



2018

# Quantum Chemical Analysis of Stable Noble Gas Cations for Astrochemical Detection

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*Quantum Chemical Analysis of Stable Noble Gas Cations for  
Astrochemical Detection*

An Honors Thesis submitted in partial fulfillment of the requirements for Honors in the  
Department of Chemistry and Biochemistry

By

Carlie M. Novak

Under the mentorship of Dr. Ryan C. Fortenberry

ABSTRACT

The search for possible, natural, noble gas molecules has led to quantum chemical, spectroscopic analysis of  $\text{NeCCH}^+$ ,  $\text{ArNH}^+$ ,  $\text{ArCCH}^+$ , and  $\text{ArCN}^+$ . Each of these systems have been previously shown to be a stable minimum on its respective potential energy surface. However, no spectroscopic data are available for laboratory detection or interstellar observation of these species, and the interstellar medium may be the most likely place, in nature, where these noble gas cations are found. The bent shape of  $\text{NeCCH}^+$  is confirmed here with a fairly large dipole moment and a bright C – H stretching frequency at  $3101.9 \text{ cm}^{-1}$ . Even if this molecule is somewhat unstable, it is likely observable now that the spectral ranges of where to look have been established.  $\text{ArCCH}^+$  is much more stable but has dim double harmonic intensities for the vibrational fundamentals and a dipole moment below 0.5 D making its rotational transitions likely buried in the astronomical weeds. Even so,  $\text{ArCCH}^+$  cannot be excluded as a possibility in laboratory experiments of hydrocarbons in argon-rich environments.  $\text{ArCN}^+$ , on the other hand, has a dipole moment of greater than 3.5 D, an observable C – N stretching fundamental at  $2189.6 \text{ cm}^{-1}$  (4.567 microns), and a viable formation pathway through HCN, a highly-abundant interstellar molecule. Consequently, the result of this work provides novel high-level spectroscopic data to aid in the search for covalently bound noble gas molecules in observable regions of outer space.

Thesis Mentor: \_\_\_\_\_

Honors Director: \_\_\_\_\_

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# Chapter 1

## Introduction

### 1.1 Astrochemistry

Astrochemistry is defined as the study of molecules and their subsequent reactions in environments beyond the Earth. Environments of interest include solar system bodies, exoplanets along with their atmospheres, and the interstellar medium (ISM) among many, many others. Through this discipline, the formation, atomic and chemical composition, and evolution of molecular gas clouds can be studied in order to predict or describe how solar systems are formed. Spectroscopy is a particularly important tool in astrochemistry because we can not collect samples or study the molecules directly. Astrochemical spectroscopy uses various telescopes to measure the absorption and emission of light from molecules and atoms in different interstellar environments. By comparing astronomical observations with experimental

measurements, chemists can infer numerous physical and chemical qualities of stars and gas clouds based on their rotational and vibrational characteristics.

The astrochemist's periodic table consists of only 11 elements<sup>50</sup>, whereas the other 81 are more commonly associated with terrestrial chemistry. These elements are largely inaccessible in the ISM as their abundances are too low to be considered for most astrochemistry. Three of these 11 elements are the noble gases: helium, neon, and argon. Noble gases species are popularly assumed not to partake in chemical reactions, as they are full valence atoms with high ionization energies that are stable on their own. Through the use of quantum chemical analysis, theoretical astrochemistry allows us to challenge standard chemical assumptions, and discover new and bizarre molecules that break the rules of traditional "terrestrial" chemistry.

### 1.1.1 Noble Gas Chemistry

Proceeding its theoretical characterization in the early 1990s, argonium,  $\text{ArH}^+$ , was detected in the Crab nebula in 2013<sup>25</sup>. Despite the previous knowledge that noble gases do not possess the reactivity necessary to form bonds, work in recent years has cast doubt on this idea<sup>1-7</sup>. It was discovered that the reason it took so long to find the  $\text{ArH}^+$  molecule was because astronomers were looking for argon in its most experimentally available isotope, <sup>40</sup>Ar. However, this is only true of the atom within the confines of Earth's atmosphere. In the ISM, argon is most abundant in its isotope, <sup>36</sup>Ar. Now that the correct isotope, specifically



for argon, is known, more accurate predictions regarding novel noble gas molecules can be made.

In order to expand the list of potential noble gas molecules, highly-accurate QFFs methods are employed here to analyze unique noble gas radical cations for the first time. Recent work has explored and produced quantum chemical spectroscopic data for  $\text{ArH}_2^+$ ,  $\text{ArH}_3^+$ ,  $\text{ArOH}^+$ , and their neon analogues using established QFF techniques<sup>4,8,9</sup>.

## 1.2 Theoretical Chemistry

Theoretical chemistry is extremely useful for rotational astrochemistry because the low pressures, densities, and temperatures of the ISM are better at creating nearly perfectly isolated molecules than any experiments in terrestrial laboratories. Quantum chemical computations of lone molecules can be physically interpreted to be infinitely separated from any other molecular species and are treated without consideration for temperature since such would not make sense for a lone molecule. Additionally, modern quantum chemical computations, especially coupled cluster theory at the singles, doubles, and perturbative triples [CCSD(T)] level are exceptionally adept at providing molecular structures<sup>10</sup>. From such structures, related rotational constants are easily computed, providing reference for rotational spectra. Dipole moments are also readily determined from these structures and from electron probability computations allowing for inferences related to the intensities of the rotational lines.

### 1.2.1 Quantum Chemical Techniques

The basis of quantum chemistry is to solve the Schrödinger equation, a typical Eigenvalue equation (Eq. 1.1) specifically constructed to deal with molecular wavefunctions and Hamiltonians. The Hamiltonian, (Eq. 1.2), contains the operations associated with kinetic and potential energies of the entire molecular system. A majority of quantum chemical studies use the Born-Oppenheimer (BO) Approximation, which assumes that the nucleus is at rest and therefore  $\hat{T}_N = 0$ . This also assumes that the  $\hat{V}_{eN}$  terms is a constant since the nuclei are implied not to be moving. The Hamiltonian is then reduced to include its electronic components and is shown in Eq. 1.3.

$$\hat{H}\Psi = E\Psi \tag{1.1}$$

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{eN} + \hat{V}_{ee} + \hat{V}_{NN} \tag{1.2}$$

$$\hat{H}_{BO} = \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee} \tag{1.3}$$

The Hartree-Fock (HF) method is an approximation for the determination of the wave function and the energy of a quantum many-body system in a stationary state. The HF method is also known as the Self-Consistent Field (SCF) method, in which Hartree equation requires

the final field as computed from the charge distribution to be the "self-consistent" with the assumed initial field. In the HF method, the effect of other electrons are accounted for in a mean-field theory context. SCF is used to approximate the wavefunctions as a product of single-electron wavefunctions, also known as atomic orbitals<sup>11-14</sup>. In order to minimize the energy of a molecule, the SCF method optimizes the molecular orbitals of the system using the variational principle. Also used in conjunction with HF Theory is the Moller-Plesset Perturbation Theory, which is an economical way to partially correct for the lack of dynamic electron correlation in the HF Theory. It improves the description of molecular energies, although being slightly more time consuming. The result of the Schrödinger equation is a set of structural parameters at the minimum energy that represents the ground state.

### 1.2.2 Coupled Cluster Theory

Coupled cluster (CC) theory is more advanced than HF and MP2 and, hopefully, remains a majority of the correlation energy. The essential idea in CC theory is the ground state wave function  $|\Psi_0\rangle$  can be enhanced by the exponential ansatz (Eq. 1.4). It uses this ansatz to correct the reference wavefunction, making it a highly accurate computational quantum chemical theory<sup>15,16</sup> for the least cost. Coupled cluster theory takes the basis Hartree-Fock molecular orbital method and constructs a multi-electron wavefunction using the exponential cluster operator (Eq. 1.5) to account for electron correlation. In the CC wavefunction,  $e^{\hat{T}}$  represents the power series expansion of the cluster operator,  $\hat{T}$ . The expansion of the cluster operator is determined by the maximum substitution level shown in Eq. 1.6, where the  $\Phi_0$

is the reference wavefunction in which HF wavefunctions are commonly used as the basis for computations<sup>17</sup>.

$$|\Psi_{CC}\rangle = e^{\hat{T}}|\Phi_0\rangle \quad (1.4)$$

$$= e^{-\hat{T}}|\Psi_{CC}\rangle \quad (1.5)$$

$$\Psi_{CC} = (1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \dots)|\Phi_0\rangle \quad (1.6)$$

CC theory allows for two or more different electrons in a system to excite into a new orbital at the same time, and multiply them by one another, resulting in a Taylor series. This theory is the perturbative variant of the many electron theory and provides the exact solution to the time-independent Schrödinger equation. A highly accurate perturbative correction is added to the singles and doubles energies to create the full couple cluster singles, doubles, and perturbative triples method<sup>18</sup>, again, CCSD(T).

$$E_{CCSD(T)} = E_{CCSD} + E_T \quad (1.7)$$

This method is used to generate the energies of the various molecules as it is faster than comparable methods.

### 1.2.3 Quartic Force Fields

A quartic force field (QFF) is a 4<sup>th</sup> ordered Taylor series expansion of the potential portion of the internuclear Hamiltonian (Eq. 1.7). The Schrödinger equation can be applied differently here to solve for the structural and internuclear parameters of a molecular system. These parameters include the Cartesian coordinates of atomic positions or the internal coordinates such as bond lengths, angles, and torsions. The structure should ultimately describe the molecule at equilibrium based upon a global minimum of its potential energy surface (PES). Combining this selective and efficient PES formulation with vibrational and rotational perturbation theories has routinely produced exceptional *ab initio* comparison to experiment for vibrational frequencies. In a nutshell, QFF's are used to generate an approximation of our wavefunction for various vibrational and rotational modes.

$$V = \frac{1}{2} \sum_{ij} F_{ij} \Delta_i \Delta_j + \frac{1}{6} \sum_{ijk} F_{ikj} \Delta_i \Delta_j \Delta_k + \frac{1}{24} \sum_{ijkl} F_{ikjl} \Delta_i \Delta_j \Delta_k \Delta_l, \quad (1.8)$$

In Eq. 1.9,  $\Delta_i$  are the displacements of the internal coordinates and  $F_{ikj}$  are force constant terms. These displacements are in increments of 0.005 Å for the bond length and 0.005 radians for the bond angles. A least-squares fitting of the energies produces the equilibrium geometry and energy. Refitting the displacement to the new minimum will yield much more accurate force constants with zero gradient. The geometry and force constants are then input into second-order vibrational perturbation theory that treats the vibrational and rotational components. The SPECTRO<sup>19</sup> program is then used to generate the spectroscopic dataset

that contains the anharmonic vibrational frequencies and rational constants that can be used to compare with experimental spectroscopic data. Finally, this methodology involves a complete basis set (CBS) limit extrapolation, an additive factor for the energy difference between core and noncore electron correlating computations, and a similar additive difference for scalar relativity. The shorthand for this approach is "CcCR" with the "C" term from the CBS energy, "cC" for core correlation, and "R" for relativity.

## Chapter 2

# Covalency in a Noble Gas Compound: ArNH<sup>+</sup> Analyzed from Quartic Force Fields

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### 2.1 Introduction

Even though isolated complexes involving argon and neon have been known for some time<sup>5,20-24</sup>, the discovery of the first naturally-occurring noble gas molecule, ArH<sup>+</sup> initially discovered astronomically toward the Crab Nebula<sup>25</sup>, has reignited the chemical study of these seemingly inert atoms. Noble gasses can make bonds, especially if they are ionized<sup>26,27</sup>. In fact, ArH<sup>+</sup> is now believed to be relatively ubiquitous in the interstellar medium (ISM) leading to questions as to the viability of other noble gas compounds that may occur in nature.

