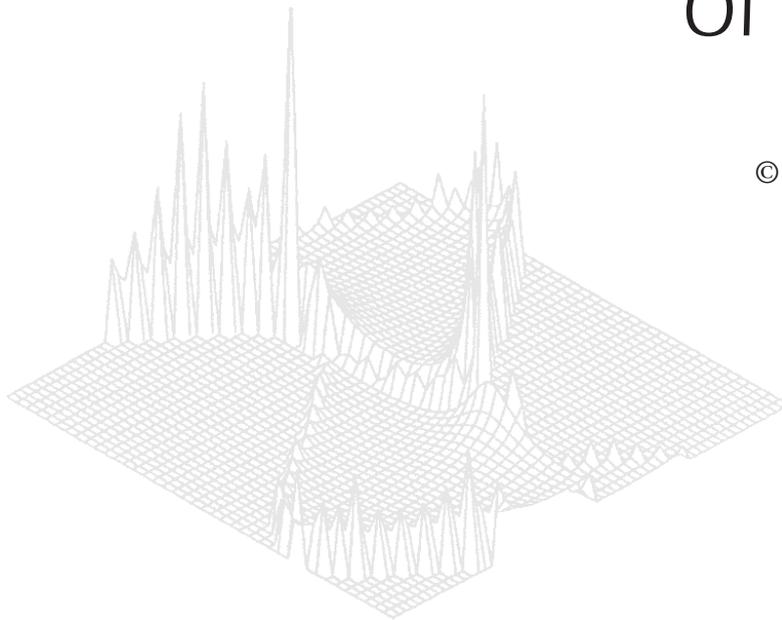

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Australian Journal of Physics

Volume 50, 1997
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Ab Initio Investigations of the Electronic Structure of HeNH⁺ and HeNH²⁺

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Abstract

Electronic structures of HeNH⁺ and HeNH²⁺ were investigated using the all-electron coupled cluster single, double and triple excitation (CCSD(T)_AE) method coupled with an augmented correlation-consistent polarised core valence triple zeta basis set (aug-cc-pCVTZ). For HeNH⁺ and HeNH²⁺, the CCSD(T)_AE/aug-cc-pCVTZ model yielded cations of C_s symmetry with ²A'' and ¹A' ground electronic states possessing optimised geometrical parameters {r_{N-H}, r_{N-He}, θ_{H-N-He}} of {1.064 Å, 1.517 Å, 88.5°} and {1.192 Å, 1.309 Å, 96.2°} respectively. Of all the linear isomeric forms possible for these two cations, the only converged minimum energy structures were for the ⁴Σ⁻ states of HeHN⁺ and HeNH⁺ yielding optimised structural parameters of {1.093 Å, 2.403 Å, 180.0°} and {1.117 Å, 1.364 Å, 180.0°} respectively. These two linear structures were calculated to be 9.6 and 18.6 kJ mol⁻¹ respectively above the C_s structure. The calculated harmonic frequencies were real for all these states and their magnitudes were sensitive to the incorporation of electron correlation.

1. Introduction

The chemistry of interstellar gas clouds has centred on the chemistry of hydrogen, since the chemistry of helium was thought to be of little consequence due to its inert nature (e.g. Green 1981). Although both these two elements do not possess p orbitals in their valence space, the chemistry of hydrogen containing compounds has dominated organic chemistry for over a century and a half, whereas it is only in more recent times that van der Waals complexes containing helium atoms have become of interest to both experimentalist and theoreticians alike (e.g. Tang and Toennies 1978).

Investigations on the chemistry of helium uncovered that the cationic species were more strongly bound than their neutral counterparts (e.g. Koch *et al.* 1986, 1987; Frenking *et al.* 1989*a*, 1989*b*, 1990*a*, 1990*b*). So far there have been no reported experimental or theoretical investigations on HeNH⁺ and HeNH²⁺, even though these ions may be of importance in modelling interstellar chemistry. Moreover, these cations may be detected since experimentalists are now able to spectroscopically characterise metastable species such as N₂⁺-(He)_n (n = 1, 2, 3) (Bieske *et al.* 1992) and He-HN₂⁺ and He₂-HN₂⁺ (Meuwly *et al.* 1996). Theoretical

investigations of HeXH^+ and HeXH^{2+} (where $X = \text{C, O}$) have been reported by Hughes and von Nagy-Felsobuki (1997*c*, 1997*d*) and so this investigation concludes the series.

