The $ArNH_2^+$ Noble Gas Molecule: Stability, Vibrational Frequencies, and Spectroscopic Constants

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Abstract

The detection of ArH^+ in the Crab nebula has led to speculation of other noble gas-containing molecules existing beyond the laboratory. Here, the previously unreported $ArNH_2^+$ molecule is shown through high-level coupled cluster theory quartic force field computations to possess a notable Ar−N bond strength (36.8 kcal/mol), a sizable dipole moment (2.78 D), near-prolate rotational character, and fairly bright vibrational transitions at 3256.0 cm^{-1} and 475.7 cm^{-1} on opposite ends of the infrared scale. Three of the other vibrational frequencies have observable intensities, and all of these data are provided for the three main isotopes of argon: $^{36}ArNH_2^+$, $^{38}ArNH_2^+$, and $^{40}ArNH_2^+$. These spectroscopic data should be useful in assisting any potential observations of the molecule whether in astrophysical or laboratory environments even if in the latter $ArNH_2^+$ could be a contaminant in argon matrix spectroscopic studies.

Keywords: Noble gas chemistry; rovibrational spectroscopy; quantum chemistry; quartic force fields; astrochemistry

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1. Introduction

Thus far, the only noble gas molecule known in nature is the argonium cation (ArH^+) [1–3], but the inventory of potential noble gas molecules is growing, especially due in large part to structural and spectroscopic data generated by highly-accurate quantum chemical computations. Most notably, the predicted existence and spectral features of the $ArOH^+$ cation [4–6] preceded the laboratory detection of this simple noble gas hydroxide [7]. Interstellar conditions are likely best for observation of noble gas molecules outside of the laboratory, and argon is one of the group-of-eleven most abundant atoms in the observable Universe [8, 9]. Hence, molecules containing this noble gas atom may yet be observable if only their spectroscopic data be determined.

Argon atoms bonded in proton-bound complexes [10], to ethynyl or cyano groups [11, 12], hydrogen clusters [13–18], water [19, 20], and even CH_2 [21, 22] have been documented and largely rovibrationally characterized by various groups including our own. Most notably, the experimental rotational constants [23] for $^{40}ArH_3^+$ compare with our

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theoretical values to within 60 MHz for the B and C constants and D_J values within 6.0 kHz [17]. In general, rotational constants for strongly bound systems agree between our standard approach and gas phase experiment to within 30 MHz and vibrational frequencies within 5.0 cm^{-1} and sometimes to within 1.0 cm^{-1} [24–36]. Hence, further analysis of more strongly-bound argon-containing cations should provide more accurate rotational constants and vibrational frequencies for laboratory or even astrophysical detection.

The commonality of carbon and its strong bonding characteristics has naturally led to more studies on molecules containing Ar−C bonds. However, Ar−O and even Ar−N bonds have been shown previously to possess relatively high bond strengths. Most notably, the Ar−O bond in $ArOH^+$ has been computed to be 73.70 kcal/mol in its ground doublet state and 16.35 kcal/mol in its excited triplet state [5]. $ArNH^+$ is also known to be well-bound and has been characterized theoretically [37]. However, NH^+ has conspicuously not been observed in the interstellar medium (ISM) [38] implying that $ArNH^+$ may not be a common interstellar species for reasons agnostic to a noble gas atom's willingness to bond. Hence, a step beyond to $ArNH_2{}^+$ may provide a more likely interstellar, noble gas molecular cation. Both NH [39] and NH_2 [40] are known in the ISM, and several molecules of the $R-NH_2$ format are known [41] including the simplest (and one of the first known interstellar species) ammonia [42], methylamine [43], and amino acetonitrile [44]. Hence, bonding an argon to the amino cation is possible in the ISM. Additionally, such bonding is also possible in argon matrix, condensed phase experiments where $ArNH_2{}^+$ may be a contaminant in any spectrum of NH_2 derivatives. This work will explore the rotational and vibrational properties of this molecule in order to aid in growing the number of physically observed noble gas molecules.

