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The gas and solution phase acidities of HNO, HOONO, HONO, and $HONO_2$

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Abstract

The acidities of HNO_x (where $x = 1–3$) have been calculated in the gas phase and in solution by using high level ab initio molecular orbital theory. Coupled cluster (CCSD(T)) energies, extrapolated to the complete basis set (CBS) limit, were used to determine thermodynamic properties of the species in the gas phase, and the fully polarizable continuum model (FPCM) was used to calculate the effect of solvent on the energy changes. The calculated gas phase heats of formation in $\mathrm{kcal\,mol^{-1}}$ at 0 K, based on extrapolations through the aug-cc-pVQZ basis set, are: $\Delta H_f(\mathrm{NO}) = 22.07$ (calculated) vs. 21.46 ± 0.04 (experimental); $\Delta H_f(\mathrm{HNO}) = 26.39$ (calculated) vs. 26.3 ± 1 (experimental); $\Delta H_f(\mathrm{NO_2}) = 10.12$ (calculated) vs. 8.59 ± 0.2 (experimental); $\Delta H_f(\mathrm{HONO_2}) = -29.87$ (calculated) vs. -29.75 ± 0.1 (experimental); $\Delta H_f(\mathrm{HONO}) = -15.79$ (calculated) vs. -17.37 ± 0.32 (experimental); $\Delta H_f(\mathrm{HOONO}) = -0.89$ (calculated); $\Delta H_f(\mathrm{NO_2}^-) = -41.95$ (calculated) vs. -43.8 ± 0.2 (experimental); $\Delta H_f(\mathrm{NO_3}^-) = -70.76$ (calculated) vs. -71.7 ± 0.30 (experimental); and $\Delta H_f(\mathrm{ONOO^-}) = -16.74$ (calculated). The electron affinity of NO is calculated to be $0.62\,\mathrm{kcal\,mol^{-1}}$, based on extrapolations up through the aug-cc-pV5Z basis set, and falls within $0.02\,\mathrm{kcal\,mol^{-1}}$ of the experimental value. The corresponding heats of formation at 0 K in $\mathrm{kcal\,mol^{-1}}$ of the anions are: $\Delta H_f(\mathrm{HNO}) = 26.93$ (calculated); $\Delta H_f(\mathrm{NO}) = 22.28$ (calculated); $\Delta H_f(\mathrm{NO^-}) = 21.66$ (calculated) vs. 20.86 ± 0.16 (experimental). The calculated gas phase acidities of HNO, HONO, HOONO, and $HONO_2$ are found to be in excellent agreement with experiment to within $1\,\mathrm{kcal\,mol^{-1}}$. Solvation calculations show that the free energy change for K_a in aqueous solution for $HONO_2$, HONO, and HNO can be calculated within ~2, 3, and $5\,\mathrm{kcal\,mol^{-1}}$ of experiment, respectively. However, the agreement for HCN (with an established pK_a) and HOONO is much worse and the calculated results suggest that the effect of the directly interacting solvent shells around HCN and HOONO are quite different from those around $HONO_2$, HONO, or HNO in terms of the solution phase acidity. Contrary to the view that HNO is an acid in aqueous solution, the pK_a is estimated to be between 10 and 13 for HNO consistent with the latest experimental result. This suggests that the behavior of HNO in biological systems warrants further investigation as it is not an acid as has previously been accepted.

Keywords: Ab initio calculations; Gas phase acidity; Solvation effects

1. Introduction

The NO radical is a key signaling molecule in many biological systems [1]. NO can participate in a number

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of reactions in aqueous media under biological conditions to form different species. For example, peroxynitrite ($OONO^-$), a potent oxidant of biomolecules, can be formed from the reaction of superoxide ($O_2{}^-$) and NO and, upon protonation, forms peroxonitrous acid, HOONO, another key biological intermediate [2] which is an isomer of nitric acid, $HONO_2$. Most of the discussions in the literature on the biological reactions of NO have focused on oxidation reactions as described above and not on the formation of the reduced species, NO^- and HNO. Little is known about the solution phase chemistry of NO^- and HNO. NO^- in the gas phase is very unstable as NO has an electron affinity of only 0.026 eV (0.6 kcal mol^{-1}) [3]. The ground state of NO^- in the gas phase is a triplet like the isoelectronic O_2 and the first excited singlet state is ∼17 kcal mol^{-1} higher in energy [4]. The acidity of HNO in solution is not well-established. There is one report of the pK_a of HNO based on a pulsed radiolysis study and a value of 4.7 was found [5]. A later study of the reactions of $NO_2{}^{2-}$ ions suggested that the actual product in the pulsed radiolysis study was NOH, not HNO. This more recent study reported a value of −0.81 V(nhe) for the NO/NO^- standard redox potential [6]. The redox potential can be combined with a quite reliable value [7] of $\Delta G_f^\circ(\text{NO}) = 24.4$ kcal mol^{-1} in aqueous solution and an estimated value [7] of $\Delta G_f^\circ(\text{HNO}) = 26.1$ kcal mol^{-1} in aqueous solution to give pK_a = 12.6 at 298 K for HNO.[1] This pK_a value is clearly different from that of the pulsed radiolysis study. A modest level theoretical chemistry study (B3LYP/6-311+G* plus a PCM solvent calculation followed by an empirical linear fitting process) has been used to predict the acidity in solution of HNO [8]. By using these calculations and the known experimental pK_a's of a number of acids, they obtained an estimated value of pK_a(HNO) = 7.2. However, this level of calculation is not adequate to predict the proton affinity of NO^- to within 10 kcal mol^{-1} in the gas phase. In addition, the solvation calculations at the PCM level (using Gaussian 94) do not explicitly include the volume polarization which is important for ionic solutes. Part of the difficulty in calculating the acidity (solution or gas phase) of HNO is, of course, the very small electron affinity of NO. We have recently calculated the heats of formation of HOONO and $HONO_2$ as well as other H_yNO_x species in order to explain the possible homolytic decomposition reactions of HOONO and $HONO_2$ in the gas phase and in solution [9].

We report here high level ab initio electronic structure calculations on HNO, HONO, $OONO^-$, $NO_3{}^-$, HNO, NO and NO^- and use these in conjunction with our previously calculated values to calculate the gas phase acidities of HNO, $HONO_2$, HOONO, and HONO as well as their acidities in aqueous solution. The latter quantities are calculated by using a self-consistent reaction field approach.

