

Thermochemistry of Ammonium Nitrate, NH_4NO_3 , in the Gas Phase

Karl K. Irikura

*Chemical and Biochemical Reference Data Division,
National Institute of Standards and Technology, Gaithersburg, MD 20899-8320*

Abstract

Hildenbrand and coworkers have shown recently that the vapor above solid ammonium nitrate includes molecules of NH_4NO_3 , not only NH_3 and HNO_3 as previously believed. Their measurements led to thermochemical values that imply an enthalpy change of $D_{298} = 98 \pm 9 \text{ kJ mol}^{-1}$ for the gas-phase dissociation of ammonium nitrate into NH_3 and HNO_3 . Using updated spectroscopic information for the partition function leads to the revised value $D_{298} = 78 \pm 21 \text{ kJ mol}^{-1}$ [accompanying paper in this journal by Hildenbrand, Lau, and Chandra]. In contrast, high-level ab initio calculations, detailed in the present report, predict a dissociation enthalpy half as large as the original result, $50 \pm 3 \text{ kJ mol}^{-1}$. These are frozen-core CCSD(T) calculations extrapolated to the limiting basis set aug-cc-pV ∞ Z, using an anharmonic vibrational partition function and a variational treatment of the NH_3 rotor. The corresponding enthalpy of formation is $\Delta_f H_{298}^\circ(\text{NH}_4\text{NO}_3, g) = -230.6 \pm 3 \text{ kJ mol}^{-1}$. The origin of the disagreement with experiment remains unexplained.

Introduction

Ammonium nitrate is a commodity chemical, with annual production of about 7×10^9 kg in the United States alone.¹ It is best known for its importance as an agricultural fertilizer and as an oxidizer in explosive mixtures, but it is also a significant component of atmospheric aerosols.^{2,3} Despite its importance, it was discovered only recently that heating the solid material produces gas-phase NH_4NO_3 molecules in addition to vapors of ammonia and nitric acid.⁴ Further experimental investigation led to a determination of the enthalpy of vaporization and to a value for the gas-phase enthalpy of formation, $\Delta_f H_{298}^\circ(\text{NH}_4\text{NO}_3, g) = -278 \pm 9 \text{ kJ mol}^{-1}$.⁵ This experimental report concluded with an invitation for computational thermochemistry on this system, which motivated the present study.

Computational Methods and Results

The aug-cc-pVnZ series of basis sets^{6,7} were used for principal computations. Only valence electrons were correlated in post-Hartree-Fock calculations. Molecular geometries and vibrations were from the MP2/aug-cc-pVTZ model. External symmetry numbers of 3, 1, and 1 were assigned based upon the respective point groups: C_{2v} (NH_3), C_s (HNO_3), and C_s (NH_4NO_3). Harmonic vibrational frequencies were all real-valued, verifying that stationary points were energy minima. Aside from the internal rotor in NH_4NO_3 (see below), vibrational zero-point energies and rotational constants were determined from anharmonic vibrational calculations using second-order perturbation theory,⁸ as implemented in the Gaussian03 computer program.^{9,10} Vibrational partition functions were computed from explicit lists of vibrational levels, up to 6000 cm^{-1} , as

determined from the anharmonic spectroscopic constants (truncating when necessary to avoid unphysical, negative energy increments).

