Check for updates

OPEN ACCESS

EDITED BY Mario Siciliani de Cumis, Italian Space Agency (ASI), Italy

REVIEWED BY Somnath Bhowmick, The Cyprus Institute, Cyprus

*CORRESPONDENCE Masatomi lizawa, ⊠ masatomi.iizawa@tu-braunschweig.de

RECEIVED 12 November 2024 ACCEPTED 21 March 2025 PUBLISHED 18 July 2025

CITATION

lizawa M and Narita Y (2025) The cooling prospect of hydrogenated nitrogen ions for quantum defect integration. *Front. Phys.* 13:1527062. doi: 10.3389/fphy.2025.1527062

COPYRIGHT

© 2025 lizawa and Narita. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.

The cooling prospect of hydrogenated nitrogen ions for quantum defect integration

Masatomi lizawa¹* and Yasuhito Narita^{1,2}

¹Institut für Theoretische Physik, Technische Universität Braunschweig, Braunschweig, Germany, ²Max Planck Institute for Solar System Research, Göttingen, Germany

KEYWORDS

synthesizing quantum material, qubit integration, NV color center, laser cooling, Paul trap, ion micro beam, dissociation, autodetachment

1 Introduction

Diamond nitrogen-vacancy (NV) color centers and other point defects are promising candidates for solid-state qubits, but there are problems with their integration [1, 2]. Recently, a one-by-one irradiation device with the positional accuracy of dopant atoms on the Ångström order has been developed [3–5] or is under development [6–9]. However, the dopant atom $X^{n+/-}$ is limited to be laser-coolable, and even the alternative method of sympathetic cooling has various problems as an irradiation device. Therefore, the hydrogenated molecules $XH_m^{n+/-}$ could be focused on as irradiation ions because the hydrogenated ions have long attracted attention as laser-coolable molecules [10, 11], and proton irradiation does not have a negative effect on the substrate.

In this paper, we review the cooling prospects of hydrogenated nitrogen $NH_m^{n+/-}$ to achieve the integration of the most studied quantum defect, the NV center. We summarize the chemical stability of each hydrogenated nitrogen, both the electronic ground state and the optically transitive excited states from the ground state. The term *chemical stability* here refers to no dissociation and, for anions, no autodetachment. Transitions excited by other than visible or near light, such as vibrational transitions that do not involve electronic transitions, are excluded.

We do not pursue the validity of the transition cycle for cooling, including Rosa's three fundamental requirements for cooling molecules [10], because the electronic structure of most of the molecules listed here is not sufficiently investigated. We discuss which hydrogenated nitrogen should be the focus of future cooling research to develop precision irradiation.

2 Chemical stability of hydrogenated nitrogens

Hydrogenated nitrogen, namely, hydronitrogen $N_l H_m^{n+/-}$, has a variety with l, m, and n as variables. For a one-by-one irradiation of nitrogen, the molecules must be composed of single nitrogens, so we will only consider l = 1. The molecule of m > 5 has not been found, and there is a density functional theory (DFT) calculation that m = 5 is stable above 55 GPa [12]. Therefore, only $m \le 4$ should be considered.

The following is a comprehensive description of previous research. It makes it clear that knowledge of the electronic structures of hydronitrogens is still insufficient to propose Doppler cooling schemes. The following section gives a concise summary of Tables 1 and 2.

2.1 Monovalent cations

2.1.1 **NH**⁺ (mono-hydrogenation, monovalence cation)

The monovalent cations or monocations (n = 1), such as NH⁺, NH₂⁺, NH₃⁺, and NH₄⁺, are all stable at low temperatures and pressures [13]. A cooling proposal has already been published for NH⁺, one of the most promising candidates. The transition for cooling cycle is $1^{2}\Pi (v'' = 0) \leftrightarrow 1^{2}\Sigma^{+} (v' = 0)$ with the light of 438.5 nm (see Figure 1), and the temperature estimated to be achieved to 6.63 µK [14].

2.1.2 \mathbf{NH}_{2}^{+} (di-hydrogenation, monovalence cation)

The amidogen cation NH₂⁺ has the electronic states $\tilde{X}^{3}B_{1}$, $\tilde{a}^{1}A_{1}$, $\tilde{b}^{1}B_{1}$, and $\tilde{c}^{1}\Sigma_{g}^{+}$ in order from the ground state [15]. However, $\tilde{X}^{3}B_{1} \rightarrow \tilde{a}^{1}A_{1}$ is spin-forbidden. In addition, transitions between $\tilde{a}^{1}A_{1}$, $\tilde{b}^{1}B_{1}$, and $\tilde{c}^{1}\Sigma_{g}^{+}$ are allowed transitions, but the potential energy curve for $\tilde{b}^{1}B_{1}$ already has no local minima [16]. Therefore, NH₂⁺ is not laser-coolable.