2. Calculations

In an effort to predict uniformly accurate thermochemical properties across a range of small-to-intermediate size chemical systems, we have developed a composite theoretical approach without recourse to empirical parameters [10]. This approach starts with existing, reliable thermodynamic values obtained from either experiment or theory. Normally we adopt experimental atomic heats of formation, which are difficult to obtain theoretically, as well as molecular and atomic spin-orbit splittings (if any) and use experimental information about molecular vibrations to calculate zero point energies where possible. High-level ab initio electronic structure methods are then used to complete the calculation of the molecular atomization energy.

The energy of the valence electrons is calculated by using coupled cluster methods, including single, double, and connected triple excitations (CCSD(T)), with the latter being handled perturbatively [11]. The CCSD(T) energies are extrapolated to the complete

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[1] $\Delta G_{aq}^\circ(\text{NO} + e^- \rightarrow \text{NO}^-) = 0.81\,\text{eV} \approx 18.9$ kcal mol^{-1}, leading to $\Delta G_f^\circ(\text{NO}^-) = \Delta G_f^\circ(\text{NO}) + \Delta G_{aq}^\circ(\text{NO} + e^- \rightarrow \text{NO}^-) \approx 43.3$ kcal mol^{-1}. These data give $\Delta G_a^\circ(\text{HNO} \rightarrow \text{NO}^- + \text{H}^+) = \Delta G_f^\circ(\text{NO}^-) - \Delta G_f^\circ(\text{HNO}) = 17.2$ kcal mol^{-1} and pK_a(HNO) = 12.6 at $T = 289$ K. Note that $\Delta G_f^\circ(\text{H}^+) = 0$ in aqueous solution in the usual convention.

basis set (CBS) limit [12], a step facilitated by the uniform convergence properties of the correlation consistent basis sets (cc-pVXZ) from Dunning and coworkers [13]. For this study, we used the diffuse function augmented (aug-cc-pVXZ) basis sets for X = D, T, and Q for the valence correlation energy calculations. For the calculation of the electron affinity of NO and the acidity (gas phase and solution) of HNO, we also used the aug-cc-pV5Z basis set. The basis set names are abbreviated as aVXZ. Only the spherical components (5-d, 7-f, and 9-g) of the Cartesian basis functions were used. All of the correlation energy calculations were performed with the programs MOLPRO [14], NWChem [15], and Gaussian 98 [16].

A number of coupled cluster methods have been proposed for treating open-shell systems. At present, little is known about which open-shell coupled cluster method produces the best agreement with the exact full configuration interaction (FCI) results. For this study, we have used the R/UCCSD(T) method which is based on an RHF wavefunction but the spin constraint is relaxed in the coupled cluster calculation as a reasonable compromise [17]. In order to extrapolate to the frozen core CBS limit, we used a three-parameter, mixed exponential/Gaussian function of the form:

$$E(x) = A_{\mathrm{CBS}} + B\exp[-(x-1)] + C\exp[-(x-1)^2] \quad (1)$$

where $x = 2$ (aVDZ), 3 (aVTZ), and 4 (aVQZ) for the extrapolation of these energies [12].

The geometries were optimized at the MP2/cc-pVTZ level [18] and CCSD(T)/aug-cc-pVDZ levels unless higher level calculations were available. In all cases where the results were checked, the use of the MP2 optimized geometries led to extrapolated total valence electronic binding energies that were larger than the ones based on the CCSD(T) optimized geometries by ~0.5 kcal mol^{-1}, so we used the results based on the MP2 geometries. (See Appendix A.)

Additional corrections to the CCSD(T)(FC) atomization electronic energies are needed when trying to achieve accuracies for the gas phase heats of formation on the order of 1 kcal mol^{-1}. For HONO, HOONO, $HONO_2$, NO_2^-, NO_3^-, $ONOO^-$, HCN, and CN^-, core/valence corrections to the bonding energies (ΔE_{CV}) were calculated at the fully correlated CCSD(T)/cc-pCVTZ level at the MP2 geometries. For HNO, NO, and NO_2, ΔE_{CV} was obtained with the cc-pCVQZ basis set at the optimal CCSD(T)/aug-cc-pVTZ geometry. For the calculations on NO and NO^- for the electron affinity of NO, ΔE_{CV} was obtained from calculations with the aug-cc-pCVQZ basis set [19] at the CCSD(T)/aug-cc-pVQZ geometries. The differential effects of relativity must also be considered. Most electronic structure computer codes do not correctly describe the lowest energy spin multiplet of an atomic state. Instead, the energy is a weighted average of the available multiplets. For N in the ^{4}S state, no such correction is needed, but a correction is needed for the ^{3}P state of O. In order to correct for this effect, we apply an atomic spin-orbit correction of 0.22 kcal mol^{-1} for O and one of 0.08 kcal mol^{-1} for C based on the excitation energies of Moore [20]. For NO, the spin orbit correction is from Huber and Herzberg [21]. Molecular scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI-SD level of theory using the cc-pVTZ basis set in the frozen core approximation. The scalar relativistic correction to the electron affinity of NO was obtained with the aug-cc-pVQZ basis set. ΔE_{SR} is taken as the sum of the mass–velocity and one-electron Darwin (MVD) terms in the Breit-Pauli Hamiltonian [22].

The molecular zero point energies were obtained as follows. For the diatomic NO, the zero point energy was evaluated as $0.5\omega_e - 0.25\omega_e x_e$, with the ω_e and $\omega_e x_e$ values taken from Huber and Herzberg [21]. For $^3NO^-$ and CN^-, we used $0.5\omega_e$ with ω_e taken to be the unscaled frequency calculated at the CCSD(T)/aug-cc-pVQZ level. For HCN, we used the value obtained by Allen et al. [23] For HNO, we used the zero point energy calculated from an ab initio anharmonic force field at the CCSD(T)/cc-pVQZ level [24]. For NO_2, we took one half the experimental frequencies from the latest values [25]. For $HONO_2$, and HOONO, we took the zero point energies from our previous work [9]. For HONO, we used the average of the experimental anharmonic frequencies [26,27] with the CCSD(T)/TZ2P harmonic frequencies of Lee and Rendell [28]. For NO_2^-, we used the average of the experimental [29–31] and the MP2 calculated frequencies. For $ONOO^-$, and NO_3^-, we used the MP2/cc-pVTZ frequencies. Thermal corrections to the enthalpy and entropies were calculated for all molecules at the MP2/cc-pVTZ level or taken from experiment, if available [32].