Recent work has explored and produced quantum chemical spectroscopic data for  $\text{ArH}_2^+$ ,  $\text{ArH}_3^+$ ,  $\text{ArOH}^+$ , and their neon analogues using established quartic force field (QFF) techniques<sup>4,8,9</sup>. These fourth-order Taylor series expansions of the potential piece within the internuclear Hamiltonian have been shown to produce highly-accurate results when compared with experiment. Vibrational frequencies, especially hydride stretches, can be reproduced to within  $1 \text{ cm}^{-1}$  of experiment<sup>28-33</sup>; B- and C-type rotational constants also match experiment to within 20 MHz<sup>28,31,34-36</sup>. Often accuracies of  $5 \text{ cm}^{-1}$  for vibrational frequencies are more common<sup>34,35,37</sup>, but rotational constants rarely deviate in well-bound systems.

Besides the efficacy of QFFs in general, the other reason for this accuracy comes in the energy description for the points that define the QFF as a potential energy surface<sup>28,38,39</sup>. The energy at each point is produced compositely based on coupled cluster theory<sup>17,40</sup> at the singles, doubles, and perturbative triples [CCSD(T)] level<sup>18</sup>. The aug-cc-pVXZ series<sup>41</sup> of basis sets with X = T, Q, and 5 is extrapolated to the complete basis set (CBS) limit via a three-point formula<sup>42</sup> giving the “C” term in the proscribed shorthand. Core correlation, the “cC” term, is included by utilizing the Martin-Taylor (MT) core correlating basis set<sup>43</sup> and computing the difference in the CCSD(T) energy with and without the inclusion of the core electrons. Scalar relativity<sup>44</sup> is appended to the composite energy in the “R” term by taking the difference between the energy also computed with and without the correction included at the CCSD(T)/aug-cc-pVTZ level. Consequently, the CcCR QFFs are reliable computational tools for physical interpretation of spectroscopic data.

Bond strengths are often considered to be proportional to the harmonic force constants of the



corresponding internal stretching mode. These force constants give an indication of molecular stability especially for seemingly bizarre species like noble gas cations. Hence, the diagonal second-derivatives produced within a QFF are a good measure of bond strength. From experimental work on  $\text{ArH}^+$ <sup>3,25,45</sup>, the  $\text{ArH}^+$  harmonic force constant is easily computed to be 3.882 845 mydne/ $\text{\AA}^2$ . A hydride stretch in many hydrocarbons or alcohols is closer to 7.0 mydne/ $\text{\AA}^2$ , but the Ar–H force constant certainly is strong enough to be considered covalent.  $\text{ArH}_2^+$  has been suggested as an intermediate in the formation of  $\text{ArH}^+$  from  $\text{Ar}^+$  and  $\text{H}_2$  or, nearly energetically equivalently, Ar and  $\text{H}_2^+$  even though the isolation of  $\text{ArH}_2^+$  in such a reaction is unlikely.<sup>46,47</sup> The Ar–H CcCR force constant in  $\text{ArH}_2^+$  is nearly half that of  $\text{ArH}^+$  at 1.895 279 mydne/ $\text{\AA}^2$ . Unlike  $\text{ArH}_2^+$ ,  $\text{ArH}_3^+$  has been observed experimentally<sup>21,24,48</sup> even though its Ar–H CcCR force constant is much smaller at 0.478 761 mdyne/ $\text{\AA}^2$ <sup>9</sup>. However,  $\text{H}_3^+$  is a common and stable interstellar species<sup>49–51</sup> making complexes with argon much more likely<sup>26,27</sup>. It is  $\text{ArOH}^+$  that actually has a covalent-level CcCR noble gas force constant at 2.987 668 mdyne/ $\text{\AA}^2$ <sup>4</sup>. Several noble gas compounds are known to be covalent,<sup>5,6</sup> but  $\text{ArH}^+$  and  $\text{ArOH}^+$  are the first analyzed whose constituent atoms have high enough interstellar abundances<sup>52</sup> to allow the parent molecule potentially to be observed in the ISM. The neon analogues of these discussed systems are all much less strongly bound if at all. Helium will likely be even less. The larger krypton and xenon are more polarizable, but their abundance in nature (especially in the ISM) is significantly less than argon since they are heavier than iron.

Hence, this work employs the CcCR QFF as a means to produce for the first time the

structural, vibrational, and rotational data of another candidate for noble gas covalency,  $\text{ArNH}^+$ .  $\text{NH}$ ,  $\text{NH}_2$ ,  $\text{HCNH}^+$ , and  $\text{HNCNH}$  are known to exist in the ISM<sup>53–56</sup>, but  $\text{NH}^+$  has conspicuously not been detected<sup>57</sup>. Furthermore, the argon atomic cation has been experimentally known to bind with the nitrogen molecule allowing for a potential interstellar tracer of nitrogen molecular gas.<sup>58</sup> Consequently, the role that ionized argon could play in the nitrogen chemistry of the ISM is open-ended. Furthermore, there is nothing reported in the literature on this open-shell cation, and its discussion here is aimed at increasing the number of analyzed, covalent, noble gas molecules that may naturally exist somewhere in the larger universe.

## 2.2 Computational Details

$\text{ArNH}^+$  is open-shell requiring the use of the restricted-open shell reference wavefunction<sup>59–61</sup>. The PSI4 suite of quantum chemical programs<sup>62</sup> is utilized for all computations except the scalar relativistic terms that employ the MOLPRO 2010.1 program<sup>63</sup> and the Møller-Plesset<sup>64</sup> second-order perturbation theory (MP2) aug-cc-pVTZ double-harmonic vibrational intensities computed with Gaussian09<sup>65</sup>.  $\text{ArNH}^+$  is a  $C_s$  triatomic structure where such connectivity has heritage within our group<sup>4,8,37,66–71</sup>. The CcCR QFF defined above for  $\text{ArNH}^+$  requires 129 points originating from displacements of 0.005 Å for the bond length coordinates and 0.005 radians for the bond angle coordinates based on a reference geometry. Coordinate 1 represents the Ar–N bond, coordinate 2 is N–H bond, and coordinate 3 is the bend. The

reference geometry is computed by taking the optimized CCSD(T)/aug-cc-pV5Z geometry and adding the difference in the core- and non-core-including geometrical parameters from CCSD(T)/MT geometry optimizations. The CcCR energies are then computed from this surface.

A least-squares fitting of the CcCR energies creates an initial QFF and the equilibrium geometry. Refitting the points creates zero gradients and the resulting force constants utilized. The INTDER<sup>72</sup> program transforms the internal coordinate force constants into Cartesian coordinates. Rotational<sup>73</sup> and vibrational<sup>74,75</sup> second-order perturbation theory (VPT2) computations within the SPECTRO program<sup>19</sup> then produce the anharmonic frequencies and spectroscopic data. Only a  $2\nu_3 = \nu_2$  type-1 Fermi resonance is necessary for inclusion in the VPT2 computations.

## 2.3 Results and Discussion

The least-squares fitting that produces the force constants is exceptionally tight for this molecule on the order of  $10^{-18}$  a.u.<sup>2</sup> indicating that the computations are very well-behaved. The force constants for ArNH<sup>+</sup> are given in Table 2.1 according to the coordinates described previously. The  $F_{11}$  force constant at gives insight into the essence of the Ar–N bond, a crucial piece for this molecule’s natural viability. At 1.865 943 mdyne/Å<sup>2</sup>, the Ar–N bond is roughly half the strength of the Ar–H bond in ArH<sup>+</sup>, two-thirds that of the more covalent ArOH<sup>+</sup>, and about the same as that from ArH<sub>2</sub><sup>+</sup> making this bond four times stronger

than the argon bond in the experimentally observed  $\text{ArH}_3^+$ . It is not surprising that the less polarizing nitrogen atom does not pull in electrons as strongly as the oxygen atom in  $\text{ArOH}^+$ , but the argon bond strength of  $\text{ArNH}^+$  is still notable among noble gas species. The  $F_{22}$  N–H stretch is of the same magnitude at  $5.794\,198\text{ mdyne}/\text{\AA}^2$  as one would expect for a hydride stretch.

Preliminary tests on the analogous  $\text{NeNH}^+$  molecule could not establish a minimum on the potential energy surface before free dissociation into Ne and  $\text{NH}^+$  takes place. This is not an unexpected result due to neon's propensity to remain as an isolated atom as was also observed for  $\text{NeH}_3^+$ .<sup>9</sup> As a further illustrative point regarding the bonding present in the title molecule, the bond strength of  $\text{ArNH}^+$  is a third again stronger than that in  $\text{NeOH}^+$ .<sup>4</sup>

The geometrical and spectroscopic data for  $\text{ArNH}^+$  are all given in Table 2.2. This includes substitution for all three major isotopes of argon ( $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ , and  $^{40}\text{Ar}$ ) and for deuterium, as well. The vibrationally-averaged ( $R_\alpha$ ) bond lengths are longer for  $\text{ArNH}^+$  than they are in the corresponding hydroxide cation. For instance the  $1.723\,854\text{ \AA}$  Ar–O bond in  $^{40}\text{ArOH}^+$  is over  $0.1\text{ \AA}$  longer than the Ar–N bond in  $^{40}\text{ArNH}^+$  at  $1.847\,154\text{ \AA}$ . The hydride bond is about  $0.05\text{ \AA}$  longer in the nitride. Deuteration increases these bond lengths as does isotopic substitution of the argon atom but to a lesser degree in the latter case. The bond angles are nearly unaffected by the heavier argon masses but shift by one-tenth of a degree for inclusion of deuterium. Additionally, the bond angles are just over four degrees closer to orthogonality in  $\text{ArNH}^+$  than in  $\text{ArOH}^+$ .

The rotational constants of  $\text{ArNH}^+$  also behave in a quasilinear fashion as one would expect

for such a system where the mass is largely dominated by a single atom, argon in this case.  $A_0$  for  $^{40}\text{ArNH}^+$  is over 40 times larger than  $B_0$  ( $0.44894\text{ cm}^{-1}$ ) and  $C_0$  ( $0.43651\text{ cm}^{-1}$ ) with the B- and C-type constants differing by only  $0.01243\text{ cm}^{-1}$ . Similar quasi-linear behavior is present in the other isotopologues. The quartic and sextic distortion constants are also given in Table 2.2 in order to provide for a more complete rotational description of this radical cation and its isotopologues.

The center-of-mass CCSD(T)/aug-cc-pVTZ dipole moment of 2.28 D computed for  $^{40}\text{ArNH}^+$  indicates that this molecule will be a strong rotational absorber. The  $\mu_x$  component is dominated by the two heavy atoms, while the nearly equivalent  $\mu_y$  component is a result of the off-linear hydrogen atom. The nitrogen atom is nearly electroneutral while the argon atom contains 61% of the net positive charge and the hydrogen atom is responsible for 36% of the charge. Consequently, the separation of the positive charge, as opposed to its exclusive presence on the argon atom, in addition to the Ar-N bond strength support the classification of  $\text{ArNH}^+$  as a covalently bonded molecule.

The  $\nu_1$  N-H stretching mode of  $\text{ArNH}^+$  is independent of the argon isotope utilized for our level of precision and falls at  $3236.3\text{ cm}^{-1}$ . This is within  $20\text{ cm}^{-1}$  of the symmetric N-H stretch in the  $\text{NH}_2$  radical at  $3219.37\text{ cm}^{-1}$ <sup>76</sup>. Previous work on the related  $\text{NH}_2^-$  system produces a CcCR symmetric hydride stretching frequency within  $6\text{ cm}^{-1}$  of experiment<sup>39</sup>. As such, it appears as though the N-H stretch of  $\text{ArNH}^+$  closely follows that from the astrophysically known  $\text{NH}_2$  radical.

The  $\nu_2$  bending mode and  $\nu_3$  Ar-N stretch, naturally, are affected by the heavier argon

isotopes, but are all relatively close together. Both the bend at  $1209.4\text{ cm}^{-1}$  and heavy atom stretch at  $516.4\text{ cm}^{-1}$  for  $^{40}\text{ArNH}^+$  are over  $100\text{ cm}^{-1}$  less than the corresponding values in  $^{40}\text{ArOH}^+$ .<sup>4</sup> The decrease in both values is a consequence of the smaller force constants in the nitrogen-containing radical cation brought about, in turn, by the slightly more weakly bound nature of  $\text{ArNH}^+$ .

