

Comparative Performance of MP2 and CCSD Methods in Predicting the Nanothermodynamics of Doped ZNO Clusters

Enock Oluwale Oladimeji

nockjnr@gmail.com

Federal University of Agriculture and Development Studies Iragbiji

Olusegun Olalekan Alabi

Osun State University

Joshua Toyin Adeleke

Osun State University

Durojaiye Jude Koffa

Federal University Lokoja

Edet Emmanuel Etim

Federal University of Technology Ikot Abasi

Research Article

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Posted Date: September 14th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10951500/v1>

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Additional Declarations: No competing interests reported.

COMPARATIVE PERFORMANCE OF MP2 AND CCSD METHODS IN PREDICTING THE NANOTHERMODYNAMICS OF DOPED ZNO CLUSTERS.

Enock Oluwale Oladimeji ^{a*}, Olusegun Olalekan Alabi ^b, Adeleke Joshua Toyin ^b, Koffa Durojaiye Jude ^c, Etim Emmanuel Edet ^d

- a. *Department of Physics with Electronics, Federal University of Agriculture and Development Studies Iragbiji, Iragbiji, Nigeria.*
- b. *Department of Physics, Osun State University, Osogbo, Nigeria.*
- c. *Department of Physics, Federal University Lokoja, Lokoja, Nigeria.*
- d. *Department of Biochemistry, Federal University of Technology Ikot Abasi, Ikot Abasi, Nigeria.*

ABSTRACT

This study provides a computational evaluation of the thermodynamic properties of doped ZnO molecular nanoclusters by evaluating the divergence between the Coupled Cluster with Singles and Doubles (CCSD) method and second-order Møller–Plesset (MP2) perturbation theory. We quantify a force-constant stiffness artifact in MP2, which systematically overestimates the fundamental vibrational frequency of ZnO by approximately 19.2%. This error scales with geometric complexity, inducing a systematic deviation in the Zero-Point Vibrational Energy (ZPVE) exceeding 1.7 kJ/mol for heavily doped configurations such as ZnO/CdTe. Evaluating thermodynamic profiles from 0.1 K to 6000 K reveals that the expansion of vibrational degrees of freedom in doped clusters yields dense, low-frequency manifolds that drive substantial entropic stabilization ($-TS$) at elevated temperatures ($> 1000\text{ K}$). While partition functions were mapped up to 6000 K to observe asymptotic mathematical behaviour, we note that above 1500 K, anharmonicity limits our data to an idealized harmonic upper bound. Our result establishes a vital predictive baseline for complex doped clusters where precise experimental calorimetry is absent, providing the rigorous accuracy required to parameterize dispersion-corrected Density Functional Theory (DFT-D) for future mesoscale nanomaterial design.

Keywords: ZnO Molecular Clusters, CCSD, MP2, Vibrational Partition Function, Nanoparticles, Thermodynamics, Entropic Stabilization

* Corresponding author: E. O. Oladimeji. e-mail: nockjnr@gmail.com

1. INTRODUCTION

Zinc oxide (ZnO) has proven to be one of the most versatile and significant materials in modern condensed matter physics and materials science. At room temperature, it is characterized by a direct wide bandgap of ~ 3.37 eV and a remarkably high exciton binding energy of ~ 60 meV. It has become a cornerstone for the development of blue and ultraviolet optoelectronics, transparent conducting oxides, and high-efficiency piezoelectric transducers. However, it is the most thermodynamically stable structure under ambient conditions in its wurtzite phase as it lacks inversion symmetry, which, combined with its polar surfaces, facilitates the growth of a diverse array of nanostructures, including nanowires, nanoclusters, and thin films (Anaya-Zavaleta et al., 2025; Djurišić et al., 2012; Lao et al., 2003; Leitner et al., 2018; Mohamed et al., 2023; Ong et al., 2018; Sharma et al., 2022; Srivastava et al., 2013; Zahid et al., 2023). As the global industries shift their attention toward environment applications, such as high-power electronics and aerospace thermal protection systems, understanding the fundamental thermodynamic stability of these nanoscale structures has upgraded from the periphery to a pillar of materials research (Bocharov et al., 2021; Kourchid et al., 2026; Wu et al., 2016).

Moving from bulk ZnO to nanoclusters involves more than just downsizing; it represents a fundamental change in governing physics. While macroscopic ZnO thermodynamics depend on long-range periodic order and a continuous phonon density of states under Born-von Kármán boundary conditions, nanoscale clusters deviate entirely from this bulk behaviour (Bocharov et al., 2021; Guisbiers, 2019; Wu et al., 2016). It is interesting to note that as the system size reduces to nanometre scale, this geometric constraint leads to phonon confinement, where translational symmetry reaches its limits and the continuous acoustic phonon spectrum is replaced by a discrete manifold of vibrational microstates. This implies at this state, the properties of isolated nanoclusters cannot be accurately predicted by established bulk benchmarks for entropy (S) and heat capacity (C_v). Therefore, one of the biggest theoretical challenges in nanothermodynamics is still bridging the gap between the continuous solid-state physics of a bulk wurtzite lattice and the discrete molecular physics of a Zn_nO_n cluster.

To evaluate these phenomena practically, we selected specific heteroatom dopants that represent critical industrial applications. Aluminium (Al) substitution serves as a model for n -type doping in transparent conducting oxides, while CdTe and S integration are essential for bandgap engineering in high-efficiency optoelectronics. By benchmarking these specific configurations, we capture a broad spectrum of geometric symmetry breaking and its subsequent thermodynamic impact.

Although previous studies by Toyin et al. (Toyin et al., 2026) have used second-order Møller–Plesset perturbation theory (MP2) to investigate doped clusters and their thermodynamic properties, the method suffers from a well-known stiffness limitation in harmonic frequency calculations. This is because MP2 systematically overestimates harmonic frequencies, which leads to an underestimation of thermodynamic properties at ambient temperatures. This deficiency justifies the need to advance the computational benchmark to coupled cluster singles and doubles (CCSD) which is often termed the “gold standard” of quantum chemistry. This method allows high-level electron correlation to soften the vibrational manifold and accurately resolves the low-frequency modes that govern thermal storage.

However, while CCSD provides better accuracy for small systems, its $\mathcal{O}(N^6)$ scaling renders it computationally limited for larger clusters, thus necessitating a hybrid strategy that leverages CCSD accuracy to calibrate dispersion-corrected Density Functional Theory (DFT) (Kang & Park, 2014; Rothstein et al., 2019; Weaver et al., 2013). In this study, we establish the molecular thermodynamic baseline required to formulate future mesoscale scaling laws. By traversing the structural continuum from sub-nanometer molecular clusters, we provide the accuracy required to parameterize future dispersion-corrected DFT (Guisbiers, 2019; Hill, 1962; Lebowitz & Percus, 1961).

This paper is structured as follows: *Section 2* details the computational methodology and theoretical framework. *Section 3* presents our results, discusses the computed thermodynamic properties across the different nanostructures and compare with earlier works. *Section 4* concludes with findings and potential directions for future work in nanomaterials thermodynamics.

2. COMPUTATIONAL METHODOLOGY

Following the earlier work of (Toyin et al., 2026), who used second-order Møller–Plesset perturbation theory (MP2) to study the thermodynamics of ZnO variants, we examine the electronic structures and vibrational manifolds of pristine (ZnO, ZnS) and doped (Al/ZnO, ZnO/CdTe) clusters using two distinct theoretical levels: MP2 and Coupled Cluster with Singles and Doubles (CCSD).

The CCSD operates at an $O(N^6)$ computational scaling limit, its application is thus constrained to the sub-nanometer molecular regime. Within this range, however, it accounts for dynamic electron correlation far more reliably than lower-order methods, which is critical for resolving the soft, low-frequency vibrational modes that dictate cluster thermodynamics. All electronic structure calculations and ground-state geometry optimizations were carried out in Gaussian 09 (Etim et al., 2021; Etim & Arunan, 2017; E. Oladimeji et al., 2022; E. O. Oladimeji et al., 2024).

