Beyond the Harmonic Approximation: Impact of Anharmonic Molecular Vibrations on the Thermochemistry of Silicon Hydrides

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Thermodynamic state function (enthalpy, entropy, and heat capacity) were calculated for several types of silicon hydrides taking into account the strongly anharmonic character of some of the molecular vibrations (internal rotation, inversion, and pseudorotation). The anharmonic motions were treated as one-dimensional motions taking place along the harmonic normal coordinates, neglecting anharmonic coupling terms. Partition functions were calculated from the idealized numerical eigenvalue spectrum in the case of pseudorotation; for the other types of large amplitude motions, we used quantum-corrected classical partition functions. Following the work of Knyazev and Tsang, we derived a novel partition function for an asymmetric double well potential. We then used the data to calculate enthalpies, entropies and free energies of reaction for several types of chemical reactions among silicon hydrides, at both the harmonic and the anharmonic level. Differences arising from the inclusion of anharmonicity are discussed.

1. Introduction

The calculation of thermodynamic properties of substances by means of ab initio molecular computations is an important task of quantum chemistry. Such computations apply the principles of statistical thermodynamics and use additional approximations to treat electronic and nuclear motions. For the nuclear motion, which is the concern of this work, the harmonic oscillator approximation is the most important one, sometimes limiting the accuracy of the results.

Although the harmonic approximation is sufficient to describe nuclear motion in most molecules at room temperature,[1] this is not necessarily true at higher temperatures, when some vibrational degrees of freedom become highly excited: the amplitude of the nuclear motion increases, and finally the system leaves the part of the potential energy surface where the harmonic approximation to the potential energy surface holds. Motions with amplitudes that large are called “large amplitude motions”. Molecules showing this kind of behavior are often referred to as “floppy”, but at sufficiently high temperatures, most molecules will exhibit one or more vibrational degrees of freedom with substantially “floppy” character.[2]

Floppiness puts an end to the validity of the harmonic approximation. Yet no general procedure is in common use that allows for improved treatment of floppy, or strongly anharmonic, molecular vibrations. In his pioneering work on internal rotation, Pitzer,[3−6] calculated tables of partition functions of internal rotators. These data is still valid today, but the thermochemistry modules of the most widely used quantum chemical packages do not take advantage of it. Neither has the work of Witschel[7−9] and Gibson[10] on anharmonic oscillators found a way into mainstream quantum chemistry. Recently, Ayala, and Schlegel[11] have developed a partially automatic method for the treatment of internal rotations; their method has been included into the latest release of the Gaussian quantum chemical package.

In the meanwhile, thermodynamic data on floppy molecules is scarce for temperatures well above 300 K. Internal rotations are an extremely common feature in organic compounds; yet collections of thermochemical data at high temperatures, like the JANAF tables,[12] contain only few organic molecules showing internal rotation; for example, fundamental species such as C_2H_6 and C_3H_8 are omitted from the JANAF tables. Clearly, this is a disadvantage hindering the understanding of high-temperature gas-phase reactions involving such species, like combustion and chemical vapor deposition (CVD) processes.

In previous work,[13,14] our group has studied the energetics of small and medium-sized silicon hydride compounds. For lack of available methods, the discussion of bond strengths, relative isomer stabilities, and reaction ratios was limited to 300 K, although the CVD processes[15] that end in the deposition of Si films from an SiH_4 atmosphere take place at much higher temperature. We therefore decided to search for a more general method to account for the strong anharmonicities found in floppy molecules and calculate thermodynamic state functions beyond the regime of the harmonic approximation.

2. Thermodynamics

Statistical thermodynamics allows to calculate thermodynamic (macroscopic) observables from knowledge of molecular (microscopic) data. Each degree of freedom of the microscopic system contributes to all thermodynamic quantities; if the degree of freedoms can be assumed independent, then also their thermodynamic contributions can be calculated separately.

In molecules, the degrees of freedom are electronic motion and nuclear motion, which can be further subdivided into translation, rotation and vibration. The molecular partition function can be written as a product

$$Q(\beta) = q_{\mathrm{trans}}(\beta)\cdot q_{\mathrm{rot}}(\beta)\cdot q_{\mathrm{vib}}(\beta)\cdot q_{\mathrm{elec}}(\beta) \qquad (1)$$

where $\beta = 1/RT$ and R is the gas constant, $R = 8.3144$ J mol^{-1} K^{-1}.

In most molecules, electron motion results only in a temperature-independent contribution to the internal energy, $U(0)$, and so we will not further consider electronic degrees of freedom.

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The contributions of translation and rotation depend only on the mass and moment of inertia of the molecule, and they are thus easy to calculate using the simple models of the particle in a box and the rigid rotator, respectively. In contrast, the vibrational contributions are, in general, difficult to evaluate, and thus are the prime issue of this work.

For an N-atomic nonlinear molecule, the vibrational problem is $3N - 6$ dimensional. If one assumes the harmonic oscillator approximation to be valid, then this $3N - 6$ dimensional problem can be reduced to $3N - 6$ independent one-dimensional harmonic oscillators, and the vibrational partition function can be written as a product of one-mode partition functions

$$q_{\mathrm{vib}}(\beta) = q^{(1)}(\beta)\cdot q^{(2)}(\beta)\cdots q^{(3N-6)}(\beta) \tag{2}$$

where each of the $q^{(i)}$ is a sum of Boltzmann factors using the eigenvalue spectrum of the ith normal mode

$$q^{(i)} = \sum_j \exp(-\beta\epsilon_j^{(i)}) \tag{3}$$

By plugging in the eigenvalues of the one-dimensional oscillator

$$\epsilon_n^{(i)} = \hbar\omega^{(i)}(n + {}^1/_2) = E^{(i)}(n + {}^1/_2) \tag{4}$$

we can write the partition function for one single vibrational degree of freedom in the harmonic approximation as

$$q^{(i)}(\beta) = \frac{\exp(-{}^1/_2\beta E^{(i)})}{1 - \exp(-\beta E^{(i)})} \tag{5}$$

where $E^{(i)} = -\hbar\omega^{(i)}$ is the spacing between energy levels of the ith normal mode. In this formulation of the partition function, the zero-point energy has been included into the temperature-dependent part of the internal energy, and there is no need to consider it separately.

If one wants to go beyond the harmonic oscillator level, then two different problems arise: First, the partition function of an harmonic oscillator must be replaced by a partition function of an anharmonic oscillator, and, second, the individual vibrational degrees of freedom couple with each other, which means the product form for the total vibrational partition function (eq 2) is no longer valid. For that reason, the anharmonic problem is inherently multidimensional, and both difficult and time-consuming to solve.

In this work, however, we will retain the separation of the various vibrational degrees of freedom, eq 2, as an *approximation* inherited from the harmonic approximation, although some vibrational degrees of freedom will be treated as anharmonic oscillators. We will, instead, concentrate on the derivation of anharmonic partition functions that can replace eq 5 to account for the anharmonic character of a particular vibrational degree of freedom.

From knowledge of the partition function and its derivatives with respect to β, thermodynamic quantities such as internal energy U, absolute entropy S and isochorous heat capacity C_v can be calculated very easily at any given temperature T (or β). The formulas are the same for all kind of partition functions; this is, thermodynamic quantities for the whole molecule, for the rotational or vibrational contributions alone, even for a single vibration, can be calculated by the same formalism from the corresponding partition function

$$U(T) - U(0) = \frac{q'}{q} \qquad S(T) = R\ln q - \frac{q'}{Tq}$$
$$C_v(T) = \frac{q''q - q'^2}{RT^2q^2} \tag{6}$$

In this equation, $U(0)$ refers to the temperature-independent part of the internal energy. Enthalpies, Gibbs functions and isobar heat capacities can be obtained from U, S, and C_v using the elementary relations of phaenomenologic thermodynamics.

An important thermodynamic function is the standard enthalpy of formation

$$\Delta_f H(\mathrm{molecule}) = H(\mathrm{molecule}) - \sum_{\mathrm{elements}} H(\mathrm{element}) \tag{7}$$

$$= \sum_{\mathrm{elements}} \Delta_{\mathrm{at}}U(\mathrm{element}) - \Delta_{\mathrm{at}}U - \Delta(pV) \tag{8}$$

where the molecular atomization energy consists of electronic, vibrational, translational, and rotational contributions

$$\Delta_{\mathrm{at}}U = \Delta E_{\mathrm{el}} + U_{\mathrm{vib}} + U_{\mathrm{rot}} + \Delta_{\mathrm{at}}U_{\mathrm{tr}} \tag{9}$$

The symbol $\Delta_{\mathrm{at}}U$(element) denotes the atomization energies of the element phases in their reference states; these energies are needed to establish the conventional zero point of $\Delta_f H$. In the equations of this paragraph, all quantities U and H depend on the temperature.

The electronic atomization energy, ΔE_{el}, is by far the largest contribution to $\Delta_{\mathrm{at}}U$ and thus to $\Delta_f H$; therefore, it dominates over both the molecular vibration energy, U_{vib}, and the dissociation energy contributions arising from rotation and translation, U_{rot} and $\Delta_{\mathrm{at}}U_{\mathrm{tr}}$.

The vibrational part, U_{vib}, is the largest temperature-dependent contribution to the dissociation energy. However, anharmonic corrections to U_{vib} typically amount to only a small fraction of the total value; therefore, these corrections are very small compared to the electronic dissociation energy. To include anharmonic effects reasonably in U and $\Delta_f H$ presupposes that the electronic energies have been calculated to a "chemical accuracy" of a few kJ/mol, or better. This is a very difficult goal to archive by pure ab initio means even for small molecules,[16,17] and for molecules the size of Si_5H_{10}, one has to resort to empirical corrections of the electronic dissociation energy.[13,14]

3. Types of Anharmonic Motions

To devise an approximation that goes beyond the limits of the harmonic oscillator approximation, it is useful to review shortly the most important types of anharmonic nuclear motions in molecules. We are only concerned with anharmonic motions that significantly and even qualitatively differ from purely harmonic motions; the small anharmonicities often dealt with in spectroscopy by polynomial expansions or Morse potentials are of little significance for thermodynamic applications, and will not be considered here.

