Quantitative Molecular Thermochemistry Based on Path Integrals

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Abstract

The calculation of thermochemical data requires accurate molecular energies and heat capacities. Traditional methods rely upon the standard harmonic normal mode analysis to calculate the vibrational and rotational contributions. We utilize path integral Monte Carlo (PIMC) for going beyond the harmonic analysis, to calculate the vibrational and rotational contributions to *ab initio* energies. This is an application and extension of a method previously developed in our group [J. Chem. Phys. 118(4), 1596–1603 (2003)].

I. INTRODUCTION

It is well known that accurate thermodynamic molecular properties are needed for a variety of reasons, including the calculation of reaction rates and equations of state (EOS). Approaches must include a quantum thermal energy (QTE) term that includes the quantum mechanical zero-point energy (ZPE) and the thermal energy. This quantum correction is essential, because vibrations are inherently quantum mechanical and the ZPE is larger than the desired accuracy of 1–2 kcal/mol. The QTE calculation done in the traditional electronic structure calculations is based upon the harmonic approximation of normal modes generated from the second-derivative of the energy at the ground state equilibrium geometry.[1] Rotations are treated through a rigid rotor approximation. This approach ignores vibrational

1

anharmonicity and vibration/rotation coupling. The importance of anharmonic effects in molecules is well documented.[2,3] The overall anharmonic contribution to the molecular energy may either increase or decrease with temperature due to canceling repulsive and attractive terms. Failure to include anharmonic effects limits the overall accuracy of thermochemical calculations, even if the basis set and level of theory are both converged.[4−7]

II. PATH INTEGRAL THERMOCHEMISTRY

We utilize a quantum mechanical treatment of the nuclei using the path integral Monte Carlo (PIMC) method[8−10] instead of the harmonic normal mode approximation. The PIMC method has found wide application in quantum physics and chemistry,[4,11−16] and the reader is directed to these references for a full discussion of the method and the underlying physics. The path integral thermochemistry method intrinsically includes all rotation-vibration interactions and anharmonicities. Unlike the more traditional sum over states approach, the path integral method performs well even when there are numerous thermally accessible states. This is important because the rotation-vibration interactions and anharmonicites that the path integral method includes become more important at high temperatures. Path integral thermochemistry suffers from no inherent approximations: the approximations of basis set, level of electronic structure theory, and the discretization of the path are all well defined and systematically improvable. The goal of path integral thermochemistry is the calculation of internal energy E, entropy $\mathcal{S}$, enthalpy $\mathcal{H}$, free energy $\mathcal{G}$, and heat capacity C_V for gas phase molecules and clusters as a function of temperature T. We utilize *ab initio* methods to calculate the underlying Born-Oppenheimer potential V.

Recently, Glaesemann and Fried[4] proposed a numerically efficient scheme for path integrals using a Born-Oppenheimer potential V, that is calculated from numerous *ab initio* electronic structure calculations. Glaesemann and Fried found that dynamically generated

sparse interpolation tables for V could substantially accelerate the path integral calculation. Protocols for optimally choosing a real space path discretization were presented. In addition, the use of centroid thermodynamic estimators was found to substantially reduce numerical noise[14,15]. It was found that the anharmonic portion of the thermodynamic energy could be as high as 2.5 kcal/mol.

The previous study, however, found strong sensitivities in the calculated thermodynamic energy to the basis set and level of *ab initio* calculation used. This could make practical application of the method problematic. In the present study, we employ several improvements that allow us to quantitatively converge *ab initio* path integral simulations of rot-vibrational molecular enthalpies to within 0.2 kcal/mol when compared to experimentally-based enthalpies. We find that correlation-consistent basis sets provide excellent convergence properties. Both double and triple zeta basis sets are compared. Correlation consistent double zeta basis sets adequately represent the vibrational anharmonicity. We find that an unrestricted second order many body perturbation theory (UMBPT2) or density functional theory (DFT) treatment of electron correlation can provide a reliable estimate of thermochemical properties. The MP2 method is compared to other electronic structure methods, such as coupled cluster theory and density functional theory.

III. METHODOLOGY

We apply PIMC to a variety of molecules and compare to the harmonic approximation and to JANAF tables.[17] JANAF tables are calculated from a selection of available experimental data, including spectroscopic information. We use our own path integral Monte Carlo code. The code uses the discrete path method with normal mode sampling instead of the Fourier method.[18−22] The difference is that the discrete method treats the path between the discrete points as a set of linear segments, while the Fourier method treats the path as a

