The Interstellar Formation and Spectra of the Noble Gas, Proton-Bound HeHHe\(^+\), HeHNe\(^+\), & HeHAr\(^+\) Complexes

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ABSTRACT

The sheer interstellar abundance of helium makes any bound molecules or complexes containing it of potential interest for astrophysical observation. This work utilizes high-level and trusted quantum chemical techniques to predict the rotational, vibrational, and rovibrational traits of HeHHe\(^+\), HeHNe\(^+\), and HeHAr\(^+\). The first two are shown to be strongly bound, while HeHAr\(^+\) is shown to be more of a van der Waals complex of argonium with a helium atom. In any case, the formation of HeHHe\(^+\) through reactions of HeH\(^+\) with HeH\(^3+\) is exothermic. HeHHe\(^+\) exhibits the quintessentially bright proton-shuttle motion present in all proton-bound complexes in the 7.4 micron range making it a possible target for telescopic observation at the mid-IR/far-IR crossover point and a possible tracer for the as-of-yet unobserved helium hydride cation. Furthermore, a similar mode in HeHNe\(^+\) can be observed to the blue of this close to 6.9 microns. The brightest mode of HeHAr\(^+\) is dimmed due the reduced interaction of the helium atom with the central proton, but this fundamental frequency can be found slightly to the red of the Ar–H stretch in the astrophysically detected argonium cation.

1 INTRODUCTION

Helium and hydrogen make up nearly all of the observable matter in the universe leaving chemists to squabble over the remaining scraps. These scraps are what compose the planets, our bodies, and most other things engineered by human beings. Nearly all other processes depend upon atoms much more interesting than the first two on the periodic table. Even so, helium and hydrogen can engage in chemistry with one another almost certainly combining to make HeH\(^+\) (Hogness & Lunn 1925). This cation should be produced in detectable amounts if for no other reason than the sheer abundance of the constituents in the interstellar medium (ISM) (Roberge & Dalgarno 1982). However, such an interstellar observation of this diatomic cation has yet to be reported in the literature. It was the analogous ArH\(^+\) that has been observed toward various astronomical sources (Barlow et al. 2013; Schilke et al. 2014; Roueff, Alekseev & Bourlot 2014; Neufeld & Wolfire 2016) making the argonium and not helium (helium hydride) cation the first noble gas molecule detected in nature. The smaller and more abundant helium and even neon hydride cations have not been observed, yet.

The chemistry of helium is likely the least voluminous for any of the elements between hydrogen and iron even in controlled laboratory conditions. However, helium will make complexes and form some bonds. Helium cationic clusters have been predicted, He\(_n^+\) clusters have been synthesized, dication complexes observed, and even hydrogen-like replacement structures analyzed (Frenking & Cremer 1990; Roth, Dopfer & Maier 2001; Grandinetti 2004; Savic et al. 2014; Zicler et al. 2014). In all cases, the issue is that the helium cation binding in any of these complexes is relatively weak making long-lifetime molecules and high enough abundances for observable interstellar spectra of such chemical combinations quite unlikely.

Like unto helium, neon is reluctant to form bonds. There is little surprise here due to the high ionization potentials and relatively poor polarizabilities in these smallest of noble gas compounds (Taylor et al. 1989; Rice et al. 1991; Pauzat & Ellinger 2003, 2007; Pauzat et al. 2009, 2013). Neonium (NeH\(^+\)) has been well-characterized (Ram, Bernath & Braul 1983; Matsushima et al. 1998; Gamallo, Huarte-Larranaga & González 2013; Koner et al. 2014; Coxon & Hajigeorgiou 2016), but it has yet to be conclusively observed in any astrophysical environment. While the reaction of Ar\(^+\) with ubiquitous hydrogen gas leads to ArH\(^+\) and hydrogen atoms in the ISM, the analogous reaction with neon will initially lead to neutral neon atoms
and ionized hydrogen gas \cite{TheisMorganFortenberry2013}. More complicated neon structures beyond NeH\(^+\) have been proposed and even synthesized, but few have bond strengths in the covalent range \cite{FrenkingCremer1996, Grandinetti2011}. Notable exceptions include NeOH\(^+\) and NeCCH\(^+\) recently characterized theoretically at high level \cite{TheisFortenberry2016, NovakFortenberry2017}, but these are several factors less stable than their argon counterparts. With helium and neon being so very abundant in the ISM, neon even more so than nitrogen \cite{SavageSembach1996}, molecules containing these atoms may still be awaiting detection.

These molecules in waiting could be proton-bound complexes. These structures involve a mostly bare proton situated between two other atoms or molecules where the mutual attraction of the ligands to the proton creates fairly strong interactions. These structures are of additional significance to astrochemistry and astrophysical observation due to their proton “rattle” or “shuttle” motion. In such vibrational modes, basically only the proton moves. Hence, little of the mass but nearly all of the charge is moving creating an immense change in dipole moment. As a result, such vibrational transitions are incredibly strong absorbers/emitters meaning that small column densities of materials are required to create observable spectral features. OCHCO\(^+\), NNHNN\(^+\), and the heteromolecular combinations have been analyzed recently showing that these bright vibrational modes can be found from the near- to mid- and even far-IR wavelengths \cite{TerrillNesbitt2014, Cotton2012, Fortenberry2013, Yu2013, FortenberryLeeFrancisco2016, BegumSubramanian2016} making them tantalizing targets for the epoch of growth in IR telescopic power in which we are currently in the midst.

