Identification and treatment of internal rotation in normal mode vibrational analysis

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A procedure that automatically identifies internal rotation modes and rotating groups during the normal mode vibrational analysis is outlined, and an improved approximation to the corrections for the thermodynamic functions is proposed. The identification and the characterization of the internal rotation modes require no user intervention and make extensive use of the information imbedded in the redundant internal coordinates. Rigid-rotor internal rotation modes are obtained by fixing stretching, bending, and out-of-plane bending motions and solving the vibrational problem for the constrained system. Normal vibrational modes corresponding to internal rotations are identified by comparing them with the constrained modes. The atomic composition of the rotating groups is determined automatically and the kinetic energy matrix for internal rotation is given by either the constrained Wilson-G matrix or the Kilpatrick and Pitzer protocol. The potential periodicity, the rotating tops' symmetry numbers, and the well-multiplicity are obtained using simple rules. These parameters can be altered by user input. An improved analytical approximation to the partition function for a one-dimensional hindered internal rotation has been developed that reproduces the accurate values tabulated by Pitzer and Gwinn to $\pm 0.4\%$ with a maximum error of 2.1%. This approximation is shown to behave better than previously available approximations over a wider range of regimes. The one-dimensional rotor treatment is generalized to give useful approximations to the multidimensional rotor thermodynamic functions that can be a good start for more thorough studies. © *1998 American Institute of Physics.* [S0021-9606(98)02006-6]
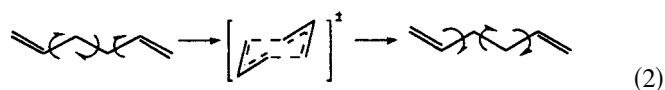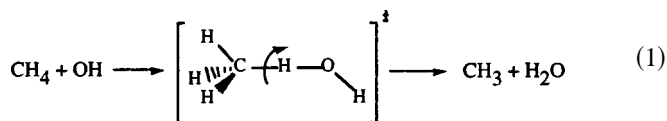
I. INTRODUCTION

Statistical thermodynamics can be used to calculate the enthalpy, heat capacity, and entropy of a gas-phase molecule using its geometry and vibrational frequencies. However, significant errors can result if the harmonic oscillator approximation is used to calculate the partition function for low frequency modes that represent hindered internal rotation, as shown in Scheme 1.
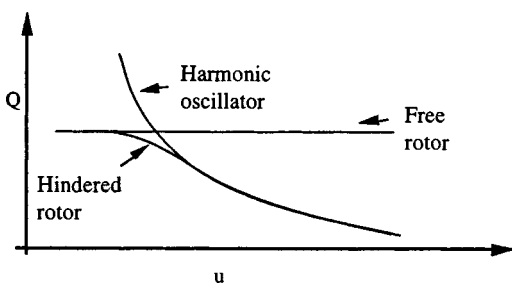
Scheme 1: A representation of the partition function Q for a free rotor, hindered rotor, and harmonic oscillator as a function of $u = h\nu/kT$, where ν is the vibrational frequency and T is the temperature.

Treating internal rotation is especially important in transition states, where several motions may have to be treated as hindered rotors, as in the hydrogen abstraction reaction $CH_4 + OH \rightarrow CH_3 + H_2O$ shown in Eq. (1).[1–4] Conversely, internal rotation degrees of freedom may disappear as a reaction takes place and failure to treat them properly causes significant errors. For instance, the harmonic oscillator treatment of the three internal rotations in 1,5-hexadiene is thought to cause an overestimation of the entropy in the Cope reaction, Eq. (2), by as much a 7 cal/mol-K.[5]

$$CH_4 + OH \longrightarrow \left[\begin{array}{c} H \\ H\text{''}C\text{---}H\text{---}O \\ H \end{array} \right]^{\ddagger} \longrightarrow CH_3 + H_2O \qquad (1)$$

$$(2)$$

The general quantum mechanical problem of multidimensional internal rotation can be complicated and cumbersome to solve. In particular, it requires the multidimensional torsional potential which can be expressed in terms of Fourier series.[6] The case of a one-dimensional but asymmetric internal rotation[7,8] can even involve a level of complexity that makes solving the hindered rotor problem impractical for many applications. In many cases, however, reducing the multidimensional problem to a product of one-dimensional rotors with simple cosine torsional potentials would constitute a good approximation. Here, we seek, first, to identify the internal rotation modes and, second, to generalize the

treatment of a single rotor to the general case of multiple internal rotors, and, third, to develop a useful approximation to the thermodynamic functions without requiring the user's intervention.

Pitzer and co-workers[8] long ago tabulated the thermodynamic functions for the minimal case of a molecule with a rigid symmetric, or nearly symmetric, rotating top. Formulas are available to interpolate the partition function between that of a free rotor, hindered rotor, and harmonic oscillator.[8–10] The approximation by Truhlar[9] has been used in many studies in recent years.[11–13] This formula has the desirable feature of being a smooth approximation from free rotor to harmonic oscillator, a useful feature for treating transitional bending modes.[14] Another formula, by McClurg, Flagan, and Goddard,[10] is based on the asymptotic behavior of the quantum mechanical partition function at low temperature and the classical partition function at high temperature. Pitzer and Gwinn's formula[8] is an improvement of the classical hindered rotor treatment. These three approximations have a well defined range of applicability within which they perform remarkably well.

For large electronic structure calculations, one would ideally like to recognize internal rotations without requiring the user's intervention or expertise, and automatically compute a correction to the thermodynamic functions. In this work, we are only concerned about internal rotation around clearly defined chemical bonds. For simple systems such as acyclic molecules, the internal rotations can take place about each nonterminal single bond. The rotating subgroups of atoms can then be determined and the reduced moments of inertia for internal rotation can be computed, with or without approximations.[7–10,15–21] Making this rotor identification procedure automatic for a general molecule can be complicated and can involve many special cases, since it would require first the identification of rings and multiple bonds. Most of the problem, however, resides in the identification of the internal rotation modes. Large molecules can have a large number of low frequency modes which can include not only internal rotations but also large amplitude collective bending motions of atoms. Moreover, some of the low frequency modes can be a mixture of the aforementioned motions, and the expertise of the user is needed to identify the internal rotations.

Generally, the necessary information required for characterization of internal rotations cannot be obtained solely from the linear displacements represented by the Cartesian normal modes. In particular, one cannot determine which subgroups of atoms are rotating about each other and cannot obtain the information needed to calculate the axis of rotation and/or the moment of inertia of each rotating subgroup. To solve this problem, we have used redundant internal coordinates[22,23] to describe the vibrations in terms of bond stretches, valence angle bends, and dihedral angle changes. The internal rotations can be described by linear combinations of dihedral angle changes, which can be isolated from stretching and bending motions. Therefore, a vibrational analysis in redundant internal coordinates offers the possibility of automatically identifying the internal rotation modes,

and treating them as free or hindered rotors rather than harmonic oscillators.

II. IDENTIFICATION OF ROTATIONAL MODES

The treatment of a vibrational mode as an internal rotation has been studied by many authors over the years and most of the mathematical details have long been documented.[15–21] The primary task is to find which subgroups of the molecule are rotating so that one can define the kinetic energy matrix of the rotating system. Then, one needs to identify which of the vibrational modes are internal rotations. Inspection of the normal modes in Cartesian coordinates does not yield this information easily and various problems can arise. For example, in a hypothetical four-atom molecule (A-B-B-A with $m_A \ll m_B$) such as in Scheme 2,
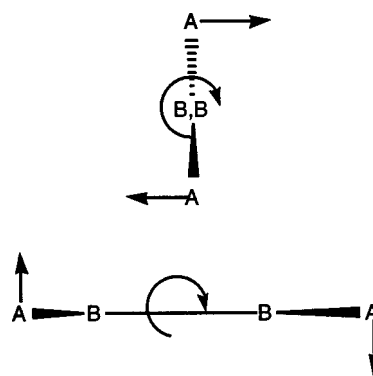
Scheme 2: In all *trans* conformation of A–B–B–A, using the Cartesian normal mode, one can correctly assign the B–B bond as the axis of rotation and the two A–B groups as rotors. However, a *cis* conformation, the Cartesian normal mode would indicate that the two A atoms rotate around an axis perpendicular to the B–B bond.

one can see that without knowing how the atoms are bonded to each other, the normal modes in Cartesian coordinates can lead to the wrong conclusion. Problems of this sort can be overcome easily by using internal coordinates, since this motion can be described by a A-B-B-A dihedral angle change.