The best known and also best investigated[11,18] case of a strongly anharmonic molecular motion is *internal rotation*. It is the most important case both because is occurs very frequently in chemistry, and the deviations from the harmonic oscillator can grow to quite large magnitude.

The prototype of a system showing internal rotation is ethane, CH_3-CH_3. Starting from the *staggered* minimum, the internal rotation leads via the *eclipsed* maximum to another minimum, which is identical to the starting minimum in this case. The barrier to internal rotation is about 13 kJ/mol at the RHF level of theory: For energies far below the barrier, the system may behave harmonically in good approximation, and for energies far above the barrier, the system's properties converge toward those of a free rotator. Because harmonic oscillation and free rotation have quite different partition functions and, thus, thermodynamic properties, the harmonic oscillator treatment for internal rotations will necessarily give great errors at high temperatures.

Another type of strongly anharmonic motion is associated with the inversion at nonplanar trivalent centers, e.g., the inversion of ammonia. The characteristic feature of this motion is the existence of two stable configurations separated by an energy barrier. The harmonic approximation remains valid as long as the thermal energy stays below the barrier, but as soon as the thermal energy approaches, or exceeds, the barrier, the molecule becomes much more conformationally free (floppy), and significant anharmonic effects may be expected.

Almost the same type of motion is also found in small ring compounds ("ring inversion"). Ring inversion can take place in nonplanar rings of four or more atoms. Low barriers, and therefore significant anharmonicities, are often found in four- and five-membered rings.

Certain small rings show another type of strongly anharmonic motion: *pseudorotation*,[19] which is a concerted motion of several atoms along a periodic coordinate. The textbook example of pseudorotation is cyclopentane, C_5H_{10}, where the *bent* (*envelope*) and *twisted* conformers interconvert via a pseudorotation process. The same type of pseudorotation appears in cyclopentasilane, Si_5H_{10}.[15,20] Although in general there is a barrier to pseudorotation, this barrier is often found to have negligible size: In this case, we speak of "free pseudorotation". As there is no potential in free pseudorotation, the harmonic approximation is invalid even at temperatures as low as room temperature.

4. Anharmonic Potentials

In this section, we shall introduce analytical potentials that can be used to describe internal rotation and inversion. The third case of strongly anharmonic nuclear motion, pseudorotation, needs no potential in its description if free pseudorotation is assumed.

4.1 Periodic cos Potential. The potential used to describe an internal rotation must depend on an angular coordinate and display several maxima and minima within one cycle. An obvious choice is a single cosine[3] function

$$V(x) = \frac{V_0}{2}(1 - \cos nx) \tag{10}$$

This potential has n equal minima at $x = 0$, $2\pi/n$, $4\pi/n$,... $2(n-1)\pi/n$ which are separated by n maxima of height V_0. The parameter n is referred to as the *periodicity* of the potential, and V_0 is called *barrier height.* Because of the existence of a barrier, motion in potential 10 is often referred to as *hindered rotation*.

The cosine potential, eq 10, is a good approximation for internal rotations involving identical conformers, as in ethane or propane. In general, internal rotation about highly substituted bonds may give rise to different conformers which usually differ in energy; the torsion potential then becomes asymmetric, having minima and maxima at different energies, and cannot be accurately described by a single cosine function. It is often found that the minima have similar energies, and then eq 10 can serve as a useful approximation.

4.2 Symmetric and Unsymmetrical cos−tan^2 Potentials. To treat inversions and similar processes with two stable configurations, one needs a double-well potential. Among the double-well potentials found in the literature, the most popular ones are polynomial potentials of fourth and sixth order. These are, however, not well suited for thermodynamic applications, as the calculation of the partition function is not possible in closed form, and computing enough eigenvalues numerically to calculate the partition function according to eq 3 is a tiresome and expensive process.

Knyazev and Tsang[21] have introduced a novel double-well potential which is here written in a slightly different form: With the auxiliary potential

$$V^{\dagger}(x, V_0) = \begin{cases} \dfrac{V_0}{2}(1 + \cos\pi x) & 0 \le x \le 1 \\ V_0\gamma^2\tan^2\left(\dfrac{\pi}{2\gamma}(x-1)\right) & 1 < x < \gamma + 1 \end{cases} \tag{11}$$

we can define a symmetric double well potential

$$V(x) = \begin{cases} V^{\dagger}(-x, V_0) & -(\gamma+1) < x < 0 \\ V^{\dagger}(x, V_0) & 0 \le x < \gamma + 1 \end{cases} \tag{12}$$

which is twice continuous differentiable. It depends on a dimensionless (relative) coordinate x limited to the interval $(-1-\gamma,\ 1+\gamma)$. There are two equivalent minima at $x = \pm 1$ separated by a central maximum of height V_0. The parameter γ relates the width of the barrier to the width of the outer, repulsive part of the potential; a high value of γ indicates a narrow barrier. At the end points of the interval, the potential grows to $+\infty$, which means that it is steeper than any polynomial potential.

The symmetric cos−tan^2 potential is suited for inversion motions such as the inversion of NH_3 or the ring inversion of cyclobutane, where two identical species are involved. In less symmetric molecules, the two species produced by inversion are not degenerate (e.g., the equatorial and axial conformers of substituted cyclobutane); for such cases, we propose an unsymmetrical double well potential.

The symmetric cos−tan^2 potential in eq 12 can be easily modified to become unsymmetrical

$$V(x) = \begin{cases} V^{\dagger}(-\sqrt{V_0/(V_0-\delta)}x,\ V_0-\delta) + \delta \\ \qquad -\sqrt{(V_0-\delta)/V_0}(1+\gamma) < x < 0 \\ V^{\dagger}(x, V_0) \\ \qquad 0 \le x < 1 + \gamma \end{cases} \tag{13}$$

This new potential is also twice continuous differentiable, and for $x > 0$ it is identical to the symmetric cos−tan^2 potential; for $x < 0$, it is raised vertically by δ and scaled horizontally and vertically in order to yield a smooth transition at $x = 0$. The minimum of the left branch lies at $x = (V_0/(V_0 - \delta))^{1/2}$. The energetic difference between the two minima is given by δ. We will assume $0 \le \delta < V_0$.

5. Partition Functions

The calculation of quantum mechanic partition functions requires knowledge of the QM energy spectrum $\{\epsilon_i\}$. For the pseudorotation, the energy spectrum is the same as for rigid rotation in one dimension[2,19]

$$\epsilon_n = hc\bar{B}\,n^2 \text{ for } n = ..., -2, -1, 0, 1, 2,... \tag{14}$$

where $\bar{B}$ (or $hc\bar{B}$ in other literature) is called the pseudorotational constant. Therefore, it is possible to compute the partition function by numerical summation (eq 3). In many cases, however, a so-called "high temperature approximation" is employed, replacing the sum in eq 3 by an integral

$$q(\beta) = \sum_{n=-\infty}^{\infty} \exp(-\beta hc\bar{B}n^2) \approx \int_{-\infty}^{\infty} \exp(-\beta hc\bar{B}n^2) dn = \sqrt{\frac{\pi}{hc\bar{B}\beta}} \quad (15)$$

This procedure has the advantage of yielding a simple closed expression for the partition function, but may be inadequate for some types of pseudorotation with large pseudorotational level spacing.[20]

For most anharmonic oscillators, the energy spectrum is *not* known, which means that application of eq 3 is not straightforward for anharmonic oscillators corresponding to the potential shapes discussed in the previous section. Numerical solutions of the eigenvalue problem are possible yet time-intensive.

At this point, classical partition functions are a viable alternative. The classical partition function is defined as an integral over normalized phase space elements, $dx\, dp/h$

$$q_{cl}(\beta) = \frac{1}{h\sigma}\int \exp(-\beta(T(p) + V(x)))dx\, dp \qquad (16)$$

where $T(p) = p^2/2m$ is the kinetic and $V(x)$ is the potential energy; h is Planck's constant and σ is a symmetry number. The classical partition function can be used in the same way as the quantum mechanical one to calculate state functions, but as it does not incorporate quantum effects, it will fail at deep energies, and its use is justified only in the high-temperature regime.

The main advantage of the classical partition function over the quantum mechanical partition function is that it can be evaluated analytically for many nontrivial potentials. The classical partition function for hindered rotation (eq 10) is[3,22]

$$q_{cl}(\beta) = \frac{n}{\sigma E}\sqrt{\frac{V_0\pi}{\beta}}\exp\left(-\frac{\beta V_0}{2}\right)I_0\left(\frac{\beta V_0}{2}\right) \qquad (17)$$

A very similar formula that contains some correction for the zero point energy was derived by McClurg et al.;[23] in their expression, V_0 in the argument of the exponential function of eq 17 is replaced by a corrected potential barrier

$$V_1 = V_0 - \frac{E^2}{E + 8V_0} \qquad (18)$$

Knyazev and Tsang[21] have described a method that allows to solve the phase space integral via the classical density-of-states function; their method can be used to construct classical density-of-states functions, sum-of-states functions and partition functions for the potentials eqs 10 and 12. For the symmetric double well potential, the classical partition function is given by

$$q_{cl}(\beta) = \frac{1}{\sigma E}\sqrt{\frac{V_0\pi}{\beta}}q^{\dagger}(\beta, V_0) \qquad (19)$$

where $q^{\dagger}$ is an auxiliary function

$$q^{\dagger}(\beta, V_0) = \exp\left(-\frac{\beta V_0}{2}\right)I_0\left(\frac{\beta V_0}{2}\right) + \gamma\, \mathrm{erfc}(\sqrt{\beta V_0\gamma^2})\exp(\beta V_0\gamma^2) \quad (20)$$

In these equations, E is the energy of an harmonic oscillator with the same curvature at the minimum, I_0 is the modified Bessel function of the first kind and erfc is the complementary error function. The symmetry numbers σ do not follow from the potential, but from symmetry properties of the molecule: They reflect the number of distinguishable minimum structures. For the internal rotation about an n-fold bond, in most cases σ is either 1 or n, whereas for inversion motions, σ can be either 1 or 2. If all potential minima belong to distinguishable structures, then $\sigma = 1$ for all partition functions.