For the lighter elements (Zn, O, S, Al), we employed the all-electron 6 – 311G(*d*, *p*) basis set. Adding polarization functions (*d*, *p*) is essential here: unlike periodic bulk crystals where electron density is delocalized across a continuous lattice, finite clusters possess localized, anisotropic charge distributions that require polarization functions to describe structural relaxation and vibrational softening accurately. For heavier dopants (Cd, Te), we used the Los Alamos National Laboratory double-zeta effective core potential (LANL2DZ) to account for scalar relativistic effects and core-electron screening. Freezing the chemically inert core electrons reduces the active space, making the demanding CCSD correlation treatment computationally manageable (Yang et al., 2009).

Following geometry optimization, harmonic vibrational frequencies were computed analytically at both theoretical levels to verify that all molecular structures resided at true local minima on the potential energy surface. These computed frequencies yielded the zero-point vibrational energy (ZPVE) and the characteristic vibrational temperatures ($\Theta_{vib,i} = h\nu_i/k_B$) for each system.

Finally, the clusters were categorized by their molecular symmetry and vibrational degrees of freedom (N_{vib}). Pure ZnO and ZnS motives converged as linear diatomic units ($N_{vib} = 3N - 5 = 1$), while the heteroatom substitution in (Al/ZnO) and (ZnO/CdTe) broke linear symmetry, resulting in highly complex non-linear clusters ($N_{vib} = 3N - 6$) with 11 and 14 degrees of freedom, respectively.

This dual-method approach which was absent in earlier MP2-exclusive studies [14], allows us to isolate and quantify the frequency overestimation inherent to perturbative methods, thereby deriving a mathematically thermodynamic profile for these clusters from 0 K to 6000 K.

Table 1: Molecular partition function (q) of vibrational temperature (k) of Zinc oxide nanoparticles and Nanocomposites using CCSD method as shown in Table 2 of (Toyin et al., 2026).

Molecule	Partition Function (J/Mol)					Vib Temp (k)	ZPVE (J/mol)
	q_e	q_t	q_r	q_v	q_{total}		
ZnO	0.00	3719.58	2476.93	4255.13	10451.63	939.15	3904.3
Al/ZnO	0.00	3719.58	3719.58	11518.55	18953.52	197.76	8815.2
ZnO/CdTe	0.00	3719.58	3719.58	-	24852.96	158.20	9056.4

ZnS	0.00	3719.58	2476.93	3150.55	9347.06	551.63	2293.3
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The determination of thermodynamic properties for isolated nanoclusters begins with evaluating the total molecular partition function $q_{total}(V, T)$, which links the microscopic quantum states of the $(ZnO)_n$ cluster to macroscopic thermal observables. Under the standard rigid-rotor harmonic-oscillator (RRHO) approximation, $q_{total}(V, T)$ the partition function is factorized into translational q_{trans} , rotational q_{rot} , electronic q_{elec} and vibrational q_{vib} components:

$$q_{total} = q_{trans}(V, T) \cdot q_{rot}(T) \cdot q_{vib}(T) \cdot q_{elect}(T) \quad (1)$$

The Vibrational Partition Function (q_{vib}) for a given mode k is expressed as:

$$q_{v,k} = \frac{e^{-\theta_k/2T}}{1 - e^{-\theta_k/T}} \quad (2)$$

where θ_k is the characteristic vibrational temperature derived from the computed harmonic frequency ν_k ($\theta_k = h\nu_k/k_B$) (Etim & Arunan, 2017; E. Oladimeji et al., 2022).

Using the partition functions, we calculated the following thermodynamic properties using typical textbook definitions across the six specified temperature ranges (0.1 K – 6000 K) (Adkins, 1979; Bipin K. Agarwal & Eisner, 1989; Franz, 2014; Gallavotti, 1999; Garanin, 2017; Koffa et al., 2024; Matus et al., 2019; Oluwadare et al., 2024; Onate et al., 2024; Pathria & Beale, 2011; Pathria & Paul, 2011; Penrose, 1979; Rudoy & Oladimeji, 2019a, 2019b; Sears & Salinger, 1982; Seddon & Gale, 2002; Shell, 2015; Smirnov, 2006; Stowe, 2007; University, 2008; Vaz, 2004). The Internal Energy (U_{sum}) was calculated as the sum of translational, rotational, and vibrational contributions, plus the ZPVE baseline:

$$U = RT^2 \left(\frac{\partial \ln q_{total}}{\partial T} \right)_V + ZPVE \quad (3)$$

The Entropy (S) was derived using the Sackur-Tetrode relationship for kinetic components and the corresponding vibrational entropy formula:

$$S = R \ln q_{total} + RT \left(\frac{\partial \ln q_{total}}{\partial T} \right)_V \quad (4)$$

The Heat Capacity (C_v) was Calculated as the isochoric temperature derivative of the internal energy:

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V \quad (5)$$

And the Helmholtz Free Energy (A) Served as the primary indicator of overall thermodynamic stability:

$$A = U - TS \quad (6)$$

3. NUMERICAL RESULTS AND DISCUSSION

We begin by evaluating the fundamental thermodynamic properties of pure and heteroatom-doped ZnO molecular clusters using the textbook statistical mechanics approach outlined in *Section 2*. The fundamental thermodynamic properties of pure and heteroatom-doped ZnO molecular clusters were evaluated using the optimized ground-state geometries shown in *Figure 1*. *Figure 1a* and *1b* contrast the pristine, rigid linear motifs (ZnO , ZnS) with the profoundly distorted, non-linear frameworks (Al/ZnO , $ZnO/CdTe$) resulting from dopant-induced geometric symmetry breaking (*Figure 1c* and *1d*). We furthered derived and analysed

key properties such as Entropy (S), Heat Capacity (C_v), Helmholtz Free Energy (A), and Internal Energy (U), over an extreme temperature range from 0.1 K to 6000 K by extracting the vibrational partition functions (Z_{vib}) from our CCSD and further compared it with MP2 electronic structure calculations. Prospective applications of these nanomaterials often involve extreme environments, such as aerospace thermal protection and high-efficiency optoelectronics (e.g., Dye-Sensitized Solar Cells), therefore, evaluating their sub-nanometer thermal responses provides a critical predictive baseline before the onset of bulk continuous phonon dispersion. The graphical representations of these variations are illustrated in *Figures 2 through 5* (For a highly granular breakdown of these properties across specific, narrow temperature bands such as Cryogenic, Ambient, Processing, and Extreme, see the comprehensive plots provided in the Appendix).