A. Transformation of force constants from Cartesian to internal coordinates

In most *ab initio* molecular orbital packages the energy derivatives are computed in Cartesian coordinates. Before performing the vibrational analysis in internal coordinates it is thus necessary to transform the energy derivatives from Cartesian to internal coordinates. In the Wilson, Decius, and Cross definition,[24] internal coordinates are coordinates that are unaffected by translation and rotation of the molecule. One such set of coordinates {$\mathbf{q}$} can be made up of bond lengths, bond angles, and torsion angles. For a nonlinear molecule with N atoms, there are $3N$-6 linearly independent internal coordinates. However, it may be desirable to use a larger numberof internal coordinates, (i.e., redundant internal coordinates) to represent the bonding in the molecule.

Redundant internal coordinates are used in the GAUSSIAN 94 suite of programs[25] for geometry optimization.[23] Given

Cartesian coordinates for the molecule, a suitable set of redundant internal coordinates is generated automatically and reflects the bonding and connectivity of the molecule. Atoms A and B are considered bonded if the interatomic distance is less than 1.3 times the sum of the covalent radii. A valence angle coordinate is assigned to A, B, and C if A is bonded to B and B is bonded to C. If the value of a bond angle lies between 175 and 180°, the valence angle and any related dihedral angle are replaced by a pair of linear angle coordinates. Finally, a dihedral angle (or torsion angle) is assigned to A, B, C, and D if A is bonded to B, B is bonded to C, and C is bonded to D. If no dihedral angles can be generated in the previous procedure, as is the case for a molecule such as H_2CO, the A-B-C-D and D-B-C-A dihedral angles are added to the set of internal coordinates in order to account for out-of-plane motions.

For the purpose of identifying internal rotations, these internal coordinates are modified slightly. In a molecule such as ethylene, the out-of-plane bending motions of the CH_2 groups are described by linear combinations of the four dihedral angle changes, and the bond torsion is also represented by a linear combination of the same four dihedral angles. Since our goal is to identify bond torsions by inspection of the changes in the dihedral angles of the molecules, out-of-plane bending motions would clearly interfere with this process. To avoid this problem, explicit out-of-plane bending coordinates are added for each tricoordinate planar center (i.e., if A is bonded to B, C, and D, then dihedral angles B-A-C-D and D-A-C-B are added). When these out-of-plane motions are frozen, then the remaining change in dihedral angles can only describe bond torsion. Identification of a planar center is simply made by inspecting the sum of the three valence angles. If the sum of the valence angles is between 355 and 360°, the two extra dihedral angles are added.

Transformation from infinitesimal Cartesian coordinate displacements to internal coordinate displacements is simple, $\delta\mathbf{q} = B\,\delta\mathbf{x}$, using the Wilson B matrix ($B = \partial q/\partial x$). Transformations of the forces or gradients, $\mathbf{g}$, and force constants or Hessian matrix, H, from Cartesian (subscript x) to internal (subscript q) are more complicated,

$$\mathbf{g}_q = (B^{-1})\mathbf{g}_x; \quad H_q = (B^{-1})H_x(B^{-1})^t + \left(\frac{dB^{-1}}{d\mathbf{q}}\right)\mathbf{g}_x. \quad (3)$$

A generalized inverse must be used since B is rectangular,

$$G = BuB^t; \quad B^{-1} = G^{(-)}Bu, \quad (4)$$

where u is an arbitrary nonsingular matrix. If the set of internal coordinates is redundant, i.e., $\{\mathbf{q}\}$ contains more than $3N-6$ variables, $G^{(-)}$ can be formed by diagonalization and inverting only the $3N-6$ nonzero eigenvalues,

$$V^tGV = \begin{bmatrix} \Lambda & 0 \\ 0 & 0 \end{bmatrix}; \quad G^{(-1)} = V\begin{bmatrix} \Lambda^{-1} & 0 \\ 0 & 0 \end{bmatrix}V^t. \quad (5)$$

The transformation of the force constants can be reformulated so that

$$H_q = (B^{-1})\left(H_x - \frac{dB}{d\mathbf{x}}\mathbf{g}_q\right)(B^{-1})^t. \quad (6)$$

The $(dB/d\mathbf{x})\,\mathbf{g}_q$ term is needed for general Hessian calculations, but it is zero for vibrational frequencies at stationary points or perpendicular to a mass-weighted reaction path.

When a redundant set of internal coordinates is used, the redundancy is projected out of the displacements, gradient, and force constant matrix by using $P = GG^{(-)}$ as a projector. For optimizations using redundant internal coordinates, arbitrarily large eigenvalues are assigned to the remaining space,

$$H' = PHP + (I-P)A(I-P) = PHP + \alpha(I-P), \quad (7)$$

where A is the identity matrix I times α (a large constant, e.g., 1000. au).

B. Normal modes of vibration in internal coordinates

The vibrational normal mode problem at a stationary point can be solved easily in mass-weighted Cartesian coordinates. If H_{Mx} is the mass-weighted Cartesian Hessian with rigid-body translations and rotations projected out, $\mathbf{L}_{Mx}^i$ the mass-weighted ith normal mode and μ, a diagonal matrix consisting of the inverse square root of the nuclear masses, then,

$$H_{Mx} = \mu H_x \mu,$$

$$\mathbf{L}_{Mx}^i = \mu \mathbf{L}_x^i,$$

$$H_{Mx}\mathbf{L}_{Mx}^i = \lambda_i \mathbf{L}_{Mx}^i. \quad (8)$$

In internal coordinates, the kinetic energy T of the molecule can be written as $2T = d\mathbf{q}^t/dt\ G^{(-)}d\mathbf{q}/dt$ if u in Eq. (4) is diagonal and consists of triplets of the inverse nuclear masses (i.e., $u = \mu^2$). The secular equation for the normal modes $\{\mathbf{L}_q^i\}$ can then be written as[24]

$$H_q\mathbf{L}_q^i = G^{(-1)}\lambda_i\mathbf{L}_q^i. \quad (9)$$

This is not a standard eigenvalue problem. However, by means of symmetric orthogonalization, the problem can be transformed into an eigenvalue problem in mass-weighted coordinates,

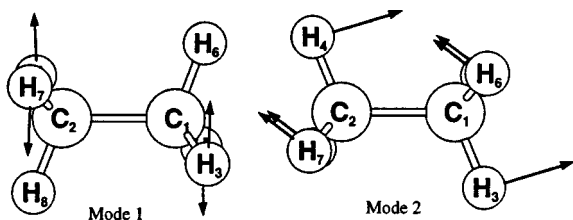$$G^{1/2}H_qG^{1/2}\mathbf{L}_{Mq}^i = \lambda_i\mathbf{L}_{Mq}^i,$$

and

$$\mathbf{L}_q^i = G^{1/2}\mathbf{L}_{Mq}^i. \quad (10)$$

Alternatively, if the normal modes in Cartesian coordinates $\{\mathbf{L}_x^i\}$ are available, the normal modes in internal coordinates can be easily obtained by
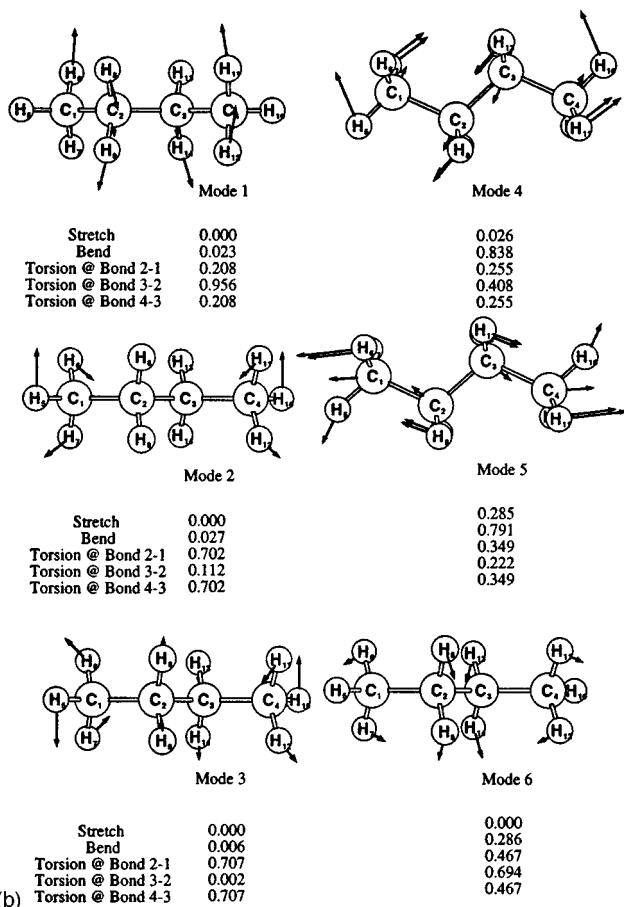
$$\mathbf{L}_q^i = B\mathbf{L}_x^i. \quad (11)$$

For problems such as variational transition state theory,[26] one needs to perform a normal mode analysis for the vibrations perpendicular to the reaction path. In this case, in addition to rigid body translation and rotation, the motion along the path needs to projected out of the mass-weighted Hessian.[27] If the path corresponds to a steepest descent reaction path in mass-weighted coordinates, i.e., an intrinsic reaction coordinate,[28] then the mass-weighted gradient is parallel to the path and is projected out. Hence, the projected $(dB/d\mathbf{x})\,\mathbf{g}_q$ term is zero and is not needed for the transformation of the projected Hessian to internal coordinates.