The partition function of the unsymmetrical double well potential, eq 13, can be derived from eq 19 in the following way: We first split the phase space integral at $x = 0$

$$\begin{aligned} q_{cl}(\beta) &= \frac{1}{h}\int_{x=-f(1+\gamma)}^{1+\gamma} \exp(-\beta(T(p) + V(x)))\, dp\, dx = \\ &= \frac{1}{h}\int_{x=-f(1+\gamma)}^{0} \exp(-\beta(T(p) + V^{\dagger}(-fx, V_0 - \delta) + \delta))\, dp\, dx + \\ &\quad \frac{1}{h}\int_{x=0}^{1+\gamma} \exp(-\beta(T(p) + V^{\dagger}(x, V_0)))\, dp\, dx \end{aligned} \quad (21)$$

where f stands for $((V_0 - \delta)/V_0)^{1/2}$. We observe that the second summand is just one-half of the symmetric cos−tan^2 potential partition function, eq 19, with $\sigma = 1$. In the first part, we can move the term $\exp(-\beta\delta)$ before the integral, switch the integral limits, and substitute a new integration variable in place of fx. The integral then becomes the partition function of a symmetric double well oscillator with a modified barrier height

$$\begin{aligned} &\frac{1}{h}\int_{x=-f(1+\gamma)}^{0} \exp[-\beta(T(p) + V^{\dagger}(-fx, V_0 - \delta) + \delta)]\, dp\, dx = \\ &\frac{\exp(-\beta\delta)}{h}\int_{x=-f(1+\gamma)}^{0} \exp[-\beta(T(p) + V^{\dagger}(-fx, V_0 - \delta))]\, dp\, dx = \\ &\frac{\exp(-\beta\delta)}{h}\int_{x=0}^{f(1+\gamma)} \exp[-\beta(T(p) + V^{\dagger}(fx, V_0 - \delta))]\, dp\, dx = \\ &\frac{f\exp(-\beta\delta)}{h}\int_{y=0}^{1+\gamma} \exp[-\beta(T(p) + V^{\dagger}(y, V_0 - \delta))]\, dp\, dy = \\ &\frac{1}{E}\sqrt{\frac{\pi V_0}{\beta}}\frac{\exp(-\beta\delta)}{2}fq^{\dagger}(\beta, V_0 - \delta) \end{aligned} \qquad (22)$$

The complete partition function of the asymmetric double well potential is thus

$$q_{cl}(\beta) = \frac{1}{E}\sqrt{\frac{\pi V_0}{\beta}}\frac{\exp(-\beta\delta)}{2}\left(\exp(\beta\delta)q^{\dagger}(\beta, V_0) + \sqrt{\frac{V_0 - \delta}{V_0}}q^{\dagger}(\beta, V_0 - \delta)\right) \quad (23)$$

Clearly, there is no symmetry number involved in the statistical description of motion in an unsymmetrical double well potential.

6. Quantum Correction

The classical partition function is not a reasonable description for the system at low temperatures, as it will not reproduce some essential features that have their origin in quantum effects: zero point energy, “freezing” of degrees of freedom and the Third Law. Pitzer and Gwinn[3] have suggested an easy correction scheme that will include quantum effects in the classical partition function under the condition that the anharmonic oscillator can be approximated by a harmonic oscillator in the low-temperature limit.

The basic idea of the so-called *Pitzer−Gwinn correction* is to construct a partition function that approaches (a) the *quantum mechanical harmonic* oscillator partition function at low temperature and (b) the *classical anharmonic* partition function at high temperature; they suggested the following formula

$$q^{ao} = q^{ao}_{cl} \cdot \frac{q^{ho}}{q^{ho}_{cl}} \tag{24}$$

The anharmonic quantum mechanical partition function q^{ao} is thus approximated by the anharmonic classical partition function, q^{ao}_{cl} and a correction factor which is the ratio of quantum mechanical and classical partition function of an harmonic oscillator. The partition functions q^{ho} (eq 5) and $q^{ho}_{cl} = 1/\beta E$ refer to an harmonic oscillator fitted to the anharmonic potential at the minimum.

The correction term becomes unity in the high-temperature limit, when the quantum mechanical and the classical partition functions of the harmonic oscillator converge. In the low-temperature limit, vibrational amplitudes are small, and one can suppose $q^{ao}_{cl} \approx q^{ho}_{cl}$ in most cases; in this case, eq 24 reduces to $q^{ao} \approx q^{ho}$ which is the correct behavior.

7. Validation

7.1 Calculated Energy Levels. The Pitzer−Gwinn (PG) correction is an ad hoc method that can be judged only by its success (or lack of success) in realistic situations. It is therefore necessary to validate the PG correction scheme, which can be done by comparing results obtained from PG corrected classical partition functions with results from partition functions obtained by numerical summation over energy levels, eq 3.

We obtained inversion potentials for several test molecules by pointwise RHF geometry optimizations at fixed out of plane angles (5° increments). The data were then fitted by a symmetric double well potential (eq 12), and the exact vibrational levels were determined solving the corresponding one-dimensional Schrödinger equation, applying the Fourier Grid Hamiltonian method of Balint-Kurti.[24]

We then calculated the exact QM partition function by numerical summation and compared it to the classical and PG corrected ones. In the literature, such comparisons have been performed[3,25] at the level of the values of partition function and its derivatives; we, however, decided not to compare the values of the partition function directly, but rather the thermodynamic quantities calculated therefrom: Internal energy U, entropy S and isochorous heat capacity C_v (eq 6).

U depends only on the relative changes of q with respect to the temperature, but S depends mostly on the low-temperature behavior of q and also on its absolute magnitude. The calculation of C_v involves the second derivative of the partition function and will, therefore, unveil even small inaccuracies in the temperature-dependence at all temperatures.

Tables 1 and 2 show the calculated U, S, and C_v of the inversion mode of ammonia, NH_3, and trisilylsilyl, $Si(SiH_3)_3$, for temperatures between 100 K and 1000 K. The two molecules were chosen because they represent different types of double well oscillators: In NH_3, the calculated barrier to inversion is high and broad (V_0 = 33 kJ mol^{-1}, γ = 5.7), and also the harmonic energy (E = 13 kJ mol^{-1}) is well above thermal energy in the temperature interval considered. $Si(SiH_3)_3$, on the other hand, has a low and narrow barrier (V_0 = 6.5 kJ mol^{-1}, γ = 12.9) and the harmonic energy separation is much smaller (E = 1.2 kJ mol^{-1}).

TABLE 1: Internal Energy *U*, Entropy *S* and Isochorous Heat Capacity C_v for the Umbrella Mode of NH_3, Calculated from Classical, PG-Corrected, and Quantum Mechanic Partition Functions

	U/kJ mol^{-1}			S/J mol^{-1} K^{-1}			C_v/J mol^{-1} K^{-1}		
T/K	class	PG	QM	class	PG	QM	class	PG	QM
100	0.83	6.46	6.29	−14.43	0.05	0.00	8.37	0.05	0.00
200	1.67	6.47	6.30	−8.61	0.14	0.05	8.43	0.33	0.30
300	2.52	6.56	6.39	−5.18	0.46	0.38	8.52	1.48	1.57
400	3.38	6.78	6.63	−2.71	1.10	1.05	8.64	3.02	3.16
500	4.25	7.16	7.01	−0.77	1.93	1.91	8.80	4.42	4.54
600	5.14	7.66	7.52	0.85	2.84	2.84	8.94	5.52	5.60
700	6.04	8.25	8.12	2.23	3.75	3.76	9.04	6.33	6.37
800	6.95	8.91	8.79	3.44	4.64	4.65	9.08	6.90	6.90
900	7.85	9.62	9.50	4.51	5.47	5.48	9.06	7.27	7.24
1000	8.76	10.36	10.23	5.46	6.25	6.26	8.99	7.50	7.46

TABLE 2: Internal Energy *U*, Entropy *S* and Isochorous Heat Capacity C_v for the Umbrella Mode of $Si(SiH_3)_3$, Calculated from Classical, PG-Corrected and Quantum Mechanic Partition Functions

	U/kJ mol^{-1}			S/J mol^{-1} K^{-1}			C_v J mol^{-1} K^{-1}		
T/K	class	PG	QM	class	PG	QM	class	PG	QM
100	0.85	0.99	0.99	5.60	6.29	6.29	8.82	7.51	7.53
200	1.76	1.83	1.82	11.84	12.02	12.02	8.99	8.63	8.62
300	2.62	2.67	2.66	15.35	15.44	15.43	8.27	8.11	8.10
400	3.41	3.45	3.44	17.64	17.68	17.68	7.60	7.51	7.51
500	4.15	4.18	4.17	19.28	19.31	19.30	7.15	7.10	7.10
600	4.85	4.87	4.86	20.56	20.58	20.57	6.87	6.83	6.84
700	5.53	5.55	5.54	21.60	21.62	21.61	6.70	6.67	6.67
800	6.19	6.21	6.20	22.49	22.50	22.50	6.59	6.57	6.57
900	6.84	6.86	6.85	23.26	23.27	23.27	6.52	6.51	6.51
1000	7.49	7.51	7.50	23.95	23.95	23.95	6.48	6.47	6.47

Due to its high E, NH_3 has a high characteristic vibrational temperature, $\theta = E/R$ = 1552 K, and quantum effects are visible even at 1000 K; below 500 K, they are essential. On the other side, NH_3 has a large barrier to inversion, and anharmonicity is a comparatively small correction. This can be seen in the classical heat capacity, which in the complete temperature interval does not deviate much from the ideal value for a harmonic oscillator, R = 8.31 J mol^{-1} K^{-1}.

Because quantum effects dominate, the uncorrected classical results in Table 1 are seriously in error. But it is reassuring that the PG correction works well and corrects the classical results toward the quantum mechanical with a deviation of about 1% (or 0.1 kJ mol^{-1} and 0.1 J mol^{-1} K^{-1}, respectively).

