of-states and sum-of-states functions of a one-dimensional hindered rotor obtained via the ILT of expression III are analyzed. Formulas are developed for the densities and sums of states that provide for better agreement with the quantum partition function than those obtained with the purely classical treatment (expression II) while preserving physically realistic functional forms.

For a one-dimensional sinusoidally hindered rotor, three components of formula III are obtained as follows: Q_{class} is given by formula I,

$$Q_{\mathrm{class}}^{\mathrm{HO}} = (h\nu\beta)^{-1}$$

and

$$Q_{\mathrm{quant}}^{\mathrm{HO}} = \exp(-(1/2)h\nu\beta)(1 - \exp(-h\nu\beta))^{-1}$$

where h is Planck constant and ν is the frequency of the corresponding harmonic oscillator. Here, the bottom of the classical potential is taken as an energy reference point for all partition functions. The density-of-states function $\rho(E)$ is given by the ILT of $Q_{\mathrm{quant}}^{\mathrm{approx}}(\beta)$:

$$\rho(E) = L^{-1}\left[Q_{\mathrm{class}}\frac{Q_{\mathrm{quant}}^{\mathrm{HO}}}{Q_{\mathrm{class}}^{\mathrm{HO}}}\right]$$

Mathematically, this is equivalent to having two degrees of freedom, one with a "partition function"

$$\tilde{Q}(\beta) = Q_{\mathrm{class}}/Q_{\mathrm{class}}^{\mathrm{HO}}$$

and the other being a harmonic oscillator. Overall density-of-states and sum-of-states functions $\rho(E)$ and $W(E)$ can be obtained by a convolution of $\tilde{\rho}(E) = \mathrm{L}^{-1}[\tilde{Q}(\beta)]$, the harmonic oscillator density of states $\rho_{\mathrm{HO}}(E)$, and the harmonic oscillator sum of states $W_{HO}(E)$:[2,15]

$$\rho(E) = \int_0^E \tilde{\rho}(E - x)\, \rho_{\mathrm{HO}}(x)\, \mathrm{d}x; \qquad W(E) = \int_0^E W_{\mathrm{HO}}(E - x)\, \tilde{\rho}(x)\, \mathrm{d}x \quad \text{(IV)}$$

For any function $F(\beta)$, the ILT of $\beta\mathrm{F}(\beta)$ is given by

$$L^{-1}[\beta F(\beta)] = f'(E) + f(0)\,\delta(E)$$

where

$$f(E) = L^{-1}[F(\beta)]$$

as can be checked via integration by parts.[16] $\tilde{\rho}(E)$, therefore, can be obtained as

$$\tilde{\rho}(E) = L^{-1}[\mathrm{h}\nu\beta Q_{\mathrm{class}}(\beta)] = h\nu\{\rho_{\mathrm{h}}'(E) + \rho(0)\,\delta(E)\}$$

where $\rho_{\mathrm{h}}(E)$ is given by expression II. Since

$$\rho_{\mathrm{HO}}(E) = \sum_{i=0}^{N(E)} \delta(E - h\nu(i + 1/2))$$

and

$$W_{\mathrm{HO}}(E) = \sum_{i=0}^{N(E)} H(E - h\nu(i + 1/2))$$

where $N(E) = \mathrm{int}[(E/h\nu) - (1/2)]$ ($\mathrm{int}(x)$ means integer part), and $H(x)$ is the Heaviside step function, we can obtain via the convolution formulas IV

$$\begin{aligned}\rho(E) &= h\nu\int_0^E [\rho_{\mathrm{h}}'(E - x) + \delta(E - x)\,\rho_{\mathrm{h}}(0)]\sum_{i=0}^{N(x)} \delta(x - h\nu(i + 1/2))\,\mathrm{d}x \\ &= h\nu \sum_{i=0}^{N(E)} [\rho_{\mathrm{h}}'(E - h\nu(i + 1/2)) + \rho_{\mathrm{h}}(0)\,\delta(E - h\nu(i + 1/2))] \quad \text{(V)}\end{aligned}$$

and

$$\begin{aligned}W(E) &= h\nu\int_0^E [\sum_{i=0}^{N(E-x)} H((E - x) - h\nu(i + 1/2))][\rho_{\mathrm{h}}'(x) + \delta(x)\,\rho_{\mathrm{h}}(0)]\,\mathrm{d}x \\ &= h\nu\sum_{i=0}^{N(E)} \rho_{\mathrm{h}}(E - h\nu(i + 1/2)) \quad \text{(VI)}\end{aligned}$$

The first derivative $\rho_{\mathrm{h}}'(E)$ of the $\rho_{\mathrm{h}}(E)$ function (formula II) is easily calculated,[15] but the resultant $\rho(E)$ function V acquires an analytical form that is not a very pleasant one to deal with due to the abundance of discontinuities and δ-functions. This analytical form of $\rho(E)$ will not be used in this article and, therefore, is not given here.