By combining our computed ΣD_0 values with the known heats of formation [32] at 0 K for the elements ($\Delta H_f^\circ(N) = 112.53\,\text{kcal mol}^{-1}$, $\Delta H_f^\circ(O) = 58.98\,\text{kcal mol}^{-1}$, $\Delta H_f^\circ(C) = 169.98 \pm 0.1\,\text{kcal mol}^{-1}$ and $\Delta H_f^\circ(H) = 51.63\,\text{kcal mol}^{-1}$), we can derive ΔH_f° values for the molecules under study in the gas phase.

Solvent shifts of the energies were evaluated by using a recently developed GAMESS [33] implementation of the surface and volume polarization for electrostatic interactions (SVPE) [34]. The SVPE model is known as the fully polarizable continuum model (FPCM) [34,35] because it fully accounts for both surface and volume polarization effects in the self-consistent reaction field (SCRF) calculation. This SVPE procedure is currently the only implementation capable of directly determining the volume polarization for a general irregularly-shaped solute cavity through an efficient three-dimensional integration algorithm [34a] in addition to the more commonly treated surface polarization. In other SCRF implementations, volume polarization effects are ignored or approximately modeled by modifying the surface polarization charge distribution through a simulation and/or charge renormalization, or the solute charge distribution is simply represented by a set of point charges at the solute nuclei. It has been shown that for evaluating solvation free energies of ions, the volume polarization effects are critical and must be accurately accounted for in the solvation calculations [35,36]. Since the solute cavity surface is defined as a solute electron charge distribution isodensity contour determined self-consistently during the SVPE iteration process, the SVPE results, converged to the exact solution of Poisson's equation with a given numerical tolerance, depend only on the contour value at a given dielectric constant and the level of the quantum chemical calculation [34]. This single parameter value has been calibrated as 0.001 a.u. and this contour was used for all the SVPE calculations [34b]. Previous continuum solvation calculations with the SVPE method indicate that the effects of electron correlation effects on the solvent shifts at the SVPE level are not large [36]. This issue was further tested in the present study by performing the SVPE calculations at both the HF/cc-pVTZ and MP2/cc-pVTZ levels. The dielectric constant of water used in this study is 78.5. For the SVPE calculations at the MP2 level, the MP2 perturbation procedure was performed for the electron correlation correction after the converged HF wave function of solute in reaction field is obtained. Once the solute cavity is defined and the dielectric constant is known, the accuracy of the SVPE numerical computation depends only on the number of surface nodes (N) representing the cavity surface and number of layers (M) describing the volume polarization charge distribution within a certain, sufficiently large three-dimensional space outside the solute cavity. If one could use an infinite number of nodes and an infinite number of layers, then the numerical results obtained from the SVPE computation would be exactly the same as those determined by the exact solution of the Poisson's equation for describing the solvent polarization potential [34]. We examined the accuracy of the SVPE numerical computations employed in this study with $N = 590$ and $M = 41$ (for a step size of 0.3 Å) and showed that the accuracy is higher than required for this work. For example, the use of more surface nodes (974) does not change the free energy by more than 10^{-7} a.u.

3. Results and discussion

The optimized geometry parameters are given in Table 1 and compared to experiment [37] where

Table 1
Calculated geometries for H_xNO_y molecules and ions. Bond distances in Å and angles in degrees (°)

Molecule	Parameter	Value				
		Method				
		Experimental [37a]	CCSD(T)/ aug-cc-pVDZ	CCSD(T)/ aug-cc-pV5Z	MP2/cc-pVTZ	
HNO	*r*(NO)	1.212 ± 0.001	1.2256	1.2103	1.2207	
	r(NH)	1.063 ± 0.002	1.0660	1.0532	1.0502	
	HNO	108.6 ± 0.2	107.7	108.0	107.5	
		Method				
		Experimental [21]	UCCSD(T)/ aug-cc-pVDZ	UCCSD(T)/ aug-cc-pV5Z		
NO	*r*(NO)	1.1508	1.1640	1.1484		
		Method				
		Experimental [37a]	CCSD(T)/ aug-cc-pVDZ	CCSD(T)/ aug-cc-pVQZ		
NO_2	*r*(NO)	1.1946	1.2102	1.1954		
	ONO	133.85	133.95	134.17		
		Method				
		Experimental [37b]	CCSD(T)/ aug-cc-pVDZ	MP2/ cc-pVTZ	MP4STDQ-FC/ 6-311+G** [26]	CCSD(T)/TZ2P [28]
HONO	*r*(N=O)	1.169	1.1838	1.1774	1.182	1.173
	r(NO)	1.442	1.4494	1.4234	1.452	1.453
	r(OH)	0.959	0.9739	0.9673	0.970	0.966
	ONO	110.6	110.30	110.76	111.0	110.5
	NOH	102.1	101.82	101.21	101.5	101.4
		Method				
			CCSD(T)/ aug-cc-pVDZ	MP2/ cc-pVTZ		
HOONO	*r*(N=O)		1.2010	1.1960		
	r(NO)		1.4014	1.3762		
	r(OO)		1.4558	1.4245		
	r(OH)		0.9888	0.9836		
	ONO		114.38	114.41		
	NOO		112.96	113.06		
	OOH		100.23	99.97		
		Method				
		Experimental [37a]	CCSD(T)/ aug-cc-pVDZ	MP2/ cc-pVTZ	CCSD(T)/TZ2P [38]	
$HONO_2$[a]	*r*(NO1)	1.210 ± 0.003	1.2231	1.2123	1.216	
	r(NO2)	1.203 ± 0.003	1.2081	1.2006	1.200	
	r(NO)	1.406 ± 0.003	1.4198	1.4046	1.418	
	r(OH)	0.959 ± 0.005	0.9768	0.9711	0.969	
	ONO1	116.1 ± 0.3	115.75	115.51	115.4	
	ONO2	113.9 ± 0.3	113.80	113.81	114.0	
	NOH	101.9 ± 0.5	101.94	101.51	101.5	

Table 1 (*Continued*)

Molecule	Parameter	Value		
		Method		
			CCSD(T)/ aug-cc-pVDZ	MP2/ cc-pVTZ
NO_3^-	*r*(NO)		1.2698	1.2581
		Method		
		Experimental [41]	CCSD(T)/ aug-cc-pVDZ	MP2/ cc-pVTZ
$ONOO^-$	*r*(NO)	1.16	1.2284	1.2342
	r(NO)	1.35	1.3823	1.3361
	r(OO)	1.41	1.4080	1.3605
	ONO		115.63	115.42
	NOO		116.50	117.89
	ONOO		0.0	0.0
		Method		
			CCSD(T)/ aug-cc-pVDZ	MP2/ cc-pVTZ
NO_2^-	*r*(NO)		1.2742	1.2661
	ONO		116.25	115.90
		Method		
		Experimental [3]	UCCSD(T)/ aug-cc-pVDZ	UCCSD(T)/ aug-cc-pVQZ
$^3NO^-$	*r*(NO)	1.271 ± 0.005	1.2829	1.2661
		Method		
		Experimental [37a]	CCSD(T)/ aug-cc-pVDZ	CCSD(T)/ aug-cc-pVQZ
HCN	*r*(CN)	1.1532	1.1758	1.1567
	r(CH)	1.0650	1.0816	1.0670
		Method		
			CCSD(T)/ aug-cc-pVDZ	CCSD(T)/ aug-cc-pVQZ
CN^-	*r*(CN)		1.2016	1.1814

