Supporting Information for

Isomeric Structures of Isolated Ammonium Nitrate and Its Hydrogenated Species Identified Through PES Experiments and DFT Calculations

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More low lying isomers of $(NH_4NO_3 + nH)^-$ (n = 1-5) anions are summarized in Figures S5, S7 to S10 in the Supporting Information. Note that the figure numbers in the S.I. document are related to those of the text figures, as for example Figure S5 ⇔ Figure 5.

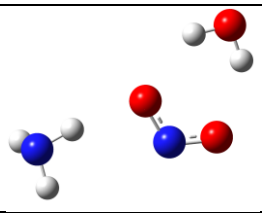
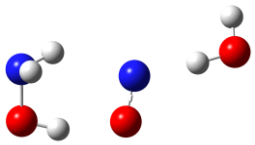
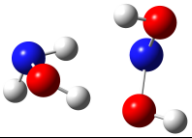
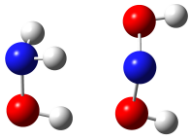
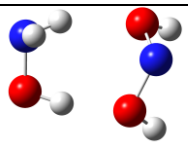
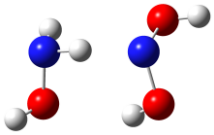
Optimized Anionic Structures				
ΔE (eV)	00	3.28	4.34	4.42
VDE (eV)	**4.02**	**1.60**	**1.71**	**1.82**
Optimized Anionic Structures				
ΔE (eV)	4.44	4.56		
VDE (eV)	**1.77**	**1.37**		

Figure S5 Optimized geometries of the typical low lying anionic isomers of $(NH_4NO_3 + H)^-$ based on ωb97XD/aug-cc-pvtz DFT calculations. The relative energies and calculated VDEs are indicated.

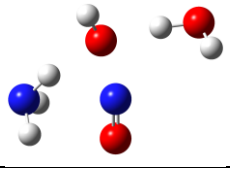
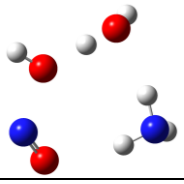
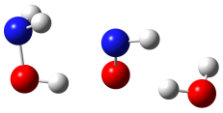
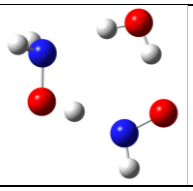
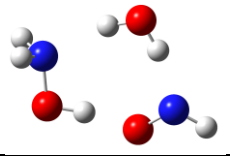
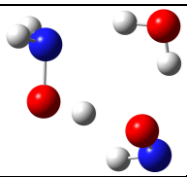
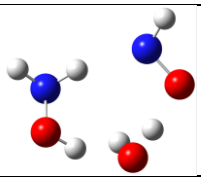
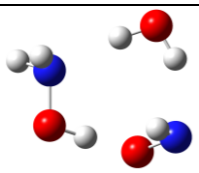
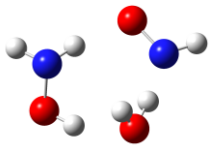
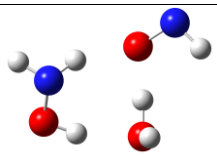
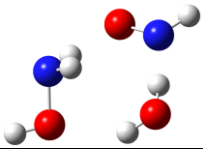
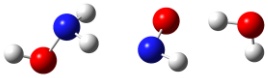
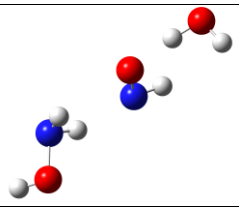
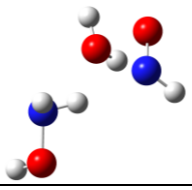
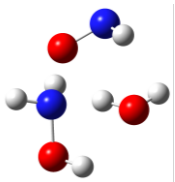
Optimized Anionic Structures				
ΔE (eV)	0.00	0.11	1.45	1.49
VDE (eV)	**3.26**	**2.94**	**3.08**	**2.52**
Optimized Anionic Structures				
ΔE (eV)	1.52	1.58	1.60	1.61
VDE (eV)	**2.55**	**2.61**	**2.65**	**2.56**
Optimized Anionic Structures				
ΔE (eV)	1.61	1.69	1.73	1.77
VDE (eV)	**2.55**	**2.72**	**2.35**	**2.50**
Optimized Anionic Structures				
ΔE (eV)	1.77	1.84	1.64	1.98
VDE (eV)	**2.50**	**2.27**	**2.43**	**2.20**

Figure S7 Optimized geometries of the typical low lying anionic isomers of $(NH_4NO_3 + 2H)^-$ based on ωb97XD/aug-cc-pvtz DFT calculations. The relative energies and calculated VDEs are indicated.