Theoretical calculations by Koch *et al.* (1986, 1987) and Frenking *et al.* (1989*a*, 1989*b*, 1990*a*, 1990*b*) have been used to model the underlying bonding mechanism of a number of helide compounds of the form XHe_n^{m+} (where X is equal to carbon, nitrogen or oxygen). Although both HeN^{2+} and He_2N^{2+} were calculated to be bound in their ground electronic states, the calculations nevertheless predicted that both these molecules were thermodynamically unstable (Koch *et al.* 1986, 1987; Frenking *et al.* 1989*a*, 1989*b*, 1990*a*, 1990*b*). For the ${}^2\text{B}_1$ and ${}^2\text{A}_1$ states of He_2N^{2+} their MP2/6-31G(d,p) calculations yielded ($r_{\text{N-He}}$, $\theta_{\text{He-N-He}}$) structural parameters of size (1.326 Å, 87.9°) and (1.038 Å, 109.9°) respectively. The ‘frozen core’ MP4(SDTQ)_FC/6-311G(2df,2pd)//MP2/6-31G(d,p) model yielded the ${}^2\text{B}_1$ state to be the lowest bound state for He_2N^{2+} . The energy difference between the ${}^2\text{B}_1$ and ${}^{12}\text{A}_1$ states was 574.0 kJ mol⁻¹. Extensive calculations performed by Hughes and von Nagy-Felsobuki (1996) on the energy hypersurface of He_2N^{2+} using the CCSD(T)_AE/cc-pCVTZ model confirmed that the ground electronic state was of ${}^2\text{B}_1$ symmetry yielding ($r_{\text{N-He}}$, $\theta_{\text{He-N-He}}$) structural parameters of size (1.329 Å, 88.6°) (which were in close agreement to the less rigorous MP2 model).

The binding nature of some helide compounds has been studied by Koch *et al.* (1989*a*, 1989*b*, 1990*a*, 1990*b*) and Frenking *et al.* (1989, 1990). They have shown that for the He-X^+ dimers (where $X = \text{Li to Ne}$) electrostatic interactions were responsible for the binding force, whereas for the dication counterparts covalent bonding prevailed. In the case of polyatomic ions, such as the Ng_2N^{2+} (where $\text{Ng} = \text{He, Ne and Ar}$), all the ${}^2\text{B}_1$ states were classified as semi-polar covalent in nature.

To rationalise the calculated bondlengths, stabilities and dissociation energies of these helide compounds, a donor-acceptor model was invoked (see Frenking *et al.* 1989*a*, 1989*b*, 1990*a*, 1990*b*). According to this model, the electronic properties were critically dependent upon electron donation of He 1s atomic orbitals (AOs) into either empty 2s or 2p AOs of the N^{2+} fragment. Using this model it was anticipated that a much shorter $r_{\text{N-He}}$ bondlength would occur for the ${}^2\text{A}_1$ state than for the ${}^2\text{B}_1$ state, because the N^{2+} fragment was a better electron acceptor in the ${}^2\text{D}$ state (with the 2s AO of nitrogen dication being half empty) than in the ${}^2\text{P}$ state (with the 2s AO of nitrogen dication being doubly filled). An extension of the donor-acceptor model to the isoelectronic amino radical yielded qualitative agreement with the MP2_AE/6-31G(d,p) calculations, which predicted that the $r_{\text{N-He}}$ bondlength was longer than the $r_{\text{N-H}}$ bondlength for the ${}^2\text{B}_1$ state and slightly longer for the ${}^2\text{A}_1$ state.

