

# Helium Bonding in Singly and Doubly Charged First-Row Diatomic Cations $\text{HeX}^{n+}$ (X = Li-Ne; $n = 1, 2$ )

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With the use of ab initio calculations at the MP4(SDTQ)/6-311G(2df,2pd)//MP2/6-31G(d,p) level of theory, equilibrium geometries, dissociation energies, and vibrational frequencies are reported for singly and doubly charged  $\text{HeX}^{n+}$  cations (X = Li-Ne;  $n = 1, 2$ ). The calculations were performed for the electronic ground states and selected excited states of  $\text{HeX}^{n+}$ . The trends in the interatomic distances and bond strengths of the helium bonds are discussed in terms of donor-acceptor interactions between neutral He as the donor and the cationic  $\text{X}^{n+}$  fragment as the acceptor. In addition, the mechanism of bonding is analyzed by utilizing the properties of the calculated electron density  $\rho(\mathbf{r})$  and its associated Laplace concentration  $-\nabla^2\rho(\mathbf{r})$ .  $\text{HeX}^+$  ions in their ground states represent van der Waals complexes stabilized by charge-induced dipole interactions. In those excited states in which  $\text{X}^+$  becomes a stronger acceptor, covalent bonds are predicted. In contrast to the singly charged  $\text{HeX}^+$  ground-state species, all  $\text{HeX}^{2+}$  dications investigated in this work can be considered as covalently bonded molecules. Calculated properties of  $\text{HeX}^{n+}$  such as interatomic distances  $r_e$  and dissociation energies  $D_e$  are nicely explained within the donor-acceptor model. The results show that the electronic structure of  $\text{X}^{n+}$  is more important for the stability of the corresponding  $\text{HeX}^{n+}$  system than the positive charge of  $\text{X}^{n+}$ .

## Introduction

In recent theoretical studies<sup>1,2</sup> of the structures, stabilities, and bonding of singly and doubly charged cations as well as neutral molecules containing helium, it was predicted that He may be bound very strongly in positively charged compounds such as  $\text{HeCCHe}^{2+}$ ,  $\text{HeCC}^{2+}$ , and  $\text{HeCCH}^+$  and that even a neutral He compound,  $\text{HeBeO}$ , is stable toward dissociation. The analysis of the helium bonds in a variety of molecules showed that the strength of the He-X bond is primarily determined by its electronic structure rather than the charge or electronegativity of X. Only when X provides low-lying empty orbitals suitable for donor-acceptor interactions with the weak electron donor He is a helium bond formed. For example, the He,X bonds in  $\text{HeCCHe}^{2+}$ ,  $\text{HeNNHe}^{2+}$ , and  $\text{HeOOHe}^{2+}$  become much weaker in this order, which is opposite to changes in the H,X bond strength encountered for the isoelectronic hydrogen compounds  $\text{HCCH}$ ,  $\text{HNNH}$ , and  $\text{HOOH}$ .<sup>2</sup> This may be explained by the increase in the number of occupied  $\sigma$  orbitals from  $\text{CC}^{2+}$  to  $\text{NN}^{2+}$  and  $\text{OO}^{2+}$ . The dominant principle of helium bonding, that is, donor-acceptor interactions, is clearly different from that of hydrogen chemistry.<sup>3</sup> Helium chemistry is also different from the chemistry of the heavier noble-gas elements. For example, for xenon strong bonds are found only when Xe combines with strongly electronegative elements such as fluorine and oxygen.<sup>4</sup> In this paper, we present the results of our ab initio study on first-row mono- and dications  $\text{HeX}^{n+}$  ( $n = 1, 2$ ) comprising a "first-row sweep" of X from Li to Ne. We calculated the ground states and, for most systems, the first excited states of  $\text{HeX}^{n+}$ . The results, in particular the interatomic distances  $r_e$  and dissociation energies  $D_e$ , are discussed in terms of donor-acceptor interactions.

Several theoretical studies of diatomic cations  $\text{HeX}^{n+}$  containing first-row elements X have been published, although most work has been carried out at the Hartree-Fock level only.<sup>5</sup>  $\text{HeLi}^+$  was the subject of several theoretical studies<sup>6</sup> with four of them<sup>6c,d,f,h</sup> carried out with explicit inclusion of correlation energy. One pseudopotential study for  $\text{HeLi}^+$  has been reported.<sup>6i</sup>  $\text{HeLi}^+$  is one of the very few  $\text{HeX}^{n+}$  systems investigated here for which experimental data are available: Results from scattering experiments<sup>7</sup> indicate a potential well of 1.1-1.6 kcal/mol at equilibrium

(1) (a) Koch, W.; Frenking, G. *Int. J. Mass Spectrom. Ion Processes* **1986**, *74*, 133. (b) Koch, W.; Frenking, G. *J. Chem. Soc., Chem. Commun.* **1986**, 1095. (c) Koch, W.; Frenking, G.; Luke, B. T. *Chem. Phys. Lett.* **1987**, *139*, 149.

(2) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D.; Collins, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5917.

(3) A systematic comparison of isoelectronic hydrogen and helium (1+) compounds is presented by the following: Frenking, G.; Koch, W.; Liebman, J. F. In *Molecular Structure and Energetics: Isoelectronic and Plemioelectronic Reasoning*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, in press.

(4) (a) Bartlett, N. *The Chemistry of the Noble Gases*; Elsevier: Amsterdam, 1971. (b) Holloway, J. H. *Chem. Br.* **1987**, 658. (c) Holloway, J. H. *Noble Gas Chemistry*; Methuen: London, 1968.

(5) A compilation of experimental and theoretical studies on noble-gas compounds including those of helium up to 1976 is presented by: Hawkins, D. T.; Falconer, W. E.; Bartlett, N. *Noble-Gas Chemistry. A Bibliography: 1962-1976*; IFI/Plenum: New York, 1978.

(6) (a) Catlow, C. W.; McDowell, M. R. C.; Kaufman, J. J.; Sachs, L. M.; Chang, E. S. *J. Phys. B* **1970**, *3*, 833. (b) Krauss, M.; Maldonado, P.; Wahl, A. C. *J. Chem. Phys.* **1971**, *54*, 4944. (c) Hariharan, P. C.; Staemmler, V. *Chem. Phys.* **1976**, *15*, 409. (d) Senff, U. E.; Burton, P. G. *Mol. Phys.* **1986**, *58*, 637. (e) Pyykko, P.; Sundholm, D.; Laaksonen, I. *Mol. Phys.* **1987**, *60*, 597. (f) Tatewaki, H.; Tanaka, K.; Ohno, Y.; Nkamura, T. *Mol. Phys.* **1984**, *53*, 233. (g) Viehland, L. A. *Chem. Phys.* **1983**, *78*, 279. (h) Cooper, D. L.; Gerratt, J.; Raimondi, M. *Mol. Phys.* **1985**, *56*, 611. (i) Fuentealba, P. *J. Phys. B* **1986**, *L235*.

(7) (a) Dalgarno, A.; McDowell, M. R. C.; Williams, A. *Phil. Trans. R. Soc. London, A* **1958**, *250*, 411. (b) Mason, E. A.; Schamp, H. W., Jr. *Ann. Phys.* **1958**, *4*, 233. (c) Polark-Dingels, P.; Rajan, M. S.; Gislason, E. A. *J. Chem. Phys.* **1982**, *77*, 3983.

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geometries between 1.95 and 2.22 Å. No theoretical or experimental data have been published for doubly charged HeLi<sup>2+</sup>.

In case of HeBe<sup>n+</sup>, some theoretical studies have been carried out for doubly charged HeBe<sup>2+</sup>,<sup>8</sup> one of them<sup>8d</sup> at a correlated level. Only one LCAO study has been reported for HeB<sup>+</sup>,<sup>9</sup> but none have been reported for the dication HeB<sup>2+</sup>.

A number of theoretical studies are available for HeC<sup>n+</sup>.<sup>1,10</sup> Hartree-Fock calculations on HeC<sup>+</sup> and HeC<sup>2+</sup> have been reported by Harrison et al.<sup>10a</sup> and by Cooper and Wilson,<sup>10b</sup> who also presented results for singly and doubly charged HeN<sup>n+</sup> and HeO<sup>n+</sup>. Correlated studies have recently been presented for HeC<sup>+1a,2,10c</sup> and HeC<sup>2+1b,2</sup> and a CASSCF investigation of the low-lying electronic states of HeC<sup>2+</sup> was published by two of the present authors.<sup>1c</sup>

Liebman and Allen<sup>11a,b</sup> discussed HeN<sup>+</sup> in several electronic states based on LCAO calculations, and they compared their results for HeN<sup>+</sup> with HeO<sup>+</sup> and HeF<sup>+</sup>. Other theoretical data on HeN<sup>+</sup> are available, at both the SCF<sup>10b</sup> and correlated level.<sup>1b,2</sup> The only results for doubly charged HeN<sup>2+</sup> have been reported by Cooper and Wilson.<sup>10b</sup>

The potential energy curves for all valence states of HeO<sup>+</sup> have been calculated with a minimum basis set and full configuration interaction by Augustin et al.<sup>12a</sup> Several LCAO<sup>10b,11,12b,c</sup> studies as well as correlation corrected<sup>1b,2</sup> calculations on HeO<sup>+</sup> have been published. In addition, two theoretical studies of doubly charged HeO<sup>2+</sup> are known to us.<sup>10b,12c</sup>

The singly charged HeF<sup>+</sup> has been studied theoretically at the SCF level by Liebman and Allen.<sup>11</sup> A subsequent experimental attempt by Berkowitz and Chupka<sup>13a</sup> to detect HeF<sup>+</sup> in the gas phase failed, and an earlier report<sup>13b</sup> that claimed the observation of HeF<sup>+</sup> was questioned.<sup>13a</sup> No theoretical data of HeF<sup>2+</sup> are available.

Ab initio calculations<sup>14a-i</sup> have been performed for HeNe<sup>+</sup>, and a theoretical model<sup>14j</sup> to estimate the low-lying electronic states of HeNe<sup>+</sup> has been introduced. Also experimental data for the spectroscopic constants of HeNe<sup>+</sup> are available.<sup>15</sup> The potential energy surface of doubly charged HeNe<sup>2+</sup> has been investigated in two theoretical studies at the SCF-CI level.<sup>16</sup>

Previous theoretical investigations do not provide sufficient knowledge about helium bonding in ground and excited states of first-row cations HeX<sup>n+</sup>. In particular, few studies address the problem of a systematic comparison of HeX<sup>n+</sup> along the first-row elements. Only the papers by Liebman and Allen<sup>11</sup> about HeN<sup>+</sup>,

HeO<sup>+</sup>, HeF<sup>+</sup> and by Cooper and Wilson<sup>10b</sup> about HeC<sup>n+</sup>, HeN<sup>n+</sup>, HeO<sup>n+</sup> compare the trends in interatomic distances and dissociation energies. In the latter paper, the authors conclude that "The various trends in stability are easily understood in terms of the effective nuclear charges on the two centres."<sup>10b</sup> As shown later in the present paper, this conclusion is misleading because it compares the ground states of HeC<sup>+</sup> and HeN<sup>+</sup> with the excited state of HeO<sup>+</sup>. It will become clear from our calculated results for ground and excited states of HeX<sup>n+</sup> that the trends in interatomic distances and dissociation energies are primarily a function of the electronic state of X<sup>n+</sup> rather than the electronic charge. This is true for very weakly bounded systems with binding energies of 1 kcal/mol or less as well as strongly bound, covalent molecules. By application of the model of donor-acceptor interactions in helium molecules, useful predictions on bonding and the nature of He,X<sup>n+</sup> interactions can be made.

We want to comment on the accuracy of the calculated data presented here. Our theoretical results for the equilibrium geometries and dissociation energies of HeX<sup>n+</sup> cations are certainly more reliable and accurate than earlier studies carried out mostly at the Hartree-Fock LCAO level.<sup>6,8-12,14</sup> In a recent theoretical study<sup>17</sup> of the atomization energies of hydrides XH<sub>n</sub> (X = Li-F) at a comparable level of theory, dissociation energies *D*<sub>0</sub> have been predicted that differ from experiment by less than 2 kcal/mol. However, the calculated stabilization energies of some HeX<sup>+</sup> cations in their ground states are in the range of 2 kcal/mol. These species are bound by charge-induced dipole interactions between X<sup>+</sup> and He. The calculated data can only be assumed to be reliable if the theoretical level predicts accurately the atomic polarizability of helium. As shown later, this is the case for the theoretical method used in our study. Nevertheless, our primary goal is an analysis of the *trends* in interatomic distances and bond strength rather than the spectroscopic accuracy of the calculated properties. The major purpose of this paper is to provide an understanding of bonding in helium-containing molecules and to show how the model of donor-acceptor interactions previously used<sup>2</sup> for the analysis of helium bonding can be employed to predict qualitatively and even semiquantitatively trends in first-row diatomic cations HeX<sup>n+</sup>. For a more quantitative description of the ground and excited states of HeX<sup>n+</sup> molecules, the complete potential energy curves have to be computed with multireference methods such as CASSCF or MRD-CI. We have recently started to carry out such studies.<sup>1c</sup> The results obtained<sup>1c</sup> by the CASSCF method for the equilibrium distances and dissociation energies of the X<sup>1</sup>Σ<sup>+</sup> ground state and <sup>3</sup>Π excited state of HeC<sup>2+</sup> are in excellent agreement with the results reported here. This gives us confidence in the accuracy of our calculated data.

