

## Supporting Information

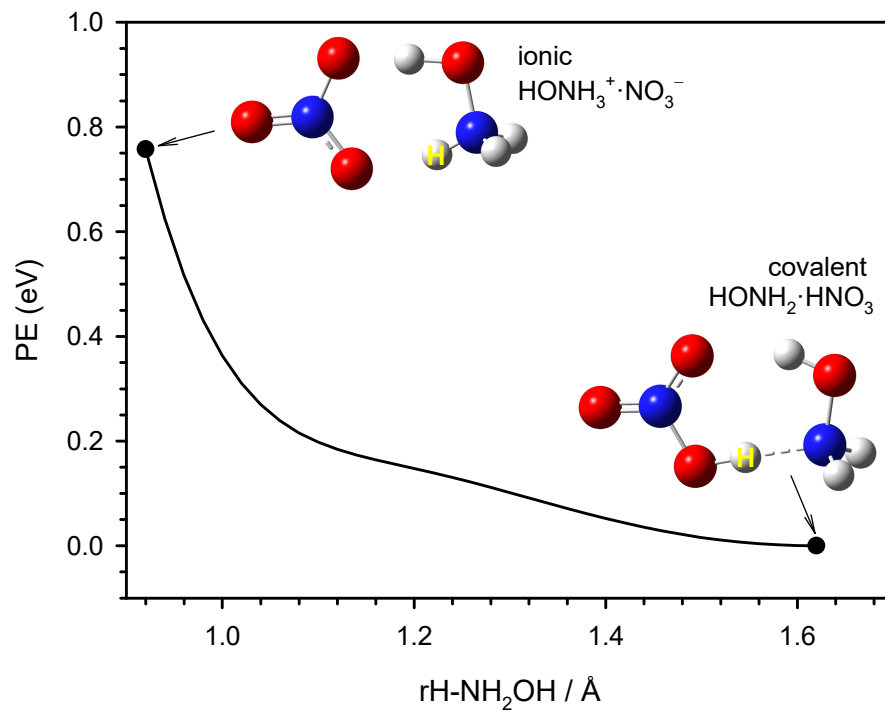
Structures, Proton Transfer and Dissociation of Hydroxylammonium Nitrate (HAN)  
Revealed by Tandem Electrospray Ionization Mass Spectrometry and Molecular Dynamics Simulations