smooth curve that goes through all the discrete points. The number of Monte Carlo cycles and number of discretization points (sometimes called "beads" or "replicas") were chosen to converge the energy to within at least 0.01 kcal/mol. The number of discretization points used are as follows: 128 at 300K, 96 at 1000K, 64 at 2000K, 48 at 3000K, 32 at 4000K, and 24 at 5000K. All calculations were run for at least 10^8 Monte Carlo cycles, with most run for 10^9 Monte Carlo cycles. Monte Carlo step sizes were optimized to obtain acceptance rates of about 60%. For ease of comparision to other's work, the standard thermodynamic energy estimator (ϵ_T) and thermodynamic heat capacity estimator (C_V^T) was used in all calculations.[14,15] The data caching scheme described in reference 4 is utilized to improve efficiency of the computations. A multi-linear interpolation is used in the cache. The data caches contained between 42,427 and 998,338 entries. The cache sparcity varied from 0.14 to 0.36. The cache spacing was 0.04 Bohr and 0.04 Radians.[23−25] Although multiplying calculated frequencies by an empirical constant is common, we use unscaled frequencies for comparison. Scaling factors are generally used to correct for the anharmonicity, for using an imperfect basis set, and for imperfect theory. The scaling factors vary greatly depending upon: the level of theory, the basis set used, the temperature, and what property is being fit.[2,26] For Hartree-Fock (HF) theory and 3-21G basis set the scaling factors ranged from 0.9085 to 1.0075, depending on whether one is fitting ω, $1/\omega$, QTE(T), $\Delta\mathcal{H}_{vib}(T)$, or $\mathcal{S}_{vib}(T)$.[2]

Molecules were studied with V calculated with UMBPT2[27,28], unrestricted coupled-cluster with single and double substitutions and non-iterative triples (CCSD(T))[29−33], and DFT methods.[34,35] Our PIMC code was interfaced to the GAMESS code[36,37] for the calculation of V for all nuclear configurations accessed during the simulation. An unrestricted reference wavefunction was used to avoid the ambiguity that exists among the multitude of RO-MBPT2 methods,[28,38,39] and to minimize the possibility of a divergence in the perturbation expansion.[40] All comparisons were made to single point frequency calculations[41−43]

using either Molpro,[44] Gaussian98[45] or GAMESS.

We use Dunning's correlation consistent basis sets.[46−52] These basis sets were designed to converge consistently to the correct answer as the basis set size is increased. They are designed with the intent of properly treating correlated methods, like MBPT and CC. For computational efficiency, the rotated versions are used, which give the same answers as the unrotated versions.[53]

IV. RESULTS

In Table I, we study the convergence of the the anharmonic part of the energy

$$\alpha \equiv E^{\mathrm{PIMC}} - E^{\mathrm{harmonic}} \tag{1}$$

for H_2O at 3000K. Here, E^{PIMC} is the total thermodynamic energy calculated with our path integral Monte Carlo method. E^{harmonic} is the total energy calculated with the standard harmonic oscillator/rigid rotor approximation. α can be converged to within 0.04 kcal/mol using coupled cluster theory and a triple zeta basis set. The anharmonic part of the energy is converged to within 0.09 kcal/mol using MBPT2 and a triple zeta basis set. The B3LYP results are similar to the MBPT2 results. DFT is preferable to MBPT2 and CC methods away from equilibrium, since DFT does not suffer from pathological divergences.[40,54] The difference between the energy calculated with the MBPT2 method and the CC method is 0.25 kcal/mol. This is less than the typical error of 1–2 kcal/mol in a thermochemical method such as G2[55].

The enthalpy can be written as a sum of an equilibrum energy and a rot-vibrational contribution:

$$H(T) = E_0 + E_{vr}(T) + pV_m \tag{2}$$

Here, E_0 is the energy at the equilibrium nuclear configuration. E_{vr} is the rot-vibrational correction to the enthalpy. p is the pressure, and V_m is the molar volume. The calculated enthalpy is sensitive to errors in E_0. We find that a higher level treatment of electron correlation and larger basis set typically is required to converge E_0 to the same accuracy than is required to converge $E_{vr}(T)$ to the same accuracy. In our work we use the ideal gas approximation for $pV_m = RT$, where R is the ideal gas constant. All calculations are performed at a standard pressure of 1 ATM.

Although the calculation of E_0 is addressed below, we find it convenient to compare our calculated results to the enthalpy of heating

$$\Delta H_h^{(x)}(T) \equiv H^{(x)}(T) - H^{(x)}(298) \tag{3}$$

Here, $x = (c, j)$ is used to denote calculated or JANAF quantities, respectively. ΔH_h does not depend on E_0. In Figure 1a we show enthalpy of heating as given by the JANAF tables as a function of temperature for H_2O. Note that in the classical limit $k_B T > \hbar\omega$, the enthalpy of heating is a linear function of temperature (ignoring anharmonicities). Figure 1 shows that $\Delta H_h^c(T)$ becomes a nearly linear function of temperature above 2000K.

In Figure 1b, we consider errors in the calculated enthalpy of heating. Calculations employing both path integral and harmonic approximations are considered. We find that both calculations perform acceptably over the temperature considered, with a maximum error of 1.4 kcal/mol for the harmonic approximation. Nonetheless, the PIMC calculation substantially reduces the maximum error to 0.2 kcal/mol. We note that the PIMC error is roughly constant with increasing temperature, while the error in the harmonic approximation grows rapidly with increasing temperature.

We next consider the effect of electron correlation treatment on the anharmonic energy α. In Figure 2, we show the anharmonic energy calculated with the B3LYP exchange-correlation density functional[35], CCSD, and MBPT2 methods using a cc-pDZV basis set.