2. Computational Details

The spectroscopic constants and vibrational frequencies are computed via a fourth-order Taylor series expansion of the potential portion of the internuclear Hamiltonian or, more commonly, a quartic force field (QFF). This energy is determined here through a composite scheme [45, 46, 24, 25] but all computations rely on coupled cluster theory at the singles, doubles, and perturbative triples [CCSD(T)] level [47, 48], the MOLPRO2015.1 program [49, 50], and all correlation consistent basis sets include the extra tight d functions for the argon atom. The reference geometry is based on CCSD(T)/aug-cc-pV5Z [51, 52] optimized parameters with correction for the Martin-Taylor (MT) core correlating basis set [53] coming from differences in those optimized geometries including and excluding the core elections. From this reference geometry, displacements of 0.005 Å, and 0.005 radians are made based on the below coordinates utilized in previous studies of non-planar, tetraatomic, C_s molecules [54, 22]:

$$S_1(a') = r(\mathrm{Ar-N}) \tag{1}$$

$$S_2(a') = \frac{1}{\sqrt{2}}[r(\mathrm{H_1-N}) + r(\mathrm{H_2-N})] \tag{2}$$

$$S_3(a') = \frac{1}{\sqrt{2}}[\angle(\mathrm{H_1-N-Ar}) + \angle(\mathrm{H_2-N-Ar})] \tag{3}$$

$$S_4(a') = \angle(\mathrm{H_1-N-H_2}) \tag{4}$$

$$S_5(a'') = \frac{1}{\sqrt{2}}[r(\mathrm{H_1-N}) - r(\mathrm{H_2-N})] \tag{5}$$

$$S_6(a'') = \frac{1}{\sqrt{2}}[\angle(\mathrm{H_1-N-Ar}) - \angle(\mathrm{H_2-N-Ar})]. \tag{6}$$

At each of the 665 total points, CCSD(T)/aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z energies are computed and extrapolated to the complete basis set (CBS) limit via a three-point formula [55]. Then, corrections for the CCSD(T)/MT with core and CCSD(T)/MT without core energies are added to this. Furthermore, CCSD(T)/cc-pVTZ-DK scalar relativistic [56] corrections are added from computations with such relativity turned on and turned off. This creates the so-called CcCR QFF [25] so named for CBS ("C"), core correlation ("cC"), and relativity ("R").

The points are then fit via a least-squares procedure with a sum of squared residuals of 2.5×10^{-18} a.u.^{2}. Refitting zeroes the gradients and produces the CcCR equilibrium geometry and final force constants that define the QFF. The INTDER program [57] transforms the symmetry-internal coordinates into Cartesian coordinates for more flexibility in the rotational [58] and vibrational [59, 60] second-order perturbation theory (VPT2) computations within the SPECTRO program [61]. Only a ν_5/ν_4 C-type Coriolis resonance is present in this molecule.

The ^{36}Ar, ^{38}Ar, and ^{40}Ar isotopes are included in this study since the last is most common on Earth while the other two are much more abundant in the ISM than their heavier brother. The CCSD(T)/aug-cc-pV5Z dipole moment is computed with the origin at the center-of-mass, and the double-harmonic vibrational intensities are computed with second-order Møller-Plesset perturbation theory (MP2) with the 6-31+G(d) basis set in the Gaussian09 program [62–64] which has been shown to produce good agreement with more advanced theory for semi-quantitative interpretations of the vibrational intensities [65, 66].

3. Results and Discussion

First, $\mathrm{ArNH_2}^+$ is a stable system. The CCSD(T)/aug-cc-pV5Z Ar−N dissociation energy is 36.8 kcal/mol. Additionally, the F_{11} force constant for the harmonic frequency of the Ar−N stretch in Table 1 is 1.869 mdyne/Å^2. The numbering of the force constants comes from the numbering of the displacements given in the previous section. The F_{11} value is nearly exactly the same as the 1.865 mdyne/Å^2 F_{11} value in ArNH^+ [37]. Hence, the two species will have similar behavior in the heavy-atom stretch and will have notable bonding. This is carried out in the vibrational frequencies given in Table 2. The anharmonic ν_6 Ar−N stretch in $^{40}\mathrm{ArNH_2}^+$ is 475.7 cm^{-1} which is less than the

Table 1: The $ArNH_2{}^+$ CcCR Simple-Internal Force Constants (in mdyn/Å^n·rad^m).