The zero-point energies decrease by  $2\text{ cm}^{-1}$  with each more massive argon atom and by  $590\text{ cm}^{-1}$  for each deuterium. Deuteration of the molecule also decreases the fundamental vibrational frequencies and rotational constants expectedly. The vibrationally-excited rotational constants are also listed in Table 2.2 as are the double harmonic intensities of each mode given in parenthesis beside the  $^{40}\text{ArNH}^+$  harmonic frequencies. The intensities are all roughly of the same order of magnitude, but the bend is the weakest absorber at  $38\text{ km/mol}$ . The two stretches at  $70\text{ km/mol}$  and  $94\text{ km/mol}$ , respective of  $\omega_1$  and  $\omega_3$  are more intense. The Ar–N stretch is slightly brighter than the N–H. The larger partial positive charge on the argon atom combined with its near-zero displacement vector for the N–H fundamental stretch is likely what makes the heavy atom stretch a better infrared absorber.

Table 2.1: The ArNH<sup>+</sup> CcCR Simple-Internal Force Constants (in mdyn/Å<sup>n</sup>·rad<sup>m</sup>).

|                  |            |                  |          |                   |        |                   |       |
|------------------|------------|------------------|----------|-------------------|--------|-------------------|-------|
| F <sub>11</sub>  | 1.865 943  | F <sub>221</sub> | 0.3088   | F <sub>1111</sub> | 34.18  | F <sub>3222</sub> | -0.12 |
| F <sub>21</sub>  | -0.161 926 | F <sub>222</sub> | -37.3959 | F <sub>2111</sub> | 0.80   | F <sub>3311</sub> | 0.98  |
| F <sub>22</sub>  | 5.794 198  | F <sub>311</sub> | -1.5860  | F <sub>2211</sub> | -0.75  | F <sub>3321</sub> | 0.49  |
| F <sub>31</sub>  | 0.321 521  | F <sub>321</sub> | -0.1825  | F <sub>2221</sub> | -0.22  | F <sub>3322</sub> | -1.10 |
| F <sub>32</sub>  | -0.030 373 | F <sub>322</sub> | 0.0695   | F <sub>2222</sub> | 211.53 | F <sub>3331</sub> | 2.28  |
| F <sub>33</sub>  | 0.938 397  | F <sub>331</sub> | -1.5064  | F <sub>3111</sub> | 4.67   | F <sub>3332</sub> | -0.27 |
| F <sub>111</sub> | -8.7623    | F <sub>332</sub> | -0.1424  | F <sub>3211</sub> | 1.39   | F <sub>3333</sub> | 1.52  |
| F <sub>211</sub> | 0.1951     | F <sub>333</sub> | -0.9633  | F <sub>3221</sub> | -0.32  |                   |       |

## 2.4 Conclusions

In the exploration for small, covalent noble gas molecules, the ArNH<sup>+</sup> radical cation indicates that it is relatively well-bound. Granted, it is not as tightly held together as the known ArH<sup>+</sup> or hypothesized ArOH<sup>+</sup> systems, but the ArNH<sup>+</sup> spectroscopic data provided in this work indicate that it should be a viable molecule. The Ar–N bond strength is half that of Ar–H in ArH<sup>+</sup>, but it is still four times greater than that in the known ArH<sub>3</sub><sup>+</sup> system. While the argon-trihydrogen cation is described as a van der Waals complex, ArNH<sup>+</sup> exhibits expected behavior in the Ar–N stretch that would be produced from a covalent system. This fundamental vibrational frequency is also the strongest absorber for the three modes in this system, and ArNH<sup>+</sup> has a large dipole moment (2.28 D) making its rotational, vibrational, or rovibrational detection an achievable experimental endeavor.

Table 2.2: The CcCR QFF ArNH<sup>+</sup> Equilibrium and Zero-Point ( $R_\alpha$ ) Structures, Spectroscopic Constants, Vibrational Frequencies, and Harmonic Intensities (in parenthesis in km/mol) for the <sup>36</sup>Ar, <sup>38</sup>Ar, <sup>40</sup>Ar, H, and D-Including Isotopologues.

|                                      | <sup>36</sup> ArNH <sup>+</sup> | <sup>36</sup> ArND <sup>+</sup> | <sup>38</sup> ArNH <sup>+</sup> | <sup>38</sup> ArND <sup>+</sup> | <sup>40</sup> ArNH <sup>+</sup> | <sup>40</sup> ArND <sup>+</sup> |
|--------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| $r_e(\text{Ar-N}) \text{ \AA}$       | 1.834 795                       | -                               | -                               | -                               | -                               | -                               |
| $r_e(\text{N-H}) \text{ \AA}$        | 1.045 833                       | -                               | -                               | -                               | -                               | -                               |
| $\angle(\text{Ar-N-H})$              | 97.116                          | -                               | -                               | -                               | -                               | -                               |
| $A_e \text{ cm}^{-1}$                | 16.84399                        | 9.11126                         | 16.84379                        | 9.11096                         | 16.84360                        | 9.11068                         |
| $B_e \text{ cm}^{-1}$                | 0.46734                         | 0.44087                         | 0.46011                         | 0.43375                         | 0.45359                         | 0.42732                         |
| $C_e \text{ cm}^{-1}$                | 0.45472                         | 0.42052                         | 0.44788                         | 0.41404                         | 0.44170                         | 0.40817                         |
| $r_0(\text{Ar-N}) \text{ \AA}$       | 1.847 259                       | 1.845 719                       | 1.847 204                       | 1.845 663                       | 1.847 154                       | 1.845 611                       |
| $r_0(\text{N-H}) \text{ \AA}$        | 1.059 404                       | 1.055 885                       | 1.059 399                       | 1.055 879                       | 1.059 395                       | 1.055 873                       |
| $\angle(\text{Ar-N-H})$              | 97.295                          | 97.196                          | 97.295                          | 97.197                          | 97.295                          | 97.197                          |
| $A_0 \text{ cm}^{-1}$                | 16.71836                        | 9.06659                         | 16.71802                        | 9.06619                         | 16.71772                        | 9.06582                         |
| $B_0 \text{ cm}^{-1}$                | 0.46253                         | 0.43714                         | 0.45538                         | 0.43009                         | 0.44894                         | 0.42372                         |
| $C_0 \text{ cm}^{-1}$                | 0.44934                         | 0.41617                         | 0.44260                         | 0.40977                         | 0.43651                         | 0.40399                         |
| $A_1 \text{ cm}^{-1}$                | 16.08356                        | 8.81923                         | 16.08322                        | 8.81882                         | 16.08292                        | 8.81846                         |
| $B_1 \text{ cm}^{-1}$                | 0.46121                         | 0.43605                         | 0.45408                         | 0.42902                         | 0.44768                         | 0.42267                         |
| $C_1 \text{ cm}^{-1}$                | 0.44772                         | 0.41476                         | 0.44100                         | 0.40838                         | 0.43494                         | 0.40263                         |
| $A_2 \text{ cm}^{-1}$                | 17.10951                        | 9.23031                         | 17.10887                        | 9.22967                         | 17.10830                        | 9.22910                         |
| $B_2 \text{ cm}^{-1}$                | 0.45853                         | 0.43487                         | 0.45145                         | 0.42784                         | 0.44505                         | 0.42150                         |
| $C_2 \text{ cm}^{-1}$                | 0.44435                         | 0.41275                         | 0.43769                         | 0.40641                         | 0.43167                         | 0.40068                         |
| $A_3 \text{ cm}^{-1}$                | 16.71076                        | 9.06089                         | 16.71045                        | 9.06053                         | 16.71018                        | 9.06021                         |
| $B_3 \text{ cm}^{-1}$                | 0.45825                         | 0.43307                         | 0.45120                         | 0.42612                         | 0.44485                         | 0.41984                         |
| $C_3 \text{ cm}^{-1}$                | 0.44517                         | 0.41223                         | 0.43852                         | 0.40597                         | 0.43252                         | 0.40027                         |
| $D_J \text{ MHz}$                    | 0.040                           | 0.033                           | 0.038                           | 0.032                           | 0.037                           | 0.031                           |
| $D_{JK} \text{ MHz}$                 | 0.896                           | 0.603                           | 0.875                           | 0.587                           | 0.856                           | 0.572                           |
| $D_K \text{ MHz}$                    | 62.521                          | 19.245                          | 62.534                          | 19.254                          | 62.546                          | 19.262                          |
| $d_1 \text{ kHz}$                    | -1.010                          | -1.448                          | -0.965                          | -1.382                          | -0.925                          | -1.324                          |
| $d_2 \text{ kHz}$                    | -0.034                          | -0.087                          | -0.032                          | -0.082                          | -0.030                          | -0.077                          |
| $H_J \text{ Hz}$                     | 0.016                           | 0.0004                          | 0.015                           | 0.005                           | 0.015                           | 0.0007                          |
| $H_{JK} \text{ Hz}$                  | 5.100                           | 2.782                           | 4.900                           | 2.662                           | 4.724                           | 2.556                           |
| $H_{KJ} \text{ Hz}$                  | 181.782                         | 65.241                          | 176.875                         | 62.975                          | 172.519                         | 60.975                          |
| $H_K \text{ kHz}$                    | 16.666                          | 3.585                           | 16.658                          | 3.581                           | 16.650                          | 3.577                           |
| $h_1 \text{ mHz}$                    | 2.541                           | 2.536                           | 2.398                           | 2.399                           | 2.275                           | 2.278                           |
| $h_2 \text{ mHz}$                    | 0.515                           | 1.162                           | 0.477                           | 1.073                           | 0.445                           | 0.998                           |
| $h_3 \text{ mHz}$                    | 0.036                           | 0.134                           | 0.033                           | 0.122                           | 0.031                           | 0.112                           |
| $\mu_x \text{ D}$                    |                                 |                                 |                                 |                                 | 1.58                            |                                 |
| $\mu_y \text{ D}$                    |                                 |                                 |                                 |                                 | 1.65                            |                                 |
| $\mu \text{ D}$                      |                                 |                                 |                                 |                                 | 2.28                            |                                 |
| $\omega_1 \text{ N-H cm}^{-1}$       | 3236.3                          | 2366.8                          | 3236.3                          | 2366.8                          | 3236.3 (70)                     | 2366.8                          |
| $\omega_2 \text{ Bend cm}^{-1}$      | 1247.3                          | 915.2                           | 1246.9                          | 914.8                           | 1246.6 (38)                     | 914.4                           |
| $\omega_3 \text{ Ar-N cm}^{-1}$      | 538.7                           | 532.7                           | 534.6                           | 528.4                           | 530.8 (94)                      | 524.5                           |
| Harmonic Zero-Point $\text{cm}^{-1}$ | 2511.2                          | 1907.3                          | 2508.9                          | 1905.0                          | 2506.9                          | 1902.8                          |
| $\nu_1 \text{ N-H cm}^{-1}$          | 3075.2                          | 2280.9                          | 3075.2                          | 2280.9                          | 3075.2                          | 2280.9                          |
| $\nu_2 \text{ Bend cm}^{-1}$         | 1209.7                          | 894.0                           | 1209.7                          | 893.6                           | 1209.4                          | 893.3                           |
| $\nu_3 \text{ Ar-N cm}^{-1}$         | 524.0                           | 520.2                           | 520.0                           | 516.0                           | 516.4                           | 512.3                           |
| Zero-Point $\text{cm}^{-1}$          | 2476.4                          | 1887.8                          | 2474.2                          | 1885.5                          | 2472.2                          | 1883.4                          |



# Chapter 3

## The Rovibrational Spectra of Three, Stable Noble Gas Molecules: $\text{NeCCH}^+$ , $\text{ArCCH}^+$ , and $\text{ArCN}^+$

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### 3.1 Introduction

The astrochemist's periodic table contains only 11 elements.<sup>50</sup> The other 81 commonly associated with terrestrial chemistry are largely inaccessible in the interstellar medium (ISM) as their abundances are too low to be considered for most astrochemistry. This is either due to the presence of relatively unstable nuclei or the simple fact that the atoms are heavier than iron, the last stable nucleus formed in stellar nucleosynthesis. In any case, these available 11 elements include: the overabundant hydrogen; the triumvirate of carbon, nitrogen, and oxygen; and the precocious iron. Even so, three of these elements are the noble gases:

helium, neon, and argon.<sup>50,52</sup> It is often assumed that such species do not engage in chemistry. However, why would the astrochemist handicap himself or herself by neglecting over a quarter of the elements in the available chemical set?