	Number of modes	Min. torsion %
Ethane	1	100.0
Ethanol	1	97.3
Propane	2	97.9
Butane	3	97.3
Pentane	4	92.0

(a)

Frequency in cm**(-1)	317.670	980.950
Stretch	0.000	0.003
Bend	0.000	0.761
D(4, 2, 1, 3)	0.333	0.000
D(4, 2, 1, 5)	0.333	-0.187
D(4, 2, 1, 6)	0.333	0.187
D(7, 2, 1, 3)	0.333	-0.187
D(7, 2, 1, 5)	0.333	-0.375
D(7, 2, 1, 6)	0.333	0.000
D(8, 2, 1, 3)	0.333	0.187
D(8, 2, 1, 5)	0.333	0.000
D(8, 2, 1, 6)	0.333	0.375
Torsion @ Bond 2-1	1.000	0.649

(b)

	Mode 1	Mode 4
Stretch	0.000	0.026
Bend	0.023	0.838
Torsion @ Bond 2-1	0.208	0.255
Torsion @ Bond 3-2	0.956	0.408
Torsion @ Bond 4-3	0.208	0.255

	Mode 2	Mode 5
Stretch	0.000	0.285
Bend	0.027	0.791
Torsion @ Bond 2-1	0.702	0.349
Torsion @ Bond 3-2	0.112	0.222
Torsion @ Bond 4-3	0.702	0.349

	Mode 3	Mode 6
Stretch	0.000	0.000
Bend	0.006	0.286
Torsion @ Bond 2-1	0.707	0.467
Torsion @ Bond 3-2	0.002	0.694
Torsion @ Bond 4-3	0.707	0.467

FIG. 1. (a) First two normal modes of ethane at the HF/STO-3G level of theory. (b) First six normal modes of n-butane at the HF/STO-3G level of theory.

C. Internal rotor identification: Method 1

A normal vibrational mode corresponding to a hindered internal rotation has unusually large components for some dihedral angles. Figure 1(a) shows some of the normal modes of ethane and butane. For instance, in the case of ethane, the torsion components of the normal mode account for 100% of the motion in the lowest frequency vibrational mode by symmetry. An internal rotation is generally well described under the rigid rotor approximation, but because most molecules do not have as much symmetry as ethane and/or posses more than one rotating group, the normal modes representing internal rotation may have nonzero components for bond stretches and angle bending. However, these components should be much smaller in magnitude than the torsions [see Fig. 1(b)]. Table I shows the minimum amount of torsion present in the normal modes typically assigned as hindered internal rotation for five simple test molecules.

Based on Table I, it should be possible to identify an internal rotation by using a cut-off value α (close to 100%) for the minimum amount of torsion present in a normal mode. For the jth mode, one can tabulate the magnitude of the dihedral components for each bond [i.e., $T(\text{B–C},j) = (\Sigma_{(\text{A,D})}L^2_{j(\text{A,B,C,D})})^{1/2}$] for each unique (B,C), where the L_j's are the dihedral components for mode j). Provided that the cut-off value is chosen so as to identify the correct number of torsional modes (equal to the number of rotating groups), the bonds about which rotation occurs can be determined by inspecting the dihedral components. The bonds involved in internal rotation would then be the bonds which have the largest $\Sigma T(\text{B–C},j)$ when summed over the internal rotation modes.

For each bond about which internal rotation occurs, the two rotating groups can be identified using the bonding information present in the set of internal coordinates. Once the rotors (the rotating groups) have been identified, one can set up the kinetic energy matrix according to Kilpatrick and Pitzer[19] and obtain the reduced moments of inertia by diagonalizing the kinetic energy matrix.[15]

Even though this approach is successful in identifying both the internal rotation modes and the rotors, it is sensitive to the cut-off value used. Furthermore, there can be instances where vibrational modes mix extensively with the internal rotation modes, making their characterization very difficult. The normal modes of 3-hexene illustrate this point. As can be seen in Fig. 2, mode 4 and mode 6 are virtually indistinguishable on the basis of their torsional components. Only a 1.5% difference exists in the amount of torsion in these two modes. Modes 4 and 6 both correspond to the rotation of the methyl groups. However, mode 6 features a greater mixing with the C–C–C bending and out-of-plane bending motions. Also, because the sp^2 carbons are not exactly planar, the

Mode 1		Mode 2	
Stretch	0.005		0.004
Bend	0.079		0.078
Out-of-Plane	0.045		0.046
Torsion @ 2-1	0.074		0.055
Torsion @ 3-1	0.701		0.703
Torsion @ 4-3	0.048		0.024
Torsion @ 5-2	0.701		0.703
Torsion @ 6-5	0.048		0.024

Mode 3		Mode 4	
Stretch	0.012		0.007
Bend	0.335		0.012
Out-of-Plane	0.219		0.108
Torsion @ 2-1	0.393		0.008
Torsion @ 3-1	0.393		0.044
Torsion @ 4-3	0.450		0.700
Torsion @ 5-2	0.393		0.044
Torsion @ 6-5	0.450		0.700

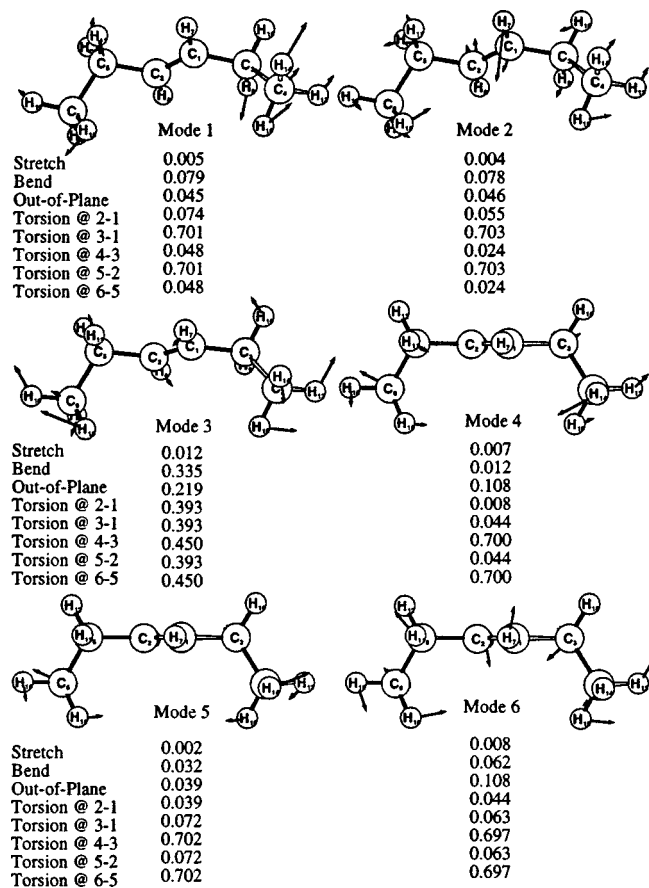| Mode 5		Mode 6	
Stretch	0.002		0.008
Bend	0.032		0.062
Out-of-Plane	0.039		0.108
Torsion @ 2-1	0.039		0.044
Torsion @ 3-1	0.072		0.063
Torsion @ 4-3	0.702		0.697
Torsion @ 5-2	0.072		0.063
Torsion @ 6-5	0.702		0.697

FIG. 2. First six normal modes of *trans* 3-hexene at the HF/STO-3G level of theory.

out-of-plane bending and bond torsion motions are heavily mixed in mode 3.