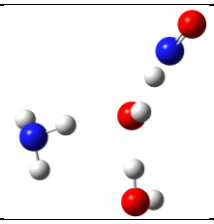
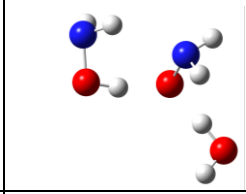
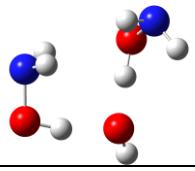
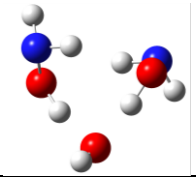
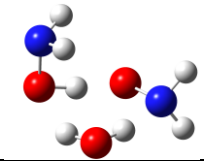
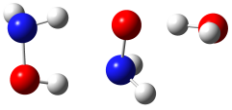
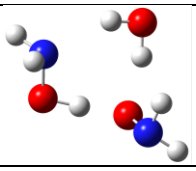
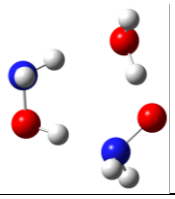
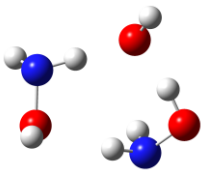
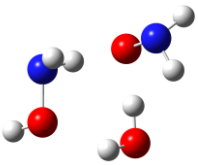
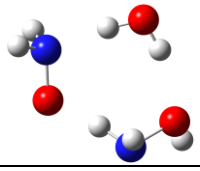
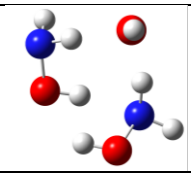
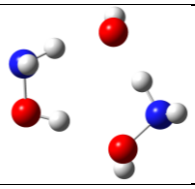
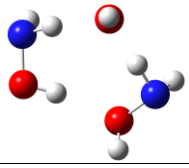
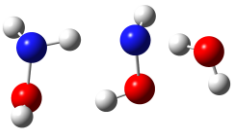
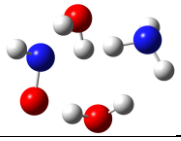
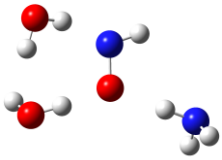
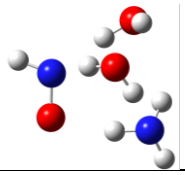
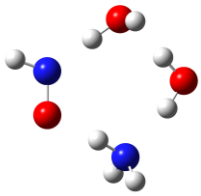
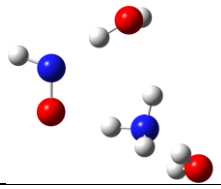
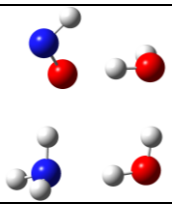
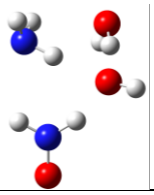
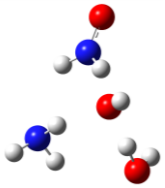
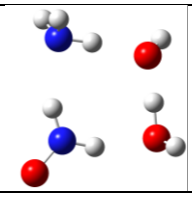
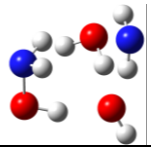
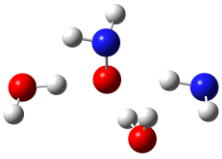
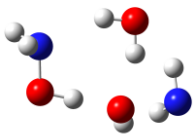
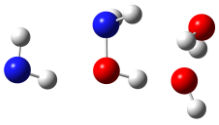
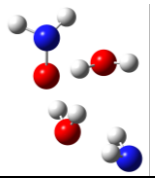
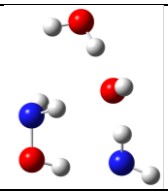
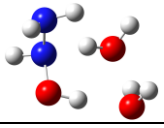
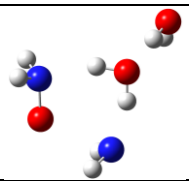
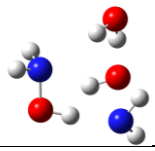
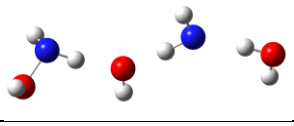
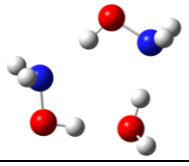
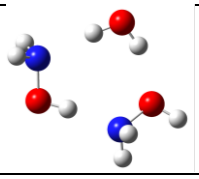
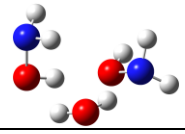
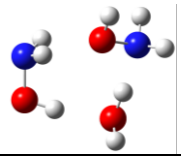
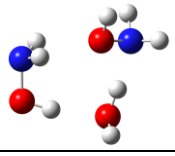
Optimized Anionic Structures				
ΔE (eV)	0.00	1.01	1.01	1.07
VDE (eV)	**3.81**	**3.09**	**4.19**	**3.88**
Optimized Anionic Structures				
ΔE (eV)	1.08	1.12	1.12	1.13
VDE (eV)	**2.89**	**2.98**	**2.84**	**2.75**
Optimized Anionic Structures				
ΔE (eV)	1.18	1.38	1.38	1.41
VDE (eV)	**2.95**	**3.61**	**3.67**	**2.46**
Optimized Anionic Structures				
ΔE (eV)	1.49	1.49	1.55	1.57
VDE (eV)	**2.25**	**2.25**	**2.19**	**3.48**
Optimized Anionic Structures				
ΔE (eV)	1.57	1.58	1.62	1.62
VDE (eV)	**2.94**	**2.94**	**3.50**	**3.50**
Optimized Anionic Structures				
ΔE (eV)	1.63	2.02		
VDE (eV)	**3.53**	**2.23**		

Figure S8 Optimized geometries of the typical low lying anionic isomers of $(NH_4NO_3 + 3H)^-$ based on ωb97XD/aug-cc-pvtz DFT calculations. The relative energies and calculated VDEs are indicated.