Astrochemistry is the cauldron of chemical assumption refinement. The Earth represents a small fraction of the conditions possible in the universe, and, most notably, the cold, diffuse ISM is populated with well-known species but also with strange, bizarre, and beautiful molecules that are in no way common terrestrially.<sup>77-79</sup> Noble gas compounds are now a part of that mix.

Argonium,  $\text{ArH}^+$ , was reported as detected in the Crab Nebula in 2013.<sup>25</sup> In the time since, it has also been conclusively observed toward TMC-1 and the center of the galaxy in Sgr B2(N).<sup>2,3,45</sup>  $\text{ArH}^+$  had been the study of some experimental work in the preceding decades<sup>20,80</sup> since its existence had been theoretically characterized in the early 1990s.<sup>1,5</sup> One of the reasons for its lack of previous discovery came from argon's isotopic structure. While  $^{40}\text{Ar}$  is the most common isotope on earth,  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  are orders of magnitude more common in the ISM. Consequently, the difference in conditions on the earth and in space kept argonium hidden from observation for some time.

It is believed that argonium is formed through cosmic ray ionization of argon atoms followed by collisions with the ubiquitous  $\text{H}_2$  to create argonium and a hydrogen atom.<sup>25,47,81</sup> However, it has recently been shown that ionization of the hydrogen molecule leads to a near isoenergy value for such a reaction initiating with the argon atom and  $\text{H}_2^+$ .<sup>8</sup> Since the hydrogen molecule is more abundant than argon atoms, this "alternative" pathway is equally viable.

As a part of either process,  $\text{ArH}_2^+$  is the global minimum on the potential energy surface (PES), but the bending motion easily leads to dissociation of the terminal hydrogen atom.<sup>8,47</sup> The analogous reaction with neon is not as favorable with the ionization of the neon atom requiring nearly 5 eV more energy than ionization of  $\text{H}_2$ . Furthermore, while  $\text{NeH}_2^+$  is the global minimum on the PES,<sup>24</sup> the most stable set of products is the neon atom and the hydrogen molecular cation, different from  $\text{ArH}^+$  and a hydrogen atom.<sup>8</sup>

This is somewhat disappointing as argon is less abundant than neon with only H, He, O, and C more abundant than Ne.<sup>52</sup> As a result, the search for neon-containing molecules could have significant implications for astrochemistry if only such compounds could be clearly predicted or experimentally isolated. Recent work in our group has shown that the hydroxyl cation is polarizing enough for the valence  $2p$  orbitals in Ne to bond to the oxygen to create  $\text{NeOH}^+$  with a Ne–O bond strength of more than 25% that present in the Ar–H bond in  $\text{ArH}^+$ .<sup>4</sup> Unfortunately, more neon-containing molecules have largely remained elusive, but argon, which is much more polarizable,<sup>6,26,27,82,83</sup> is more keen to bond with various electron-withdrawing ligands. Notable examples include  $\text{ArOH}^+$ ,  $\text{ArNH}^+$ ,  $\text{ArCCH}^+$ , and  $\text{ArCN}^+$ <sup>4,79,84,85</sup> with some stability present in the Ar–H bond(s) of  $\text{ArH}_3^+$  and  $\text{Ar}_2\text{H}_3^+$ .<sup>9,86</sup>

The only further neon-containing molecule that has shown any promise as a stable molecule beyond  $\text{NeOH}^+$  is  $\text{NeCCH}^+$ .<sup>1,85</sup>  $\text{NeON}^+$ ,  $\text{ArON}^+$ , and  $\text{NeCN}^+$  were shown not to be stable molecular systems except as potential van der Waals complexes with neutral neon atoms. Unlike its third-row analogue in  $\text{ArCCH}^+$ ,  $\text{NeCCH}^+$  exhibits a strangely bent,  $C_s$  minimum structure. The in-plane  $\pi$  orbital appears to be involved in the Ne–C bonding somewhat.<sup>1</sup>

Even so, the dissociation energy of the Ne–C bond is a paltry but non-negligible 21.8 kcal/mol<sup>85</sup> compared to 45.1 kcal/mol for the Ne–O bond in NeOH<sup>+</sup>.<sup>4</sup> Regardless, the fact that NeCCH<sup>+</sup> exists as a stable minimum on its potential energy surface indicates that enough of this material could be present in the ISM for detection. As a further disappointment, no gas-phase mechanisms involving known or hypothesized interstellar molecular reactants could produce favorable reaction energetics for NeCCH<sup>+</sup> unlike the argon species: ArNH<sup>+</sup>, ArCCH<sup>+</sup>, and ArCN<sup>+</sup>.<sup>85</sup> However, adsorption of the neutral noble gas atom onto a polycyclic aromatic hydrocarbon (PAH) surface is shown to catalyze the formation reaction of NeCCH<sup>+</sup> and even ArCCH<sup>+</sup> as well as ArCN<sup>+</sup>.<sup>85</sup> Hence, the presence of NeCCH<sup>+</sup> could be an indirect indicator for the presence of PAHs.

In any case, the vibrational frequencies, rotational constants, and general rovibrational spectroscopic data for NeCCH<sup>+</sup>, ArCCH<sup>+</sup>, and ArCN<sup>+</sup> are completely unknown. Hence, this work will produce these data at high-level for comparison to experimental or even astronomical spectra taken with modern telescopic instruments such as the Stratospheric Observatory for Infrared Astronomy (SOFIA), the Atacama Large Millimeter Array (ALMA), or even the upcoming James Webb Space Telescope (JWST) where noise levels have been significantly reduced increasing the amount of usable signal created. Quantum chemical *ab initio* vibrational frequencies computed via fourth-order Taylor series expansions of the internuclear Hamiltonian (known as quartic force fields or QFFs)<sup>38,87</sup> have reproduced known experimental vibrational fundamental frequencies to within as good as 1.0 cm<sup>-1</sup> in some cases and rotational constants to within 50 MHz or better.<sup>28,29,31–33,37–39,88</sup> In building the presumably,

highly-accurate spectroscopic data for such noble gas cations, more molecules involving atoms from the right-most column on the periodic table are hoped finally to be detected in nature, even if in the often extremely cold and diffuse ISM.

## 3.2 Computational Details

NeCCH<sup>+</sup>, ArCCH<sup>+</sup>, and ArCN<sup>+</sup> are all closed-shell molecules that use a restricted Hartree-Fock reference wave function<sup>89</sup>. The PSI4 suite of quantum chemical programs<sup>62</sup> and coupled cluster theory<sup>17,40</sup> at the singles, doubles, and perturbative triples [CCSD(T)] level<sup>18</sup> is used for all computations. However, the scalar relativistic terms utilize the MOLPRO 2010.1 program,<sup>63</sup> and Møller-Plesset<sup>64</sup> second-order perturbation theory (MP2) with the 6-31+G\* basis set double-harmonic vibrational intensities are computed with Gaussian09.<sup>64,65,90</sup> The reference geometry for any of the molecules is computed by taking the optimized CCSD(T)/aug-cc-pV5Z geometry, with the (5+d) additional functions for Ar,<sup>41,91</sup> and adding the difference in the core- and non-core-including geometrical parameters from the CCSD(T) geometry optimizations with the Martin-Taylor (MT) core correlating basis set.<sup>43</sup>

The NeCCH<sup>+</sup> QFF is described by 805 total points defined from 743 symmetry-unique points that originate from displacements on the reference geometry of 0.005 Å for bond length coordinates and 0.005 radians for the bond angle and torsional coordinates. The

coordinates defined for this molecule are:

$$S_1(a') = \text{Ne} - \text{C} \quad (3.1)$$

$$S_2(a') = \text{C} - \text{C} \quad (3.2)$$

$$S_3(a') = \text{C} - \text{H} \quad (3.3)$$

$$S_4(a') = \angle(\text{Ne} - \text{C} - \text{C}) \quad (3.4)$$

$$S_5(a') = \angle(\text{C} - \text{C} - \text{H}) \quad (3.5)$$

$$S_6(a'') = \tau(\text{Ne} - \text{C} - \text{C} - \text{H}). \quad (3.6)$$

This is the same coordinate system utilized previously and successfully with a number of  $C_s$ , tetra-atomic species.<sup>31,36,92</sup> The coordinate system for the linear  $\text{ArCCH}^+$  cation requires 625 total points utilizing the following symmetry-internal coordinates also with heritage:<sup>93</sup>

$$S_1(\Sigma^+) = \text{Ar} - \text{C} \quad (3.7)$$

$$S_2(\Sigma^+) = \text{C} - \text{C} \quad (3.8)$$

$$S_3(\Sigma^+) = \text{C} - \text{H} \quad (3.9)$$

$$S_4(\Pi_{xz}) = \angle \text{Ar} - \text{C} - \text{C} - \mathbf{y} \quad (3.10)$$

$$S_5(\Pi_{xz}) = \angle \text{C} - \text{C} - \text{H} - \mathbf{y} \quad (3.11)$$

$$S_6(\Pi_{yz}) = \angle \text{Ar} - \text{C} - \text{C} - \mathbf{x} \quad (3.12)$$

$$S_7(\Pi_{yz}) = \angle \text{C} - \text{C} - \text{H} - \mathbf{x}. \quad (3.13)$$

Finally, the  $\text{ArCN}^+$  system requires 55 symmetry-unique and 69 total points constructed in the same way as other triatomic, linear,  $C_{\infty v}$  systems:<sup>8,37,69,94</sup>

$$S_1(\Sigma^+) = \text{Ar} - \text{C} \quad (3.14)$$

$$S_2(\Sigma^+) = \text{C} - \text{N} \quad (3.15)$$

$$S_3(\Pi_{xz}) = \angle \text{Ar} - \text{C} - \text{N} - \mathbf{y} \quad (3.16)$$

$$S_4(\Pi_{yz}) = \angle \text{Ar} - \text{C} - \text{N} - \mathbf{x}. \quad (3.17)$$

The energy produced at each point is compositely based again on CCSD(T). Within the aug-cc-pVXZ basis set series with X= T, Q, and 5, the CCSD(T) energy is extrapolated to the complete basis set (CBS) limit via a three-point formula<sup>42</sup>. MT basis set corrections (the energy difference computed with and without core electrons) are appended to the CCSD(T)/CBS energies. Therefore, the CcC QFF is constructed where the "C" is for the CBS energy, and the "cC" is for the core correlation computed again by taking the difference in the MT and MT energies with and without the 1s electrons for Ne, C, and N and the 1s2s2p electrons for Ar. Scalar relativity<sup>44</sup> is added to the composite energy in the "R" term by taking the difference between the energy also computed with and without the relativity included at the CCSD(T)/aug-cc-pVTZ-DK level.<sup>95</sup> The outcome of the CcCR QFFs are reliable computational tools for physical interpretation of spectroscopic data.