Proton-bound complexes of noble gases have been known for some time. In fact, the simplest, HeHHe\(^+\), was noted for its relatively strong bonds nearly 35 years ago \cite{Dykstra1983}. However, a complete and reliable set of rovibrational spectroscopic data have yet to be produced for this simple system while other insights into its nature have been explored theoretically \cite{BaccarelliGianturcoSchneider1997, PandaSathyaprakash2003, Bartl2013}. Other data for related noble gas molecules have been produced including those with helium \cite{FridgenParrin1995, LundellPetterssonRasanen1991, KonerVatsPanda2012, Koner2014, BorocciGiordaniGrandinetti2015, Grabowski2016, Koner2016}, but full spectral characterization is still lacking for most of these structures.

Very recently, the vibrational spectra of ArH\(^+\) complexes were characterized experimentally including ArHAr\(^+\) \cite{McDonaldII2016} with its bright proton motion at 10.11 microns with dissociation not occurring until 1.74 microns (or 0.711 eV). Simultaneously, theoretical work on this complex produced a very similar dissociation energy (0.719 eV) and comparable vibrational frequencies \cite{Fortenberry2016}. The NeHNe\(^+\) and NeHAr\(^+\) complexes were also analyzed. \cite{Fortenberry2017} showed that the NeHNe\(^+\) complex is actually more strongly bound than ArHAr\(^+\) indicating that, for once, the neon bonds are actually stronger than the more polarizable argon bonds in a cation. The NeHNe\(^+\) dissociation is higher at 0.867 eV, but interstellar synthesis of NeHNe\(^+\) is most likely in the gas phase from reactions of NeH\(^+\) with NeH\(^+\). Again, the former has yet to be observed, and the latter is only weakly bound \cite{TheisFortenberry2015}. ArHAr\(^+\) is also favorably created from ArH\(^+\) and ArH\(^+\) where the former is, again, known in the ISM and the latter is a viable interstellar candidate \cite{PauzatEllinger2005, Pauzat2013, TheisFortenberry2015}. Additionally, ArHAr\(^+\) has a much brighter and longer wavelength proton shuttle motion making it more likely to be observed in the ISM \cite{Fortenberry2017}.

Consequently, the question lingers as to whether proton-bound complexes involving the abundant helium atom are viable interstellar detection candidates. Furthermore, combinations of noble gas atoms in such complexes with helium are known to be fairly stable \cite{KonerVatsPanda2012, Grabowski2016} and those with other noble gas atoms have been classified at high-level with good comparison to experiment \cite{Fortenberry2017}. As a result, this work will employ the same methodology as that utilized previously on proton-bound complexes \cite{FortenberryLeeFrancisco2016, Fortenberry2017} where comparison in other molecules to gas phase experimental results has provided exceptional accuracy on the order of 0.01 micron accuracy for vibrational features and 30 MHz for rotational constants \cite{HuangLee2008, HuangLee2009, HuangTaylorLee2011, ZhaoDoneyLinnartz2014, Fortenberry2014, FortenberryLeeMuller2014, KitchensFortenberry2016, FortenberryRoueffLee2016}. These data will be useful for the spectral characterization of such molecules in the ISM with current and upcoming ground- and space-based telescopes such as the upcoming James Webb Space Telescope. Potentially expanding the noble gas molecular budget of the ISM will grow our understanding of interstellar chemical bonding and provide novel chemical pathways for these so-called “inert” and noble gases.

## 2 COMPUTATIONAL DETAILS

The \textit{ab initio}, quantum chemical computational methodology employed here has been detailed elsewhere \cite{HuangLee2008, HuangLee2009, HuangTaylorLee2011, Fortenberry2011a, Fortenberry2011b} and specifically for proton-bound complexes of noble gas cation dimers by \cite{Fortenberry2017}. For completeness, coupled cluster theory \cite{CrawfordSchaeferIII2000, ShavittBartlett2003} at the singles, doubles, and perturbative triples [CCSD(T)] level \cite{Raghavachari1989} is employed in all computations within the PS4 quantum chemistry package \cite{Turney2012}. The geometries of these linear complexes are treated at the aug-cc-pV5Z level \cite{Dunning1989} and corrected for core correlation with the Martin-Taylor (MT) core correlation basis set \cite{MartinTaylor1994}. From these geometries, 0.005 Å displacements of the bond lengths and 0.005 radian displacements of the bond angle within the symmetry-internal coordinates defined below are computed to produce a fourth-order Taylor series.
expansion of the internuclear Hamiltonian called a quartic force field (QFF). The coordinates for HeHHe⁺ are defined as:

\[ S_1(\Sigma_u) = \frac{1}{\sqrt{2}}[(\text{He}_1 - H) + (\text{He}_2 - H)] \]  
\[ S_2(\Sigma_u) = \frac{1}{\sqrt{2}}[(\text{He}_1 - H) - (\text{He}_2 - H)] \]  
\[ S_3(\Pi_{u+}) = \sqrt{2} (\text{He} - H - \text{He} - y) \]  
\[ S_4(\Pi_{u-}) = \sqrt{2} (\text{He} - H - \text{He} - x). \]  

