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Exploring the effect of anharmonicity of molecular vibrations on thermodynamic properties

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Thermodynamic properties of selected small and medium size molecules were calculated using harmonic and anharmonic vibrational frequencies. Harmonic vibrational frequencies were obtained by normal mode analysis, whereas anharmonic ones were calculated using the vibrational self-consistent field (VSCF) method. The calculated and available experimental thermodynamic data for zero point energy, enthalpy, entropy, and heat capacity are compared. It is found that the anharmonicity and coupling of molecular vibrations can play a significant role in predicting accurate thermodynamic quantities. Limitations of the current VSCF method for low frequency modes have been partially removed by following normal mode displacements in internal, rather than Cartesian, coordinates. © 2006 American Institute of Physics. [DOI: [10.1063/1.2395940](https://doi.org/10.1063/1.2395940)]

I. INTRODUCTION

Ab initio calculations provide data that can be used in evaluating, interpreting, or predicting experimental results pertaining to spectral and thermodynamic properties of molecules. This is especially important for larger molecules, for which obtaining and identifying all vibrational frequencies from experiment alone are quite often a very difficult task. Calculated frequencies and their intensities may be used to simulate vibrational spectra and compare them to experimental data to assign the experimental frequencies. Furthermore, the calculated frequencies can also be used to calculate thermodynamic properties that are not easy to obtain experimentally, and which impact the accuracy of *ab initio* calculations such as enthalpies of formation, reaction enthalpies, and activation energies.

The goal of the present work is to explore the effect of anharmonicity and coupling of molecular vibrations on the accuracy of calculated thermodynamic properties. Anharmonic, coupled vibrational frequencies were calculated using the vibrational self-consistent field (VSCF) method, which was first introduced in the late 1970s (Ref. 1) and further developed into the *ab initio* VSCF method with a second order perturbation theory correction²⁻⁴ that is used in the present work.

For some species, low vibrational frequencies calculated by the VSCF method overestimate experimental values by such a magnitude that it is impossible to obtain reliable thermodynamic properties. For these cases a different approach for generating the potential energy surface (PES), in which normal modes are displaced in internal,⁵ rather than Cartesian⁶ coordinates, is shown to be more reliable.

II. COMPUTATIONAL METHODS

A. Thermodynamic functions

Statistical thermodynamics is used to obtain macroscopic properties such as enthalpy, entropy, and heat capacity from molecular energy level *ab initio* calculations. Formulas for the thermodynamic functions of interest are summarized in Table I. Molecular partition functions can be expressed as products of translational, rotational, and vibrational partition functions, assuming that these types of motion are separable and noting that usually the electronic partition function can be taken as the degeneracy of the ground electronic state, which is unity for closed shell molecules. The rotational and translational partition functions were obtained using the usual rigid rotor-ideal gas approximations. Although vibrational thermodynamic functions apply rigorously only within the harmonic approximation, anharmonic frequencies can, as noted by Truhlar and Isaacson,⁷ be used to construct a simple approximation to the correct vibrational partition functions. This approximation has been shown to provide good agreement with more rigorous calculations.^{7,8} Among all thermodynamic properties entropy is, as shown in Appendix A, particularly sensitive to changes in low vibrational frequencies, which are frequently the most heavily affected by anharmonicity and coupling.

One can calculate the zero point vibrational energy in more than one way. A simple approach is to use the anharmonic frequencies in the simple (harmonic) energy expression given in Table I, where ν_i are the anharmonic frequencies obtained from VSCF calculations,^{2,4} as suggested by Truhlar and Isaacson.⁷ Alternatively, one can employ the VSCF vibrational energy levels to calculate the zero point energy (ZPE). The first method is consistent with both the approach described above for calculating the thermodynamic

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TABLE I. Thermodynamic functions. The volume $V=RT/p$, at pressure p and temperature T ; R is the gas constant; m is the mass of the molecule; k is Boltzmann's constant; h is planck's constant; I_A , I_B , and I_C are the principle moments of inertia; σ is the symmetry factor; f is the number of vibrational degrees of freedom ($3N-5$ for linear and $3N-6$ for nonlinear molecule with N being the number of atoms in the molecule); ν_i is the i th vibrational frequency.

Thermodynamic property	Function
Molecular partition function	$Q = Q_{tr} Q_{rot} Q_{vib} Q_{el}$
Translational partition function	$Q_{tr} = (2\pi mkT)^{3/2} h^{-3} V$
Translational enthalpy	$[H(T) - H(0)]_{tr} = (5/2)RT$
Translational entropy	$S_{tr} = R[(3/2)\ln(2\pi m/h^2) + (5/2)\ln(kT) - \ln(p) + 5/2]$
Translational heat capacity	$C_{p,tr} = (5/2)R$
Rotational partition function	$Q_{rot} = \frac{8\pi^2}{\sigma h^3} (2\pi kT)^{3/2} (I_A I_B I_C)^{1/2}$
Rotational enthalpy	$[H(T) - H(0)]_{rot} = (3/2)RT$
Rotational entropy	$S_{rot} = R[\ln(8\pi^2/\sigma) + (3/2)\ln(2\pi kT/h^2) + (1/2)\ln(I_A I_B I_C) + 3/2]$
Rotational heat capacity	$C_{p,rot} = (3/2)R$
Vibrational partition function	$Q_{vib} = \prod_{i=1}^f (1 - e^{-h\nu_i/kT})^{-1}$
Vibrational enthalpy	$[H(T) - H(0)]_{vib} = RT \sum_{i=1}^f \left(\frac{h\nu_i}{kT} \right) \frac{e^{-h\nu_i/kT}}{(1 - e^{-h\nu_i/kT})}$
Vibrational entropy	$S_{vib} = -R \sum_{i=1}^f \ln(1 - e^{-h\nu_i/kT}) + R \sum_{i=1}^f \left(\frac{h\nu_i}{kT} \right) \frac{e^{-h\nu_i/kT}}{(1 - e^{-h\nu_i/kT})}$
Vibrational heat capacity	$C_{p,vib} = R \sum_{i=1}^f \left(\frac{h\nu_i}{kT} \right)^2 \frac{e^{-h\nu_i/kT}}{(1 - e^{-h\nu_i/kT})}$
Total enthalpy	$[H(T) - H(0)]_{tot} = [H(T) - H(0)]_{tr} + [H(T) - H(0)]_{rot} + [H(T) - H(0)]_{vib}$
Total entropy	$S_{tot} = S_{tr} + S_{rot} + S_{vib}$
Total heat capacity	$C_{p,tot} = C_{p,tr} + C_{p,rot} + C_{p,vib}$
Zero point energy	$ZPE = \frac{1}{2} \sum_{i=1}^f \nu_i$

properties and the manner in which ZPEs, are reported in the NIST database,⁹ while the second method is directly related to the VSCF approach. Both sets of zero point energies are reported below.

B. Vibrational self-consistent field (VSCF) method

The foundation for the VSCF method is obtaining an accurate potential energy surface. As there is no analytic expression for the PES, one needs to calculate it on a grid. In order to choose grid points, the first step is to calculate the equilibrium geometry to obtain a starting point from which

the potential energy surface of the molecule may be explored. Then, a normal mode analysis at this structure provides normal mode frequencies and normal mode displacements, which define, respectively, how far and in which direction the PES will be explored. A normal mode displacement can be expressed in terms of Cartesian or internal coordinates (e.g., bond lengths, angles, and torsions). Since normal modes are delocalized, with more than one internal coordinate involved in a particular vibrational motion, one can express each vibrational motion as a sum of contributions of all internal coordinates, such that this sum satisfies completeness and symmetry requirements.

As the normal mode analysis is done in the harmonic approximation without coupling of molecular vibrations, one may generate the PES by making two types of displacements from the equilibrium geometry: along each normal mode separately or along two or more normal modes simultaneously. The first type of displacement generates the so-called diagonal potential, which reflects the anharmonicity along each normal mode. The second type of displacement gives rise to the coupling potential, which measures the coupling of vibrations involved in the displacement.