[a] O1 is *cis* to the OH and O2 is *trans* to the OH.

available and to appropriate calculated values. Overall, the calculated geometries are in excellent agreement with experiment. The MP2 and CCSD(T) geometries for HNO and $HONO_2$ are in good agreement with each other and experiment as well as that of $HONO_2$ calculated by Lee at the CCSD(T)/TZ2P level [38]. The bond distance for $^3NO^-$ is predicted to be much longer than that for NO and in excellent agreement with the experimentally estimated value [3]. It is also similar to the value found by McCarthy et al. at the CCSD(T)/aVTZ level [39]. For HONO, the *trans* geometry was used as it is the lowest energy conformer [32]. For $OONO^-$, the cisoid geometry was used as it was lower in energy than the *trans* conformer. This is consistent with the findings of other workers [40]. As expected, the biggest differences between the MP2 and

CCSD(T) results are found for the molecules HOONO and $OONO^-$. The MP2 bond distances for the long N–O single bond and the O–O single bond are shorter than the CCSD(T) bond distances by ∼0.03 Å. The largest variation in the geometry parameters is found for $OONO^-$. The MP2 bond distances are shorter than the long N–O single bond and the O–O single bond distances at the CCSD(T) level by ∼0.05 Å. There is no good experimental structure for $ONOO^-$, only a disordered crystal structure [41]. The averaged crystal structure results show that the molecules has a cisoid geometry with a torsion angle of ∼22°. The calculated distances at the CCSD(T) level for the long N–O single bond and the O–O single bond are in good agreement with the experimental estimates. The short NO bond from the experiment is far too short for this type of molecule as exemplified by HOONO and we prefer the calculated value. Our MP2 geometries for HOONO and $ONOO^-$ are in good agreement with the previously calculated values at the MP2/6-311+G(2df), MP2/TZ2PF+(diffuse s, p), and CCSD/6-311+G(d) levels for $ONOO^-$ and at the MP2/6-311++G(d,p) and CCSD/6-311++G(d,p) levels for HOONO [40].

The calculated frequencies are given in Table 2 where they are compared to the appropriate experimental values [21,23,26–31,42–46] and to other computational values where appropriate. In general, the available coupled cluster frequencies are, in better agreement with experiment than the MP2 frequencies. For $^3NO^-$, we obtain values that are in reasonable agreement with the matrix isolation value of Jacox and Thompson [44] of 1370 cm^{-1} and the result given by Huber and Herzberg [21] of 1363 cm^{-1} but not with the result of Maricq et al. [45] of 1284 cm^{-1} from a study of the vibrational autodetachment spectrum. We also note that our calculated values at the UCCSD(T) level do not agree within 100 cm^{-1} with those given by McCarthy et al. [39] with the same basis sets. The frequency for $^3NO^-$ is significantly lower than that for NO, consistent with the large difference in bond lengths as previously noted by McCarthy et al. [39] The QCISD and MP2 frequencies are both in reasonable qualitative agreement with experiment for HOONO [43]. We expect that we can use the MP2 frequencies for $ONOO^-$ also based on this and the fact that the MP2 geometry is in qualitative agreement with the CCSD(T) geometry for HOONO. The calculated frequencies for $ONOO^-$ are in good agreement with the previous MP2/6-311+G(d) results and in qualitative agreement with the CCSD/6-311+G(d) frequencies [40].

Table 3 shows the various energy components used in calculating the total dissociation energies for the molecules under study. The results for $HONO_2$, HOONO, HNO, NO_2, and NO using basis sets up through aug-cc-pVQZ are taken from our previous work [9] and repeated here for completeness. The heats of formation of the molecules in the gas phase at 0 K are given in Table 4. Reasonable agreement between the calculated and experimental heats of formation [32,47] is found. The largest error for the HNO_y neutral molecules is predicted for HONO with an error of 1.58 kcal mol^{-1}, similar to the error of 1.53 kcal mol^{-1} found for NO_2. Our calculated value for ΔH_f(HNO) is in excellent agreement with that of Lee and Dateo [48] of 26.7 kcal mol^{-1} based on two variations of a CCSD(T) approach extrapolated to the complete basis set limit. We agree with their conclusion that the JANAF value [32] is incorrect. A much better experimental value of 26.3±1 kcal mol^{-1} can be obtained from the NASA Tables (values at 298 K from [47] corrected to 0 K by use of [32]) which is based on the highly accurate value of 26.29±0.6 kcal mol^{-1} obtained by reinterpretation of the spectral data [49]. For HCN, we are in better agreement with the value from Gurvich et al. [50] than from the JANAF tables [32].

The electron affinity of NO was computed as a reliability check on the calculation of the gas phase acidity of HNO. To do so required an even larger basis set as the additional electron on NO^- only becomes bound at the aV5Z level. Instead of using the mixed exponential/Gaussian CBS extrapolation formula, for basis sets of this size, it is more appropriate to use a function in $\ell_{\max}^m$ where $\ell_{\max}$ is the highest angular momentum value in the basis set. The expression we used for this fit is [51]:

$$E(n) = E_{\mathrm{CBS}} + A\ell_{\max}^{-3} \tag{2}$$

Table 2
Calculated frequencies for HNO_y molecules and ions in cm^{-1}

Molecule	Frequency			
	Method			
	Experimental [21] (harmonic)	Experimental [21] (anharmonic)	UCCSD(T)/ aug-cc-pVQZ	
NO	1904	1876	1943	
	Method			
	Experimental [24]	CCSD(T)/aug-cc-pVDZ	MP2/cc-pVTZ	CCSD(T)/cc-pVQZ [24]
HNO	2684(a′)	2905	3029	2954
	1565(a′)	1578	1586	1604
	1501(a′)	1520	1487	1546
	Method			
	Experimental [25]	MP2/cc-pVTZ		
NO_2	1349(a_1)	1417		
	760(a_1)	802		
	1671(b_1)	1339		
	Method			
	Experimental [26,27]	MP2/cc-pVTZ	MP4STDQ-FC/ 6-311+G** [26]	CCSD(T)/TZ2P [28]
HONO	3591(a′)	3795	3775	3785
	1700(a′)	1673	1650	1696
	1263(a′)	1297	1280	1308
	790(a′)	834	817	796
	596(a′)	619	580	590
	544(a″)	590	559	544
	Method			
	Experimental [43]	MP2/cc-pVTZ	QCISD/cc-pVDZ	
HOONO	3285	3510(a′)	3563	
	1600	1580(a′)	1706	
	1395	1450(a′)	1484	
	927	982(a′)	974	
	794	849(a′)	839	
	629	745(a′)	671	
		532(a″)	411	
		406(a′)	335	
		377(a″)	506	
	Method			
	Experimental [42]	MP2/cc-pVTZ	CCSD(T)/TZ2P [38]	
$HONO_2$	3550(a′)	3749	3747	
	1708(a′)	1872	1722	
	1331(a′)	1351	1349	
	1325(a′)	1334	1310	
	879(a′)	910	895	
	647(a′)	672	649	
	579(a′)	593	580	

Table 2 (*Continued*)

Molecule	Frequency			
	Method			
	Experimental [42]	MP2/cc-pVTZ	CCSD(T)/TZ2P [38]	
	762(a″)	783	761	
	456(a″)	498	469	
	Method			
	Experimental [29–31]	MP2/cc-pVTZ		
NO_2^-	776	802		
	1242	1339		
	1284	1417		
	Method			
		MP2/cc-pVTZ		
NO_3^-		1532(e′)		
		1075(a_1')		
		860(a_2'')		
		725(e′)		
	Method			
		MP2/cc-pVTZ		
$ONOO^-$		1433(a′)		
		1003(a′)		
		962(a′)		
		862(a′)		
		360(a′)		
		562(a″)		
	Method			
	Experimental	UCCSD(T)/aug-cc-pVDZ	UCCSD(T)/aug-cc-pVQZ	MP2/cc-pVTZ
$^3NO^-$	1284 ± 10 [45]	1408	1391	1494
	1363 [21]			
	1370 [44]			
	Method			
	Experimental [46] (harmonic)	Experimental [46] (anharmonic)	CCSD(T)/aug-cc-pVTZ	MP2/cc-pVTZ
HCN	3442 (σ)	3311	3434	3476
	2129 (σ)	2097	2108	2027
	727 (π)	712	717	719
	Method			
		CCSD(T)/aug-cc-pVDZ	CCSD(T)/aug-cc-pVQZ	MP2/cc-pVTZ
CN^-		2016	2061	2002

Table 3
Energy decomposition for calculating heats of formation in kcal mol^{-1}

Molecule	ΣD_e(elec)[a]	ΔE_{CV}[b]	ΔE_{SR}[c]	ΔE_{SO}[d]	ΣD_e	ZPE[e]	ΣD_0
HNO	205.26	0.39	−0.18	−0.21	205.26	8.56	196.70
NO	151.92	0.36	−0.08	−0.05	152.15	2.71	149.44
NO_2	226.16	0.63	−0.59	−0.43	225.77	5.40	220.37
HOONO	356.94	0.87	−0.83	−0.64	356.34	14.35	341.99
$HONO_2$	387.77	1.29	−1.02	−0.64	387.40	16.43	370.97
HONO	310.97	0.50	−0.84	−0.43	310.20	12.29	297.91
NO_3^-	369.80	1.02	−1.43	−0.64	368.75	9.22	359.53
$ONOO^-$	314.82	0.65	−1.21	−0.64	313.62	7.41	306.21
NO_2^-	278.26	0.58	−0.88	−0.43	277.53	5.09	272.44
HCN	311.37	2.08	−0.02	−0.08	313.35	9.95	303.40
CN^-	268.75	1.00	−0.19	−0.08	269.48	2.94	266.54
HNO (aq5)[f]	204.98	0.39	−0.18	−0.21	204.98	8.51	196.47
NO (aq5)[f]	151.81	0.41	−0.23	−0.05	151.94	2.71	149.23
$^3NO^-$ (aq5)[f]	152.04	0.40	−0.39	−0.21	151.84	1.99	149.85

[a] Mixed Gaussian extrapolation of CCSD(T)/aug-cc-pVXZ energies, X = D, T, Q to complete basis set limit (CBS) valence electronic energies.

[b] Core-valence electronic energy corrections.

[c] Scalar-relativistic electronic energy corrections.

[d] Spin-orbit energy corrections.

[e] Zero point energy corrections. See text for details.

[f] ℓ_{max} Extrapolation of the CCSD(T)/aug-cc-pVQZ and CCSD(T)/aug-cc-pV5Z energies. Also, ΔE_{CV} for NO and $^3NO^-$ were calculated with the aug-cc-pCVQZ basis set and ΔE_{SR} was calculated with the aug-cc-pVQZ basis set. See text for details.

Table 4
Calculated and experimental heats of formation in kcal mol^{-1}

Molecule	ΔH_f (calculated, 0 K)	ΔH_f (experimental, 0 K)[a]
HNO	26.44 (26.72)[b]	26.29 ± 0.06[c], 26.3 ± 1[d]
NO	22.07 (22.28)[b]	21.46 ± 0.04
NO_2	10.12	8.59 ± 0.2
HONO	−15.79	−17.37 ± 0.32, −17.40 ± 0.14[e]
HOONO	−0.89	
$HONO_2$	−29.87	−29.75 ± 0.1
NO_3^-	−70.76	−71.7 ± 0.30[f]
$ONOO^-$	−16.74	
NO_2^-	−41.95	−43.8 ± 0.2[g]
HCN	30.74	32.4 ± 2, 31.6 ± 1[e]
CN^-	15.97	17.7 ± 2.3[h]
$^3NO^-$	(21.66)[b]	20.86 ± 0.16[i]
H^+		365.22

[a] Experimental values are from Ref. [32].

[b] Values in parentheses calculated with the ℓ_{max} extrapolation of the CCSD(T)/aug-cc-pVQZ and CCSD(T)/aug-cc-pV5Z energies. See Table 3 and text for additional details.

[c] Ref. [49].

[d] Value at 298 K from Ref. [47] corrected to 0 K by use of Ref. [32].

[e] Ref. [50].

[f] From Ref. [52] converted to 0 K.

[g] From electron affinity measurement, Ref. [30].