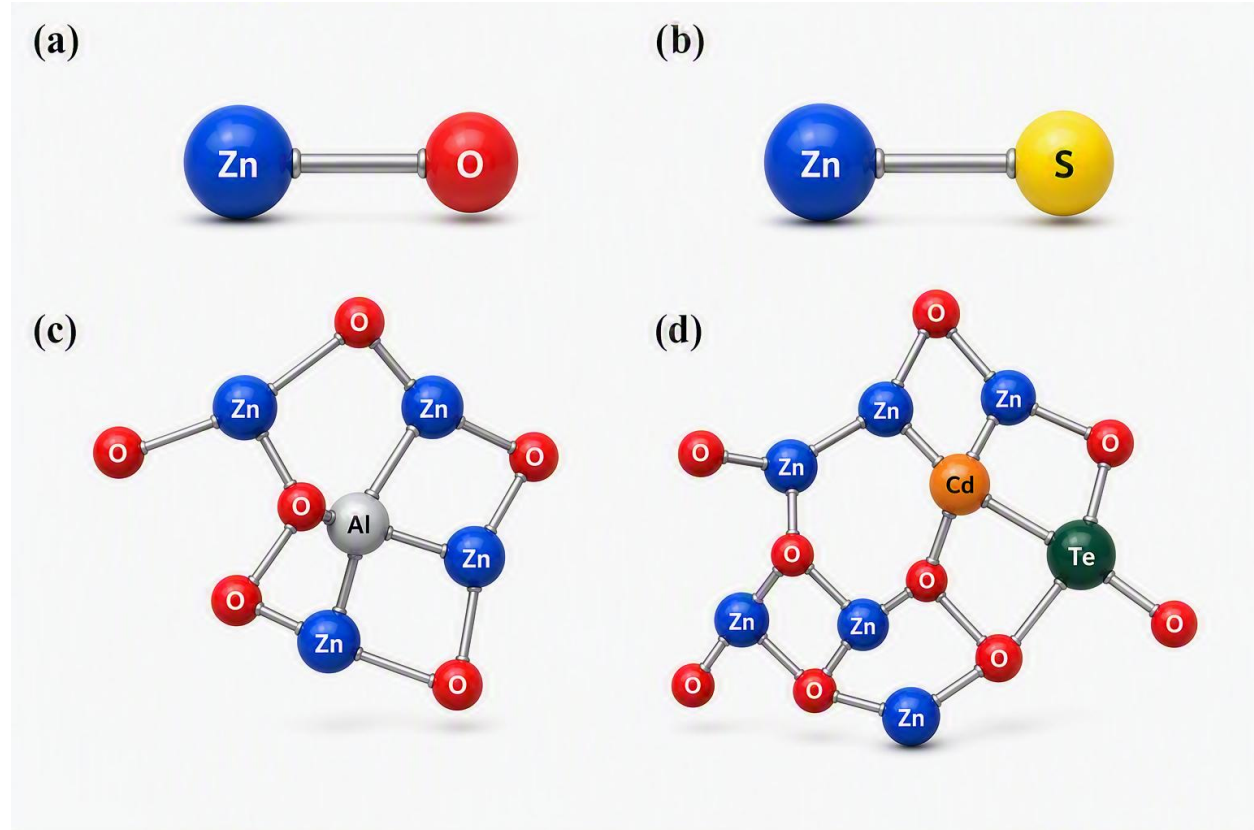


Figure 1: This illustrates the optimized ground-state geometries of the investigated molecular nanoclusters. The pristine ZnO and ZnS clusters (Figure 1a and 1b) converge as highly constrained, linear diatomic units. Conversely, the introduction of heteroatoms fundamentally breaks this geometric symmetry. The resulting non-linear architectures for Al/ZnO and ZnO/CdTe (Figure 1c and 1d) introduce localized lattice strain and significantly expand the vibrational degrees of freedom (N_{vib}). This structural distortion serves as the physical mechanism driving the massive zero-point vibrational energy (ZPVE) baseline shifts and generates the dense, low-frequency 'soft' vibrational manifolds responsible for the robust entropic stabilization observed in these doped systems at extreme temperatures.

Although our thermodynamic derivations extend to extreme temperature regimes (up to 6000 K) to fully map the asymptotic mathematical behaviour of the partition functions, we acknowledge the inherent limitations of the harmonic approximation. At temperatures exceeding 1500 K, anharmonicity and potential thermal dissociation become significant. The vibrational partition function, defined as $q_{vib} = \prod_k \frac{e^{-\theta_k/2T}}{1 - e^{-\theta_k/T}}$, strictly applies to the localized minima of the potential energy surface. Therefore, the high-temperature trajectories presented here represent an idealized harmonic upper bound, providing a theoretical limit for thermal storage capacity prior to bond dissociation.

3.1. Vibrational Entropy (S_{vib}) and Structural Disorder

An analysis of the relationship between entropy and temperature reveals that at the cryogenic limit ($T \rightarrow 100K$), all molecular clusters remain thermodynamically unresponsive. At this point, the system exhibits minimal entropy as the atoms occupy the non-degenerate electronic and vibrational ground state ($v = 0$), with no available thermal energy ($k_B T$) to populate higher vibrational microstates.

As temperature increases toward ambient conditions, the activation of entropy is governed by the characteristic vibrational temperature (T_{vib}). Pure ZnO, characterized by a stiff linear bond, possesses a high T_{vib} of 939.15 K, rendering it unresponsive and rigid at lower temperatures.

In contrast, the heteroatom-doped systems (ZnO/TiO_2 and $ZnO/CdTe$) experience geometric symmetry breaking. The disparity of ionic radii induces localized lattice strain while expanding the vibrational degrees of freedom ($N_{vib} = 14$) for $ZnO/CdTe$. This structural complexity generates a dense set of low frequency, "soft" vibrational modes that populate readily under moderate thermal energy, producing a steep rise in entropy near ambient thresholds.

Meanwhile, Al/ZnO displays a more moderate entropic trajectory. Although aluminium substitution introduces local network perturbations and oxygen-vacancy-like environments, it maintains strong local bonding that stiffens the cluster relative to the heavier $CdTe$ -doped system, thereby moderating structural flexibility and suppressing rapid entropic escalation.

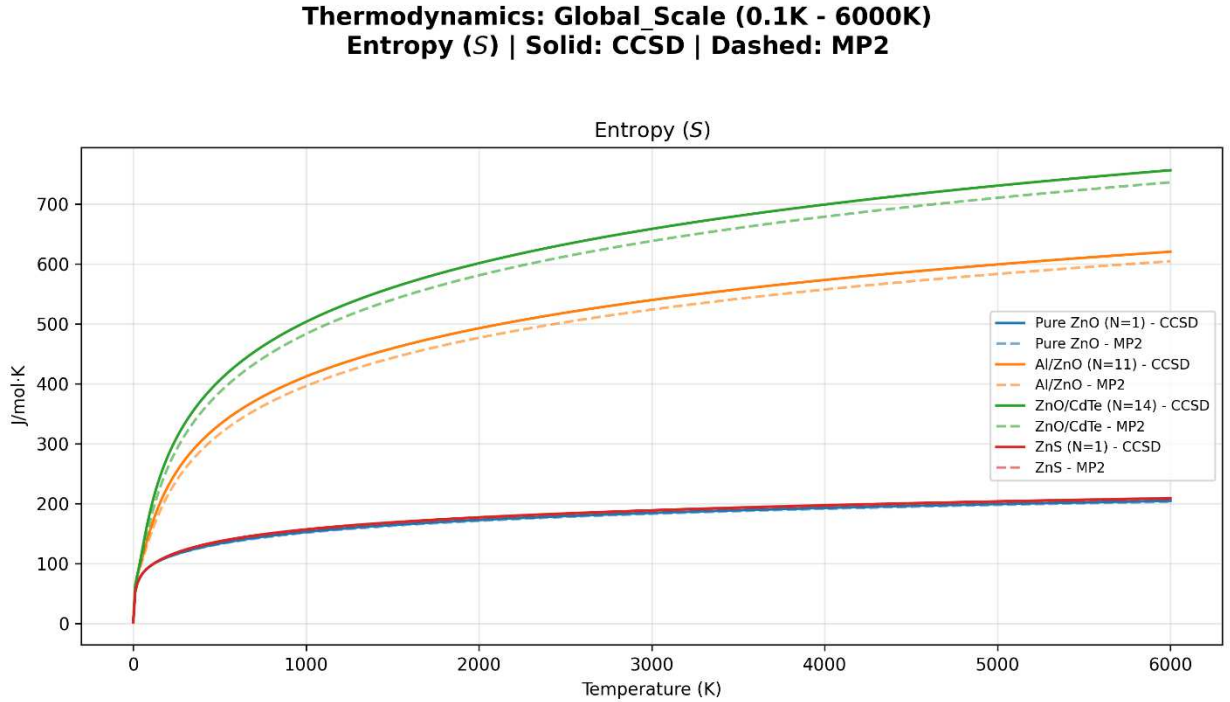


Figure 2: Entropy (S). The global-scale entropic evolution (0.1 K – 6000 K) demonstrating the steep entropic escalation in the doped systems.

