The Journal of Physical Chemistry A

© Copyright 1997 by the American Chemical Society VOLUME 101, NUMBER 22, MAY 29, 1997

LETTERS

Theoretical Investigations of the Electronic Structure of $HeHO^+$ and $HeHO^{2+}$

Jason M. Hughes and Ellak I. von Nagy-Felsobuki*

Department of Chemistry, The University of Newcastle, Callaghan, NSW 2308, Australia

Received: November 14, 1996; In Final Form: April 3, 1997[⊗]

The $^3\Sigma^-$ and $^1A'$ of $HeHO^+$ and $^2A''$ ground electronic states of $HeHO^{2+}$ have been investigated using the all-electron coupled cluster single, double, and triple-excitation (CCSD(T)) method coupled with an augmented correlation-consistent polarized core valence triple-ζ basis set (aug-cc-pCVTZ). For the $^3\Sigma^-$ and $^1A'$ states of $HeHO^+$, the CCSD(T)/aug-cc-pCVTZ model yielded optimized geometrical parameters (r_{O-H}, r_{O-He}, θ_{H-O-He}) of (1.036 Å, 2.608 Å, 180°) and (1.150 Å, 1.009 Å, 94.7°) respectively, with the triplet state being more stable by 40.4 kcal mol^{-1}. For the $^2A''$ ground electronic state of $HeHO^{2+}$, the optimized structural parameters were (1.247 Å, 1.158 Å, 101.3°) respectively. The calculated harmonic frequencies were real for all these states, and their magnitudes were sensitive to the incorporation of configuration interaction.

1. Introduction

With the advent of molecular beam mass spectrometers, the structural and spectroscopic properties of a number of van der Waals molecules containing rare gas atoms have been characterized.[1,2] So far there has been no reported experimental or theoretical investigations on the mixed hydrogen helide compounds, such as $HeHO^+$ and $HeHO^{2+}$, even though experimentalists are now able to spectroscopically characterize metastable species. (The former molecule is isoelectronic with the water molecule, while the latter is isoelectronic with the hydroxyl radical.) A theoretical investigation into the electronic structure of $HeHO^+$ and $HeHO^{2+}$ is of importance, since these ions are not just examples of a foreign ion residing in a helium cluster but showcase the molecular chemistry of helium itself. Moreover, it is anticipated that detailing the chemistry of helium with fragment ions, such as HO^+ and HO^{2+}, will have an important bearing in our understanding interstellar chemistry.

Theoretical calculations by Frenking, Koch, and co-workers[3-8] 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, and oxygen). In the case of the ground electronic state of He_2O^{2+}, they showed that it was not thermodynamically stable, but rather metastable. Nevertheless, it was predicted to possess a potential energy minimum, yielding short and very strong helium−oxygen bonds. For example, their MP2/6-31G(d, p) calculations yielded structural parameters (r_{C-He}, $\theta_{He-O-He}$) of (1.148 Å, 92.4°) respectively.[3,4] Moreover, an extensive CCSD(T)/cc-pCVTZ calculation performed by von Nagy-Felsobuki and co-workers[9] confirmed these results, yielding an optimized geometry with C_{2v} symmetry and with a r_{O-He} bond length of 1.168 Å and a bond angle of 92.6°.

Electrostatic interactions were thought to be responsible for the binding force of most of the $He-X^+$ monocations (where X = Li to Ne), whereas covalent bonding is postulated to prevail for their dication counterparts.[5] The polyatomic analogues of the Ng_2X^{2+} (where Ng = He, Ne, Ar and X = C, N, O) have been predicted to have semipolar covalent bonding with respect to the $^1A_1$ electronic states.[6]

The singlet−triplet energy separations for He_2X^{2+} and the analogous hydrides have been of considerable interest. Frenking, Koch, and Liebman[8] have given qualitative insight into the underlying interactions that affect the magnitudes of these

---

* Author to whom correspondence should be addressed. Telephone: 61-49-215482. Fax: 61-49-215472. E-mail: chvo@cc.newcastle.edu.au. Telex: NEWUN AA28194.

[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1997.

S1089-5639(96)03802-9 CCC: $14.00 © 1997 American Chemical Society

separations. Their analysis suggest that for C_{2v} molecules the singlet−triplet splitting is critically dependent on the fact that two of the MO's ($2a_1$ and $3a_1$) favor smaller bond angles, while only one ($1b_2$) will increase in energy. The overall result is a smaller bond angle for He_2C^{2+} (yielding a singlet ground state) compared with CH_2 (which yields a triplet ground state).