[h] From electron affinity measurement, Ref. [58]. See also Ref. [32].

[i] From electron affinity measurement, Ref. [3].

For HNO and NO, the agreement with experiment for ΔH_f worsened by 0.2–0.3 kcal mol^{-1} when we used the larger basis sets suggesting that higher order correlation corrections play a role for these compounds. The core-valence correction was obtained with the large aug-cc-pCVQZ basis set, as use of the smaller cc-pCVQZ basis set led to unreliable values. In fact, the electron was not bound with the smaller basis set. The experimental electron affinity of NO is small, 0.026 eV or 0.60 kcal mol^{-1} [3]. The electron only becomes bound at the CCSD(T)/aug-cc-pV5Z level where the valence electronic affinity is 0.08 kcal mol^{-1}. We calculate a valence electronic binding energy at the CBS limit of NO of 0.23 kcal mol^{-1}. This is essentially eliminated by the scalar relativistic correction of −0.16 kcal mol^{-1} and the spin-orbit correction so that the electron is unbound by 0.10 kcal mol^{-1} (0.004 eV) electronically. However, the difference in zero point energies between NO and NO^- is calculated to be 0.72 kcal mol^{-1}, yielding a calculated electron affinity of 0.62 kcal mol^{-1} in excellent agreement with the experimental value of 0.60 kcal mol^{-1}. Thus, all of the electron affinity of NO is due to the difference in zero point energies. The same conclusion has been reached by McCarthy et al. [39] based on CCSD(T) calculations with a smaller basis set where the electron is not bound. The error in the calculated absolute $\Delta H_f(NO^-)$ is similar to the error in the calculated $\Delta H_f(NO)$. As the electron affinity is calculated correctly, it seems that the origins of the error in $\Delta H_f(NO^-)$ are similar to those in the calculation of the atomization energy of NO.

The electron affinity of NO_2 of 2.271 eV (52.37 kcal mol^{-1}) based on the calculated heats of formations is in excellent agreement with the experimental value of 2.273 ± 0.005 eV (52.42 ± 0.12 kcal mol^{-1}) from photoelectron spectroscopy [30]. Again as the electron affinity is being calculated accurately, it is likely that the error in $\Delta H_f(NO_2^-)$ is due to the difficulty in calculating the atomization energy of NO_2. The heat of formation for NO_3^- has been measured [52] from an equilibrium measurement of the reaction at 298 K.

$$HBr + NO_3^- \rightarrow HONO_2 + Br^- \quad (3)$$

The agreement between our calculated value for $\Delta H_f(NO_3^-)$ and the experimental value obtained from reaction (3) and corrected to 0 K is better than 1 kcal mol^{-1}.

The gas phase acidities are given in Table 5. As noted above, the errors in $\Delta H_f(HNO)$ and $\Delta H_f(NO)$ are similar so that the gas phase acidity of HNO is calculated to be in excellent agreement with that obtained from experiment [3,32]. A similar result is found for the gas phase acidity of HONO which can be obtained from the gas phase heats of formation of the neutrals and the ion [30,32]. The calculated gas phase acidity of $HONO_2$ is within 1.1 kcal mol^{-1} of the experimental value [52]. These results suggest that the gas phase acidity for HOONO is good to ∼1 kcal mol^{-1}. The gas phase acidities show that $HONO_2$ is the strongest acid followed by HONO, 14.4 kcal mol^{-1} less acidic, and then HOONO, 25 kcal mol^{-1} less acidic. The least acidic molecule is HNO, 35.5 kcal mol^{-1} less acidic than $HONO_2$.

In order to calculate the contribution of the solvation energies to the free energy for the solution phase acidity calculations, the absolute solvation energy of the proton is needed. By using high level ab initio electronic structure calculations, we have recently calculated the absolute hydration free energy of the proton to be −262.4 kcal mol^{-1} [53]. This is consistent with a previous ab initio calculation [54] and in excellent agreement with a value obtained by extrapolating results on cluster experiments [55]. This result for the proton is for the solvation free energy determined as the free energy change from the hypothetical 1 bar standard state of gas phase solute at 298.15 K to the 1 M solution at 298.15 K and 1 bar. (Note that 1 atm = 1.013 bar and the difference between 1 atm and 1 bar for our results is <0.01 kcal mol^{-1}.) By using this value with the solvation free energies calculated as described above, we can calculate the free energy changes in aqueous solution based on this choice of the standard state for the solvation energy of the proton. In Table 5, we report the differences in the free energies of solvation for the HA/A^- pair as $\Delta\Delta G_{solv}$. As shown in Table 5, the differences between the $\Delta\Delta G_{solv}$ values calculated at

Table 5
Acidity reaction energies at 298 K in kcal mol^{-1}

Reaction	ΔH (calculated)[a]	ΔH (experimental)[b]	ΔG (calculated)[c]	ΔG (experimental)[d]	$\Delta\Delta G_{solv}$[e]	ΔG_{aq}[f] (calculated)	ΔG_{aq}[g] (experimental/ calculated)	ΔG_{aq}[h] (experimental)
	Gas							
$HONO_2 \rightarrow H^+ + NO_3^-$	325.6	325.5 ± 0.2	319.3	317.8 ± 0.2	−56.9 (−55.9)	0.0	−1.5	−1.9
$HOONO \rightarrow H^+ + ONOO^-$	350.6		343.2		−62.7 (−63.4)	18.1		9.0
$HONO \rightarrow H^+ + NO_2^-$	339.7	340.2 ± 0.2	332.7	333.7 ± 0.3	−62.8 (−62.5)	7.5	8.5	4.6
$HNO \rightarrow H^+ + NO^-$	361.3	361.3 ± 0.2	354.2	354.7 ± 0.4	−69.8 (−69.4)	22.0	22.5	17.2,[i] 6.4
$HCN \rightarrow H^+ + CN^-$	351.6	351.1 ± 2.1	344.3	343.8 ± 2.0	−61.8 (−61.0)	20.0	19.6	11.9
		348.3 ± 2.0		341.0 ± 2.1			16.8	

[a] Calculated using theoretical heats of formation at 0 K and corrected to 298 K.

[b] Calculated using experimental heats of formation at 0 K and corrected to 298 K.

[c] Calculated from column 1.

[d] Calculated from column 2.

[e] Differential solvation energy at the FPCM-MP2/cc-pVTZ level excluding the solvation energy of the proton, i.e., $\Delta\Delta G_{solv} = \Delta G_{solv}(A^-) - \Delta G_{solv}$ (AH). $\Delta G_{solv}(H^+) = -262.4$ kcal mol^{-1}. The corresponding values at the HF/cc-pVTZ level are indicated in the parentheses for comparison.