We also want to comment on the use of the term "donor-acceptor" interactions in the context of our investigation. Generally, the notation of a donor and acceptor fragment implies interactions between a Lewis acid-base pair.<sup>18</sup> Donor-acceptor complexes constitute an important area of inorganic chemistry.<sup>19</sup> The acceptor fragment is usually a neutral or cationic metal atom, and the donor fragment is often an atom or molecule with a high-lying doubly occupied orbital such as the "lone-pair" orbitals of CO, CN, Cl<sup>-</sup>, etc.<sup>20a</sup> These interactions are often discussed in terms of the frontier orbitals of the donor and acceptor fragments, i.e., the highest occupied molecular orbital (HOMO) of the donor, and the lowest unoccupied molecular orbital (LUMO) of the acceptor.<sup>20</sup> In the present case, the donor fragment is the He atom and the acceptor fragment is the singly or doubly charged X<sup>n+</sup> cation. Our donor-acceptor model of HeX<sup>n+</sup> is primarily based on a frontier orbital description of the possible interactions between He and X<sup>n+</sup>. Accordingly, trends in the calculated He,X

(8) (a) Hayes, E. F.; Gole, J. L. *J. Chem. Phys.* **1971**, *55*, 5132. (b) Harrison, S. W.; Massa, L. J.; Solomon, P. *J. Chem. Phys.* **1973**, *59*, 263. (c) Alvarez-Rizzatti, M.; Mason, E. A. *J. Chem. Phys.* **1975**, *63*, 5290. (d) Schleyer, P. v. R. *Adv. Mass Spectrom.* **1985**, *10a*, 287.

(9) Liebman, J. F.; Allen, L. C. *Inorg. Chem.* **1972**, *11*, 1143.

(10) (a) Harrison, S. W.; Henderson, G. A.; Masson, L. J.; Solomon, P. *Astrophys. J.* **1974**, *189*, 605. (b) Cooper, D. L.; Wilson, S. *Mol. Phys.* **1981**, *44*, 161. (c) Wong, M. W.; Nobes, R. H.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1987**, 233.

(11) (a) Liebman, J. F.; Allen, L. C. *J. Am. Chem. Soc.* **1970**, *92*, 3539. (b) Liebman, J. F.; Allen, L. C. *Int. J. Mass Spectrom. Ion Phys.* **1971**, *7*, 27.

(12) (a) Augustin, S. D.; Miller, W. H.; Pearson, P. K.; Schaefer, H. F., III *J. Chem. Phys.* **1973**, *58*, 2845. (b) Fereday, R. J.; Sinha, S. P. *J. Chim. Phys.* **1977**, *74*, 88. (c) Masse, J. L.; Masse-Baerlocher, M. *J. Chim. Phys.* **1967**, *64*, 417.

(13) (a) Berkowitz, J.; Chupka, W. *Chem. Phys. Lett.* **1970**, *7*, 447. (b) Bochin, V. P.; Zakurin, N. V.; Kapyshev, V. K. *Russ. J. High Energy Chem.* **1967**, *1*, 159.

(14) (a) Olson, R. E.; Smith, F. T. *Phys. Rev. A* **1971**, *3*, 1607. (b) Sidis, V.; Lefebvre-Brion, H. *J. Phys. B* **1971**, *4*, 1040. (c) Gaussorgues, C. *J. Phys. B* **1973**, *6*, 675. (d) Bobbio, S. M.; Doverspike, L. D.; Champion, R. L. *Phys. Rev. A* **1973**, *7*, 526. (e) Blint, B. J. *Phys. Rev. A* **1976**, *14*, 971. (f) Barat, M.; Brenot, J. C.; Dhucq, D.; Pommier, J.; Sidis, V.; Olson, R. E.; Shipsec, E. J.; Browne, J. C. *J. Phys. B* **1976**, *9*, 269. (g) Cooper, D. L.; Wilson, S. *J. Chem. Phys.* **1982**, *76*, 6088. (h) Kuntz, P. J.; Doran, M.; Hillier, I. H. *Chem. Phys.* **1979**, *43*, 197. (i) Kendrick, J.; Kuntz, P. J. *J. Chem. Phys.* **1979**, *70*, 736. (j) Hausamann, D.; Morgner, H. *Mol. Phys.* **1985**, *54*, 1085.

(15) (a) Dabrowski, I.; Herzberg, G. *J. Mol. Spectrosc.* **1978**, *73*, 183. (b) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(16) (a) Montabonel, M.-C. B.; Cimiriaglia, R.; Persico, M. *J. Phys. B* **1984**, *17*, 1931. (b) Cimiriaglia, R.; Malrieu, J.-P.; Persico, M.; Spiegelmann, F. *J. Phys. B* **1985**, *18*, 3073.

(17) Pople, J. A.; Frisch, M. J.; Luke, B. T.; Binkley, J. S. *Int. J. Quant. Chem. Quantum Chem. Symp.* **1983**, *17*, 307.

(18) Jensen, W. B. *Chem. Rev.* **1978**, *78*, 1.

(19) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.

(20) (a) Hoffmann, R.; Chen, M. M.-L. *Inorg. Chem.* **1977**, *16*, 503. (b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.

distances and dissociation energies are rationalized by investigating the properties of the LUMO of X<sup>n+</sup>.

Although the frontier orbital description of cations HeX<sup>n+</sup> is both simple and useful, a caveat in this connection is necessary. Investigation of the LUMO of X<sup>n+</sup> does not reveal whether interactions between He and X<sup>n+</sup> are those typical of a van der Waals complex or a covalently bonded molecule. In the first case, there is hardly any transfer of negative charge from He to X<sup>n+</sup> and, therefore, one may doubt the usefulness of a frontier orbital approach. The stability of a van der Waals complex is dominated by electrostatic interactions, in the case of HeX<sup>n+</sup> by charge-induced dipole attractions. These in turn depend on the anisotropy of the electron density distribution of X<sup>n+</sup>. If the electrons of X<sup>n+</sup> are isotropically arranged, interactions will be relatively low. However, if there is a hole in the electronic structure of X<sup>n+</sup> in the direction of an approaching He atom, attraction will be relatively strong.

It is reasonable to assume that shape and energy of the LUMO of X<sup>n+</sup> are related to the location and depth of a hole in the electronic structure. We will elaborate this point by investigating the Laplace concentration of the electrons, which is given by the negative Laplacian of the electron density distribution  $\rho(\mathbf{r})$ , namely,  $-\nabla^2\rho(\mathbf{r})$ .<sup>21</sup> It has been shown that the lumps in the Laplace concentration can be associated with inner shell, bonding, and lone-pair electrons. Concentration holes in the valence region of an atom ( $\nabla^2\rho(\mathbf{r}) > 0$ ) indicate those locations that are prone to a nucleophilic attack. They are the result of the electron configuration of an atom; i.e., they depend on the shape of the occupied MOs. Since the LUMO is orthogonal to all occupied MOs, it possesses its largest amplitude where the Laplace concentration indicates the holes in the valence electronic structure. The larger and the deeper a valence shell hole is, the stronger should be the acceptor ability of the respective atom and a possible donor-acceptor bond. Even if such a donor-acceptor bond can be established, the hole will influence charge polarization at the donor and, therefore, electrostatic interactions between a potential donor such as He and a potential acceptor such as X<sup>n+</sup>. In short, the LUMO of X<sup>n+</sup> is not only responsible for the extent of charge transfer between donor and acceptor but also for charge-induced dipole attractions in a van der Waals complex.<sup>22</sup>

A frontier orbital analysis is satisfactory in all those cases, in which only relatively few MO interactions have to be considered as is the case in HeX<sup>n+</sup>. Nevertheless, we will substantiate the conclusions drawn from the analysis of the frontier orbitals by investigation of the Laplace concentration, which comprises the effects of all occupied MOs and which immediately reveals failures of the frontier orbital approach.<sup>21</sup> In addition, investigation of the Laplace concentration in connection with the corresponding analysis of  $\rho(\mathbf{r})$  provides a basis to distinguish between bonding and closed-shell interactions and to describe the nature of the He,X bond in a unique and quantitative way. This has already been demonstrated in the case of the He,C bound in helium organic cations.<sup>2</sup> As described in more detail elsewhere,<sup>23</sup> we expect a covalent bond (a) if there exists a path of maximum electron density (MED) between the corresponding atomic nuclei (necessary condition) and (b) if the energy density  $H(\mathbf{r})$  is found to be stabilizing ( $H(\mathbf{r}) < 0$ ) at the path critical point (sufficient condition).

A MED path is always found between bonded atoms, and therefore, it can be considered as an image of the chemical bond. It can be characterized by the properties of  $\rho(\mathbf{r})$  at the path critical point  $\mathbf{r}_b$ , which corresponds to a saddle point of  $\rho(\mathbf{r})$ : The electron density adopts a minimum along the path at  $\mathbf{r}_b$  but is a maximum

in all directions perpendicular to the MED path. If conditions a and b are fulfilled, we will denote  $\mathbf{r}_b$  as a bond critical point and we will characterize the corresponding bond by the electron density  $\rho(\mathbf{r}) = \rho_b$ , the Laplace concentration  $\nabla^2\rho(\mathbf{r}_b) = \nabla^2\rho_b$ , and the energy density  $H(\mathbf{r}_b) = H_b$ .

Since it is very difficult to determine the amount of negative charge transferred from He to X<sup>n+</sup> (see next section), we will describe all cations investigated within the donor-acceptor model outlined above, no matter whether a covalently bonded cation or a van der Waals complex is predicted.

A final word shall be said concerning the use of the term "stable" in the context of our investigation. We consider a HeX<sup>n+</sup> species as thermodynamically stable if its energy is lower than all possible dissociation products in every electronic state, even if such a dissociation is a spin and/or spatial symmetry forbidden reaction. If a local minimum is found, but at a higher energy than the energetically lowest-lying combination of the respective product ions, we call this species metastable or kinetically stable. This is the case for many dications and for the excited states of the singly charged HeX<sup>+</sup> molecules. Such species might still be observable if a sufficiently high activation barrier prevents spontaneous dissociation. With one exception transition states have not been calculated because we think that a multiconfiguration method should be employed especially for the doubly charged cations. Such calculations are part of our ongoing studies of multiply charged cations.<sup>24</sup>

### Theoretical Methods

Standard ab initio calculations have been performed using the programs GAUSSIAN 82<sup>25</sup> and COLOGNE 87.<sup>26</sup> Equilibrium geometries and vibrational frequencies have been obtained at MP2/6-31G(d,p). The latter data and the corresponding zero-point energies (ZPE) are scaled by a factor of 0.93.<sup>27</sup> For a few higher lying states with the same spin symmetry as the ground state, numeric differentiation leads to oscillations between different electronic states. In these cases minima were verified by energy calculations with a slightly different bond length than the equilibrium distance. Single-point energy calculations for ions XHe<sup>n+</sup> and their atomic fragments were carried out at the MP4-(SDTQ)/6-311G(2df,2pd) level using MP2/6-31G(d,p) optimized geometries. Basis set superposition errors (BSSE) have been estimated by using the counterpoise method.<sup>28</sup>

The dissociation energies  $D_0$  have been calculated in most cases as the energy differences between the HeX<sup>n+</sup> cation and the respective atomic fragments in the corresponding electronic state at MP4(SDTQ)/6-311G(2df,2pd)//MP2/6-31G(d,p), corrected by ZPE and BSSE data. In a few cases where excited D states of X<sup>n+</sup> were involved, we have chosen a different method. Because D states are poorly described when only one determinant is used, we calculated the dissociation energy yielding the respective ground state of X<sup>n+</sup> and subtracted the experimentally determined<sup>29</sup> excitation energy for X<sup>n+</sup>.

The electron density distribution,  $\rho(\mathbf{r})$ , its associated Laplace concentration,  $-\nabla^2\rho(\mathbf{r})$ , and the energy density,  $H(\mathbf{r})$ , have been analyzed along the lines established earlier.<sup>21,23,30</sup> First, the MED paths and the corresponding path critical points have been determined. Then, the energy density has been analyzed and, finally, the Laplace concentration in the valence shell and the bonding

(24) (a) Koch, W.; Frenking, G.; Chang, C. C. *J. Chem. Phys.* **1986**, *84*, 2703. (b) Koch, W.; Frenking, G. *J. Chem. Phys.* **1987**, *86*, 5617. (c) Koch, W.; Liu, B.; Frenking, G. *J. Chem. Phys.* Submitted for publication.

(25) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82; Carnegie-Mellon University: Pittsburgh, PA.

(26) Gauss, J.; Kraka, E.; Cremer, D. COLOGNE 87; Universität Köln.

(27) Hout, R. F.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234.

(28) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(29) Moore, C. E. *Atomic Energy Levels*; National Bureau of Standards; U.S. Government Printing Office: Washington, DC, 1971; NSRDS-NBS 35.

(30) (a) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1984**, *106*, 1594. (b) Bader, R. F. W.; Essen, H. *J. Chem. Phys.* **1984**, *80*, 1943.

(21) Cremer, D. In *Theoretical Models of Chemical Bonding*; Springer Verlag: Heidelberg, in press.

(22) This has been found a useful approach when investigating van der Waals complexes of He, Ne, and Ar: Frenking, G.; Koch, W.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1988**, *110*, 8007.

(23) (a) Cremer, D.; Kraka, E. In *Conceptual Approaches in Quantum Chemistry Models and Applications*. *Croat. Chem. Acta* **1984**, *57*, 1259. (b) Cremer, D. In *Modelling of Structure and Properties of Molecules*; Maksic, Z. B., Ed.; Ellis Horwood: Chichester, 1987; p 87.