In $Si(SiH_3)_3$ (Table 2), the behavior is more anharmonic, as seen by the low classical heat capacities, and quantum effects play a minor role; therefore, the classical results already resemble the exact quantum mechanical ones, and the PG correction has less work to do. The PG corrected results agree with the purely quantum mechanical results excellently.

Because most of the interesting cases of molecular inversions fall between the extremes of NH_3 and $Si(SiH_3)_3$, it appears that the PG correction is sufficient to include quantum effects in classical partition functions for anharmonic molecular vibrations.

7.2 Experimentally Observed Energy Levels. In the previous section, the two partition functions compared were both derived theoretically from the same potential energy function by the methods of classical mechanics and quantum chemistry,

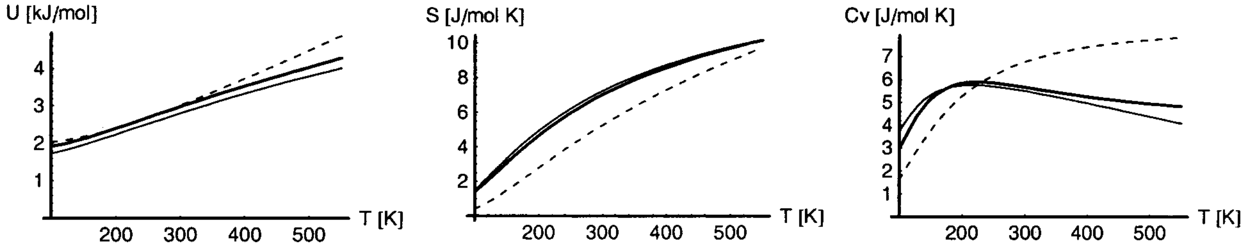

Figure 1. Thermodynamic contribution of internal rotation in methanol to internal energy U, entropy S, and heat capacity C_v. Harmonic curves dashed, experimental solid thin, anharmonic theoretical solid bold.

respectively. Their numerical equivalency demonstrates the validity of the PG correction, but is does not in any way guarantee that the thermodynamical data calculated therefrom compares well to experimental data from these molecules.

It is difficult to find a reference system where thermodynamical data has been experimentally determined with sufficient accuracy; but it is possible to calculate partition functions from spectroscopically observed energy levels and compare these with our PG corrected classical partition functions. By this procedure, the choice of potential function, the choice of potential parameters and the PG correction can be validated. We performed this test for the internal rotation of methanol, whose first fifteen energy levels are known both theoretically and experimentally.[26,27]

We optimized the minimum structure of methanol at the RHF level of theory and scaled the harmonic frequencies by a factor of 0.900; from that, E was determined to 3.61 kJ mol^{-1}. From the Hessian eigenvectors, we estimated[28] the barrier to internal rotation to $V_0 = 5.11$ kJ mol^{-1}, which compares favorably to both the RHF value (5.16 kJ mol^{-1}) and the experimental[29] one (4.76 kJ mol^{-1}). We used McClurg's formula[23] for the partition function of a hindered rotator.

The internal energy, entropy, and heat capacity contributions of the internal rotation mode in CH_3OH are shown in Figure 1. Although the harmonic approximation (dashed) is seriously in error, the results from the PG corrected partition function (bold) agree very well with those of the QM partition function (solid).

At higher temperatures, the heat capacity calculated from the QM partition function can be seen to decrease below the theoretical high-temperature limit of $R/2 = 4.16$ J mol^{-1} K^{-1}. This is not a physical effect, but an artifact due to the limited number of states included in the partition function. The internal energy is affected in lesser degree.

8. Methods

Molecular structures and electronic energies for all molecules discussed here were calculated following the path of the previous work of our group:[13,14] For geometry optimization, we used RHF (restricted Hartree−Fock) for closed-shell species, ROHF (restricted open-shell Hartree−Fock) for radicals and MCSCF (multiconfiguration self-consistent field) for singlet states of diradicalic systems (disilenes, silylenes); these calculations were performed with the GAMESS[30] program. Electronic energies were calculated using MOLPRO[31] as single point energies at the ACPF (average coupled pair functional) level of theory; for these calculations, we used an ANO (atomic natural orbitals) basis set of quadruple ζ quality employing f functions for silicon and d functions for hydrogen. The core electrons of Si were dealt with by a local pseudopotential.[32]

The electronic parts of the standard enthalpy of formation were calculated from atomization enthalpies; incompleteness in the one electron basis was corrected by an empirical correction scheme described earlier.[14]

The vibrational contributions to all thermodynamic functions were determined at the basis of independent motion along different vibrational degrees of freedom (eq 2), using anharmonical partition functions wherever appropriate. This approach is similar to that of Ayala and Schlegel,[11] although these authors applied it only to internal rotation.

We have developed a method that allows to estimate the free parameters (V_0, n, σ, γ) of the partition functions for internal rotation and double well oscillations from the minimum structure and the Hessian eigenvalues and eigenvectors. We use Hessian eigenvectors in redundant internal coordinates[1] to identify internal rotations[11] and to estimate barrier heights; periodicity and symmetry numbers are derived from careful analysis of the equilibrium structure alone. Technical details of this method will be published in a separate paper shortly.[28]

In general, it is not necessary to perform additional ab initio calculations in order to get the anharmonic parameters, except in the case of δ in eq 23. We did, however, perform such calculations in many cases to ensure that the automatic guesses were correct.

9. Results and Discussion

In this section, we will present our results using anharmonic partition functions. This section is not meant to give an overview on silicon hydride chemistry, but on the possible extent of anharmonic terms in thermochemistry. We will therefore discuss the nature, origin and magnitude of anharmonic contributions in several example molecules, and explore the importance of anharmonic corrections in observable quantities such as heats of reaction and equilibrium constants.

9.1 Anharmonic Contributions to Molecular Quantities.

9.1.1 Internal Rotation. The simplest example of internal rotation in a silicon hydride occurs in disilane, SiH_3-SiH_3. This system has a low barrier to internal rotation (4 kJ mol^{-1} at the RHF level), and one can expect the onset of anharmonic behavior at or slightly above room temperature.

The upper row of Figure 2 shows thermodynamic state functions (internal energy, entropy, isochorous heat capacity) for the internal rotation degree of freedom of Si_2H_6, calculated both with a harmonic (eq 5) and an anharmonic (eq 17) partition function. At room temperature, harmonic energy and entropy are well reproduced by the harmonic partition function, but the heat capacity already is influenced by anharmonicity. In the temperature range between 1000 and 2000 K, inclusion of anharmonic effects become essential to stay within "chemical accuracy". The anharmonic contribution to U is 4.3 kJ mol^{-1} at 1500 K.

It is interesting to compare the anharmonicities of disilane and its carbon analogue, ethane (Figure 2, second row). At RHF level, the barrier to torsion in ethane is 12.5 kJ mol^{-1}, and thus anharmonicity manifests itself at somewhat higher temperatures than in disilane.

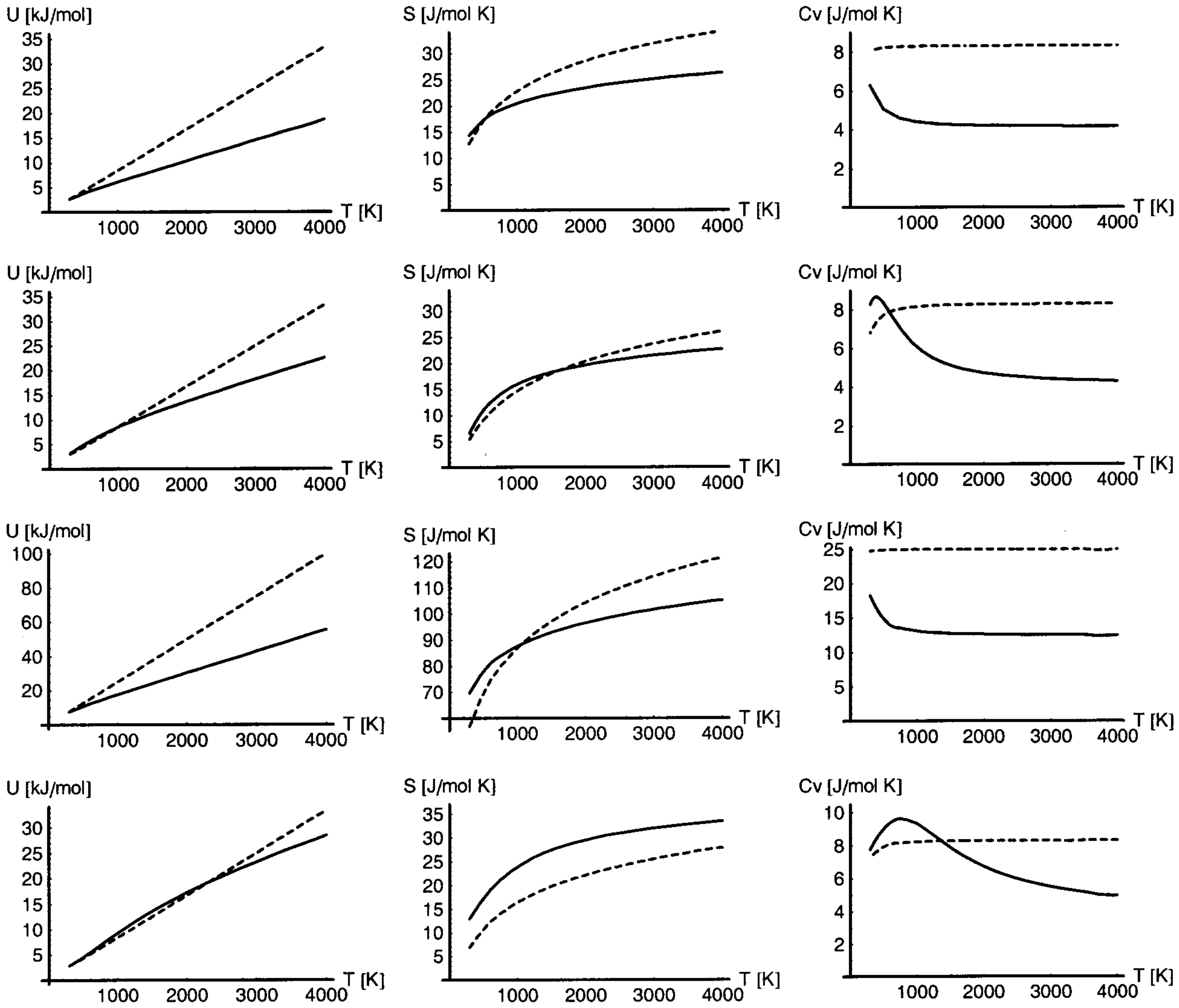

Figure 2. Thermodynamic contribution of internal rotation degrees of freedom to internal energy *U*, entropy *S*, and heat capacity C_v. Top row: One internal rotation in disilane, $SiH_3{-}SiH_3$. Second row: One internal rotation in ethane, C_2H_6. Third row: Three internal rotations in tetrasilane, Si_4H_{10}. Fourth row: One internal rotation in cyclotrisilanyl silylene, $Si_3H_5{-}SiH$. Harmonic curves dashed, anharmonic curves solid.