As an extension of ab initio investigations into the electronic structure of helide cations (Hughes and von Nagy-Felsobuki 1996, 1997*a*, 1997*b*, 1997*c*, 1997*d*) we wish to detail an ab initio investigation on the ground and linear electronic states of HeHN^+ , HeNH^+ and HeNH^{2+} and so conclude the HeXH^{n+} ($n = 1, 2$ and $X = \text{C, O, N}$) series. It is hoped that this study will assist and encourage experimentalists to detect and identify these mixed hydrogen helide cations, thereby detailing more clearly the molecular ion chemistry of helium.

2. Computational Details

The GAUSSIAN 94 suite of programs (Frisch *et al.* 1995) was employed to study the structural parameters of the electronic states of HeHN^+ , HeNH^+ and HeNH^{2+} . The electron correlation method selected was the all-electron coupled cluster method, using both single and double excitations with a perturbative estimate of the effect of triple excitations (e.g. Cizek 1969; Purvis and Bartlett 1982; Bartlett 1989; Raghavachari *et al.* 1989) which is denoted as CCSD(T)_AE. For the open-shell states the unrestricted CCSD(T)_AE model was utilised (Frisch *et al.* 1995). All minimum energy structures were obtained using the Fletcher and Powell (1963) algorithm and stationary points characterised by calculating the harmonic frequencies.

The construction of the basis set is critical in theoretical investigations of metastable complexes, such as HeNH^+ and HeNH^{2+} , since the accurate modelling of the electron affinities of their fragments (e.g. $\text{He}+\text{NH}^+$ etc.) are important in mimicking their bonding characteristics. Recently, Woon and Dunning (1994, 1995) have developed families of correlation-consistent polarised valence basis sets, which have been optimised for correlated calculations. These basis sets have been extended by Woon and Dunning (1994, 1995) to include not only the valence–valence correlation, but also to include the core–core and core–valence correlation effects. The aug-cc-pCVTZ basis set of Kendall and Dunning (1992) were employed in all the calculations below, since it was shown that within the MRSD-CI ansatz this basis set yielded the most accurate electron affinities for first row atoms. The correct modelling of the helium electron affinity is critical in all these studies, since previous bonding mechanisms of their dihelide counterparts (e.g. Frenking *et al.* 1989*a*, 1989*b*) have suggested that bond formation arises from electron density donation of helium to the ion fragment (and not the reverse). In addition Martin (1995) has shown that for structural properties the neglect of core correlation causes bondlengths to be over estimated by 0.001 Å for single bonds. He has also shown that the triple zeta core-correlation basis set yielded structural parameters, such as bondlengths and harmonic frequencies to within 0.0004 Å and 10 cm^{-1} respectively of a quadruple basis set. Hence the aug-cc-pCVTZ basis set of Kendall and Dunning (1992) is appropriate for studies involving helium containing cations.*

3. Results and Discussion

Fig. 1 gives the optimised geometries of HeHN^+ , HeNH^+ and HeNH^{2+} using the aug-cc-pCVTZ basis set at the HF and the CCSD(T)_AE level of theory. In all cases the optimised $r_{\text{N-He}}$ bondlengths were sensitive to the inclusion of electron correlation (i.e. significantly shortened).

* Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, PO Box 999, Richland, Washington 99352, USA, and funded by the US Department of Energy. The Pacific Northwest Laboratory is a multi-program Laboratory operated by Battelle Memorial Institute for the US Department of Energy under contract DE-AC06-76LO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.