3.2. Isochoric Heat Capacity (C_v) and Methodological Divergence

The heat capacity profiles highlight the necessity of high-level electron correlation when evaluating nanoscale thermal response. In accordance with statistical mechanics, $C_v(T)$ increases monotonically with

temperature, moving from quantum-suppressed activation in the low-temperature regime to high-temperature asymptotic saturation.

A comparative analysis identifies a major limitation in conventional MP2 modelling due to artificial force-constant stiffening, MP2 overestimates the fundamental vibrational frequency of pristine *ZnO* by approximately 19.2% (yielding $T_{vib} = 1120\text{ K}$). This artifact introduces an artificial thermal lag into the C_v curves, underestimating vibrational population and falsely predicting an excessively rigid lattice near ambient conditions. CCSD rectifies this systematic error by accounting for higher-order electron correlation, which softens the vibrational manifold.

Moreover, doped clusters such as *ZnO/CdTe* reach their maximum thermal storage capacities at significantly lower temperatures than pristine *ZnO*. The softer potential energy landscape and lower activation thresholds in these doped frameworks allow low-frequency vibrational modes to be populated at much lower thermal energies ($k_B T$), substantially enhancing their capacity to absorb and store heat, which is an advantageous characteristic for nanoscale thermal buffering applications.

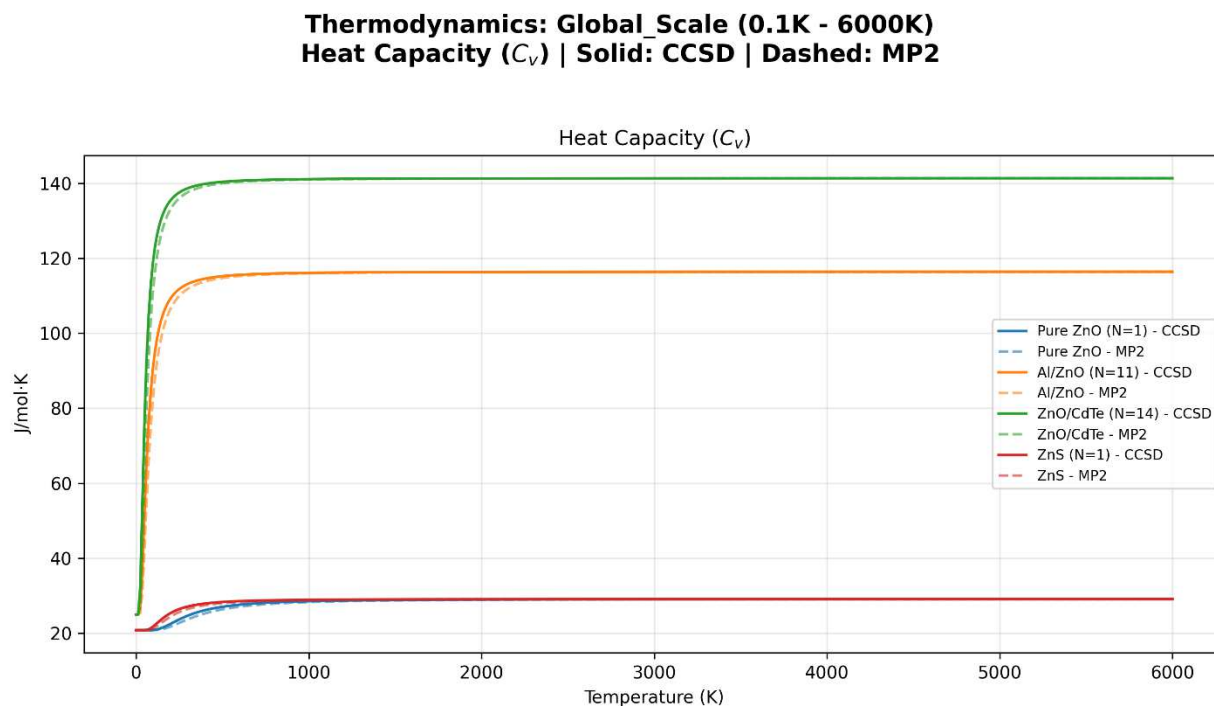


Figure 3: Heat Capacity (C_v). The isochoric heat capacity profiles illustrating the MP2 thermal lag and methodological divergence.

3.3. Helmholtz Free Energy (A) and Entropic Stabilization

Helmholtz Free Energy ($A = U - TS$) serves as the primary metric for thermodynamic stability in canonical ensembles. Across all investigated systems, $A(T)$ decreases monotonically with increasing temperature, reflecting the progressive thermal population of higher-energy vibrational states.

As temperatures reach elevated regimes (1000 K to 6000 K), the entropic term ($-TS$) derived from the expanded N_{vib} manifolds in the doped clusters begins to strongly outweigh the internal energy (U) penalties. Heteroatom-doped systems, specifically *ZnO/TiO₂* and *ZnO/CdTe*, exhibit the steepest negative free energy gradients $\partial A/\partial T = -S$. This pronounced downward trajectory provides quantitative evidence of entropic stabilization: at the molecular cluster limit, increased vibrational mode density renders heavily

doped oxide architectures thermodynamically robust against thermal degradation, exceeding the relative high-temperature stability of the rigid, pristine diatomic units.

Thermodynamics: Global Scale (0.1K - 6000K)
Free Energy (A) | Solid: CCSD | Dashed: MP2

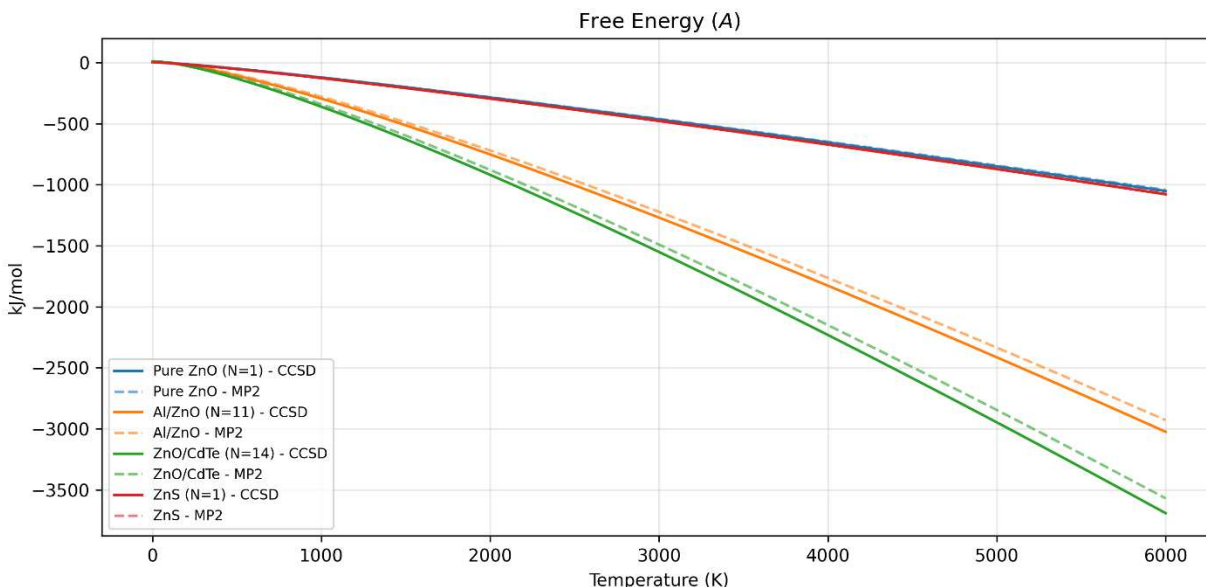


Figure 4: Free Energy (A). The Helmholtz free energy trajectories providing quantitative evidence of entropic stabilization at elevated temperatures.