[f] Free energy change in aqueous solvent $= \Delta G(\text{column } 3) + \Delta\Delta G(\text{column } 5) + \Delta G_{solv}(H^+)$.

[g] Free energy change in aqueous solvent $= \Delta G(\text{column } 4) + \Delta\Delta G(\text{column } 5) + \Delta G_{solv}(H^+)$.

[h] Experimental values converted from pK_a given in Refs. [5,55,56].

[i] Calculated as described in text using values from Refs. [6,7].

Table 6
Calculated and experimental acidity constants

Reaction	K (calculated)[a]	K (calculated)[b]	K (calculated)[c]	K (experimental)[d]
$HONO_2 \rightarrow H^+ + NO_3^-$	1	4.5		24
$HOONO \rightarrow H^+ + ONOO^-$	5.4×10^{-14}			2.50×10^{-7}
$HONO \rightarrow H^+ + NO_2^-$	3.2×10^{-6}	1.0×10^{-6}		4.5×10^{-4}
$HNO \rightarrow H^+ + NO^-$	7.5×10^{-17}	3.2×10^{-17}	10^{-10} to 10^{-13}	2.5×10^{-13}, 2.0×10^{-5}
$HCN \rightarrow H^+ + CN^-$	2.1×10^{-15}	1.8×10^{-15} 4.8×10^{-13}		2.0×10^{-9}

[a] Calculated from ΔG in column 6, Table 5.
[b] Calculated from ΔG in column 7, Table 5.
[c] Best estimate for K_a.
[d] Calculated from ΔG in column 8, Table 5.

the MP2/cc-pVTZ level and those at the HF/cc-pVTZ level are all within 1.0 kcal mol^{-1}. The MP2 values were used in the solvation free energy calculations. The calculated free energies for the solution phase acidity process are given in Table 5 together with the experimental values where known. The K_a's obtained from the free energy changes are then given in Table 6.

The calculated values for the best-established free energy changes in solution, those of HONO and $HONO_2$, are in reasonable agreement with the experimental values [56]. For the NO_x^- series, the solvation effect on the free energy increases as the size of the anion decreases. The calculated free energies are too high by 1.9 kcal mol^{-1} for $HONO_2$ and 2.9 kcal mol^{-1} for HONO. A larger difference of 4.8 kcal mol^{-1} is noted for the comparison of the solution phase acidity of HNO with the latest experimental estimate [6,7]. These differences are consistent with the fact that we are not including any direct solvent interactions (predominantly hydrogen bonding) to the neutrals or anions. This effect is expected to be most important for the anions and the size of this effect is expected to increase as the size of the anion decreases due to the localization of the negative charge.

Another option for the calculation of K_a for HNO is to base it on an acid/anion pair of similar size whose solution phase acidity is known; we chose the HCN/CN^- pair for this comparison. We have calculated the gas phase acidity of HCN using the approach given above (see Table 5 for the final results) and find it to be in good agreement with the value from the acidity scale [32,57] but not with the value based on the electron affinity of CN [58]. This difference is due in part to errors in the experimental heats of formation of HCN and CN. The calculated value for the solution phase acidity of HCN is too high by 8.1 kcal mol^{-1} if we use our calculated values and by smaller differences depending on which experimental values for the gas phase acidity that we choose to use. This allows us to bracket the value of K_a for HNO in solution. At the low end, we predict $pK_a = 10.2$ ($K_a = 6 \times 10^{-11}$) based on taking the difference between the calculated values for HNO and HCN and correcting the calculated value of HCN to the experimental value [56] for $K_a(HCN) = 2.0 \times 10^{-9}$ ($pK_a = 8.7$). If we use the lowest energy experimental value for the gas phase acidity of HCN together with the gas phase experimental value for HNO, we get $pK_a = 12.9$ ($K_a = 1 \times 10^{-13}$) for HNO. These results are clearly in accord with the value of 3×10^{-13} given above based on the results from Stanbury [7] and the new redox measurement of the NO/NO^- couple [6]. The calculated results are clearly different form the older pulse radiolysis experimental value [5] of $K_a = 2 \times 10^{-5}$. Our calculation of the K_a of HNO also differs from Houk and coworkers' theoretical value of 6×10^{-8} [8]. (Houk and co-workers (private communication) have suggested that their original value for the pK_a should be revised upwards and are now in agreement with our proposed range.) This difference from our value is due to the difference in the gas phase acidity enthalpies as well as to the lower level treatment of the solvation correction in the Houk and co-workers' work. We used Houk and coworkers' empirical linear relationship to predict pK_a of HCN and obtained pK_a(HCN) $= 6.4$, ~3 pK_a units smaller than the well-established experimental value of 9.21. We note that the Houk and coworkers pK_a value of 0.6 predicted for HNO_2 by the same relationship is also ~3 pK_a units smaller than the corresponding experimental value of 3.3. Thus, their empirical relationship systematically underestimates the pK_a values of the molecules that we are studying. Nevertheless, the difference in pK_a calculated for HNO and HCN is in good agreement with ours; the pK_a of HNO is slightly larger, in magnitude, than that of HCN. Since the experimental pK_a of HCN is 9.21, use of the Houk and coworker's relationship would predict that pK_a of HNO is ~10, in excellent agreement with our lower limit. Thus, the calculated results are in agreement with the latest experimental results and show that HNO is not an acid in aqueous solution, and its chemistry will be dominated by HNO chemistry, not NO^- chemistry in biological systems.