Trisilane, $SiH_3{-}SiH_2{-}SiH_3$ is the simplest example of a silicon hydride with two internal rotations. Both internal rotations give similar anharmonic contributions as the single internal rotation in Si_2H_6, and the resulting anharmonic correction to the state functions of Si_3H_8 is about twice as large as for disilane.

In tetrasilane, $SiH_3{-}SiH_2{-}SiH_2{-}SiH_3$, we have a new situation, as internal rotation about the central Si$-$Si bond produces three distinguishable isomers. This has two consequences: First, the usage of potential eq 10 and partition function eq 17 is an additional approximation, as it neglects the different heights of the minima and maxima along the internal rotation path. The error induced hereby is expected to be small: The antiperiplanar and synclinal minima of Si_4H_{10} differ by only 1.5 kJ mol^{-1}.

Second and probably more important, the symmetry number is affected ($\sigma = 1$ in eq 17). The large amplitude character of this vibration therefore contributes a temperature-independent increment of $R \ln 3 = 9.1$ J mol^{-1} K^{-1} to the calculated entropy. The third row of Figure 2 shows the sum of the thermodynamic contributions of all three internal rotations in this molecule; apart from the increment to the entropy, the curves look very much like those of the upper row in Figure 2 multiplied by three: The anharmonic contributions of internal rotations about Si$-$Si bonds in silanes do not much depend on the molecular environment.

Internal rotations occur not only in silanes but in all open-chain silicon hydrides. In most cases, the barriers to internal rotation, and thence the anharmonic contributions, resemble those we already reported for silanes. There are, however, exceptions to that: For example, the internal rotation about an Si$=$Si double bond in disilenes has a periodicity of $n = 1$ and a high barrier; it is, thus, best treated as an harmonic vibration.

Another exception arises in the context of silylenes. Although in most silylenes the barriers to internal rotation are similar, or even slightly smaller, than in silanes, this is not the case for three-ring substituted silylenes, e. g., cyclotrisilanyl silylene ($Si_3H_5{-}SiH$). In these species,[33] the periodicity is reduced to $n = 2$, and the barriers range around $V_0 = 30$ kJ mol^{-1}; consequently, the anharmonic contributions to the energy are smaller than in isomeric silylenes such as $Si_3H_3{-}SiH_3$, and the existence of two distinguishable isomers affects the entropy (Figure 2, bottom row).

In Figure 2 (and in the subsequent figures), the thermodynamic functions are plotted up to temperatures of at least 4000 K. Although we do not hold that all species for which we plot thermodynamic data are stable up to these high temperatures, we are aware that such data is still useful for calculating

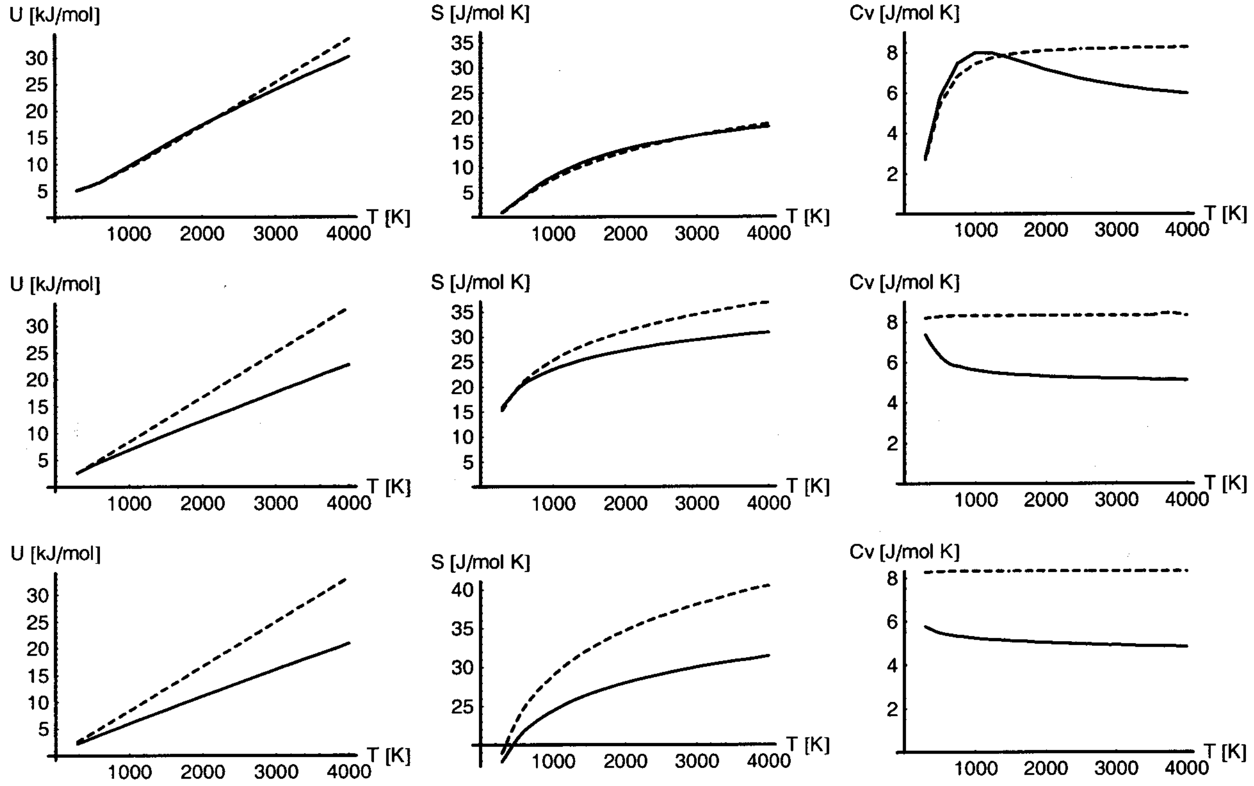

Figure 3. Thermodynamic contribution of the inversion ("umbrella") mode to internal energy *U*, entropy *S* and heat capacity C_v. Top row: Inversion in silyl, SiH_3. Middle row: Inversion in trisilylsilyl, $Si(SiH_3)_3$. Bottom row: Ring inversion in Cyclotetrasilane. Harmonic curves dashed, anharmonic curves solid.

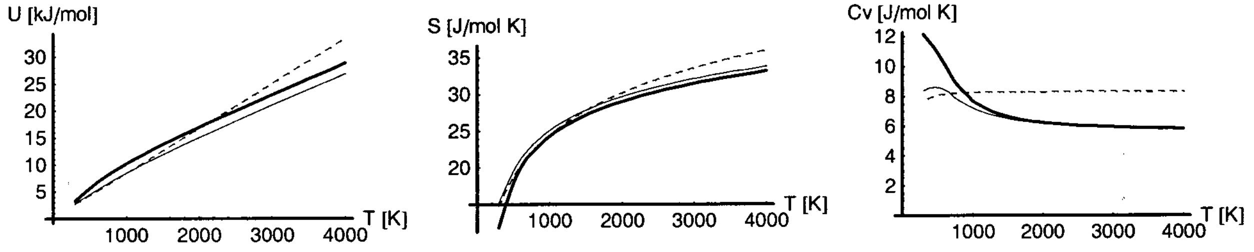

Figure 4. Thermodynamic contributions of symmetric and unsymmetrical inversion to internal energy *U*, entropy *S*, and heat capacity C_v. The underlying potentials do not correspond to real molecules; see the text for the potential parameters chosen. Harmonic curves are dashed, symmetric double well solid thin, asymmetric double well solid bold.

equilibrium concentrations, even if these are very small. Furthermore, anharmonic effects often become clearer at very high temperatures.

9.1.2 Inversion. Silyl radicals feature a trivalent Si atom with pyramidal coordination; thus, they exhibit an "umbrella mode" just like NH_3. The barrier to inversion, however, depends on the degree of substitution; at the RHF level of theory, it is 36.5 kJ mol^{-1} for silyl, SiH_3, but only 6.3 kJ mol^{-1} for trisilylsilyl, $Si(SiH_3)_3$. Therefore, also the magnitude of the anharmonic correction depends on substitution.

Figure 3 shows the anharmonic corrections to both silyl (upper row) and trisilylsilyl (middle row); for the latter species, contributions arising from the three internal rotations are omitted. It can be seen that in SiH_3, anharmonicity is of minor importance, whereas in $Si(SiH_3)_3$ the anharmonic correction for the inversion mode is almost as large as the anharmonic correction for the internal rotation of Si_2H_6.

Disilenes (e.g., disilene $SiH_2{=}SiH_2$) have a puckered minimum geometry and therefore show the same type of planarization mode. Like in silyl radicals, the barrier depends on the degree of substitution: In disilene, it is 19 kJ mol^{-1} and in tetrasilyldisilene it is 12 kJ mol^{-1} at the MCSCF level. The anharmonic corrections are therefore larger than in SiH_3 but smaller than in $Si(SiH_3)_3$.

Unsymmetrically substituted silyl radicals and disilenes can exist in two degenerate distinguishable configurations; therefore, $\sigma = 1$ in eq 19, and the calculated entropy increases by $R \ln 2 = 5.8$ J mol^{-1} K^{-1}.