The values of α obtained generally agree to within 0.1 kcal/mol. In addition the shape of $\alpha(T)$ is very similar for each method. This indicates that more inexpensive methods, such as DFT or MBPT2, are adequate to determine the anharmonic part of the enthalpy. In our previous work, we found DFT to be more difficult to converge, but that result did not use the correlation consistent basis sets, which we have found to provide a more balanced approach.[4] The anharmonic energy α increases with temperature in Fig. 2. This is expected, because as T increases, the amplitude of vibrations away from equilibrium increases, thus enhancing the contribution of anharmonicities.

The path integral thermochemistry method is also applicable to radicals. When treating radicals, it is important to consider the importance of excited electronic states. We consider CH_2 here. For this molecule, the first excited $^1A_1$ state lies at 9280 cm^{-1} above the lowest singlet state ($^1A_1$) and the first excited triplet state lies more than 21000 cm^{-1} above the ground triplet state.[56,57] This state is not thermally accessible at the maximum temperature of 4000K considered here. If excited states are thermally populated, it becomes necessary to conduct separate path integral simulations for each state. Results can then be combined with an appropriate Boltzmann weighting factor. In Figure 3a we show $\Delta H_h^j(T)$. This is a nearly linear function of T, similar to H_2O. The difference between the calculated and JANAF enthalpy of heating is shown in Figure 3b. We find a maximum error for the harmonic calculation of 1.8 kcal/mol. This compares with a maximum error of 0.3 kcal/mol for the PIMC calculation. The magnitude of the error for the harmonic calculation is similar to that of H_2O, indicating that radicals do not necessarily have a larger vibrational anharmonicity than closed-shell molecules.

For triplet CH_2, the anharmonic energy α varies non-monotonically with temperature in Fig. 4. This contrasts with the monotonic variation found in Fig. 3. Therefore, there is not a simple *ad hoc* correction for the anharmonicity.

The path integral thermochemistry method can be applied to linear and non-linear

7

molecules without modification. We have applied the path integral thermochemistry method to CO_2 as a demonstration of its applicability to linear molecules. In Fig. 5a, we show $\Delta H_h^j(T)$. We show calculated differences from JANAF values in Fig. 5b. Similar to other cases, the PIMC calculation is substantially closer to JANAF values than the harmonic calculation.

The path integral thermochemistry method can also be straightforwardly applied to floppy molecules or molecules undergoing isomerizations. For HCN at the cc-pVDZ/CCSD level of theory, isomerizations between HNC and HCN are found at 4000K. Note that we use coupled cluster theory, since MBPT2 is likely to be inaccurate for large amplitude nuclear motions. The calculated anharmonic energy is shown in Figure 6. Once isomerizations begin, the calculated anharmonic energy increases rapidly with temperature. For higher temperatures, the anharmonicity grows significantly (over 11 kcal/mol at 5000K).

The heat capacity can also be directly calculated with the path integral thermochemistry method. This is of interest, since the entropy can be generated through the integral of $C_v(T)/T$. Given the entropy and the enthalpy, other thermodynamic potentials, such as the Gibbs free energy, can be easily computed. We show the constant volume heat capacity given by JANAF (C_v^j) for CO_2 in Fig. 7a. We show the difference between calculated (C_V^c) and JANAF heat capacities in Fig. 7b. At lower temperatures (300K), the heat capacity is dominated by rotational terms. Thus, the harmonic approximation is sufficiently accurate. The PIMC result for this case has a somewhat higher error than the harmonic approximation, most likely because too few discretization points were used (128, which was more than adequate for calculating E). We note that the heat capacity is more sensitive than energy to the number of discretization points.[4] For intermediate temperatures (1000K), both the harmonic approach and the PIMC approach match JANAF to within 0.1 cal/mol-K. At higher temperatures (2000K), the PIMC results are clearly better than the harmonic results.

The enthalpy of formation is calculable with PIMC. This requires the accurate determi-

nation of E_0. A simple method is utilized. The G2 method is used to calculate the enthalpy of formation at 298.15K.[58,55,59,60] The PIMC enthalpy of heating is added to this G2 value to obtain $H(T)$:

$$H(T) = H^{\mathrm{G2}}(298) + \Delta H_h^c(T) \tag{4}$$

This provides a straightforward method to extend the accuracy of G2 to higher temperatures. The enthalpy of formation is then calculated by subtracting the appropriate absolute entropies:

$$\Delta H = H(T) - \sum_i y_i H_i(T) \tag{5}$$

Here, $H(T)$ is the absolute enthalpy of the compound of interest, while $H_i(T)$ is the enthalpy of the ith element in its standard state. y_i is a stoichiometric coefficient. For H_2O, the G2 enthalpy of formation was calculated using G2 enthalpies of H_2O, H_2, and O_2. For atoms for which the standard state is not easily calculated (such as carbon: graphite), the enthalpy would be calculated for a single gas atom and then corrected with JANAF data for C(gas) vs. G(graphite). The PIMC calculation used the cc-pVDZ basis set and MBPT2. The results for H_2O are presented in Fig. 8. The JANAF results differ by less than 0.2 kcal/mol from the PIMC results, but at higher T the scaled harmonic approximation has an error as large as 0.9 kcal/mol. In the harmonic enthalpy of formation calculation we used scaled frequencies to be consistent with the underlying G2 method. We have not corrected the 298.15K G2 numbers for anharmonicity, because the empirical corrections built into the G2 method may partially take that into account.