**TABLE I: Theoretically Determined Bond Lengths,  $r_e$  (in Å), Total Energies,  $E_{\text{tot}}$  (in hartrees), Zero-Point Vibrational Energies, ZPE, BSSE Data, and Dissociation Energies,  $D_0$  (in kcal/mol), for Low-Lying Electronic States of HeX<sup>+</sup> Monocations (Calculated Total Energies of Atomic Fragments)**

struct	sym	MP2/6-31G(d,p)			MP4/6-311G(2df,2pd) <sup>a</sup>		
		$r_e$	$E_{\text{tot}}$	ZPE	$E_{\text{tot}}$	BSSE	$D_0$
HeLi <sup>+</sup>	X <sup>1</sup> Σ <sup>+</sup>	2.062	-10.1190	0.3	-10.1356	0.1	+1.2
HeBe <sup>+</sup>	X <sup>2</sup> Σ <sup>+</sup>	3.132	-17.1597	0.1	-17.1740	0.1	+0.2
HeBe <sup>+</sup>	<sup>2</sup> Π	1.415	-17.0343		-17.0522	0.2	+15.6 <sup>b</sup>
HeB <sup>+</sup>	X <sup>1</sup> Σ <sup>+</sup>	2.912	-27.1526	0.1	-27.1877	0.1	+0.4
HeB <sup>+</sup>	<sup>3</sup> Π	1.454	-27.0084	0.6	-27.0306	0.2	+5.0
HeC <sup>+</sup>	X <sup>2</sup> Π	2.406	-40.2161	0.2	-40.2615	0.1	+0.9
HeC <sup>+</sup>	<sup>4</sup> Σ <sup>-</sup>	1.168	-40.0828	1.7	-40.1177	0.3	+27.6
HeN <sup>+</sup>	X <sup>3</sup> Σ <sup>-</sup>	1.749	-56.8143	0.4	-56.8797	0.3	+3.7
HeN <sup>+</sup>	<sup>3</sup> Π	1.007	-56.4859		-56.5638	0.9	+68.9 <sup>b</sup>
HeO <sup>+</sup>	X <sup>4</sup> Σ <sup>-</sup>	2.473	-77.2875	0.2	-77.3737	0.1	+0.6
HeO <sup>+</sup>	<sup>2</sup> Π	1.191	-77.1517	2.6	-77.2587	1.0	+1.8
HeF <sup>+</sup>	X <sup>3</sup> Π	2.123	-101.7532	0.2	-101.8779	0.3	+1.2
HeF <sup>+</sup>	<sup>1</sup> Σ <sup>+</sup>	1.024	-101.7144	2.4	-101.8576	1.1	+45.1
HeNe <sup>+</sup>	X <sup>2</sup> Σ <sup>+</sup>	1.406	-130.7464	1.3	-130.9196	1.3	+9.1
Li <sup>+</sup>	<sup>1</sup> S		-7.2359		-7.2358		
Be <sup>+</sup>	<sup>2</sup> S		-14.2786		-14.2762		
Be <sup>+</sup>	<sup>2</sup> P		-14.1319		-14.1298		
B <sup>+</sup>	<sup>1</sup> S		-24.2715		-24.2896		
B <sup>+</sup>	<sup>3</sup> P		-24.1230		-24.1242		
C <sup>+</sup>	<sup>2</sup> P		-37.3344		-37.3624		
C <sup>+</sup>	<sup>4</sup> P		-37.1640		-37.1733		
N <sup>+</sup>	<sup>3</sup> P		-53.9293		-53.9755		
O <sup>+</sup>	<sup>4</sup> S		-74.4062		-74.4751		
F <sup>+</sup>	<sup>3</sup> P		-98.8712		-98.9780		
Ne <sup>+</sup>	<sup>2</sup> P		-127.8494		-128.0037		
He	<sup>1</sup> S		-2.8806		-2.8972		

<sup>a</sup> At MP2/6-31G(d,p) optimized geometries. <sup>b</sup>  $D_e$  value (without correction for ZPE).

region has been investigated. This three-step approach has been found very useful when describing bonding in hydrocarbons,<sup>31</sup> Si-containing molecules,<sup>32</sup> three-membered rings and  $\pi$ -complexes,<sup>33</sup> dications,<sup>34</sup> He organic compounds,<sup>2</sup> van der Waals complexes,<sup>35</sup> and many other systems.<sup>21</sup>

The electron density,  $\rho(\mathbf{r})$ , has been investigated at the Hartree-Fock level throughout, although in some cases (e.g., HeNe<sup>+</sup>, HeNe<sup>m+</sup>) correlation corrections to  $\rho(\mathbf{r})$  turned out to be important. These cases have not been pursued since the calculation of correlation corrected electron density distributions is beyond the scope of the present work. For the same reason, only estimates of partial charges have been obtained on the basis of a Mulliken population analysis.<sup>36</sup> The Mulliken values do not comprise correlation effects. In addition, they strongly depend on the basis set used (functions located at one atom may describe charge distributions at the other atom) and the artificial dissection of the overlap populations.<sup>36</sup> Numerical integration of a correlation corrected electron density over a quantum mechanically defined atomic basis would yield better atomic charges. However, the numerical effort is far too large to justify these calculations. Therefore, we content ourselves with a qualitative discussion of the Mulliken populations.

### Singly Charged HeX<sup>+</sup> Cations

Table I shows the theoretically predicted interatomic distances and energies for ground and selected excited states of monocations HeX<sup>+</sup>. The excited states discussed here have been chosen because they are well suited to demonstrate the donor-acceptor interactions in helium cations. The calculated dissociation energies  $D_e$  and  $D_0$ , which are corrected by the values for the respective BSSE, refer to the dissociation of HeX<sup>+</sup> into He and X<sup>+</sup> in the corresponding electronic states as shown in Chart I. The total energies

**CHART I: Dissociation Reactions of Ground and Excited States of HeX<sup>+</sup> Cations: Calculated Dissociation Energies  $D_0$  and  $D_e$  (in kcal/mol) at MP4(SDTQ)/6-311G(2df,2pd)//MP2/6-31G(d,p) and Theoretically Predicted Charge-Induced Dipole Interaction Energies,  $E_{\text{ind}}$  (in kcal/mol)**

	$D_0$	$D_e$	$E_{\text{ind}}$
HeLi <sup>+</sup> (X <sup>1</sup> Σ <sup>+</sup> ) → He( <sup>1</sup> S) + Li <sup>+</sup> ( <sup>2</sup> S)	+1.2	+1.5	+1.9
HeBe <sup>+</sup> (X <sup>2</sup> Σ <sup>+</sup> ) → He( <sup>1</sup> S) + Be <sup>+</sup> ( <sup>2</sup> S)	+0.2	+0.3	+0.4
HeBe <sup>+</sup> ( <sup>2</sup> Π) → He( <sup>1</sup> S) + Be <sup>+</sup> ( <sup>2</sup> P)		+15.6	+8.5
HeB <sup>+</sup> (X <sup>1</sup> Σ <sup>+</sup> ) → He( <sup>1</sup> S) + B <sup>+</sup> ( <sup>1</sup> S)	+0.4	+0.5	+0.5
HeB <sup>+</sup> ( <sup>3</sup> Π) → He( <sup>1</sup> S) + B <sup>+</sup> ( <sup>3</sup> P)	+5.0	+5.6	+7.6
HeC <sup>+</sup> (X <sup>2</sup> Π) → He( <sup>1</sup> S) + C <sup>+</sup> ( <sup>2</sup> P)	+0.9	+1.1	+1.0
HeC <sup>+</sup> ( <sup>4</sup> Σ <sup>-</sup> ) → He( <sup>1</sup> S) + C <sup>+</sup> ( <sup>4</sup> P)	+27.6	+29.3	+18.3
HeN <sup>+</sup> (X <sup>3</sup> Σ <sup>-</sup> ) → He( <sup>1</sup> S) + N <sup>+</sup> ( <sup>3</sup> P)	+3.7	+4.1	+3.6
HeN <sup>+</sup> ( <sup>3</sup> Π) → He( <sup>1</sup> S) + N <sup>+</sup> ( <sup>3</sup> D)		+68.9 <sup>a</sup>	+33.1
HeO <sup>+</sup> (X <sup>4</sup> Σ <sup>-</sup> ) → He( <sup>1</sup> S) + O <sup>+</sup> ( <sup>4</sup> S)	+0.6	+0.8	+0.9
HeO <sup>+</sup> ( <sup>2</sup> Π) → He( <sup>1</sup> S) + O <sup>+</sup> ( <sup>2</sup> D)	+1.8 <sup>a</sup>	+4.4 <sup>a</sup>	+16.9
HeF <sup>+</sup> (X <sup>3</sup> Π) → He( <sup>1</sup> S) + F <sup>+</sup> ( <sup>3</sup> P)	+1.2	+1.4	+1.7
HeF <sup>+</sup> ( <sup>1</sup> Σ <sup>+</sup> ) → He( <sup>1</sup> S) + F <sup>+</sup> ( <sup>1</sup> D)	+45.1 <sup>a</sup>	+47.5 <sup>a</sup>	+30.9
HeNe <sup>+</sup> (X <sup>2</sup> Σ <sup>+</sup> ) → He( <sup>1</sup> S) + Ne <sup>+</sup> ( <sup>2</sup> P)	+9.1	+10.4	+8.7

<sup>a</sup> Calculated by using the atomic ground states and excitation energies shown in Table II.

**TABLE II: Calculated (MP4(SDTQ)/6-311G(2df)) and Experimentally Derived<sup>29</sup> Excitation Energies (in kcal/mol) for Some Singly and Doubly Charged Atomic Ions**

	excitation	calcd	exptl
Be <sup>+</sup>	<sup>2</sup> S → <sup>2</sup> P	91.8	91.2
B <sup>+</sup>	<sup>1</sup> S → <sup>3</sup> P	103.7	106.7
C <sup>+</sup>	<sup>2</sup> P → <sup>4</sup> P	118.6	122.9
N <sup>+</sup>	<sup>3</sup> P → <sup>3</sup> D		263.5
O <sup>+</sup>	<sup>4</sup> S → <sup>2</sup> D		76.6
F <sup>+</sup>	<sup>3</sup> P → <sup>1</sup> D		59.6
B <sup>2+</sup>	<sup>2</sup> S → <sup>2</sup> P	139.2	138.2
C <sup>2+</sup>	<sup>1</sup> S → <sup>3</sup> P	145.7	149.5
N <sup>2+</sup>	<sup>2</sup> P → <sup>4</sup> P	157.4	163.4
O <sup>2+</sup>	<sup>3</sup> P → <sup>3</sup> D		342.9
F <sup>2+</sup>	<sup>4</sup> S → <sup>2</sup> D		97.4
Ne <sup>2+</sup>	<sup>3</sup> P → <sup>1</sup> D		73.8

for the atomic fragments are also listed in Table I. To give an estimate for the accuracy of our computed results of excited states,

(31) Cremer, D.; Schmidt, T. *J. Org. Chem.* **1985**, *50*, 2684.

(32) Cremer, D.; Gauss, J.; Kraka, E. *J. Mol. Struct. (THEOCHEM)*, in press.

(33) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800, 3811.

(34) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1986**, *108*, 5808.

(35) Curtiss, L.; Kraka, E.; Gauss, J.; Cremer, D. *J. Chem. Phys.* **1987**, *91*, 1080. See also ref 8b.

(36) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

TABLE III: Theoretically Predicted Vibrational Frequencies,  $\nu$  (cm<sup>-1</sup>), Partial Charges,  $q$  (He), and Overlap Populations,  $p$  (He-X), for Singly and Doubly Charged HeX<sup>n+</sup> Cations Calculated at MP2/6-31G(d,p) Optimized Geometries

	$n = 1$				$n = 2$			
	state	$\nu$	$q(\text{He})$	$p(\text{He-X})$	state	$\nu$	$q(\text{He})$	$p(\text{He-X})$
HeLi <sup>n+</sup>	X <sup>1</sup> $\Sigma^+$	198	0.04	0.036				
HeBe <sup>n+</sup>	X <sup>2</sup> $\Sigma^+$	68	0.01	0.005	<sup>1</sup> $\Sigma^+$	829	0.19	0.141
HeBe <sup>n+</sup>	<sup>2</sup> $\Pi$		0.15	0.123				
HeB <sup>n+</sup>	X <sup>1</sup> $\Sigma^+$	87	0.01	0.003	<sup>2</sup> $\Sigma^+$	956	0.26	0.115
HeB <sup>n+</sup>	<sup>3</sup> $\Pi$	450	0.13	0.030	<sup>2</sup> $\Pi$	1488	0.34	0.222
HeC <sup>n+</sup>	X <sup>2</sup> $\Pi$	142	0.01	0.006	<sup>1</sup> $\Sigma^+$	609	0.18	0.034
HeC <sup>n+</sup>	<sup>4</sup> $\Sigma^-$	1196	0.28	0.077	<sup>3</sup> $\Pi$	1425	0.40	0.154
HeN <sup>n+</sup>	X <sup>3</sup> $\Sigma^-$	250	0.07	0.018	<sup>2</sup> $\Pi$	1011	0.36	0.074
HeN <sup>n+</sup>	<sup>3</sup> $\Pi$		0.50	0.194	<sup>4</sup> $\Sigma^-$	1809	0.57	0.215
HeO <sup>n+</sup>	X <sup>4</sup> $\Sigma^-$	118	<0.01	0.001	<sup>3</sup> $\Sigma^-$	1669	0.58	0.130
HeO <sup>n+</sup>	<sup>2</sup> $\Pi$	1824	0.34	0.053	<sup>3</sup> $\Pi$		0.83	0.237
HeF <sup>n+</sup>	X <sup>3</sup> $\Pi$	162	0.01	0.003	<sup>2</sup> $\Pi$	2675	0.78	0.195
HeF <sup>n+</sup>	<sup>1</sup> $\Sigma^+$	1656	0.55	0.140				
HeNe <sup>n+</sup>	X <sup>2</sup> $\Sigma^+$	892	0.21	0.014	<sup>1</sup> $\Sigma^+$	1692	0.94	0.205

we compare in Table II experimentally determined and theoretically predicted excitation energies for atomic states of X<sup>n+</sup> which are important here. The agreement between theory and experiment is good. Excitation energies involving D states have not been calculated. Table III shows the calculated vibrational frequencies and results of the Mulliken population analysis<sup>36</sup> for HeX<sup>n+</sup>.