2.1.3 \mathbf{NH}_{3}^{+} (tri-hydrogenation, monovalence cation)

The electronic structure of NH₃⁺ on the ground state $\tilde{X} {}^{2}A_{2}''$ and the first excited state $\tilde{A} {}^{2}E$ are investigated both experimentally and theoretically. The transition $\tilde{X} {}^{2}A_{2}'' \rightarrow \tilde{A} {}^{2}E$ is optically allowable; however, $\tilde{A} {}^{2}E$ have rapid radiationless relaxation processes of 30 fs [17], which means that a simple cooling process that excites and de-excites between two levels cannot be constructed.

2.1.4 NH₄⁺ (tetra-hydrogenation, monovalence cation; ammonium ion)

We could not find any studies on the electronic excited states of the ammonium ion NH_4^+ . However, the rotational spectrum v_3 band with vibrational transitions is well studied [18–25]. Such vibrational

transitions could be used for cooling using near-ultraviolet lasers. Future research is desired.

2.2 Divalent cations

The cooling feasibility of high-valence ions is rarely noticed. However, high-valence ions are more appropriate for precision irradiation applications because irradiating them can lower the acceleration voltage to achieve the same beam energy.

2.2.1 NH²⁺ (mono-hydrogenation, divalence cation)

The stability of the dication of the diatomic molecule XY^{2+} can be briefly evaluated by the large value of the Δ in Equation 1:

$$\Delta := I(\mathbf{X}) - I(\mathbf{Y}^+), \tag{1}$$

where *I* is the ionization energy; that is, I(X) is the first ionization energy of X, and $I(Y^+)$ is the second ionization energy of Y [26, 27]. This means that the energy potential curve of $A^{2+} + B$ is placed at a position well below the curve of $A^+ + B^+$. Because the first ionization energy of hydrogen is 13.6 eV [28], the atoms with a second ionization energy sufficiently higher than 13.6 eV can form stable dications. The second ionization energy of nitrogen is 29.6 eV [28]. There is still a possibility that NH²⁺ is stable. However, NH²⁺ is predicted to dissociate spontaneously, according to the calculation of *ab initio* molecular orbital (MO) theory [29]. The dissociation study from NH₃²⁺ [30] also pointed out that NH²⁺ is unstable. There have been reports of observing a long-lived state [31], but NH²⁺ is not a candidate for cooling because even the ground state is metastable.

2.2.2 NH_2^{2+} (di-hydrogenation, divalence cation)

 NH_2^{2+} was observed by charge stripping using neutral gas [32] and by electron impact [30, 33, 34]. There are some theoretical reports on the calculation regarding the electronic ground state

TABLE 1 Investigation status of the stability of the hydrogenated nitrogen cations NH_m^{n+} . Good candidates: the ions for which cooling proposals can be found. Unstable: the ions for which the ground state or the lowest excited state that can be optically transitive from the ground state are known to be unstable. Poorly documented: the others.

NH_m^{n+}						
Ionization	1 H	2 H	3 H	4 H		
+	Good candidate	Unstable	Poorly documented	Poorly documented		
++	Unstable	Poorly documented	Poorly documented	Unstable		
Higher	Poorly documented	Poorly documented	Unstable	Unstable		

TABLE 2 Investigation status of the stability of the hydrogenated nitrogen anions NH_m^{n-} . The legend is the same as Table 1.

NH_m^{n-}						
ionization	1 H	2 H	3 H	4 H		
_	Unstable	Poorly documented	Unstable	Poorly documented		
Higher	Poorly documented	Poorly documented	Poorly documented	Poorly documented		



[29, 35–37] and excited states [38]. There is also an experimental report that an excited state of $\rm NH_2^{2+}$ has been observed [34]. This excited state was caused by a collision with helium, resulting in a transition of X ${}^2\rm A_1 ({}^2\rm \Pi_u) \rightarrow {}^2\rm A_1 ({}^2\Sigma_g^+)$. ${}^2\Sigma_g^+$ was thought to be the first electronic excited state, but later theoretical research has suggested that there is a lower excited state than ${}^2\Sigma_g^+$ [38]. $\rm NH_2^{2+}$ can take chemically (quasi-)stable excited states. Research on these excited states is inadequate, and there has been no progress for more than 30 years. Further research is desired in the future.

2.2.3 NH_3^{2+} (tri-hydrogenation, divalence cation)

 NH_3^{2+} is the most well-investigated dication of hydronitrogen. NH₃²⁺ was experimentally found through electron impact ionization [30, 33, 39-43], photoionization by synchrotron radiation [44-49], and by the other photon sources [50-52]. Auger electron spectroscopy (AES) [53-55] and doubly charged transfer spectroscopy (DCT spectroscopy, DCS) [56-58] were also carried out, and there are several theoretical works [29, 47-49, 59-67]. The dissociation studies from highly excited rovibrational states or excited electronic states of NH₃²⁺ [30, 41, 43, 44, 46, 48, 49, 68] are useful for considering the stability of the cooling cycle. The excited states of NH₃²⁺ have been well studied both experimentally and theoretically. However, their studies have been mainly motivated by the dissociation process through coincidence measurement. We could not find any studies on the existence of low-lying excited states, which are difficult to dissociate, or on the transitions between states of NH₃²⁺. Because divalent ions are convenient for high energy irradiation, NH₃²⁺ should be thoroughly investigated in the future.