V. CONCLUSIONS

We have calculated quantum anharmonic corrections to the enthalpy of *ab initio* electronic structure calculations using PIMC. We have demonstrated that correlation-consistent

9

basis functions combined with MBPT2 or DFT electronic structure yields a rot-vibrational enthalpy of formation that is within roughly 0.2 kcal/mol of JANAF thermochemical enthalpy data. Similarly, we find that the PIMC method can improve the calculation of the heat capacity. The path integral thermochemistry method is of particular importance for temperatures above 2000K. Such temperatures are common in combustion processes. The anharmonic effects included in the PIMC method could also be important for floppy molecules and clusters at lower temperatures. The difference between PIMC and the traditional harmonic normal mode approximation is not always the same sign or magnitude, therefore there is clearly no simple scaling relationship that can be consistently exploited. The method presented allows the calculation of temperature dependent enthalpies without any experimental input. Although we have considered only triatomics here, the method is extendable to larger molecules. A typical calculation reported here required 2 weeks of computer time on a single processor. A massively parallel computation would make it possible to study larger systems. Of particular interest are molecules with partially hindered rotations, which are difficult to account for simply in traditional thermochemical methods.[7]

VI. ACKNOWLEDGMENTS

10

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TABLES

V	α (kcal/mol)
cc-pVDZ/B3LYP	-0.85
cc-pVTZ/B3LYP	-0.73
cc-pVDZ/MBPT2	-0.70
cc-pVTZ/MBPT2	-0.79
cc-pVDZ/CCSD	-0.54
cc-pVTZ/CCSD	-0.58
cc-pVDZ/CCSD(T)	-0.54
cc-pVTZ/CCSD(T)	-0.54