Optimized Anionic Structures				
ΔE (eV)	0.00	0.01	0.02	0.08
VDE (eV)	**2.98**	**3.03**	**2.78**	**2.71**
Optimized Anionic Structures				
ΔE (eV)	0.09	0.12	0.16	0.16
VDE (eV)	**2.68**	**2.82**	**4.14**	**4.14**
Optimized Anionic Structures				
ΔE (eV)	0.23	1.51	1.56	1.60
VDE (eV)	**4.30**	**5.80**	**5.62**	**5.93**
Optimized Anionic Structures				
ΔE (eV)	1.61	1.62	1.76	1.78
VDE (eV)	**6.46**	**5.78**	**5.98**	**-0.28**
Optimized Anionic Structures				
ΔE (eV)	1.93	2.09	2.14	2.93
VDE (eV)	**3.36**	**4.08**	**5.69**	**-0.46**
Optimized Anionic Structures				
ΔE (eV)	3.03	3.04	3.05	3.05
VDE (eV)	**-0.12**	**0.14**	**0.06**	**0.06**

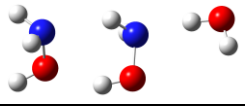
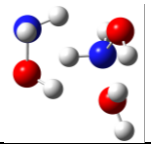
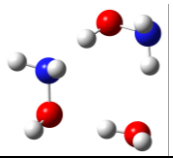
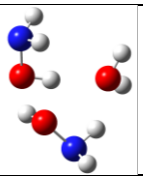
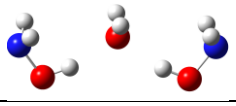
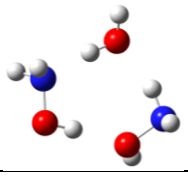
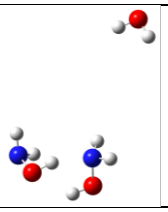
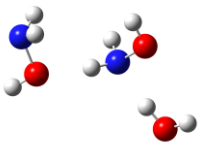
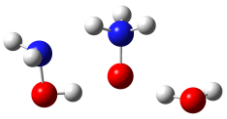
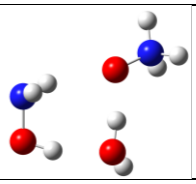
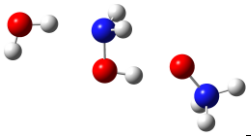
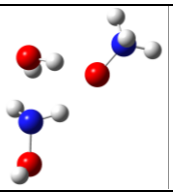
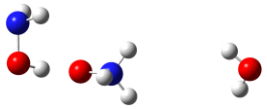
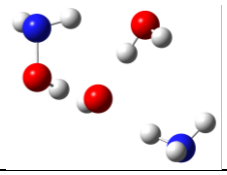
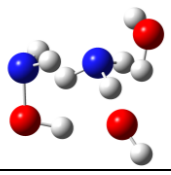
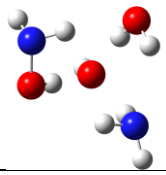
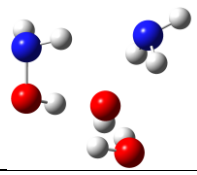
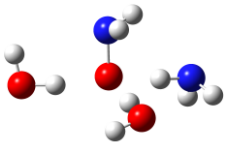
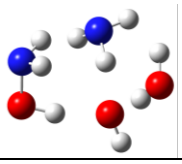
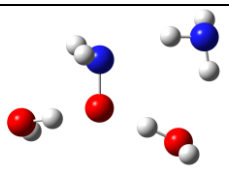
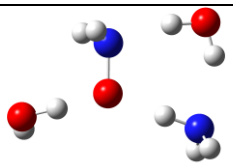
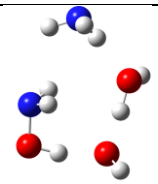
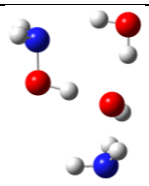
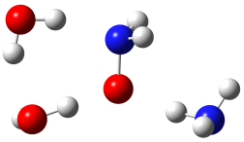
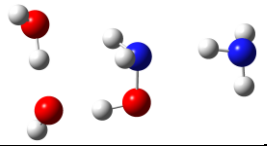
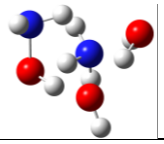
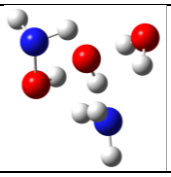
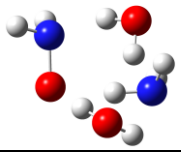
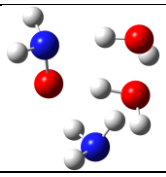
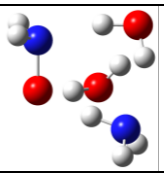
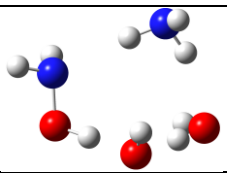
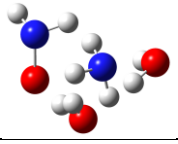
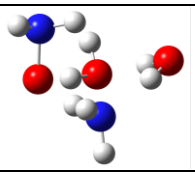
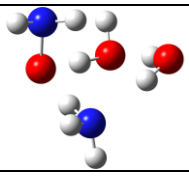
Optimized Anionic Structures				
ΔE (eV)	3.06	3.06	3.08	3.10
VDE (eV)	**0.05**	**-0.03**	**0.16**	**0.03**
Optimized Anionic Structures				
ΔE (eV)	3.10	3.13	3.23	3.25
VDE (eV)	**0.28**	**-0.44**	**-0.06**	**-0.14**
Optimized Anionic Structures				
ΔE (eV)	3.30	3.30	3.36	3.37
VDE (eV)	**0.05**	**-0.08**	**0.43**	**0.36**
Optimized Anionic Structures				
ΔE (eV)	3.51	3.51		
VDE (eV)	**0.22**	**0.51**		

Figure S9 Optimized geometries of the typical low lying anionic isomers of $(NH_4NO_3 + 4H)^-$ based on ωb97XD/aug-cc-pvtz DFT calculations. The relative energies and calculated VDEs are indicated.