There are several approaches for generating a PES on a grid. Two of these were employed in this work, namely, direct and quartic force field (QFF) methods. In the direct approach² electronic structure calculations are done at 16 points along each normal mode to explore anharmonicity of the particular mode, and 16×16 grid points following the simultaneous displacements along two normal modes in order to describe pairwise coupling of molecular vibrations. The direct method yields accurate results, but it is computationally very demanding, so for larger molecules the PES was generated in the QFF approximation,⁴ a fourth order Taylor expansion of the PES as a function of mass-weighted normal coordinates. The expansion coefficients are determined by differentiation of the energy, which requires electronic structure calculations at only 6 points along each normal mode and 12 points along each pair of normal modes. These expansion coefficients are then used to calculate the potential for 16 points along each normal mode and 16×16 grid points for pairwise coupling. The obtained PES is used to solve the vibrational Schrödinger equation in mass-weighted normal coordinates Q_i given by

$$\hat{H}_{vib} \Psi_n(Q_1, \dots, Q_f) = E_n \Psi_n(Q_1, \dots, Q_f), \quad (1)$$

where the vibrational Hamiltonian \hat{H}_{vib} is

$$\hat{H}_{vib} = -\frac{1}{2} \sum_{i=1}^f \frac{\partial^2}{\partial Q_i^2} + V(Q_1, \dots, Q_f). \quad (2)$$

The VSCF method is based on the separability of normal mode vibrations:

$$\Psi_n(Q_1, \dots, Q_f) = \prod_{i=1}^f \psi_i^{(n)}(Q_i). \quad (3)$$

One can then rewrite the Schrödinger equation in terms of a set of single-mode VSCF equations:

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + \bar{V}_i^{(n)}(Q_i) \right] \psi_i^{(n)}(Q_i) = \varepsilon_i^{(n)} \psi_i^{(n)}(Q_i), \quad (4)$$

where $\bar{V}_i^{(n)}(Q_i)$ is an effective potential energy operator

$$\bar{V}_i^{(n)}(Q_i) = \left\langle \prod_{j \neq i} \psi_j^{(n)}(Q_j) \middle| V(Q_1, \dots, Q_f) \middle| \prod_{j \neq i} \psi_j^{(n)}(Q_j) \right\rangle. \quad (5)$$

The potential energy, $V(Q_1, \dots, Q_f)$, is a sum of diagonal and coupling potentials calculated on the grid:

$$V(Q_1, \dots, Q_f) = \sum_{i=1}^f V_i(Q_i) + \sum_i \sum_{j < i} V_{ij}(Q_i, Q_j). \quad (6)$$

Equations (4) and (5) are solved self-consistently using the collocation method¹⁰ to obtain the vibrational energy levels at the VSCF level of theory:

$$E_n^{\text{VSCF}} = \sum_{i=1}^f \varepsilon_i^{(n)} - (f-1) \times \left\langle \prod_{i=1}^f \Psi_i^{(n)}(Q_i) \middle| V(Q_1, \dots, Q_f) \middle| \prod_{i=1}^f \Psi_i^{(n)}(Q_i) \right\rangle. \quad (7)$$

In this sense, the VSCF equations are analogous to the Hartree-Fock equations in electronic structure theory. From this analogy, it follows that the VSCF method alone will not generally provide sufficient accuracy. One approach for further improvement is to employ second order perturbation theory. The second order perturbation theory corrected vibrational energy levels (VSCF-PT2) are given by

$$E_n^{\text{VSCF-PT2}} = E_n^{\text{VSCF}} + \sum_{m \neq n} \frac{\left| \left\langle \prod_{i=1}^f \psi_i^{(n)}(Q_i) \middle| \Delta V \middle| \prod_{i=1}^f \psi_i^{(m)}(Q_i) \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}}, \quad (8)$$

where the perturbation potential ΔV is

$$\Delta V = V(Q_1, \dots, Q_f) - \sum_{i=1}^f \bar{V}_i^{(n)}(Q_i),$$

and the $E_n^{(0)}$ and $E_m^{(0)}$ are the sums of single-mode energies in the reference and excited states, respectively.

Anharmonic, coupled VSCF-PT2 vibrational frequencies are obtained as fundamental excitations from vibrational energy levels calculated at the VSCF-PT2 level of theory.^{2,4}

III. COMPUTATIONAL DETAILS

All computations were done using the GAMESS program suite,¹¹ and molecules were visualized in MacMolPlt.¹²

The basis sets used in this work include 6-31G(*d,p*),¹³ MIDI,¹⁴ pVTZ (Ref. 15) with diffuse functions,¹⁶ aug-cc-pVDZ,¹⁷ and aug-cc-pVTZ,¹⁷ with the Hartree-Fock [RHF (Ref. 18)], second order perturbation theory [MP2 (Ref. 19)], or coupled cluster [CCSD(T) (Ref. 20)] levels of theory. Details are given in the tables in the following section. The calculations on homonuclear and heteronuclear di-

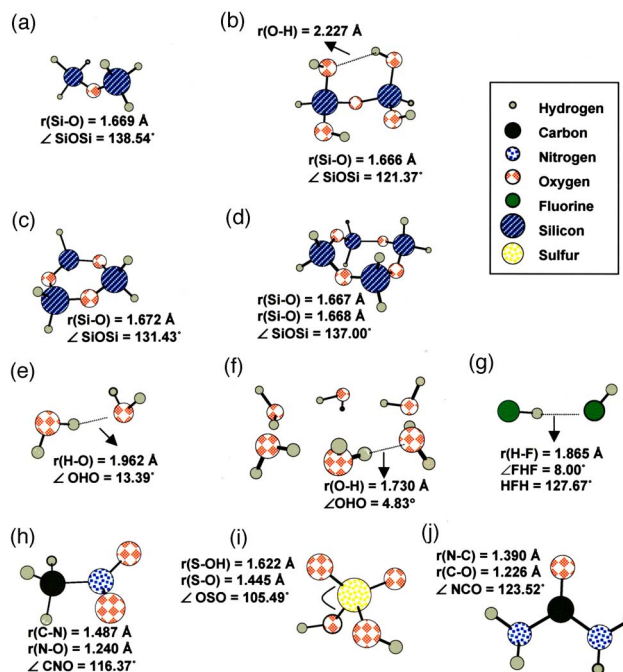


FIG. 1. MP2 optimized structures. Basis set is 6-31G(*d,p*), except for (HF)₂ where pVTZ with diffuse functions was used. (a) Disiloxane [(H₃Si)₂O] in C_{2v}; (b) 1,1,3,3-disiloxanetetrol (Si₂O₃H₆) in C₁; (c) Cyclotrisiloxane [(H₂SiO)₃] in D_{3h}; (d) Cyclotetrasiloxane [(H₂SiO)₄] in C₁; (e) Water dimer [(H₂O)₂] in C_s; (f) Water hexamer [(H₂O)₆] in C₁; (g) Hydrogen fluoride dimer [(HF)₂] in C_s; (h) Nitro-methane (CH₃NO₂) in C₁; (i) Sulfuric acid (H₂SO₄) in C₂; (j) urea [(H₂N)₂CO] in C₂.

atomic molecules employed *D*_{4h} and *C*_{4v} symmetries, respectively, while the remaining molecules were considered in their full point groups. Additional details can be found in Fig. 1.

The geometries for all of the molecules studied were tightly optimized²¹ with the largest component of the gradient required to be less than 1×10^{-5} hartree/bohr. CCSD(T) geometry optimizations were accomplished using numerical gradients. A normal mode analysis⁶ was performed, and the resulting harmonic frequencies and normal mode displacements were used to generate the PES on a 16×16 grid. VSCF calculations^{2,4} were done yielding anharmonic, VSCF-PT2 frequencies. Harmonic frequencies and VSCF-PT2 frequencies were then used to calculate thermodynamic properties of the molecules.