The theoretically predicted dissociation energies  $D_0$  of the HeX<sup>+</sup> ions in their electronic ground states are very low; the values are between 0.2 kcal/mol for (X<sup>2</sup> $\Sigma^+$ ) HeBe<sup>+</sup> and 9.1 kcal/mol for (X<sup>2</sup> $\Sigma^+$ ) HeNe<sup>+</sup>. The low dissociation energies correspond to rather long equilibrium distances of the HeX<sup>+</sup> ground states (Table I). The interatomic distances become significantly shorter in the calculated excited states of HeX<sup>+</sup> (Table I). In agreement with the much shorter bond lengths there is a substantial increase in dissociation energy (with the notable exception of the <sup>2</sup> $\Pi$  state of HeO<sup>+</sup>), vibrational frequencies, and Mulliken overlap population  $p(\text{He-X})$  for the HeX<sup>+</sup> excited states (Tables I and III). Thus, stronger binding is predicted for the calculated excited states than the ground states.

The trend in the interatomic distances and dissociation energies for the HeX<sup>+</sup> ground states is quite interesting. Figure 1 illustrates the sequence of the equilibrium distances in comparison with the experimentally known<sup>15b</sup> bond lengths for isoelectronic XH molecules. Since NeH does not form a stable molecule in its ground state, HeNe<sup>+</sup> has not been included in Figure 1. Then, the shortest (and strongest) bond is predicted for HeN<sup>+</sup>, and HeLi<sup>+</sup> has even a slightly shorter (and stronger) bond than HeF<sup>+</sup>. This is in striking contrast to the isoelectronic HX molecules, which exhibit a monotonic decrease in the bond length from HLi to HF.<sup>15b</sup> The differences between isoelectronic hydrogen and helium(+) structures have been discussed in detail somewhere else.<sup>3</sup>

Chart I lists our calculated dissociation energies,  $D_0$  and  $D_e$ , for ground and excited states of HeX<sup>+</sup>. The very low  $D_0$  and  $D_e$  values for the ground states suggest that the attractions are caused by charge-induced dipole interactions. The energy  $E_{\text{ind}}$  of these interactions may be estimated by

$$E_{\text{ind}} = -0.5\alpha q^2/r^4 \quad (1)$$

Here,  $q$  is the atomic charge of atom X,  $r$  is the interatomic distance, and  $\alpha$  is the atomic polarizability of He. Using the recommended<sup>37</sup> value of  $\alpha(\text{He}) = 1.385 a_0^3$  and the theoretically predicted equilibrium distances, we have obtained the energies  $E_{\text{ind}}$  shown in Chart I. For the ground states,  $D_e$  and  $E_{\text{ind}}$  values are very close. In order to see whether this agreement is fortuitous, we have calculated the atomic polarizability of helium,  $\alpha(\text{He})$ . At the MP4(SDTQ)/6-311G(2df,2pd) level the calculated  $\alpha(\text{He})$  deviates only 10% from the recommended value,<sup>37</sup> provided the complete basis of HeX<sup>+</sup> is employed.<sup>38</sup> We interpret this together with the agreement between  $D_e$  and  $E_{\text{ind}}$  values as strong indication

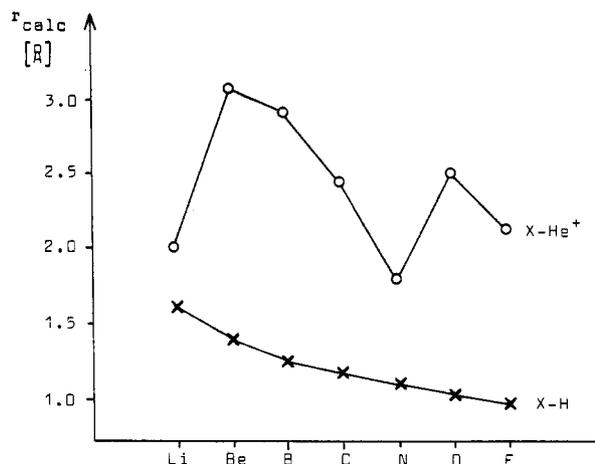


Figure 1. Variation of the calculated bond length (in Å) at MP2/6-31G(d,p) for the electronic ground states of helium cations HeX<sup>+</sup> and isoelectronic hydrides XH from X = Li to Ne.

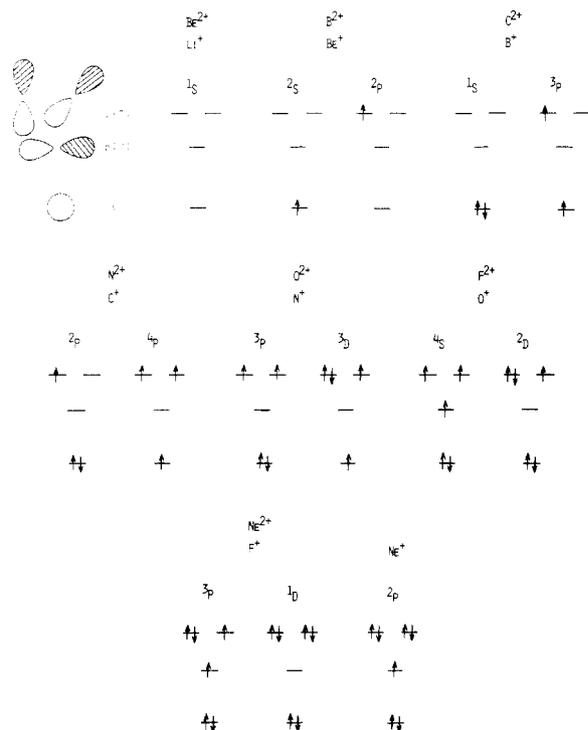
that binding is caused predominantly by electrostatic interactions between the positive charge at X<sup>+</sup> and the induced dipole at the He atom. Larger differences between  $D_e$  and  $E_{\text{ind}}$  values are found for the excited states (Chart I). However, eq 1 is only valid for large interatomic distances and may not be appropriate when the distances are as short as calculated for the higher lying states. Therefore, we can not make a statement whether the excited states are chemically bound species, although the rather large dissociation energies and Mulliken overlap populations indicate covalent bonding for (<sup>3</sup> $\Pi$ ) HeN<sup>+</sup> and (<sup>1</sup> $\Sigma^+$ ) HeF<sup>+</sup> (Chart I, Table III).

The trend in He,X bonds for the HeX<sup>+</sup> ground states and the dramatic changes between HeX<sup>+</sup> ground and excited states find a consistent explanation when the interaction between neutral He and X<sup>+</sup> in its respective electronic state is analyzed by using the model of donor-acceptor interactions with He as donor and X<sup>+</sup> as acceptor. The donor-acceptor interactions may be considered as being dominated by the interactions between the highest occupied orbital of He (1s HOMO) and the lowest unoccupied orbital (LUMO) or singly occupied orbital (SOMO) of X<sup>+</sup>. It will be seen that the predictions based on this model are valid for weakly bound systems such as the HeX<sup>+</sup> ground states as well as for stronger bound HeX<sup>+</sup> excited states, and also for HeX<sup>2+</sup> dications.

The valence orbitals of the first-row elements consist of the 2s AO and the triply degenerate p AO. Upon approach of a helium atom, this degeneracy is split into a p( $\sigma$ ) AO, and a pair of degenerate p( $\pi$ ) AOs. This is schematically shown in Figure 2 for all electronic states of X<sup>+</sup> and X<sup>2+</sup> which are important for the discussion here. The orbital scheme of Figure 2 will provide a basis for the discussion of the interactions between He and X<sup>n+</sup>. Since the ionization energies (IE) of atoms X are frequently used in the text, we show the experimentally observed first and second ionization energies in Table IV. We will consider in the following

(37) Miller, T. M.; Bederson, B. *Adv. At. Mol. Phys.* 1977, 13, 1.

(38) Collins, J. R.; Frenking, G., to be submitted.



**Figure 2.** Schematic representation of some electronic states of first-row atomic ions  $X^+$  and  $X^{2+}$ ,  $X = \text{Li-Ne}$ , upon approach of a helium atom. Note that the symmetry assignments refer to the isolated atoms and that only one term for the delta states is shown.

**TABLE IV: Experimentally Observed<sup>39</sup> First and Second Ionization Energies, IE (in eV), for He and First-Row Elements X**

atom	IE <sub>1</sub>	IE <sub>2</sub>	atom	IE <sub>1</sub>	IE <sub>2</sub>
He	24.587	54.416	N	14.534	29.601
Li	5.392	75.638	O	13.618	35.116
Be	9.322	18.211	F	17.422	34.970
B	8.298	25.154	Ne	21.564	40.962
C	11.260	24.383			

monocations  $\text{HeX}^+$ , starting with  $\text{HeLi}^+$ .

**HeLi<sup>+</sup>.**  $\text{Li}^+(^1\text{S})$  has an empty valence shell (Figure 2). The 2s LUMO is energetically not very low lying (IE of Li, 5.392 eV<sup>39</sup>), and interactions with He yield a rather weak bond in ( $X^1\Sigma^+$ )  $\text{HeLi}^+$  with a dissociation energy  $D_e$  of only 1.5 kcal/mol (Chart I). ( $^1\Sigma^+$ )  $\text{HeLi}^+$  is well described at the Hartree-Fock level, and the previously computed data with or without correlation corrections but without ZPE corrections<sup>6</sup> predict interaction energies between 1.5 and 1.6 kcal/mol. There is good agreement with experimental values,<sup>7</sup> which are between 1.4 and 1.5 kcal/mol. Since the potential energy curve is very flat near the equilibrium distance, larger differences are found for the He,Li interatomic distance. The previously reported values<sup>6</sup> for  $r_e$  are between 1.85 and 1.98 Å, somewhat smaller than our value of 2.06 Å. The experimentally observed<sup>7</sup>  $r_e$  values are between 1.85 and 2.05 Å.

**HeBe<sup>+</sup>.** The  $^2\Sigma^+$  ground state of  $\text{HeBe}^+$  is theoretically predicted to be the weakest bound  $\text{HeX}^+$  system investigated here with a dissociation energy of only 0.2 kcal/mol and a He,Be interatomic distance of 3.132 Å. The corresponding electronic state of  $\text{Be}^+$ , the  $^2\text{S}$  ground state, has a singly occupied 2s AO (Figure 2). HOMO-SOMO interactions are mostly smaller than HOMO-LUMO interactions, and they may even be repulsive at large distances.<sup>40</sup> This is probably the reason for the weak interactions between He and  $\text{Be}^+$  yielding a long interatomic distance in the ground state. However, if the valence electron of

$\text{Be}^+$  is excited to the 2p AO in the  $^2\text{P}$  state of  $\text{Be}^+$  (Figure 2), HOMO-LUMO interactions with He yield a significantly shorter distance ( $r_e = 1.415$  Å) and larger dissociation energy ( $D_e = 15.6$  kcal/mol) in the corresponding  $^2\Pi$  state of  $\text{HeBe}^+$ .

**HeB<sup>+</sup>.** The He,B distance (2.912 Å) and  $D_e$  value (0.5 kcal/mol) in the  $X^1\Sigma^+$  ground state of  $\text{HeB}^+$  are comparable to those in the  $X^2\Sigma^+$  ground state of  $\text{HeBe}^+$  (Table I, Chart I). The corresponding  $^1\text{S}$  ground state of  $\text{B}^+$  has a doubly occupied 2s AO, and HOMO-LUMO interactions with He involve the 2p( $\sigma$ ) AO (Figure 2). The 2p( $\sigma$ ) AO is less effective than the 2s AO in HOMO-LUMO interactions due to its higher energy. Therefore,  $\text{HeB}^+$  is less stabilized in its  $X^1\Sigma^+$  ground state than ( $X^1\Sigma^+$ )  $\text{HeLi}^+$ . In the excited  $^3\text{P}$  state of  $\text{B}^+$  (Figure 2), HOMO-SOMO interactions with He involving the singly occupied 2s AO of  $\text{B}^+$  increase the dissociation energy  $D_e$  in excited  $^3\Pi$   $\text{HeB}^+$  to 5.6 kcal/mol (Chart I). However, this is much less compared with the  $D_e$  value for the  $^2\Pi$  excited state of  $\text{HeBe}^+$  which benefits from HOMO-LUMO interactions.

In a previous theoretical study of  $\text{HeB}^+$  at the SCF level, Liebman and Allen<sup>9</sup> predicted a repulsive curve for the  $^1\Sigma^+$  ground state. However, the interactions of a charged atom  $X^+$  with He must yield a weakly bound energy minimum structure due to charged-induced dipole interactions as calculated in this work.