The case of 3-hexene provides an opportunity to stress an important point in the relationship between hindered internal rotation and harmonic vibrational frequency. For a simple hindered rotor with a periodic potential $V = V_0(1 - \cos(\sigma\tau))/2$, where τ is the twist angle and σ the periodicity of the potential, the harmonic vibrational frequency, ν, is given by

$$I_r \frac{d^2\tau}{dt^2} + \frac{V_0\sigma^2}{2} \tau = 0; \quad \tau = \tau_0 \cos(2\pi\nu t), \quad (12)$$

where I_r is the reduced moment of inertia for internal rotation. Clearly, the internal rotation barrier height is proportional to the square of the vibrational frequency and to the reduced moment of inertia,

$$V_0 = 8\pi^2\nu^2 I_r/\sigma^2. \quad (13)$$

In the case of a carbon–carbon double bond, the rotation barrier height V_0 is large (50 to 60 kcal/mol) and mostly independent of the nature of the substituents attached to the olefin; however, the reduced moment of inertia I_r will depend on the mass of these substituents and can take large values, such as in the case of hexene, where an ethyl group is attached at each end of the double bond. This explains why the vibrational frequency for the double bond torsion mode is so small in 3-hexene (150 cm^{-1} compared to 1250 cm^{-1} in

ethylene). Likewise, the C–C bond torsion frequency in ethane is approximately 2.5 times greater than that in butane. Trying to identify the internal rotation modes on the basis of the vibrational frequencies can thus be misleading. A better diagnostic would be based upon an estimate of the torsional barrier height. The C=C double bond torsional mode is not an internal rotation and is best treated as a harmonic oscillator no matter how small the associated frequency. Alternatively, one can treat this torsional mode as an internal rotation using thermodynamic functions that reach the proper harmonic oscillator limit for high rotational barrier height. Clearly, in difficult cases like this one, using the preceding approach would require some user intervention. An alternative, perhaps more automatic, procedure is described next.

D. Internal rotor identification: Method 2

Instead of identifying internal rotations by inspection of the normal mode components, one can separate the internal rotations out before the normal mode problem is solved. The internal coordinates consist of stretches, bends, out-of-plane bends, and dihedrals; one can construct a projector that removes all of the stretches, bends, and out-of-plane motions, leaving only the bond torsions. If P is the projector for the allowed internal motions $[P = GG^{(-)}$ for redundant internals], then the stretches, bends, and out-of-plane bends can be constrained by using the projector P' given by,[23,24]

$$P' = P - PC(CPC)^{-1}CP, \quad (14)$$

where C is a diagonal matrix with 1's for the constrained coordinates and 0's for the remaining coordinates. The constrained G matrix, G', is constructed likewise. The secular equation for the projected normal mode problem for the internal rotors is,

$$G'H_q'\mathbf{L'}_q^i = \lambda'_i\mathbf{L'}_q^i,$$
$$H_q' = P'H_qP', \quad (15)$$

and transformed to mass-weighted coordinates, it becomes,

$$G'^{1/2}H'_qG'^{1/2}\mathbf{L'}_{Mq}^i = \lambda'_i\mathbf{L'}_{Mq}^i. \quad (16)$$

The mass-weighted Hessian for internal rotation, $G'^{1/2}H'_qG'^{1/2}$, is singular with a rank equal to the number of bonds about which internal rotation is possible. In most cases, the projected vibrational frequencies will be very similar to the actual ones (see Table II). A significant shift in frequency would indicate coupling with stretching, bending, and out-of-plane modes.

Next, one must identify which of the actual normal modes are internal rotations by determining which have the greatest similarity with the modes of the projected, internal rotation problem, Eq. (16). This is simply done by considering their overlap. Using this procedure, the internal rotation modes are identified without ambiguity.

Central to the statistical thermodynamical treatment of hindered internal rotation are the periodicity of the potential and the symmetry number of the rotating top. Assuming a single cosine potential, the ratio of periodicity over the symmetry number represents the degeneracy of the energy levels. For example, if the potential is threefold and the three posi-

TABLE II. Harmonic vibrational frequencies for internal rotation and projected frequencies (in cm^{-1}) for selected molecules at the HF/STO-3G level of theory.

Molecule	Frequencies for torsional modes	Projected frequencies	Overlap
Ethane	317.6	317.6	1.00
Methanol	399.0	400.2	0.99
n-butane	123.8, 232.4, 267.0	126.0, 238.5, 267.3	0.99, 0.99, 0.99
1,5-hexadiene[a]	63.5, 97.5, 103.74	71.9, 107.2, 114.9	0.99, 0.99, 0.96
3-hexane	55.4, 124.0, 198.1, 248.5	59.8, 133.2, 237.9, 241.5	0.99, 0.99, 0.98, 0.99
1,2-dichloroethane	108.76	111.12	0.99

[a]At the B3LYP/6-31G* level of theory.

tions (0, 120, and 120°) correspond to indistinguishable structures, such as in ethane, one only needs to account for the energy levels in the region $0 \pm 60°$. However, if the three positions are distinguishable, to account for all the energy levels, one can consider the full range ($0 \pm 180°$) or, alternatively, consider the range $0 \pm 60°$, but count the energy levels three times. Failure to recognize this can be the source of large errors in the thermodynamic functions. For instance, let us consider the internal rotation about the C3–C4 bond in 1,5-hexadiene. The potential energy profile for this bond torsion was obtained using the method described in Ref. 29 and is shown in Fig. 3. Even though the rotating top is clearly asymmetric (symmetry number equal to 1), to a good approximation, the torsional potential can be represented by a single cosine function with a periodicity of 3.

In order to identify the symmetry number of each rotating top, one first needs to identify which atoms belong to the top. As mentioned earlier, this can be done by using the bonding information present in the set of redundant internal coordinates. If one chooses to do this, special attention must be paid for ring-containing molecules. A simpler approach consists of incrementing, by a small quantity, such as $\pi/12$ or $\pi/6$, all the dihedral angles pertaining to the bond under consideration and solving for the new set of Cartesian coordinates given by $\Delta \mathbf{q} = B \Delta \mathbf{x}$. The old and new set of Carte-

sian coordinates can then be compared using a fixed Cartesian orientation defined by the bond under consideration and a bond within one of the rotating group; an atom belongs to the rotating top if its Cartesian coordinates have changed. Once the composition of the rotating top is known, one can simply identify the symmetry number by repeatedly rotating (by $\pi/12$ or $\pi/6$, for instance) the Cartesian coordinates around the bond connecting the top to the rest of the molecule until the difference between the starting set and the new set of Cartesian coordinates and atomic numbers is below threshold.

The periodicity of the torsional potential can be obtained by performing a series of *ab initio* energy calculations at different conformations. In most cases, however, the periodicity of a torsional potential can be obtained by using simple rules depending on the hybridization of the bond atoms. Here we followed the rules set by Mayo, Olafson, and Goddard for their generic force field DREIDING.[30] The coordination of an atom is used in order to assign a hybridization character. For instance, a tricoordinated carbon is assumed sp^2 whereas a doubly coordinated oxygen is assumed sp^3.

In many cases, the torsional potential differs greatly from a single cosine function; the parameter that we called periodicity up to now remains nevertheless of great importance. Just as in the standard case of a particle in a box where the energy levels depend upon the size of the box, the energy levels for the hindered rotor will depend upon the width of the potential energy well. In the case of 1,2-dichloroethane for instance, the torsional potential differs greatly from a single cosine function with a periodicity of 3 (see Fig. 4). As it will be seen later, a good approximation to the thermodynamic function of 1,2-dichloroethane can be obtained by considering only the deepest well, that is by only considering the region $\tau = 180 \pm 60°$. It is thus important to still use 3 as a periodicity number for the torsional potential in 1,2-dichloroethane.

No discrimination against bonds like carbon–carbon double bonds has been made so far. As mentioned for the case of hexene, there are instances where there is no pure bond torsion mode, but there are, instead, modes that are varying mixtures of out-of-plane bending and bond torsions. Since these modes are best treated using the harmonic oscillator approximation, there is no need to try to identify which one of these modes is more akin to a bond torsion. A very hindered bond torsion can be detected by inspection of the
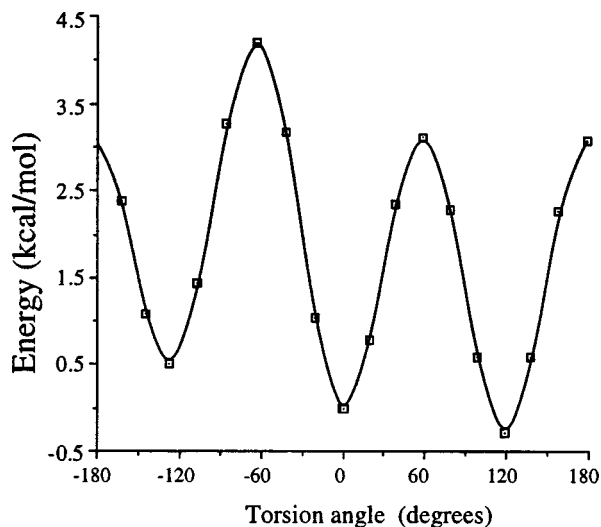

FIG. 3. Torsional potential for the C3–C4 bond in 1,5-hexadiene at the HF/STO-3G level of theory in the *gauche–gauche* conformation.
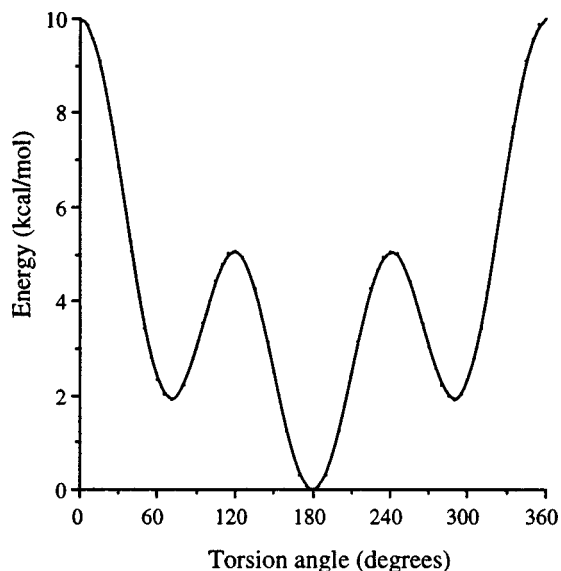
FIG. 4. Torsional potential for 1,2-dichloroethane at the HF/6−31G* level of theory.

diagonal element of the force constant matrix, $k_{\tau\tau}$. Assuming no coupling with the other internal rotations, the torsional barrier height is given by $V_0 = 2\sigma^2 k_{\tau\tau}$. If V_0 is higher than threshold (20 kcal/mol at 300 K, for instance), the bond torsion is not considered.