Two sets of calculations were performed to generate potential energy surfaces. For the first set of calculations harmonic frequencies and normal mode displacements in Cartesian coordinates were used to generate a PES on a grid directly² for all except the larger molecules such as (H₂O)₆, ((OH)₂HSi)₂O, (H₂SiO)₃, and (H₂SiO)₄ where a QFF (Ref. 4) generated PES was used instead. For the second set of calculations, for water, water dimer, sulfuric acid, and urea, normal mode displacements in both internal and Cartesian coordinates were used to generate a direct PES.² For infinitesimal displacements, there is no difference between the use of Cartesian or internal coordinates. However, since the VSCF procedure involves several finite steps along each normal mode direction, different points on the PES are sampled, depending on whether Cartesian or internal coordinates are

TABLE II. Zero point energies [$\delta(\text{har-anh})=ZPE_{\text{har}}-ZPE_{\text{anh}}$; $\delta(\text{har-calc})=ZPE_{\text{har}}-ZPE_{\text{calc(exptfreq)}}$; $\delta(\text{anh-calc})=ZPE_{\text{anh}}-ZPE_{\text{calc(exptfreq)}}$; $\delta(\text{expt-calc})=ZPE_{\text{expt}}-ZPE_{\text{calc(exptfreq)}}$; $\delta(\text{ELC-expt})=ZPE(0)_{\text{ELC}}-ZPE_{\text{expt}}$. Level of theory/basis set: MP2/6-31G(*d,p*), MP2/aug-cc-pVTZ, CCSD(T)/aug-cc-pVTZ, MP2/MIDI, and MP2/p-TZV with diffuse functions], (kcal/mol) calculated using harmonic formula: harmonic (ZPE_{har}), anharmonic (ZPE_{anh}), and experimental frequencies. Experimental frequencies are taken from Ref. 9 for all except diatomic molecules (Ref. 26), (HF)₂ (Ref. 41), (H_2O)₂ (Ref. 42).] ($ZPE_{\text{calc(exptfreq)}}$). $ZPE(0)_{\text{ELC}}$ is obtained directly from vibrational energy level calculations, whereas ZPE_{expt} is obtained from calculations using experimental constants for diatomic molecules (Ref. 39) or in the case of water molecule from PES defined in Ref. 40. H_2O_2 data are obtained from the vibrational results exchanged privately between Truhlar and Koput as published in Ref. 26.

Molecule	ZPE_{har}	ZPE_{anh}	$ZPE(0)_{\text{ELC}}$	$ZPE_{\text{calc(exptfreq)}}$	ZPE_{expt}	$\delta(\text{har-anh})$	$\delta(\text{har-calc})$	$\delta(\text{anh-calc})$	$\delta(\text{expt-calc})$	$\delta(\text{ELC-expt})$
H_2^{a}	6.59	6.26	6.53	5.94	6.38	0.33	0.64	0.32	0.43	0.15
H_2^{b}	6.29	5.94	6.23	5.94	6.38	0.35	0.35	-0.01	0.43	-0.15
HF^{a}	5.99	5.73	5.94	5.66	5.98	0.26	0.33	0.07	0.32	-0.04
HF^{b}	5.90	5.65	5.84	5.66	5.98	0.25	0.24	-0.01	0.32	-0.14
F_2^{a}	1.42	1.40	1.42	1.28	1.32	0.02	0.15	0.12	0.04	0.10
F_2^{c}	1.43	1.41	1.43	1.28	1.32	0.03	0.16	0.13	0.04	0.11
F_2^{b}	1.31	1.28	1.30	1.28	1.32	0.03	0.03	0.00	0.04	-0.02
Cl_2^{a}	0.77	0.77	0.77	0.79	0.80	0.01	-0.02	-0.03	0.01	-0.03
Br_2^{a}	0.47	0.47	0.47	0.47	0.47	0.00	0.01	0.00	0.00	0.00
I_2^{d}	0.33	0.33	0.33	0.31	0.31	0.00	0.02	0.02	0.00	0.02
$\text{H}_2\text{O}^{\text{a}}$	13.73	13.06	13.54	12.88	13.26	0.67	0.86	0.18	0.38	0.28
NH_3^{a}	22.26	21.02	21.87	20.63		1.23	1.63	0.39		
CH_4^{a}	29.20	28.22	28.83	27.11		0.99	2.10	1.11		
$\text{H}_2\text{O}_2^{\text{a}}$	16.73	15.71	16.46	15.90	16.37	1.02	0.83	-0.20	0.47	0.09
$\text{H}_2\text{S}_2^{\text{a}}$	12.14	11.61	11.97	11.16		0.53	0.98	0.45		
$\text{H}_2\text{SO}_4^{\text{a}}$	24.70	23.37	24.70	23.91		1.33	0.79	-0.54		
$\text{CH}_3\text{NO}_2^{\text{a}}$	32.32	31.55	32.13			0.77				
urea ^a	41.12	39.92	40.95	38.65		1.21	2.47	1.27		
$(\text{HF})_2^{\text{c}}$	13.69	14.11	14.25	12.81		-0.42	0.88	1.30		
$(\text{H}_2\text{O})_2^{\text{a}}$	29.73	29.34	30.44	27.51		0.38	2.22	1.84		
$(\text{H}_2\text{O})_6^{\text{a}}$	96.05	97.43	97.66			-1.38				
$(\text{H}_3\text{Si})_2\text{O}^{\text{a}}$	35.77	35.18		35.71		0.60				
$((\text{HO})_2\text{HSi})_2\text{O}^{\text{a}}$	52.82	52.00	53.22			0.82				
$(\text{H}_2\text{SiO})_3^{\text{a}}$	44.18	43.77	44.08			0.41				
$(\text{H}_2\text{SiO})_4^{\text{a}}$	59.34	58.43	59.18			0.92				

^aMP2/6-316(*d,p*).

^bCCSD(T)/aug-cc-pVTZ.

^cMP2/aug-cc-pVTZ.

^dMP2/MIDI.

^eMP2/p-TZV with diffuse functions.

employed. The larger the displacement, the more important this distinction becomes. For stiff modes with high vibrational frequencies, small linear (Cartesian) displacements provide a reasonable accounting of the region of the PES sampled during the VSCF procedure. For low frequency modes, frequently dominated by angle bends and torsions, a more sensible region of the PES is sampled if one chooses internal coordinates. A more rigorous approach, as discussed in detail by Gerber and co-workers,²²⁻²⁵ would be to reformulate the vibrational Hamiltonian in terms of internal or angular coordinates. However, it is shown below that the simple procedure used here can be very effective.

IV. RESULTS AND DISCUSSION

Molecules were chosen for this study based on the availability of experimental data, as well as the likelihood that some vibrational modes would exhibit significant anharmonicity. The latter include molecules with anharmonic modes due to hydrogen bonding, such as water dimer [$(\text{H}_2\text{O})_2$] and hydrogen-fluoride dimer [$(\text{HF})_2$], as well as some larger cyclic molecules with floppy vibrational motions, such as cyclotrisiloxane [$(\text{H}_2\text{SiO})_3$] and cyclotetrasiloxane [$(\text{H}_2\text{SiO})_4$]

(see Fig. 1). The largest molecule studied was the cyclic water hexamer [$(\text{H}_2\text{O})_6$] that combines both hydrogen bonding and floppy motions [Fig. 1(f)].

ZPE, enthalpy (ΔH^0), and entropy (ΔS^0) are given in Tables II-IV, while heat capacity (C_p^0) data are tabulated in Table VIII. Subscripts har, anh, and calc(exptfreq) represent calculations that employ a particular basis set and level of theory in which harmonic, anharmonic, or experimental frequencies, respectively, were used in partition functions in the rigid-rotor-harmonic-oscillator approximation. ZPE and thermodynamic properties calculated using experimental frequencies represent the limits of the approach in which harmonic partition functions are used. The subscript expt stands for experimental data.