Optimized Anionic Structures				
ΔE (eV)	0.00	0.01	0.03	0.04
VDE (eV)	**4.38**	**4.25**	**4.21**	**4.18**
Optimized Anionic Structures				
ΔE (eV)	0.04	0.04	0.06	0.06
VDE (eV)	**3.24**	**4.33**	**3.23**	**3.09**
Optimized Anionic Structures				
ΔE (eV)	0.06	0.07	0.08	0.08
VDE (eV)	**3.27**	**4.33**	**3.15**	**3.11**
Optimized Anionic Structures				
ΔE (eV)	0.08	0.09	0.09	0.09
VDE (eV)	**4.18**	**3.17**	**4.22**	**3.92**
Optimized Anionic Structures				
ΔE (eV)	0.09	0.10	0.10	0.12
VDE (eV)	**3.92**	**2.94**	**2.93**	**2.80**
Optimized Anionic Structures				
ΔE (eV)	0.14	0.15	0.15	0.15
VDE (eV)	**4.09**	**2.84**	**2.85**	**2.84**

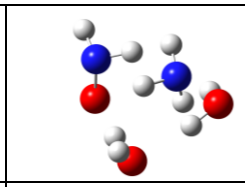
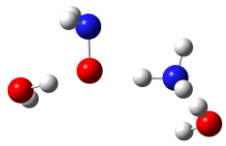
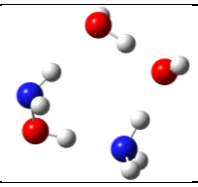
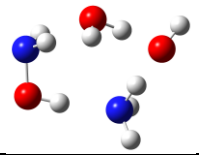
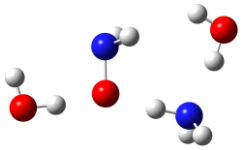
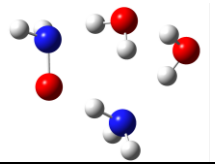
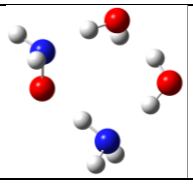
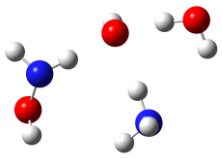
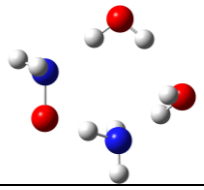
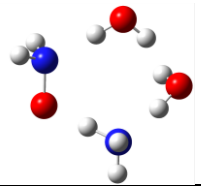
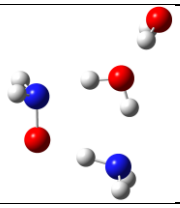
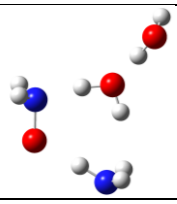
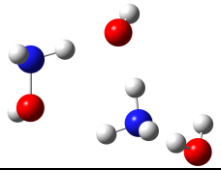
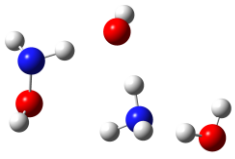
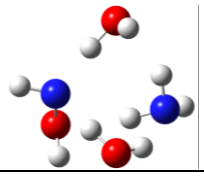
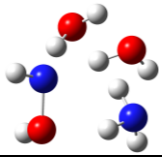
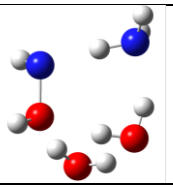
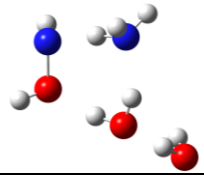
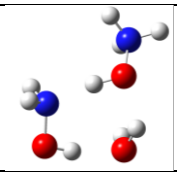
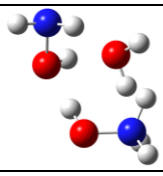
Optimized Anionic Structures				
ΔE (eV)	0.16	0.21	0.23	0.23
VDE (eV)	**2.84**	**2.95**	**4.19**	**4.20**
Optimized Anionic Structures				
ΔE (eV)	0.24	0.39	0.39	0.39
VDE (eV)	**2.88**	**2.65**	**2.65**	**4.02**
Optimized Anionic Structures				
ΔE (eV)	0.41	0.41	0.42	0.44
VDE (eV)	**2.55**	**2.55**	**2.53**	**3.62**
Optimized Anionic Structures				
ΔE (eV)	0.51	0.59	0.62	0.66
VDE (eV)	**2.50**	**3.63**	**3.62**	**2.91**
Optimized Anionic Structures				
ΔE (eV)	0.70	0.70	1.01	1.08
VDE (eV)	**2.83**	**2.83**	**2.37**	**2.31**
Optimized Anionic Structures				
ΔE (eV)	5.67	5.76		
VDE (eV)	**0.36**	**0.41**		

Figure S10 Optimized geometries of the typical low lying anionic isomers of $(NH_4NO_3 + 5H)^-$ based on ωb97XD/aug-cc-pvtz DFT calculations. The relative energies and calculated VDEs are indicated.