Once the rotating groups have been identified, one can proceed to calculate the reduced moments of inertia using Kilpatrick and Pitzer's protocol.[19] Alternatively, one can extract this information from the projected G matrix, G', since it corresponds to the kinetic energy matrix of the molecule under the rigid-rotor approximation with overall translation and rotation projected out. The periodicity of the internal rotation potential can be taken into account by scaling G' by σ, where σ is a diagonal matrix consisting of inverse n_m-tuplets of the bond periodicity numbers (i.e., $G'' = \sigma^{1/2} G' \sigma^{1/2}$).

Since the rotation about a given bond is equally well described by any one of the dihedral angles associated with this bond, the dimension of G' can be reduced to an n by n matrix. This can be done by making the appropriate variable change in the kinetic energy matrix to leave n^2 terms, or by simply dropping the rows and columns of G' corresponding to the extra dihedral angles, as noted by Wilson et al.[24]

Throughout this section, we have assumed that n, the number of degrees of freedom for the constrained systems, is equal to the number of bonds about which internal rotation is possible. This is always the case for acyclic molecules; however, for cyclic molecules featuring rings bigger than six-membered rings there are ring torsional modes (the ring-puckering modes have been projected out since they would involve bending). The presence of these ring torsions is usually recognizable from the fact that the projector P' has non-zero off-diagonal components for dihedral angles about a number of bonds, since such motions involve correlated motions about several bonds. Similar to internal rotations, ring torsions can cause problems in the evaluations of thermodynamic functions. In the present analysis they are not treated.

III. CORRECTION TO THERMODYNAMIC FUNCTIONS

If a low vibrational frequency mode, such as a hindered rotation, is treated as a harmonic oscillator, the partition function is too large, approaching infinity as the frequency goes to zero. If this mode is treated as a free rotor, the partition function is correct for a zero frequency, but is overestimated for a nonzero frequency (see Scheme 1). Determining an accurate density of states for multiple hindered rotors is a difficult problem and is not our objective. Here, we propose to use some simple approximations to obtain suitable estimates of the partition function.

For a free rotor, the classical partition function is

$$Q^{\text{free rot.}} = \left(\frac{2\pi kT}{h^2}\right)^{1/2} \int_0^{2\pi/\sigma} I_r^{1/2} d\tau.$$

For a simple hindered rotor with a periodic potential $V = V_0(1 - \cos(\sigma\tau))/2$, the classical limit to the partition function is

$$Q = \left(\frac{2\pi kT}{h^2}\right)^{1/2} \int_0^{2\pi/\sigma} I_r^{1/2}$$

$$\times \exp[-V_0(1 - \cos(\sigma\tau))/2kT]d\tau. \quad (17)$$

For the rotation of a symmetric top, the reduced moment of inertia I_r is constant. For the rotation of an asymmetric top, I_r can vary greatly with the twist angle. In the case of 1,2-dichloroethane, the reduced moment of inertia more than doubles as the twist angle is varied. Although the reduced moment of inertia varies, the partition function for free rotation can often be reliably approximated by $Q^{\text{free rot.}} \approx (8\pi^3 kT/\sigma^2 h^2)^{1/2} I_r^{1/2}$. In the case of 1,2-dichloroethane, using a simple 25-point trapezoid integral, the error is estimated to be 1.9%. For the free rotation of an asymmetric top, however, the moments of inertia for overall rotation, $I_a I_b I_c$, would vary with the twist angle as well, and one needs to also consider the variation of the overall rotation partition function. In the case of 1,2-dichloroethane, neglecting the variation of the moments of inertia for both external and internal rotation produces an error of approximately 12.3%. Even though treating the internal rotation of asymmetric tops can be complicated, it is important to recognize that in many cases the same formalism used to treat the rotation of symmetric tops can provide a fairly good approximation.

If the reduced moment of inertia is constant, then the classical partition function in Eq. (17) can be expressed in terms of the Bessel function $J_0(iV_0/2kT)$,[8]

$$Q^{\text{hin. rot.}} = \left(\frac{8\pi^3 kT}{\sigma^2 h^2}\right)^{1/2} I_r^{1/2} \exp[-V_0/2kT]J_0(iV_0/2kT)$$

$$= Q^{\text{free rot.}} \exp[-V_0/2kT]J_0(iV_0/2kT). \quad (18)$$

As mentioned in the Introduction, Pitzer and Gwinn[8] solved for the energy levels for a cosine potential representing the hindered rotation of a symmetrical top attached to a rigid frame, and tabulated the thermodynamic functions for a one-dimensional internal rotation using the barrier height for internal rotation V_0 and $1/Q^{\text{free rot.}}$ as reduced variables. The quantum and classical partition functions for the harmonic oscillator with a vibrational frequency ν are given by,

$$Q^{\text{h.o.q.}}=\frac{e^{-u/2}}{1-e^{-u}}; \quad Q^{\text{h.o.cl}}=\frac{1}{u} \quad \text{with} \quad u=\frac{h\nu}{kT}. \qquad (19)$$

The thermodynamic functions for the free energy, energy, the entropy, and the heat capacity of the gas-phase molecule[31] are

$$G=-kT\ln(Q); \quad E=kT^2\frac{\partial \ln(Q)}{\partial T},$$

$$S=k\ln(Q)+kT\frac{\partial \ln(Q)}{\partial T},$$

$$C_V=2kT\frac{\partial \ln(Q)}{\partial T}+kT^2\frac{\partial^2 \ln(Q)}{\partial T^2}. \qquad (20)$$

Using the relationship in Eq. (13), it is possible to directly compare the thermodynamic functions for the harmonic oscillator to the ones for the hindered rotor as tabulated by Pitzer and Gwinn. Both G/T and S start to differ significantly for rotational barrier heights, V_0, of the order of kT and very large errors occur for $V_0 \ll kT$, as the free-rotor limit is approached. Although the entropy for hindered rotation can be much smaller than for the corresponding harmonic oscillator, it is never more than 0.5 cal/mol-K greater than that of the harmonic oscillator for the range covered by the Pitzer and Gwinn tables.

Pitzer and Gwinn solved for the energy levels for a region $2\pi/(\sigma a)$ wide, where σ is the symmetry number of the top and σa is the periodicity of the potential, as explained in Sec. II D. The free-rotor partition function is thus taken as

$$Q^{\text{free rot.}}=\left(\frac{2\pi kT}{h^2}\right)^{1/2}\int_0^{2\pi/\sigma a}I_r^{1/2}d\tau$$

rather than the correct

$$Q^{\text{free rot.}}=\left(\frac{2\pi kT}{h^2}\right)^{1/2}\int_0^{2\pi/\sigma}I_r^{1/2}d\tau.$$

In the instances where the potential periodicity is greater than the top symmetry number, the tabulated values for S and $-G/T$ need to be increased by $k\ln(a)$. It should be emphasized that $k\ln(a)$ should only be added in the cases where the potential resembles very closely $V=V_0(1-\cos(\sigma a\tau))/2$.