It is more convenient to analyze $\rho(E)$ and $W(E)$ resulting from expressions V and VI by visualizing the $W(E)$ dependence which is presented in Figure 1 (lower solid-line curve on the (b) plot). As can be seen from the plot, $W(E)$ increases with energy at energies E below the amplitude of hindered rotation V_0 but exhibits non-monotonic behavior at higher energies. This nonmonotonic behavior corresponds to negative values of the density-of-states function $\rho(E)$, which are completely unrealistic. At the same time, the $W(E)$ dependence, on average, follows the classical sum-of-states function of the hindered rotor, $W_{\mathrm{h}}(E)$, represented by the dotted line.

Considering the above analysis, one can recommend for further use the corrected for quantum effects sum-of-states function $W_{\mathrm{h}}^{\mathrm{Q}}$ constructed from $W(E)$ and $W_{\mathrm{h}}(E)$ functions: at energies below the hindrance barrier ($E < V_0$) $W_{\mathrm{h}}^{\mathrm{Q}}(E) = W(E)$ and $W_{\mathrm{h}}^{\mathrm{Q}}(E) = W_{\mathrm{h}}(E)$ above the barrier:

$$W_{\mathrm{h}}^{\mathrm{Q}}(E) = \begin{cases} W_{\mathrm{h}}{}^{\mathrm{Q}}{}_1(E) = h\nu \displaystyle\sum_{i=0}^{\mathrm{int}(E/\mathrm{h}\nu - 1/2)} \rho_{\mathrm{h}}(E - h\nu(i + 1/2)), & 0 < E < V_0 \\ W_{\mathrm{h}}{}^{\mathrm{Q}}{}_2(E) = \dfrac{4}{\pi\sigma}\sqrt{\dfrac{E}{B}}\,\boldsymbol{E}\left(\sqrt{\dfrac{V_0}{E}}\right), & E > V_0 \end{cases} \quad \text{(VII)}$$

where $\rho_{\mathrm{h}}(E)$ is given by expression II. Here one can use a simple (first approximation) relation between the vibrational frequency ν and parameters of the rotor: $h\nu = n\sqrt{BV_0}$, where n is the symmetry number of the hindering potential. Care must be taken to assure a smooth connection in the region $E \approx V_0$, where $W_{\mathrm{h}}{}^{\mathrm{Q}}{}_1(E)$ may have to be extended a little above the barrier if $W_{\mathrm{h}}{}^{\mathrm{Q}}{}_1(V_0) > W_{\mathrm{h}}{}^{\mathrm{Q}}{}_2(V_0)$, or, alternatively, $W_{\mathrm{h}}{}^{\mathrm{Q}}{}_2(E)$ can be extended a little below the barrier. This small degree of arbitrariness in making the smooth connection does not affect the resultant partition function to any noticeable extent.

The density-of-states function $\rho_{\mathrm{h}}{}^{\mathrm{Q}}(E)$ of the hindered rotor is similarly constructed from the parts of expressions V and II.