Those for the HeHNe⁺ and HeHAr⁺ molecules are produced from (with Ng representing either Ne or Ar):

\[ S_1(\Sigma^+) = \text{He} - H \]  
\[ S_2(\Sigma^+) = \text{Ng} - H \]  
\[ S_3(\Pi_{u+}) = \sqrt{2} (\text{He} - H - \text{Ng} - y) \]  
\[ S_4(\Pi_{u-}) = \sqrt{2} (\text{He} - H - \text{Ng} - x). \]  

As a consequence of the differences in geometrical connectivities and atomic symmetries, HeHHe⁺ requires the use of 57 total points, while HeHNe⁺ and HeHAr⁺ require 69 to define the QFF.

At each displacement point, CCSD(T)/aug-cc-pVTZ, -pVQZ, and -pV5Z energies are extrapolated to the complete basis set (CBS) limit via a three-point formula (Martin & Lee 1998) and augmented for inclusion of core correlation from the MT basis sets as well as scalar relativity (Douglas & Kroll 1974). This produces the CcCR QFF for “CBS,” “core correlation,” and “relativity.” The relativistic computations are made with the MOLPRO 2010.1 quantum chemistry package (Werner et al. 2010). A least-squares fitting of the points produces the equilibrium geometry, and refitting the points produces zero gradients and the subsequent force constants. The fitting is tight with a sum of squared residuals on the order of \(10^{-17}\) a.u.\(^2\) for the Ne and Ar complexes and \(10^{-18}\) a.u.\(^2\) for HeHHe⁺. The force constants are transformed from the symmetry-internal coordinates into more generic Cartesian coordinates with the INTDER program (Allen & coworkers 2004). Then, second-order vibrational perturbation theory (VPT2) and rotational perturbation theory are employed to provide the frequencies and spectroscopic constants (Mills 1972; Watson 1973; Papousek & Alix 1982) within the SPECTRO program (Gaw et al. 1991). Double-harmonic intensities are computed with the Gaussian09 program and the MP2/6-31+G* level of theory (Møller & Plesset 1934; Hehre, Ditchfield & Pople 1972; Frisch et al. 2009) which has been shown to provide notable agreement for the vibrational intensities of NNHHN⁺ with a more advanced and time-consuming semi-global dipole moment surface (Yu et al. 2013).

3 RESULTS AND DISCUSSION

The interstellar presence for any of these proton-bound complexes can be established by observing the necessary rotational or vibrational transitions. However, the possible formation of these species must be established in order for such searches to be deemed even plausible before observation can begin. In light of such, high-level computations at

Table 1. CCSD(T)/aug-cc-pV5Z Formation/Destruction Energetics.

| Reactions                        | kcal/mol | eV   |
|----------------------------------|----------|------|
| He + HeH⁺ → HeHHe⁺               | -13.2    | -0.57|
| 2He + H⁺ → HeHHe⁺                | -60.3    | -2.62|
| 2HeH⁺ → HeHHe⁺ + H⁺              | 33.8     | 1.47 |
| HeH⁺ + HeH⁺ → HeHHe⁺ + H⁺        | -11.9    | -0.52|
| He + H₃⁺ → HeH⁺                  | -1.3     | -0.06|
| Ne + HeH⁺ → HeHNe⁺               | -11.9    | -0.52|
| NeH⁺ + NeH⁺ → HeHNe⁺ + H⁺        | -21.9    | -0.95|
| HeH⁺ + NeH⁺ → HeHNe⁺ + H⁺        | 35.2     | 1.52 |
| NeH⁺ + HeH⁺ → HeHNe⁺ + H⁺        | -10.6    | -0.46|
| HeH⁺ + NeH⁺ → HeHNe⁺ + H⁺        | -15.4    | -0.67|
| Ne + H₃⁺ → HeH⁺                  | -6.5     | -0.28|
| He + ArH⁺ → HeAr⁺                | -2.1     | -0.09|
| Ar + HeH⁺ → HeAr⁺                | -49.0    | -2.13|
| HeH⁺ + ArH⁺ → HeAr⁺ + H⁺         | 45.0     | 1.95 |
| ArH⁺ + HeH⁺ → HeAr⁺ + H⁺         | -0.8     | -0.03|
| HeH⁺ + ArH⁺ → HeAr⁺ + H⁺         | -40.0    | -1.73|
| Ar + H₃⁺ → ArH⁺                  | -9.1     | -0.39|

| F₁₁ 3.061 326 | F₂₂ 0.632 926 | F₃₃ 0.101 838 |
| F₁₁ 85.54 | F₂₂ 45.26 211 | F₃₃ 1.43 343 |
| F₂₂ 45.0 1.95 | F₃₃ 1.43 344 |

\(\text{a}1 \text{ mdyn} = 10^{-8} \text{ N}; n \text{ and } m \text{ are exponents corresponding to the number of units from the type of modes present in the specific force constant.}\)
NeCCH$^+$ is -0.93 eV, and NeHNe$^+$ -0.87 eV. Helium reacting with NeH$_2$ favors creation of HeHNe$^+$ and the ubiquitous H$_3^+$ with -0.67 eV. Reacting neon with He$_3^+$ is also exothermic but less favorable at -0.46 eV.