In 1,2-dichloroethane, for example, the rotating top has a symmetry number of one and the torsional potential is threefold, but differing greatly from $V=V_0(1-\cos(3\tau))/2$, as was shown in Fig. 4. We have seen earlier that a good approximation for the free-rotor partition function is given by $Q^{\text{free rot.}}=(8\pi^3kT/h^2)^{1/2}I_r^{1/2}$. At the HF/6-31G* level of theory, the vibrational frequency corresponding to the internal rotation is $128\,\text{cm}^{-1}$. Using Eq. (13) with a symmetry number of 3 yields a rotational barrier height of 5.3 kcal/mol, which is very close to the actual *antigauche* barrier. Accounting for the energy levels in the region $180\pm60°$ constitutes a fair approximation, as long as kT is less than the *antigauche* endothermicity (2 kcal/mol). With a rotational barrier of 5.3 kcal/mol and $I_r=58.9$ amu A^2, the entropy contribution due to internal rotation is estimated to be $S=3.12$ cal/mol-K at 298 K using Pitzer and Gwinn's tables.
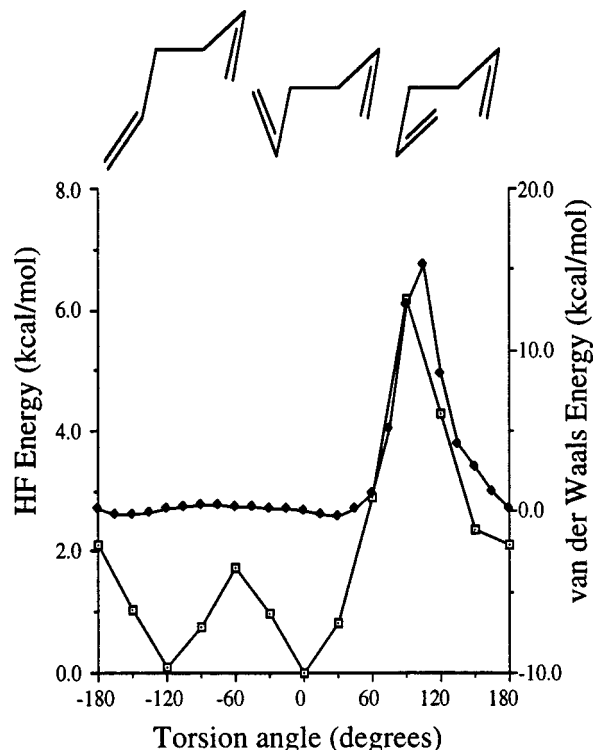

FIG. 5. Torsional potential for the C2–C3 bond in 1,5-hexadiene at the HF/STO-3G (open squares) and van der Waals energy (filled diamonds).

Chung-Phillips[7] solved for the internal rotation energy levels of 1,2-dichloroethane; using the first 18 nondegenerate energy levels, the entropy contribution is $S=3.16$ cal/mol-K. Using the next 12 doubly degenerate energy levels, the first of which being at $730\,\text{cm}^{-1}$ (2.1 kcal/mol), increases the entropy by 0.25 cal/mol-K. The doubly and triply degenerate energy levels would only contribute significantly when $kT \gg 2-3$ kcal/mol, that is, when the free-rotor regime is approached and when $I_r=58.9$ amu A^2 is the value that needs to be used.

Determining how many wells need to be considered is best decided upon inspection of the actual torsional potential. The asymmetry of the torsional potential is, however, often due to strong steric hindrances, and the expense of determining the actual torsional potential is not always justified. In order to help in the determination of the well multiplicity, one can consider the variation of a van der Waals potential with the twist angle. In the case of 1,5-hexadiene for instance, assuming $V=V_0(1-\cos(3\tau))/2$ is valid between -180 and $60°$ only; the third well in the model torsional potential is missing due to the steric hindrance because the two double bonds are too close to each other, as shown in Fig. 5. This steric hindrance is reflected in the van der Waals potential as well. In the present implementation of our procedure, we have used the same van der Waals parameters as in the DREIDING force field. A well is judged too high in energy or missing if the van der Waals energy change is greater than 2 RT. We should emphasize that this protocol is only meant to address the most obvious cases of steric hindrance.

Truhlar[9] noted that a great number of approximations are made in treating internal rotation, and suggested a simple way to evaluate the partition function with minimal effort by interpolating between the harmonic oscillator and free-rotor limits,

$$Q_i^{hin} \approx Q_i^{h.o.q} \tanh(Q_i^{free\ rot.}/Q_i^{h.o.cl})$$

$$= Q_i^{h.o.q} \tanh((\pi V_0/kT)^{1/2}), \tag{21}$$

where $Q_i^{h.o.q}$ and $Q_i^{h.o.cl}$ are the quantum and classical partition function, the harmonic oscillator for the ith normal mode being treated as an internal rotation. This function approaches the free-rotor partition function for $u_i \to 0$ and the harmonic oscillator partition function for $u_i \to \infty$. It reproduces the results tabulated by Pitzer and Gwinn with an average absolute deviation of 6.9% for $Q^{free\ rot}$ $= \{0.05, 0.25, 0.50\}$ and $V_0/kT = \{0.2, 0.4, 0.8, 1, 3, 5, 10, 20\}$, which is acceptable for most applications.[9] Truhlar's interpolating function can be compared with the $(\pi V_0/kT)^{1/2}$ $\times \exp[-V_0/2kT]J_0(iV_0/2kT)$ factor which plays the same role in the approximation proposed by Pitzer and Gwinn,[8]

$$Q_i^{hin.} = (Q_i^{h.o.q}/Q_i^{h.o.cl})\left(\frac{8\pi^3 kT}{\sigma^2 h^2}\right)^{1/2} I^{1/2}$$

$$\times \exp[-V_0/2kT]J_0(iV_0/2kT)$$

$$= Q_i^{h.o.q}(\pi V_0/kT)^{1/2} \exp[-V_0/2kT]J_0(iV_0/2kT). \tag{22}$$

When the vibrational frequency for internal rotation is small and/or the temperature is high, the ratio $(Q_i^{h.o.q}/Q_i^{h.o.cl})$ is close to one and Eq. (22) is nearly identical to the classical hindered rotation partition function which requires only the rotational barrier heights and the reduced moments of inertia. The approximation in Eq. (22) is good for large systems or at high temperature, when the classical treatment is justified.[8] Because $J_0(iV_0/2kT)$ grows as $(\pi V_0/kT)^{-1/2} \exp[V_0/2kT]$ for high values of $V_0/2kT$, Pitzer and Gwinn's formula approaches the harmonic oscillator limit for very hindered internal rotation, just as Truhlar's formula does. McClurg and co-workers[10] use Pitzer and Gwinn's formula along with a Padé approximant, Eq. (23), to correct for the overestimation of the zero point energy in the harmonic oscillator partition function,

$$Q_i^{hin.} = \exp[\Delta E/kT]Q_i^{h.o.q}(\pi V_0/kT)^{1/2}$$

$$\times \exp[-V_0/2kT]J_0(iV_0/2kT)$$

$$\text{with} \quad \Delta E = \frac{h\nu^2}{2h\nu + 16V_0}. \tag{23}$$

In Figs. 6 and 7, the accurate values for the hindered rotor partition function tabulated by Pitzer and Gwinn are compared to the harmonic oscillator partition function, Truhlar's approximation, Eq. (21), and Pitzer and Gwinn's approximation, Eq. (22). For $V_0/kT > 1$, the harmonic oscillator treatment of the hindered rotation is within 10%–15% of the tabulated values, but for $0 < V_0/kT \leqslant 1$, Eqs. (21) or (22) should be used. Truhlar's formula does poorly for high values of $Q^{free\ rot.}$ and Pitzer and Gwinn's formula deteriorates
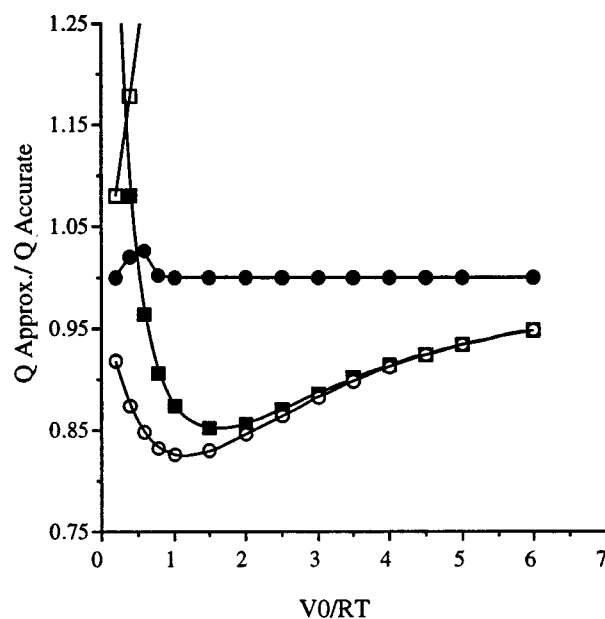

FIG. 6. Comparison between the tabulated hindered rotor partition function, the harmonic oscillator partition function (filled squares), the free-rotor partition function (open squares), Truhlar's approximation (Ref. 9) (open circles), and Pitzer and Gwinn's approximation (Ref. 8) (filled circles) as a function of the reduced barrier height V_0/RT for $Q^{free\ rot.} = 20$.