2.2.4 \mathbf{NH}_{4}^{2+} (tetra-hydrogenation, divalence cation)

 $\rm NH_4^{2+}$ is predicted to be unstable as a MO calculation [29], multireference configuration interaction (MRCI) calculation [35, 36], and coupled cluster (CC) calculation [69]. There is a report to possibly generate $\rm NH_4^{2+}$ by the charge stripping with neutral gas and instantly dissociate to $\rm NH_3^+ + H^+$ [32]. $\rm NH_4^{2+}$ is chemically unstable and therefore not a cooling target.

2.3 Trivalent and higher valence cations

For NH_2^{3+} , no reports were found for either experiments or calculations. There is a dissociation study of NH_3^{n+} (n = 3, 4, 5) obtained by polyvalent argon irradiation [70], and NH_3^{3+} was obtained by ionization by proton irradiation [68]. These reports show that NH_3^{3+} should be dissociated, which means unstable. As CC calculation [69], there is no local minimum on the potential energy curve of NH_4^{3+} ; therefore, NH_4^{3+} does not even have a metastable state. This result is not surprising, as even NH_4^{2+} was unstable.

2.4 Anions

The polyvalence anion is first discussed. The reports of dianions, that is, divalent anions, are mostly related to large organic molecules, and the relatively small ones are AX_3^{2-} (A = Li, Na, K and X = F, Cl), which is a compound of alkali metals and halogens [71, 72], EX_4^{2-} (E = Be, Mg and X = F, Cl), which is a compound of alkaline earth metals and halogens [73, 74], and a compound of metals and pseudohalogens CN [75]. Only molecules with strong correlations, such as metal-halide, may allow stable dianions. Therefore, we will only consider monovalent anions (*n* = 1).

2.4.1 **NH**⁻ (mono-hydrogenation, monovalence anion)

NH⁻ is experimentally well investigated, and the ground states are chemically stable [76]. NH⁻ realizes the similar transition as the prominent cooling candidate NH⁺, but NH⁻ of the excited state is theoretically estimated to be neutralized by autodetachment [14]. Therefore, NH⁻ should not be a cooling candidate.

2.4.2 **NH**⁻₂ (di-hydrogenation, monovalence anion)

The ground state of NH_2^- is known as stable [77]. NH_2^- is autodetached through photoelectron spectroscopy of the $\tilde{X}\,^1A_1 \rightarrow \,^1B_1$ transition excited by a 3.408 eV photon [77]. It is not known whether 1B_1 is the lowest excited state.

2.4.3 NH_3^- (tri-hydrogenation, monovalence anion)

The stability report of NH_3^- cannot be found because all of the p subshells in N are half-filled, so it is difficult for four more electrons to form a stable system with sufficient separation from each other. The possibility remains that there are states with finite lifetimes due to vibrational rotational degrees of freedom, but in any case, NH_3^- cannot be used for cooling.

2.4.4 \mathbf{NH}_{4}^{-} (tetra-hydrogenation, monovalence anion)

While NH_3^- is unstable, NH_4^- is stabilized in two forms: $H^-(NH_3)_1$, which is stabilized by the ion-dipole interaction [78–82], and NH_4^- as a double Rydberg anion (DBA), which is stabilized by the two Rydberg-like electrons attached to NH_4^+ [80–90]. The dissociation studies of $H^-(NH_3)_1$ and NH_4^- have been well investigated. However, we could not find any research focusing on the electronic excited states that can be reached through optical transitions. Further research is needed.

3 Discussion and outlook

The above discussion is summarized in Table 1 for the cations and Table 2 for the anions. The electronic structures of the hydrogenated nitrogens have hardly been investigated. Although there have been previous studies on the cooling potential of NH⁺ and NH⁻, this does not mean that NH⁺ is the only promising candidate. The electronic structures of the ions listed here, namely, NH⁺_m (m = 1, 3, 4), NH²⁺_m (m = 2, 3), NH³⁺₂, NH⁻_m (m = 2, 4), and H⁻(NH₃), have not yet begun to be studied other than NH⁺.

In order to investigate the cooling capability of hydrogenated nitrogens, the energy potential curves of the ground state and the optically transitive excited states should be derived by *ab initio* calculations. The study of some hydrogenated molecules stagnated for about 30 years, but more recently, calculations using large basis sets have become practically feasible. *Ab initio* calculations are the first step in the study of Doppler cooling. We strongly emphasize the importance of *ab initio* calculations of hydrogenated nitrides for integrating solid-state qubits. We encourage quantum chemistry theorists to conduct intensive research on hydrogenated nitrides.