The $\text{H}_3\text{N-HNO}_3$ complex has three vibrational frequencies below 200 cm^{-1} . The lowest ($\omega_{21} = 55\text{ cm}^{-1}$, a'' symmetry) corresponds to internal rotation of the NH_3 unit. This torsional barrier is only 43 cm^{-1} at the MP2/aug-cc-pVTZ level [45 cm^{-1} at QCISD/6-311+G(d,p), 46 cm^{-1} at MP2/6-31G(d), but 64 cm^{-1} at B3LYP/6-311++G(d,p)]. The relaxed torsional potential was mapped in 12° increments and energy levels computed variationally¹¹ using a value of $2.611 \times 10^{-20}\text{ u m}^2$ for the reduced moment of inertia. An internal symmetry number of 3 was used for this manifold (ground-state tunneling-splitting = 4.3 cm^{-1}). The second-lowest frequency ($\omega_{20} = 73\text{ cm}^{-1}$, a'' symmetry) corresponds to motion of the NH_3 unit out of the plane of the HNO_3 unit; it resembles the OH torsion mode of free HNO_3 , but with the NH_3 moiety attached. This torsional motion has a barrier of about 2870 cm^{-1} , which is high enough for the single-well treatment to be reasonable. The third-lowest frequency ($\omega_{14} = 120\text{ cm}^{-1}$, a' symmetry) is a bending motion that resembles the reaction path for degenerate, internal H-atom exchange.^{3,12} Scanning this bending coordinate shows the barrier to be about 4000 cm^{-1} , again high enough for standard anharmonic treatment. The well known inversion of the NH_3 molecule (barrier $\approx 1780\text{ cm}^{-1}$)^{13,14} was ignored; this is the most severe physical approximation made in the present partition functions.

Computed rotational constants for the equilibrium geometry are listed in [Table 1](#). The anharmonic vibrational treatment provides values averaged over the ground vibrational state, which are more appropriate for comparison with experimental

measurements. These values are also included in Table 1. No corrections were made for tunneling of the NH₃ rotor.

Harmonic and fundamental vibrational frequencies, vibrational constants, and torsional levels up to 5000 cm⁻¹, are summarized in the [Supporting Information](#), including comparison with experimental fundamentals tabulated by Shimanouchi^{13,14} for NH₃ and HNO₃. As shown in the Supporting Information, our results are similar to those obtained previously, also using vibrational perturbation theory, by Xantheas¹⁵ for HNO₃ (using the aug-cc-pVDZ basis sets) and by Kumarasiri et al.¹⁶ for all three species, NH₃, HNO₃, and NH₄NO₃ [using B3LYP/6-311++G(d,p) potential energy functions]. Our vibrational zero-point energies are 7467, 5755, and 13867 cm⁻¹ for NH₃, HNO₃, and NH₄NO₃ respectively.

Electronic energies were determined by extrapolating Hartree-Fock (HF) and correlation energies, separately, to the limit aug-cc-pV ∞ Z. HF energies were computed using aug-cc-pVnZ basis sets ($n = 3, 4, 5$) and extrapolated assuming exponential dependence upon n .¹⁷ CCSD(T) correlation energies were computed for $n = 3$ and 4 and extrapolated assuming n^{-3} behavior.¹⁸ Energies and atomic coordinates are tabulated in the [Supporting Information](#).

The present results provide estimates for the thermochemistry for gas-phase dissociation, reaction (1).



Predictions are summarized in [Table 2](#). The enthalpy of formation at 298.15 K was computed via the dissociation reaction by using the reference values $\Delta_f H_{298}^{\circ}(\text{NH}_3) = -45.94 \pm 0.35 \text{ kJ mol}^{-1}$ and $\Delta_f H_{298}^{\circ}(\text{HNO}_3) = -134.3 \pm 0.5 \text{ kJ mol}^{-1}$.^{19,20} The dissociation

reaction was selected because it shows excellent correlation balance ($\Delta E_{\text{corr}} = 11 \text{ kJ mol}^{-1}$), in contrast to the atomization reaction ($\Delta E_{\text{corr}} = -1449 \text{ kJ mol}^{-1}$).²¹ Although atomization reactions were not used in this analysis, the present calculations are adequate to make them tractable. For example, we find $\Delta_f H_{298}^{\circ}(\text{NH}_3) = -44.7 \text{ kJ mol}^{-1}$ and $\Delta_f H_{298}^{\circ}(\text{HNO}_3) = -132.8 \text{ kJ mol}^{-1}$ by atomization, which are both within 2 kJ mol^{-1} of the reference values cited above. The standard uncertainty associated with our predictions for NH_4NO_3 is estimated to be somewhat larger, 3 kJ mol^{-1} , because of the challenging vibrational structure. Temperature-dependent thermodynamic functions are summarized in [Table 3](#). For temperatures other than 298.15 K, enthalpy functions for the elements in their standard states were taken from the JANAF tables.²²