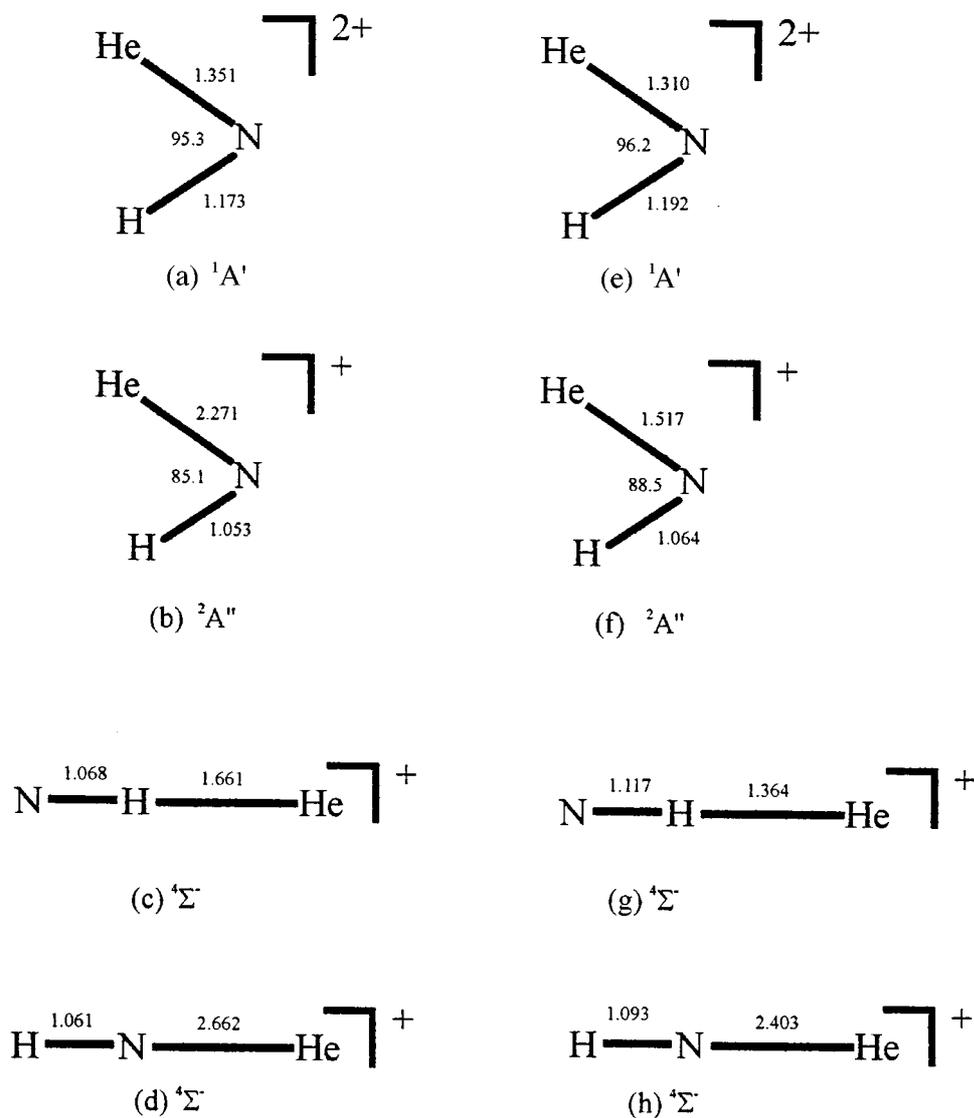


Fig. 1. Optimised geometries of HeHN^+ , HeNH^+ and HeNH_2^+ using the aug-cc-pCVTZ basis set at: (a)–(d) the HF level of theory; (e)–(h) the CCSD(T)_AE level of theory.

For HeNH_2^+ the ${}^1A'$ state (bent geometry) was calculated to be the ground electronic state. None of the linear structures were bound. However, for the linear structures of HeHN^+ and HeNH^+ the ${}^4\Sigma^-$ states were bound and were calculated to be 9.6 and 18.6 kJ mol^{-1} respectively above the bent structure. These barriers do not highlight the correlations that exist between the linear and bent configurations. For example, in the HeNH^+ case (within the HF model) the open shell configuration of $\dots(1\pi_g)^2(4\sigma_g)^1\text{MO}$ for the ${}^4\Sigma^-$ state correlates to the valence shell configuration of $\dots(4a')^1(1a'')^1$ for the ${}^2A''$ state of the bent configuration.