As a next step, absorption, photoelectron, and various active spectra should be obtained over a wide range of wavenumbers for each hydrogenated nitrogen ion. In particular, because the energy levels of the excited state are difficult to match with the calculation results, the spectra must be scanned over a wide range. Obtaining such comprehensive data is less likely to produce immediate scientific results than the effort required for the experiment. Therefore, a cooling investigation driven by engineering and social demands to develop solid-state quantum devices is necessary. As with semiconductor research in the past, research based on engineering and social demands will lead to the development of science.

In addition, a method for analyzing the obtained large-scale spectral data should be developed. Currently, the rovibrational spectra of small molecules are assigned semi-manually using software such as PGOPHER [91–94]. For extensive data sets, semi-manual assignments are unrealistic. Modern pattern recognition techniques should be applied based on physical understanding. Furthermore, scientific software packages are often developed by individual researchers, and the development is sometimes not stable. PGOPHER also stopped being updated in 2022 because the author passed away. Standard assignment tools should be systematically developed to analyze large data sets.

The science of molecular cooling must assist in achieving the integration of the NV color centers. As we have discussed, the science of molecular cooling, at least of hydrogenated nitrogen, is

References

1. Atatüre M, Englund D, Vamivakas N, Lee SY, Wrachtrup J. Material platforms for spin-based photonic quantum technologies. *Nat Rev Mater* (2018) 3:38–51. doi:10.1038/s41578-018-0008-9

2. Wan NH, Lu TJ, Chen KC, Walsh MP, Trusheim ME, De Santis L, et al. Large-scale integration of artificial atoms in hybrid photonic circuits. *Nature* (2020) 583:226–31. doi:10.1038/s41586-020-2441-3

3. Jacob G, Groot-Berning K, Wolf S, Ulm S, Couturier L, Dawkins ST, et al. Transmission microscopy with nanometer resolution using a deterministic single ion source. *Phys Rev Lett* (2016) 117:043001. doi:10.1103/physrevlett.117. 043001

not sufficiently advanced. We hope this will be a case where pure science evolves dramatically due to engineering needs.

Author contributions

MI: writing-original draft and writing-review and editing. YN: writing-review and editing.

Funding

The author(s) declare that financial support was received for the research and/or publication of this article. We acknowledge support by the Open Access Publication Funds of Technische Universität Braunschweig.

Acknowledgments

MI would like to thank K. Chartkunchand for insightful discussions.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Generative AI statement

The author(s) declare that no Generative AI was used in the creation of this manuscript.

Publisher's note

All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors, and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

4. Groot-Berning K, Kornher T, Jacob G, Stopp F, Dawkins ST, Kolesov R, et al. Deterministic single-ion implantation of rare-earth ions for nanometer-resolution color-center generation. *Phys Rev Lett* (2019) 123:106802. doi:10.1103/physrevlett.123.106802

5. Groot-Berning K, Jacob G, Osterkamp C, Jelezko F, Schmidt-Kaler F. Fabrication of $^{15}\rm NV^-$ centers in diamond using a deterministic single ion implanter. *New J Phys* (2021) 23:063067. doi:10.1088/1367-2630/ac0753

 Muroo K, Okamoto H, Miyawaki N, Yuri Y. Simulation study of ultrahighprecision single-ion extraction from a linear Paul trap. Prog Theor Exp Phys (2023) 2023:063G01. doi:10.1093/ptep/ptad071 7. Miyawaki N, Ishii Y, Yuri Y, Narumi K, Muroo K, Ito K, et al. Calculation study of selective ion extraction from ion source with Paul-trap-type laser cooling device. *Nucl Instrum Methods Phys Res B* (2023) 542:183–7. doi:10.1016/j.nimb.2023.06.015

8. Ishii Y, Ohkubo T, Miyawaki N, Yuri Y, Onoda S, Narumi K, et al. Design of an apertureless two-stage acceleration lens for a single-ion implantation system. *Nucl Instrum Methods Phys Res B* (2023) 541:200–4. doi:10.1016/j.nimb.2023.05.021

9. Yuri Y, Miyawaki N, Hosaka K, Ishii Y, Hosoya S, Kashiwagi H, et al. Investigating ultralow-emittance nanobeam formation using a coulomb crystal. *Prog Theor Exp Phys* (2025) 2025:023G01. doi:10.1093/ptep/ptaf019

10. Rosa MD. Laser-cooling molecules: concept, candidates, and supporting hyperfine-resolved measurements of rotational lines in the A-X(0, 0) band of CaH. *Eur Phys J D* (2004) 31:395–402. doi:10.1140/epjd/e2004-00167-2

11. Nguyen JHV, Viteri CR, Hohenstein EG, Sherrill CD, Brown KR, Odom B. Challenges of laser-cooling molecular ions. *New J Phys* (2011) 13:063023. doi:10.1088/1367-2630/13/6/063023