As an extension of our earlier work on the electronic structure on seeded helium clusters,[9−11] we wish to detail an ab initio investigation of the $^3\Sigma^-$ and $^1A'$ states of $HeHO^+$ and $^2A''$ ground electronic states of $HeHO^{2+}$. It is hoped that this study may assist and encourage experimentalists to detect and identify these mixed hydrogen helide compounds, thereby detailing more clearly the molecular chemistry of helium.

2. Computational Details

We have employed the GAUSSIAN 94 suite of programs[12] to study the structural parameters of the electronic states of $HeHO^+$ and $HeHO^{2+}$. The configuration interaction method selected was the coupled cluster method, using both single and double excitations with a perturbative estimate of the effect of triple excitations (i.e. denoted as CCSD(T)).[13−16] For the open-shell states the unrestricted CCSD(T) model was employed.

Recently, Dunning and co-workers[17−19] have developed families of correlation-consistent polarized valence basis sets, which have been optimized for correlated calculations. These basis sets have been extended by Woon and Dunning[18] to include not only the valence−valence correlation but also the core−core and core−valence correlation effects. As the electronegativity of the fragments of these molecules (e.g. He + OH^+, etc.) may be critical in reproducing their bonding characteristics, we have employed the aug-cc-pCVTZ basis set of Kendall and Dunning,[20] since they have demonstrated that within the MRSD-CI ansatz, this basis set yielded the most accurate electron affinities for first-row atoms. The correct modeling of the helium electron affinity is critical in a these helide studies, since previous bonding mechanisms[8] have suggested that bond formation arises from electron density donation of helium to the ion fragment (and not the reverse). Furthermore, Martin[21] has shown that the neglect of core correlation causes bond lengths to be over estimated by 0.001 Å for single bonds. He has also shown[21] that triple-ζ core-correlation basis sets yield structural parameters, such as bond lengths and harmonic frequencies, to within 0.0004 Å and 10 $cm^{-1,}$ respectively, of quadrupole basis sets. Hence the aug-cc-pCVTZ basis set of Kendall and Dunning[20] is appropriate for studies involving helium-containing molecules.

The minimum energy structures were obtained using the Fletcher−Powell algorithm[22] and the stationary points characterized by calculating the harmonic frequencies.

3. Results and Discussion

Figure 1 gives the optimized geometries of $HeHO^+$ and $HeHO^{2+}$ using the aug-cc-pCVTZ basis set at the Hartree−Fock (HF) and the CCSD(T) levels of theory. For $HeHO^{2+}$ the linear structures were not bound. However, for $HeHO^+$ the $^3\Sigma^-$ linear state was lower than the $^1A'$ state by 40.4 kcal mol^{-1}. Within the HF model, the 4σ MO was lower in energy than the 1π MO, with the result that for the bent geometry the LUMO was the $1a''$ MO. Hence for this geometry the lowest energy state is the singlet state, whereas for the linear structure the lowest energy state is the triplet state.

For $^3\Sigma^-$ and $^1A'$ states of $HeHO^+$ the CCSD(T)/aug-cc-pCVTZ model yielded optimized structural parameters (r_{O-H}, r_{O-He}, θ_{H-O-He}) of (1.036 Å, 2.608 Å, 180°) and (1.150 Å, 1.009 Å, 94.7°) respectively. It should be noted that we could not find a stable (or even transition state) geometry for $^1\Sigma^+$ state of $OHHe^+$ at the CCSD(T) level of theory nor could we find a local minimum for both the $^1\Sigma^+$ and $^3\Sigma^-$ states of $HOHe^+$ at this level of theory, although we have found a second-order saddle point for the $^3\Sigma^-$ state of $HOHe^+$. Also the analogous HHO ($^3\Sigma^-$) ion was found to be a transition state (with one imaginary frequency).