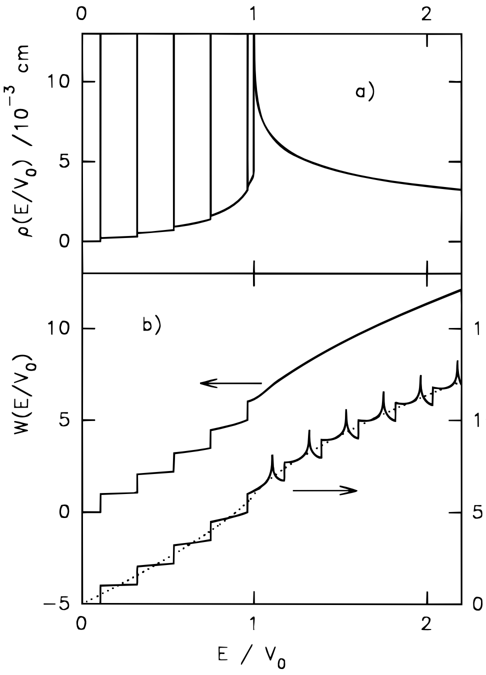

Figure 1. Plots of recommended density-of-states (a) and sum-of-states (b) functions of a hindered internal rotor given by formulas VII and VIII. For comparison, the sum-of-states function obtained via the ILT of the classical partition function corrected for quantum effects is shown (formula VI, lower solid line in plot b), as well as the corresponding classical sum-of-states function (dotted line). Parameters of the $-CH_3$ hindered rotor in the butane molecule were used in the calculations.

It is equal to $\rho(E)$ (formula V) at energies below the barrier and to $\rho_h(E)$ above the barrier:

$$\rho_h^{Q}(E) = \begin{cases} h\nu \sum_{i=0}^{N(E)} [\rho_h'(E - h\nu(i = 1/2)) + \rho_h(0)\,\delta(E - h\nu(i + 1/2))], & 0 < E < V_0 \\ \rho_h(E) & E > V_0 \end{cases} \qquad \text{(VIII)}$$

In many practical applications, in calculating densities of states and performing numerical manipulations of related functions (e.g., solving master equations for unimolecular reactions[2]), the energy scale is divided into an array of energy bins of small size, and continuous functions are replaced with arrays. In such cases, at energies below or in the vicinity of the hindering barrier height, it is advisable to calculate the value of the density-of-states function for each energy bin as an increment of the $W_h^{Q}(E)$ function between the upper and lower borders of the bin divided by the bin width:

$$\rho_h^{Q}(E) = \frac{\delta W_h^{Q}(E)}{\delta E} \qquad \text{(IX)}$$

The recommended $W_h^{Q}(E)$ and $\rho_h^{Q}(E)$ dependencies given by expressions VII and VIII are illustrated in Figure 1. The $W_h^{Q}(E)$ function of formula VII satisfies the requirement of realistically representing the physics of the problem. At low energies, it increases in a stepwise manner, as appropriate for a torsional oscillator. Although the energy "distance" between the steps does not reduce at energies approaching the hindering barrier, this inaccuracy is compensated for by the fact that $W_h^{Q}(E)$ grows faster than a simple sum of step functions, resembling, on average, an upward curvature of the classical $W_h(E)$ at $E < V_0$. At energies above V_0, where quantum effects are not as important, the $W_h^{Q}(E)$ dependence follows that of the classical $W_h(E)$. It has been shown for a large variety of torsional parameters ($0.15 < B < 15$ cm^{-1}, $0.5 < V_0 < 50$ kJ mol^{-1}) that, with sufficiently small energy bin sizes, the partition function obtained by a numerical integration of the densities of states given by formulas VIII and IX with Boltzmann factors is equal to that obtained from formula III with an accuracy of 1%.

III. Density of States and the Separability of the External and Internal Rotational Degrees of Freedom

Robertson and Wardlaw[9] and Gang et al.[10,11] applied ILT of the classical (or classical corrected for quantum effects[11] via formula III) rotational partition function to determine rotational and rovibrational densities of states of i-C_3H_7,[9] n-C_4H_{10},[10] n-C_5H_{12},[10] and sec-C_4H_9.[11] Rotational partition functions were derived from exact kinetic and potential energy functions, including explicit accounting for (1) interaction between rotations internal and external (overall) and (2) hindrances associated with internal rotations. After the rotational densities of states were obtained by the ILT of the full rotational partition functions, vibrational degrees of freedom were included by the Beyer−Swinehart algorithm to obtain the total (rovibrational) densities of states. Below in this section, the rotational and rovibrational densities of states of the above species obtained by Robertson and Wardlaw[9] and Gang et al.[10,11] are compared with those calculated in this work by (1) assuming the separability of the rotational degrees of freedom and (2) applying formulas II or VII−IX to calculate the density-of-state functions of hindered internal rotations. The choice of purely classical or classical corrected for quantum effects treatment reproduced that of the authors of references 9−11: internal rotations in i-C_3H_7, n-C_4H_{10}, and n-C_5H_{12} were treated classically, and quantum corrections were used for those in sec-C_4H_9. The structures of all species used in the current work conform to those used in refs 9−11. In calculating the moments of inertia, properties of the lowest-energy conformations were used. The methods of Pitzer and Gwinn[5,17] were used to obtain the reduced moments of inertia of all internal rotations (Table 1).