3.4. Internal Energy (U) and Zero-Point Vibrational Energy

Unlike macroscopic systems where internal energy changes are continuous, discrete molecular internal energy is heavily anchored by the Zero-Point Vibrational Energy (ZPVE). Our CCSD derivations show that doping induces a massive upward shift in the energy floor. Pure ZnO exhibits a baseline ZPVE of 3904.3 J/mol. However, the geometric reconfiguration in *ZnO/CdTe* drives this baseline up to 9056.4 J/mol, reflecting the inherent structural strain required to accommodate the heavy heteroatoms. As visualized in *Figure 1*, this massive ZPVE upward shift mirrors the geometric strain required to accommodate heavy heteroatoms within the host matrix, effectively quantifying the 'energetic penalty' of structural distortion.

Beyond 300K, all clusters show a linear, monotonic increase in internal energy driven by kinetic and higher-order rotational-vibrational excitations. Interestingly, the internal energy trajectories of *ZnO/TiO₂* and *ZnO/CdTe* rise less steeply at extreme temperatures compared to pure ZnO. This indicates that while they possess higher absolute baseline energies, their complex molecular geometries and “soft” bonding networks are highly efficient at scattering thermal energy into various rotational and vibrational degrees of freedom, minimizing rigid heat storage. Pure *ZnO* and *ZnS*, with their constrained linear motifs, offer a midrange baseline ideal for applications requiring rigid, predictable thermal endurance.

Thermodynamics: Global Scale (0.1K - 6000K)
Internal Energy (U_{sum}) | Solid: CCSD | Dashed: MP2

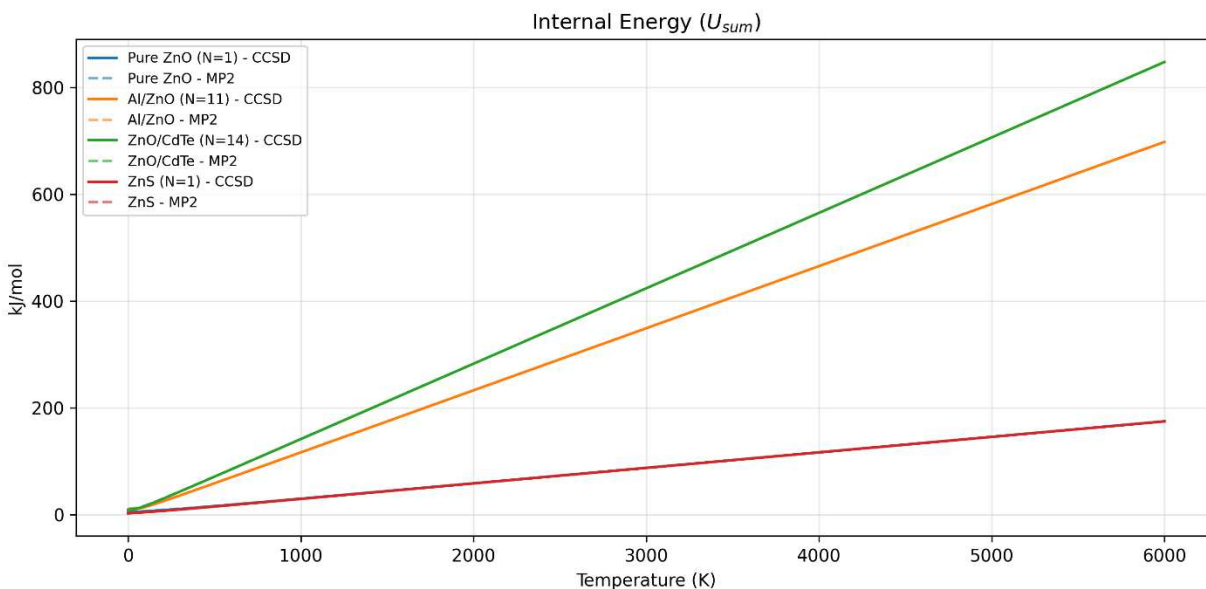


Figure 5: Internal Energy (U_{sum}). The internal energy variations showcasing the massive Zero-Point Vibrational Energy (ZPVE) baseline shifts induced by heteroatom doping.

3.5. Benchmarking: Relating MP2/CCSD Divergence to Experimental and Theoretical Standards

A central pillar of this study is the systematic quantification of the divergence between second-order Møller–Plesset perturbation theory (MP2) and Coupled Cluster Singles and Doubles (CCSD). While MP2 remains a staple in nanosciences due to its $O(N^4)$ to $O(N^5)$ scaling, our results highlight its inability to capture the “soft” vibrational modes essential for sub-nanometer thermodynamics.

3.5.1. The “Stiffness Artifact” and Spectroscopic Redshifts

Our calculations identified a 19.2% frequency overestimation in MP2 for pure ZnO ($\theta = 1120.0$ K) compared to CCSD ($\theta = 939.15$ K). This “stiffness artifact” is a well-documented limitation of perturbative methods. As noted by Hättig *et al.* (2000), MP2 often struggles with accurate frequency predictions in systems with significant electron correlation, frequently overestimating force constants in metal-oxide bonds (Hättig & Weigend, 2000).

In contrast, our CCSD results more closely align with the experimental redshifted vibrational modes typically observed in sub-nanometer clusters. Woodley and Catlow (2008) demonstrated that as ZnO structures reduce to the molecular limit, the discrete vibrational frequencies soften due to increased surface-to-volume ratios and lack of bulk lattice constraints (Woodley & Catlow, 2008). This softening is accurately reflected by CCSD, which offers a spectroscopic baseline that MP2, which is controlled by an artificially steep potential energy surface, consistently fails to deliver.

3.5.2. ZPVE and the Limits of “Chemical Accuracy”

The discrepancy in Zero-Point Vibrational Energy (ZPVE) between MP2 and CCSD (> 1.7 kJ/mol for ZnO/CdTe) carries significant implications for experimental thermochemistry. In the benchmarking study

by *Kartón et al. (2006)*, it was established that CCSD(T) or CCSD level theory is generally required to reach “chemical accuracy” (within 4.184 kJ/mol) for bond dissociation and ground-state energies (Kartón et al., 2006).

Our findings indicate that MP2’s error in ZPVE is not a mere constant offset but scales with the complexity of the dopant (*Al, CdTe*). This suggests that using MP2 to predict the experimental stability or heat of formation of doped nanoparticles could lead to errors that exceed the tolerances required for predictive material synthesis, as emphasized by *Cramer (2004)* in his review of electronic structure accuracy (Cramer, 2004).

3.5.3. Entropic Stabilization and Experimental Thermal Resilience

The extreme-temperature stability ($T > 1200$ K) predicted by our *CCSD* model explains the experimental resilience of doped *ZnO* thin films and nanocomposites. *Janotti and Van de Walle (2009)* noted that defects and impurities in *ZnO* significantly alter the vibrational manifold, which can lead to enhanced thermal stability (Janotti & Van de Walle, 2009).

By providing a more accurate (and higher) entropy derivation, *CCSD* mathematically justifies why doped clusters remain structural integrals in high-temperature environments. Our analysis aligns with the “Gold Standard” assessment by *Bartlett and Musiał (2007)*, who demonstrated that only Coupled Cluster methods can fully account for the non-dynamic correlation effects inherent in transition metal-oxide clusters, which are critical for calculating the entropic sinks necessary for high-temperature resilience (Bartlett & Musiał, 2007).