All calculations have been carried out using the GAUSSIAN 94 suite of programs (Frisch *et al.* 1995). For the singly charged cations, the open-shell reference wavefunction was the spin and symmetry UHF wavefunction. Using the UHF method, the variational wavefunction no longer needs to be an eigenfunction of the spin operator S^2 with expectation value $S(S+1)$. The spin operator S^2 has the form (Amos and Snyder 1964)

$$S^2 = -\frac{1}{4}N(N-4) + \frac{1}{2}\sum' P_{ij}, \quad (1)$$

where P_{ij} interchanges the spin of the i th and j th electrons, the prime on the summation indicates $i \neq j$ and N is the total number of α and β electrons. A ‘pure’ doublet state [with expectation value $0.5(0.5+1)$ or 0.75] may mix with a low-lying excited quartet state (with expectation value of 3.75). Therefore the eigenvalue of the spin operator indicates the level of contamination of the wavefunction with an excited spin state. Codes are available to annihilate the excited spin state from the ground state wavefunction (e.g. Amos and Snyder 1964; Frisch *et al.* 1995). However, even after such a spin annihilation procedure has been performed, the spin expectation value may still indicate an unwanted level of contamination. As a result, the optimised UHF geometry may be a local minimum for the contaminated wavefunction on the energy hypersurface rather than the global minimum for the respective ‘pure’ wavefunction. Care must also be taken to avoid such features as saddle points on the energy hypersurface (i.e. no imaginary frequencies). The expectation of the S^2 operator (before, after) annihilation of the doublet and quartet states of HeHN⁺ (bent), HeHN⁺ (linear) and HeNH⁺ (linear) structures is $(0.90, 0.75)$, $(3.75, 3.75)$ and $(3.75, 3.75)$ respectively, indicating an uncontaminated wavefunction after annihilation. However, it should be noted that Bartlett (1995) showed that for the CN radical, even though spin contamination was high for the UHF wavefunction, there was a near equivalence between the UHF-CCSD and ROHF-CCSD wavefunctions. A similar result is expected for these calculations.

The CCSD(T)/aug-cc-pCVTZ level of theory aims for high accuracy. For a large number of molecules containing first row atoms, Oliphant and Bartlett (1994) have shown that the CCSD(T) method coupled with a triple zeta basis set augmented with polarisation functions yields average differences between theory and experiment for bondlengths, bond angles, vibrational frequencies, atomisation energies and dipole moments of the order of 0.005 \AA , 1.9° , 30 cm^{-1} , 48.1 kJ mol^{-1} and 0.10 D respectively. For a semi-polar covalent bond such as in HF, they also showed that average errors are only 0.002 \AA , 2 cm^{-1} , 19.7 kJ mol^{-1} and 0.01 D respectively. Using the CCSD(T)/aug-cc-pCVTZ model the calculated equilibrium geometry should reflect similar inaccuracies.

For the bent HeNH⁺ and HeNH²⁺, the CCSD(T)___AE/aug-cc-pCVTZ model yielded cations of C_s symmetry with ²A'' and ¹A' ground electronic states possessing optimised geometrical parameters $\{r_{\text{N-H}}, r_{\text{N-He}}, \theta_{\text{H-N-He}}\}$ of $\{1.064 \text{ \AA}, 1.517 \text{ \AA}, 88.5^\circ\}$ and $\{1.192 \text{ \AA}, 1.309 \text{ \AA}, 96.2^\circ\}$ respectively. Using the same level of theory, the ⁴Σ⁻ state of HeHN⁺ and HeNH⁺ gave optimised structural parameters of $\{1.093 \text{ \AA}, 2.403 \text{ \AA}, 180.0^\circ\}$ and $\{1.117 \text{ \AA}, 1.364 \text{ \AA}, 180.0^\circ\}$ respectively. The He₂N²⁺ molecule is isoelectronic with HeNH⁺. Calculations by Hughes and von Nagy-Felsobuki (1996) using the CCSD(T)___AE model

showed that the doubly charged species is also bent, with the 2B_1 state yielding optimised structural parameters ($r_{\text{N-He}}$, $\theta_{\text{He-N-He}}$) of (1.329 Å, 88.6°). It should be noted that HeNH^+ molecules are not just complexes of the HeH^+ moiety, since at the CCSD(T)/aug-cc-pCVTZ level of theory the HeH^+ singlet state is lowest in energy with a bondlength of 0.776083 Å (Hughes and von Nagy-Felsobuki 1996). It is significant that the bond angles of these isoelectronic species are in close agreement, whereas the $r_{\text{N-He}}$ bondlengths are not.