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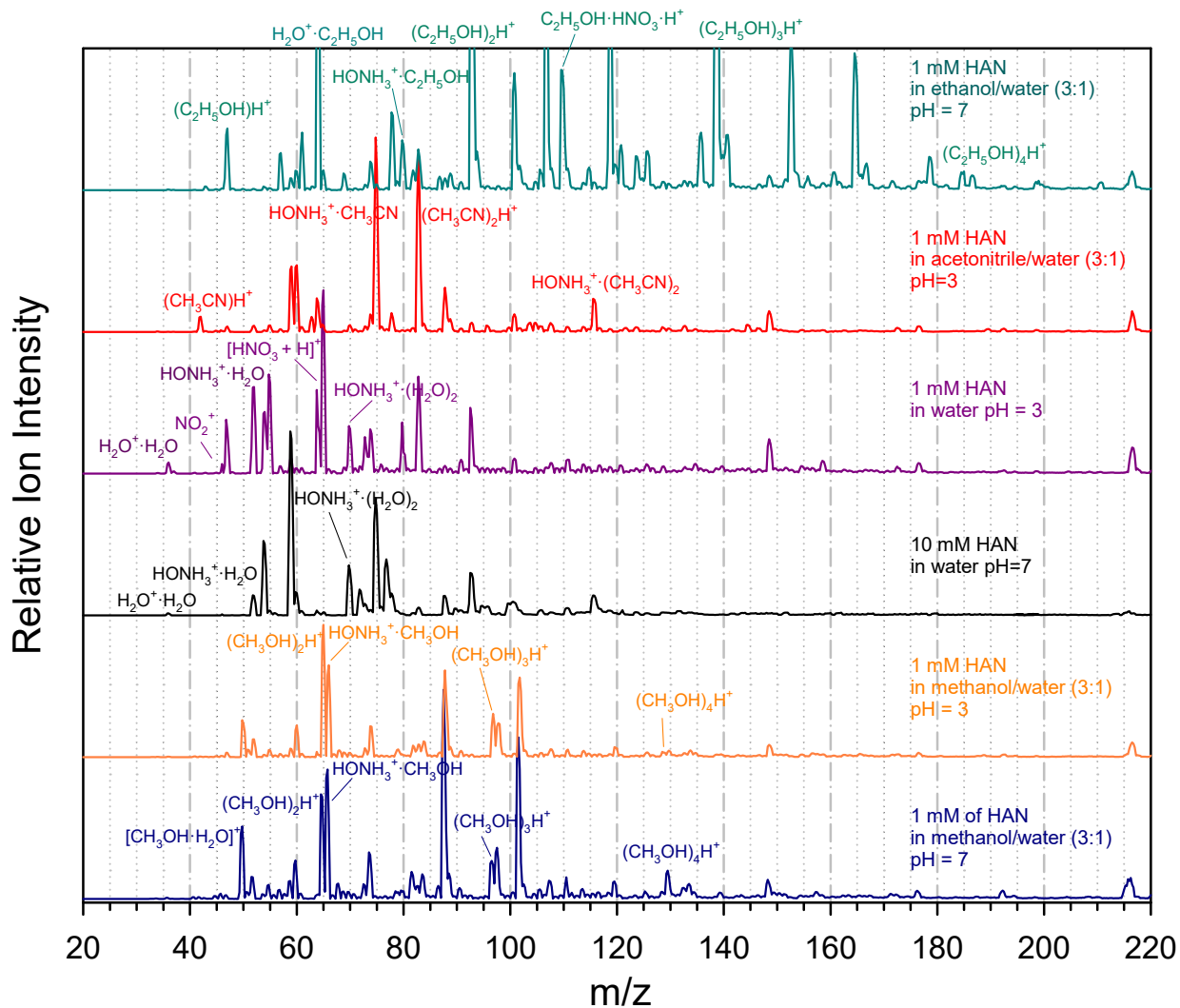
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**Fig. S1** A relaxed PES scan along the proton transfer coordinate within HONH<sub>2</sub>·HNO<sub>3</sub>, calculated at the  $\omega$ B97XD/6-31+G(d,p) level of theory.



**Fig. S2** Positive ESI mass spectra of HAN measured in various solvents and at pH = 3 and 7, respectively. Note that the ESI ion intensity of a typical 1 mM cation solution is  $\sim 1 \times 10^6$  counts/s measured at an ESI voltage of  $\sim +2.3$  kV. However, a much higher voltage (+3.4 kV) was required to initiate electrospray of HAN solutions, and the maximum ion intensity in these mass spectra was only  $< 5 \times 10^4$  counts/s. The lack of any obvious intact HAN species in the positive ESI mass spectra indicates the use of HAN in electrospray could result in a significant loss of thrust because of neutralization and/or the presence of other reactive channels.

**Cartesian coordinates optimized at  $\omega$ B97XD/6-31+G(d,p)****HONH<sub>2</sub>·HNO<sub>3</sub>**

N1 1.971556 0.649636 -0.000106  
 H2 2.447331 1.025105 -0.818687  
 H3 2.446977 1.025483 0.818508  
 O4 2.247171 -0.737888 0.000278  
 H5 1.361950 -1.138561 0.000124  
 N6 -1.272523 -0.071090 -0.000036  
 O7 -0.639365 1.114339 -0.000028  
 H8 0.374782 0.922287 -0.000344  
 O9 -0.575833 -1.083584 -0.000316  
 O10 -2.472508 -0.028384 0.000241