TABLE I. H_2O rot-vibrational anharmonic energy α at 3000K
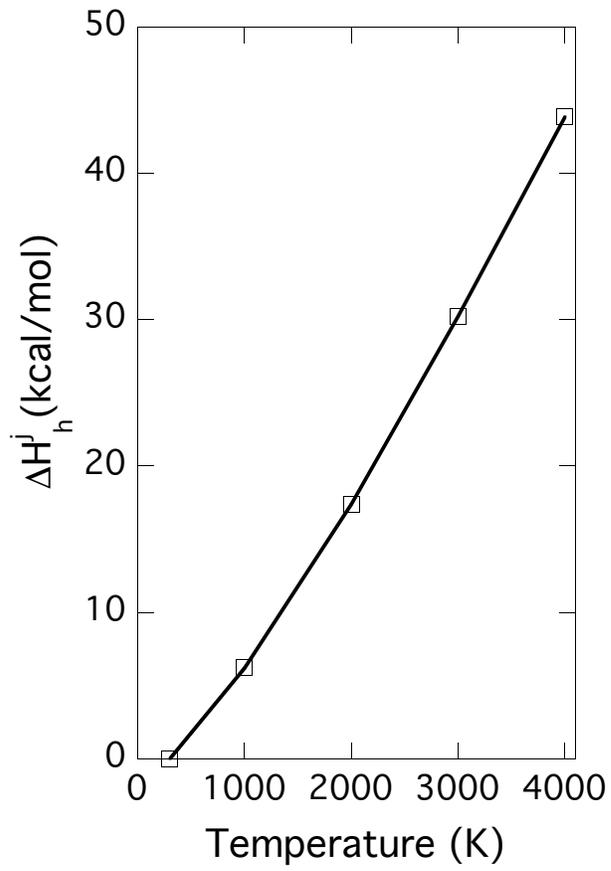
FIG. 1a. JANAF enthalpy of heating of H_2O.
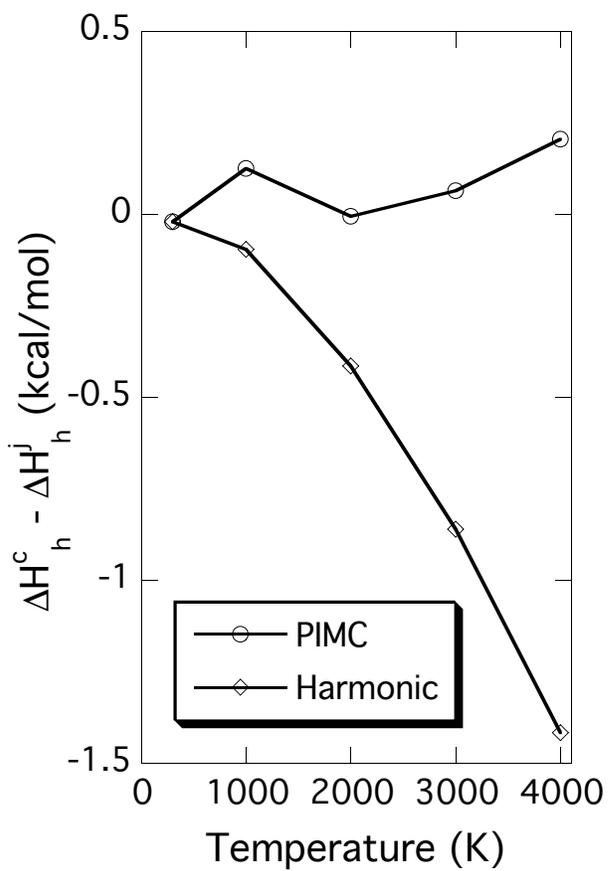
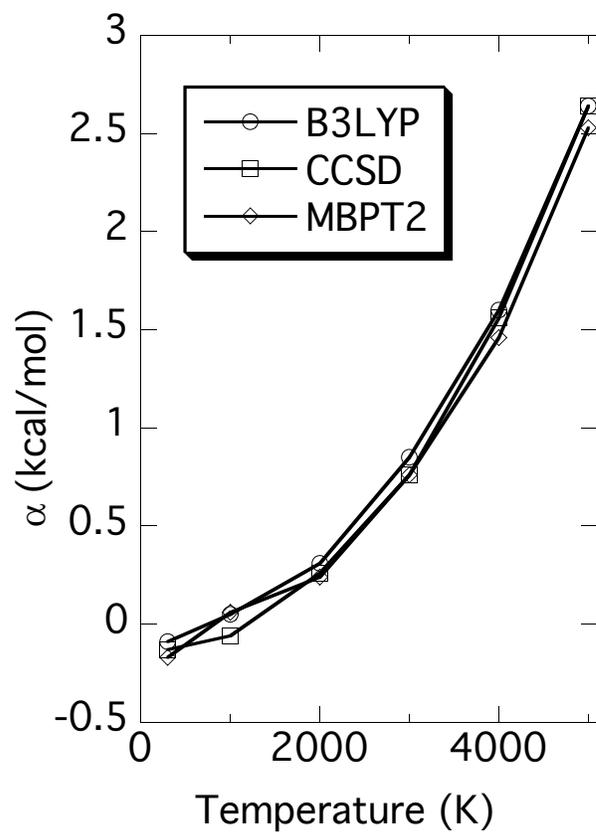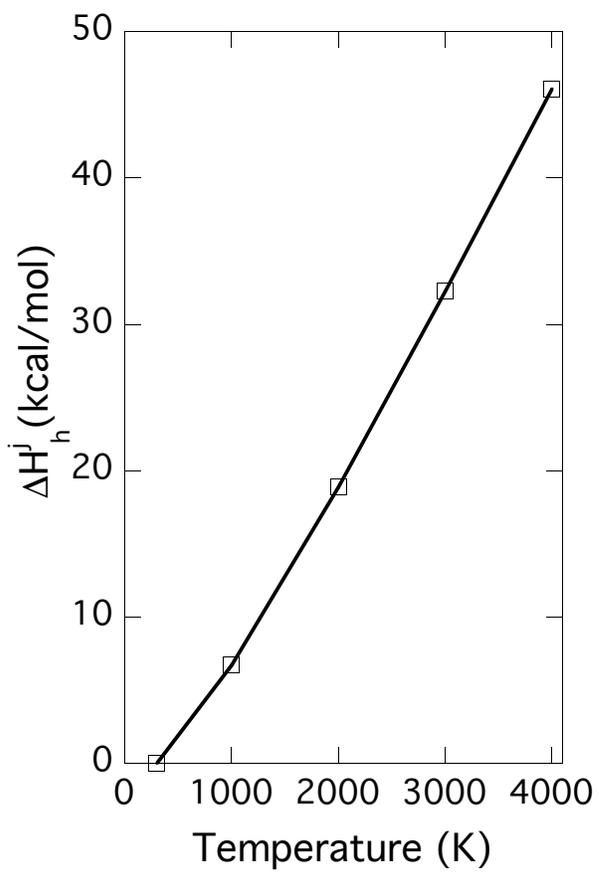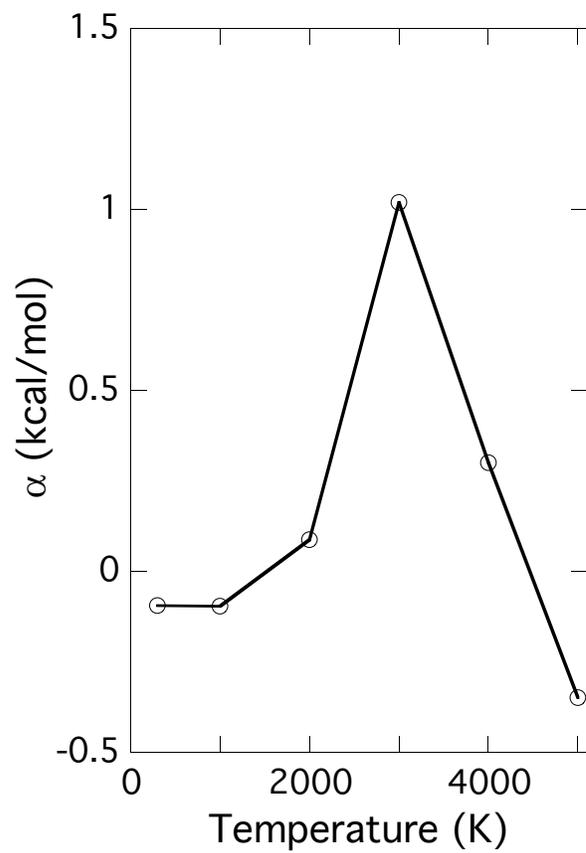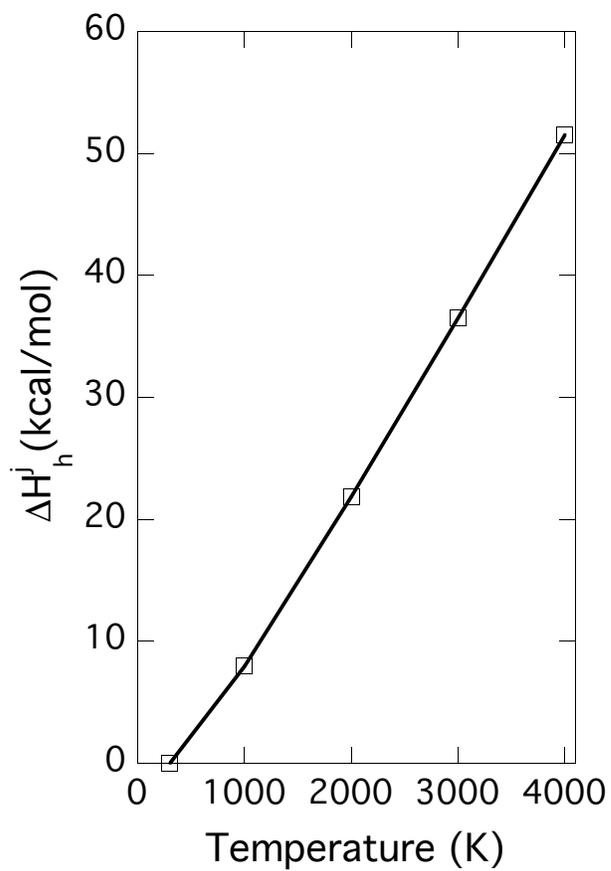FIG. 1b. Difference from JANAF values at the cc-pVDZ/MBPT2 level of theory.