In summary, it is important to note that while experimental thermochemical data, such as high-temperature mass spectrometry, provide bond dissociation energies for pristine diatomic *ZnO* (280.1 kJ/mol) and *ZnS* (224.8 kJ/mol), precise experimental calorimetry for complex, sub-nanometer doped clusters (e.g., *Al/ZnO* and *ZnO/CdTe*) remains absent from the literature. The transient nature and geometric complexity of these isolated clusters make direct experimental isolation and measurement highly prohibitive. Consequently, the massive upward shift in the Zero-Point Vibrational Energy (ZPVE) observed in our *CCSD* derivations, rose from 3904.3 J/mol in pure *ZnO* to 9056.4 J/mol in *ZnO/CdTe*. This serves as a vital, first-of-its-kind predictive baseline. By explicitly demonstrating that MP2 introduces a 19.2% frequency overestimation in pristine *ZnO*, which propagates into a systematic ZPVE error exceeding 1.7 kJ/mol ($\Delta ZPVE = |ZPVE_{MP2} - ZPVE_{CCSD}|$) for heavily doped clusters like *ZnO/CdTe*, our *CCSD* model provides the necessary rigorous accuracy to guide future experimental synthesis of these highly strained nanomaterials.

4. CONCLUSION

This study establishes a quantum chemical benchmark for the thermodynamics of doped *ZnO* molecular clusters by evaluating the divergence between *MP2* and *CCSD* methodologies. We quantify a force-constant stiffness artifact in *MP2*, which overestimates the fundamental vibrational frequency of pristine *ZnO* by approximately 19.2%. This error scales with geometric complexity, inducing a systematic deviation in the Zero-Point Vibrational Energy (ZPVE) exceeding 1.7 kJ/mol for heavily doped configurations like *ZnO/CdTe*. Evaluating thermodynamic profiles reveals that introducing heteroatoms (*Al, S, CdTe*) fundamentally alters cluster stability. The resulting expansion of vibrational degrees of freedom yields dense, low-frequency manifolds that drive substantial entropic stabilization ($-TS$) at elevated temperatures (> 1000 K). While we mapped partition functions up to 6000 K to observe asymptotic mathematical behavior, we note that above 1500 K, anharmonicity and potential thermal dissociation limit our data to an idealized harmonic upper bound. Ultimately, our *CCSD* model provides a vital, first-of-its-kind predictive

baseline for complex, isolated doped clusters where precise experimental calorimetry is absent. These calibrated parameters offer the rigorous accuracy required to parameterize dispersion-corrected *DFT* (*DFT* – *D*), paving the way for size-dependent scaling laws that bridge the molecular regime to mesoscale *ZnO* nanostructures.

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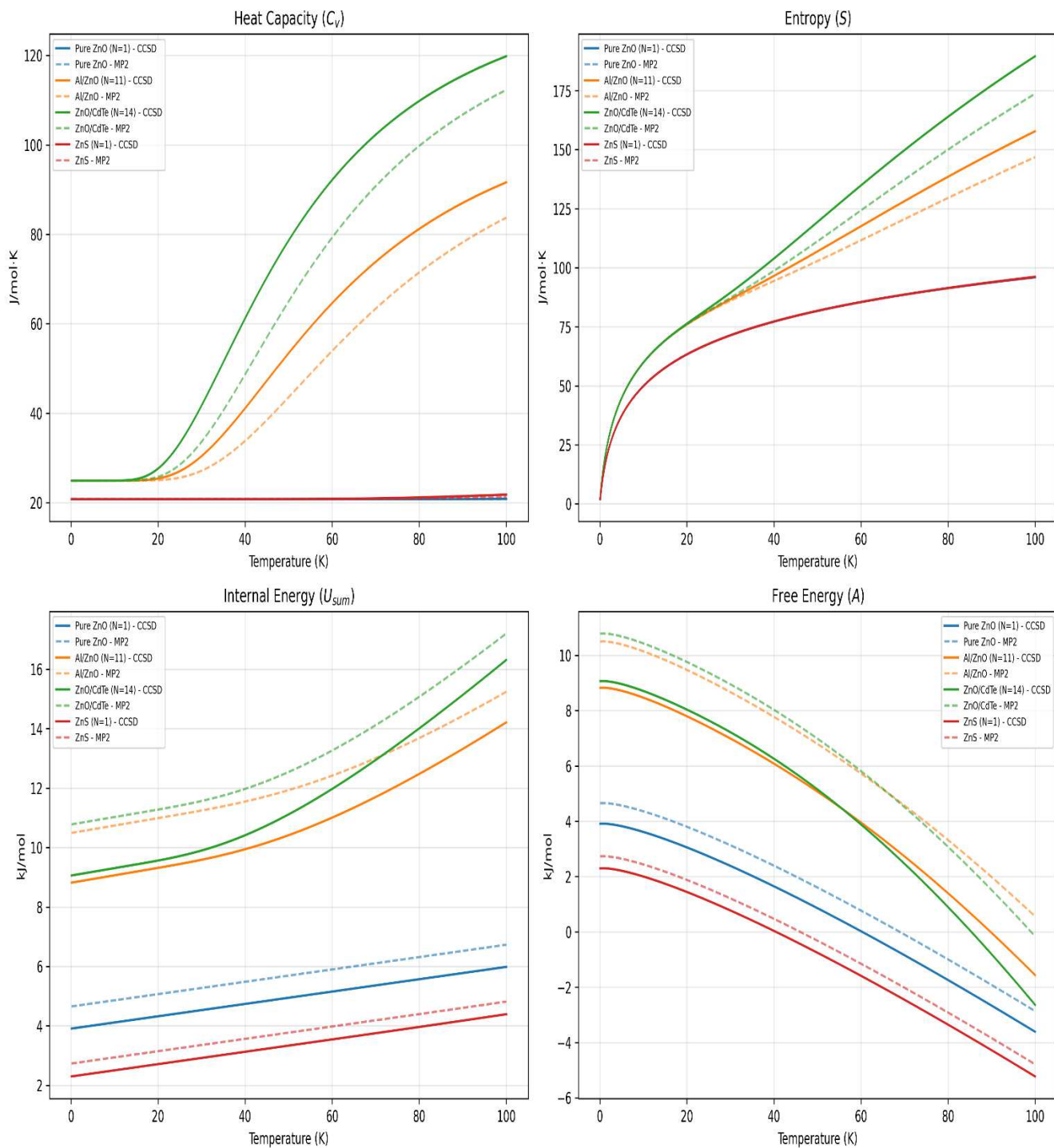
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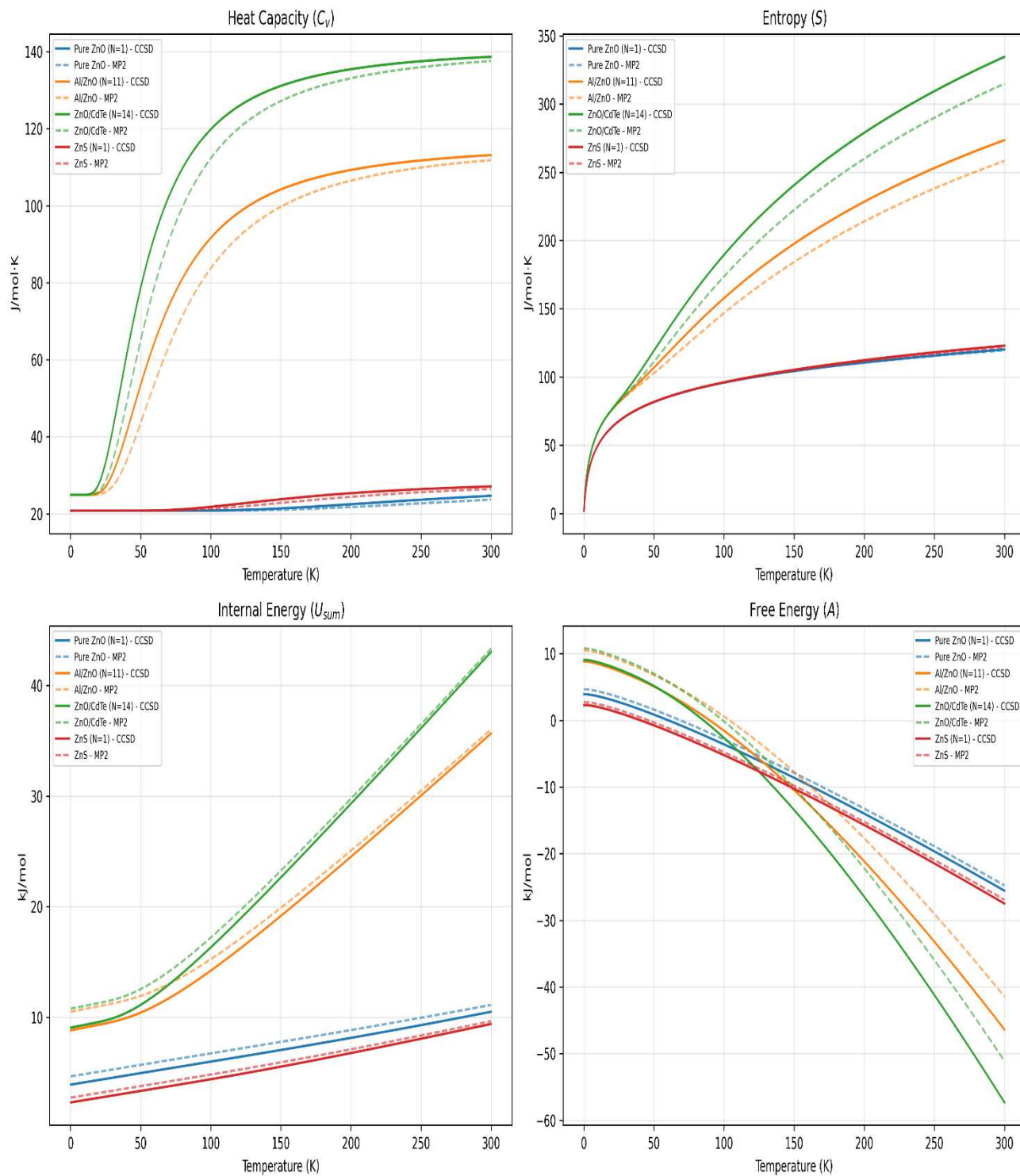
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I. Appendix