F_{66}	0.833612	F_{662}	-0.0945	F_{6665}	-0.29	F_{6532}	-0.45	F_{3331}	2.48
F_{65}	-0.073616	F_{652}	0.1008	F_{6655}	-0.51	F_{5532}	-0.04	F_{6621}	0.42
F_{55}	6.408817	F_{552}	-28.7448	F_{6555}	-0.06	F_{4432}	0.18	F_{6521}	-0.32
F_{44}	0.633115	F_{442}	-0.3744	F_{5555}	116.21	F_{4332}	0.13	F_{5521}	-0.27
F_{43}	-0.017270	F_{432}	0.1158	F_{6644}	0.61	F_{3332}	0.02	F_{4421}	0.00
F_{33}	0.966241	F_{332}	0.0671	F_{6544}	0.03	F_{6622}	-0.54	F_{4321}	-0.18
F_{42}	0.296459	F_{422}	-0.4570	F_{5544}	-0.89	F_{6522}	-0.15	F_{3321}	-0.14
F_{32}	0.032223	F_{322}	0.0255	F_{4444}	-0.71	F_{5522}	115.20	F_{4221}	-0.16
F_{22}	6.291929	F_{222}	-28.8205	F_{6643}	0.08	F_{4422}	0.35	F_{3221}	-0.37
F_{41}	0.037066	F_{661}	-1.5360	F_{6543}	0.06	F_{4322}	0.08	F_{2221}	-0.16
F_{31}	0.525248	F_{651}	-0.0992	F_{5543}	0.05	F_{3322}	-0.53	F_{6611}	1.56
F_{21}	-0.196890	F_{551}	0.3343	F_{4443}	-0.05	F_{4222}	-0.12	F_{6511}	1.27
F_{11}	1.869259	F_{441}	0.0657	F_{6633}	0.32	F_{3222}	-0.18	F_{5511}	-0.98
F_{664}	-0.3429	F_{431}	0.3219	F_{6533}	-0.17	F_{2222}	114.54	F_{4411}	-0.10
F_{654}	-0.0314	F_{331}	-1.1118	F_{5533}	-0.51	F_{6641}	0.29	F_{4311}	-0.43
F_{554}	0.2516	F_{421}	0.0093	F_{4433}	0.61	F_{6541}	0.06	F_{3311}	0.06
F_{444}	-0.7069	F_{321}	-0.2555	F_{4333}	0.36	F_{5541}	-0.06	F_{4211}	-0.38
F_{663}	-0.6863	F_{221}	0.2318	F_{3333}	2.94	F_{4441}	-0.05	F_{3211}	0.87
F_{653}	-0.0722	F_{411}	-0.0864	F_{6642}	0.15	F_{6631}	1.51	F_{2211}	-0.32
F_{553}	0.0184	F_{311}	-2.2473	F_{6542}	0.05	F_{6531}	0.35	F_{4111}	-0.32
F_{443}	-0.0020	F_{211}	0.0721	F_{5542}	-0.81	F_{5531}	-0.21	F_{3111}	4.99
F_{433}	0.5642	F_{111}	-9.9053	F_{4442}	0.82	F_{4431}	0.34	F_{2111}	1.82
F_{333}	-0.4233	F_{6666}	1.52	F_{6632}	-0.20	F_{4331}	0.51	F_{1111}	41.97

same frequncy in $^{40}ArNH^+$ at 516.4 cm^{-1}. However, they are of the same magnitude, and the additional mass of the hydrogen atom is likely responsible for the decrease in the vibrational frequency. Regardless, the dissociation energy is 12870.1 cm^{-1} indicating that the molecular system cannot undergo vibrational predissociation upon single-mode vibrational excitation from the amino cation moiety. The barrier to inversion through the C_{2v} saddle point is computed here via CCSD(T)/aug-cc-pVTZ to be 6271 cm^{-1} providing a deep enough well for the present VPT2 computations to be reliable and the structure to be C_s. With respect to the ν_4 mode, several quanta of excitation would be required to overcome the barrier.