FIG. 2. Anharmonic energy α of H_2O with cc-pVDZ basis set.

FIG. 3a. JANAF enthalpy of heating of CH$_2$.
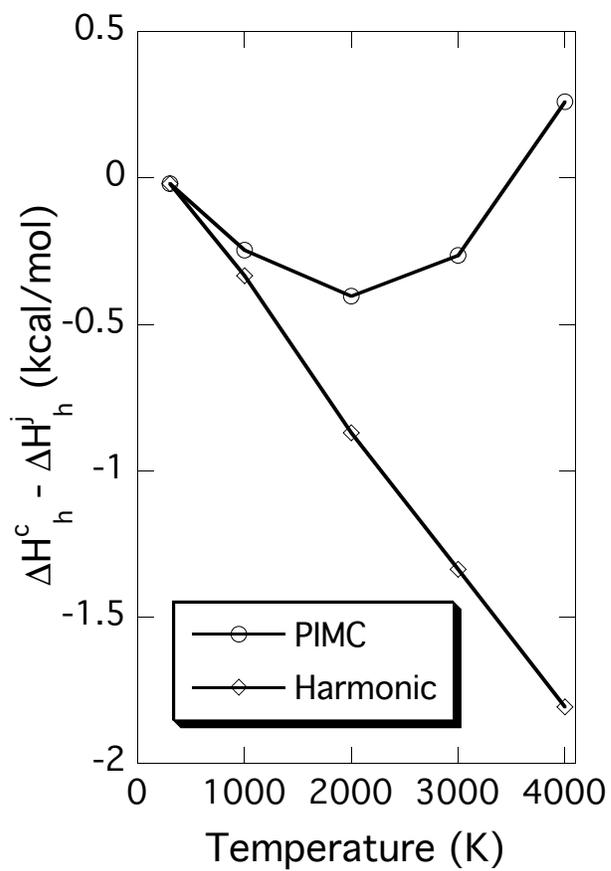
FIG. 3b. Difference from JANAF values at the cc-pVDZ/MBPT2 level of theory.