The simple donor-acceptor model (Koch *et al.* 1986, 1987; Frenking *et al.* 1989*a*, 1989*b*, 1990*a*, 1990*b*) employed the fragment ion as the acceptor, with the helium atom donating electron density into the fragment ion's lowest unoccupied molecular orbital structure. For these molecules, the NH fragment ion has MO structure: $1\sigma(\text{N}1s)2\sigma(\text{N}2s)3\sigma(\text{N}2p_\sigma+\text{H}1s)1\pi(\text{N}2p_\pi)$. For the bent structures, the approaching helium atom would split the π MOs on the NH fragment ion, enabling electron donation into a π component along the $r_{\pi\text{-He}}$ reaction coordinate. The use of this simple approach suggests that for HeHN^+ and He_2N^{2+} the bond angle would be in the vicinity of ninety degrees (with the widening of the $\theta_{\text{H-N-He}}$ bond angle in HeHN^{2+} being indicative of a reduction of in-plane bond pair-lone pair repulsions). The optimised CCSD(T)_AE/aug-cc-pCVTZ bondlengths for NH^+ (${}^2\Pi$) and NH^{2+} (${}^1\Sigma^+$) were calculated to be 1.071 and 1.326 Å respectively, which is consistent with the bonding characteristics of the occupied fragment MOs. The electron affinity of the NH^+ fragment is not as strong as the NH^{2+} fragment due to double charge of the latter significantly relaxing the $1\pi(\text{N}2p_\pi)$ MO relative to the $3\sigma(\text{N}2p_\sigma+\text{H}1s)$ MO and so enabling a more efficient He donation. [It should be noted that the first ionisation energy of helium is 24.587 eV (Moore 1971)]. Hence, the $r_{\text{N-He}}$ bondlength of HeNH^+ is longer when compared with HeNH^{2+} . Although such qualitative models give insight into bonding characteristics of these hydrogen helide ions, care must be taken not to over interpret these CCSD(T)_AE results in terms of simple MO theory.

Table 1 compares the various properties for the electronic states of HeHN^+ , HeNH^+ and HeHN^{2+} using the HF and CCSD(T)_AE methods. For all these calculations the harmonic frequencies were real and their magnitudes sensitive to the level of theory employed. For example, the poorest agreement between the HF and CCSD(T)_AE methods is for HeNH^+ (${}^2A''$), where the symmetric stretch and bend modes are significantly in disagreement (i.e. 1146 and 467 cm^{-1} compared with 285 and 154 cm^{-1} respectively). Smaller percentage discrepancies were observed for the other structures. Pertinent to these variations, Lee and Scuseria (1995) have found that the difference between CCSD(T) and experimental harmonic or fundamental vibrational frequencies for X-H stretching and bending frequencies were not very systematic and therefore not amenable to employing an appropriate 'correction' factor. They have also shown that for compounds containing very electronegative atoms it was necessary in the CCSD(T) level of theory to include diffuse basis functions in the basis set (i.e. such as those incorporated in these calculations) in order to describe more correctly the ionic behaviour of a molecule. As these cations contain helium and as any donation of electron density by the helium atom would render the helium moiety very electronegative, it would be anticipated that the CCSD(T)/aug-cc-pCVTZ model should yield results more closely aligned with experiment compared

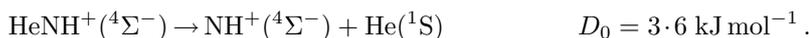
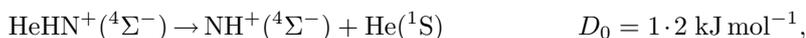
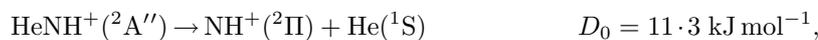
with those level of theories unable to accurately model electron affinities (e.g. such as the HF model).