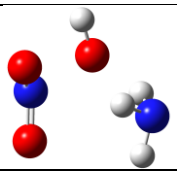
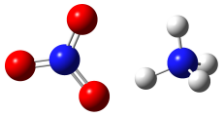
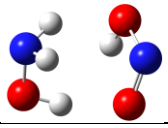
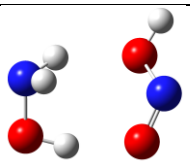
Optimized Anionic Structures				
ΔE (eV)	0.00	0.62	0.53	0.59
VDE (eV)	**3.87**	**0.43**	**2.18**	**2.12**

Figure S14 Optimized geometries of the typical low lying anionic isomers of parent anion $NH_4NO_3^-$ based on M062X/aug-cc-pvtz DFT calculations. The relative energies and calculated VDEs are indicated. The isomers have nearly identical structures with respect to the corresponding isomers optimized at ωb97XD/aug-cc-pvtz DFT level of theory.

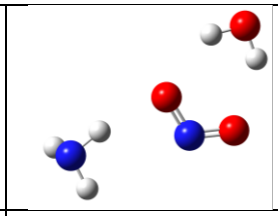
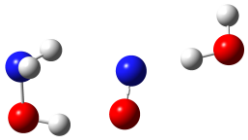
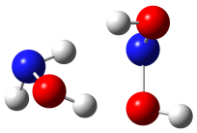
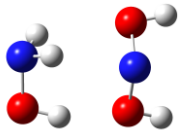
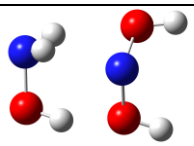
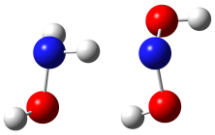
Optimized Anionic Structures				
ΔE (eV)	0.00	3.17	4.14	4.24
VDE (eV)	**4.28**	**1.79**	**1.85**	**1.97**
Optimized Anionic Structures				
ΔE (eV)	4.24	4.39		
VDE (eV)	**1.96**	**1.54**		

Figure S15 Optimized geometries of the typical low lying anionic isomers of $(NH_4NO_3 + H)^-$ based on M062X/aug-cc-pvtz DFT calculations. The relative energies and calculated VDEs are indicated.

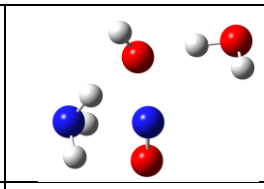
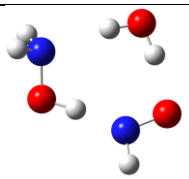
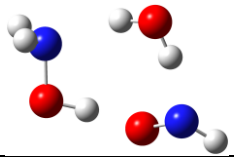
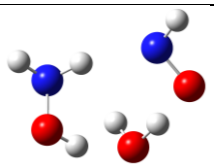
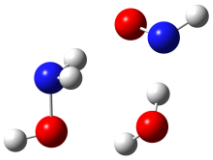
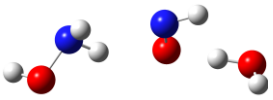
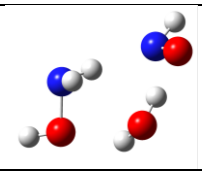
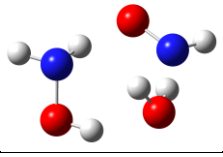
Optimized Anionic Structures				
ΔE (eV)	0.00	1.35	1.42	1.45
VDE (eV)	**3.68**	**3.21**	**2.68**	**2.74**
Optimized Anionic Structures				
ΔE (eV)	1.51	1.53	1.66	1.69
VDE (eV)	**2.77**	**2.61**	**2.43**	**2.64**
Optimized Anionic Structures				
ΔE (eV)	1.67	1.53		
VDE (eV)	**2.48**	**2.61**		

Figure S16 Optimized geometries of the typical low lying anionic isomers of $(NH_4NO_3 + 2H)^-$ based on M062X/aug-cc-pvtz DFT calculations. The relative energies and calculated VDEs are indicated.