The initial QFF is fit from a least-squares means on the CcCR energy. This fitting also provides the equilibrium geometry, and refitting the points creates zero gradients and the

subsequent force constants utilized. The internal coordinate force constants are transformed into Cartesian coordinates with the INTDER<sup>72</sup> program so that general force constants definitions can be utilized. Rotational<sup>73</sup> and vibrational<sup>74,75</sup> second-order perturbation theory (VPT2) is then used to derive the anharmonic frequencies and spectroscopic data from the SPECTRO program.<sup>19</sup> Resonances can be input into SPECTRO, and NeCCH<sup>+</sup> requires a  $2\nu_6 = \nu_6 + \nu_5 = \nu_3$  Fermi resonance polyad, an additional  $2\nu_2 = \nu_1$  type-1 Fermi resonance,  $\nu_4/\nu_3$  and  $\nu_6/\nu_5$  Darling-Denison resonances, and a  $\nu_4/\nu_3$  A-type as well as a  $\nu_6/\nu_5$  C-type Coriolis resonance. ArCCH<sup>+</sup> possesses a  $\nu_5 + \nu_3 = \nu_4$  type-2 Fermi resonance and  $\nu_4/\nu_3$  Darling-Denison resonance. ArCN<sup>+</sup> only requires a  $2\nu_3 = \nu_2$  type-1 Fermi resonance.

## 3.3 Results and Discussion

### 3.3.1 NeCCH<sup>+</sup>

In the analysis of these cationic species, the search for neon-containing species leads the discussion to begin with NeCCH<sup>+</sup>. The force constants that define the QFF from the composite CcCR energy are given in Table 3.1. Most notably, the mirroring of the small, but non-negligible 21.8 kcal/mol Ne–C bond energy<sup>85</sup> is present in the  $F_{11}$  force constant of 0.658 276 mdyne/Å<sup>2</sup>. This is less than the Ne–H harmonic, diagonal force constant in NeH<sub>2</sub><sup>+</sup><sup>8</sup>. Consequently, the Ne–C bond is notably weak. However, the  $F_{22}$  value of 10.396 521 mdyne/Å<sup>2</sup> corresponding to the C–C bond is less than what one would assume is present



in a triple bond, which is typically closer to  $15.0 \text{ mdyne}/\text{\AA}^{2.96}$ . Examining the aug-cc-pVTZ Mulliken population electron density gives a 0.32 value to Ne, 0.60 for the adjacent carbon atom, a -0.56 for the other carbon atom, and 0.63 for H. Clearly some electron density is shared throughout the system even if the Ne–C bond is weak. Consequently, the neon’s desire to fill its octet is being balanced to a large degree by similar forces in the  $\text{C}_2\text{H}^+$  ligand making  $\text{NeCCH}^+$  a viable molecule for study in darker and cooler regions of the ISM.

The  $\text{NeCCH}^+$  structural and spectroscopic values are produced in Table 3.2. The Ne–C bond is fairly long for a bond comprised of second-row atoms, but neither bond angle is anywhere close to linear in accordance with the aforementioned properties. Additionally, the dipole moment, computed with the center-of-mass at the origin, is fairly large at 2.82 D with most of this vector coming along the near-prolate  $a$  axis. Vibrational-averaging ( $R_\alpha$ ) increases the Ne–C bond length notably thus influencing the rotational constants of this prolate top. Deuteration and inclusion of  $^{22}\text{Ne}$  also reduces the rotational constants.

The vibrational frequencies are given at the bottom of Table 3.2. The double harmonic intensities show that the C–H stretch is a fairly bright mode with the C–C–H bend and Ne–C stretch also being noteworthy in any infrared spectrum of this molecule. The  $\nu_1$  C–H stretch at  $3101.9 \text{ cm}^{-1}$  should be well-characterized here based on previous experience with hydride stretches and the fact that there is no notable coupling to any Ne-containing modes. Furthermore, the  $\nu_2$  C–C stretch at  $1661.8 \text{ cm}^{-1}$  is also reliable with expected levels of anharmonicity and trustworthy force constants.

The modes that involve Ne are somewhat more problematic. The Ne–C–C bend exhibits

almost no anharmonicity which is likely. However, the  $\nu_4$  torsion and the  $\nu_6$  Ne–C stretch are largely anharmonic with the former being positively anharmonic. Consequently, the  $\nu_4$  value is likely not reliable here and is such due possibly to coupling with the  $\nu_6$  fundamental. Such a large anharmonicity of 66% in the  $\nu_6$  Ne–C stretch is typically not indicative of a computation that will compare well with experiment. Similar errors in QFF/VPT2 computations have been shown for stable systems with loosely bonded interactions<sup>97,98</sup> like the Ne–C coordinate here. Even so, those fundamentals that do not couple strongly to such modes or are enough above the energies are likely well-described while modes such as the present  $\nu_4$  and  $\nu_6$  of NeCCH<sup>+</sup> are not well-behaved.

As a result, the Ne–C bond can be interpreted to be fairly weak, but not enough for this molecule to be immediately dismembered. The bright rotational lines and the strong C–H stretching fundamental may provide enough signal for detection either in the laboratory or in the ISM. If this molecule is formed in the adsorbed phase, these transition energies may aid in further tracing of regions where PAHs are present.<sup>85</sup>

### 3.3.2 ArCCH<sup>+</sup>

Fortunately, the ArCCH<sup>+</sup> system is more strongly bound than NeCCH<sup>+</sup><sup>85</sup> indicating that the CcCR QFF VPT2 results should all be reliable. The previously computed 67.0 Ar–C bond energy is qualitatively in line with the  $F_{11}$  value given in Table 3.3, but the 4.524 874 mdyne/Å<sup>2</sup> Ar–C force constant is the largest such value computed thus far for a noble gas system. Hence, the VPT2 results here will not have problems within the QFF, and the

Table 3.1: The NeCCH<sup>+</sup> CcCR Internal Force Constants (in mdyne/Å<sup>n</sup>·rad<sup>m</sup>).

|                  |            |                  |         |                   |        |                   |       |                   |       |
|------------------|------------|------------------|---------|-------------------|--------|-------------------|-------|-------------------|-------|
| F <sub>11</sub>  | 0.658 276  | F <sub>431</sub> | -0.0375 | F <sub>1111</sub> | 39.81  | F <sub>4432</sub> | 0.15  | F <sub>5531</sub> | -0.15 |
| F <sub>21</sub>  | -0.590 956 | F <sub>432</sub> | -0.0435 | F <sub>2111</sub> | 9.90   | F <sub>4433</sub> | 0.01  | F <sub>5532</sub> | -0.34 |
| F <sub>22</sub>  | 10.396 521 | F <sub>433</sub> | -0.0053 | F <sub>2211</sub> | 23.04  | F <sub>4441</sub> | 3.50  | F <sub>5533</sub> | -0.45 |
| F <sub>31</sub>  | -0.076 363 | F <sub>441</sub> | -1.0887 | F <sub>2221</sub> | 32.74  | F <sub>4442</sub> | 1.51  | F <sub>5541</sub> | 0.42  |
| F <sub>32</sub>  | -0.128 263 | F <sub>442</sub> | -0.0364 | F <sub>2222</sub> | 286.57 | F <sub>4443</sub> | 0.27  | F <sub>5542</sub> | -0.60 |
| F <sub>33</sub>  | 5.669 585  | F <sub>443</sub> | -0.0419 | F <sub>3111</sub> | 0.55   | F <sub>4444</sub> | 2.58  | F <sub>5543</sub> | -0.05 |
| F <sub>41</sub>  | 0.276 421  | F <sub>444</sub> | -0.9553 | F <sub>3211</sub> | 0.48   | F <sub>5111</sub> | -2.01 | F <sub>5544</sub> | -0.37 |
| F <sub>42</sub>  | 0.508 570  | F <sub>511</sub> | -0.5403 | F <sub>3221</sub> | 0.65   | F <sub>5211</sub> | -0.91 | F <sub>5551</sub> | 0.55  |
| F <sub>43</sub>  | -0.007932  | F <sub>521</sub> | -0.5486 | F <sub>3222</sub> | -2.53  | F <sub>5221</sub> | 5.19  | F <sub>5552</sub> | -1.37 |
| F <sub>44</sub>  | 0.515 881  | F <sub>522</sub> | -0.4315 | F <sub>3311</sub> | -0.63  | F <sub>5222</sub> | 11.63 | F <sub>5553</sub> | -0.19 |
| F <sub>51</sub>  | 0.075 624  | F <sub>531</sub> | 0.0393  | F <sub>3321</sub> | 0.60   | F <sub>5311</sub> | -0.49 | F <sub>5554</sub> | 0.05  |
| F <sub>52</sub>  | 0.351 929  | F <sub>532</sub> | -0.2081 | F <sub>3322</sub> | -0.76  | F <sub>5321</sub> | -0.50 | F <sub>5555</sub> | -0.50 |
| F <sub>53</sub>  | 0.079 501  | F <sub>533</sub> | -0.0245 | F <sub>3331</sub> | 0.34   | F <sub>5322</sub> | -0.49 | F <sub>6611</sub> | -0.35 |
| F <sub>54</sub>  | 0.026 129  | F <sub>541</sub> | 0.0308  | F <sub>3332</sub> | -0.60  | F <sub>5331</sub> | 0.44  | F <sub>6621</sub> | -0.41 |
| F <sub>55</sub>  | 0.247 393  | F <sub>542</sub> | 0.1849  | F <sub>3333</sub> | 165.02 | F <sub>5332</sub> | 0.11  | F <sub>6622</sub> | 0.68  |
| F <sub>66</sub>  | 0.073 062  | F <sub>543</sub> | 0.0088  | F <sub>4111</sub> | 2.43   | F <sub>5333</sub> | -0.56 | F <sub>6631</sub> | 0.09  |
| F <sub>111</sub> | -6.7752    | F <sub>544</sub> | -0.0297 | F <sub>4211</sub> | -2.27  | F <sub>5411</sub> | -0.82 | F <sub>6632</sub> | 0.07  |
| F <sub>211</sub> | 0.0337     | F <sub>551</sub> | -0.2937 | F <sub>4221</sub> | -1.54  | F <sub>5421</sub> | -1.72 | F <sub>6633</sub> | 1.53  |
| F <sub>221</sub> | 1.2037     | F <sub>552</sub> | 0.0515  | F <sub>4222</sub> | 16.21  | F <sub>5422</sub> | -3.26 | F <sub>6641</sub> | 5.19  |
| F <sub>222</sub> | -60.3656   | F <sub>553</sub> | -0.2036 | F <sub>4311</sub> | 0.22   | F <sub>5431</sub> | -0.33 | F <sub>6642</sub> | 0.10  |
| F <sub>311</sub> | 0.0468     | F <sub>554</sub> | -0.1078 | F <sub>4321</sub> | -0.10  | F <sub>5432</sub> | 0.26  | F <sub>6643</sub> | 0.00  |
| F <sub>321</sub> | 0.0869     | F <sub>555</sub> | -0.1224 | F <sub>4322</sub> | 0.66   | F <sub>5433</sub> | -0.04 | F <sub>6644</sub> | 0.66  |
| F <sub>322</sub> | -0.0606    | F <sub>661</sub> | -0.0605 | F <sub>4331</sub> | 0.34   | F <sub>5441</sub> | 0.71  | F <sub>6651</sub> | 0.99  |
| F <sub>331</sub> | -0.1026    | F <sub>662</sub> | -0.0864 | F <sub>4332</sub> | -0.71  | F <sub>5442</sub> | 0.45  | F <sub>6652</sub> | 0.27  |
| F <sub>332</sub> | 0.0848     | F <sub>663</sub> | -0.0078 | F <sub>4333</sub> | -0.26  | F <sub>5443</sub> | -0.13 | F <sub>6653</sub> | -0.17 |
| F <sub>333</sub> | -32.5100   | F <sub>664</sub> | -0.0122 | F <sub>4411</sub> | 1.53   | F <sub>5444</sub> | -0.01 | F <sub>6654</sub> | -0.88 |
| F <sub>411</sub> | -1.5938    | F <sub>665</sub> | -0.0993 | F <sub>4421</sub> | 0.89   | F <sub>5511</sub> | -1.03 | F <sub>6655</sub> | 0.62  |
| F <sub>421</sub> | -1.8664    |                  |         | F <sub>4422</sub> | -4.85  | F <sub>5521</sub> | -0.26 | F <sub>6666</sub> | 2.02  |
| F <sub>422</sub> | -2.7806    |                  |         | F <sub>4431</sub> | 0.35   | F <sub>5522</sub> | 1.39  |                   |       |

Ar–C bond is strong even if not as strong as Badger’s rule may indicate. Furthermore, the C–C,  $F_{22}$  16.753 422 mdyne/Å<sup>2</sup> value is over 50% larger than the same value in NeCCH<sup>+</sup> showing that this moiety is closer to what would be expected of a triple bond. ArCCH<sup>+</sup> is linear, after all.