A. Diatomic molecules

First, consider diatomic molecules. Heavier molecules, such as Cl_2 , Br_2 , and I_2 , do not exhibit significant anharmonic effects on the ZPEs. As shown in Table II, the ZPEs are very similar, regardless of the computational method: harmonic (ZPE_{har}), anharmonic (ZPE_{anh}), experimental frequencies ($ZPE_{\text{calc(exptfreq)}}$), VSCF energy level calculations

TABLE III. Enthalpy [$\Delta H = [H(0 \text{ K}) - H(298.15 \text{ K})]$]. $\delta(\text{anh-calc}) = \Delta H_{\text{calc}}^0 - \Delta H_{\text{calc}(\text{exptfreq})}^0$; $\delta(\text{har-anh}) = \Delta H_{\text{har}}^0 - \Delta H_{\text{anh}}^0$; $\delta(\text{har-expt}) = \Delta H_{\text{har}}^0 - \Delta H_{\text{expt}}^0$; $\delta(\text{anh-expt}) = \Delta H_{\text{anh}}^0 - \Delta H_{\text{expt}}^0$; $\delta(\text{calc-expt}) = \Delta H_{\text{calc}(\text{exptfreq})}^0 - \Delta H_{\text{expt}}^0$. Level of theory/basis set: MP2/6-31G(*d,p*), MP2/aug-cc-pVTZ, CCSD(T)/aug-cc-pVTZ, MP2/MIDI, and MP2/p-TZV with diffuse functions.] (kcal/mol) calculated using harmonic formula with harmonic (ΔH_{har}^0), anharmonic, (ΔH_{anh}^0), and experimental frequencies [Experimental frequencies are taken from Ref. 9 for all except diatomic molecules (Ref. 26) (HF)₂ (Ref. 41, and (H₂O)₂ (Ref. 42). ($\Delta H_{\text{calc}(\text{exptfreq})}^0$). Experimental enthalpy is given as ΔH_{expt}^0 . Experimental enthalpies are taken from Ref. 9, except for I₂ which is taken from Ref. 43.]

Molecule	ΔH_{har}^0	ΔH_{anh}^0	$\Delta H_{\text{calc}(\text{exptfreq})}^0$	ΔH_{expt}^0	$\delta(\text{anh-calc})$	$\delta(\text{har-anh})$	$\delta(\text{har-expt})$	$\delta(\text{anh-expt})$	$\delta(\text{calc-expt})$
H ₂ ^a	2.07	2.07	2.07	2.02	0.00	0.00	0.05	0.05	0.05
H ₂ ^b	2.07	2.07	2.07	2.02	0.00	0.00	0.05	0.05	0.05
HF ^a	2.07	2.07	2.07	2.06	0.00	0.00	0.01	0.01	0.01
HF ^b	2.07	2.07	2.07	2.06	0.00	0.00	0.01	0.01	0.01
F ₂ ^a	2.10	2.10	2.11	2.11	-0.01	0.00	-0.01	-0.01	0.00
F ₂ ^c	2.10	2.10	2.11	2.11	-0.01	0.00	-0.01	-0.01	0.00
F ₂ ^b	2.11	2.11	2.11	2.11	0.00	0.00	0.00	0.00	0.00
Cl ₂ ^a	2.20	2.20	2.19	2.19	0.01	0.00	0.01	0.00	0.00
Br ₂ ^a	2.31	2.31	2.32	2.32	-0.01	0.00	-0.01	-0.01	-0.01
I ₂ ^d	2.40	2.40	2.41	2.42	-0.01	0.00	-0.02	-0.02	-0.01
H ₂ O ^a	2.37	2.37	2.37	2.37	0.00	0.00	0.00	0.00	0.00
NH ₃ ^a	2.39	2.40	2.40	2.40	-0.01	-0.01	-0.01	0.00	0.00
CH ₄ ^a	2.39	2.39	2.40	2.39	-0.01	0.00	0.00	0.00	0.01
H ₂ O ₂ ^a	2.65	2.67	2.63	2.67	0.04	-0.02	-0.02	0.00	-0.04
H ₂ S ₂ ^a	2.72	2.75	2.76		-0.01	-0.03			
H ₂ SO ₄ ^a	3.87	4.07	3.85	3.95	0.22	-0.20	-0.08	0.12	-0.10
CH ₃ NO ₂ ^a	3.31	3.10		3.08		0.21	0.23	0.02	
urea ^a	3.28	3.30	3.46	3.49	-0.16	-0.01	-0.21	-0.19	-0.03
(HF) ₂ ^c	3.41	3.04	3.54		-0.50	0.37			
(H ₂ O) ₂ ^a	4.25	3.56	4.55		-0.99	0.69			
(H ₂ O) ₆ ^a	10.23	8.22				2.01			
(H ₃ Si) ₂ O ^a	4.35	4.13				0.21			
((HO) ₂ HSi) ₂ O ^a	6.54	6.20				0.34			
(H ₂ SiO) ₃ ^a	5.48	5.25				0.24			
(H ₂ SiO) ₄ ^a	7.41	7.12				0.29			

^aMP2/6-31G(*d,p*).

^bCCSD(T)/aug-cc-pVTZ.

^cMP2/aug-cc-pVTZ.

^dMP2/MIDI.

^eMP2/p-TZV with diffuse functions.

(ZPE(0)_{ELC}), or anharmonic ZPE calculated from an expansion in anharmonic constants²⁶ (ZPE_{expt}). On the other hand, light molecules such as H₂, HF, and F₂ do show discrepancies between ZPE_{har} and ZPE_{anh}, with the latter being closer to ZPE calculated from experimental frequencies.

Different levels of theory and different basis sets were utilized in order to explore convergence of ZPE_{anh} to ZPE_{calc(exptfreq)} for these light diatomic molecules. The MP2 level of theory with the small 6-31G(*d,p*) basis set gives better agreement than MP2 with the larger aug-cc-pVTZ basis set. On the other hand, CCSD(T) with the larger basis set gives excellent agreement between ZPE_{anh} and ZPE_{calc(exptfreq)}, while ZPE_{har} is off by ~ 0.25 kcal/mol, so that high accuracy in fundamental frequencies is achieved by including both very accurate electronic structure theory and a proper accounting for anharmonicity. The deterioration of MP2 predictions with improvements in the basis set has been noted previously.²⁷ It is likely that an even better basis set is needed to reach convergence of ZPE(0)_{ELC} to ZPE_{expt} for very light molecules such as H₂ and HF.

Although H₂, HF, and F₂ do show significant anharmonicity, thermodynamic properties such as enthalpy, entropy, and heat capacity are well described in the harmonic ap-

proximation for all diatomic molecules (see Tables III, IV, and VIII). Since the thermodynamic properties of interest are inversely proportional to the frequencies, changes in high frequencies due to anharmonicity do not result in significant changes in thermodynamic properties.

B. Molecules with stiff modes

Next, consider molecules with relatively stiff vibrational motions, such as H₂O, NH₃, and CH₄, or a relatively small degree of anharmonicity, as in H₂O₂, H₂S₂, H₂SO₄, CH₃NO₂, and urea (Table II).

Comparison of ZPE_{har} and ZPE_{anh} with ZPE_{calc(exptfreq)} demonstrates that ZPE_{anh} is ~ 1 kcal/mol more accurate than ZPE_{har}, because the calculated anharmonic vibrational frequencies are more accurate than harmonic ones. Next, compare ZPE_{anh} and ZPE(0)_{ELC}, obtained from vibrational energy level calculations, with ZPE_{expt}, obtained by extrapolation from experimental vibrational levels. For H₂O and H₂O₂, ZPE(0)_{ELC} are ~ 0.2 and ~ 0.6 kcal/mol, respectively, closer to ZPE_{expt} than ZPE_{anh}. Indeed, in general, the two methods used to calculate ZPE based on VSCF anharmonic frequencies are in very good agreement with each

TABLE IV. Entropy (cal/mol K) [$\delta(\text{anh-calc})=S_{\text{anh}}^0-S_{\text{calc(exptfreq)}}^0$; $\delta(\text{har-anh})=S_{\text{har}}^0-S_{\text{anh}}^0$; $\delta(\text{har-expt})=S_{\text{har}}^0-S_{\text{expt}}^0$; $\delta(\text{anh-expt})=S_{\text{anh}}^0-S_{\text{expt}}^0$; $\delta(\text{calc-expt})=S_{\text{calc(exptfreq)}}^0-S_{\text{expt}}^0$. Level of theory/basis sets: MP2/6-31G(*d,p*), MP2/aug-cc-pVTZ, CCSD(T)/aug-cc-pVTZ, MP2/MIDI, and MP2/p-TZV with diffuse functions.] calculated using harmonic formula with harmonic (S_{har}^0), anharmonic (S_{anh}^0), and experimental frequencies [Experimental frequencies are taken from Ref. 9, except diatomic molecules (Ref. 26), (HF)₂ (Ref. 41), and (H₂O)₂ (Ref. 42).] ($S_{\text{calc(exptfreq)}}^0$). Experimental entropy is S_{expt}^0 [Experimental entropies are taken from Ref. 9, except for H₂O₂ (Ref. 26) and I₂ (Ref. 43).].