as both $Q^{free\ rot.}$ and V_0/kT become small. Not shown in Figs. 6 and 7 is the behavior of the formula of McClurg et al., Eq. (23). Equation (23) reproduces the tabulated results remarkably well for values of $Q^{free\ rot.}$ greater than 3 to 4 and V_0/kT less than 10. Over this range of values, the maximum error is no more than 8%. However, for values of $Q^{free\ rot.}$ less than 4, the error is consistently greater than 3% and the good behavior of Eq. (23) deteriorates very quickly. This approximation can thus be viewed as a modest improvement over Pitzer and Gwinn's. In defense of McClurg et al.,
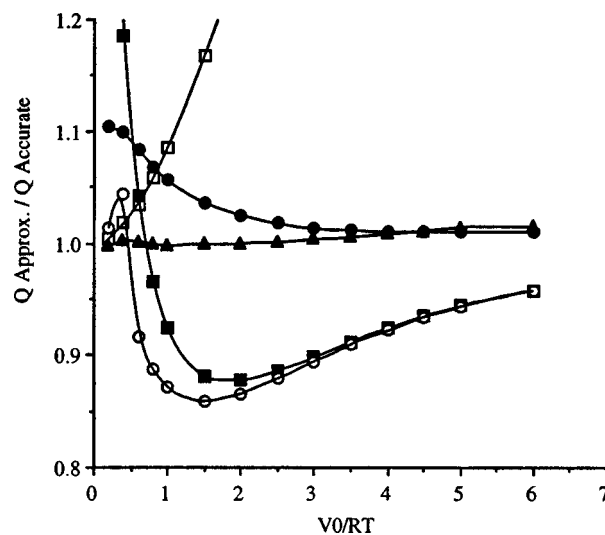

FIG. 7. Comparison between the tabulated hindered rotor partition function, the harmonic oscillator partition function (filled squares), the free-rotor partition function (open squares), Truhlar's approximation (Ref. 9) (open circles), Pitzer and Gwinn's approximation (Ref. 8) (filled circles), and the present work (filled triangles) as a function of the reduced barrier height V_0/RT for $Q^{free\ rot.} = 2$.

TABLE III. Deviation from Pitzer and Gwinn's tabulated accurate values for the hindered rotor partition function for various approximations.

	Truhlar[a]	McClurg[b]	Pitzer and Gwinn[c]	Present work
Abs. mean deviation	4.5%	4.3%	1.3%	0.4%
Maximum deviation	17.4%	23.8%	12.2%	2.1%
$Q^{\text{free rot.}}$ at max. dev.	20.0	1.818	1.818	1.818
V_0/kT at max. dev.	1.0	14.0	0.2	8.0

[a]See Ref. 9.
[b]See Ref. 10.
[c]See Ref. 8.

one could argue that their formula is most effective in a range of values most often encountered. For instance, the free-rotor partition function for the internal rotation in ethane is 3.35 at 500 K.

As shown in Table III, over the full range of Pitzer and Gwinn's tables ($1.818 \leq Q^{\text{free rot.}} \leq 20.0$ and $0.2 \leq V_0/kT \leq 14$, a total of 220 values), Truhlar's formula has a mean absolute deviation of 4.5% (maximum deviation = 17.4% for $Q^{\text{free rot.}} = 20$ and $V_0/kT = 1$). That Truhlar's formula is in error for high values of $Q^{\text{free rot.}}$ is not surprising. However, even for low values of $Q^{\text{free rot.}}$ (e.g., $Q^{\text{free rot.}}$ approximately 2), Truhlar's formula is in error by more than 10% for $1 \leq V_0/kT \leq 3$. Pitzer and Gwinn's formula has a mean absolute deviation of 1.3% (maximum deviation = 12.2% for $Q^{\text{free rot.}} = 1.818$ and $V_0/kT = 0.2$) and does well over the whole range of the table. Even though Truhlar's formula has slightly larger errors, it has the very desirable feature of being a smooth approximation over the entire range from free rotor to harmonic oscillator. However, as it will be seen below, the use of Truhlar's formula causes large errors in the entropy estimation, in contrast to Pitzer and Gwinn's formula which performs remarkably well. Pitzer and Gwinn's formula seems to reproduce the tabulated values fairly well except for lower values of both $Q^{\text{free rot.}}$ and V_0/kT.

Since our aim is to treat the case of a molecule with multiple internal rotors, it is desirable to have a formalism that accurately treats the single rotor case so as to minimize compounding errors. Using the tabulated accurate values, it is possible to improve upon Pitzer and Gwinn's formula. For small values of values of V_0/kT, Eq. (22) can be written as

$$Q_i^{\text{hin.}} = (Q_i^{\text{h.o.q}}/Q_i^{\text{h.o.cl}})Q_i^{\text{free rot.}}$$
$$\times \exp[-V_0/2kT]J_0(iV_0/2kT)$$
$$= Q_i^{\text{free rot.}}(1 + P_1 \exp[-V_0/2kT]), \quad (24)$$

where P_1 is a polynomial function of $1/Q_i^{\text{free rot.}}$ and $(V_0/kT)^{1/2}$. Likewise, the accurate values for the hindered rotor partition function can be fitted for small values of V_0/kT to

$$Q_{i(\text{accurate})}^{\text{hin.}} = Q_i^{\text{free rot.}}(1 + P_2 \exp[-V_0/2kT]), \quad (25)$$

where P_2 is another polynomial function of $1/Q_i^{\text{free rot.}}$ and $(V_0/kT)^{1/2}$. A new approximation to the hindered rotor partition function is then given by,

$$Q_i^{\text{hin.}} = (Q_i^{\text{h.o.q}}/Q_i^{\text{h.o.cl}})Q_i^{\text{free rot}} \frac{(1 + P_2 \exp[-V_0/2kT])}{(1 + P_1 \exp[-V_0/2kT])}$$
$$\times \exp[-V_0/2kT]J_0(iV_0/2kT). \quad (26)$$

This type of function keeps the good characteristics of Eq. (22) for high V_0/kT while improving its behavior for low V_0/kT. Using fifth-order polynomials[32] for P_1 and P_2 over the range $1.818 \leq Q^{\text{free rot.}} \leq 20.0$ and $0.2 \leq V_0/kT \leq 3$, Eq. (26) reproduces the tabulated values with an average deviation of 0.4% (maximum deviation = 2.1% for $Q^{\text{free rot.}} = 1.818$ and $V_0/kT = 8$) over the whole range of Pitzer's table. Figure 6 shows the behavior of Eq. (26) for low values of $Q^{\text{free rot.}}$.

The formulas discussed above are for one mode involving a single rotating group with a clearly defined reduced moment of inertia. For a system involving several coupled rotating groups (and, therefore, several normal modes), to the best of our knowledge, similar approximations do not exist. The rotors are coupled by both the kinetic and potential energy terms, and little may be known about the potential energy surface. Nevertheless, it would be very desirable to obtain an estimate of the coupled hindered rotor partition function that is better than the harmonic oscillator approximation.

For a system with n free rotors, Eidinoff and Alston[15] expressed the classical partition function of the system in terms of the determinant of the kinetic energy matrix for rotation and translation. If the rigid-body motions are projected out, the kinetic energy T is expressed as

$$2T = \sum_{ij}^{n} A_{ij}\dot{\tau}_i\dot{\tau}_j, \quad (27)$$

then the partition function Q for free rotors is given by:

$$Q = \left(\frac{2\pi kT}{h^2}\right)^{n/2} \int_{-\alpha_1}^{\beta_1} \cdots \int_{-\alpha_n}^{\beta_n} (\text{Det}[A])^{1/2}d\tau_1 \cdots d\tau_n. \quad (28)$$

In a first approximation, the determinant of A can be assumed to be constant and the partition function for free internal rotation is given by

$$Q^{\text{free rot.}} = \left(\frac{8\pi^3 kT}{h^2}\right)^{n/2}(\text{Det}[A])^{1/2}$$
$$= \left(\frac{8\pi^3 kT}{h^2}\right)^{n/2}\prod_{i=1}^{n} I_i^{1/2}. \quad (29)$$

The projected $G^{(-)}$ matrix used in Sec. IID corresponds to the kinetic energy matrix A, n is the number of internal rotors (equal to the rank of this matrix), and the I_j's are the reduced moments of inertia (equal to the nonzero eigenvalues of the kinetic energy matrix).