The subsequent geometrical values are given at the top of Table 3.4. The Ar–C bond length is shorter in ArCCH<sup>+</sup> than the Ne–C bond length in NeCCH<sup>+</sup> in line with previous

comparisons between  $\text{NeOH}^+/\text{ArOH}^+$  and  $\text{ArH}_2^+/\text{NeH}_2^+$ .<sup>4,8</sup> Since the ISM and the Earth's primary isotopes of argon differ, data is given for  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ , and  $^{40}\text{Ar}$ . The rotational constants reflect these shifts in mass, but the dipole moment is fairly small at 0.46 D. Hence, the abundances of  $\text{ArCCH}^+$  must be fairly high in order for this molecule to be observed in the ISM. Unfortunately, only one favorable gas phase reaction has been shown for the formation of  $\text{ArCCH}^+$  from ionized argon atomic cations and  $\text{HCCNC}$ .<sup>85</sup>

The vibrational modes of  $\text{ArCCH}^+$  are all fairly dim with the C–H stretch coming in as the brightest fundamental. Even so, it is fortunate that the Ar–C stretch is not the lowest frequency mode giving further evidence beyond the large  $F_{11}$  value that  $\text{ArCCH}^+$  is a stable system and is well-described with the present tools. The Ar–C stretching frequency at  $674.8\text{ cm}^{-1}$  for  $\nu_3$  is in close proximity to the  $\nu_4$  C–C–H bend at  $661.4\text{ cm}^{-1}$ , but, again, neither are strong absorbers or emitters. The Ar–C–C bend is positively anharmonic, but such anharmonicities have been observed in other linear molecules.<sup>99,100</sup> While the dim modes may make interstellar detection unlikely, laboratory observation is certainly not out of the question, especially as a byproduct of chemical reactions involving experiments where ethynyl cations may be present in argon matrices, carried by argon carrier gases, or demarked with argon tags.

### 3.3.3 $\text{ArCN}^+$

The  $\text{ArCN}^+$  CcCR force constants are reported in Table 3.5. The Ar–C bond is fairly strong at  $52.8\text{ kcal/mol}$  which is corroborated with the  $F_{11}$  value for  $\text{ArCN}^+$ . The C–N bond  $F_{22}$

force constant is very large owing to the strength of the  $\text{C}\equiv\text{N}$  bond which is of the magnitude expected for triple bonds. The  $\text{Ar}-\text{C}$  bond length in Table 3.6 is the shortest of the noble gas bonds that are not hydride bonds computed thus far. Hence,  $\text{ArCN}^+$  is a tightly compacted molecule but with a large dipole moment of 3.65 D indicating that it will be easily observed rotationally.

The intensities of the vibrational modes for  $\text{ArCN}^+$  are largely in line with those from  $\text{ArCCH}^+$ , but the  $\nu_1$  C–N stretch is somewhat brighter. This fundamental frequency at  $2189.6\text{ cm}^{-1}$  will sit in the mid-infrared in a region that is largely under-explored due to the frequency dichotomy of hydride and heavy-atom stretches. The  $\text{Ar}-\text{C}$  stretch at  $602.6\text{ cm}^{-1}$  is well-above the bend at  $245.8\text{ cm}^{-1}$  for  $^{36}\text{ArCN}^+$  (and similar for the other isotopologues), and neither fundamental is largely anharmonic. Heavy-atom motions, especially those involving third-row atoms, are often not greatly anharmonic<sup>70,71,92,101</sup> lending credence to the reliability of the frequencies reported here.

Furthermore,  $\text{ArCN}^+$  can form from simple reactions of ionized argon atomic cations with the abundant HCN. As a result,  $\text{ArCN}^+$  is likely the best candidate for interstellar detection of the three reported here. Although the C–N stretch is only moderately intense, it will fall slightly to the red of the same stretch in the cyano radical, but the rotational transitions of this molecule will be much more clearly observed due to the linear geometry and the large dipole moment.

## 3.4 Conclusions

In the search for naturally-occurring noble gas molecules, the ISM is likely the best place to look. The various regions of this astrophysical environment offer a diversity of physical conditions with many being cold and diffuse. In such regions, seemingly unstable molecules can form. Argonium is known,<sup>25</sup> but other species containing elements from the last column of the periodic table could be present. This work has built upon the previous knowledge to provide data useful for the detection of such noble gas cations in the ISM or even in the laboratory where studies on these types of systems can further the understanding of chemical bonding and electron-sharing.

While He is the second-most abundant element in the universe, it is unlikely that its chemistry will have any long-lived products capable of observation, although  $\text{CHe}^{2+}$  has been a tantalizing recent suggestion<sup>7</sup>. Neon is the fifth-most abundant element, but the reaction schema that lead to  $\text{ArH}^+$  are not analogous for neon making detection of neonium unlikely. While  $\text{NeOH}^+$  may form from a neon atom and hydrogen peroxide, no other gas phase reactions that could lead to a neon-containing molecule cation have emerged.<sup>79,85</sup>  $\text{NeCCH}^+$  is a stable minimum on its PES,<sup>85</sup> but surface catalysis of some type is likely required for it to form. At any rate, the rovibrational data provided here will aid in the search for this molecule even if just in the laboratory.

Natural noble gas chemistry, especially in the ISM, will likely be dominated by argon. It is orders of magnitude more abundant than krypton and much more polarizable than neon.

Consequently,  $\text{ArOH}^+$ ,  $\text{ArNH}^+$ ,  $\text{ArCCH}^+$ , and  $\text{ArCN}^+$  may be lurking in the depths of the ISM. The present work has shown that  $\text{ArCCH}^+$  will be relatively dark, spectroscopically speaking. This combined with its weakly favored formation<sup>85</sup> will likely hinder its observation beyond controlled conditions in the terrestrial laboratory.  $\text{ArCN}^+$ , on the other hand, is rotationally bright, has a decent intensity for the C–N stretching fundamental frequency, and can form from HCN, one of the most common molecules in space. Consequently, the spectroscopic data provided here will aid in the classification of these molecules where, previously, little if any chemical or spectroscopic data have been derived. Additionally, the zero-point vibrational frequencies computed will be necessary for any interstellar chemical reaction models in which these cations take part. Thus, the chemical inventory of natural noble gas molecules may be greater than previously believed since now we know where to look.

Table 3.2: The NeCCH<sup>+</sup> CcCR QFF Equilibrium and Zero-Point ( $R_\alpha$ ) Structures, Spectroscopic Constants, Vibrational Frequencies, and Harmonic Intensities (in parenthesis in km/mol) for the <sup>20</sup>Ne, <sup>22</sup>Ne, H, and D Isotopologues.

|                                      | <sup>20</sup> NeCCH <sup>+</sup> | <sup>20</sup> NeCCD <sup>+</sup> | <sup>22</sup> NeCCH <sup>+</sup> | <sup>22</sup> NeCCD <sup>+</sup> |
|--------------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| $r_e(\text{Ne-C}) \text{ \AA}$       | 1.672 347                        | –                                | –                                | –                                |
| $r_e(\text{C-C}) \text{ \AA}$        | 1.278 409                        | –                                | –                                | –                                |
| $r_e(\text{C-H}) \text{ \AA}$        | 1.083 835                        | –                                | –                                | –                                |
| $\angle(\text{Ne-C-C})$              | 117.8758                         | –                                | –                                | –                                |
| $\angle(\text{C-C-H})$               | 143.7248                         | –                                | –                                | –                                |
| $A_e \text{ cm}^{-1}$                | 3.584 645                        | 3.512 081                        | 3.560 995                        | 3.485 967                        |
| $B_e \text{ cm}^{-1}$                | 0.294 424                        | 0.266 885                        | 0.281 614                        | 0.255 389                        |
| $C_e \text{ cm}^{-1}$                | 0.272 077                        | 0.248 037                        | 0.260 976                        | 0.237 956                        |
| $\mu_x \text{ D}$                    | 2.77                             |                                  |                                  |                                  |
| $\mu_y \text{ D}$                    | 0.55                             |                                  |                                  |                                  |
| $\mu \text{ D}^a$                    | 2.82                             |                                  |                                  |                                  |
| $r_0(\text{Ne-C}) \text{ \AA}$       | 1.735 353                        | 1.729 503                        | 1.734 509                        | 1.728 650                        |
| $r_0(\text{C-C}) \text{ \AA}$        | 1.286 132                        | 1.285 243                        | 1.286 030                        | 1.285 143                        |
| $r_0(\text{C-H}) \text{ \AA}$        | 1.076 372                        | 1.079 473                        | 1.076 314                        | 1.079 409                        |
| $\angle(\text{Ne-C-C})$              | 116.5281                         | 116.6827                         | 116.5439                         | 116.6993                         |
| $\angle(\text{C-C-H})$               | 142.5738                         | 142.6947                         | 142.5857                         | 142.7068                         |
| $A_0 \text{ cm}^{-1}$                | 3.430 836                        | 3.386 171                        | 3.412 007                        | 3.364 812                        |
| $B_0 \text{ cm}^{-1}$                | 0.284 285                        | 0.259 095                        | 0.271 913                        | 0.247 932                        |
| $C_0 \text{ cm}^{-1}$                | 0.261 483                        | 0.239 782                        | 0.250 874                        | 0.230 087                        |
| $A_1 \text{ cm}^{-1}$                | 3.370 864                        | 3.329 972                        | 3.352 778                        | 3.309 488                        |
| $B_1 \text{ cm}^{-1}$                | 0.281 719                        | 0.256 669                        | 0.269 444                        | 0.245 599                        |
| $C_1 \text{ cm}^{-1}$                | 0.258 948                        | 0.237 411                        | 0.248 437                        | 0.227 808                        |
| $A_2 \text{ cm}^{-1}$                | 3.293 095                        | 3.269 289                        | 3.276 085                        | 3.249 583                        |
| $B_2 \text{ cm}^{-1}$                | 0.281 675                        | 0.257 280                        | 0.269 393                        | 0.246 180                        |
| $C_2 \text{ cm}^{-1}$                | 0.258 474                        | 0.237 634                        | 0.247 992                        | 0.228 032                        |
| $A_3 \text{ cm}^{-1}$                | 3.444 714                        | 3.419 971                        | 3.427 515                        | 3.400 936                        |
| $B_3 \text{ cm}^{-1}$                | 0.282 950                        | 0.258 582                        | 0.270 646                        | 0.247 476                        |
| $C_3 \text{ cm}^{-1}$                | 0.260 077                        | 0.239 100                        | 0.249 548                        | 0.229 482                        |
| $A_4 \text{ cm}^{-1}$                | 3.351 422                        | 3.340 459                        | 3.333 024                        | 3.312 862                        |
| $B_4 \text{ cm}^{-1}$                | 0.280 839                        | 0.256 967                        | 0.268 568                        | 0.245 858                        |
| $C_4 \text{ cm}^{-1}$                | 0.258 259                        | 0.237 902                        | 0.247 748                        | 0.228 253                        |
| $A_5 \text{ cm}^{-1}$                | 3.418 216                        | 3.305 464                        | 3.425 721                        | 3.315 669                        |
| $B_5 \text{ cm}^{-1}$                | 0.280 864                        | 0.253 785                        | 0.269 364                        | 0.243 760                        |
| $C_5 \text{ cm}^{-1}$                | 0.257 703                        | 0.234 423                        | 0.247 910                        | 0.225 795                        |
| $A_6 \text{ cm}^{-1}$                | 3.399 085                        | 3.400 054                        | 3.358 946                        | 3.358 024                        |
| $B_6 \text{ cm}^{-1}$                | 0.277 383                        | 0.255 706                        | 0.264 658                        | 0.243 805                        |
| $C_6 \text{ cm}^{-1}$                | 0.254 249                        | 0.235 715                        | 0.243 407                        | 0.225 419                        |
| $D_J \text{ MHz}$                    | 0.0257                           | 0.0193                           | 0.0240                           | 0.0180                           |
| $D_{JK} \text{ MHz}$                 | 0.5259                           | 0.3745                           | 0.5049                           | 0.3594                           |
| $D_K \text{ MHz}$                    | 46.7791                          | 48.7125                          | 45.935                           | 47.8376                          |
| $d_1 \text{ kHz}$                    | -1.5569                          | -1.1472                          | -1.3964                          | -1.0335                          |
| $d_2 \text{ kHz}$                    | -0.1421                          | -0.0963                          | -0.1241                          | -0.0844                          |
| $H_J \text{ Hz}$                     | -0.3944                          | -0.2520                          | -0.3575                          | -0.2295                          |
| $H_{JK} \text{ Hz}$                  | -37.4720                         | -29.0763                         | -34.1209                         | -26.5428                         |
| $H_{KJ} \text{ Hz}$                  | -175.6746                        | -242.5649                        | -155.8071                        | -223.0992                        |
| $H_K \text{ kHz}$                    | 63.6195                          | 65.0924                          | 61.9612                          | 63.4156                          |
| $h_1 \text{ mHz}$                    | -4.9511                          | 0.2151                           | -4.9108                          | -0.2121                          |
| $h_2 \text{ mHz}$                    | -3.0974                          | -1.8612                          | -2.5716                          | -1.5532                          |
| $h_3 \text{ mHz}$                    | 0.8251                           | 0.5615                           | 0.6640                           | 0.4531                           |
| $\omega_1 \text{ C-H cm}^{-1}$       | 3239.6 (210)                     | 2431.4                           | 3239.6                           | 2431.4                           |
| $\omega_2 \text{ C-C cm}^{-1}$       | 1690.4 (2)                       | 1633.3                           | 1690.2                           | 1633.1                           |
| $\omega_3 \text{ C-C-H cm}^{-1}$     | 674.8 (95)                       | 544.8                            | 674.3                            | 543.9                            |
| $\omega_4 \text{ Torsion cm}^{-1}$   | 593.8 (21)                       | 450.7                            | 593.6                            | 450.4                            |
| $\omega_5 \text{ Ne-C-C cm}^{-1}$    | 315.4 (1)                        | 294.7                            | 310.8                            | 288.7                            |
| $\omega_6 \text{ Ne-C cm}^{-1}$      | 278.5 (77)                       | 272.8                            | 274.3                            | 270.1                            |
| Harmonic Zero-Point $\text{cm}^{-1}$ | 1132.1                           | 937.95                           | 1130.5                           | 936.3                            |
| $\nu_1 \text{ C-H cm}^{-1}$          | 3101.9                           | 2351.9                           | 3102.0                           | 2352.1                           |
| $\nu_2 \text{ C-C cm}^{-1}$          | 1661.8                           | 1611.1                           | 1661.8                           | 1611.0                           |
| $\nu_3 \text{ C-C-H cm}^{-1}$        | 652.8                            | 512.5                            | 652.3                            | 516.7                            |
| $\nu_4 \text{ Torsion cm}^{-1}$      | 856.0                            | 579.8                            | 856.3                            | 579.9                            |
| $\nu_5 \text{ Ne-C-C cm}^{-1}$       | 314.1                            | 269.3                            | 308.7                            | 275.1                            |
| $\nu_6 \text{ Ne-C cm}^{-1}$         | 94.2                             | 152.0                            | 94.7                             | 141.4                            |
| Zero-Point $\text{cm}^{-1}$          | 3387.8                           | 2789.9                           | 3383.9                           | 2785.9                           |