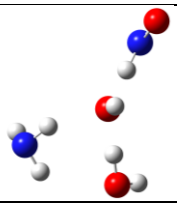
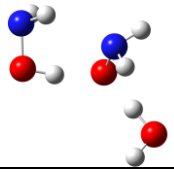
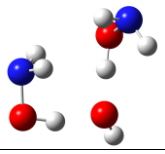
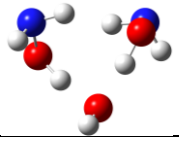
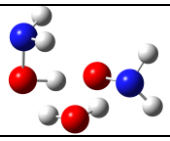
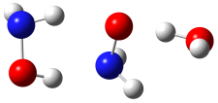
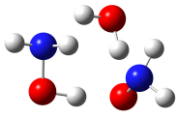
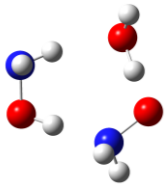
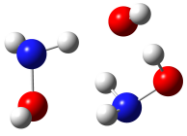
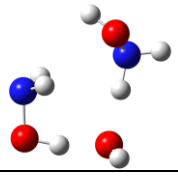
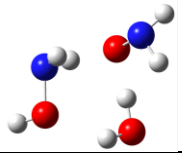
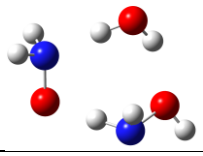
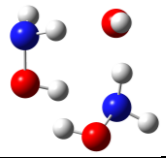
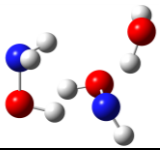
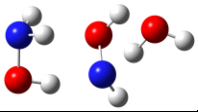
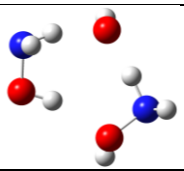
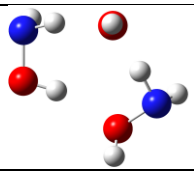
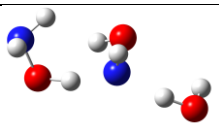
Optimized Anionic Structures				
ΔE (eV)	0.00	0.89	0.88	0.85
VDE (eV)	**4.03**	**3.44**	**4.51**	**4.44**
Optimized Anionic Structures				
ΔE (eV)	0.93	1.00	0.98	0.99
VDE (eV)	**3.20**	**3.34**	**3.20**	**3.23**
Optimized Anionic Structures				
ΔE (eV)	1.09	1.30	1.29	1.33
VDE (eV)	**3.33**	**3.87**	**3.93**	**2.76**
Optimized Anionic Structures				
ΔE (eV)	1.40	1.40	1.49	1.51
VDE (eV)	**2.52**	**2.52**	**2.44**	**3.70**
Optimized Anionic Structures				
ΔE (eV)	1.42	1.43	1.59	1.59
VDE (eV)	**3.21**	**3.24**	**3.72**	**3.72**
Optimized Anionic Structures				
ΔE (eV)	0.89	1.46		
VDE (eV)	**3.42**	**3.23**		

Figure S17 Optimized geometries of the typical low lying anionic isomers of $(NH_4NO_3 + 3H)^-$ based on M062X/aug-cc-pvtz DFT calculations. The relative energies and calculated VDEs are indicated.

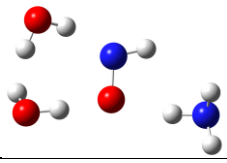
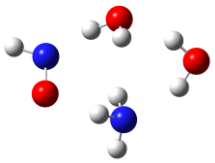
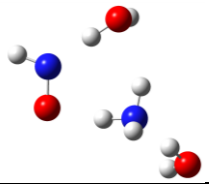
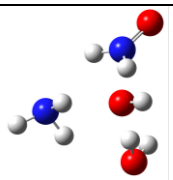
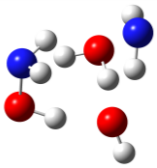
Optimized Anionic Structures				
ΔE (eV)	0.00	0.03	0.13	0.15
VDE (eV)	**3.10**	**3.14**	**2.82**	**2.78**
Optimized Anionic Structures				
ΔE (eV)	0.21	1.43	1.50	
VDE (eV)	**4.22**	**6.16**	**6.01**	

Figure S18 Optimized geometries of the typical low lying anionic isomers of $(NH_4NO_3 + 4H)^-$ based on M062X/aug-cc-pvtz DFT calculations. The relative energies and calculated VDEs are indicated.

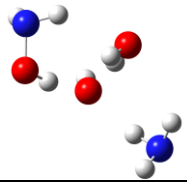
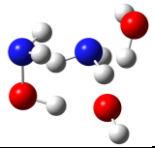
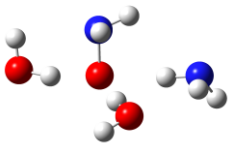
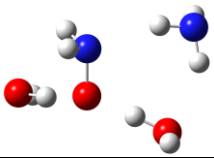
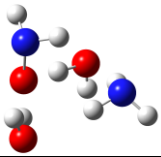
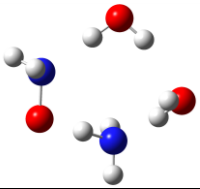
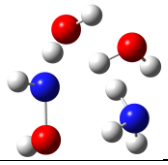
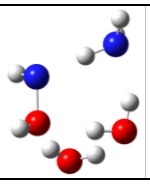
Optimized Anionic Structures				
ΔE (eV)	0.03	0.00	0.04	0.08
VDE (eV)	**3.31**	**4.48**	**3.57**	**3.20**
Optimized Anionic Structures				
ΔE (eV)	0.05	0.11	0.43	0.44
VDE (eV)	**3.46**	**3.06**	**2.74**	**2.73**
Optimized Anionic Structures				
ΔE (eV)	0.64	1.00	1.08	
VDE (eV)	**3.04**	**2.52**	**2.44**	

Figure S19 Optimized geometries of the typical low lying anionic isomers of $(NH_4NO_3 + 5H)^-$ based on M062X/aug-cc-pvtz DFT calculations. The relative energies and calculated VDEs are indicated.