In Figure 2, ratios of the rotational density-of-states functions obtained in the current treatment to those calculated by Gang et al.[10] for butane and pentane are plotted vs energy. As can be seen from the plot, significant differences between the two methods are observed at low rotational energies: up to factors of 2.6 and 5.7 at $E = 350$ cm^{-1} for butane and pentane, respectively. At higher energies this disagreement decreases, becoming negligible (less than 5 %) at $E > 4000$ cm^{-1} (48 kJ mol^{-1}). Including vibrational densities of states does not increase the maximum values of disagreement but somewhat propagates the difference to higher energies (Figure 3). The rovibrational density-of-states ratios for butane and pentane are still as high as 1.34 at $E = 4000$ cm^{-1} and decrease below 1.10 only at $E > 14\,000$ cm^{-1} (166 kJ mol^{-1}).

At the same time, the rovibrational densities of states for isopropyl and sec-butyl radicals calculated in the current work show significantly better agreement with the results of the exact treatment of Robertson and Wardlaw[9] and Gang et al.[11] (Figure 3). For the isopropyl radical, the agreement is virtually complete.[18] For sec-butyl, disagreement is less than a factor of 1.5 at its maximum and becomes negligible at a low energy of $E = 1000$ cm^{-1} (12 kJ mol^{-1}). Different degrees of disagreement between the densities of states obtained in the current work under the assumption of separability of the

TABLE 1: Rotational Constants (B, cm^{-1}), Symmetry Numbers (σ), and Torsional Barriers (V_0, kJ mol^{-1}) of Molecules Used in the Calculations

	i-C_3H_7[a]	*sec*-C_4H_9	n-C_4H_{10}	n-C_5H_{12}
overall	$B = 1.2958, 0.2690, 0.2415$, $\sigma = 2$	$B = 0.8887, 0.1210, 0.1138$, $\sigma = 1$	$B = 0.7360, 0.1250, 0.1168$, $\sigma = 2$	$B = 0.5358, 0.06714, 0.06344$, $\sigma = 2$
$-CH_3$ rotors	$B = 6.9704$, $\sigma = 3$, $V_0 = 3.05$	$B = 5.560$, $\sigma = 3$, $V_0 = 3.13$ $B = 5.562$, $\sigma = 3$, $V_0 = 13.77$	$B = 5.713$, $\sigma = 3$, $V_0 = 13.43$	$B = 5.419$, $\sigma = 3$, $V_0 = 13.43$
C_2-C_3 rotors		$B = 1.741$, $\sigma = 1$, $V_0 = 9.04$	$B = 1.487$, $\sigma = 1$, $V_0 = 16.48$	$B = 1.317$, $\sigma = 1$, $V_0 = 11.04$

[a] Structure of the isopropyl radical (bond lengths and angles) is based on the ab initio results of Chen et al.[21] However, a planar structure of the radical center was used to conform to the model of Robertson and Wardlaw.[9]

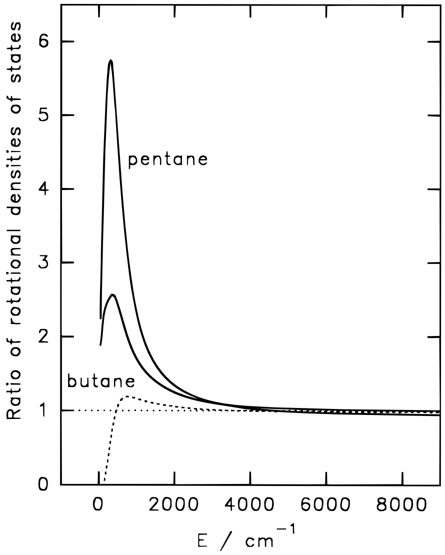

Figure 2. Ratios of rotational densities of states of butane and pentane obtained in the current work under the assumption of the separability of external and internal rotations to those calculated by Gang et al.[10] via ILT of the exact classical partition function with internal−external rotational coupling taken into account (solid lines). Dashed line: same ratio obtained for butane in the case where the minimum of the approximating sinusoidal potential is "shifted" relative to the absolute minimum of the real C_2-C_3 torsional potential by 100 cm^{-1} (see text).