<sup>a</sup>The geometry utilized for the dipole moment is that computed from the center-of-mass: Ne,-1.166174,0.1308715,0.000000; C,0.372036,-0.5253712,0.000000; C,1.365269,0.2795017,0.000000; H,2.447860,0.3314011,0.000000.



Table 3.3: The ArCCH<sup>+</sup> CcCR Symmetry-Internal Force Constants (in mdyn/Å<sup>n</sup>·rad<sup>m</sup>).

|                  |            |                   |         |                   |       |                   |       |
|------------------|------------|-------------------|---------|-------------------|-------|-------------------|-------|
| F <sub>11</sub>  | 4.524 874  | F <sub>551</sub>  | -0.0674 | F <sub>4421</sub> | -0.95 | F <sub>6633</sub> | 0.38  |
| F <sub>21</sub>  | -0.003 061 | F <sub>552</sub>  | -0.8975 | F <sub>4422</sub> | 0.72  | F <sub>6644</sub> | 1.93  |
| F <sub>22</sub>  | 16.753 422 | F <sub>553</sub>  | -0.1422 | F <sub>4431</sub> | 0.10  | F <sub>6654</sub> | -1.53 |
| F <sub>31</sub>  | -0.025 245 | F <sub>661</sub>  | -0.5410 | F <sub>4432</sub> | -0.99 | F <sub>6655</sub> | 0.47  |
| F <sub>32</sub>  | -0.174 122 | F <sub>662</sub>  | -1.3785 | F <sub>4433</sub> | 0.21  | F <sub>6666</sub> | 2.20  |
| F <sub>33</sub>  | 6.117 647  | F <sub>663</sub>  | -0.0355 | F <sub>4444</sub> | 1.90  | F <sub>7611</sub> | -2.10 |
| F <sub>44</sub>  | 0.082 193  | F <sub>761</sub>  | -0.0765 | F <sub>5411</sub> | -1.71 | F <sub>7621</sub> | 0.90  |
| F <sub>54</sub>  | -0.125 213 | F <sub>762</sub>  | -0.3572 | F <sub>5421</sub> | 0.87  | F <sub>7622</sub> | 0.03  |
| F <sub>55</sub>  | 0.300 960  | F <sub>763</sub>  | 0.0158  | F <sub>5422</sub> | 0.35  | F <sub>7631</sub> | -1.74 |
| F <sub>66</sub>  | 0.082 181  | F <sub>771</sub>  | -0.0674 | F <sub>5431</sub> | -1.72 | F <sub>7632</sub> | 0.71  |
| F <sub>76</sub>  | -0.125 199 | F <sub>772</sub>  | -0.8976 | F <sub>5432</sub> | 0.66  | F <sub>7633</sub> | 0.30  |
| F <sub>77</sub>  | 0.300 953  | F <sub>773</sub>  | -0.1423 | F <sub>5433</sub> | 0.64  | F <sub>7644</sub> | 1.71  |
| F <sub>111</sub> | -25.7391   | F <sub>1111</sub> | 122.19  | F <sub>5444</sub> | 0.47  | F <sub>7654</sub> | -1.08 |
| F <sub>211</sub> | -0.7150    | F <sub>2111</sub> | 2.73    | F <sub>5511</sub> | -0.48 | F <sub>7655</sub> | -0.02 |
| F <sub>221</sub> | -0.6704    | F <sub>2211</sub> | 0.02    | F <sub>5521</sub> | -2.77 | F <sub>7666</sub> | 0.08  |
| F <sub>222</sub> | -99.5102   | F <sub>2221</sub> | -0.93   | F <sub>5522</sub> | 0.69  | F <sub>7711</sub> | -0.32 |
| F <sub>311</sub> | -0.0526    | F <sub>2222</sub> | 484.62  | F <sub>5531</sub> | -0.02 | F <sub>7721</sub> | -2.81 |
| F <sub>321</sub> | -0.0808    | F <sub>3111</sub> | -0.79   | F <sub>5532</sub> | 0.40  | F <sub>7722</sub> | 0.83  |
| F <sub>322</sub> | -0.0645    | F <sub>3211</sub> | -1.34   | F <sub>5533</sub> | -0.64 | F <sub>7731</sub> | -0.01 |
| F <sub>331</sub> | -0.0154    | F <sub>3221</sub> | -1.14   | F <sub>5544</sub> | -0.11 | F <sub>7732</sub> | 0.42  |
| F <sub>332</sub> | 0.2425     | F <sub>3222</sub> | -0.08   | F <sub>5554</sub> | -0.65 | F <sub>7733</sub> | -0.47 |
| F <sub>333</sub> | -34.6553   | F <sub>3311</sub> | -0.23   | F <sub>5555</sub> | -0.52 | F <sub>7744</sub> | 0.41  |
| F <sub>441</sub> | -0.5410    | F <sub>3321</sub> | -0.80   | F <sub>6611</sub> | 2.20  | F <sub>7754</sub> | 0.52  |
| F <sub>442</sub> | -1.3783    | F <sub>3322</sub> | -1.09   | F <sub>6621</sub> | -0.95 | F <sub>7755</sub> | 0.08  |
| F <sub>443</sub> | -0.0355    | F <sub>3331</sub> | -1.17   | F <sub>6622</sub> | 0.91  | F <sub>7766</sub> | 0.18  |
| F <sub>541</sub> | -0.0766    | F <sub>3332</sub> | -1.65   | F <sub>6631</sub> | 0.08  | F <sub>7776</sub> | -1.05 |
| F <sub>542</sub> | -0.3577    | F <sub>3333</sub> | 177.06  | F <sub>6632</sub> | -0.96 | F <sub>7777</sub> | -0.43 |
| F <sub>543</sub> | 0.0158     | F <sub>4411</sub> | 1.97    |                   |       |                   |       |

Table 3.4: The CcCR QFF ArCCH<sup>+</sup> Equilibrium and Zero-Point ( $R_\alpha$ ) Structures, Spectroscopic Constants, Vibrational Frequencies, and Harmonic Intensities (in parenthesis in km/mol) for the <sup>36</sup>Ar, <sup>38</sup>Ar, <sup>40</sup>Ar, H, and D-Including Isotopologues.