HeHAr$^+$ is much more dichotomous. The helium is not well-bound (-0.09 eV), but the argon atom very much is (-2.13 eV). This trend is carried through the other formation and destruction reactions listed in Table 3. However, ArH$_3^+$ has the strongest Ng$^-$H bond of all the noble gas-hydride cations and is hypothesized to exist in the ISM (Theis & Fortenberry 2013; Pauzat et al. 2013). Reacting this specie with the almost guaranteed interstellar HeH$^+$ produces HeHAr$^+$ and -1.73 eV of energy.

Hence, HeHAr$^+$ is the most energetically-favored product, but interstellar abundances still point to HeHHe$^+$ as the most likely to be observed. In any case, only spectroscopic observation in the ISM can determine the presence for any of these compounds. The following data for each complex should be able to assist in the laboratory or even interstellar observation of these noble gas, molecular cations.

### 3.1 HeHHe$^+$

The force constants, those needed to construct the QFF potential within the Hamiltonian, for the proton-bound, helium cation dimer are given in Table 2. The harmonic, diagonal force constants can be viewed as proportional to bond strength. Breaking these symmetry-internal coordinates (from Eqs. 1-4) down into simple-internal coordinates, i.e. He$^-$H coordinates, produces a 2.165 mdyne/Å$^2$ force constant for the He$^-$H stretch. This is nearly identical to the 2.158 mdyne/Å$^2$ Ne$^-$H force constant in NeHNe$^+$ and greater than that in ArHAr$^+$ (Fortenberry 2017). This is greater even than the force constant in NeOH$^+$ (Theis & Fortenberry 2016). Consequently, the notable bond energy discussed previously for the removal of the helium atom from HeHHe$^+$ is corroborated by the internal molecular structure, as well.

Further corroboration comes from the He$^-$H bond length given in Table 3. This value is 0.946 Å, which is 0.17 Å longer than the same bond in the helium hydride cation. However, the He$^-$H bond length is still significantly less than bond lengths in helium van der Waals complexes which often approach 3 Å. The rotational constants are also given even though HeHHe$^+$ possesses no permanent dipole moment. The distortion constants are fairly large since the molecule has a fairly small mass and a labile proton. On the other hand, the vibrationally-excited rotational constants ($B_e$), notably $B_3$ and $B_2$, can be utilized for rovibrational spectral modeling.

Furthermore, the vibrational intensities indicate that the proton-shuttle motion will be have a large transition moment/be a strong absorber or emitter as would be expected for such a complex. The double-harmonic 2661 km/mol intensity for $\omega_1$ is nearly the same as NeHNe$^+$ and roughly half that of ArHAr$^+$ which are all two orders of magnitude greater than most vibrational intensities. The anharmonic shuttle motion, $\nu_1$, lies at 1345.2 cm$^{-1}$ or 7.43 microns at the red end of the mid-IR. Deuteration drops this value into the far-IR at 1030.8 cm$^{-1}$ or 9.70 microns. Inclusion of the lighter $^3$He isotope blueshifts the frequencies slightly for each inclusion. The $\nu_2$ bending mode also has a notable intensity and is actually quite bright relative to more traditional vibrational modes. The anharmonic frequency for the bend (or perpendicular proton motion) is 884.9 cm$^{-1}$ or 11.30 microns. The two-quanta combination bands and overtones are also given in Table 3. Those modes containing $\nu_2$ will also be bright as has been shown for ArHAr$^+$ (McDonald II et al. 2014).

### 3.2 HeHNe$^+$

The HeHNe$^+$ force constants are given in Table 4. Immediately, the He$^-$F$_{11}$ force constant shows weakening in this bond upon inclusion of the neon atom. However, the F$_{22}$ Ne$^-$H force constant is quite close to that in NeHNe$^+$ and actually is even greater by a small margin corroborating the energetic data from Table 4. The He$^-$H bond length consequently grows to 0.977 Å in HeHNe$^+$ relative to the helium dimer, and the Ne$^-$H bond length is small at 1.124 Å, as shown in Table 3. This is shorter than the 1.156 Å Ne$^-$H bond length in NeHNe$^+$ (Fortenberry 2017).

HeHNe$^+$ is rotationally active and has a large dipole moment of 3.10 D computed with the center-of-mass at the origin from CCSD/aug-cc-pVTZ. The dipole moment and subsequent rotational constants provided in Table 5 will assist in pointing closely towards the placement for the rotational lines of this linear complex. Isotopic substitution with $^3$He actually has more of an effect than D in this case since the helium atoms are on the outside of the molecule and the hydrogen is closer to the center-of-mass. Again, the vibrationally-excited rotational lines are also given in Table 5 in order to provide complete rovibrational analysis of HeHNe$^+$. The magnitudes of the distortion constants are not as large in this complex as they are in HeHHe$^+$, and scale, at least for $D_e$, with the mass of neon relative to helium.