Truncating the vibrational manifold is a mathematical approximation that reduces the calculated entropy and heat capacity. For example, truncating at 4500 cm^{-1} instead of 6000 cm^{-1} , a worse approximation, changes the computed properties of molecular NH_4NO_3 at $T = 500 \text{ K}$: S by $-3.0 \text{ J mol}^{-1} \text{ K}^{-1}$, C_p by $-20.6 \text{ J mol}^{-1} \text{ K}^{-1}$, $H(500) - H(0)$ by -1.4 kJ mol^{-1} , and $\Delta_f H$ by -1.3 kJ mol^{-1} . These are substantial changes. However, at $T = 400 \text{ K}$ the changes are much smaller: S by $-0.4 \text{ J mol}^{-1} \text{ K}^{-1}$, C_p by $-4.5 \text{ J mol}^{-1} \text{ K}^{-1}$, $H(400) - H(0)$ by -0.1 kJ mol^{-1} , and $\Delta_f H$ by -0.1 kJ mol^{-1} . The values at 500 K ($kT \approx 348 \text{ cm}^{-1}$) are the most uncertain in the Tables. The errors in the partition functions from physical approximations, described above, remain unquantified but are probably larger than that from truncation at 6000 cm^{-1} .

Discussion

Earlier computations established that free molecules of ammonium nitrate are not ionic, but strongly hydrogen-bonded.^{3,12,16,23-25} This is confirmed by an experimental microwave study by Ott and Leopold.²⁶ However, detailed structural interpretation of the microwave data was hindered by the sensitivity of the results to assumed geometries of the monomers within the complex. Moreover, the *A* and *B* rotational constants (but not *C*) depend upon the internal NH₃ rotor.²⁶ Experimental values of these constants are compared with the present values in Table 1. The theoretical structure appears to be slightly too extended.

Literature values of the zero-temperature enthalpy change for reaction (1) are summarized in Table 4. The present CCSD(T) result, which has been extrapolated to the aug-cc-pV ∞ Z basis-set asymptote, is in good agreement with more approximate calculations, as anticipated by Nguyen et al.³ However, theory is not in agreement with the experimental measurement.

Compared with theoretical predictions, the experimental thermochemistry corresponds to greater stability of gaseous NH₄NO₃. A possible explanation could be that dimers, (NH₄NO₃)₂, exist in the gas, but that they are overlooked because their mass spectra do not show parent ions. This would exaggerate the apparent abundance of NH₄NO₃ in the vapor, causing an increased stability to be inferred. Earlier work^{12,16} established that the gas-phase dimer has an ionic structure, unlike the neutral, hydrogen-bonded monomer, but its energetics has not been investigated. As a check, we performed routine G3(MP2) calculations²⁷ to determine the stability of the dimer (expected uncertainty = 10 kJ mol⁻¹). At 298 K, the prediction for dissociation into two molecules

of NH_4NO_3 is $\Delta H^\circ = 58 \text{ kJ mol}^{-1}$, $\Delta S^\circ = 202 \text{ J mol}^{-1} \text{ K}^{-1}$, and $\Delta G^\circ = -2 \text{ kJ mol}^{-1}$. This corresponds to an equilibrium constant $K = \exp(-\Delta G^\circ/RT) = p_{\text{monomer}}^2/p_{\text{dimer}} \approx 2 \text{ bar}$. At equilibrium, the corresponding pressure is $p_{\text{dimer}} = p_{\text{monomer}}^2/K = p_{\text{monomer}} (p_{\text{monomer}}/K)$. Since $K \approx 2 \text{ bar}$ and $p_{\text{monomer}} \approx 10^{-7} \text{ bar}$,⁵ $p_{\text{dimer}} \ll p_{\text{monomer}}$ and the dimer is not expected to interfere with the experiment. The disagreement between theory and experiment remains unexplained.