Molecule	S_{har}^0	S_{anh}^0	$S_{\text{calc(exptfreq)}}^0$	S_{expt}^0	$\delta(\text{anh-calc})$	$\delta(\text{har-anh})$	$\delta(\text{har-expt})$	$\delta(\text{anh-calc})$	$\delta(\text{calc-expt})$
H ₂ ^a	31.08	31.08	31.08	31.23	0.00	0.00	-0.15	-0.15	-0.15
H ₂ ^b	31.13	31.13	31.13	31.23	0.00	0.00	-0.10	-0.10	-0.10
HF ^a	41.48	41.48	41.48	41.53	0.00	0.00	-0.05	-0.05	-0.05
HF ^b	41.48	41.48	41.48	41.53	0.00	0.00	-0.05	-0.05	-0.05
F ₂ ^a	48.40	48.41	48.45	48.47	-0.04	-0.01	-0.07	-0.06	-0.02
F ₂ ^c	48.34	48.34	48.44	48.47	-0.09	-0.01	-0.13	-0.13	-0.03
F ₂ ^b	48.42	48.44	48.39	48.47	0.05	-0.01	-0.05	-0.03	-0.08
Cl ₂ ^a	53.29	53.30	53.26	53.32	0.04	-0.01	-0.03	-0.02	-0.06
Br ₂ ^a	58.57	58.58	58.59	58.67	-0.01	-0.01	-0.10	-0.09	-0.08
I ₂ ^a	62.18	62.18	62.29	62.31	-0.11	-0.01	-0.13	-0.13	-0.02
H ₂ O ^a	45.09	45.09	45.06	45.13	0.03	0.00	-0.04	-0.04	-0.07
NH ₃ ^a	45.94	45.98	46.00	46.07	-0.02	-0.04	-0.13	-0.09	-0.07
CH ₄ ^a	44.43	44.44	44.46	44.54	-0.02	-0.01	-0.11	-0.10	-0.08
H ₂ O ₂ ^a	54.57	54.71	54.46	55.68	0.25	-0.14	-1.11	-0.97	-1.22
H ₂ S ₂ ^a	60.05	60.21	60.27	60.33	-0.06	-0.16	-0.28	-0.12	-0.06
H ₂ SO ₄ ^a	71.31	74.15	71.31	71.53	2.84	-2.85	-0.22	2.62	-0.22
CH ₃ NO ₂ ^a	69.38	65.61		65.77		3.77	3.61	-0.16	
urea ^a	64.82	65.01	65.92	66.42	-0.91	-0.19	-1.60	-1.41	-0.50
(HF) ₂ ^c	62.74	60.58	63.87	62.36	-3.29	2.16	0.38	-1.78	1.51
(H ₂ O) ₂ ^a	70.10	64.28	72.95		-8.67	5.82			
(H ₂ O) ₆ ^a	126.17	106.12				20.05			
(H ₃ Si) ₂ O ^a	77.23	73.11				4.12			
((HO) ₂ HSi) ₂ O ^a	94.21	91.32				2.90			
(H ₂ SiO) ₃ ^a	87.70	82.76				4.94			
(H ₂ SiO) ₄ ^a	107.47	101.83				5.64			

^aMP2/6-31G(*d,p*).

^bCCSD(T)/aug-cc-pVTZ.

^cMP2/aug-cc-pVTZ.

^dMP2/MIDI.

^eMP2/p-TZV with diffuse functions.

other at least for molecules with stiff vibrations, although if one strives for high accuracy the method of choice should be $ZPE(0)_{\text{ELC}}$.

Thermodynamic properties for polyatomic molecules with primarily stiff modes, such as water, ammonia, and methane (Tables III, IV, and VIII), do not exhibit significant discrepancies among the values calculated using the harmonic formula with harmonic, VSCF-PT2, or experimental frequencies, versus experimental data. The enthalpy (Table III) is well described in the harmonic approximation, with errors relative to experiment lower than 0.2 kcal/mol. This error can be reduced to <0.1 kcal/mol by using the harmonic partition function formula with accurate anharmonic frequencies ($\Delta H_{\text{calc(exptfreq)}}$).

Comparison of entropy values listed in Table IV for H₂S₂, CH₃NO₂, and urea shows the following trend in errors compared to experimental data: $S_{\text{har}}^0 > S_{\text{anh}}^0 > S_{\text{calc(exptfreq)}}^0$. This is to be expected, since the entropy is more sensitive to changes in low frequencies that are treated more accurately when anharmonicity is included in the calculation. Note that an unexpectedly high S_{anh}^0 is obtained for H₂SO₄. This is due to the error encountered when one uses Cartesian displacements in the VSCF-PT2 calculations for low frequency modes. This will be discussed in more detail below.

Although the main focus of this paper is on comparisons of calculated thermodynamic properties with available experimental data, it is worth mentioning the theoretical results obtained by Truhlar and co-workers employing accurate vibrational-rotational partition functions for CH₄ (Ref. 28) and H₂O₂ (Refs. 29 and 30) molecules. The calculated vibrational partition functions obtained in this work for CH₄ are 1.004 and 1.005 in the harmonic and anharmonic approximations, respectively. Both are in very good agreement with the 1.008 value predicted by Truhlar *et al.* This is to be expected at room temperature, since, as noted by Truhlar *et al.*, the rigid-rotor-harmonic-oscillator approximation is already very close to the accurate rovibrational partition function due to the lack of floppy modes in CH₄. For H₂O₂, the calculated $ZPE(0)_{\text{ELC}}=16.46$ kcal/mol is in very good agreement with the value of ~ 16.37 kcal/mol estimated by Lynch *et al.*³⁰ Finally, the calculated room temperature standard-state Gibbs free energy of 13.64 kcal/mol underestimates by less than 0.5 kcal/mol the more accurate values obtained by Lynch *et al.*²⁹ and Dorofeeva *et al.*³¹

C. Molecules with low frequency modes

Now, consider larger, highly anharmonic systems with hydrogen bonding and other floppy motions. These mol-

TABLE V. MP2 vibrations of H₂O and (H₂O)₂. Experimental frequencies are taken from Ref. 9 for H₂O and Ref. 42 for (H₂O)₂. [acc: hydrogen acceptor molecule; donor: hydrogen donor molecule; $\nu 1$ refers to symmetric stretch, $\nu 2$ to bend, $\nu 3$ to asymmetric stretch; OPB: out-of-plan bend; IPB: in-plane bend; S: intermolecular stretch; AT: acceptor twist; AW acceptor wag; DT: donor torsion.]