The bottom row in Figure 3 shows the thermodynamic properties of the ring inversion (puckering mode) in cyclotetrasilane. The barrier is very low (2 kJ mol^{-1}), and consequently, there are large anharmonic corrections to the thermodynamic functions.

The partition function for the asymmetric double-well potential, eq 23, gives us an opportunity to study the effect of slight symmetry breaking. Figure 4 shows the thermodynamic functions of a hypothetical symmetric double-well oscillator ($E = 200$ cm^{-1}, $V_0 = 15$ kJ mol^{-1}, $\gamma = 3$, $\sigma = 1$) in comparison to an asymmetric double well oscillator with $\delta = 6$ kJ mol^{-1} and otherwise identical parameters.

Asymmetry mainly affects the heat capacity at low temperatures; consequently both the internal energy and the entropy

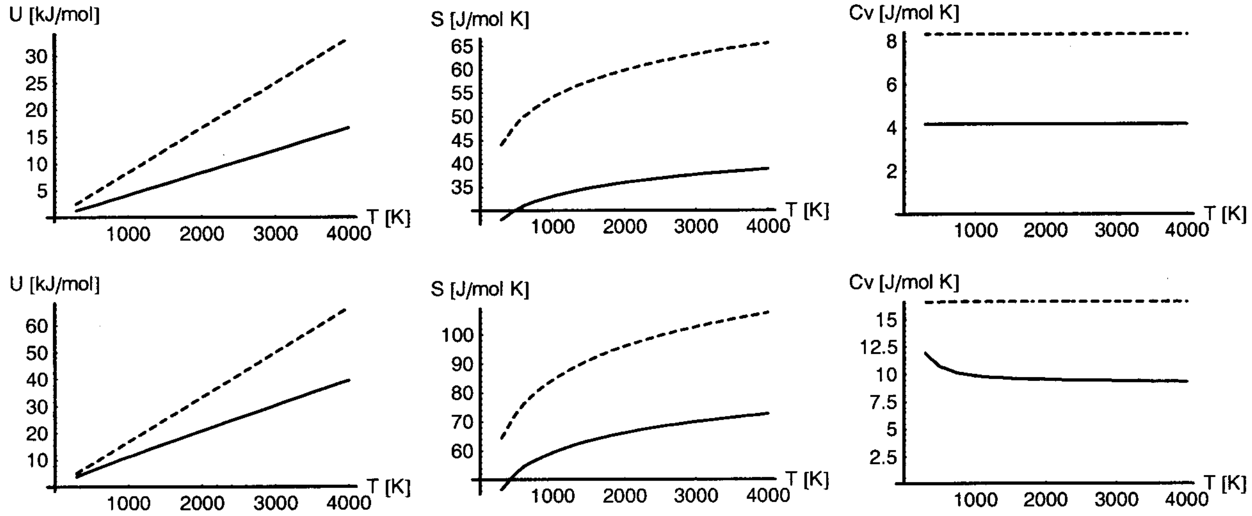

Figure 5. Thermodynamic contribution of anharmonic modes in cyclopentasilane to internal energy U, entropy S and heat capacity C_v. Top row: Pseudorotation. Bottom row: Pseudorotation plus ring puckering. Harmonic curves dashed, anharmonic curves solid.

are shifted vertically by rather small values: The internal energy is increased by about 2 kJ mol^{-1} and the entropy is decreased by about 0.7 Jmol^{-1} K^{-1}. We note that the actual shift in the internal energy is much smaller than the energetic difference between the two different isomers, δ.

From this finding, it appears that small asymmetries in the order of a few kJ mol^{-1} can be neglected safely. We have reason to believe that the same is also true for asymmetric internal rotations, where we have no partition function at hand to test the assumption.

9.1.3 Pseudorotation. Pseudorotation is best known in puckered five-ring systems, although it is not restricted to these molecules. We will limit our discussion to cyclopentasilane as the simplest case of pseudorotation in silicon hydride compounds. The pseudorotation constant, $\bar{B}$, is needed to generate the eigenvalue spectrum and, thus, the partition function (eq 3); it was calculated[20] to about 1 cm^{-1}.

In cyclopentasilane, there are two strongly anharmonic modes: Pseudorotation and ring puckering. Both give rise to anharmonic corrections, but the dominating contributions come from the pseudorotation mode (Figure 5). Both entropy and heat capacity are strongly affected even at room temperature.

9.2 Anharmonic Contributions to Reaction Quantities. Reaction-specific quantities such as the enthalpy of reaction ($\Delta_r H$) are calculated as differences of substance-specific quantities such as the enthalpy of formation ($\Delta_f H$) for reactants and products. Anharmonic corrections to the individual enthalpies of formation will, therefore, in some cases cancel each other and in other cases enforce each other. Moreover, some thermodynamic functions ($\Delta_r H$, $\Delta_r S$) may be more sensitive to anharmonic corrections than others ($\Delta_r G$).

Strongly anharmonic oscillations are associated with floppiness and conformational freedom; whenever a chemical reaction converts a comparatively rigid system into a floppy one, strong effects of anharmonicity on the heat of reaction and entropy can be expected. If, however, products and reactants show a similar degree of floppiness, anharmonic corrections are likely to remain small, even if the individual molecules have many anharmonic degrees of freedom by themselves.

9.2.1 Si−H Dissociation. The dissociation of Si−H bonds does not alter the conformational flexibility of the silicon backbone much; it does, however, create a tricoordinate center that can show an anharmonic inversion mode. We have seen before that the anharmonicity of these inversions depends on the number of silyl substituents. From that, it will appear that the dissociation of a tertiary Si−H bond will need more anharmonic correction than the dissociation of a primary Si−H bond. On the other side, cleavage of a Si−H bond in an SiH_3 group will often increase the number of distinguishable isomers, and thus add an extra increment to $\Delta_r S$.

These considerations can be exemplified by the reactions of disilane, trisilane, and isotetrasilane to disilanyl, 1-trisilanyl and trisilylsilyl, respectively (Figure 6). The first two examples involve the formation of a primary silyl radical and both show only small anharmonic corrections to the enthalpy of reaction, but in the second example, the entropy of reaction (and consequently, the Gibbs function) is affected by the existence of three different conformers in 1-trisilanyl, $SiH_3-SiH_2-SiH_2$.

In the last example, anharmonicity affects both the enthalpy and entropy of reaction. Although the anharmonic corrections to $\Delta_r H$ and $\Delta_r S$ are larger than in the previous example, the net effect on $\Delta_r G$ is smaller because the anharmonic corrections are negative for both $\Delta_r H$ and $\Delta_r S$, and error cancellation occurs when $\Delta_r G$ is calculated.

9.2.2 H_2 Elimination. In this section, we will discuss the 1,1 elimination and 1,2 elimination of H_2 from silanes, yielding silylenes and disilenes, respectively.

1,1 elimination converts a silane to a silylene, both of which have the same number of internal rotations and lack other nonharmonic degrees of freedom. In most cases, the barriers to internal rotation are almost the same in a silane and all the silylenes derived from it. Still, the number of distinguishable conformers in the silylene may be higher, and then $\Delta_r S$ and $\Delta_r G$ can be influenced. An example for that is the formation of trisila-1,1-diyl (SiH_3-SiH_2-SiH, three conformers) from trisilane ($SiH_3-SiH_2-SiH_3$, one conformer).

Figure 7 (upper row) shows the 1,1 H_2 elimination reaction of silylcyclotrisilane ($Si_3H_5-SiH_3$, one conformer) to cyclotrisilylsilylene (Si_3H_5-SiH, two conformers). Although the internal rotation in the reactant is only slightly hindered (V_0 = 5 kJ mol^{-1}), there is considerable hindrance in the product (V_0 = 30 kJ mol^{-1}), which behaves more harmonically. The figure shows than both enthalpy and entropy of reaction are affected; in the free energy, however, the effects on $\Delta_r H$ and $\Delta_r S$ partially cancel each other.

Formally, disilenes result from the 1,2 elimination of H_2 from silanes. They have one internal rotation less than the corresponding silane, but on the other side exhibit an inversion mode