**HeC<sup>+</sup> and HeN<sup>+</sup>.** Frontier orbital interactions between He and the ground states of  $\text{B}^+$ ,  $\text{C}^+$ , and  $\text{N}^+$  all involve the 2p( $\sigma$ ) LUMO of  $X^+$  and the 1s AO of He, because the additional electrons occupy the 2p( $\pi$ ) AOs of ( $^2\text{P}$ )  $\text{C}^+$  and ( $^3\text{P}$ )  $\text{N}^+$ , respectively (Figure 1). Since the energy level of the 2p( $\sigma$ ) AO becomes lower in the sequence  $\text{B} > \text{C} > \text{N}$ , the HOMO-LUMO interactions with He increase in the same order. This is reflected by  $r_e$  and  $D_e$  values in the ground state of  $\text{HeB}^+$ ,  $\text{HeC}^+$ ,  $\text{HeN}^+$ , which become more stable with  $\text{HeB}^+ < \text{HeC}^+ < \text{HeN}^+$ . The same sequence is found for the excited states of the three cations (Table I, Chart I). Figure 2 shows that, for the excited states, HOMO-SOMO interactions involving the 2s AO of  $X^+$  are possible for the  $^3\text{P}$ ,  $^4\text{P}$ , and  $^3\text{D}$  state<sup>41</sup> of  $\text{B}^+$ ,  $\text{C}^+$ , and  $\text{N}^+$ , respectively. Since the 2s orbital becomes lower in energy in the same order as the 2p( $\sigma$ ) AO, a parallel shortening of the interatomic distances for ground and excited states is found for  $\text{HeB}^+$ ,  $\text{HeC}^+$ , and  $\text{HeN}^+$  (Table I). The dissociation energy of the  $^3\Pi$  state of  $\text{HeN}^+$  ( $D_e = 68.9$  kcal/mol) is the largest value of all  $\text{HeX}^+$  ions discussed here (Chart I). Also, ( $^3\Pi$ )  $\text{HeN}^+$  possesses the shortest bond length (1.007 Å) of all  $\text{HeX}^+$  species shown in Table I.

Previous ab initio studies of  $\text{HeC}^+$  in its  $X^2\Pi$  ground state predict at the Hartree-Fock level dissociation energies  $D_e$  of  $\geq 0.55$  kcal/mol at  $r_e = 2.59$  Å<sup>10a</sup> and  $D_e$  ca. 0.57 kcal/mol at  $r_e = 2.275$  Å.<sup>10b</sup> Our result for  $D_e$  is slightly larger (1.1 kcal/mol; Chart I). Due to the rather shallow potential energy curve, differences in  $r_e$  values are larger. Experimentally, a molecular ion  $\text{HeC}^+$  has been observed<sup>42</sup> in discharge studies involving graphite and He. However, no spectroscopic data are available.

For the  $X^2\Sigma^+$  ground state of  $\text{HeN}^+$  two LCAO studies predict stabilization energies  $D_e$  of 1.7 kcal/mol at  $r_e = 1.693$  Å<sup>10b</sup> and  $D_e$  ca. 1 kcal/mol at  $r_e = 2.12$  Å.<sup>11a</sup> Again, our  $D_e$  value of 4.1 kcal/mol obtained at a correlated level is higher (Chart I). While the  $^3\Pi$  excited state of  $\text{HeN}^+$  has not been studied previously, another excited state of  $\text{HeN}^+$ , the  $^1\Sigma^+(4\pi)$ , was calculated by Liebman and Allen.<sup>11a</sup> They obtained  $r_e = 1.06$  Å and  $D_e = 127$  (!) kcal/mol, which can be easily rationalized using the donor-acceptor model used here. The electronic state of  $\text{N}^+$  corresponding to  $^1\Sigma^+(4\pi)$   $\text{HeN}^+$  is the highly excited  $^1\text{D}(4\pi)$  state with two doubly occupied p( $\pi$ ) orbitals. This state has a low-lying 2s LUMO (compare Figure 2) leading to strong HOMO-LUMO interactions with He.

**HeO<sup>+</sup>.** The main difference between  $\text{HeN}^+$  and  $\text{HeO}^+$  is that the additional electron in the corresponding  $^4\text{S}$  ground state of

(39) Moore, C. E. *Analyses of Optical Spectra*; National Bureau of Standards; U.S. Government Printing Office: Washington, DC, 1970; NSRDS-NBS 34.

(40) Bernardi, F.; Epiotis, N. D.; Cherry, W.; Schlegel, H. B.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 469.

(41) Figure 2 shows only one component of the D state in terms of real orbitals, which is sufficient for the discussion presented here. For a more complete presentation of atomic D and molecular  $\Delta$  states, see: Salem, L. *Electrons in Chemical Reactions*; Wiley: New York, 1982.

(42) Young, S. E.; Coggiola, M. J. *Int. J. Mass. Spectrom. Ion Processes* **1986**, *74*, 137.

TABLE V: Nature of the He,X Interactions As Described by the Properties of the Electron Density Distribution Calculated at the HF/6-31G(d,p) Level<sup>a</sup>

HeX <sup>n+</sup> (state)	r <sub>b</sub>	ρ <sub>b</sub>	∇ <sup>2</sup> ρ <sub>b</sub>	H <sub>b</sub>	D <sub>e</sub> (IA) <sup>d</sup>	interactions
HeX <sup>+</sup>						
HeLi <sup>+</sup> (X <sup>1</sup> Σ <sup>+</sup> )	1.159	0.04	1.06	0.02	1.5	electrostatic
HeBe <sup>+</sup> (X <sup>2</sup> Σ <sup>+</sup> ) <sup>b</sup>	1.396	0.01	0.17	0.00 <sub>2</sub>	0.3	electrostatic
HeB <sup>+</sup> (X <sup>1</sup> Σ <sup>+</sup> )	1.287	0.02	0.33	0.01	0.5	electrostatic
HeB <sup>+</sup> ( <sup>3</sup> Π) <sup>c</sup>	0.903	0.34	8.95	-0.08	5.6	(covalent)
HeC <sup>+</sup> (X <sup>2</sup> Π)	1.109	0.05	0.93	0.02	1.1	electrostatic
HeC <sup>+</sup> ( <sup>4</sup> Σ <sup>-</sup> ) <sup>c</sup>	0.737	0.98	39.12	-0.76	29.3	covalent
HeN <sup>+</sup> (X <sup>3</sup> Σ <sup>-</sup> )	0.829	0.26	5.60	0.07	4.1	electrostatic
HeN <sup>+</sup> ( <sup>3</sup> Π)	0.630	2.06	73.36	-3.51	68.9	covalent
HeO <sup>+</sup> (X <sup>4</sup> Σ <sup>-</sup> )	1.146	0.04	0.75	0.01	0.8	electrostatic
HeO <sup>+</sup> ( <sup>2</sup> Π)	0.576	1.51	10.79	-1.21	4.4	covalent
HeF <sup>+</sup> ( <sup>3</sup> Π)	0.998	0.09	1.98	0.03	1.4	electrostatic
HeF <sup>+</sup> (X <sup>1</sup> Σ <sup>+</sup> )	0.470	2.63	12.82	-2.72	47.5	covalent
HeNe <sup>+</sup> (X <sup>2</sup> Π)	0.625	0.80	18.08	0.01	10.4	(electrostatic)
HeX <sup>2+</sup>						
HeB <sup>2+</sup> (X <sup>2</sup> Σ <sup>+</sup> )	0.835	0.57	8.80	-0.19	26.8	covalent
HeB <sup>2+</sup> ( <sup>2</sup> Π)	0.727	0.82	29.68	-0.16	64.5	covalent
HeC <sup>2+</sup> (X <sup>1</sup> Σ <sup>+</sup> )	0.757	0.55	3.25	-0.11	17.7	covalent
HeC <sup>2+</sup> ( <sup>3</sup> Π) <sup>c</sup>	0.738	1.24	19.23	-1.39	67.0	covalent
HeN <sup>2+</sup> (X <sup>2</sup> Π)	0.642	1.19	0.08	-0.80	48.2	covalent
HeN <sup>2+</sup> ( <sup>4</sup> Σ <sup>-</sup> )	0.648	2.16	9.19	-4.06	127.9	covalent
HeO <sup>2+</sup> (X <sup>3</sup> Σ <sup>-</sup> )	0.537	1.96	-5.11	-1.86	98.4	covalent
HeO <sup>2+</sup> ( <sup>3</sup> Π)	0.468	2.88	-15.18	-3.59	223.3	covalent
HeF <sup>2+</sup> ( <sup>2</sup> Π)	0.450	2.82	-9.16	-2.93	143.0	covalent
HeNe <sup>2+</sup> (X <sup>1</sup> Σ <sup>+</sup> )	0.415	2.92	-5.87	-2.58	240.1	covalent

<sup>a</sup>The position r<sub>b</sub> is given in Å with respect to the position of the nucleus of He. Electron density ρ<sub>b</sub> at r<sub>b</sub> is given in e Å<sup>-3</sup>, Laplacian ∇<sup>2</sup>ρ<sub>b</sub> in e Å<sup>-5</sup>, energy density H<sub>b</sub> in hartrees Å<sup>-3</sup>, and D<sub>e</sub> (without ZPE) in kcal mol<sup>-1</sup>. <sup>b</sup>At the HF/6-31G(d,p) level, ρ(r) is badly described for HeBe<sup>+</sup>. Only those results are shown that could be interpreted. <sup>c</sup>A minimum rather than a maximum was found in a direction perpendicular to the internuclear axis indicating insufficient description of ρ(r). <sup>d</sup>For HeX<sup>2+</sup>, IA values are given.

O<sup>+</sup> occupies the 2p(σ) AO (Figure 2). Frontier orbital interactions involve the SOMO of (<sup>4</sup>S) O<sup>+</sup>, and therefore, they are weaker than in (X<sup>3</sup>Σ<sup>-</sup>) HeN<sup>+</sup>. This is clearly reflected by the He,O distance (2.473 Å) and the D<sub>e</sub> value (0.8 kcal/mol). However, the <sup>2</sup>D excited state of O<sup>+</sup> yields the same kind of HOMO-LUMO interactions involving the 2p(σ) AO of X<sup>+</sup> and the 1s AO of He as the ground states of B<sup>+</sup>, C<sup>+</sup>, and N<sup>+</sup> (Figure 2). Because of the lower energy level of the 2p(σ) AO in O<sup>+</sup>, the interatomic distance in (<sup>2</sup>Π) HeO<sup>+</sup> is shorter than in (<sup>3</sup>Σ<sup>-</sup>) HeN<sup>+</sup>. On the other hand, the computed dissociation energy D<sub>e</sub> for the <sup>2</sup>Π excited state (4.4 kcal/mol), although larger than for the X<sup>4</sup>Σ<sup>-</sup> ground state, is surprisingly small in view of the short interatomic distance of 1.191 Å. A previous SCF-CI study of the potential curves of HeO<sup>+</sup> by Augustin et al.<sup>12a</sup> gave a stabilization energy of ca. 6 kcal/mol for (<sup>2</sup>Π)HeO<sup>+</sup>. This is in good agreement with our D<sub>e</sub> value of 4.4 kcal/mol (Chart I).

Inspection of Figure 2 reveals that frontier orbital interactions in the ground state of HeC<sup>+</sup> and HeN<sup>+</sup> are of the same type as in the excited state of HeO<sup>+</sup>, all involving the 2p(σ) AO of X<sup>+</sup>. In this series, the trend in the He,X distance is easily understood as a consequence of the lowering of the 2p(σ) AO, which in turn is caused by the increase in nuclear charge from C<sup>+</sup> to O<sup>+</sup>. In part, Cooper and Wilson<sup>10b</sup> were correct when pointing out the decisive role of the nuclear charge for the stability of (<sup>2</sup>Π) HeC<sup>+</sup>, (<sup>3</sup>Σ<sup>-</sup>) HeN<sup>+</sup>, and (<sup>2</sup>Π) HeO<sup>+</sup>. However, these authors did not realize that they were comparing ground states of HeC<sup>+</sup> and HeN<sup>+</sup> with an excited state of HeO<sup>+</sup>. The large He,X<sup>+</sup> distance in the <sup>4</sup>Σ<sup>-</sup> ground state of HeO<sup>+</sup> cannot be explained with an increase in the nuclear charge. The dominant factor in the He,X<sup>+</sup> interactions is the electronic structure of X<sup>+</sup>.

The only previous theoretical study<sup>12a</sup> on the X<sup>4</sup>Σ<sup>-</sup> ground state of HeO<sup>+</sup> predicts a purely repulsive potential energy curve at the SCF-CI level using a minimum basis set. The stronger bound <sup>2</sup>Π excited state of HeO<sup>+</sup> has been the subject of several LCAO studies which predict interatomic distances of 1.323 Å,<sup>10b</sup> 1.5 Å,<sup>11b</sup> and 1.74 Å.<sup>12c</sup> Augustin et al.<sup>12a</sup> reported the SCF-CI potential curve of the <sup>2</sup>Π state without giving the energy minimum distance. From the plotted curve and the listed energy values, a value for r<sub>e</sub> of ca. 1.25 Å can be deduced which is in reasonable agreement with our result of 1.191 Å. The large deviations of the SCF

values<sup>10b,11b,12c</sup> can be explained by the very flat potential energy curve of the <sup>2</sup>Π state.<sup>12a</sup>

**HeF<sup>+</sup> and HeNe<sup>+</sup>.** The orbital diagrams for the electronic states of F<sup>+</sup> and Ne<sup>+</sup> shown in Figure 2 suggest HOMO-SOMO interactions involving the singly occupied 2p(σ) AO of (<sup>3</sup>P) F<sup>+</sup> and (<sup>2</sup>P) Ne<sup>+</sup> in the X<sup>3</sup>Π and X<sup>2</sup>Σ<sup>+</sup> ground states of HeF<sup>+</sup> and HeNe<sup>+</sup>, respectively. Since the energy of the SOMO increases from (<sup>4</sup>S) O<sup>+</sup> to (<sup>3</sup>P) F<sup>+</sup>, frontier orbital interactions should increase. This is in agreement with the calculated decrease in r<sub>e</sub> and increase in dissociation energy for the corresponding HeX<sup>+</sup> ions (Table I, Chart I). In the case of HeF<sup>+</sup>, the <sup>1</sup>D valence excited state of F<sup>+</sup> (Figure 2) entails the same type of HOMO-LUMO interactions for the <sup>1</sup>Σ<sup>+</sup> excited state of HeF<sup>+</sup> as in (<sup>2</sup>Π) HeO<sup>+</sup>. Compared to (<sup>2</sup>Π) HeO<sup>+</sup>, r<sub>e</sub> is shorter and D<sub>e</sub> much higher (47.5 kcal/mol, Chart I) in (<sup>1</sup>Σ<sup>+</sup>) HeF<sup>+</sup>. Again, this can be considered as a result of the low-lying LUMO.