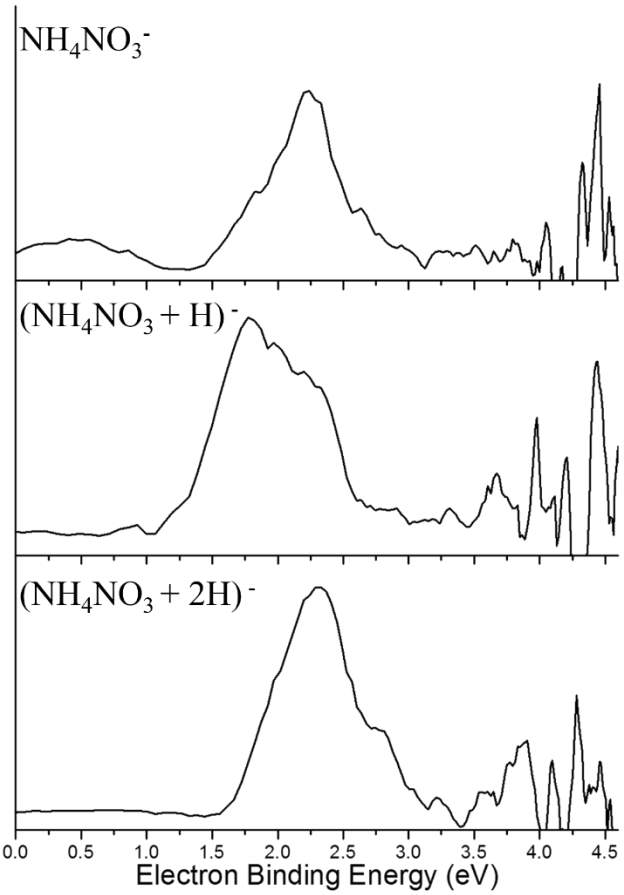


Figure S20 Photoelectron spectra of $(NH_4NO_3 + nH)^-$ (n = 0-2) recorded with 266 nm photons. The features around 4 eV come from noise.

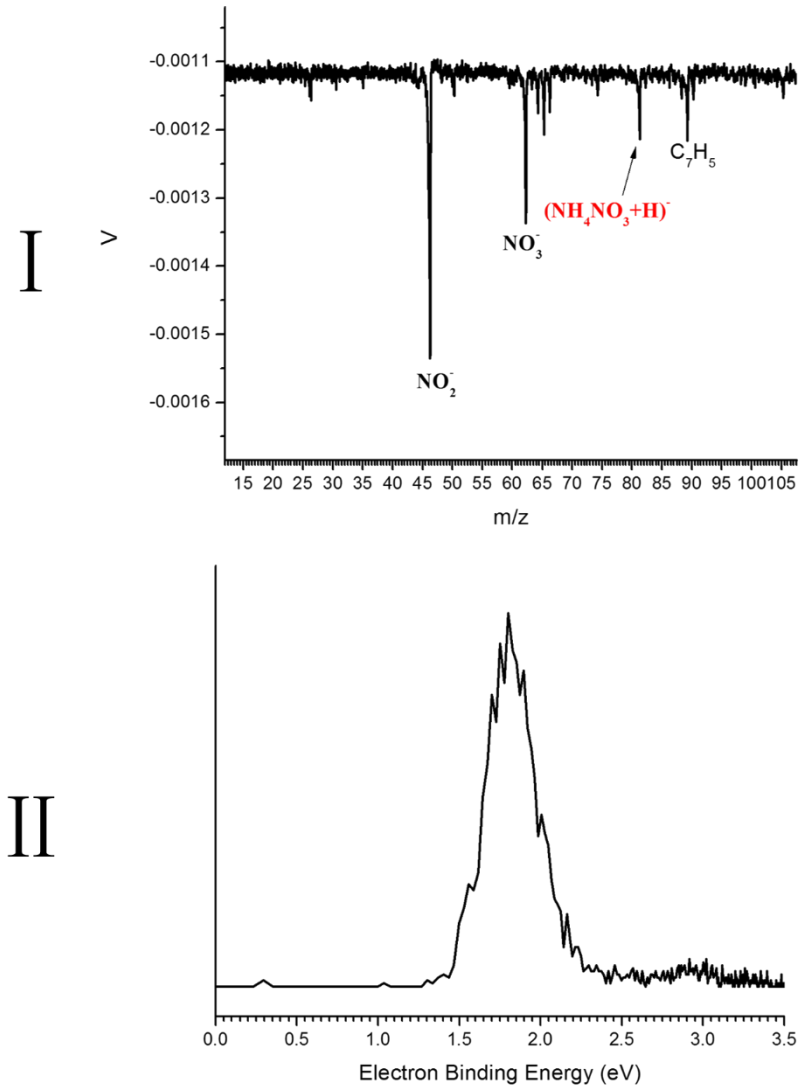


Figure S21 (I) Mass spectrum of $(NH_4NO_3 + H)^-$ with sample (NH_4NO_3/DCM) spayed on a Zn substrate. (II) Photoelectron spectrum of $(NH_4NO_3 + H)^-$ recorded with 355 nm photons with sample (NH_4NO_3/DCM) spayed on a Zn substrate.