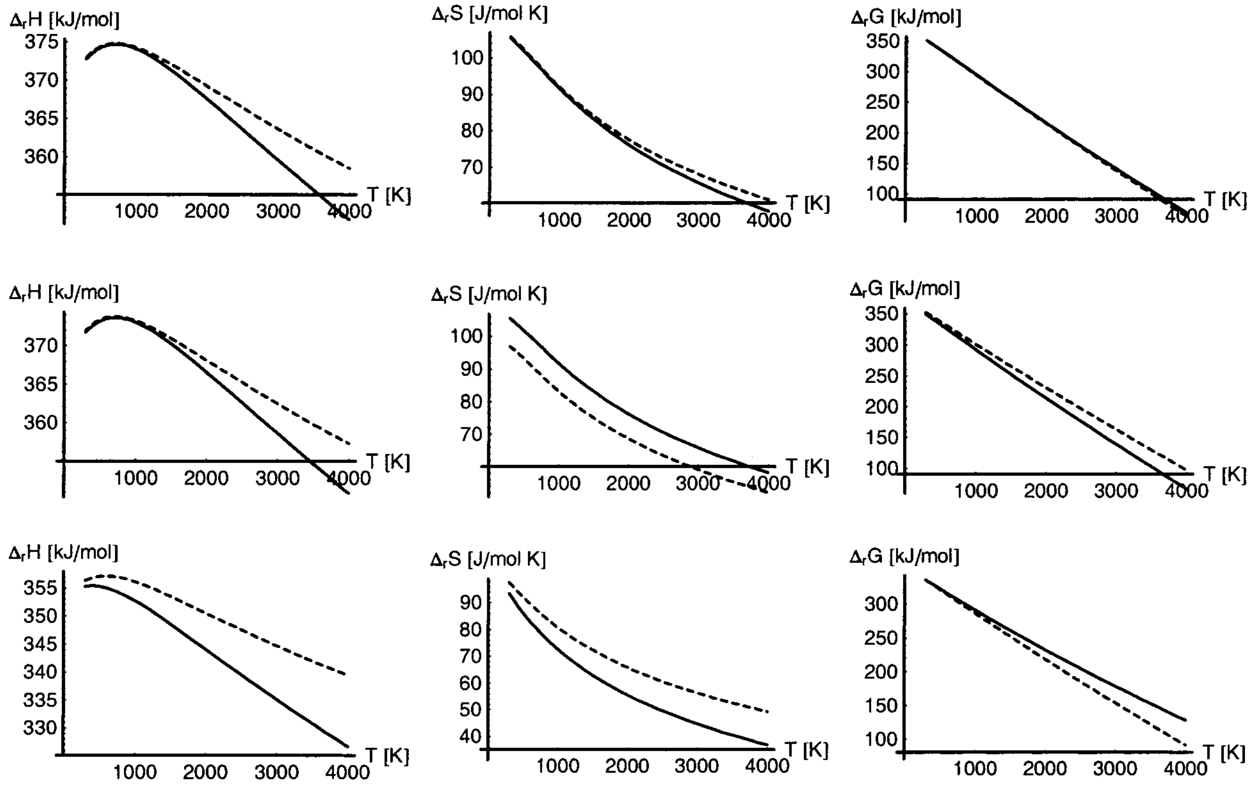

Figure 6. Effects of anharmonicity on Si−H dissociation reactions. Top row: $Si_2H_6 \rightarrow H + Si_2H_5$. Middle row: $Si_3H_8 \rightarrow H + SiH_3{-}SiH_2{-}SiH_2$. Bottom row: $SiH(SiH_3)_3 \rightarrow H + Si(SiH_3)_2$. Harmonic curves dashed, anharmonic curves solid.

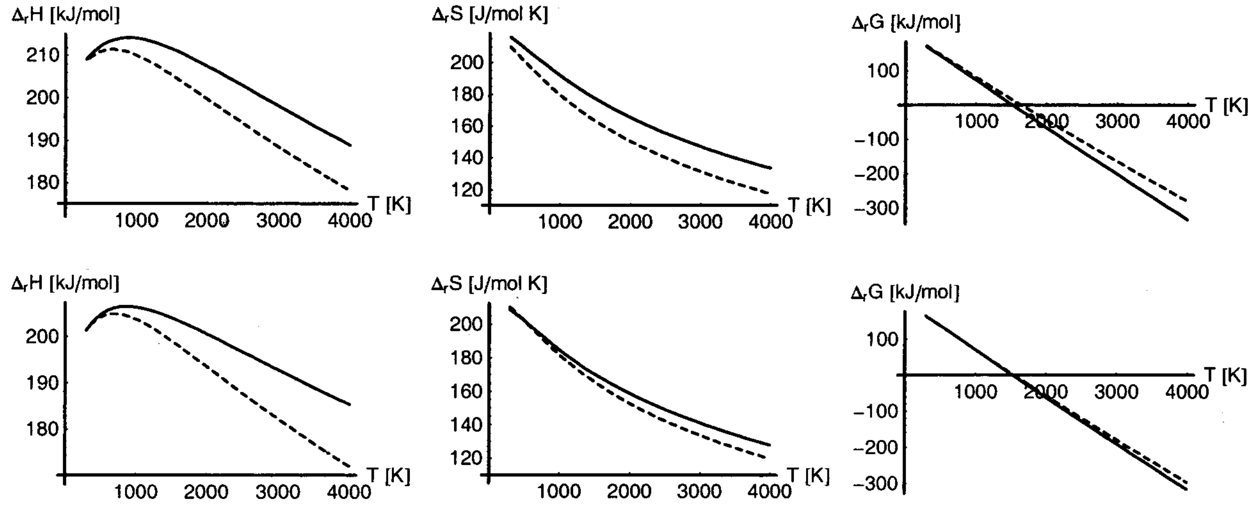

Figure 7. Effects of anharmonicity on H_2 elimination reactions. Top row: *cyclo*-$Si_3H_5{-}SiH_3 \rightarrow H_2 +$ *cyclo*-$Si_3H_5{-}SiH$. Bottom row: $Si_2H_6 \rightarrow H_2 + SiH_2{=}SiH_2$. Harmonic curves dashed, anharmonic curves solid.

lacking from their silane counterparts. As the anharmonic contributions of a double well oscillator are smaller that those of an internal rotator, anharmonicity can influence the thermodynamics of such reactions.

In Figure 7 (lower row), thermodynamic functions for the 1,2 elimination of disilane to disilene are shown. The anharmonic corrections are, however, quite small; they are most pronounced for the enthalpy of reaction, (7 kJ mol^{-1} at 2000 K); entropy and particularly free energy show even smaller anharmonic corrections.

9.2.3 Cyclization Reactions. Formation of cyclic structures is always associated with a loss of conformational freedom; therefore, anharmonic effects can be expected to grow to significant size.

As an example, we take the formation of cyclotrisilane from trisilane via H_2 elimination (Figure 8, upper row). In the course of this reaction, two internal rotation degrees of freedom vanish, and the product cyclotrisilane does not show any significantly anharmonic modes. The figure shows that anharmonicity affects both enthalpy and entropy of reaction with the same sign; therefore, error compensation keeps the effect of anharmonicity on $\Delta_r G$ small.

Anharmonic effects are particularly strong in reactions that form five membered rings. The lower row of Figure 8 shows the isomerization of 1-pentasilene ($SiH_2{=}SiH{-}SiH_2{-}SiH_2{-}SiH_3$) to cyclopentasilene. Although the reactant has nine different conformers produced by internal rotations about the central Si−Si single bonds, the product, although floppy, has

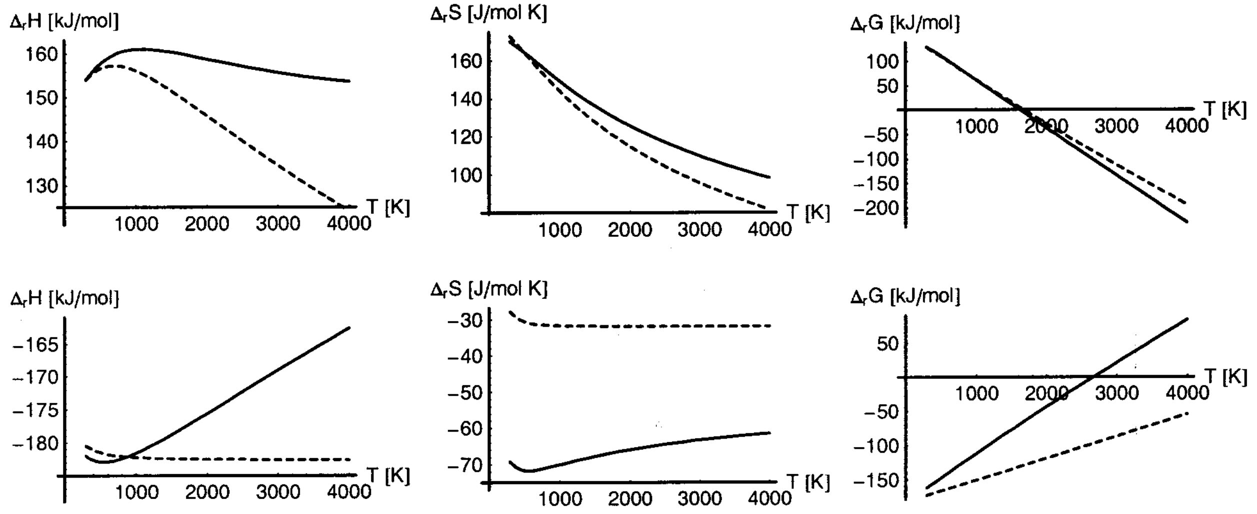

Figure 8. Effects of anharmonicity on cyclization reactions. Top row: $Si_3H_8 \rightarrow H_2 + cyclo\text{-}Si_3H_6$. Bottom row: $SiH_2{=}SiH{-}SiH_2{-}SiH_2{-}SiH_3 \rightarrow cyclo\text{-}Si_5H_{10}$. Harmonic curves dashed, anharmonic curves solid.

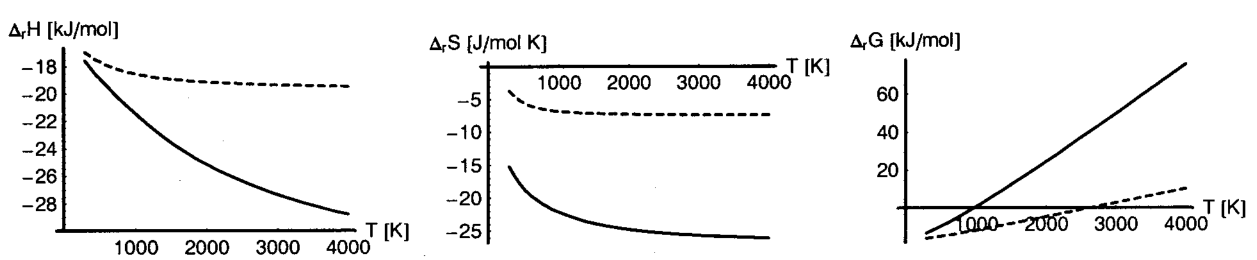

Figure 9. Effects of anharmonicity on radical isomerization $SiH(SiH_3)_2{-}SiH_2 \rightarrow Si(SiH_3){-}SiH_3$. Harmonic curves dashed, anharmonic curves solid.

less conformational entropy. As a consequence, we find that all functions, Δ_rH, Δ_rS and Δ_rG, are heavily affected; at temperatures above 2000 K, the harmonic and the anharmonic results for Δ_rG have different sign and show almost no resemblance.

9.2.4 Hydrogen Migration. In the examples discussed so far, the most important types of anharmonic motions were internal rotations (and pseudorotations in the case of five-membered rings). Because internal rotations show larger deviations from harmonic behavior than inversions, the former tend to dominate over the latter in the net effect.