The <sup>1</sup>Σ<sup>+</sup> excited state of HeF<sup>+</sup> has been calculated before at the Hartree-Fock level.<sup>11a,43</sup> The bond length was predicted as 1.33 Å and the dissociation energy D<sub>e</sub> as 33 kcal/mol. Our results predict a much shorter and stronger bond for <sup>1</sup>Σ<sup>+</sup> HeF<sup>+</sup> (r<sub>e</sub> = 1.024 Å, D<sub>e</sub> = 47.5 kcal/mol; Table I, Chart I). Experimental attempts to observe HeF<sup>+</sup> in the gas phase analogous to the successful formation of XeF<sup>+</sup>, KrF<sup>+</sup>, and ArF<sup>+</sup> failed<sup>13a</sup> for reasons we will discuss below. The rather large dissociation energy predicted for the <sup>1</sup>Σ<sup>+</sup> excited state of HeF<sup>+</sup> should be sufficient to observe metastable HeF<sup>+</sup> in a suitable experiment.

For HeNe<sup>+</sup> the results of a spectroscopic study<sup>15a</sup> are available which give a dissociation energy D<sub>0</sub> of 15.9 kcal/mol at an

(43) In ref 11a and 13a, the ground state of HeF<sup>+</sup> was assumed to have <sup>3</sup>Σ<sup>+</sup>(2π) symmetry. The <sup>3</sup>Π state was not considered. Both electronic states are related to the <sup>3</sup>P state of F<sup>+</sup> (Figure 2). The difference is that, in the <sup>3</sup>Σ<sup>+</sup>(2π) state, the 2p(σ) AO of F<sup>+</sup> is doubly occupied, and the two p(π) orbitals are occupied each by an electron. At large He-F distances, the two states become degenerate. At shorter distances, the <sup>3</sup>Π state encounters weak donor-acceptor attraction involving the singly occupied 2p(σ) AO as discussed in the text. Since this orbital is doubly occupied in the <sup>3</sup>Σ<sup>+</sup>(2π) state, there are no attractive orbital interactions involving the valence orbitals of F<sup>+</sup>, and the potential energy curve of this state will be slightly higher in energy than the <sup>3</sup>Π state. Consequently, the <sup>3</sup>Π state of HeF<sup>+</sup> should be considered the ground state.

equilibrium distance of 1.30 Å for the  $X^2\Sigma^+$  ground state. This indicates somewhat stronger He,Ne interactions as calculated here ( $D_0 = 9.1$  kcal/mol; Table I). A model calculation<sup>14j</sup> gave results that are similar to the experimental results; i.e.,  $D_0 = 16.1$  kcal/mol at  $r_e = 1.375$  Å. Several ab initio studies<sup>14a-1</sup> predict dissociation energies between 0 kcal/mol<sup>14a</sup> and 30 kcal/mol.<sup>14f</sup> In those studies where minima have been located, interatomic distances are predicted between 1.455 Å<sup>14f</sup> and 1.49 Å.<sup>14e</sup>

### Analysis of the Electron Density Distribution and the Bonding Mechanism

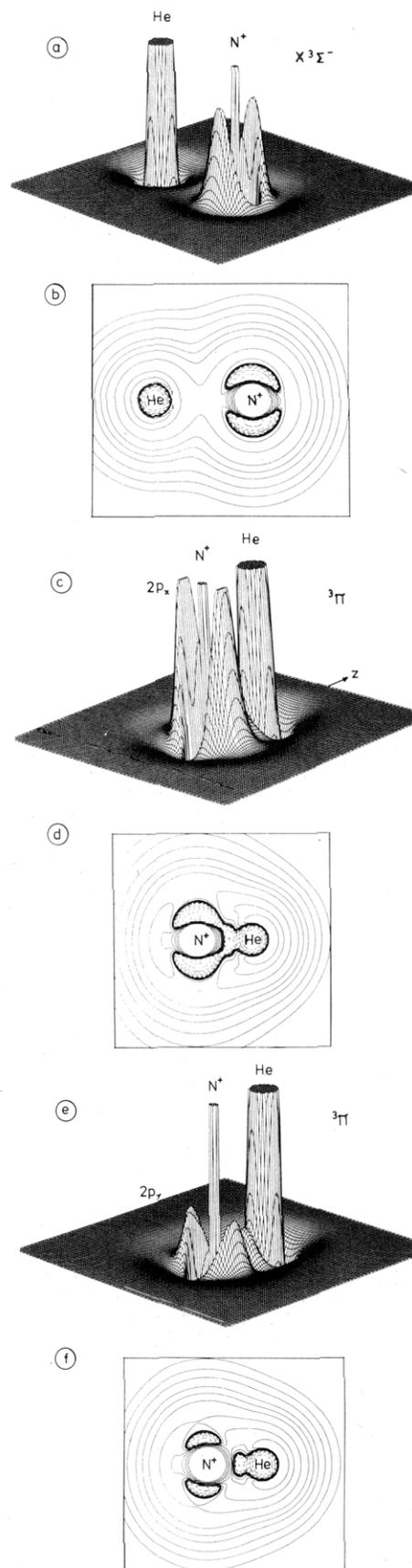
Table V summarizes the results of the electron density analysis. For all cations investigated a MED path and a path critical point  $r_b$  have been found. However, for the electronic ground states of  $HeX^+$  monocations the electron density  $\rho_b$  at the path critical point is extremely small ranging from 0.01 ( $X = Be$ ) to 0.26  $e \text{ \AA}^{-3}$  ( $X = N$ ). Only ( $X^2\Pi$ )  $HeNe^+$  possesses a somewhat larger value of  $\rho_b = 0.90 e \text{ \AA}^{-3}$  (Table 5). Since  $\rho_b$  of covalent bonds is typically 1.5–3  $e \text{ \AA}^{-3}$ , the calculated  $\rho_b$  values suggest that the  $HeX^+$  cations in the ground state are bound by electrostatic forces, with perhaps some covalent contributions in case of  $HeNe^+$ .

As noted above, both electrostatic and covalent interactions depend on the position and the size of electron holes in the valence shell of  $X^{n+}$ . The latter are nicely reflected by the Laplace concentration  $-\nabla^2\rho(\mathbf{r})$ . Figure 3 gives perspective drawings and contour line diagrams of  $-\nabla^2\rho(\mathbf{r})$  of the  $X^3\Sigma^-$  and  $^3\Pi$  states of  $HeN^+$  shown in the  $xz$  plane and the  $yz$  plane, where the  $z$  direction corresponds to the internuclear axis. There is a torus of negative charge concentration in the valence shell of  $N^+$  in ( $X^3\Sigma^-$ )  $HeN^+$  perpendicular to the internuclear axis. This torus can be associated with the electrons in the  $2p_x$  and  $2p_y$  orbitals of ( $^3P$ )  $N^+$ . Only the part of the torus in the  $xz$  plane is shown in Figure 3a,b. In the direction of the oncoming He atom, i.e., in the  $z$  axis, there is a concentration hole in the valence shell of ( $^3P$ )  $N^+$ , which can be associated with the  $p(\sigma)$  LUMO. It is this valence shell hole that imparts electron acceptor ability to ( $^3P$ )  $N^+$ . However, the acceptor ability of ( $^3P$ )  $N^+$  is not sufficient to pull electrons of He into the valence shell of the ion to establish a semipolar bond. Inspection of Figure 3a,b reveals that the Laplace concentration of the He atom in ( $X^3\Sigma^-$ )  $HeN^+$  is only slightly distorted from the isotropical distribution of an isolated He atom. There is more depletion of negative charge (solid contour lines) at the back and less in front opposite to  $N^+$ . Hence, the Laplace concentration is typical of electrostatic attraction between the two atoms.

The situation is different for the excited ( $^3\Pi$ ) state (Figure 3c,d,  $xz$  plane; Figure 3e,f,  $yz$  plane). The torus of charge concentration at  $N^+$  is enlarged in the  $x$  direction because the  $p_x$  orbital of ( $^3D$ )  $N^+$  is now occupied by two electrons, one stemming from the  $2s$  orbital. The  $2s$  orbital is singly occupied and, as a consequence, the N nucleus is less shielded, in particular in the direction of the  $2p(\sigma)$  LUMO. This is clearly reflected by the deep valence shell concentration hole in the  $z$  direction (compare Figure 3a with 3c and 3e). The acceptor ability of  $N^+$  is enlarged in the  $^3D$  state and electrons are pulled from He toward the concentration hole. Accordingly, the Laplace concentration of He is strongly distorted in ( $^3\Pi$ )  $HeN^+$ . There is a dropletlike appendix in the He,N bonding region of ( $^3\Pi$ )  $HeN^+$  (Figure 3d and 3f, respectively). Such a feature was found by us typical of a semipolar He,X bond in the case of helium compounds.<sup>2</sup> At the bond critical point of the He,N bond,  $\rho_b$  is 2.06  $e \text{ \AA}^{-3}$  and  $H_b$  is significantly smaller than zero. Hence, there is a strong semipolar covalent He,N bond in ( $^3\Pi$ )  $HeN^+$ .

All excited  $HeX^+$  states investigated in this work possess a covalent He,X bond or at least a bond with partial covalent character. The  $\rho_b$  and  $H_b$  data in Table V show that the He,B bond is the weakest, actually more electrostatic than covalent. The strongest covalent bond is found for ( $^3\Pi$ )  $HeN^+$ , which is in line with both the frontier orbital and the Laplace description of He, $X^+$  interactions (Figures 2 and 3c-f).

While first-row  $HeX^+$  cations in their ground state are van der Waals complexes, weakly stabilized by charge-induced dipole



**Figure 3.** Perspective drawings and contour line diagrams of the Laplace concentration  $-\nabla^2\rho(\mathbf{r})$  of  $HeN^+$ . Dashed contour lines are in regions of concentration of negative charge, and solid contour lines are in regions of charge depletion. Inner-shell concentration of  $N^+$  is not shown in the contour line diagrams. (a and b)  $HeN^+(X^3\Sigma^-)$  in  $xz$  plane. (c and d)  $HeN^+(^3\Pi)$  in  $xz$  plane. (e and f)  $HeN^+(^3\Pi)$  in  $yz$  plane (HF/6-31G(d,p) calculations).

attraction, the corresponding HeX<sup>2+</sup> dications are all covalently bound in the ground and excited states. This is suggested by the  $r_b$  and  $H_b$  values listed in Table V. Ionization of a second electron of X leads to an enlargement of valence shell holes and, thus, stronger attraction of the s electrons of He. Figure 4, which gives the Laplace concentration of (X<sup>2+</sup>) HeN<sup>2+</sup> in the *xz* plane (Figure 4a,b) and in the *yz* plane (Figure 4c,d), reveals that the 1s electron concentration of He is pulled toward N<sup>2+</sup> leading to a Laplace pattern typical of a semipolar covalent. There are two concentration lumps where the  $p_x$  electron of (<sup>2</sup>P) N<sup>2+</sup> should be expected and a concentration hole in the *y* direction corresponding to an empty  $p_y$  orbital. If negative charge is transferred from He to the 2p( $\sigma$ ) LUMO, electron concentration is also found in the *z* direction (Figure 4a–d).

Covalent bonding is also found for the excited states of HeX<sup>2+</sup> investigated in this work. Figure 4e clearly shows that the valence shell hole is deeper when a 2s electron is excited in a 2p( $\pi$ ) AO of (<sup>4</sup>P) N<sup>2+</sup>. As a consequence, donor–acceptor interactions are larger than in the ground state and a stronger semipolar He,N bond results (note that a direct comparison of the Laplace concentrations of N<sup>+</sup> and N<sup>2+</sup> is only possible if the smaller valence shell radius of the latter ion is considered). This observation applies to all excited states investigated (Table V). We will now discuss the HeX<sup>2+</sup> ions in more detail.