The $\omega_1$ proton-shuttle motion in HeHNe$^+$ has a similar intensity at 2610 km/mol (Table 5) as HeHHe$^+$ and NeHNe$^+$. The $\omega_3$ stretch can be classified as both the Ne and He atoms moving away from the proton, but the lighter He atom has a larger vector leading to the qualitative description of this state as the He$^-$H stretch. This fundamental will also be visible, but the change in dipole moment is quite small creating only a 15 km/mol intensity. The bend intensity is also in the same range as the bending frequency intensities in HeHHe$^+$ and NeHNe$^+$.

Replacement with the neon atom to create HeHNe$^+$ actually blue-shifts the bright $\nu_2$ fundamental vibrational frequency to 1453.6 cm$^{-1}$ (6.88 microns) relative to the bright mode in HeHHe$^+$. The other two modes red-shift as one would expect for vibrational frequencies involving a heavier atom, neon in this case. The reason for this likely lies in the non-zero, by symmetry, F$_{22}$ mixed harmonic force constant that is forbidden in HeHHe$^+$. This additional overlap is quite large at 1.169 mdyne/Å$^2$ from Table 4 and allows the two stretches to couple further since more symmetry-allowed avenues are opened. Consequently, the total interatomic interaction increases in the proton-sharing for HeHNe$^+$. The $\nu_3$ stretch in HeHNe$^+$ is further red-shifted relative to the helium proton-bound dimer since the He$^-$H$_{11}$ force constant is computed here to be significantly reduced in the CcCR QFF VPT2 computations.

Deuteration decreases the frequencies notably, but replacement with $^3$He affects the He$^-$H$_{3}$ stretch more than it
Table 3. The CcCR Zero-Point (\(R_0\) vibrationally-averaged) and Equilibrium Structures, Rotation Constants, Vibrationally Excited-Rotation Constants, Distortion Constants, and Vibrational Frequencies and Intensities\(^a\) of \(\text{HeHe}^+\) and Its Various Isotopologues.

| \(r_0(\text{He–H})\) Å | \(0.946482\) | \(0.942908\) | \(0.94044\) | \(0.941724\) | \(0.947882\) | \(0.944400\) |
| \(r_0(\text{He–H})\) Å | \(0.924908\) | \(0.924908\) | \(0.924908\) | \(0.924908\) | \(0.924908\) | \(0.924908\) |
| \(B_0\) MHz | \(73708.7\) | \(73708.7\) | \(85611.9\) | \(85484.6\) | \(97938.9\) | \(97938.9\) |
| \(B_0\) MHz | \(70816.5\) | \(71217.8\) | \(82106.4\) | \(82598.6\) | \(81486.9\) | \(82214.5\) |
| \(B_1\) MHz | \(64474.8\) | \(64051.4\) | \(74081.0\) | \(80428.6\) | \(73398.9\) | \(79997.2\) |
| \(B_2\) MHz | \(71730.3\) | \(71673.0\) | \(83067.1\) | \(82814.7\) | \(82474.5\) | \(82322.6\) |
| \(D_0\) MHz | \(69360.2\) | \(69929.3\) | \(80220.4\) | \(78564.1\) | \(79269.6\) | \(77340.9\) |
| \(D_e\) MHz | \(1.378\) | \(1.378\) | \(1.860\) | \(1.858\) | \(2.428\) | \(2.428\) |
| \(H_e\) MHz | \(12.491\) | \(12.491\) | \(18.765\) | \(16.940\) | \(29.196\) | \(29.196\) |

Table 4. The \(\text{HeHe}^+\) CcCR Reduced Simple-Internal Force Constants (in mdyn/Å\(^n\)-rad\(^m\)).

| \(F_{11}\) | \(1.560258\) | \(F_{331}\) | \(-0.2807\) | \(F_{331}\) | \(0.58\) |
| \(F_{21}\) | \(1.169047\) | \(F_{332}\) | \(-0.2682\) | \(F_{332}\) | \(1.02\) |
| \(F_{22}\) | \(2.174774\) | \(F_{441}\) | \(-0.2807\) | \(F_{442}\) | \(0.56\) |
| \(F_{33}\) | \(0.998183\) | \(F_{442}\) | \(-0.2682\) | \(F_{443}\) | \(0.46\) |
| \(F_{44}\) | \(0.998183\) | \(F_{1111}\) | \(81.86\) | \(F_{111}\) | \(0.58\) |
| \(F_{111}\) | \(-12.8685\) | \(F_{211}\) | \(8.08\) | \(F_{211}\) | \(1.02\) |
| \(F_{211}\) | \(-3.2887\) | \(F_{221}\) | \(12.05\) | \(F_{221}\) | \(0.56\) |
| \(F_{221}\) | \(-2.9577\) | \(F_{222}\) | \(6.37\) | \(F_{222}\) | \(0.29\) |
| \(F_{222}\) | \(-16.9096\) | \(F_{222}\) | \(115.32\) | \(F_{222}\) | \(0.46\) |

\(^a\)MP2/6-31+G\(^*\) double-harmonic vibrational intensities in km/mol in parentheses. The modes where the intensities are zero by symmetry have no values.