Water monomer							
6-31G(<i>d,p</i>)	Har	VSCF-PT2(Cart)	VSCF-PT2(int)	Expt.	% err(har)	% err(anh)cart	% err(anh)int
asym str $\nu 3$	4033	3938	3948	3756	7.4	4.8	5.1
sym str $\nu 1$	3893	3803	3822	3657	6.5	4.0	4.5
bend $\nu 2$	1680	1622	1628	1595	5.3	1.7	2.1
aug-cc-pVDZ	Har	VSCF-PT2(Cart)	VSCF-PT2(int)	Expt.	% err(har)	% err(anh)Cart	% err(anh)Int
asym str $\nu 3$	3811	3717	3739	3756	1.5	1.0	0.5
sym str $\nu 1$	3711	3621	3651	3657	1.5	1.0	0.2
bend $\nu 2$	1615	1557	1562	1595	1.3	2.4	2.1
aug-cc-pVTZ	Har	VSCF-PT2(cart)	VSCF-PT2(int)	Expt.	% err(har)	% err(anh)Cart	% err(anh)int
asym str $\nu 3$	3851	3837	3777	3756	2.5	2.2	0.6
sym str $\nu 1$	3723	3712	3663	3657	1.8	1.5	0.2
bend $\nu 2$	1652	1583	1598	1595	3.6	0.8	0.2
Water dimer							
6-31G(<i>d,p</i>)	Har	VSCF-PT2(Cart)	VSCF-PT2(int)	Expt.	% err(har)	% err(anh)Cart	% err(anh)int
acc $\nu 3$	4010	3700	3860	3745	7.1	1.2	3.1
donor $\nu 3$	4001	3725	3851	3735	7.1	0.3	3.1
acc $\nu 1$	3878	3635	3714	3660	6.0	0.7	1.5
donor $\nu 1$	3819	3564	3689	3601	6.1	1.0	2.5
donor $\nu 2$	1713	1671	1668	1616	6.0	3.4	3.2
acc $\nu 2$	1678	1596	1652	1599	5.0	0.2	3.3
OPB	665	742	535	523	27.1	41.9	2.3
IPB	429	589	178	311	38.0	89.4	42.9
S	204	161	182	143	42.5	12.5	27.2
AT	162	434	113	108	49.9	301.7	4.9
AW	144	313	130	103	39.9	203.9	25.9
DT	89	396	108	88	1.6	349.6	22.8
aug-cc-pVDZ	Har	VSCF-PT2(Cart)	VSCF-PT2(int)	Expt.	% err(har)	% err(anh)Cart	% err(anh)int
acc $\nu 3$	3925	3624	3801	3745	4.8	3.2	1.5
donor $\nu 3$	3905	3667	3747	3735	4.5	1.8	0.3
acc $\nu 1$	3796	3553	3629	3660	3.7	2.9	0.9
donor $\nu 1$	3705	3466	3578	3601	2.9	3.8	0.6
donor $\nu 2$	1643	1598	1598	1616	1.6	1.1	1.1
acc $\nu 2$	1624	1557	1598	1599	1.6	2.7	0.1
OPB	639	733	483	523	22.2	40.0	7.5
IPB	357	544	289	311	14.9	75.0	7.2
S	184	163	192	143	28.3	14.1	34.1
AT	150	420	122	108	39.2	289.0	12.6
AW	148	325	127	103	43.3	215.3	23.1
DT	128	431	91	88	45.0	389.7	3.1

ecules are listed in Tables II–IV starting with (HF)₂ and ending with (H₂SiO)₄. ZPE_{har} and ZPE_{anh} differ by ~0.4–1.4 kcal/mol (Table II). Similar differences are observed among harmonic and anharmonic enthalpies, entropies, and heat capacities (Tables III, IV, and VIII). Unfortunately, there are little available experimental data for comparison. Reported experimental entropies for (HF)₂ range from 57.08 (Ref. 26) to 62.36 (Ref. 9) cal/mol K, and experimental heat capacities for this species range from 10.71 (Ref. 26) to 13.89 (Ref. 9) cal/mol K. The calculated values are in the upper ends of these ranges. Nevertheless, it is interesting to note that for all these molecules, thermody-

namic properties calculated with anharmonic frequencies have lower values than those calculated using harmonic frequencies. In the absence of experimental data, this is surprising. Generally, one expects that anharmonicity and coupling will both lower vibrational frequencies and consequently increase the enthalpy, entropy, and heat capacity. Since these three thermodynamic properties increase as frequencies decrease, the observed trend should be the reverse of the predictions for these species.

The origin of this unusual behavior lies in the manner in which low frequency motions are treated in the usual VSCF computation of the PES. Comparison of VSCF-PT2 frequen-

cies with experimental frequencies shows that coupling and anharmonicity for $(\text{H}_2\text{O})_2$ and $(\text{HF})_2$ are overestimated by the VSCF method. This results in predicted frequencies that can be much too high, as illustrated in Table V. For example, for water dimer the three lowest VSCF-PT2 frequencies lying below 200 cm^{-1} calculated employing normal mode displacements in Cartesian coordinates [VSCF-PT2(Cart)] give values that overestimate experimental frequencies by $200\text{--}300\text{ cm}^{-1}$, while harmonic frequencies are off by less than 60 cm^{-1} . It is revealing that VSCF-PT2(Cart) gives much better agreement with experimental bond-stretching frequencies than with angle bends or torsions, even though the bond stretches may also be low frequency. An example is the hydrogen bonded intermolecular stretch in $(\text{H}_2\text{O})_2$ which is better described with VSCF-PT2(Cart) with an error of 20 cm^{-1} versus the harmonic approximation error of 40 cm^{-1} .

So, in general, low frequency bending and torsion motions are better described in the harmonic approximation than by VSCF-PT2 with a PES based on normal mode displacements in Cartesian coordinates. One approach to solving this problem³² might be to use harmonic frequencies for low frequency modes that are dominated by angle bends and torsions, rather than VSCF-PT2 frequencies. However, this is not a general (or satisfying) solution since low frequency modes can be rather mixed. Of course, the most desirable approach would be to reformulate the vibrational Hamiltonian in terms of curvilinear coordinates,^{22,24,25,33} but this is difficult to accomplish in the general case.

D. Cartesian versus internal displacement coordinates

To a large degree, the origin of the partial failure of the VSCF approach lies not in the VSCF method itself but rather in the manner in which the potential energy surface is generated, since the quality of the results can only be as good as the calculated PES. The VSCF method consists of two crucial steps: (1) the calculation of the diagonal frequencies and (2) the calculation of the VSCF frequencies. Each diagonal frequency is calculated from PES grid points along the corresponding normal mode, whereas the VSCF frequencies depend on the PES along n normal modes, where n is the number of normal modes that are coupled in the calculation. This means that the diagonal frequencies and the associated PES grid points should reflect the anharmonicity of the corresponding normal mode, while the VSCF frequencies and the corresponding PES grid points should reflect the coupling of molecular vibrations. Since grid points determined from normal mode displacements in Cartesian coordinates do not preserve any particular internal coordinate; the calculated diagonal frequency does not correspond to a stretch, bend, or torsion but rather to some mixture of these internal coordinates. Especially for low frequency/high amplitude vibrations, linear (Cartesian) displacements will therefore not capture the correct potential energy surface. The linear displacements result in artificially high coupling of all vibrations since they all have mixed character. Because stretching motions are essentially linear, this problem primarily impacts bends and torsions. The latter are linear only for infinitesimal

TABLE VI. MP2/aug-cc-pVDZ thermodynamic properties for the water dimerization reaction at $T=373\text{ K}$ and $P=1\text{ bar}$.

Thermodynamic property	Har	VSCF-PT2 (Cart)	VSCF-PT2 (int)	Expt.
ΔH [kcal/(mol K)]	-3.42	-3.11	-3.27	-3.59 ± 0.5^a
ΔS [cal/(mol K)]	-19.71	-25.85	-17.68	-18.59 ± 1.30^a
K_p (atm^{-1})	0.0050	0.0001	0.0113	0.0064^b 0.0110^a 0.0160^c

^aEstimated from thermal conductivity measurements by Curtiss *et al.* (Ref. 34).

^b $K_p \approx 0.0293[(e^{D_0/kT} - 1)/T]$, where $D_0 = 3.27\text{ kcal/mol}$ as fitted to thermodynamic data by Evans and Vaida (Ref. 36).

^c $K_p = -(B - b_0)/RT$, where $B(373\text{ K}) = 452.3\text{ cm}^3/\text{mol}$ was determined by Harvey and Lemmon (Ref. 35) and $b_0 = 38.5\text{ cm}^3/\text{mol}$ was estimated by Curtiss *et al.* (Ref. 34).

displacements, and the higher the amplitude of these types of vibrations, the worse the linear (Cartesian) displacements become.

Expanding the PES in terms of internal coordinate displacements can at least partially solve this problem. This new approach has been applied to water, water dimer, sulfuric acid, and urea. Water dimer is of particular importance, because it has many floppy modes that cannot be successfully treated using Cartesian displacements.