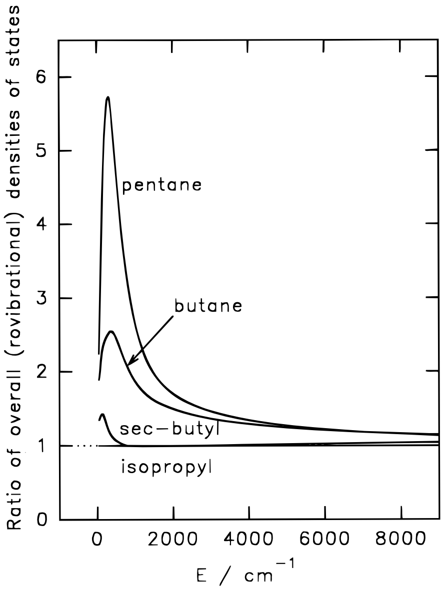

Figure 3. Ratios of overall (rovibrational) densities of states of butane, pentane, secondary butyl, and isopropyl radicals obtained in the current work under the assumption of the separability of external and internal rotations to those calculated via ILT of the exact classical (classical corrected for quantum effects for *sec*-C_4H_9) partition function with internal−external rotational coupling taken into account (results of refs 9−11 with vibrational densities of states included by the modified Beyer−Swinehart algorithm[3]). Frequencies of the lowest-energy conformations of butane,[22] pentane,[22] and secondary butyl radical[19] were used.

rotational degrees of freedom and those calculated with the exact accounting for the rotational coupling[10,11] are reflected in the ratios of corresponding rotational partition functions plotted in Figure 4 vs temperature.

Secondary butyl radical, *sec*-C_4H_9, is quite similar to butane in structure (and, therefore, in moments of inertia for internal and external rotations and in the extent of coupling between the external and internal rotations in the inertial tensor). However, the current approach based on the separability of rotational degrees of freedom gives much better results for *sec*-C_4H_9 than for butane. The explanation, most likely, lies in the major difference between these two molecules: the shapes of the C_2-C_3 torsional potentials. That of the secondary butyl radical, although quite complex in shape,[11,19] can be reasonably approximated by a sinusoidal function with one minimum ($n = \sigma = 1$) (Figure 5a). While this potential has three different wells at torsional angles of 17°, 94°, and 133° (each repeated twice), two of these are minor compared with the overall height of the hindering barrier. One of these minor wells is not deep enough to accommodate even the zeroth vibrational level, and the other one can only accommodate two (zeroth and first) vibrational levels.[19] One can consider these minor wells (and a small maximum at a torsional angle equal to 0) as a relatively small perturbation $V_1(\varphi)$ of a sinusoidal potential. The overall hindering potential $V(\varphi)$ is thus described as $V(\varphi) = (1/2)V_0(1 - \cos(\varphi)) + V_1(\varphi)$. The contribution of perturbation $V_1(\varphi)$ (which has an alternating sign) is likely to average out, to a large extent, in the classical partition function given by the expression[5]

$$Q = \sqrt{\frac{\pi}{\beta B}} \int_0^{2\pi} \exp[-\beta V(\varphi)]\, d\varphi \approx \sqrt{\frac{\pi}{\beta B}} \int_0^{2\pi} \exp\left[-\beta \frac{V_0}{2}(1 - \cos(\varphi))\right] d\varphi = Q_{\text{class}}(\beta) \qquad \text{(X)}$$

where $Q_{\text{class}}(\beta)$ is given by formula I.