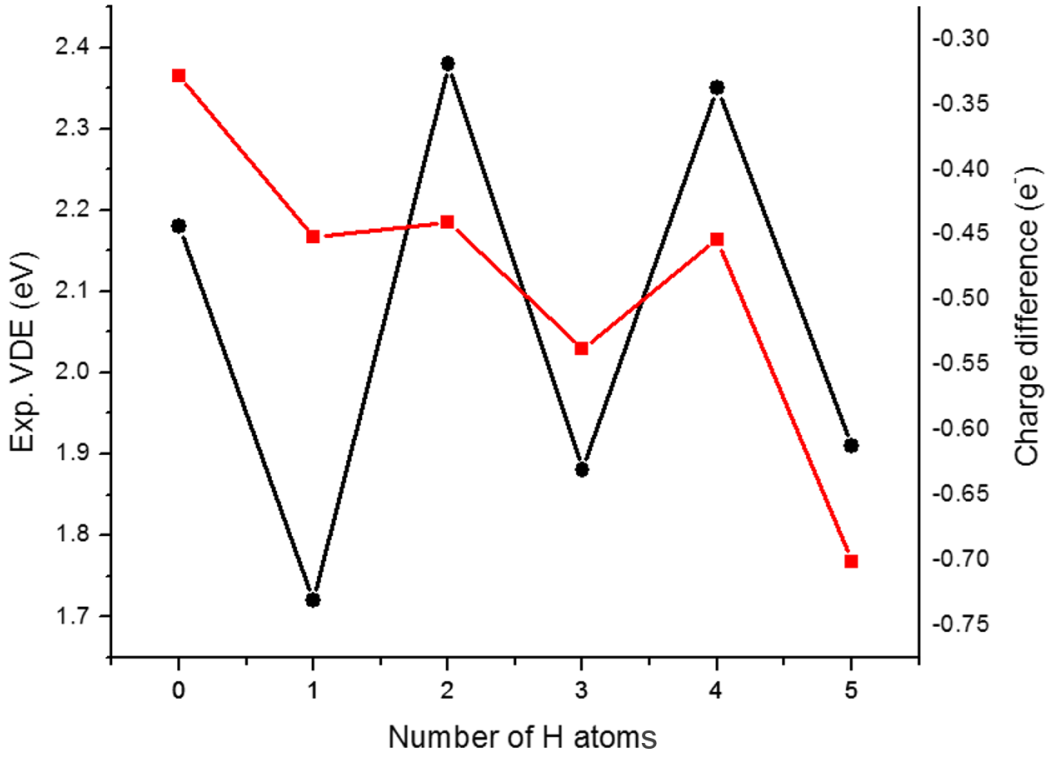


Figure S22 Experimental VDEs (black line) and charge differences (red line) between anion and corresponding neutral at the same geometry as that of anion on local atom of specific anionic isomers with increasing number of H atom. (n = 0, isomer (C); n = 1, isomer $1H^-$ (B); n = 2, isomer $2H^-$ (C); n = 3, isomer $3H^-$ (I); n = 4, isomer $4H^-$ (D); n = 5, isomer $5H^-$ (J)) Both lines show similar trend patterns. As can be seen from Figure 11 in the text, the NBO/HOMOS of these anionic isomers all show valence bound extra electron wave functions mostly localized on O/N p orbitals.

Table S1 Binding energies (eV/mol) of three anionic isomers ((A), (B), and (C)) of $NH_4NO_3^-$ parent anion.

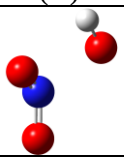
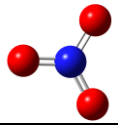
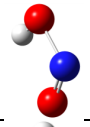
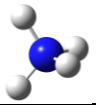
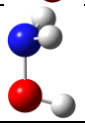
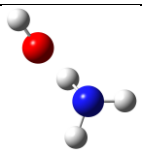
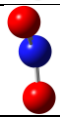
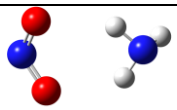
Isomer	(A)	(B)	(C)
Moiety 1			
Moiety 2			
Binding energy	0.36	1.15	0.94
BSSE		0.008	0.011
Binding energy with BSSE		1.16	0.95
Moiety 3			
Moiety 4			
Binding energy ΔH	85.59		
Moiety 5			
Moiety 6			
Binding energy ΔH	72.98		

Table S2 Chemical compound names of different moieties exhibited in the isomeric structures shown in present work.

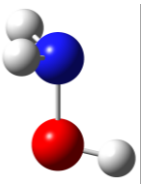
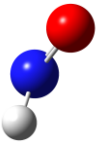
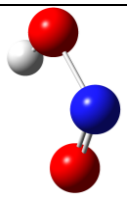
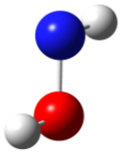
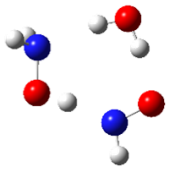
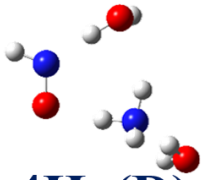
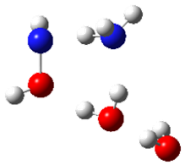
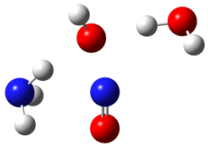
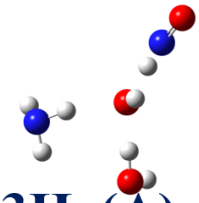
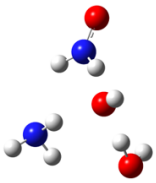
				
formula	NH_2OH	HNO	HONO	HNOH
name	hydroxylamine	nitroxyl	nitrous acid	hydroxyazanyl or aminoxyl

Table S3 Binding energies (eV/mol) of different isomers for hydrogenated cluster anions $(NH_4NO_3 + nH)^-$ (n = 2-5). The binding energies are given as the dissociation energy for losing the least strongly bound fragments.

		$(NH_4NO_3 + 2H)^-$	$(NH_4NO_3 + 3H)^-$	$(NH_4NO_3 + 4H)^-$	$(NH_4NO_3 + 5H)^-$
observed isomer		 $2H^-$ (C)	 $3H^-$ (H)	 $4H^-$ (D)	 $5H^-$ (J)
	binding energy	0.76	0.56	0.57	0.53
not observed isomer		 $2H^-$ (A)	 $3H^-$ (A)	 $4H^-$ (E)	 $5H^-$ (A)
	binding energy	0.29	0.36	0.36	0.37