12. Qian GR, Niu H, Hu CH, Oganov AR, Zeng Q, Zhou HY. Diverse chemistry of stable hydronitrogens, and implications for planetary and materials sciences. *Sci Rep* (2016) 6:25947. doi:10.1038/srep25947

13. Rednyk S, Roučka Š, Kovalenko A, Tran TD, Dohnal P, Plašil R, et al. Reaction of NH⁺, NH⁺₂, and NH⁺₃ ions with H₂ at low temperatures: the pathway to ammonia production in the interstellar medium. *Astron Astrophys* (2019) 625:A74. doi:10.1051/0004-6361/201834149

14. Zhang QQ, Yang CL, Wang MS, Ma XG, Liu WW. Spectroscopic parameters of the low-lying electronic states and laser cooling feasibility of NH⁺ cation and NH⁻ anion. *Spectrochim Acta A* (2017) 185:365–70. doi:10.1016/j.saa.2017.06.001

15. Stephens JC, Yamaguchi Y, Sherrill CD, Schaefer HE \tilde{X} ³B₁, \tilde{a} ¹A₁, \tilde{b} ¹B₁, and \tilde{c} ¹ Σ_g ⁺ Electronic States of. *J Phys Chem A* (1998) 102:3999–4006. doi:10.1021/jp980779n

16. Kabbadj Y, Huet T, Uy D, Oka T. Infrared spectroscopy of the amidogen ion, $\rm NH_2^+$. J Mol Spectrosc (1996) 175:277–88. doi:10.1006/jmsp.1996.0033

17. Webb AD, Nahler NH, Ashfold MNR. Imaging studies of the photodissociation of NH₃ $^+$ and ND₃ $^+$ cations. J Phys Chem A (2009) 113:3773–8. doi:10.1021/jp808854d

18. Yamaguchi Y, Schaefer HF. A systematic theoretical study of harmonic vibrational frequencies: the ammonium ion $\rm NH_4^{+}$ and other simple molecules. *J Chem Phys* (1980) 73:2310–8. doi:10.1063/1.440381

19. Schwarz HA. Gas phase infrared spectra of ammoniated ammonium ions. *J Chem Phys* (1980) 72:284–7. doi:10.1063/1.438892

20. Crofton MW, Oka T. Infrared studies of molecular ions. i. the v_3 band of $\rm NH_4^+$, J Chem Phys (1983) 79:3157–8. doi:10.1063/1.446147

21. Schäfer E, Begemann MH, Gudeman CS, Saykally RJ. The ν_3 vibrational spectrum of the free ammonium ion (NH_4^+). J Chem Phys (1983) 79:3159–60. doi:10.1063/1.446148

22. Schäfer E, Saykally RJ, Robiette AG. A high resolution study of the v_3 band of the ammonium ion (NH₄⁺) by velocity modulation laser absorption spectroscopy. *J Chem Phys* (1984) 80:3969–77. doi:10.1063/1.447279

23. Crofton MW, Oka T. Observation of forbidden transitions of ammonium ion (NH₄⁺) v_3 band and determination of ground state rotational constants. observation of v_3 band allowed transitions of ND₄⁺. *J Chem Phys* (1987) 86:5983–8. doi:10.1063/1.452484

24. Han H, Song H, Li J, Guo H. Near spectroscopically accurate *ab initio* potential energy surface for NH_4^+ and variational calculations of low-lying vibrational levels. *J Phys Chem A* (2015) 119:3400–6. doi:10.1021/acs.jpca.5b01835

25. Yu HG, Han H, Guo H. Full-dimensional quantum calculations of vibrational levels of NH₄⁺ and isotopomers on an accurate *ab initio* potential energy surface. *J Phys Chem A* (2016) 120:2185–93. doi:10.1021/acs.jpca.6b01946

26. Bates DR, Carson TR. Doubly charged diatomic molecular ions. *Proc Phys Soc Sec A* (1955) 68:1199–202. doi:10.1088/0370-1298/68/12/417

27. Falcinelli S, Rosi M. Production and characterization of molecular dications: experimental and theoretical efforts. *Molecules* (2020) 25:4157. doi:10.3390/molecules25184157

28. Kramida A, Ralchenko Y. NIST atomic spectra database. *NIST Stand reference database* (1999) 78. doi:10.18434/T4W30F

29. Koch W, Schwarz H. The NH_n²⁺ (n = 1-4) dications. A theoretical investigation. Int J Mass Spectrom Ion Process. (1986) 68:49–56. doi:10.1016/0168-1176(86)87067-7

30. Boyd R, Singh S, Beynon J. Delayed predissociation and collision-induced processes of the ammonia di-cation $\rm NH_3^{2+}$. *Chem Phys* (1985) 100:297–314. doi:10.1016/0301-0104(85)85013-8