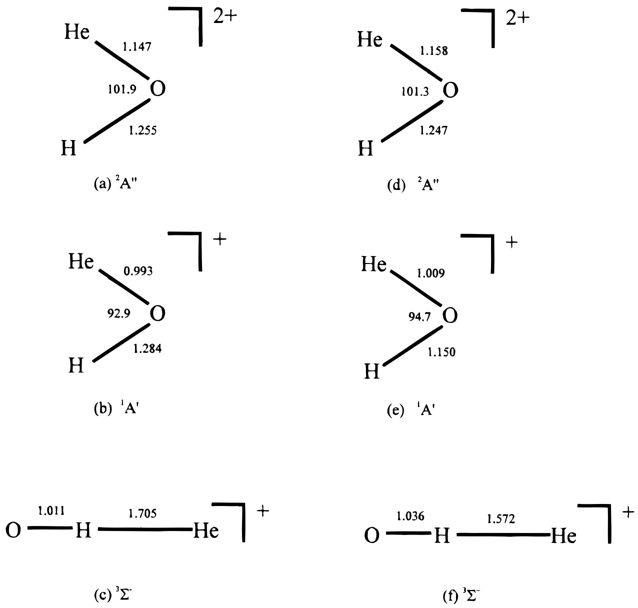

Figure 1. Optimized geometries of $HeHO^+$ and $HeHO^{2+}$ using the aug-cc-pCVTZ basis set at (a)−(c) the HF level of theory and (d)−(f) the CCSD(T) level of theory.

For the $^2A''$ ground electronic state of $HeHO^{2+}$ the optimized structural parameters were (1.247 Å, 1.158 Å, 101.3°) respectively. The calculations showed that for the bent CCSD(T) structures, the r_{O-H} and r_{O-He} bond lengths were slightly shorter and longer respectively when compared to the HF model. The reverse trend is observed for the linear structure. It is interesting to note that Koch and Frenking's[3] MP2/6-31G(d, p) calculation on He_2O^{2+} yielded structural parameters $\{r_{O-He}, \theta_{H-O-He}\}$ of (1.148 Å, 92.4°) respectively, in close agreement with those corresponding to the bent structure of $HeHO^+$. That these molecules are not just complexes of the HeH^+ moiety is evident from the CCSD(T)/aug-cc-pCVTZ level of theory, which yields the HeH^+ singlet state to be lowest in energy with a bond length of 0.776 083 Å.

Table 1 compares the various properties for the electronic states of $HeHO^+$ and $HeHO^{2+}$ using the HF and CCSD(T) methods. For all these calculations, the harmonic frequencies were real and their magnitudes sensitive to the level of theory employed and to the inclusion of diffuse functions in the basis set. For example, in the case of the bent monocation, the bend mode nearly doubled in frequency at the CCSD(T) level when compared to the HF level (i.e. 1063 compared to 547 cm^{-1} respectively). Similar large percentage discrepancies were observed for the linear structure. Hence, small variations in bond lengths and bond angle resulted in significant changes in the force constant associated with angle deformation or bond-stretching vibrational modes. Lee and Scuseria[23] 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 so employing a "correction" factor was deemed not advisable. Nevertheless, Lee and Scuseria[23] have also pointed out that for compounds containing very electronegative atoms it is necessary to include diffuse basis functions in the basis set (i.e. such as the basis set

TABLE 1: Calculated Properties of $HeHO^{n+}$ (Where n = 1, 2)

property	HF/aug-cc-pCTVZ	CCSD(T)/aug-cc-pCTVZ
(a) $HeHO^{+}(^{3}\Sigma^{-})$		
total energy[a]	−77.868921	−78.133918
ZPE[b]	5.62	5.49
sym. stretch[c]	188	242
bend[c]	228	291
asym. stretch[c]	3286	3017
(b) $HeHO^{+}(^{1}A')$		
total energy[a]	−77.741662	−78.064576
ZPE[b]	7.95	8.56
sym. stretch[c]	1478	1594
bend[c]	547	1063
asym. stretch[c]	3539	3334
(c) $HeHO^{2+}(^{2}A'')$		
total energy[a]	−76.834226	−77.116535
ZPE[b]	4.83	5.30
sym. stretch[c]	115	1263
bend[c]	891	1078
asym. stretch[c]	1372	1369

[a] Energy in hartrees. [b] Zero-point energy (ZPE) in kcal mol^{-1}. [c] Frequencies in cm^{-1}.

incorporated in these calculations) in order to describe more correctly the ionic behavior of the molecule. As these ions contain helium and as any donation of charge by the helium atom would render the helium moiety very electronegative, it is anticipated that the CCSD(T)/aug-cc-pCVTZ model would yield results more closely aligned with experiment than those obtained using basis sets without the inclusion of augmented basis functions (since the aug-cc-pCVTZ basis sets accurately model the electron affinity of first-row atoms[20]).