Table 1. Calculated properties of HeNH^{n+} (where $n = 1, 2$)

The total energy is in Hartree units, the zero-point energy (ZPE) in kJ mol^{-1} , and the frequencies in cm^{-1}

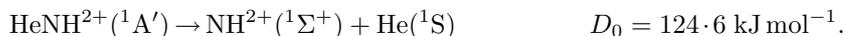
Property	HF/aug-cc-pCTVZ	CCSD(T)_AE/aug-cc-pCTVZ
(a) $\text{HeNH}^+(^2A'')$		
Total energy	-57.382107	-57.614324
ZPE	21.88	28.31
Sym. stretch ω_1	285	1146
Bend ω_2	154	467
Asym. stretch ω_3	3219	3120
(b) $\text{HeHN}^+(^4\Sigma^-)$		
Total energy	-57.407251	-57.610684
ZPE	21.61	21.72
Sym. stretch ω_1	188	319
Bend ω_2	272	466
Asym. stretch ω_3	2882	2380
(c) $\text{HeNH}^+(^4\Sigma^-)$		
Total energy	-57.405894	-57.607232
ZPE	19.37	18.00
Sym. stretch ω_1	89	133
Bend ω_2	72	75
Asym. stretch ω_3	3005	2727
(d) $\text{HeNH}^{2+}(^1A')$		
Total energy	-56.445190	-56.688006
ZPE	24.51	25.06
Sym. stretch ω_1	1205	1177
Bend ω_2	784	997
Asym. stretch ω_3	2109	2015

Due to the high ionisation energy of helium (24.587 eV) it would be expected that the lowest energy dissociation channel of these ions is along the nitrogen hydride ion and helium reaction coordinate. The CCSD(T)/aug-cc-pCVTZ model yielded a helium atom ground state energy of $-2.900836 E_h$. For the doublet and quartet state of the NH^+ fragment this level of theory yielded an energy of -54.705332 and $-54.705261 E_h$ at the optimised bondlengths of 1.071 and 1.094 Å respectively. Incorporating the zero-point energies, it is possible to calculate dissociation energies for the dissociation channels:



For the singlet state of the NH^{2+} , the CCSD(T)/aug-cc-pCVTZ model yielded an energy of $-53.732613 E_h$ at the optimised bondlengths of 1.326 Å. Incorporating

the zero-point energies, the dissociation energy for the dissociation channel of the doubly charged ion is



The $\text{He}^+({}^2S)+\text{NH}^+({}^2\Pi)$ dissociation channel lies 49.8 kJ mol^{-1} below the $\text{HeNH}^{2+}({}^1A')$ minimum and so can only be accessed if there are two potential curves which cross. The NHe^+ ground state was calculated by Frenking *et al.* (1989*b*) to be a ${}^3\Sigma^-$ and so for $\text{HeNH}^{2+}({}^1A')$ the dissociation channel $\text{NHe}^+({}^3\Sigma^-)+\text{H}^+$ should not correlate with respect to spin considerations. For HeN^+ at the CCSD(T)_FC/cc-pVTZ level the ${}^1\Sigma^+$ state lies 205 kJ mol^{-1} above the ground electronic state. Hence the latter is well beyond the $\text{NH}^{2+}({}^1\Sigma^+)+\text{He}({}^1S)$. It is clear that only the bent structures may be confidently considered as being thermodynamically stable.

Concern is often expressed of the possible influence of basis-set superposition errors (BSSE) on the energetics of weakly bound systems such as the helide cations. We have estimated BSSE using the counter-poise method for the most electron dense system, ${}^4\Sigma^- \text{HeNH}^+$. For this state and molecule the BSSE was estimated to be 0.1 kJ mol^{-1} . Hence we believe the BSSE will not alter the conclusions drawn here.