31. Hamdan M, Mazumdar S, Marathe VR, Badrinathan C, Brenton AG, Mathur D. Excited states of XH²⁺ (X = C, N, O, S) ions: a combined experimental and theoretical study. *J Phys B Mol Opt Phys* (1988) 21:2571–84. doi:10.1088/0953-4075/21/14/010

32. Proctor CJ, Porter CJ, Ast T, Bolton PD, Beynon JH. Charge stripping reactions of ions formed from methane, ammonia, water and hydrogen sulphide by protonation

and by electron impact. Org Mass Spectrom (1981) 16:454-8. doi:10.1002/oms.1210 161008

33. Märk TD, Egger F, Cheret M. Ionization of ammonia and deuterated ammonia by electron impact from threshold up to 180 eV. J Chem Phys (1977) 67:3795–802. doi:10.1063/1.435321

34. Hamdan M, Brenton A. Experimentally observed excited states of the dication NH_2^{2+} . Int J Mass Spectrom Ion Process. (1988) 84:211–4. doi:10.1016/0168-1176(88)83036-2

35. Pope SA, Hillier IH, Guest MF, Kendric J. The structure and stability of the dications, XH2+itn(X = N, O, P, S). *Chem Phys Lett* (1983) 95:247–9. doi:10.1016/0009-2614(83)87241-8

36. Pope SA, Hillier IH, Guest MF. Structure, stability and energetics of the neutral and singly and doubly ionized first- and second-row hydrides. *Faraday Symp Chem Soc* (1984) 19:109. doi:10.1039/fs9841900109

37. Wong MW, Radom L. Multiply charged isoelectronic analogs of cyclopropenyl/propargyl cation: cyclic or open chain? *J Am Chem Soc* (1989) 111:6976-83. doi:10.1021/ja00200a012

38. Gu JP, Wang ZX, Huang MB. Electronic states of the dication NH₂²⁺. *Int J Mass Spectrom Ion Process*. (1992) 120:157–61. doi:10.1016/0168-1176(92)80058-9

39. Mann MM, Hustrulid A, Tate JT. The ionization and dissociation of water vapor and ammonia by electron impact. *Phys Rev* (1940) 58:340–7. doi:10.1103/physrev.58.340

40. Dorman FH, Morrison JD. Double and triple ionization in molecules induced by electron impact. J Chem Phys (1961) 35:575–81. doi:10.1063/1.1731972

41. Locht R, Momigny J. The double ionization of ammonia. its dissociation into the doubly ionized fragment N^{2+} . Chem Phys Lett (1987) 138:391–6. doi:10.1016/0009-2614(87)80527-4

42. Leyh B, Hoxha A. Reaction window in the single-electron capture by ammonia dications. *Chem Phys* (1995) 192:65–77. doi:10.1016/0301-0104(94)00365-h

43. Wei L, Chen S, Zhang Y, Wang B, Yu W, Ren B, et al. Dissociation of NH $_3^{2+}$ induced by collision of 300 eV electrons with NH $_3$. Eur Phys J D (2020) 74:133. doi:10.1140/epjd/e2020-10094-7

44. Winkoun D, Dujardin G. Fragmentation of doubly charged ammonia cations $\rm NH_3^{++}$ studied by the photoion-photoion coincidence (PIPICO) method. Z Phys D Atoms Mol Clusters (1986) 4:57–64. doi:10.1007/bf01432498

45. Piancastelli MN, Cauletti C, Adam MY. Angle-resolved photoelectron spectroscopic study of the outer- and inner-valence shells of NH_3 in the 20–80 eV photon energy range. *J Chem Phys* (1987) 87:1982–6. doi:10.1063/1.453171

46. Stankiewicz M, Hatherly PA, Frasinski LJ, Codling K, Holland DMP. The double photoionisation of NH₃ using the triple coincidence (PEPIPICO) technique. *J Phys B: Mol Opt Phys* (1989) 22:21–31. doi:10.1088/0953-4075/22/1/006

47. Zhao YJ, Shan XB, Sheng LS, Wang ZY, Zhang J, Yu CR. Synchrotron radiation vuv double photoionization of some small molecules. *Chin Phys B* (2011) 20:043201. doi:10.1088/1674-1056/20/4/043201

48. Larsen KA, Rescigno TN, Streeter ZL, Iskandar W, Heck S, Gatton A, et al. Mechanisms and dynamics of the NH₂⁺ + H⁺ and NH⁺ + H⁺ + H fragmentation channels upon single-photon double ionization of NH₃. *J Phys B Mol Opt Phys* (2020) 53:244003. doi:10.1088/1361-6455/abc3aa

49. Larsen KA, Rescigno TN, Severt T, Streeter ZL, Iskandar W, Heck S, et al. Photoelectron and fragmentation dynamics of the $H^+ + H^+$ dissociative channel in NH₃ following direct single-photon double ionization. *Phys Rev Res* (2020) 2:043056. doi:10.1103/physrevresearch.2.043056