As the previously discussed energetics indicate, the behavior of \(\text{HeHe}^+\) is quite different from the other two proton-bound complexes described in this work and also from \(\text{HeHe}^+\). The \(F_{11}\) He–H force constant in \(\text{HeHe}^+\) is quite small at 0.105 mdyn/Å\(^2\) in Table 6. The \(F_{22}\) Ar–H force constant is quite large at 4.011 mdyn/Å\(^2\), nearly the same magnitude as that in argonium itself (Theis, Morgan & Fortenberry 2015). Table 7 corroborates the strong Ar–H bonding and relatively weak He–H bonding in the bond lengths themselves. The 1.558 Å He–H bond length is much longer than any in the other two helium proton-bound complexes, and the 1.276 Å Ar–H bond length is quite close to the 1.292 Å bond length in argonium (Cueto et al. 2014).

The longer bond lengths and the heavier argon mass increase the rotational constants such that they are roughly half as large as \(B_e\) in \(\text{HeHe}^+\) which are roughly half–again as large as \(B_e\) in \(\text{HeHe}^+\). The center-of-mass-origin, CCSD/aug-cc-pVTZ dipole moment for \(\text{HeHe}^+\) is 1.48 D smaller than that in \(\text{HeHe}^+\) making any rotational intensities less for \(\text{HeHe}^+\) than in the neon complex. The more weakly bonded nature of \(\text{HeAr}^+\) is also carried out in increases of the quartic and sextic \((D_e\) and \(H_e\), respectively) distortion constants. Both of these values are higher for \(\text{HeAr}^+\) relative to \(\text{HeHe}^+\), and the -40.138 Hz \(H_e\) in \(\text{HeAr}^+\) is of greater magnitude than the same parameter in \(\text{HeHe}^+\). The bond lengths and the distortion constants, as well as the energetics, show that the \(\text{HeAr}^+\) proton-bound complex is likely a strong van der Waals interaction between the argonium cation and a helium atom and not a covalent interaction on the helium end.

The intensities of the vibrational modes also belie a shift in the physical construction of this complex. The proton-shuttle motion is relatively dim (although still absolutely bright) with an intensity of 703 km/mol. The bend and He–H stretch are also less intense, but they do not drop in value by as much of a percentage relative to \(\text{HeHe}^+\) as \(\omega_2\). Similar behavior is reported for \(\text{ArHe}^+\) (Fortenberry 2017) making these trends highly likely to be observed physically.

The \(\nu_2\) proton shuttle motion now is actually more correctly described as the Ar–H stretch since the He–H stretching component coefficient in defining the potential does the \(\nu_2\) bend with shifts of 106.1 cm\(^{-1}\) and 9.1 cm\(^{-1}\), respectively. Inclusion of \(^{22}Ne\) affects the frequencies, as well, but the shift in relative mass is less obtrusive for this atom making its isotopic shifts far less than those for D and \(^{3}\text{He}\).
Table 5. The CcCR HeHNe+ Zero-Point ($R_n$ vibrationally-averaged) and Equilibrium Structures, Rotation Constants, vibrationally Excited-Rotation Constants, Distortion Constants, Vibrational Frequencies, and Intensities (km/mol).

|                  | HeHNe+ | HeDNe+ | HeH22Ne+ | HeD22Ne+ | 3HeHNe+ | 3HeDNe+ | 3HeH22Ne+ | 3HeD22Ne+ |
|------------------|--------|--------|----------|----------|---------|---------|----------|---------|
| $r_0$(He–H) Å    | 0.977  | 0.957  | 0.972    | 0.972    | 0.975   | 0.980   | 0.979    | 0.979   |
| $r_0$(Ne–H) Å    | 1.124  | 1.119  | 1.124    | 1.124    | 1.119   | 1.123   | 1.118    | 1.118   |
| $r_e$(He–H) Å    | 0.953  | 0.953  | 0.953    | 0.953    | 0.953   | 0.953   | 0.953    | 0.953   |
| $r_e$(Ne–H) Å    | 1.113  | 1.113  | 1.113    | 1.113    | 1.113   | 1.113   | 1.113    | 1.113   |
| $B_0$, MHz       | 34112.0| 32946.6| 33525.3  | 32607.7  | 42551.9 | 40411.7 | 41940.7  | 39737.2 |
| $B_0$, MHz       | 33114.8| 32187.5| 32543.3  | 31567.2  | 41259.1 | 39464.1 | 40669.8  | 38810.7 |
| $B_1$, MHz       | 30502.4| 30432.1| 29699.5  | 29841.4  | 37988.1 | 37398.9 | 37439.1  | 36783.9 |
| $B_2$, MHz       | 33671.5| 32353.5| 33087.3  | 31911.0  | 41957.4 | 39867.9 | 41360.4  | 39210.9 |
| $B_3$, MHz       | 32609.5| 31728.8| 30964.6  | 31214.2  | 40547.9 | 38826.5 | 39977.4  | 38184.1 |
| $D_0$, kHz       | 238.640| 218.636| 230.300   | 210.162  | 367.623 | 328.492 | 356.984   | 317.700 |
| $H_e$, mHz       | 86.700 | 323.489| 92.429    | 308.120  | 451.354 | 473.786 | 496.507   | 496.507 |