The corresponding torsional potential of butane has three distinct potential energy minima at torsional angles of 0°, 118°, and 241°, two of these being equal and positioned above the third one by 3.8 kJ mol^{-1} (Figure 5b, solid line). When such a potential (present as well in the C_2-C_3 and C_3-C_4 rotations of pentane) is approximated with a simple sinusoidal one, there is an ambiguity in the placement of the energy minimum of the sinusoidal potential relative to the three unequal minima of the real potential. In the current work, it was positioned (dashed

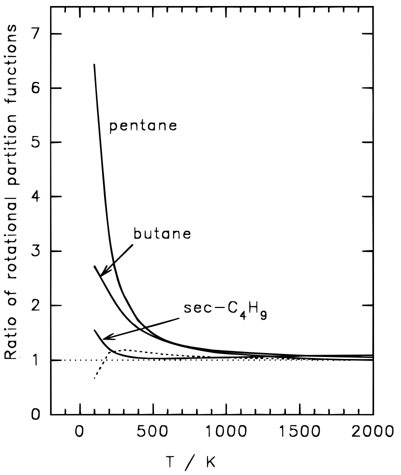

Figure 4. Ratios of rotational partition functions of butane, pentane, and secondary butyl radical obtained in the current work under the assumption of the separability of external and internal rotations to those calculated by Gang et al.[10,11] via the ILT of the exact classical (classical corrected for quantum effects for *sec*-C_4H_9) partition function with internal−external rotational coupling taken into account. Dashed line: same ratio obtained for butane in the case where the minimum of the approximating sinusoidal potential is "shifted" relative to the absolute minimum of the real C_2-C_3 torsional potential by 100 cm^{-1} (see text).

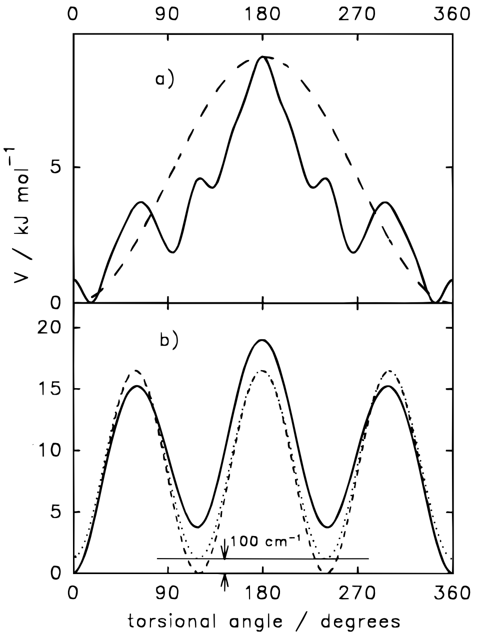

Figure 5. Torsional potentials hindering the rotation about the C_2-C_3 bond in (a) secondary butyl radical and (b) butane used in calculations of Gang et al.[10,11] Dashed lines: sinusoidal approximations used in the current work. Dotted line in plot (b): sinusoidal potential with the minimum placed between the lowest and the highest minima of the real potential, 100 cm^{-1} (1.2 kJ mol^{-1}) above the absolute minimum.

line in Figure 5b) at the absolute (lowest) minimum of the real potential, which results in a poor description of the other two minima. The analogous perturbation $V_1(\phi)$ is mostly positive and is not likely to average out. If, on the other hand, this sinusoidal potential minimum is placed between the lowest and the highest minima of the real potential, 100 cm^{-1} (1.2 kJ mol^{-1}) above the lowest one (dotted line in Figure 5b), the result is significantly better accuracy in the obtained density-of-states and corresponding partition functions (dashed lines in Figures 2 and 4). In this case, the discrepancies between the results of the current and exact[10] treatments are comparable to those obtained for the secondary butyl radical. One should admit, however, that there is no rationale for the choice of this particular value of 100 cm^{-1} for "shifting" the potential energy minimum of the approximating sinusoidal function. A similar improvement can be obtained for pentane by positioning the minimum of the sinusoidal potential between the different minima of the real nonuniform potential.

Numerical evaluation of the exact (left) and approximate (right) integrals in expression X confirms these qualitative conclusions about the role of $V_1(\varphi)$, the deviation of the real hindering potential from its sinusoidal approximation. For example, at $T = 100$ K (the lowest temperature in Figure 4, where disagreement in partition functions is the highest), ratios of approximate to exact integrals equal 3 for butane, but only 1.3 for *sec*-C_4H_9 and 0.7 for butane if a sinusoidal potential with a "shifted" minimum is used. These values correlate with the deviations of the partition functions in Figure 4.