The first ionization energy of helium is 24.587 eV,[7] and so it is expected that the lowest energy dissociation channel of these ions is along the hydrogen oxide ion and helium reaction coordinate (which is analogous to the lowest energy reaction coordinate found by Frenking and Cremer[7] for the singlet state of He_2O^{2+}). The CCSD(T)/aug-cc-pCVTZ model yielded a helium atom ground state energy of −2.900 836 hartree. This model also yielded for the singlet and triplet state of the OH^+ fragment an energy of −75.136 411 hartree and −75.229 940 hartree at the optimized bond lengths of 1.028 84 and 1.030 72 Å, respectively. Incorporating the zero-point energy of the OH^+ fragment ions, it is possible to calculate dissociation energies for the dissociation channels:

$$HeHO^{+}\ (^{1}A') \rightarrow OH^{+}\ (^{1}\Delta) + He\ (^{1}S) \qquad D_0 = 13.1\ \text{kcal mol}^{-1}$$

$$HeHO^{+}\ (^{3}\Sigma^{-}) \rightarrow OH^{+}\ (^{3}\Sigma^{-}) + He\ (^{1}S) \qquad D_0 = 0.9\ \text{kcal mol}^{-1}$$

As the doublet and quartet states of the OH^{2+} fragment were not bound, it is clear that only the singly charge species may be confidently considered as being thermodynamically stable.

The simple donor−acceptor model of Frenking, Koch, and co-workers[3−8] employs the fragment ion as the acceptor, with helium atom donating electron density into the fragment ion's LUMO structure. For these molecules, the OH fragment ion has the MO structure $1\sigma(O1s)2\sigma(O2s)3\sigma(O2p_\sigma{+}H1s)1\pi(O2p_\pi)$. For the bent structures, the approaching helium atom would split the π MO's on the OH fragment ion, enabling electron donation into a π component along the $r_{\pi-He}$ reaction coordinate. The use of this simple approach suggests that for $HeHO^+$ the bond angle would be in the vicinity of 90° (with the widening of the θ_{H-O-He} bond angle in $HeHO^{2+}$ being indicative of the reduction in the in-plane bond pair−lone pair repulsions). Although such qualitative models give insight into bonding characteristics of the these hydrogen helide ions, care must be taken not to overinterpret these configuration interaction results using these such simple models.

Acknowledgment. Calculations were performed using the VAX 3100 workstation, Sun workstations, and VP2200; the VAX was made available by the generous support of the Australian Research Grants Scheme, the Suns by the generous support of the Engineering Faculty, and the VP by generous support of the ANU. We wish to acknowledge the University of Newcastle scholarship held by J.M.H.

References and Notes

(1) Young, S. E. *Int. J. Mass Spectrom. Ion Processes* **1986**, *74*, 137.
(2) Clampitt, R.; Jefferies, D. K. *Nature* **1970**, *226*, 141.
(3) Koch W.; Frenking, G. *J. Chem. Soc., Chem. Commun.* **1986**, 1095.
(4) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D.; Collins, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5917.
(5) Frenking, G.; Koch, W.; Cremer, D.; Gauss J.; Liebman, J. F. *J. Phys. Chem.* **1989**, *93*, 3397.
(6) Frenking, G.; Koch, W.; Reichel, F.; Cremer, D. *J. Am. Chem. Soc.* **1990**, *112*, 4240.
(7) Frenking, G.; Cremer, D. In *Structure and Bonding*; Springer: Heidleberg, 1990; Vol. 73.
(8) Frenking, G.; Koch, W.; Liebman, J. F. In *From Atoms to Polymers*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1989.
(9) Hughes, J. M.; von Nagy-Felsobuki, E. I. *J. Mol. Struct: THEOCHEM*, in press.
(10) Hughes, J. M.; von Nagy-Felsobuki, E. I. *Chem. Phys.*, in press.
(11) Hughes, J. M.; von Nagy-Felsobuki, E. I. *J. Mol. Struct. THEOCHEM*, in press.
(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Ciolowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S. Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*; GAUSSIAN,Inc.: Pittsburgh, PA, 1995.
(13) Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 35.
(14) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.
(15) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697.
(16) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
(17) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1994**, *100*, 2975 and references therein.
(18) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1995**, *103*, 4572.
(19) 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 Nortwest Laboratory, P. O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram Laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76LO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.
(20) Kendall, R. A.; Dunning, T. H. *J. Chem. Phys.* **1992**, *96*, 6796.
(21) Martin, J. M. L. *Chem. Phys. Lett.* **1995**, *242*, 343.
(22) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163.
(23) Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic Publishers: Dordrecht, 1995.