For cases with multiple hindered rotors, the potential can take very complicated forms. If the potential is known, one could solve for the energy levels of the n-dimensional system and obtain the partition function. Since the potential is not known in most cases, one must make some approximations. Often, there is little potential energy coupling between rotors, and the potential energy for a given internal rotation

is well represented by a single cosine function for each torsion. Assuming that the potential energy can be expressed as $V = \Sigma_{i=1}^{n} V_i (1 - \cos(\sigma_i \tau_i))/2$, the classical approximation of Pitzer and Gwinn[8] can be extended to multiple rotors,

$$Q^{\text{hin.}} = \prod_{i=1}^{n} (Q_i^{\text{h.o.q}}/Q_i^{\text{h.o.cl}}) \left(\frac{8\pi^3 kT}{\sigma^2 h^2} \right)^{1/2} I_j^{1/2}$$

$$\times \exp[-V_i/2kT] J_0(iV_i/2kT). \qquad (30)$$

Like Eq. (22), this formula should be suitable for low barriers and does go to the harmonic oscillator limit as the barriers increase. In order to use Eq. (22), for a given vibrational frequency, the correspondence between the reduced moments of inertia and the rotational barrier height V_i needs to be established. For low barriers, most of the coupling between rotors is due to kinetic energy terms. If the potential energy coupling is ignored, then the barriers can be approximated by an extension of Eq. (13),

$$\sigma_i^2 V_i = \mathbf{L}_q''^{i\,t} H_q \mathbf{L}_q''^{i} I_i, \qquad (31)$$

where $\mathbf{L}_q''^{i}$ is the eigenvector of the projected $G^{(-)}$ matrix that corresponds to I_i. Alternatively, one can include the local potential coupling but treat the kinetic coupling in an approximate way by using the effective reduced moment of inertia for each normal mode. Provided that the redundancy in G' has been removed, the effective reduced moment of inertia for the ith mode, $I_{\text{eff},i}$ is given by

$$I_{\text{eff},i} = 1/((G'^{1/2}\mathbf{L'}_{Mq}^{i})^t \cdot (G'^{1/2}\mathbf{L'}_{Mq}^{i}))^{1/2}. \qquad (32)$$

The associated barrier height V_i is then obtained by using $I_{\text{eff},i}$ in Eq. (13). Thus, a reasonable extension of Truhlar's formula, which switches from the quantum harmonic oscillator partition function at high frequencies, to the classical rotor partition function for low frequencies, to the coupled internal rotation problem, is

$$Q^{\text{hin}} = \prod_{i=1}^{n} Q_i^{\text{h.o.q}} \tanh((\pi V_i/kT)^{1/2})$$

$$= \prod_{i=1}^{n} Q_i^{\text{h.o.q}} \tanh\left(\frac{2\pi v_i (2\pi I_{\text{eff},i}/kT)^{1/2}}{\sigma_i} \right). \qquad (33)$$

This extended formula depends only on the reduced moments of inertia and vibrational frequencies of the modes identified as internal rotors. Likewise, using Eq. (32), the multiple rotor analog of Eqs. (22) and (26) can be formulated. Although the coupling between rotors is treated only approximately, it should be suitable for most applications,

$$Q^{\text{hin.}} = \prod_{i=1}^{n} (Q_i^{\text{h.o.q}}/Q_i^{\text{h.o.cl}}) \left(\frac{8\pi^3 kT}{\sigma^2 h^2} \right)^{1/2}$$

$$\times I_{\text{eff},i}^{1/2} \exp[-V_i/2kT] J_0(iV_i/2kT), \qquad (34)$$

TABLE IV. Entropy correction for internal rotation in 1,5-hexadiene at 500 K.

Mode	$S^{\text{hin}} - S^{\text{h.o.q}}$ (cal/mol-K)	$Q^{\text{free rot.}}$	Frequency (cm^{-1})	V/RT
1	0.346	12.749	63.474	1.726
2	0.398	8.844	97.485	1.959
3	0.416	10.934	103.765	3.393

$$Q^{\text{hin.}} = \prod_{i=1}^{n} (Q_i^{\text{h.o.q}}/Q_i^{\text{h.o.cl}}) Q_i^{\text{free rot}}$$

$$\times \frac{(1 + P_2 \exp[-V_i/2kT])}{(1 + P_1 \exp[-V_i/2kT])}$$

$$\times \exp[-V_i/2kT] J_0(iV_i/2kT). \qquad (35)$$

Obtaining a good approximation for the hindered rotor partition function is critical for applications of the transition state theory. We have seen that Eqs. (21), (22), or (26) can help achieve good results. However, in many studies, the temperature dependence of the partition function plays an important role in determining the corrections to the energy, entropy, and heat capacity. We have mentioned earlier that Truhlar's formula offers only a small improvement on the evaluation of the entropy for a single hindered rotor over the free-rotor approximation. The entropy is consistently underestimated with an average deviation of -0.13 cal/mol-K and a maximum deviation of -0.51 cal/mol-K for $Q^{\text{free rot.}} = 20$ and $V_0/kT = 2.5$. Although such a deviation is intrinsically small, the use of Truhlar's formula for multiple uncoupled rotors can give rise to large compounded errors. In contrast, Pitzer and Gwinn's formula reproduces the tabulated values with an absolute deviation of 0.007 cal/mol-K (maximum deviation $= 0.04$ cal/mol-K for $Q^{\text{free rot.}} = 2$ and $V_0/kT = 1.5$). The mean absolute deviation for Eq. (26) is 0.05 cal/mol-K. Given the good overall performance of Eq. (22), there is probably no need for improvements.

IV. EXAMPLE

Throughout this paper we have used the case of internal rotation in 1,5-hexadiene to illustrate key aspects of our treatment. Here, we give quantitative results for the activation entropy of the Cope rearrangement of 1,5-hexadiene at 500 K using B3LYP/6−31G* vibrational frequencies. The internal rotation about the C2–C3, C3–C4, C4–C5 bonds is assumed threefold with a symmetry number of one. The values for the free-rotor partition functions and reduced barrier heights are shown in Table IV. The correction to the entropy is a modest 1.16 cal/mol-K.

As we have seen earlier, the multiplicity of the wells is $3 \times 2 \times 2$, which adds an extra correction of 4.94 cal/mol-K to the entropy. The total correction is thus 6.1 cal/mol-K. If the optically equivalent structures need to be taken into account, one should note that the four wells for the rotation about the C2–C3 and C4–C5 bonds are equivalent under external rotation and the mirror image of the reactant structure is obtained after rotation about the C3–C4 bond. The

quantity $R \ln(2 \times 2 \times 2)$ thus needs to be subtracted from the total correction, giving a correction of 1.96 cal/mol-K to the entropy obtained using the harmonic oscillator model. The entropy factor for the Cope [3,3] sigmatropic rearrangement of 1,5-hexadiene is thus estimated to $\Delta S^{\ddagger} = -14.0$ cal/mol-K at 500 K and can be compared to the experimental value[33] of $\Delta S^{\ddagger} = -13.8$ cal/mol-K.

V. CONCLUSIONS

We have outlined a procedure to identify internal rotation modes and provide a first approximation to the corrections for the thermodynamic functions without requiring analytical expressions of the torsional potential. The identification of the internal rotation modes requires no user intervention and makes extensive use of the information imbedded in the redundant internal coordinates. The potential periodicity, the rotating tops' symmetry numbers, and the well-multiplicity are determined using simple rules. These parameters can be altered by the user at will. We propose an analytical approximation to the partition function for a one-dimensional hindered internal rotation that reproduces the accurate values tabulated by Pitzer and Gwinn. Generalizing the one-dimensional rotor treatment gives a useful approximation to the multidimensional rotor thermodynamic functions that constitutes a good start for more thorough studies.

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$$P_1 = 0.003\,235x - 0.026\,252x^2 + 0.110\,460x^3 - 0.203\,340x^4 + 0.130\,633x^5$$
$$- 0.010\,112y^{0.5} + 0.650\,122xy^{0.5} + 0.067\,112x^2y^{0.5} + 0.088\,807x^3y^{0.5}$$
$$- 0.014\,290x^4y^{0.5} - 0.364\,852y + 0.913\,073xy - 0.021\,116x^2y$$
$$- 0.092\,086x^3y - 0.415\,689y^{1.5} - 1.128\,961xy^{1.5} + 0.233\,009x^2y^{1.5}$$
$$+ 0.421\,344y^2 + 0.505\,139xy^2 - 0.215\,088y^{2.5}$$
$$P_2 = 0.067\,113x + 0.772\,485x^2 - 3.067\,4131x^3 + 4.595\,051x^4$$
$$- 2.101\,341x^5 + 0.015\,800y^{0.5} + 0.102\,119xy^{0.5} - 0.555\,270x^2y^{0.5}$$
$$- 1.125\,261x^3y^{0.5} + 0.071\,884x^4y^{0.5} - 0.397\,330y + 2.284\,956xy$$
$$+ 0.850\,046x^2y - 0.174\,240x^3y - 0.451\,875y^{1.5} - 2.136\,226xy^{1.5}$$
$$+ 0.303\,469x^2y^{1.5} + 0.470\,837y^2 + 0.675\,898xy^2$$
$$- 0.226\,287y^{2.5} \quad \text{with} \quad x = 1/Q^{\text{free rot}} \quad \text{and} \quad y = V_0/kT.$$

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