In the formula of Gang et al.[10,11] for the classical rotational partition functions of butane and *sec*-C_4H_9, the term $\tilde{q}(\beta)$ (notation assigned here) responsible for the coupling of external and internal hindered rotations is

$$\tilde{q}(\beta) = \int_0^{2\pi} |\mathbf{A}(\theta)|^{1/2} \exp(-\beta V_3(\theta))\, \mathrm{d}\theta \qquad \text{(XI)}$$

where $\mathbf{A}(\theta)$ is the generalized inertial tensor which was assumed to depend only on θ, the C_2-C_3 torsional angle, and $V_3(\theta)$ is the C_2-C_3 torsional potential. The dependence of $|\mathbf{A}(\theta)|^{1/2}$ on θ is not very strong: for both molecules $|\mathbf{A}(\theta)|^{1/2}$ oscillates within <20% of its average value, $\mathbf{a}_0$. The $|\mathbf{A}(\theta)|^{1/2}$ vs θ dependence can be represented by a sum of θ-independent and θ-dependent parts, $|\mathbf{A}(\theta)|^{1/2} = \mathbf{a}_0 + \mathbf{a}_1(\theta)$, and the integral in formula XI will thus separate into two parts:

$$\tilde{q}(\beta) = \mathbf{a}_0 \int_0^{2\pi} \exp(-\beta V_3(\theta))\, \mathrm{d}\theta + \int_0^{2\pi} \mathbf{a}_1(\theta) \exp(-\beta V_3(\theta))\, \mathrm{d}\theta = q_0(\beta) + q_1(\beta) \qquad \text{(XII)}$$

Here, both the $q_0(\beta)$ and $q_1(\beta)$ terms are associated with the effects of the hindrance potential, $V_3(\theta)$, but only $q_1(\beta)$ describes the effects of coupling between external and internal rotations which accounts for the $|\mathbf{A}(\theta)|^{1/2}$ dependence on θ. Numerical evaluation of the relative contributions of q_0 and q_1 for butane at $T = 100-3000$ K (performed using the $|\mathbf{A}(\theta)|$ dependence reported by Gang et al.[10] and both the real $V_3(\theta)$ potential[10] and the sinusoidal approximation to it) showed that q_1 values are less than 4% of q_0. Thus, q_1 is minor compared to q_0, and its contribution, generally, can be neglected without sacrificing accuracy. This numerical comparison of the effects of (1) the separability assumption and (2) the sinusoidal approximation to the more complex hindering potential demonstrates that, indeed, disagreement between the rigorous method applied by Gang et al.[10,11] and the current simplified approach is mainly due to the use of the sinusoidal approximation and not to the separability assumption.

Robertson and Wardlaw[9] and Gang et al.[10] attempted to assess the effect of the separability assumption by comparing rotational partition functions calculated with and without this assumption for the internally unhindered models of *i*-C_3H_7[9] and *n*-C_4H_{10}.[10] The differences obtained (11% in the case of *i*-C_3H_7 and a factor of approximately 20 in the case of *n*-C_4H_{10}) apparently result from the fact that only approximate moments of inertia for the internal rotations were used instead of the appropriate reduced moments of inertia calculated by the methods of Pitzer and

Gwinn[5,17] (i-C_3H_7 and n-C_4H_{10}) and from different assignments of symmetry numbers (n-C_4H_{10}).[20]

The above comparison of the density-of-states and partition functions obtained under the assumption of the separability of rotations on one hand and in the full treatment of rotational coupling on the other demonstrates, in general, good agreement between the two approaches. This agreement in the densities of states is almost complete for isopropyl and *sec*-butyl radicals and is reasonable for butane and pentane. In all cases, disagreements in the densities of states are negligible at chemically significant energies. The significant discrepancies between these two approaches observed for butane and pentane molecules at low energies (for densities of states) and low temperatures (for partition functions) seem to mainly originate not from the inseparability of the internal and external rotational degrees of freedom but rather from the crudeness of the sinusoidal approximation to the hindering potentials. While values of the density-of-states function $\rho(E)$ are needed, in general, at high energies comparable to reaction barriers, sum-of-states function $W(E)$ values (obtained by an integration of the density-of-states function and used, for example, to calculate microcanonical rate constants via the RRKM formula[1,2]) are needed at low energies as well. Low-energy discrepancies (analogous to those observed for butane and pentane) in the $\rho(E)$ of a transition state will cause similar low-energy errors in $W(E)$ and, thus, incorrect microcanonical rate constants. Further efforts directed to accurately describing densities of states and partition functions of a one-dimensional hindered rotor with arbitrary hindering potential are needed.

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