Table V compares H_2O and $(\text{H}_2\text{O})_2$ vibrational frequencies obtained by harmonic normal mode analysis (har), VSCF based on a PES generated in Cartesian (VSCF-PT2 Cart), and internal (VSCF-PT2 int) displacements with experimental frequencies (expt). For water molecule, which has mostly stiff modes, there is still a small improvement when internal displacements are used, especially for the bend with the larger basis sets. Indeed, it seems to be a general trend that when one uses larger basis sets, the performance of internal versus Cartesian displacements improves considerably. However, for H_2O , the bend frequency is $\sim 1600\text{ cm}^{-1}$, so an improvement of $\sim 35\text{ cm}^{-1}$ (for internal versus Cartesian displacements) has only a small effect on predicted thermodynamic properties (see Table VI). Calculated enthalpy and entropy are 2.37 kcal/mol and 45.09 cal/(mol K) , which are in excellent agreement with experimental data of $[H(T) - H(0\text{ K})] = 2.37\text{ kcal/mol}$ and $S = 45.13\text{ cal/(K T)}$.

For $(\text{H}_2\text{O})_2$, the use of smaller basis sets, such as 6-31G(d), with the use of internal displacements in the VSCF method introduces errors in the higher frequency modes, especially O-H stretches. As the basis set is improved to aug-cc-pVDZ, even the errors in these stiffer modes are smaller for internal displacements than for Cartesian displacements. For the weaker, intermolecular modes, for all basis sets, one observes very large errors when Cartesian displacements are employed, for the reasons discussed above. These errors range from ~ 200 to $\sim 350\text{ cm}^{-1}$. Following the normal mode displacements in internal coordinates lowers these errors to 50 cm^{-1} or less.

The impact of using internal versus Cartesian displacements is illustrated in Fig. 2 for $(\text{H}_2\text{O})_2$. Displacements

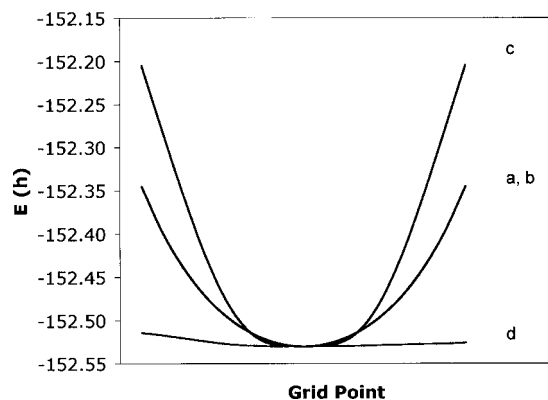


FIG. 2. Potential energy surface sampled along stiff [(a) and (b)] symmetric H–O stretch in the acceptor molecule and along floppy [(c) and (d)] donor torsion vibrational modes. (a) Diagonal potential sampled along symmetric H–O stretch in the acceptor molecule by following normal mode displacements in Cartesian coordinates. (b) Diagonal potential sampled along symmetric H–O stretch in the acceptor molecule by following normal mode displacements in internal coordinates. (c) Diagonal potential sampled along donor torsion vibration by following normal mode displacements in Cartesian coordinates. (d) Diagonal potential sampled along donor torsion vibration by following normal mode displacements in internal coordinates.

relative to the equilibrium geometry, in terms of Cartesian or internal coordinates, for two modes of $(\text{H}_2\text{O})_2$: the high frequency symmetric H–O stretch in the acceptor molecule [curves (a) and (b)] and the low frequency donor torsion vibration [curves (c) and (d)] are shown. Plotted on the y axis are the energy changes due to each displacement. Plotted on the x axis are the equally spaced displacements themselves, calculated as rms changes relative to the equilibrium geometry. The plotted displacements, in mass-weighted Cartesian coordinates, depend on whether the actual displacements are obtained in internals or Cartesians, since the internals are in general a composite of stretches, bends, and torsions. There is a dramatic difference in the PES sampled along the low frequency donor torsion vibration, depending on whether Cartesian [curve (c)] or internal [curve (d)] displacements are employed. In contrast, the PES sampled along the high frequency H–O stretching mode is independent of which displacement coordinates is used, since curves (a) and (b) are essentially indistinguishable. Typically, internal displacements (especially for angle bends and torsions) correspond to

TABLE VII. MP2/6–31G(*d,p*) vibrational frequencies of H_2SO_4 and urea molecules.

Mode	Har	H_2SO_4						
		VSCF-PT2 Cart	VSCF-PT2 int	Expt.	%err(har)	%err(anh) Cart	%err(anh) int	
1	3825	3575	3660	3567	7.2	0.2	2.6	
2	3820	3488	3653	3563	7.2	2.1	2.5	
3	1491	1467	1471	1452	2.7	1.0	1.3	
4	1228	1214	1212	1216	1.0	0.2	0.3	
5	1189	1139	1164	1157	2.8	1.6	0.6	
6	1172	1118	1131	1136	3.2	1.6	0.4	
7	873	855	860	882	1.0	3.1	2.5	
8	810	797	797	831	2.5	4.1	4.1	
9	529	543	528	558	5.2	2.7	5.4	
10	527	521	527	548	3.8	4.9	3.8	
11	477	451	473	506	5.7	10.9	6.5	
12	428	429	393	422	1.4	1.7	6.9	
13	358	351	341	379	5.5	7.4	10.0	
14	312	350	262	288	8.3	21.5	9.0	
15	240	53	216	224	7.1	76.3	3.6	
		Urea						
24	3790	3597	3715	3545	6.9	1.5	4.8	
23	3790	3585	3714	3535	7.2	1.4	5.1	
22	3662	3469	3528	3440	6.4	0.8	2.6	
21	3659	3468	3589	3440	6.4	0.8	4.3	
20	1866	1832	1840	1740	7.2	5.3	5.7	
19	1677	1635	1722	1590	5.5	2.8	8.3	
18	1667	1656	1651	1590	4.8	4.2	3.8	
17	1454	1420	1425	1393	4.4	2.0	2.3	
16	1205	1192	1184	1145	5.2	4.1	3.4	
15	1084	1079	1051	1004	7.9	7.5	4.7	
14	972	957	950	940	3.5	1.8	1.1	
13	794	809	795	785	1.1	3.1	1.3	
12	649	695	593	580	11.9	19.9	2.2	
11	595	684	642	555	7.3	23.3	15.7	
10	560	553	554	543	3.1	1.9	2.0	
9	476	485	482	500	4.8	3.0	3.5	
8	458	516	455	479	4.5	7.7	5.1	
7	409	291	388	233	75.7	24.7	66.5	

a tighter set of points (smaller displacements in Cartesian space) than do displacements that are obtained directly in Cartesian space.

More accurate frequencies are expected to lead to more accurate thermodynamic properties. There are no experimental data available for water dimer; however, experimental and calculated thermodynamic data for the reaction corresponding to water dimerization^{34–37} are compared in Table VI. Since thermodynamic properties for water monomer are not significantly affected by a small degree of anharmonicity, the calculated reaction enthalpy and entropy reflect the anharmonicity and coupling present in the water dimer. Although there is a need for more precise experimental measurements, the best calculated results (obtained from internal displacements along the PES) of $\Delta H = -3.27$ kcal/mol and $\Delta S = -17.68$ cal/(mol K) are within the experimental error bars. These values were used to calculate $K_p = \exp(-\Delta H/RT + \Delta S/R)$. The calculated $K_p = 0.0113$ atm⁻¹ using internal displacements falls within the range of available experimental data.^{34–36} Note that the use of Cartesian displacements produces thermodynamic properties for this reaction that are in much worse agreement with the experimental values. The values obtained using the harmonic approximation are not in as good agreement with experiment as are the VSCF-PT2 results if internal displacements are used, but (as noted above) the harmonic approximation is much better than VSCF-PT2 if one uses Cartesian displacements.

The calculated ΔH , ΔS , and K_p reflect the important effect of anharmonicity and coupling of molecular vibrations on thermodynamic properties. Including the anharmonicity and vibration coupling lowers both enthalpy and (especially) entropy, as suggested in Sec. II A, thereby increasing K_p . This trend in entropy and K_p behavior is in accord with the published work of Muñoz-Caro and Niño,³⁸ although their best calculated $K_p = 0.0034$ atm⁻¹ is too small compared to experiment, and they do report an increase in ΔH with anharmonic correction.