We can now apply such an analysis to the solution phase acidity of HOONO. The calculated free energy difference for the solution phase acidity of HOONO differs from the experimental value [59] by 8.9 kcal mol^{-1}. If we take HCN as the base to which to compare our values for HOONO, we obtain p$K_a = 7.3$ ($K_a = 5 \times 10^{-8}$) if we use the calculated gas phase acidities. If we use the lowest experimental gas phase acidity for HCN, we obtain p$K_a = 4.9$ ($K_a = 1 \times 10^{-5}$) which clearly brackets the experimental solution phase acidity of p$K_a = 6.5 \pm 0.1$ ($K_a = 3.2 \times 10^{-7}$). This suggests that the effects of the missing solvent molecules in determining the solvation free energy for the solution phase acidity calculation for HOONO are very similar to that of HCN (an error is 8.1 kcal mol^{-1}) but not like the other HNO_x species which have much smaller effects of 2–5 kcal mol^{-1}. This is consistent with the sizes of the differences in solvation free energies which are -62.7 kcal mol^{-1} for HOONO and -61.8 kcal mol^{-1} for HCN. A potential reason for the similarity of HCN and HOONO is the charge localization in the ion. For $NO_3{}^-$, the negative charge is equally shared by the three oxygen atoms (-0.33 e) with little change on the N (-0.02 e) as compared to $HONO_2$ based on Mulliken charges obtained at the HF/cc-pVTZ level. In $NO_2{}^-$, there is some negative charge localized on the N (-0.18 e) and the rest is delocalized on the two oxygen atoms (-0.44 e). Even for NO^-, the negative charge is delocalized with only -0.60 e on the O. For $OONO^-$, the charge is highly localized on the terminal peroxy oxygen with -0.62 e on this atom with the remaining negative charge predominantly on the N=O group. The charge distributions are consistent with the result that there must be large differences in the hydrogen bonding of the first solvation shell to the HOONO/$ONOO^-$ pair as compared to the $HONO_2/NO_3{}^-$, $HONO/NO_2{}^-$, or HNO/NO^- pairs. The charge distribution for CN^- has a charge localization of -0.70 e on the C. The larger charge localization on CN^- is consistent with the fact that the solvent model that we are applying without a first (or second) shell of solvent molecules has a larger error for the difference in solvation free energies for CN^- and $ONOO^-$. These results clearly suggest that the solvation around $ONOO^-$ is likely to be quite different from that around the other $NO_x{}^-$ ($x = 1$–3) ions.

4. Conclusion

The gas phase and aqueous thermochemistries have been calculated for HNO, HONO, HOONO, and $HONO_2$ as well as for HCN. These are the most reliable calculations of the gas phase acidities of these species. The pK_a of HNO is predicted to be in the range of 10–13 consistent with the latest experimental estimate [6] and confirming this value. This is considerably different from the value recently reported by Houk and coworkers [8] of 7.2 ± 1.0 and the value of 4.7 reported from pulse radiolysis experiments [5]. HNO is not predicted to be a weak acid in aqueous solution as previously suggested and will have minimal dissociation near neutral pH. In light of the new pK_a value for HNO, the role that HNO and NO^- play in biological processes warrants further investigation. The calculation of the pK_a of HOONO is complicated by the requirement that at least the first shell of solvent molecules must be explicitly included to get accuracy within a few kcal mol^{-1} and that the error in the calculation of the pK_a of HOONO is similar to that of HCN in the approach that we have taken.

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Appendix A

Supporting information available: Optimized Cartesian coordinates in angstroms at the MP2/cc-pVTZ level (Table A.1) and energies (Hartrees) for the CCSD(T) calculations as a function of the correlation-consistent basis set and extrapolations to the CBS limit (Table A.2).

Table A.1
Cartesian coordinates in angstroms at the MP2/cc-pVTZ level

HNO			
7	0.062607	0.590659	0.000000
1	−0.939102	0.906097	0.000000
8	0.062607	−0.630089	0.000000
HONO (*trans*)			
7	0.000000	0.518869	0.000000
8	−1.117395	0.147863	0.000000
8	0.898264	−0.585317	0.000000
1	1.753048	−0.132448	0.000000
$HONO_2$			
7	0.000000	0.152096	0.000000
8	−0.264692	−1.227308	0.000000
8	1.172900	0.458683	0.000000
8	−0.987370	0.835150	0.000000
1	0.633292	−1.596879	0.000000
HOONO (*cis*)			
7	0.000000	0.988988	−0.006788
8	0.000000	0.626072	−1.146366
8	0.000000	−0.032520	0.915358
8	0.000000	−1.324914	0.316238
1	0.000000	−1.072015	−0.634332
NO_2^-			
7	0.000000000	0.000000000	−0.883092949
8	0.000000000	2.027917470	0.386552558
8	0.000000000	−2.027917470	0.386552558
NO_3^-			
7	0.000000	0.000000	0.000000
8	−0.629062	1.089568	0.000000
8	−0.629062	−1.089568	0.000000
8	1.258125	0.000000	0.000000
$ONOO^-$			
7	−0.928299	−0.100212	0.000000
8	−0.494712	−1.255783	0.000000
8	0.000000	0.860678	0.000000
8	1.306974	0.482790	0.000000
NO^-			
7	0.000000	0.000000	−0.675562
8	0.000000	0.000000	0.591117
HCN			
6	0.00000000	0.0	0.0
7	0.00000000	0.0	1.1668
1	0.0	0.0	−1.0643
CN^- MP2			
7	0.000000	0.000000	−0.548549
6	0.000000	0.000000	0.639974

Table A.2
Total CCSD(T) energies in a.u. as a function of basis set given in the form (n, energy) where $n = 2$ aug-cc-pVDZ; $n = 3$ aug-cc-pVTZ; $n = 4$ aug-cc-pVQZ; $n = 5$ aug-cc-pV5Z

NO_3^-
2, −279.7857633
3, −280.0164492
4, −280.0903597
CBS, −280.1323357

NO_2^-
2, −204.7319162
3, −204.8987153
4, −204.9519364
CBS, −204.9821383

NO^-
4, −129.7582474
5, −129.7687295
CBS, −129.7797271

NO
4, −129.7583563
5, −129.7686023
CBS, −129.7793522

NO_2
2, −204.652345
3, −204.816669
4, −204.868852
CBS, −204.8984376

HNO
2, −130.203904
3, −130.309749
4, −130.342629
CBS, −130.3611902

HNO
4, −130.342629
5, −130.3530987
CBS, −130.3640837

$HONO_2$
2, −280.312112
3, −280.545002
4, −280.618473
CBS, −280.6600747

HONO (*trans*)
2, −205.2832781
3, −205.4521921
4, −205.5050827
CBS, −205.5349872

NO_3^-
2, −279.7857633
3, −280.0164492
4, −280.0903597
CBS, −280.1323357

Table A.2 (*Continued*)

$ONOO^-$
2, −279.7019242
3, −279.9317942
4, −280.0039193
CBS, −280.0447154

HCN
2, −93.2047108
3, −93.2811669
4, −93.3034570
CBS, −93.3158761

CN^-
2, −92.6405266
3, −92.7131052
4, −92.7354000
CBS, −92.7479575

CBS limit from mixed exponential expression: $E(x) = A_{CBS} + B\exp[-(x-1)] + C\exp[-(x-1)^2]$ except for HNO, NO and NO^- with aug-cc-pV5Z basis set where the CBS limit is from the expression: $E(n) = E_{CBS} + A\,\ell_{max}^{-3}$.

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