|   | <sup>36</sup> ArCCH <sup>+</sup> | <sup>36</sup> ArCCD <sup>+</sup> | <sup>38</sup> ArCCH <sup>+</sup> | <sup>38</sup> ArCCD <sup>+</sup> | <sup>40</sup> ArCCH <sup>+</sup> | <sup>40</sup> ArCCD <sup>+</sup> |
|---|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| $r_e(\text{Ar-C}) \text{ \AA}$                        | 1.648 048                        | –                                | –                                | –                                | –                                | –                                |
| $r_e(\text{C-C}) \text{ \AA}$                         | 1.194 963                        | –                                | –                                | –                                | –                                | –                                |
| $r_e(\text{C-H}) \text{ \AA}$                         | 1.069 704                        | –                                | –                                | –                                | –                                | –                                |
| $B_e \text{ cm}^{-1}$                                 | 0.18698                          | 0.17053                          | 0.18345                          | 0.16728                          | 0.18024                          | 0.16433                          |
| $D_e \text{ kHz}$                                     | 1.53                             | 1.20                             | 1.48                             | 1.16                             | 1.43                             | 1.12                             |
| $H_e \text{ mHz}$                                     | -0.41                            | -0.28                            | -0.39                            | -0.27                            | -0.37                            | -0.26                            |
| $r_0(\text{Ar-C}) \text{ \AA}$                        | 1.651 099                        | 1.646 892                        | 1.651 121                        | 1.646 959                        | 1.651 140                        | 1.647 020                        |
| $r_0(\text{C-C}) \text{ \AA}$                         | 1.186 769                        | 1.187 400                        | 1.187 702                        | 1.187 338                        | 1.186 642                        | 1.187 281                        |
| $r_0(\text{C-H}) \text{ \AA}$                         | 1.063 584                        | 1.059 027                        | 1.063 556                        | 1.058 998                        | 1.063 529                        | 1.058 971                        |
| $B_0 \text{ cm}^{-1}$                                 | 0.187 344                        | 0.170 513                        | 0.183 810                        | 0.167 265                        | 0.179 770                        | 0.164 317                        |
| $B_1 \text{ cm}^{-1}$                                 | 0.186 929                        | 0.170 394                        | 0.183 405                        | 0.167 150                        | 0.180 575                        | 0.164 205                        |
| $B_2 \text{ cm}^{-1}$                                 | 0.186 391                        | 0.170 477                        | 0.182 877                        | 0.167 229                        | 0.182 044                        | 0.164 282                        |
| $B_3 \text{ cm}^{-1}$                                 | 0.187 326                        | 0.170 551                        | 0.183 790                        | 0.167 301                        | 0.180 575                        | 0.164 352                        |
| $B_4 \text{ cm}^{-1}$                                 | 0.186 468                        | 0.170 613                        | 0.182 961                        | 0.167 361                        | 0.179 804                        | 0.164 409                        |
| $B_5 \text{ cm}^{-1}$                                 | 0.188 848                        | 0.170 488                        | 0.185 284                        | 0.167 242                        | 0.182 044                        | 0.164 296                        |
| $\mu \text{ D}^a$                                     |                                  |                                  |                                  |                                  | 0.46                             |                                  |
| $\omega_1 \text{ C-H cm}^{-1}$                        | 3399.9 (24)                      | 2670.6                           | 3399.9                           | 2670.6                           | 3399.9                           | 2670.5                           |
| $\omega_2 \text{ C-C cm}^{-1}$                        | 2184.3 (16)                      | 2016.8                           | 2184.1                           | 2016.5                           | 2183.9                           | 2016.3                           |
| $\omega_3 \text{ Ar-C cm}^{-1}$                       | 692.9 (6)                        | 559.0                            | 685.5                            | 559.0                            | 678.7                            | 558.9                            |
| $\omega_4 \text{ C-C-H Bend } (\pi) \text{ cm}^{-1}$  | 730.2 (6)                        | 559.0                            | 730.2                            | 559.0                            | 730.2                            | 558.9                            |
| $\omega_5 \text{ Ar-C-C Bend } (\pi) \text{ cm}^{-1}$ | 107.8 (12)                       | 105.1                            | 107.6                            | 105.0                            | 107.5                            | 104.8                            |
| Harmonic Zero-Point $\text{cm}^{-1}$                  | 3976.6                           | 3348.5                           | 3972.6                           | 3344.5                           | 3968.9                           | 3340.8                           |
| $\nu_1 \text{ C-H } (\sigma) \text{ cm}^{-1}$         | 3266.7                           | 2575.9                           | 3266.7                           | 2575.9                           | 3266.7                           | 2575.9                           |
| $\nu_2 \text{ C-C } (\sigma) \text{ cm}^{-1}$         | 2134.2                           | 1975.0                           | 2133.9                           | 1974.9                           | 2133.8                           | 1974.7                           |
| $\nu_3 \text{ Ar-C } (\sigma) \text{ cm}^{-1}$        | 675.8                            | 506.9                            | 668.8                            | 506.8                            | 662.4                            | 506.6                            |
| $\nu_4 \text{ C-C-H Bend } (\pi) \text{ cm}^{-1}$     | 661.4                            | 500.2                            | 661.3                            | 500.1                            | 661.2                            | 500.0                            |
| $\nu_5 \text{ Ar-C-C Bend } (\pi) \text{ cm}^{-1}$    | 120.2                            | 148.4                            | 120.0                            | 147.7                            | 119.8                            | 147.0                            |
| Zero-Point $\text{cm}^{-1}$                           | 3910.5                           | 3237.0                           | 3906.5                           | 3236.4                           | 3902.8                           | 3235.8                           |

<sup>a</sup>The geometry utilized for the dipole moment is that computed from the center-of-mass: Ar,0.00000,0.00000,-0.890194; C,0.00000,0.00000,0.757855; H,0.00000,0.00000,3.022523.

Table 3.5: The ArCN<sup>+</sup> CcCR Symmetry-Internal Force Constants (in mdyne/ $\text{\AA}^n \cdot \text{rad}^m$ ).

|                  |            |                   |         |                   |      |
|------------------|------------|-------------------|---------|-------------------|------|
| F <sub>11</sub>  | 3.559 545  | F <sub>331</sub>  | -0.2564 | F <sub>3311</sub> | 1.11 |
| F <sub>21</sub>  | -0.511 371 | F <sub>332</sub>  | -0.9059 | F <sub>3321</sub> | 0.68 |
| F <sub>22</sub>  | 17.262 909 | F <sub>441</sub>  | -0.2564 | F <sub>3322</sub> | 0.50 |
| F <sub>33</sub>  | 0.125 609  | F <sub>442</sub>  | -0.9059 | F <sub>3333</sub> | 0.69 |
| F <sub>44</sub>  | 0.125 609  | F <sub>1111</sub> | 107.56  | F <sub>3344</sub> | 0.39 |
| F <sub>111</sub> | -23.7124   | F <sub>2111</sub> | 7.39    | F <sub>4411</sub> | 1.11 |
| F <sub>211</sub> | -1.3462    | F <sub>2211</sub> | 4.63    | F <sub>4421</sub> | 0.68 |
| F <sub>221</sub> | 0.1335     | F <sub>2221</sub> | 1.92    | F <sub>4422</sub> | 0.50 |
| F <sub>222</sub> | -118.4939  | F <sub>2222</sub> | 615.56  | F <sub>4444</sub> | 0.69 |

Table 3.6: The CcCR QFF ArCN<sup>+</sup> Equilibrium and Zero-Point ( $R_\alpha$ ) Structures, Spectroscopic Constants, Vibrational Frequencies, and Harmonic Intensities (in parenthesis in km/mol) for the <sup>36</sup>Ar, <sup>38</sup>Ar, <sup>40</sup>Ar

|                                      | <sup>36</sup> ArCN <sup>+</sup> | <sup>38</sup> ArCN <sup>+</sup> | <sup>40</sup> ArCN <sup>+</sup> |
|--------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| $r_e(\text{Ar-C}) \text{ \AA}$       | 1.434 944                       | –                               | –                               |
| $r_e(\text{C-N}) \text{ \AA}$        | 1.110 007                       | –                               | –                               |
| $B_e \text{ cm}^{-1}$                | 0.23972                         | 0.23502                         | 0.23077                         |
| $D_e \text{ kHz}$                    | 4.290                           | 4.143                           | 4.007                           |
| $H_e \text{ mHz}$                    | -3.363                          | -3.185                          | -3.029                          |
| $r_0(\text{Ar-C}) \text{ \AA}$       | 1.440 038                       | 1.440 008                       | 1.439 981                       |
| $r_0(\text{C-N}) \text{ \AA}$        | 1.107 168                       | 1.107 132                       | 1.107 099                       |
| $B_0 \text{ cm}^{-1}$                | 0.239 227                       | 0.234 545                       | 0.230 310                       |
| $B_1 \text{ cm}^{-1}$                | 0.237 374                       | 0.232 731                       | 0.228 532                       |
| $B_2 \text{ cm}^{-1}$                | 0.237 447                       | 0.232 814                       | 0.228 625                       |
| $B_3 \text{ cm}^{-1}$                | 0.240 550                       | 0.235 841                       | 0.231 582                       |
| $\mu \text{ D}^a$                    |                                 |                                 | 3.65                            |
| $\omega_1 \text{ C-N cm}^{-1}$       | 2233.3 (33)                     | 2233.1                          | 2232.9                          |
| $\omega_2 \text{ Ar-C cm}^{-1}$      | 602.0 (8)                       | 595.3                           | 589.3                           |
| $\omega_3 \text{ Bend cm}^{-1}$      | 246.2 (5)                       | 245.8                           | 245.6                           |
| Harmonic Zero-Point $\text{cm}^{-1}$ | 1663.9                          | 1660.0                          | 1656.7                          |
| $\nu_1 \text{ C-N cm}^{-1}$          | 2189.6                          | 2189.4                          | 2189.3                          |
| $\nu_2 \text{ Ar-C cm}^{-1}$         | 602.6                           | 596.9                           | 591.8                           |
| $\nu_3 \text{ Bend cm}^{-1}$         | 245.8                           | 245.5                           | 245.3                           |
| Zero-Point $\text{cm}^{-1}$          | 1654.7                          | 1651.0                          | 1647.7                          |

<sup>a</sup>The geometry utilized for the dipole moment is that computed from the center-of-mass: Ar,0.00000,0.00000,-0.801275; C,0.00000,0.00000,0.633667; N,0.00000,0.00000,1.743677.

# Chapter 4

## Conclusions

From the beginning of time, humans have gazed out at the stars and wondered at what they were looking, from where they came, and tried to make sense of it all. As science and time progressed, astronomers, physicists, and chemists have studied the stars to learn the chemical and physical makeup of the universe. In the earliest days of scientific exploration, most astronomers believed that OH, CN, CH, and  $\text{CH}^+$  were the only molecular fragments that existed in space because gas densities were so low in nebulae, and UV radiation was so intense that any normal molecules surviving would be too scarce to be detectable. After the discovery of complex molecules in space, hundreds of new molecules have been theorized, and many have been detected.

The discovery of new molecules in the ISM is a continuing process. The results of this project provides the rovibrational spectroscopic details of four novel, noble gas cations, in hopes of future astrophysical detection.

Computational quantum chemical methods are an excellent means of classifying spectro-

scopic characteristics of these undiscovered molecules. Although a new and rather contradictory field, noble gas chemistry is on the cusp of becoming a more understood subfield of chemistry due to the advances and usability of quantum chemistry. Furthermore, the discovery of the naturally occurring noble gas compound,  $\text{ArH}^+$ , sparked a major interest in astrochemistry. Because of this, the methods used in this work focus on unidentifiable noble gas molecules both in the ISM or experimentally.

Both argon and neon were explored in this study in hopes of finding stable, covalently bound cations. Based on current, similar experimental data as well as using basic chemical knowledge of dipole moments, bond lengths and strengths, and the corresponding potential energy surface, the possibility of  $\text{NeCCH}^+$ ,  $\text{ArNH}^+$ ,  $\text{ArCCH}^+$ , and  $\text{ArCN}^+$  was predicted. Of the four novel compounds,  $\text{ArCN}^+$  was found to be the most likely candidate for ISM detection because it is rotationally bright with a detectable fundamental frequency for the C – N stretch. It is also likely that this cation can form from HCN, a highly abundant molecule in space. As a result of this study, the chemical inventory of natural noble gas molecules may be greater than previously believed and the archive of spectroscopic data for theoretical molecules is enlarged, making future detection and understanding of these compounds possible.

# Acknowledgments

My time here at Georgia Southern University has been nothing short of opportunistic in regards of undergraduate research. I would like to thank the University Honors program for the funding and resources given to me in order to not only carry out this research, but to have been able to present this work all over the country at various research conferences and expositions. Specifically, I would like to thank the Office of the Vice President of Research and Economic Development as well as the Student Government Association for providing me with external travel funds to carry out these collaborative excursions. I would also like to give much of my appreciation to the Department of Chemistry and Biochemistry faculty for continuously encouraging me to work hard and strive for excellence. It is through the inspiration of these individuals that I have become the woman in STEM that I am today, and that I have the goals and ambition to continue this research throughout a graduate education. Lastly, and most importantly, I would like to thank my research advisor and mentor Dr. Ryan Fortenberry for his guidance throughout my undergraduate research experience, it truly was an honor to work alongside him. Dr. Fortenberry provided me with the opportunity to gain experience, knowledge, and a confidence in my work that has further inspired me to progress

on to the PhD level in chemistry. Thank you to everyone who supported me and encouraged me along the way, I would not be the person I am today without you all.

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