Because sulfuric acid and urea are large molecules, only the modest 6-31G(*d,p*) basis set was used with MP2 for VSCF calculations on these molecules. Table VII lists the experimental and calculated vibrational frequencies for H₂SO₄. As noted for water dimer, the predicted frequencies for the stiffer modes deteriorate a bit. Based on the water dimer calculations, this would be corrected if a larger basis set was used. On the other hand, the use of Cartesian displacements for the lower frequency modes leads to very poor frequencies, whereas there is considerable improvement when internal displacements are used. This suggests that better basis sets are required to obtain consistently reliable VSCF calculations with internal displacements. The analogous comparison for urea is similar, although the error for the smallest known experimental frequency is larger for internal displacements than for Cartesian displacements. This may have several origins, including the need for better atomic basis sets, for higher order coupling of vibrational modes, the use of curvilinear coordinates for mapping out the potential energy surface, and possible inaccuracies in the experimental frequencies.

V. CONCLUSIONS

This paper has explored the influence of anharmonicity of molecular vibrations, as calculated by the VSCF-PT2 method, on thermodynamic properties. Entropy and heat capacity appear to be the most greatly affected by anharmonicity, although an anharmonic treatment of molecular vibrations is also important for quantitative *ab initio* calculations of other thermodynamic quantities. All calculations described here have been implemented in GAMESS.¹¹

In general, the use of internal displacements to generate the VSCF potential energy surface is more reliable than the use of Cartesian coordinates. For higher frequency modes, the accuracy of frequencies obtained with internal coordinate displacements improves dramatically when the atomic basis set and the level of theory are improved. Based on the calculations presented here, internal displacements are preferred to Cartesian displacements for mapping out the potential energy surface when low frequency floppy modes are present in the molecular system of interest.

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APPENDIX A: DEPENDENCE OF ENTROPY ON FREQUENCY

$$S_{\text{vib}} = -R \sum_i^f \ln(1 - e^{-h\nu_i/kT}) + R \sum_i^f \frac{h\nu_i}{kT} \frac{e^{-h\nu_i/kT}}{(1 - e^{-h\nu_i/kT})}.$$

The first term is

$$\begin{aligned} -\ln(1 - e^{-c\nu_i}) &= \ln \frac{1}{1 - e^{-c\nu_i}} \\ &= \ln \frac{e^{c\nu_i}}{e^{c\nu_i} - 1} \\ &= c\nu_i - \ln(e^{c\nu_i} - 1) \\ &= c\nu_i + \ln \frac{1}{e^{c\nu_i} - 1}, \end{aligned}$$

while the second term gives

$$c\nu_i \frac{e^{-c\nu_i}}{1 - e^{-c\nu_i}} = c\nu_i \frac{1}{e^{c\nu_i} - 1},$$

where $c = h/kT$.

So, both terms decrease while frequency increases.

APPENDIX B: HEAT CAPACITY (C_p^0) DATA

Table VIII shows heat capacity (C_p^0) data.

TABLE VIII. Heat capacity [cal/(mol K)] [$\delta(\text{anh-calc}) = \Delta C_{p,\text{anh}}^0 - \Delta C_{p,\text{calc}}^0(\text{exptfreq})$; $\delta(\text{har-anh}) = \Delta H_{p,\text{har}}^0 - \Delta C_{p,\text{anh}}^0$; $\delta(\text{har-expt}) = \Delta C_{p,\text{har}}^0 - \Delta C_{p,\text{expt}}^0$; $\delta(\text{anh-expt}) = \Delta C_{p,\text{anh}}^0 - \Delta C_{p,\text{expt}}^0$; $\delta(\text{calc-expt}) = \Delta C_{p,\text{calc}}^0(\text{exptfreq}) - \Delta C_{p,\text{expt}}^0$. Level of theory/basis set: MP2/6-31G(*d,p*), MP2/aug-cc-pVTZ, CCSD(T)/aug-cc-pVTZ, MP2/MIDI, and MP2/p-TZV with diffuse functions.] calculated using the harmonic formula with harmonic ($\Delta C_{p,\text{har}}^0$), anharmonic, ($\Delta C_{p,\text{anh}}^0$), and experimental frequencies [Experimental frequencies are taken from Ref. 9 except diatomic molecules (Ref. 26) (HF)₂ (Ref. 41, and (H₂O)₂ (Ref. 42).] ($\Delta C_{p,\text{calc}}^0(\text{exptfreq})$). Experimental entropy is $\Delta C_{p,\text{expt}}^0$ [Experimental data are taken from Ref. 9, except for Br₂ and I₂ which are taken from Ref. 43, and H₂O₂ (Ref. 26).]

Molecule	$\Delta C_{p,\text{har}}^0$	$\Delta C_{p,\text{anh}}^0$	$\Delta C_{p,\text{calc}}^0(\text{exptfreq})$	$\Delta C_{p,\text{expt}}^0$	$\delta(\text{anh-calc})$	$\delta(\text{har-anh})$	$\delta(\text{har-expt})$	$\delta(\text{anh-expt})$	$\delta(\text{calc-expt})$
H ₂ ^a	6.96	6.96	6.96	6.89	0.00	0.00	0.07	0.07	0.07
H ₂ ^b	6.96	6.96	6.96	6.89	0.00	0.00	0.07	0.07	0.07
HF ^a	6.96	6.96	6.96	6.96	0.00	0.00	0.00	0.00	0.00
HF ^b	6.96	6.96	6.96	6.96	0.00	0.00	0.00	0.00	0.00
F ₂ ^a	7.34	7.36	7.47	7.48	-0.11	-0.02	-0.14	-0.12	-0.02
F ₂ ^c	7.33	7.35	7.47	7.48	-0.12	-0.02	-0.15	-0.13	-0.02
F ₂ ^b	7.43	7.47	7.47	7.48	0.00	-0.03	-0.05	-0.01	-0.02
Cl ₂ ^a	8.11	8.13	8.08	8.11	0.04	-0.01	0.00	0.02	-0.03
Br ₂ ^a	8.57	8.58	8.58	8.61	-0.01	0.00	-0.04	-0.04	-0.03
I ₂ ^d	8.75	8.75	8.77	8.82	-0.02	0.00	-0.07	-0.07	-0.05
H ₂ O ^a	7.99	8.00	8.00	8.03	0.00	-0.01	-0.04	-0.03	-0.03
NH ₃ ^a	8.28	8.41	8.48	8.52	-0.07	-0.13	-0.24	-0.11	-0.04
CH ₄ ^a	8.36	8.43	8.52	8.53	-0.09	-0.07	-0.17	-0.10	-0.01
H ₂ O ₂ ^a	10.26	10.39	1.28	10.29	0.11	-0.14	-0.03	0.10	-0.01
H ₂ S ₂ ^a	11.36	11.52	11.66	11.76	-0.14	-0.16	-0.40	-0.24	-0.10
H ₂ SO ₄ ^a	19.90	20.21	19.78	20.17	0.43	-0.32	-0.27	0.04	-0.39
CH ₃ NO ₂ ^a	14.38	14.28				0.10			
urea ^a	16.89	16.75	17.63	17.09	-0.88	0.14	-0.20	-0.34	0.54
(HF) ₂ ^e	14.22	12.66	14.54	13.89	-1.89	1.57	0.33	-1.23	0.65
(H ₂ O) ₂ ^a	17.92	16.26	18.64		-2.38	1.65			
(H ₂ O) ₆ ^a	51.61	45.06				6.55			
(H ₃ Si) ₂ O ^a	20.21	20.13				0.08			
((HO) ₂ HSi) ₂ O ^a	36.32	35.23				1.09			
(H ₂ SiO) ₃ ^a	29.21	29.02				0.18			
(H ₂ SiO) ₄ ^a	40.16	39.91				0.25			

^aMP2/6-31G(*d,p*).

^bCCSD(T)/aug-cc-pVTZ.

^cMP2/aug-cc-pVTZ.

^dMP2/MIDI.

^eMP2/p-TZV with diffuse functions.

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