Rotational constants (GHz): 8.5838351 1.7886277 1.4920015

Zero-point correction= 0.071173 (Hartree/Particle)  
 Thermal correction to Energy= 0.078119  
 Thermal correction to Enthalpy= 0.079063  
 Thermal correction to Gibbs Free Energy= 0.039155  
 Sum of electronic and zero-point Energies= -412.451598  
 Sum of electronic and thermal Energies= -412.444652  
 Sum of electronic and thermal Enthalpies= -412.443708  
 Sum of electronic and thermal Free Energies= -412.483616

**<sup>-</sup>O<sub>3</sub>N·HONH<sub>3</sub><sup>+</sup>·NO<sub>3</sub><sup>-</sup>**

N1 -0.141098 0.494491 0.059375  
 H2 -1.015402 0.424225 -0.539795  
 H3 -0.503652 0.415107 1.013587  
 O4 0.499712 1.721651 -0.137889  
 H5 1.460406 1.499297 0.029094  
 N6 3.087451 -0.381106 -0.012106  
 O7 2.081226 -1.045059 -0.393567  
 H8 0.551579 -0.267003 -0.136393  
 O9 2.921703 0.820928 0.361972  
 O10 4.205098 -0.886003 0.002579  
 N11 -3.202048 -0.255415 0.028178  
 O12 -2.565230 0.131948 -1.007037  
 O13 -2.575340 -0.376128 1.111297  
 O14 -4.405052 -0.502015 -0.049182

Rotational constants (GHz): 3.4585888 0.3777837 0.3611731

Zero-point correction= 0.088034 (Hartree/Particle)  
 Thermal correction to Energy= 0.099337  
 Thermal correction to Enthalpy= 0.100281  
 Thermal correction to Gibbs Free Energy= 0.046866

Sum of electronic and zero-point Energies= -692.780781  
 Sum of electronic and thermal Energies= -692.769478  
 Sum of electronic and thermal Enthalpies= -692.768534  
 Sum of electronic and thermal Free Energies= -692.821949

*cyclic*-[HONH<sub>3</sub><sup>+</sup>·NO<sub>3</sub><sup>-</sup>·HONH<sub>3</sub><sup>+</sup>·NO<sub>3</sub><sup>-</sup>]

N1 -1.577896 -1.452901 0.852240  
 H2 -1.085875 -1.971192 0.090218  
 H3 -1.544945 -1.995275 1.713878  
 O4 -2.922254 -1.217484 0.550470  
 H5 -2.901822 -0.331744 0.109395  
 N6 -1.218835 1.625093 -0.263104  
 O7 -0.598193 1.064182 0.723973  
 H8 -1.081956 -0.532999 0.980311  
 O9 -2.331834 1.181474 -0.590473  
 O10 -0.674674 2.558982 -0.838135  
 N11 2.027697 1.405155 0.240596  
 H12 2.441985 2.329324 0.139221  
 H13 1.001318 1.469463 0.484815  
 O14 2.724820 0.748710 1.259976  
 H15 2.344913 -0.166661 1.202188  
 N16 1.119512 -1.469727 -0.618366  
 O17 1.892981 -0.826164 -1.350705  
 H18 2.117954 0.843468 -0.631025  
 O19 1.208453 -1.361810 0.645413  
 O20 0.232587 -2.197605 -1.096589

Rotational constants (GHz): 0.8878585 0.6893278 0.4883460

Zero-point correction= 0.146906 (Hartree/Particle)  
 Thermal correction to Energy= 0.161463  
 Thermal correction to Enthalpy= 0.162407  
 Thermal correction to Gibbs Free Energy= 0.103813  
 Sum of electronic and zero-point Energies= -824.931707  
 Sum of electronic and thermal Energies= -824.917151  
 Sum of electronic and thermal Enthalpies= -824.916207  
 Sum of electronic and thermal Free Energies= -824.974800