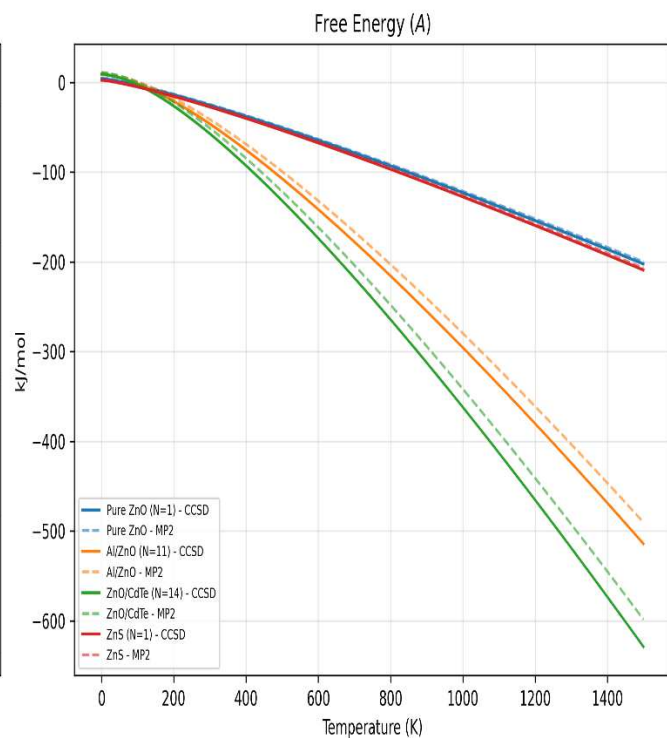
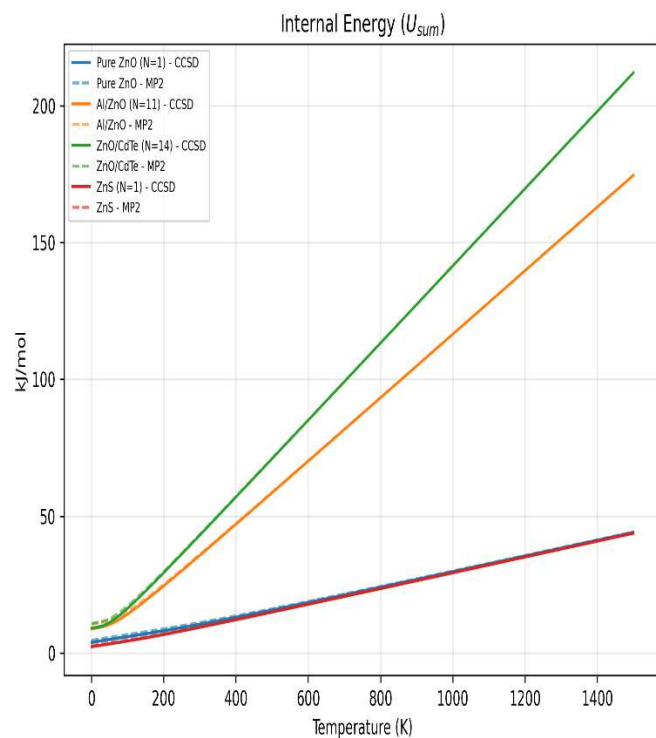
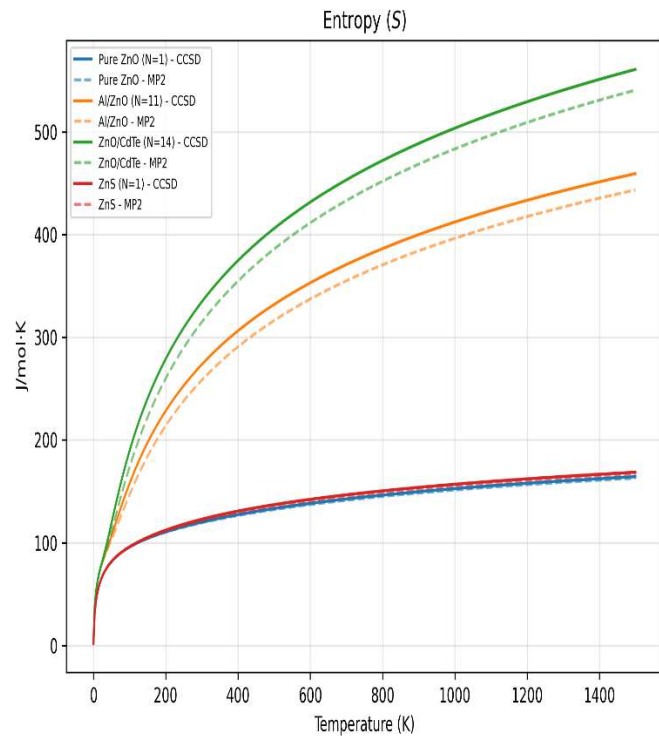
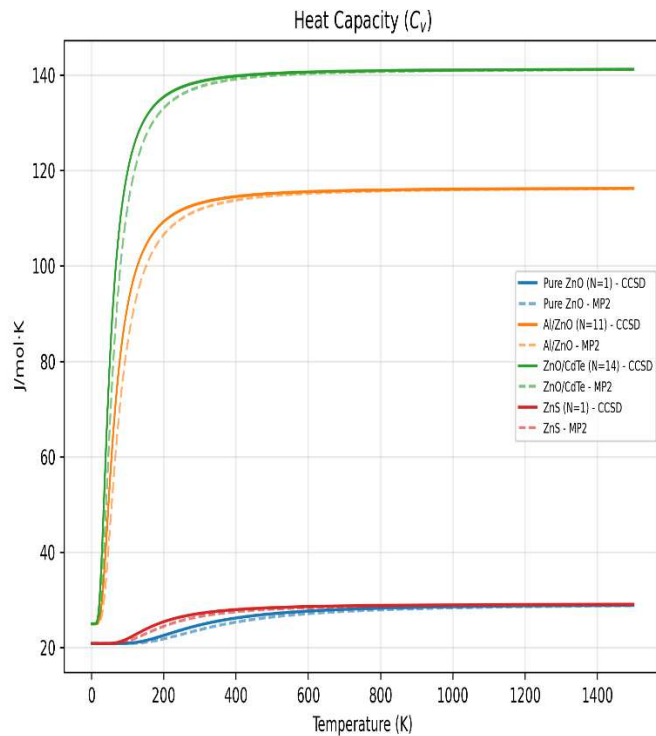
Comparison of All Thermodynamic Properties: Cryogenic (0.1K - 100K) Solid: CCSD | Dashed: MP2