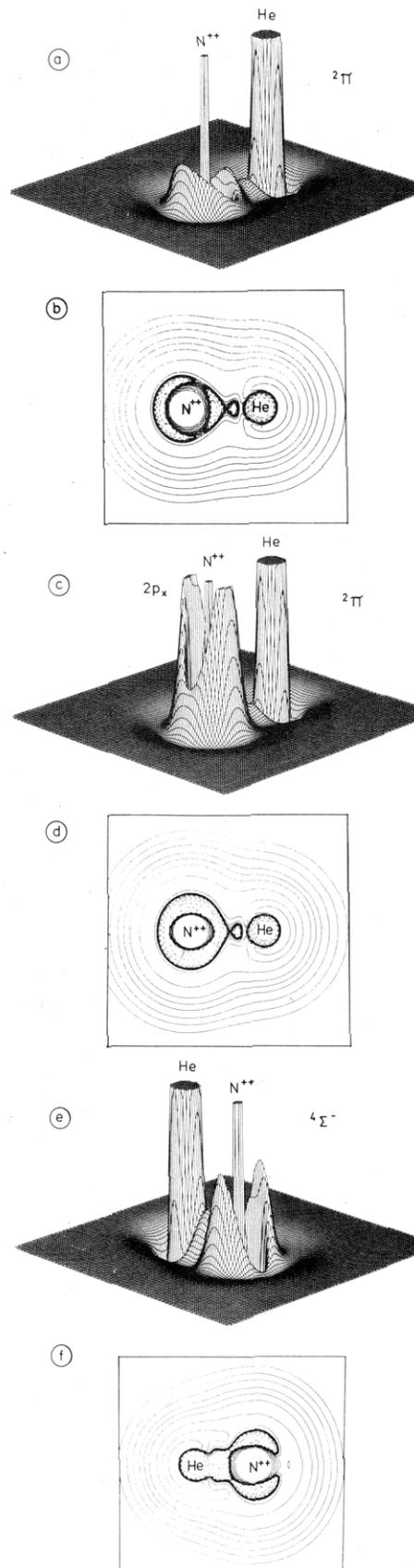
### Doubly Charged HeX<sup>2+</sup> Cations

As indicated above, donor–acceptor interactions between He and X<sup>2+</sup> should be much stronger than between He and X<sup>+</sup> since (i) the orbital vacancy is higher for X<sup>2+</sup> than for X<sup>+</sup> and, therefore, X<sup>2+</sup> can be expected to be a stronger electron acceptor than X<sup>+</sup>; (ii) the energy of the LUMO is lower in X<sup>2+</sup> than in X<sup>+</sup>, which also increases the acceptor ability of X.

However, there is a distinct difference between the dissociation of doubly charged cations HeX<sup>2+</sup> and monocations HeX<sup>+</sup>. While the latter species dissociate always to He and X<sup>+</sup>, the energetically lowest lying fragmentation of dications HeX<sup>2+</sup> may either be He + X<sup>2+</sup> or He<sup>+</sup> + X<sup>+</sup>. Provided that the reaction is spin- and space-symmetry allowed, the charge-separation reaction into He<sup>+</sup> and X<sup>+</sup> will be preferred for those dications HeX<sup>2+</sup> whose atom X has a second IE which is higher than the first IE of He (24.587 eV).<sup>39</sup> For the systems investigated here, that is the case for X = Li, B, N, O, F, and Ne. Only for HeBe<sup>2+</sup> and HeC<sup>2+</sup> the preferred dissociation reaction involves He and X<sup>2+</sup> because the second IE of Be and C is lower than the first IE of He (Table IV). Then, what is the justification to discuss dications HeX<sup>2+</sup> in terms of interactions between He and X<sup>2+</sup> in cases where the actual dissociation products are He<sup>+</sup> and X<sup>+</sup>?

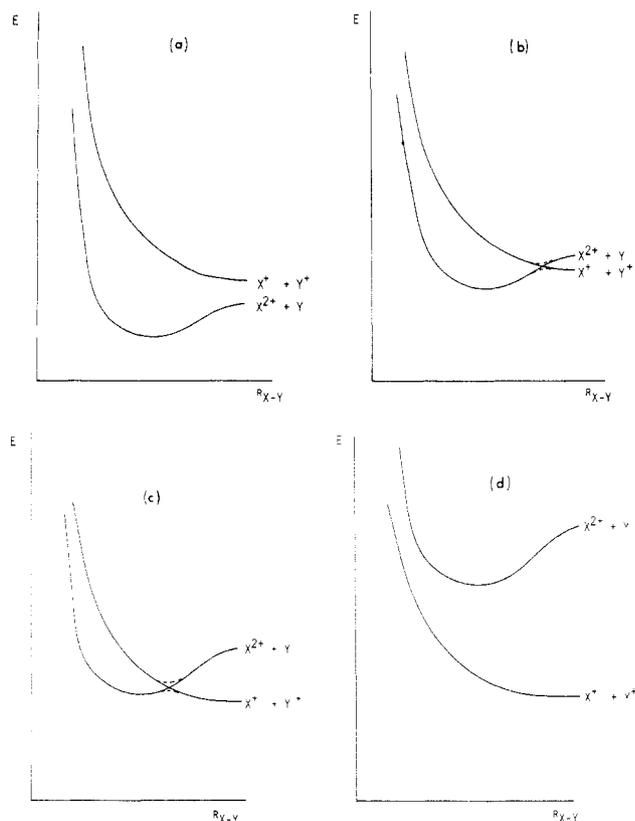
The basis of the argumentation presented here is found in Pauling's discussion of the bonding in He<sub>2</sub><sup>2+</sup> back in 1933.<sup>44</sup> Generalized for systems XY<sup>2+</sup>, where X and Y may be atoms or molecules, the principles of bonding between X and Y in XY<sup>2+</sup> are as following: The positively charged fragments X<sup>+</sup> and Y<sup>+</sup> repel each other due to Coulomb interactions, and the potential curve may be approximated by a purely repulsive 1/*r* curve. Electron excitation from X<sup>+</sup> to Y<sup>+</sup> and vice versa yields the systems X + Y<sup>2+</sup> and X<sup>2+</sup> + Y, respectively. To simplify the discussion we will consider only one of these two terms, that is X<sup>2+</sup> + Y. The interactions between atoms or molecules X<sup>2+</sup> and Y will be attractive, either due to charge–induced dipole interactions at larger distances or because of actual electron donation from Y toward X<sup>2+</sup> at a shorter range. Thus, the potential curve between X<sup>2+</sup> and Y will exhibit a minimum. Then, four qualitatively different possibilities may be envisaged depending on the ionization energies of X and Y. These four cases are schematically shown in Figure 5.

Figure 5a depicts the situation where the dissociation products X<sup>2+</sup> + Y are lower in energy than X<sup>+</sup> + Y<sup>+</sup>. The ground-state potential energy curve of XY<sup>2+</sup> is completely determined by the interactions between X<sup>2+</sup> and Y. In Figure 5b, X<sup>+</sup> + Y<sup>+</sup> are lower



**Figure 4.** Perspective drawings and contour line diagrams of the Laplace concentration  $-\nabla^2\rho(\mathbf{r})$  of HeN<sup>2+</sup>. Dashed contour lines are in regions of concentration of negative charge, and solid contour lines are in regions of charge depletion. Inner-shell concentration of N<sup>2+</sup> is not shown in the contour line diagrams. (a and b) HeN<sup>2+</sup>(X<sup>2</sup>II) in *xz* plane. (c and d) HeN<sup>2+</sup>(X<sup>2</sup>II) in *yz* plane. (e and f) HeN<sup>2+</sup>(<sup>4</sup>Σ<sup>-</sup>) in *xz* plane (HF/6-31G(d,p) calculations).

(44) Pauling, L. *J. Chem. Phys.* 1933, 1, 56.



**Figure 5.** Schematic representation of potential energy curves of dications  $XY^{2+}$  dissociating to either  $X^+ + Y^+$  or  $X^{2+} + Y$ . (a) The dissociation limit  $X^+ + Y^+$  is higher than  $X^{2+} + Y$ . (b) The dissociation limit  $X^+ + Y^+$  is lower than the dissociation limit of  $X^{2+} + Y$ , but higher than the potential energy minimum. (c) The dissociation limit  $X^+ + Y^+$  is lower than the limit  $X^{2+} + Y$  and lower than the energy of the local minimum, but the two curves are crossing in between. (d) The two curves do not cross, and the energy of  $X^{2+} + Y$  is much higher than the energy of  $X^+ + Y^+$ .

in energy than  $X^{2+} + Y$ . At some interatomic distance the two curves are crossing, and the  $X^{2+} + Y$  curve at shorter distances becomes lower in energy than the  $X^+ + Y^+$  curve. When the two curves have the same symmetry, the result will be an avoided crossing which is indicated by the dashed lines in Figure 5b. The important conclusion is that at the minimum geometry the dication  $XY^{2+}$  is better described by the term  $X^{2+} + Y$  than by  $X^+ + Y^+$ .

In Figure 5b, the energy difference between the dissociation products  $X^{2+} + Y$  and  $X^+ + Y^+$  is not very high, and the potential energy at the equilibrium geometry is lower than the dissociation limits. Thus, Figure 5b depicts a system  $XY^{2+}$  which is thermodynamically stable although the preferred dissociation reaction into  $X^+ + Y^+$  releases Coulomb repulsion. Figure 5c shows the case where the energy differences between the two dissociation limits are larger, and the fragmentation of  $XY^{2+}$  is exothermic. Here,  $XY^{2+}$  is only a metastable species. In cases where the minimum energy point of the  $X^{2+} + Y$  curve is close to the curve crossing, there might only be a flattening of the resulting potential energy curve, without a minimum energy structure. Finally, in Figure 5d we show the case where the energy differences between the two dissociation limits are too large to allow significant interactions. The ground-state curve is purely repulsive. We will see that the first-row diatomic dications  $HeX^{2+}$  in their ground states provide examples for all four cases shown in Figure 5a–d.

The qualitative model for binding in doubly charged cations outlined here has recently been used to give a rationale for some features of dication chemistry that are radically different from the chemistry of the respective neutral molecules. One example concerns the peculiar equilibrium geometries of some simple organic dications such as  $CH_3X^{2+}$  (for example,  $X = F, OH, NH_2$ , and many others). The only minima for the respective dications have a tricoordinated carbon geometry  $H_2C-XH^{2+}$  rather than

the classical tetracoordinated  $H_3C-X$  structures as in case of the neutral molecules.<sup>34,45,46</sup> This could be explained by donor–acceptor interactions between the acceptor  $CH_2^{2+}$  and the respective donor fragment  $X$ .<sup>34</sup> The second example concerns the transition structures for dissociation of dications  $XY^{2+}$  into  $X^+ + Y^+$  (Figure 5b,c). For some reactions, these transition structures have unusually long  $X, Y$  interatomic distances. Figure 5b,c indicates that the location of the transition state depends on the energy difference of the two dissociation products, i.e.,  $X^+ + Y^+$  and  $X^{2+} + Y$ . It was possible to predict rather accurately the transition states for some dissociation reaction of  $XY^{2+}$  based solely on the ionization energies of  $X$  and  $Y$ .<sup>47</sup>

From the above we conclude that it is reasonable to discuss systems  $XY^{2+}$  in terms of interactions between  $X^{2+}$  and  $Y$  even when the preferred dissociation path of  $XY^{2+}$  is the charge-separation reaction into  $X^+ + Y^+$ . Thus, our discussion of  $HeX^{2+}$  will be analogous to  $HeX^+$ .

Table VI shows the calculated interatomic distances, total energies, and ZPE and BSSE values for the ground and some excited states of dications  $HeX^{2+}$ . The energies for those atomic fragments that are not already listed in Table I are also given. In addition, the theoretically predicted dissociation energies  $D_0$  are listed which refer to the energetically most favorable symmetry-allowed atomization reactions given in Chart II. The calculated interaction energies  $IA$  for the dissociation into  $He(1S)$  and  $X^{2+}$  in the respective electronic state are also shown in Table VI. The corresponding dissociation reactions are included in Chart II. In case of the singly charged  $HeX^+$  cations,  $D_e$  and  $IA$  values are the same. For the dications it is only when the most favorable reaction path for dissociation of  $HeX^{2+}$  yields  $He + X^{2+}$  that  $D_0$  and  $IA$  values are identical. In other cases, the  $IA$  values may be taken as a measure for stabilizing donor–acceptor interactions in  $HeX^{2+}$ . From the discussion presented above a correlation may be expected between the  $IA$  values and the interatomic distances  $He-X$ .

The data in Table VI show that the interatomic distances of  $HeX^{2+}$  dications which are bound in their ground state are much shorter than those of the respective singly charged systems and that the  $IA$  values of  $HeX^{2+}$  are much higher than the  $D_e$  values of the corresponding  $HeX^+$  ions. Three dications are predicted to be thermodynamically stable in their ground states, i.e.,  $HeBe^{2+}$ ,  $HeB^{2+}$ , and  $HeC^{2+}$ . As for the monocations, the excited states of  $HeX^{2+}$  have shorter bond lengths than the ground states. Only for one excited state, the  $HeB^{2+} \ ^2\Pi$  state, the symmetry-allowed dissociation reaction is predicted to be endothermic. All other excited states calculated here exhibit very short interatomic distances  $He, X$  and, therefore, may have a sufficiently high activation energy for dissociation to be observable in the gas phase. For example, a deep potential well of 15.9 kcal/mol has theoretically been predicted<sup>1c</sup> for the  $^3\Pi$  state of  $HeC^{2+}$  based on a CASSCF study of the potential energy curve.

We calculated charge-induced dipole interactions  $E_{ind}$  for ground and excited states of  $HeX^{2+}$  using eq 1. The results are shown in Chart II. Although eq 1 is not valid at short interatomic distances, because it considers only attractive forces and not repulsive interactions, a comparison with the quantum mechanically calculated results is interesting. The  $E_{ind}$  data show nearly the same order as the calculated  $IA$  values (Chart II), and even the absolute values for  $IA$  and  $E_{ind}$  are rather close in most cases.

We will now discuss our results for  $HeX^{2+}$  dications for each molecule separately in the same fashion as the singly charged cations  $HeX^+$ .

**$HeLi^{2+}$ .** The ground-state  $^2\Sigma^+$  potential energy curve of  $HeLi^{2+}$  is calculated as purely repulsive. Using the bonding model outlined above, attractive interactions are expected for  $He + Li^{2+}$ . The second ionization energy of  $Li$  is very high (75.638 eV<sup>39</sup>), because

(45) Koch, W.; Schwarz, H. In *Structure/Reactivity and Thermochemistry of Ions*; Lias, S. G., Ausloos, P., Eds.; Reidel: Dordrecht, 1987.

(46) Yates, B. F.; Bouma, W.; Radom, L. *J. Am. Chem. Soc.* **1986**, *108*, 6545.