Table 6. The HeHar+ CcCR Reduced Simple-Internal Force Constants (in mdyn/Å·rad²).

|               | F_{11} | F_{21} | F_{31} | F_{22} | F_{32} | F_{33} | F_{41} | F_{44} | F_{111} | F_{221} | F_{222} | F_{2222} |
|---------------|--------|--------|--------|--------|--------|--------|--------|--------|---------|---------|---------|---------|
|               | 0.105  | 0.193  | 4.011  | 0.027  | 0.027  | 0.027  | 0.027  | 0.027  | -0.6979 | -0.7749 | -0.2108 | -24.1460 |
|               | 357    | 842    | 600    | 336    | 336    | 336    | 336    | 336    | 2111    | 2211    | 2221    | 2222    |
|               | 1.00   | -0.35  | -0.88  | 0.61   | 1.00   | -0.88  | 0.24   | 0.61   | 1.00    | 1.00    | 1.00    | 1.00    |

4 CONCLUSIONS

The most striking result from this study in light of the earlier work by Fortenberry (2017) is that neon and helium behave very similarly while argon does not. The intensities, fundamental vibrational frequencies, and even binding energies are not significantly changed when moving down the periodic table from helium to neon in such proton-bound complexes. Once argon is invoked, the chemistry changes fundamentally. This is likely due to the polarizability of argon and the energy proximity of the additional d orbitals close to argon’s valence orbital occupation.

In any case, the proton-bound complexes involving helium and neon (HeHeNe+, HeHeNe+, and NeHeNe+) give very intense proton shuttle motions in the range where the mid-IR becomes the far-IR. The newest generation of space-based telescopes like the upcoming James Webb Space Telescope (JWST) or even the Stratospheric Observatory for Infrared Spectroscopy can potentially be utilized to observe these vibrational frequencies. The HeHNe+ dipole moment is also large making this proton-bound complex a candidate for rotational observation with ground-based telescopes as has been the common practice for half a century. The HeHar+ complex appears to be readily formed from hypothesized interstellar species, the helium and argon trihydride cations. HeHar+ is also rotationally active and has a bright fundamental vibrational frequency, but both of these are reduced relative to HeHNe+.

The sheer abundance of helium and hydrogen as well as the relatively high abundance of neon make any molecules comprised of these species notable for interstellar chemistry.
Table 7. The CcCR $^4$HeAr$^+$ Zero-Point ($R_a$ vibrationally-averaged) and Equilibrium Structures, Rotation Constants, Vibrationally Excited-Rotation Constants, Distortion Constants, and Vibrational Frequencies (Intensities in km/mol).

|                | HeH$^{36}$Ar$^+$ | HeD$^{36}$Ar$^+$ | HeH$^{38}$Ar$^+$ | HeD$^{38}$Ar$^+$ | HeH$^{40}$Ar$^+$ | HeD$^{40}$Ar$^+$ |
|----------------|------------------|------------------|------------------|------------------|------------------|------------------|
| $r_0$(He–H) Å | 1.556 699        | 1.564 906        | 1.557 493        | 1.564 738        | 1.557 333        | 1.564 585        |
| $r_0$(Ar–H) Å | 1.275 998        | 1.282 695        | 1.276 025        | 1.282 729        | 1.276 048        | 1.282 759        |
| $r_e$(He–H) Å | 1.516 393        | 1.516 393        | 1.516 393        | 1.516 393        | 1.516 393        | 1.516 393        |
| $r_e$(Ar–H) Å | 1.294 727        | 1.294 727        | 1.294 727        | 1.294 727        | 1.294 727        | 1.294 727        |
| $B_0$ MHz     | 17147.8          | 16607.3          | 17044.4          | 16494.9          | 16951.2          | 16393.3          |
| $B_0$ MHz     | 16379.5          | 15900.3          | 16282.8          | 15794.8          | 16195.6          | 15699.4          |
| $B_0$ MHz     | 17288.3          | 16480.7          | 17184.8          | 16369.7          | 17091.5          | 16269.3          |
| $B_2$ MHz     | 15869.0          | 15757.4          | 15776.0          | 15644.1          | 15692.1          | 15542.1          |
| $B_2$ MHz     | 14955.0          | 14191.9          | 14871.1          | 14121.3          | 14795.4          | 14205.6          |
| $D_e$ kHz     | 434.842          | 373.927          | 429.277          | 368.279          | 424.287          | 363.322          |
| $H_e$ Hz      | -40.138          | -33.640          | -39.380          | -32.895          | -38.703          | -32.232          |
| $\mu$ D       | 1.48             | 1.48             | 1.48             | 1.48             | 1.48             | 1.48             |