Furthermore, the two N−H stretching vibrational frequencies are notably perturbed by the presence of the argon atom. The ν_1 symmetric stretch at 3256.0 cm^{-1} is 45 cm^{-1} lower than the 3301 cm^{-1} frequency in lone NH_2, and the ν_2 antisymmetric stretch at 3168.1 cm^{-1} is 49 cm^{-1} less than the 3219 cm^{-1} NH_2 fundamental [67]. Certainly, the mass of the argon atom plays a role in these reductions, but the atom must be bonded for it to have such an effect.

The rest of the fundamental vibrational frequencies are also given in Table 2. These fall in the 1460 cm^{-1} to 1130 cm^{-1} range in the mid-infrared. The ν_4 argon atom out-of-plane bend (OPB) can also be characterized as the symmetric, but out-of-plane deformation of the concerted hydrogen atoms. Hence, the ν_5 antisymmetric hydrogen bend (or, equivalently, NH_2 twist) is a mere 62.2 cm^{-1} less at 1136.2 cm^{-1} since both motions involve the hydrogen atoms bending about the nitrogen atom.

All but one of the vibrational frequencies have notable intensities with the bookending

ν_6 Ar−N stretch and the ν_1 symmetric N−H stretches being the brightest by basically the same amount at $\sim$ 100 km/mol. The antisymmetric hydrogen bend it practically vibrationally dark, but the other three fundamental modes have intensities on the order of the antisymmetric stretch in water.

Additionally, this molecule will have an observable rotational spectrum. Its dipole moment is quite large at 2.78 D indicating that the observed rotational lines will be marked. Even with the deformation of the hydrogen atoms out of plane due to the lone pair on the nitrogen, this molecule is near-prolate due to the large mass of the argon atom. The ^{40}ArNH$^+$ B_0 rotational constant is 12151.9 MHz, and C_0 is 11924.5 MHz, a difference of less than 2.0 %. However, the A_0 constant is over 20× larger giving classic near-prolate rotational spectroscopic structure. Additionally, the B and C constants for the different isotopologues are given in Table 2 in order to aid in radioastronomical or microwave laboratory experimental searches for this molecule. The vibrationally-excited rotational constants are also provided with the numbering now indicative of the fundamental vibrational frequencies given at the bottom of Table 2.

4. Conclusions

The ArNH$_2$$^+$ noble gas, molecular cation has a stable Ar−N bond born out through both computations of the dissociation energy and treatment of this vibrational motion. This molecule has notable absorption features both in the hydride stretching (3256.0 cm^{-1}) and in the far-infrared (475.7 cm^{-1}). Additionally, a strong dipole moment and near-prolate character should make the rotational spectrum of ArNH$_2$$^+$ relatively straight-forward to decipher in the laboratory. Laboratory synthesis of ArCH$_2$$^+$ proceeded through reactions of CH$_3$Br^{2+} and argon atoms [21], and similar reactions may be possible with NH$_3$Br^{2+} leading to ArNH$_2$$^+$ especially due to the noted stability of the ammonium cation in at least laboratory analysis. Additionally, this molecule may also form in condensed phase spectroscopic experiments in argon matrices potentially as a contaminant in any observed spectra. If so or even through other means, the present data will be helpful in spectroscopically characterizing this molecule in both the laboratory or potentially even in interstellar environments.

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Table 2: The CcCR QFF $ArNH_2^+$ Equilibrium and Zero-Point (R_α) Structures, Vibrational Frequencies, Harmonic Intensities (in parenthesis in km/mol), and Spectroscopic Constants for the ^{36}Ar, ^{38}Ar, and ^{40}Ar Isotopologues.