Table 2. Comparison of structural properties for ground electronic states of HeXH^{n+} (where $X = \text{C, O, N}$ and $n = 1, 2$)

The symbol Δ represents the difference in the properties of HeCH^{n+} to HeXH^{n+} ($n = 1, 2$ and $X = \text{N, O}$) with the subscript indicating the heavy atom involved in the ion and the superscript indicating the charge. See Hughes and von Nagy-Felsobuki (1997*c*, 1997*d*) for the HeXH^{n+} ($X = \text{N, O}$) results

Property	$\Delta^+_{\text{C-N}}$		$\Delta^{2+}_{\text{C-N}}$		$\Delta^+_{\text{N-O}}$		$\Delta^{2+}_{\text{N-O}}$	
	HF	CCSD(T)	HF	CCSD(T)	HF	CCSD(T)	HF	CCSD(T)
r_{X-H} (Å)	0.061	0.065	0.041	0.062	-0.231	-0.086	-0.041	-0.082
r_{X-He} (Å)	0.161	0.655	0.060	0.079	1.278	0.508	0.264	0.204
θ_{H-X-He} (deg.)	-5.8	-7.1	14.7	14.3	-7.8	-6.2	8.1	-6.6
ω_1 (cm^{-1})	14	-719	-304	-320	-1193	-488	-208	-90
ω_2 (cm^{-1})	-26	-278	-218	-312	-393	-596	-322	-107
ω_3 (cm^{-1})	-155	-252	-52	-200	-320	-214	688	737
ZPE (kJ mol^{-1})	-0.84	-7.53	-3.35	-10.04	-11.38	-7.50	0.84	4.30

Table 2 gives a comparison of structural properties for only the ground electronic states of HeXH^{n+} (where $X = \text{C, O, N}$ and $n = 1, 2$). The differences are expressed relative to the least electron-dense system, namely HeXH^{n+} . The CCSD(T)/aug-cc-pCVTZ calculations for HeXH^{n+} (where $X = \text{O, N}$ and $n = 1, 2$) have been reported elsewhere by Hughes and von Nagy-Felsobuki (1997*c*, 1997*d*).

The largest discrepancy in the optimised geometrical parameters between the HF and CCSD(T) models for the HeXH^{n+} ($X = \text{C, N, O}$) series was for the ground electronic state of HeNH^+ , where the $r_{\text{He-N}}$ bondlength was shortened by 0.75 \AA . A large shortening of 0.48 \AA was also calculated for the ${}^3A''$ state of HeCH^+ (Hughes and von Nagy-Felsobuki 1997*d*). In both cases, the HF r_{X-H} bond length was predicted to be much smaller and the bond angle more acute

than the corresponding CCSD(T) model. This suggests that subtle changes in the fragment ion geometry are magnified in the geometrical parameters of these helide ions.

The reduction of the $\theta_{\text{H-X-He}}$ bond angle across the series reflects the marked structural variations across the series for the $r_{\text{X-He}}$ bondlength of the singly charged cations. For these helide ions, the XH^{n+} fragment ion has MO structure: $1\sigma(\text{X}1\text{s})2\sigma(\text{X}2\text{s})3\sigma(\text{X}2\text{p}_\sigma+\text{H}1\text{s})1\pi(\text{X}2\text{p}_\pi)$ and as previously discussed the use of this simple MO approach suggests that the bond angles should be in the vicinity of ninety degrees (with a more acute bond angle being indicative of a greater in-plane bond pair-lone pair repulsion). On the other hand, for the doubly charged species the opposite trend is observed for the bond angle, with subsequent much smaller variations in the bondlengths.

The major discrepancies between the two ab initio models is in the differences of the curvatures of their potential energy surfaces. This is reflected in the fundamental vibrational modes. As the reduced masses of these systems are similar in magnitude, trends in vibrational modes across the series are more reflective of the force constants (i.e. bondlength and angle deformation force constants). For this series, the HF model generally yields flatter potentials with much smaller binding energies. Hence the HF level of theory yielded the poorest agreement with the electron correlation calculation for the bending vibrations. These modes are extremely sensitive to the $k_{\text{X-He}}$ and $k_{\Delta\theta}$ constants.

Acknowledgments

Calculations were performed using the VAX 3100 workstation, Sun workstations and VPP300; the VAX was made available by the generous support of the Australian Research Grants Scheme, the Suns by the generous support of the Faculty of Engineering (University of Newcastle) and the VP by generous support of the ANU. We wish to acknowledge the University of Newcastle scholarship held by Mr J. M. Hughes.

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Manuscript received 30 June, accepted 18 September 1997