Table 8. The CcCR $^3$HeAr$^+$ Zero-Point ($R_a$ vibrationally-averaged) and Equilibrium Structures, Rotation Constants, Vibrationally Excited-Rotation Constants, Distortion Constants, and Vibrational Frequencies.

|               | $^3$HeH$^{36}$Ar$^+$ | $^3$HeD$^{36}$Ar$^+$ | $^3$HeH$^{38}$Ar$^+$ | $^3$HeD$^{38}$Ar$^+$ | $^3$HeH$^{40}$Ar$^+$ | $^3$HeD$^{40}$Ar$^+$ |
|---------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| $r_0$(He–H) Å | 1.566 868            | 1.481 206            | 1.566 714            | 1.481 184            | 1.566 573            | 1.481 164            |
| $r_0$(Ar–H) Å | 1.276 728            | 1.272 902            | 1.276 754            | 1.272 956            | 1.276 777            | 1.273 004            |
| $r_e$(He–H) Å | 1.516 393            | 1.516 393            | 1.516 393            | 1.516 393            | 1.516 393            | 1.516 393            |
| $r_e$(Ar–H) Å | 1.294 727            | 1.294 727            | 1.294 727            | 1.294 727            | 1.294 727            | 1.294 727            |
| $B_0$ MHz     | 21839.5              | 20872.8              | 21742.7              | 20753.4              | 21662.6              | 20665.8              |
| $B_0$ MHz     | 20757.6              | 20949.4              | 20658.6              | 20829.3              | 20569.1              | 20720.9              |
| $B_0$ MHz     | 21789.1              | 20852.9              | 21773.0              | 20733.6              | 21677.1              | 20626.1              |
| $B_0$ MHz     | 20142.0              | 20164.9              | 20046.5              | 19896.0              | 19960.1              | 20787.0              |
| $B_0$ MHz     | 18638.6              | 21064.4              | 18600.2              | 20943.0              | 18524.7              | 20833.5              |
| $D_e$ kHz     | 682.267              | 554.180              | 675.061              | 546.953              | 668.595              | 540.474              |
| $H_e$ Hz      | -80.385              | -62.553              | -79.133              | -61.357              | -78.015              | -60.291              |
| $\omega_1(\sigma)$ Ar–H cm$^{-1}$ | 2542.9             | 1824.4              | 2540.9              | 1821.7              | 2539.2 (703)         | 1819.3              |
| $\omega_2(\pi)$ Bend cm$^{-1}$ | 319.1              | 253.8               | 319.1               | 253.8               | 319.0               | 253.7               |
| $\omega_3(\sigma)$ He–H cm$^{-1}$ | 250.5              | 233.8               | 250.0               | 233.8               | 249.6               | 233.7               |
| $\nu_1(\pi)$ Ar–H cm$^{-1}$ | 2474.0             | 1803.8              | 2472.4              | 1801.5              | 2470.9              | 1799.4              |
| $\nu_2(\pi)$ Bend cm$^{-1}$ | 514.6              | 357.8               | 514.4               | 357.7               | 514.3               | 357.5               |
| $\nu_3(\sigma)$ He–H cm$^{-1}$ | 266.5              | 370.2               | 266.1               | 370.1               | 265.8               | 369.9               |
| $2\nu_0(\sigma)$ cm$^{-1}$ | 4737.0             | 3518.4              | 4734.0              | 3514.0              | 4731.3              | 3510.0              |
| $2\nu_2(\pi)$ cm$^{-1}$ | 1138.5             | 780.6               | 1138.0              | 780.1               | 1137.7              | 779.7               |
| $2\nu_3(\sigma)$ cm$^{-1}$ | 466.7              | 791.6               | 466.1               | 791.2               | 465.6               | 790.9               |
| $\nu_1 + \nu_2(\sigma)$ cm$^{-1}$ | 3101.0             | 2207.2              | 3099.3              | 2204.9              | 3097.8              | 2202.9              |
| $\nu_1 + \nu_3(\pi)$ cm$^{-1}$ | 2800.2             | 2219.6              | 2798.0              | 2217.3              | 2796.1              | 2215.3              |
| $\nu_2 + \nu_3(\sigma)$ cm$^{-1}$ | 833.7              | 790.3               | 833.1               | 790.0               | 832.4               | 789.9               |
| ZPE cm$^{-1}$ | 1831.9             | 1370.5              | 1830.6              | 1369.0              | 1829.4              | 1367.8              |
and subsequent astrophysical observation. The relative energetics, zero-point energies, and spectroscopic data provided in this work will enhance further laboratory, modeling, or interstellar studies. While estimates of the actual abundances are beyond the scope of the present work, the formation energetics imply that the abundances of these proton-bound complexes are likely dependent upon the abundances of the possible precursors, notably the noble gas-hydride and -trihydride cations. As a result, HeHAr\(^+\) will likely have the highest abundance. However, the significant intensities present for the proton shuttle fundamental frequencies of the helium and neon complexes should make relatively small abundances for any of these noble gas species detectable with JWST. Consequently, the present work is showing a likely case where more, natural noble gas molecules may be detected in the ISM and the chemistries of these atoms can be further enhanced.

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