50. Samson JAR, Haddad GN, Kilcoyne LD. Absorption and dissociative photoionization cross sections of NH_3 from 80 to 1120 Å. J Chem Phys (1987) 87:6416–22. doi:10.1063/1.453472

51. Locht R, Davister M, Denzer W, Jochims H, Baumgärtel H. About the double ionization of ammonia and carbon dioxide. a comparison between photoionization and electron impact. *Chem Phys* (1989) 138:433–40. doi:10.1016/0301-0104(89)87149-6

52. Eland JH. Double photoionisation spectra of methane, ammonia and water. *Chem Phys* (2006) 323:391–6. doi:10.1016/j.chemphys.2005.09.047

53. Shaw R, Jen J, Thomas T. Auger spectrum of ammonia. J Electron Spectrosc Relat Phenom (1977) 11:91–100. doi:10.1016/0368-2048(77)85050-0

54. White J, Rye R, Houston J. Experimental auger electron spectrum of ammonia. *Chem Phys Lett* (1977) 46:146–50. doi:10.1016/0009-2614(77)85183-x

55. Camilloni R, Stefani G, Giardini-Guidoni A. The measured auger electron spectrum of ammonia vapour. *Chem Phys Lett* (1977) 50:213–7. doi:10.1016/0009-2614(77)80166-8

56. Appell J, Horsley JA. Electronic states of doubly ionized ammonia. J Chem Phys (1974) 60:3445–8. doi:10.1063/1.1681557

57. Griffiths WJ, Harris FM. An experimental determination of the energy of the first triplet doubly-ionized state of ammonia. *Rapid Commun Mass Spectrom* (1990) 4:366–8. doi:10.1002/rcm.1290041003

58. Langford M, Harris F, Fournier P, Fournier J. Determination of singletand triplet-state energies of the doubly ionized ammonia molecule by doublecharge-transfer spectroscopy. *Int J Mass Spectrom Ion Process.* (1992) 116:53–69. doi:10.1016/0168-1176(92)80019-w

59. Joshi BD. Study of BeH_3^- , BH_3 , CH_3^+ , NH_3^{++} , and OH_3^{3+} by one-center-expansion, self-consistent-field method. *J Chem Phys* (1967) 46:875–87. doi:10.1063/1.1840821

60. Økland MT, Fægri K, Manne R. Calculated auger emission spectrum of ammonia. *Chem Phys Lett* (1976) 40:185–8. doi:10.1016/0009-2614(76)85055-5

61. Jennison DR. Initial-state relaxation effects in molecular auger spectra. *Phys Rev* A (1981) 23:1215–22. doi:10.1103/physreva.23.1215

62. Tarantelli F, Tarantelli A, Sgamellotti A, Schirmer J, Cederbaum L. On the doubly ionized states of ammonia. *Chem Phys Lett* (1985) 117:577–82. doi:10.1016/0009-2614(85)80305-5

63. Brammer R. A computational study of the x-ray satellite spectrum of $\rm NH_3$. J Chem Phys (1987) 87:1153–61. doi:10.1063/1.453295

64. Sironi M, Cooper DL, Gerratt J, Raimondi M. Spin-coupled VB study of the di-cations of methane, ammonia and water. *Mol Phys* (1988) 65:251–9. doi:10.1080/00268978800101001

65. Mitra A, Mahapatra US, Majumder D, Sinha D. Multiple solutions of coupled cluster equations: an application to molecular auger spectra. *J Phys Chem A* (1998) 102:7277–85. doi:10.1021/jp972116w

66. Ida T, Ortiz JV. Second-order, two-electron dyson propagator theory: comparisons for vertical double ionization potentials. *J Chem Phys* (2008) 129:084105. doi:10.1063/1.2973533

67. Streit L, Custodio R. The auger spectra and the calculation of double-ionization potentials for H_2O and NH_3 using the diffusion quantum Monte Carlo method. *Chem Phys Lett* (2009) 482:148–52. doi:10.1016/j.cplett.2009.09.084

68. Wolff W, Luna H, Montenegro EC, Rodrigues Junior LC. Multiple fragmentation mechanisms in ammonia: collisions with protons in the intermediate velocity regime. *Phys Rev A* (2020) 102:052821. doi:10.1103/physreva.102.052821

69. Rasul G, Prakash GKS, Olah GA. XH_4^{2+} Dications and search for XH_4^{3+} Trications (X = N, P, and As). J Phys Chem A (1998) 102:8457–9. doi:10.1021/jp98 0981q

70. Bhatt P, Sairam T, Kumar A, Kumar H, Safvan CP. Formation of H_2^+ and H_3^+ in energetic highly-charged-ion collisions with NH₃. *Phys Rev A* (2017) 96:022710. doi:10.1103/physreva.96.022710