	$^{36}ArNH^+$	$^{38}ArNH^+$	$^{40}ArNH^+$
r_e(Ar−N) Å	1.856 320	–	–
r_e(N−H) Å	1.030 553	–	–
∠(Ar−N−H)	97.706	–	–
∠(H−N−H)	106.554	–	–
τ(H−Ar−N−H)	107.747	–	–
A_e MHz	253039.4	253037.8	253036.4
B_e MHz	12748.7	12545.6	12362.4
C_e MHz	12510.9	12315.3	12138.7
D_J MHz	0.033	0.032	0.031
D_{JK} MHz	0.371	0.362	0.354
D_K MHz	7.245	7.254	7.262
d_1 kHz	-0.749	-0.715	-0.684
d_2 kHz	-0.020	-0.020	-0.018
H_J Hz	-0.018	-0.017	-0.016
H_{JK} Hz	1.840	1.769	1.706
H_{KJ} Hz	35.292	34.392	33.592
H_K kHz	462.134	462.892	463.563
h_1 mHz	3.411	3.210	3.037
h_2 mHz	0.401	0.371	0.345
h_3 mHz	0.013	0.012	0.011
r_0(Ar−N) Å	1.875 057	1.874 990	1.874 928
r_0(N−H) Å	1.041 581	1.041 576	1.041 572
∠(Ar−N−H)	97.706	97.707	97.707
∠(H−N−H)	106.606	106.606	106.606
τ(H−Ar−N−H)	107.799	107.799	107.799
A_0 MHz	249491.0	249488.5	249486.2
B_0 MHz	12530.6	12331.5	12151.9
C_0 MHz	12288.9	12097.4	11924.5
A_1 MHz	245615.0	245612.5	245610.2
B_1 MHz	12481.9	12283.8	12105.0
C_1 MHz	12481.9	12058.0	11885.6
A_2 MHz	244747.0	244744.5	244742.2
B_2 MHz	12487.7	12289.4	12110.5
C_2 MHz	12246.7	12055.9	11883.6
A_3 MHz	247284.3	247279.8	247275.9
B_3 MHz	12526.6	12326.8	12146.6
C_3 MHz	12243.1	12052.2	11879.8
A_4 MHz	252090.5	252081.5	252073.4
B_4 MHz	12456.4	12259.5	12081.7
C_4 MHz	12262.3	12071.4	11898.9
A_5 MHz	250729.1	250733.0	250736.6
B_5 MHz	12392.9	12195.9	12018.0
C_5 MHz	12126.3	11937.6	11767.1
A_6 MHz	249383.5	249381.0	249378.8
B_6 MHz	12401.8	12205.7	12028.7
C_6 MHz	12162.0	11973.5	11803.1
μ_x D			1.78
μ_y D			2.13
μ D			2.78
ω_1 (a') symmetric N−H cm^{-1}	3437.4	3437.4	3437.4 (106)
ω_2 (a'') antisym. N−H cm^{-1}	3332.3	3332.3	3332.3 (65)
ω_3 (a') symmetric H−N−Ar bend cm^{-1}	1521.7	1521.7	1521.7 (77)
ω_4 (a') Ar OPB cm^{-1}	1233.7	1233.3	1233.0 (87)
ω_5 (a'') antisym. H−N−Ar bend cm^{-1}	1177.5	1177.2	1176.9 (2)
ω_6 (a') Ar−N cm^{-1}	507.2	503.2	499.5 (102)
ν_1 (a') symmetric N−H cm^{-1}	3256.0	3256.0	3256.0
ν_2 (a'') antisym. N−H cm^{-1}	3168.0	3168.1	3168.1
ν_3 (a') symmetric H−N−Ar bend cm^{-1}	1457.2	1457.2	1457.1
ν_4 (a') Ar OPB cm^{-1}	1199.1	1198.8	1198.4
ν_5 (a'') antisym. H−N−Ar bend cm^{-1}	1136.7	1136.4	1136.2
ν_6 (a') Ar−N cm^{-1}	482.9	479.1	475.7
Zero-Point cm^{-1}	5514.4	5512.1	5510.0