The experimental measurement most directly yields the enthalpy of sublimation, $\Delta_{\text{cr}}^{\text{g}}H_{298}^\circ = 107 \pm 21 \text{ kJ mol}^{-1}$, which is combined with a literature value of the enthalpy of formation of solid NH_4NO_3 to yield the corresponding gas-phase value.²⁸ Using the reference values $\Delta_{\text{f}}H_0^\circ(\text{NH}_4\text{NO}_3, \text{cr}) = -350.6 \pm 1.0 \text{ kJ mol}^{-1}$ and $\Delta_{\text{f}}H_{298}^\circ(\text{NH}_4\text{NO}_3, \text{cr}) = -365.6 \pm 1.0 \text{ kJ mol}^{-1}$,²⁹ our best computations correspond to sublimation enthalpies of $\Delta_{\text{cr}}^{\text{g}}H_0^\circ = 138.5 \pm 3 \text{ kJ mol}^{-1}$ and $\Delta_{\text{cr}}^{\text{g}}H_{298}^\circ = 135 \pm 3 \text{ kJ mol}^{-1}$.

Expressed in spectroscopic energy units, the dissociation energy [reaction (1)] is $D_0 = 4060 \pm 250 \text{ cm}^{-1}$ from theory (this work) and $D_0 = 6400 \pm 1750 \text{ cm}^{-1}$ from experiment.²⁸ Many two-quantum vibrational levels lie between these two energies. Thus, spectroscopic studies of the predissociation threshold would be valuable.

Supporting Information

10 Tables: harmonic and fundamental frequencies, anharmonicity constants x_{ij} , atomic coordinates, and electronic energies for NH_3 , HNO_3 , and NH_4NO_3 ; torsional potential and energy levels for NH_4NO_3 . This material is available free of charge via the Internet at pubs.acs.org.

Acknowledgment

The authors of ref. 5 suggested this study, and I thank Dr. Donald Hildenbrand in particular for stimulating correspondence during the course of the work.

Table 1. Rotational constants (in GHz) for gas-phase NH_4NO_3 .

Method	A	B	C	ref.
Experiment	12.4382(4)	2.6560627(4)	2.1959697(4)	²⁶
MP2/aug-cc-pVTZ (R_0)	11.975	2.649	2.195	present work
MP2/aug-cc-pVTZ (R_e)	12.042	2.673	2.213	present work
MP2/6-311++G(d,p) (R_e)	11.984	2.630	2.182	³

Table 2. Ab initio thermochemistry for the gas-phase dissociation reaction, $\text{NH}_4\text{NO}_3 = \text{NH}_3 + \text{HNO}_3$.

T (K)	$\Delta H(T)$ (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	$\Delta G(T)$ (kJ mol ⁻¹)
0	48.6		48.6
100	50.5	116.6	38.8
200	50.8	118.9	27.0
298.15	50.4	117.2	15.4
300	50.3	117.2	15.2
400	49.2	114.0	3.6
500	47.5	110.3	-7.6

Table 3. Enthalpy of formation and ideal-gas thermodynamic functions for ammonium nitrate, $\text{NH}_4\text{NO}_3(\text{g})$, implied by results in Table 2.

T (K)	S (J mol ⁻¹ K ⁻¹)	C_p (J mol ⁻¹ K ⁻¹)	$H(T) - H(0)$ (kJ mol ⁻¹)	$\Delta_f H(T)$ (kJ mol ⁻¹)
0			0	-212.1
100	261.1	58.7	4.7	-220.6
200	307.8	77.9	11.6	-226.5
298.15	342.4	97.1	20.2	-230.6
300	343.0	97.5	20.3	-230.7
400	373.9	117.8	31.1	-233.1
500	401.8	130.4	43.7	-233.9

Table 4. Zero-temperature dissociation energy of the ammonia-nitric acid complex.

Method	$\Delta_{(1)}H_0$ (kJ mol ⁻¹)	ref.
Experiment	77 ± 21	²⁸
CCSD(T) asymptote	48.6 ± 3	present work
MP2 asymptote	48.9	present work
MP2/6-311++G(d,p)	51.3	¹²
MP2/6-311++G(d,p)	51.3	³
MP2/6-311++G(d,p) ^a	54.5	²⁵
MP2/6-31+G(d)	58.5	¹²
HF asymptote	37.3	present work
HF/6-311++G(d,p) ^a	50.3	²⁵
HF/4-31G	91.4	²³
B3LYP/6-311++G(d,p)	51.8	¹²

^a With counterpoise correction for basis-set superposition error, but no vibrational zero-point correction.