71. Scheller MK, Cederbaum LS. Stability of MX_3^{2-} ions in the gas phase and when do ionic molecules have large ionization potentials. *J Chem Phys* (1993) 99:441–55. doi:10.1063/1.465768

72. Zhao XL, Litherland AE. Observation of ${\rm LIF_3}^{2-}$. Phys Rev A (2005) 71:064501. doi:10.1103/physreva.71.064501

73. Weikert HG, Cederbaum LS. Free doubly negative tetrahalides. J Chem Phys (1993) 99:8877-91. doi:10.1063/1.465556

74. Middleton R, Klein J. Experimental verification of the existence of the gas-phase dianions BeF_4^{2-} and MgF_4^{2-} . *Phys Rev A* (1999) 60:3515–21. doi:10.1103/physreva.60.3515

75. Behera S, Jena P. Stability and spectroscopic properties of singly and doubly charged anions. *J Phys Chem A* (2012) 116:5604–17. doi:10.1021/jp210095q

76. Neumark DM, Lykke KR, Andersen T, Lineberger WC. Infrared spectrum and autodetachment dynamics of NH⁻. J Chem Phys (1985) 83:4364–73. doi:10.1063/1.449052

77. Wickham-Jones CT, Ervin KM, Ellison GB, Lineberger WC. $\rm NH_2$ electron affinity. J Chem Phys (1989) 91:2762–3. doi:10.1063/1.456994

78. Kleingeld JC, Ingemann S, Jalonen JE, Nibbering NMM. Formation of the NH_4^- ion in the gas phase. J Am Chem Soc (1983) 105:2474–5. doi:10.1021/ja00346a061

79. Coe JV, Snodgrass JT, Freidhoff CB, McHugh KM, Bowen KH. J Chem Phys (1985) 83:3169–70. doi:10.1063/1.449223

80. Snodgrass JT, Coe JV, Freidhoff CB, McHugh KM, Bowen KH. Faraday Discuss Chem Soc (1988) 86:241-56. doi:10.1039/dc9888600241

81. Xu SJ, Nilles JM, Hendricks JH, Lyapustina SA, Bowen KH. J Chem Phys (2002) 117:5742–7. doi:10.1063/1.1499491

82. Hu Q, Song H, Johnson CJ, Li J, Guo H, Continetti RE. Imaging a multidimensional multichannel potential energy surface: photodetachment of $\rm H^-(NH_3)$ and $\rm NH_4^-$. J Chem Phys (2016) 144:244311. doi:10.1063/1.4954187

83. Herzberg G. Rydberg spectra of triatomic hydrogen and of the ammonium radical. *Faraday Discuss Chem Soc* (1981) 71:165. doi:10.1039/dc9817100165

84. Cardy H, Larrieu C, Dargelos A. An *ab initio* study of the tetrahedral $\rm NH_4^-$ ion. *Chem Phys Lett* (1986) 131:507–12. doi:10.1016/0009-2614(86)80573-5

85. Ortiz JV. Vertical and adiabatic ionization energies of $\rm NH_4^-$ isomers via electron propagator theory and many body perturbation theory calculations with large basis sets. *J Chem Phys* (1987) 87:3557–62. doi:10.1063/1.453000

86. Gutowski M, Simons J, Hernandez R, Taylor HL. "dougle-rydberg" molecular anions. J Phys Chem (1988) 92:6179-82. doi:10.1021/j100333a004

87. Ortiz JV. Structures and properties of double-rydberg anions. *J Phys Chem* (1990) 94:4762–3. doi:10.1021/j100375a002

88. Simons J, Gutowski M. Double-rydberg molecular anions. Chem Rev (1991) 91:669-77. doi:10.1021/cr00005a002

89. Matsunaga N, Gordon MS. A theoretical study of $\rm NH_4^-$ and $\rm PH_4^-$. J Phys Chem (1995) 99:12773–80. doi:10.1021/j100034a014

90. Ortiz JV. A double rydberg anion with a hydrogen bond and a solvated double rydberg anion: interpretation of the photoelectron spectrum of $N_2H_7^{-}$. J Chem Phys (2002) 117:5748–56. doi:10.1063/1.1499492

91. Western CM. PGOPHER: a program for simulating rotational, vibrational and electronic spectra. J Quant Spectrosc Radiat Transf (2017) 186:221-42. doi:10.1016/j.jqsrt.2016.04.010

92. Western CM, Billinghurst BE. Automatic assignment and fitting of spectra with PGOPHER. *Phys Chem Chem Phys* (2017) 19:10222–6. doi:10.1039/c7cp00266a

93. Western C. PGOPHER version (2018) 10.1. doi:10.5523/ BRIS.3MQFB4GLGKR8A2REV7F73T300C

94. Western CM, Billinghurst BE. Automatic and semi-automatic assignment and fitting of spectra with PGOPHER. *Phys Chem Chem Phys* (2019) 21:13986–99. doi:10.1039/c8cp06493h