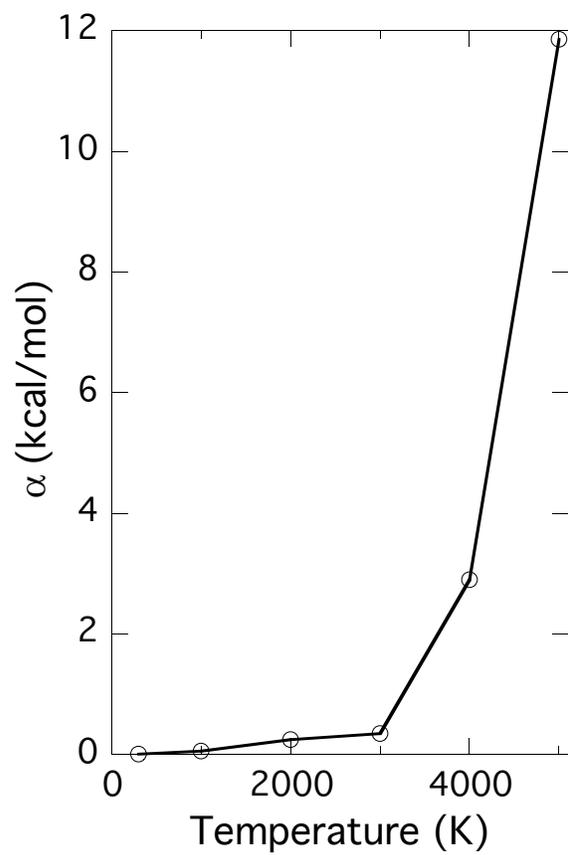FIG. 4. Anharmonic energy α of triplet CH_2 at the cc-pVDZ/UMBPT2 level of theory.

FIG. 5a. JANAF enthalpy of heating of CO_2.
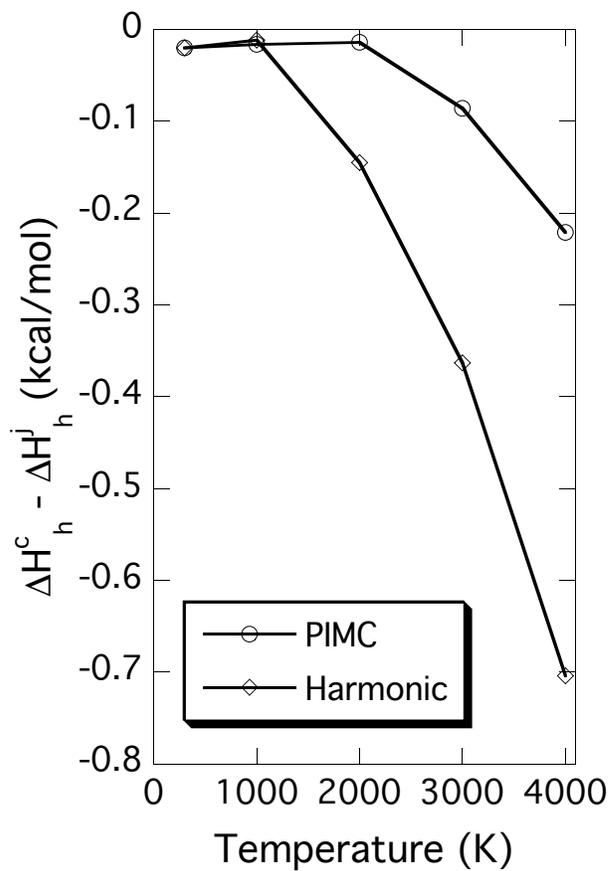
FIG. 5b. Difference from JANAF values at the cc-pVDZ/MBPT2 level of theory.

FIG. 6. Anharmonic energy α of HCN at cc-pVDZ/CCSD level of theory.
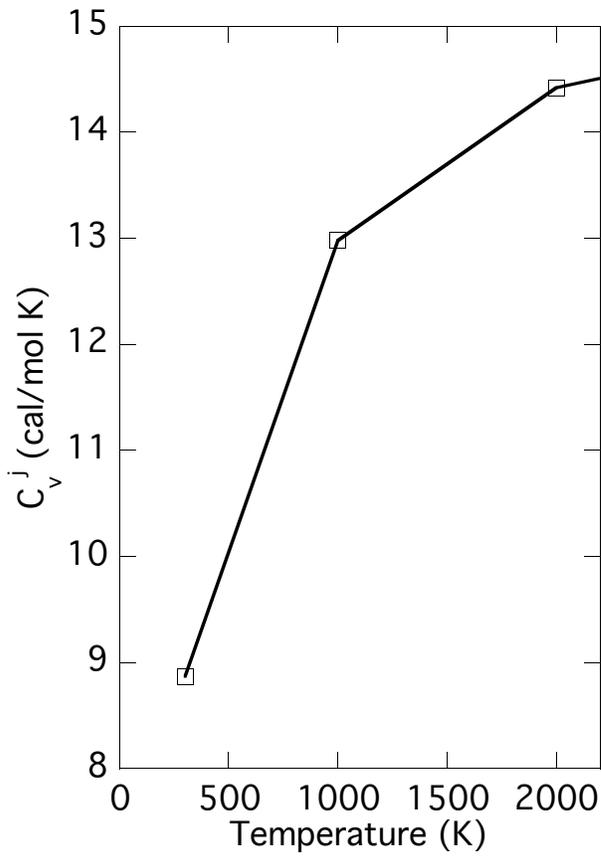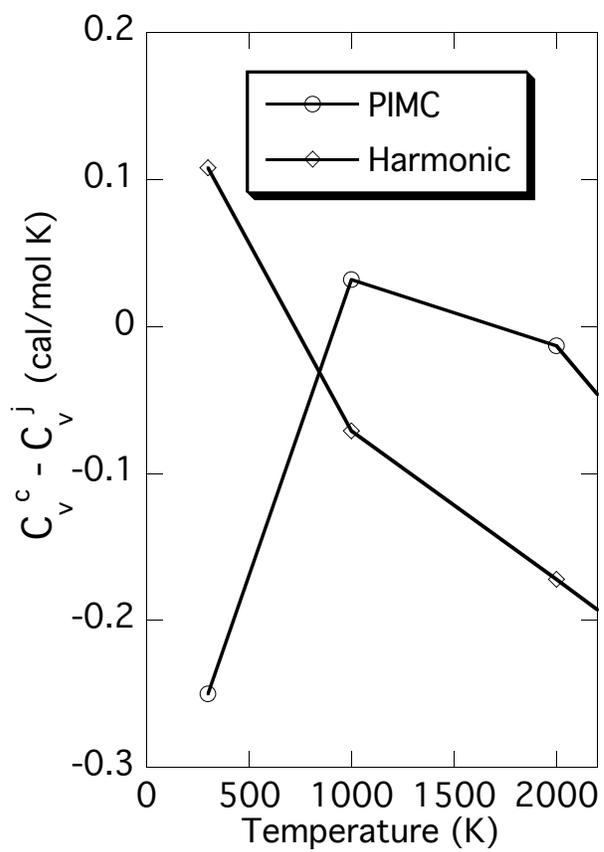
FIG. 7a. JANAF C_v of CO_2.