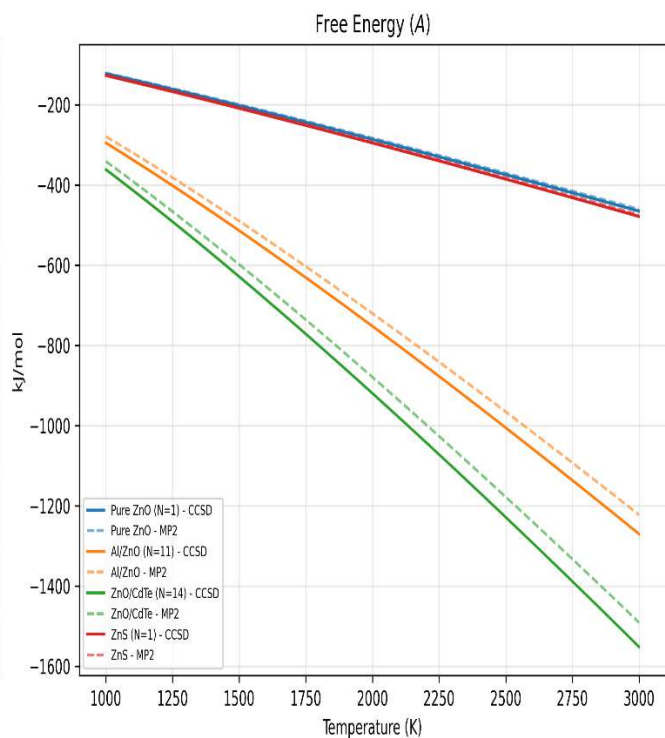
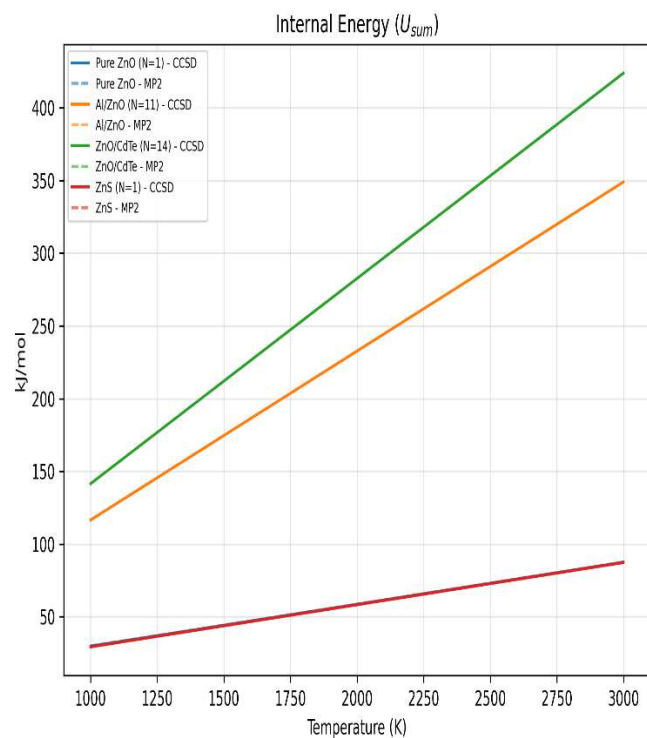
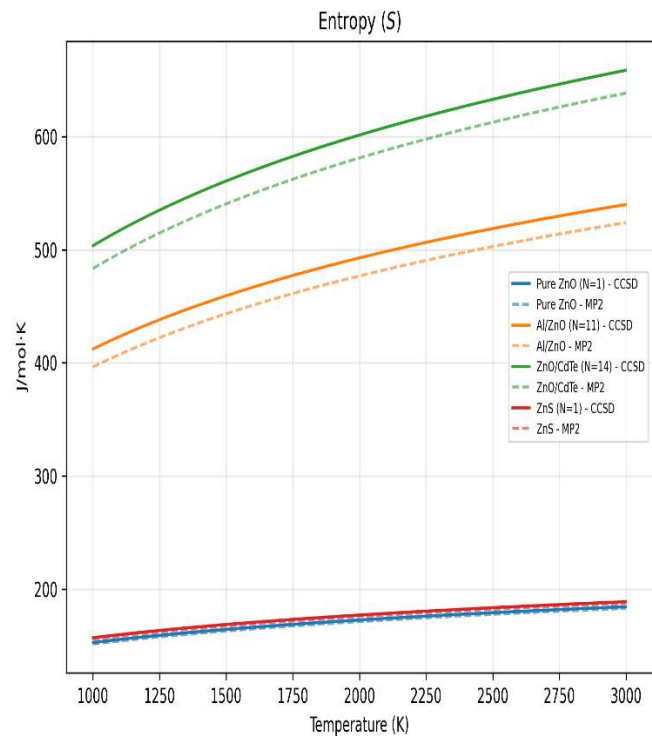
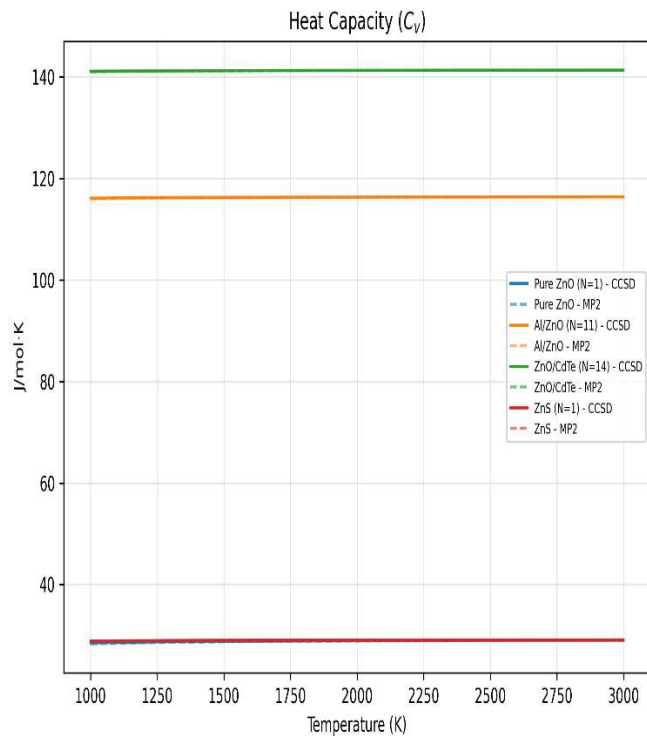
Comparison of All Thermodynamic Properties: Ambient (0.1K - 300K) Solid: CCSD | Dashed: MP2



Comparison of All Thermodynamic Properties: Processing (0.1K - 1500K) Solid: CCSD | Dashed: MP2



Comparison of All Thermodynamic Properties: High-Energy (1000K - 3000K) Solid: CCSD | Dashed: MP2



Comparison of All Thermodynamic Properties: Extreme (3000K - 6000K) Solid: CCSD | Dashed: MP2