If, however, the number of internal rotations remains constant during a reaction, and if the enthalpy (and Gibbs energy) of reaction has low absolute value, the effect of inversions may become crucial for the correct prediction of Δ_fH. As an example, we look at the isomerization of *prim*-isotetrasilanyl to *tert*-isotetrasilanyl (trisilylsilyl). It is well known[14] that electronic effects favor tertiary over primary radicals energetically, and so does anharmonicity (Figure 9).

The energetic stabilization of the tertiary radical is, however, overbalanced by its entropic destabilization, which has its source in part in the strongly anharmonic inversion, but even more so in the loss of three distinguishable isomers in the primary to only one isomer in the tertiary case. Because of the small absolute value of Δ_rH, the entropy term in the Gibbs enthalpy Δ_rG exceeds the enthalpy term even at modest temperature (500 K), and the entropy becomes the dominating factor for Δ_rG and, therefore, the equilibrium constant.

The product distribution of this reaction is shown in Figure 10; the graphic shows the mole fraction of the tertiary radical in the equilibrium mixture. The harmonic approximation leads to an dramatic overestimization of the stability and thus concentration of the tertiary radical: In the temperature range of 1000 K to 2000 K, it even predicts the dominating species incorrectly. In the high-temperature limit, the harmonic approximation is still wrong by a factor of 5 (40% vs 8%).

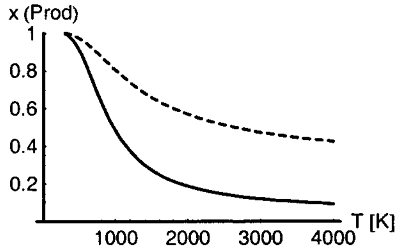

Figure 10. Effects of anharmonicity on the primary/tertiary radical equilibrium $SiH(SiH_3)_2{-}SiH_2 \rightarrow Si(SiH_3){-}SiH_3$. Harmonic curve dashed, anharmonic curve solid.

9.3 Enthalpy of Formation and Enthalpy of Reaction. All calculated thermodynamic quantities are sums of a large number of different contributions. In the special case of the enthalpy of formation, there are not only contributions arising from the molecule in question, but also contributions from the corresponding element phases due to the special choice of zero in enthalpies of formation.

The molecule-related contributions to the enthalpy of formation have different orders of magnitude, and one might ask whether small anharmonic corrections are of any practical influence. Table 3 shows these contributions to two isomeric Si_5H_{10} species, 1-pentasilene and cyclopentasilane, and also the corresponding contributions to the enthalpy of reaction of the isomerization (cf. section 9.2.3 and Figure 8). The figures are given for three different temperatures, 298, 2000, and 3000 K.

It can be seen that the electronic contribution, which is the

TABLE 3: Enthalpies of Formation for Two Si_5H_{10} Species at Different Temperatures and Enthalpy of Reaction for their Interconversion, in kJ/mol

$T =$	298 K	2000 K	3000 K
$\Delta_f H$ (1-pentasilene)	397.2	147.2	171.6
elec	−4210.6	−4210.6	−4210.6
trans	6.2	41.5	62.3
rot	3.7	24.9	37.4
vib, harmon	240.1	687.5	999.2
anharm	+0.4	−19.4	−33.2
$\Delta_f H$ (cyclopentasilane)	215.1	−28.4	2.6
elec	−4393.4	−4393.4	−4393.4
trans	6.2	41.5	62.3
rot	3.7	24.9	37.4
vib, harmon	242.2	687.7	999
anharm	−1.1	−12.4	−19.6
$\Delta_r H$ (isomerization)	−182.1	−175.6	−169.0
elec	−182.8	−182.8	−182.8
trans	0.0	0.0	0.0
rot	0.0	0.0	0.0
vib, harmon	2.2	0.2	0.2
anharm	−1.5	+7.0	+13.6

negative electronic atomization energy, is by far the largest summand, being more than 1 order of magnitude larger than the vibrational contribution at room temperature. Even at high temperatures, the anharmonic correction is only a few percent of the total vibrational contribution.

Although the atomization energy is so much larger than the vibrational contributions, and the anharmonic correction is only a tiny fraction of the latter, anharmonicity can still be an important effect, as shown in the lower third of Table 3, where the same contributions to the enthalpy of reaction are displayed. As before, the electronic energies form the dominating contribution, but as the harmonic parts of the vibrational contributions cancel almost exactly, anharmonicity is the second largest contribution at higher temperatures.

The Si_5H_{10} isomerization described here exemplifies that anharmonicity can become a matter of relevance within chemical accuracy, even if other contributions to the enthalpy of formation are larger.

10. Conclusions

We have illustrated the influence of anharmonic nuclear motion (internal rotation, inversion and pseudorotation) on thermodynamic properties such as energy, entropy, or equilibrium composition. For most single species, anharmonicity usually decreases internal energy, entropy and heat capacity in comparison to the purely harmonic results. If, however, anharmonic motions produce chemically distinguishable species (conformers, configurations), then the entropy may actually increase. When enthalpies of formation are combined to give enthalpies of reaction, or Gibbs energies are calculated from enthalpy and entropy, these effects will in some cases cancel each other but, in other cases, will reinforce each other and give substantial anharmonical net effects.

We have investigated a number of classes of silicon hydrides and reactions between them to rationalize the magnitude and sign of anharmonic corrections. When, during a reaction, floppy degrees of freedom emerge or vanish, strong effects on $\Delta_r H$ and $\Delta_r S$ can be expected, although not necessarily on $\Delta_r G$. We have found that formation of rigid ring systems from conformationally less constrained open-chain compounds is prone to large anharmonic effects.

In the high-temperature regime, the entropy is often the dominating factor for the value of $\Delta_r G$ if reactions with small $\Delta_r H$ are considered. An example of such reactions are equilibria between radicals with the same silicon backbone. We found that the number of distinguishable isomers is the key factor determining the concentrations of the various species at high temperatures, when their energetic differences become comparatively unimportant.

An online version of our program operating on data for about 200 silicon hydride compounds can be found at http://bthec11.kfunigraz.ac.at/~katzer.

References and Notes

(1) Wilson, E. B., Jr.; Decius, J. D.; Cross, P. C. *Molecular Vibrations*; Dover Publications: Mineola, New York, 1980.

(2) Lister, D. G.; Macdonald, J. N.; Owen, N. L. *Internal Rotation and Inversion*; Academic Press: New York, 1978.

(3) Pitzer, K. S.; Gwinn, W. D. *J. Chem. Phys.* **1942**, *10*, 428−440.

(4) Pitzer, K. S. *J. Chem. Phys.* **1946**, *14*, 239−243.

(5) Kilpatrick, J. E.; Pitzer, K. S. *J. Chem. Phys.* **1946**, *14*, 239−243.

(6) Pitzer, K. S. *J. Chem. Phys.* **1944**, *12*, 310−314.

(7) Witschel, W. *Chem. Phys. Lett.* **1980**, *71*, 131−134.

(8) Witschel, W. *Chem. Phys.* **1980**, *50*, 265−271.

(9) Witschel, W.; Bohmann, J. *J. Phys. A: Math. Gen.* **1980**, *13*, 2735−2750.

(10) Gibson, W. G. *J. Phys. A: Math. Gen.* **1984**, *17*, 1877−1890.

(11) Ayala, P. Y.; Schlegel, H. B. *J. Chem. Phys.* **1998**, *108*, 2314−2325.

(12) *JANAF Thermochemical Tables*, 3rd ed.; *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. No. 1.

(13) Sax, A. F.; Kalcher, J. *J. Phys. Chem.* **1991**, *95*, 1768−1783.

(14) Katzer, G.; Ernst, M.; Sax, A. F.; Kalcher, J. *J. Phys. Chem. A* **1997**, *101*, 3942.

(15) Swihart, M. T.; Girshick, S. L. *J. Phys. Chem. B* **1999**, *103*, 64−76.

(16) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **1999**, *103*, 6413−6419.

(17) Martin, J. M. L.; Taylor, P. R. *J. Phys. Chem. A* **1999**, *103*, 4427−4431.

(18) East, A. L. L.; Radom, L. *J. Chem. Phys.* **1997**, *106*, 6655−6674.

(19) Kilpatrick, J. E.; Pitzer, K. S.; Spitzer, R. *J. Am. Chem. Soc.* **1947**, *69*, 2483−2488.

(20) Katzer, G.; Sax, A. F. submitted to *J. Chem. Phys.*

(21) Knyazev, V. D.; Tsang, W. *J. Phys. Chem. A* **1998**, *102*, 9167−9176.

(22) Knyazev, V. D. *J. Phys. Chem. A* **1998**, *102*, 3916−3922.

(23) McClurg, R. B.; Flagan, R. C.; Goddard, W. A., III *J. Chem. Phys.* **1997**, *106*, 6675−6680.

(24) Marston, C. C.; Balint-Kurti, G. G. *J. Chem. Phys.* **1989**, *91*, 3571−3576.

(25) Isaacson, A. D.; Truhlar, D. G. *J. Chem. Phys.* **1981**, *75*, 4090−4094.

(26) Burkhard, D. G.; Dennison, D. M. *J. Mol. Spectrosc.* **1959**, *3*, 299−344.

(27) Muñoz-Caro, C.; Niño, A.; Senent, M. L. *Chem. Phys. Lett.* **1997**, *273*, 135−140.

(28) Katzer, G.; Sax, A. F. to be published.

(29) Herbst, E.; Messer, J. K.; de Lucia, F. C.; Helminger, P. *J. Mol. Spectrosc.* **1984**, *108*, 42.

(30) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, S.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.

(31) MOLPRO is a package of ab initio programs written by Werner, H.-J. and Knowles, P. J. with contributions from the following: Almlöf, J.; Amos, R. D.; Deegan, M. J. O.; Elbert, S. T.; Hampel, C.; Meyer, W.; Peterson, K.; Pitzer, R.; Stone, A. J.; Taylor, P. R.

(32) Janoschek, R.; Sax, A. F.; Halevi, E. *Isr. J. Chem.* **1983**, *23*, 58.

(33) Katzer, G.; Sax, A. F.; Kalcher, J. *J. Phys. Chem. A* **1999**, *103*, 7894−7899.