References

- (1) McCoy, M.; Reisch, M. S.; Tullo, A. H.; Tremblay, J.-F.; Voith, M. *Chem. Eng. News*, July 6, 2009, pp. 51-59.
- (2) Yin, J.; Allen, A. G.; Harrison, R. M.; Jennings, S. G.; Wright, E.; Fitzpatrick, M.; Healy, T.; Barry, E.; Ceburnis, D.; McCusker, D. *Atmos. Res.* **2005**, *78*, 149-165.
- (3) Nguyen, M.-T.; Jamka, A. J.; Cazar, R. A.; Tao, F.-M. *J. Chem. Phys.* **1997**, *106*, 8710-8717.
- (4) Chien, W.-M.; Chandra, D.; Lau, K. H.; Hildenbrand, D. L.; Helmy, A. M. *J. Chem. Thermodyn.* **2010**, *42*, 846-851.
- (5) Hildenbrand, D. L.; Lau, K. H.; Chandra, D. *J. Phys. Chem. B* **2010**, *114*, 330-332.
- (6) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007-1023.
- (7) Kendall, R. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1992**, *96*, 6796-6806.
- (8) Barone, V. *J. Chem. Phys.* **2004**, *120*, 3059-3065.
- (9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision E.01; Gaussian, Inc.: Wallingford, CT, 2004.
- (10) Certain commercial materials and equipment are identified in this paper in order to specify procedures completely. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.
- (11) Johnson, R. D., III. *FGHID*, revision 1.01; National Institute of Standards and Technology: Gaithersburg, MD, 1998.

- (12) Alavi, S.; Thompson, D. L. *J. Chem. Phys.* **2002**, *117*, 2599-2608.
- (13) Rajamäki, T.; Miani, A.; Halonen, L. *J. Chem. Phys.* **2003**, *118*, 10929-10938.
- (14) Léonard, C.; Carter, S.; Handy, N. C. *Chem. Phys. Lett.* **2003**, *370*, 360-365.
- (15) Xantheas, S. S. *Int. Rev. Phys. Chem.* **2006**, *25*, 719-733.
- (16) Kumarasiri, M.; Swalina, C.; Hammes-Schiffer, S. *J. Phys. Chem. B* **2007**, *111*, 4653-4658.
- (17) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104-6114.
- (18) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639-9646.
- (19) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.
- (20) Dorofeeva, O. V.; Iorish, V. S.; Novikov, V. P.; Neumann, D. B. *J. Phys. Chem. Ref. Data* **2003**, *32*, 879-901.
- (21) Irikura, K. K. In *Energetics of Stable Molecules and Reactive Intermediates*; Minas da Piedade, M. E., Ed.; Kluwer: Dordrecht, 1999; pp 353-372.
- (22) Chase, M. W., Jr. *J. Phys. Chem. Ref. Data* **1998**, *Monograph 9 (JANAF Thermochemical Tables, 4th ed.)*.
- (23) Latajka, Z.; Szczesniak, M. M.; Ratajczak, H.; Orville-Thomas, W. J. *J. Comput. Chem.* **1980**, *1*, 417-419.
- (24) Dunlap, B. I.; Doyle, R. J. *J. Phys. Chem.* **1996**, *100*, 5281-5285.
- (25) Dimitrova, Y.; Peyerimhoff, S. *Chem. Phys.* **2000**, *254*, 125-134.
- (26) Ott, M. E.; Leopold, K. R. *J. Phys. Chem. A* **1999**, *103*, 1322-1328.
- (27) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1999**, *110*, 4703-4709.
- (28) Hildenbrand, D. L.; Lau, K. H.; Chandra, D. *accompanying paper in this journal* **2010**.
- (29) *Thermodynamic Properties of Individual Substances*; 4th ed.; Gurvich, L. V.; Veyts, I. V.; Alcock, C. B., Eds.; Hemisphere: New York, 1989.