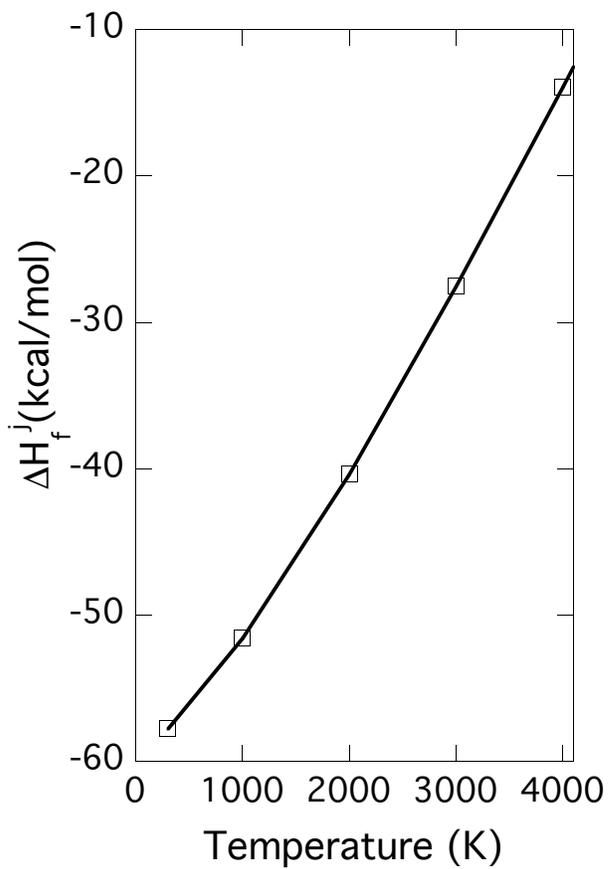FIG. 7b. Difference from JANAF values at the cc-pVDZ/MBPT2 level of theory.

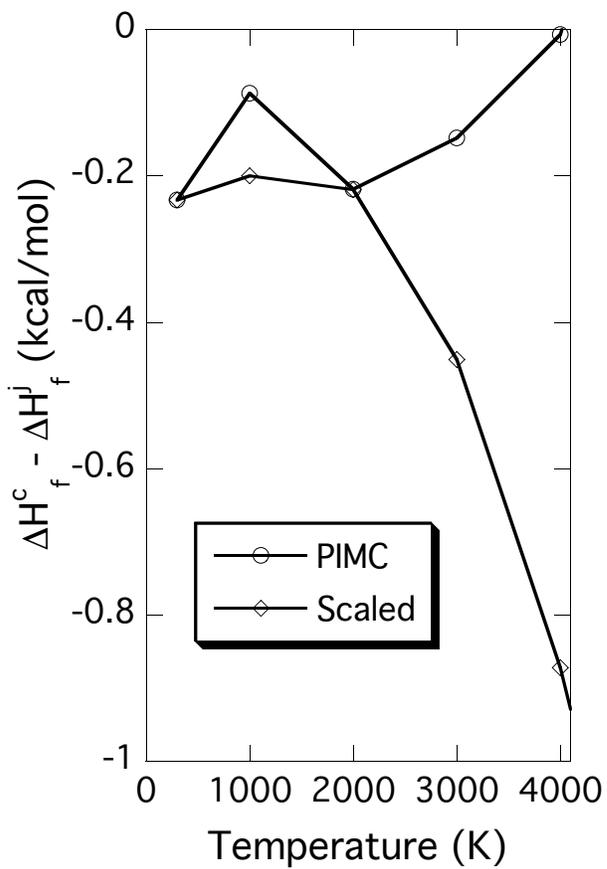FIG. 8a. JANAF enthalpy of formation of H_2O.

FIG. 8b. Difference from JANAF values for H_2O.