(47) Gill, P. M. W.; Radom, L. *Chem. Phys. Lett.* **1987**, *136*, 294.

TABLE VI: Theoretically Determined Interatomic Distances,  $r_e$  (in Å), Total Energies,  $E_{\text{tot}}$  (in hartrees), Zero-Point Vibrational Energies, ZPE, BSSE Data, Dissociation Energies,  $D_0$ , and Interaction Energies, IA (in kcal/mol), for Energetically Low Lying States of HeX<sup>2+</sup> Dications (Calculated Total Energies for Atomic Fragments)

struct	sym	MP2/6-31G(d,p)			MP4/6-311G(2df,2pd) <sup>a</sup>			
		$r_e$	$E_{\text{tot}}$	ZPE	$E_{\text{tot}}$	BSSE <sup>b</sup>	$D_0$	IA
HeLi <sup>2+</sup>	X <sup>2</sup> Σ <sup>+</sup>	diss						
HeBe <sup>2+</sup>	X <sup>1</sup> Σ <sup>+</sup>	1.453	-16.5241	1.2	-16.5400	0.2; 0.2	+18.9	+20.1
HeB <sup>2+</sup>	X <sup>2</sup> Σ <sup>+</sup>	1.339	-26.2944	1.4	-26.3143	0.3; 0.2	+15.2	+26.8
HeB <sup>2+</sup>	<sup>2</sup> Π	1.191	-26.1304		-26.1525	0.3; 0.3	+18.6 <sup>c</sup>	+64.5
HeC <sup>2+</sup>	X <sup>1</sup> Σ <sup>+</sup>	1.575	-39.3455	0.9	-39.3967	0.2; 0.2	+16.8	+17.7
HeC <sup>2+</sup>	<sup>3</sup> Π	1.167	-39.2111	2.0	-39.2432	0.6; 0.3	-76.2	+67.0
HeN <sup>2+</sup>	X <sup>2</sup> Π	1.321	-55.7923	1.4	-55.8653	0.4; 0.4	-69.7	+48.2
HeN <sup>2+</sup>	<sup>4</sup> Σ <sup>-</sup>	1.060	-55.6865	2.6	-55.7415	0.7; 0.5	-148.8	+127.9
HeO <sup>2+</sup>	X <sup>3</sup> Σ <sup>-</sup>	1.164	-76.1422	2.4	-76.2408	0.9; 0.9	-149.0	+98.4
HeO <sup>2+</sup>	<sup>3</sup> Π	1.003	-75.7916		-75.8937	1.4; 1.2	-288.2 <sup>c</sup>	+223.3
HeF <sup>2+</sup>	X <sup>4</sup> Σ <sup>-</sup>	diss						
HeF <sup>2+</sup>	<sup>2</sup> Π	1.044	-100.5377	3.8	-100.6764	1.8; 2.1	-193.5	+143.0
HeNe <sup>2+</sup>	X <sup>3</sup> Π	diss						
HeNe <sup>2+</sup>	<sup>1</sup> Σ <sup>+</sup>	1.025	-129.4862	2.4	-129.6721	2.6; 3.2	-211.7	+240.1
Be <sup>2+</sup>	<sup>1</sup> S		-13.6127		-13.6104			
B <sup>2+</sup>	<sup>2</sup> S		-23.3754		-23.3740			
B <sup>2+</sup>	<sup>2</sup> P		-23.1518		-23.1520			
C <sup>2+</sup>	<sup>1</sup> S		-36.4437		-36.4710			
C <sup>2+</sup>	<sup>3</sup> P		-36.2323		-36.2386			
N <sup>2+</sup>	<sup>2</sup> P		-52.8447		52.8906			
N <sup>2+</sup>	<sup>4</sup> P		-52.6171		-52.6396			
O <sup>2+</sup>	<sup>3</sup> P		-73.1188		-73.1853			
F <sup>2+</sup>	<sup>4</sup> S		-97.6129		-97.7032			
Ne <sup>2+</sup>	<sup>3</sup> P		-126.3593		-126.5046			
He <sup>+</sup>	<sup>2</sup> S		-1.9936		-1.9981			

<sup>a</sup> At MP2/6-31G(d,p) optimized geometries. <sup>b</sup> The first value refers to  $D_0$  data and the second to IA results. <sup>c</sup>  $D_e$  value, without ZPE correction.

a 1s core electron is ionized. In fact, the second IE of Li is even higher than the second IE of He (Table IV). Therefore, the dissociation limit He<sup>2+</sup> + Li is lower in energy than He + Li<sup>2+</sup>. On the other hand, the potential energy curves of the dissociation reactions yielding He<sup>2+</sup> + Li or He + Li<sup>2+</sup> are much higher in energy than those electronic states leading to H<sup>+</sup> + Li<sup>+</sup>, and because of the large energy difference, the states do not interact significantly. Thus, HeLi<sup>2+</sup> is an example for the case shown in Figure 5d.

**HeBe<sup>2+</sup>.** The second IE of Be is lower than the first IE of He (Table IV), and dissociation of (X<sup>1</sup>Σ<sup>+</sup>) HeBe<sup>2+</sup> yields He and (<sup>1</sup>S) Be<sup>2+</sup>. (<sup>1</sup>S) Be<sup>2+</sup> is isoelectronic with (<sup>1</sup>S) Li<sup>+</sup>, and frontier orbital interactions with He involve in both cases the 2s LUMO (Figure 2). Since the 2s (Be<sup>2+</sup>) AO is lower in energy than the 2s (Li<sup>+</sup>) AO, the He,Be distance is shorter (1.453 Å) and the dissociation energy is larger ( $D_e = 20.1$  kcal/mol) than the corresponding values for (X<sup>1</sup>Σ<sup>+</sup>) HeLi<sup>+</sup> (2.062 Å, 1.5 kcal/mol; Table I, Chart I). The calculated  $D_0$  value (18.9 kcal/mol) is very similar to previously reported values obtained at a lower level of theory (17.7,<sup>8b</sup> 18.2,<sup>8d</sup> and 18.6<sup>8a</sup> kcal/mol). HeBe<sup>2+</sup>(<sup>1</sup>Σ<sup>+</sup>) is an example for the situation shown in Figure 5a.

**HeB<sup>2+</sup>.** HeB<sup>2+</sup> is isoelectronic with HeBe<sup>+</sup>. In both cases, there are HOMO-SOMO interactions of the singly occupied 2s AO of the respective atomic ion X with He in the <sup>2</sup>Σ<sup>+</sup> ground states of the diatomics (Figure 2). Because the 2s AO of B<sup>2+</sup> is energetically lower lying than the 2s orbital of Be<sup>+</sup>, HOMO-SOMO interactions are stronger in (X<sup>2</sup>Σ<sup>+</sup>) HeB<sup>2+</sup>. Since HOMO-SOMO interactions become more attractive at shorter interatomic distances,<sup>40</sup> the bond length of HeB<sup>2+</sup>(X<sup>2</sup>Σ<sup>+</sup>) is not only shorter than that in HeB<sup>+</sup>(<sup>2</sup>Σ<sup>+</sup>), it is also shorter than the bond length in (X<sup>1</sup>Σ<sup>+</sup>) HeBe<sup>2+</sup>. This is in line with the calculated interaction energy IA for the ground state of HeB<sup>2+</sup> (26.8 kcal/mol), which is larger than that for the ground state of HeBe<sup>2+</sup> (20.1 kcal/mol). However, the ground state of HeB<sup>2+</sup> does not dissociate into He + B<sup>2+</sup>, because the second IE of B (25.154 eV<sup>39</sup>) is slightly larger than the first IE of He. Nevertheless, the interaction energy IA between He and B<sup>2+</sup> is sufficient to compensate for the energy differences of the dissociation limits. HeB<sup>2+</sup> in its X<sup>2</sup>Σ<sup>+</sup> ground state is theoretically predicted to be thermodynamically stable toward dissociation by  $D_0 = 15.2$  kcal/mol. The difference between the IA and  $D_e$  values for HeB<sup>2+</sup>(X<sup>2</sup>Σ<sup>+</sup>) (10.2 kcal/mol;

Chart II) corresponds to the difference between first IE of He and second IE of B (experiment, 13.1 kcal/mol<sup>39</sup>). HeB<sup>2+</sup>(<sup>2</sup>Σ<sup>+</sup>) is an example for the case shown in Figure 5b.

The <sup>2</sup>Π excited state of HeB<sup>2+</sup> correlates with the <sup>2</sup>P excited state of B<sup>2+</sup> (Figure 2). HOMO-LUMO interactions of the empty 2s AO with He yield a clearly shorter interatomic distance (1.191 Å) than that in the X<sup>2</sup>Σ<sup>+</sup> ground state, analogous to what has been calculated for isoelectronic HeBe<sup>+</sup>(<sup>2</sup>Π) (Table I). Parallel to the shortening of the He,B<sup>2+</sup> distance, the calculated interaction energy, IA, of HeB<sup>2+</sup>(<sup>2</sup>Π) (64.5 kcal/mol) is significantly larger than that for the X<sup>2</sup>Σ<sup>+</sup> ground state (26.8 kcal/mol). The lowest lying symmetry-allowed dissociation reaction of the <sup>2</sup>Π excited state yields He<sup>+</sup> + B<sup>+</sup>(<sup>3</sup>Π) (Chart II). The very similar  $D_e$  values for ground and excited states of HeB<sup>2+</sup> (16.6 and 18.6 kcal/mol; Chart II) are further indication that interactions are dominated by electron donation from the 1s electrons of He. The  $D_e$  values suggest that the excitation energy of B<sup>2+</sup>(<sup>2</sup>S→<sup>2</sup>P) is nearly the same as the excitation energy of HeB<sup>2+</sup>(<sup>2</sup>Σ<sup>+</sup>→<sup>2</sup>Π). It follows that the 2s electron of boron in HeB<sup>2+</sup>(<sup>2</sup>Σ<sup>+</sup>) is hardly disturbed by the presence of the helium atom. This indicates that the 2s electron does not significantly participate in the He,B bonding. Like the <sup>2</sup>Σ<sup>+</sup> ground state, the <sup>2</sup>Π excited state of HeB<sup>2+</sup> is illustrated by the potential energy curve shown in Figure 5b.

**HeC<sup>2+</sup>.** The <sup>1</sup>Σ<sup>+</sup> ground state of HeC<sup>2+</sup> dissociates to He + C<sup>2+</sup>(<sup>1</sup>S) because the second IE of carbon is slightly lower than the first IE of He (Table IV). Therefore,  $D_e$  and IA values are the same for HeC<sup>2+</sup>(X<sup>1</sup>Σ<sup>+</sup>). The dominant interactions in HeC<sup>2+</sup>(X<sup>1</sup>Σ<sup>+</sup>) involve the 2p(σ) LUMO of C<sup>2+</sup>, which is higher in energy than the 2s LUMO of Be<sup>2+</sup>. As a consequence, HeC<sup>2+</sup> has a longer (1.575 Å) and weaker ( $D_0 = 16.8$  kcal/mol) bond than HeBe<sup>2+</sup>(X<sup>1</sup>Σ<sup>+</sup>). This is parallel to what has been found for the singly charged ions HeLi<sup>+</sup> and HeB<sup>+</sup> (Table I). Although doubly charged, C<sup>2+</sup> in its <sup>1</sup>S ground state binds helium more weakly in (X<sup>1</sup>Σ<sup>+</sup>) HeC<sup>2+</sup> ( $D_e = 17.7$  kcal/mol) than singly charged C<sup>+</sup> (<sup>4</sup>S) does in (<sup>4</sup>Σ<sup>-</sup>) HeC<sup>+</sup> ( $D_e = 29.3$  kcal/mol; Chart I). This is a striking evidence that the electronic structure of a binding partner of He is more important than its positive charge. The <sup>1</sup>Σ<sup>+</sup> ground state of HeC<sup>2+</sup> is another example for the situation shown in Figure 5a.

The <sup>3</sup>Π excited state of HeC<sup>2+</sup> possesses a much shorter bond (1.167 Å) than the ground state. Bonding in HeC<sup>2+</sup>(<sup>3</sup>Π) is caused

by HOMO–SOMO interactions between the 2s (He) AO and the singly occupied 2s AO of  $C^{2+}$  (Figure 2). The shorter bond length is in agreement with the calculated IA value for the  $^3\Pi$  state of 67.0 kcal/mol (Table VI) indicating stronger bonding in the excited state. However, unlike the ground state, the  $^3\Pi$  excited state dissociates to  $He^+ + C^+(^2P)$  (Chart II) and the dissociation is highly exothermic by  $-76.2$  kcal/mol. Thus,  $HeC^{2+}$  in its  $^3\Pi$  excited state is an example for the case shown in Figure 5c.

Our calculated data for the ground state and excited state of  $HeC^{2+}$  may be compared with recent results of a CASSCF study<sup>1c</sup> of the low-lying potential energy curves of  $HeC^{2+}$ . For the  $^1\Sigma^+$  ground state, an equilibrium geometry of 1.566 Å and a dissociation energy  $D_0$  of 15.6 kcal/mol have been predicted. The corresponding data for the  $^3\Pi$  excited state are  $r_e = 1.185$  Å and a negative dissociation energy of  $-84.3$  kcal/mol.<sup>1c</sup> For the  $^1\Sigma^+$  ground state, a theoretical study at the Hartree–Fock level<sup>10b</sup> predicts a bond length of ca. 1.587 Å and an approximate well depth of 14.3 kcal/mol. Our results presented here are in agreement with these data.

**$HeN^{2+}$  and  $HeO^{2+}$ .** The  $X^2\Pi$  state of  $HeN^{2+}$  and  $X^3\Sigma^-$  state of  $HeO^{2+}$  are interpreted as the results of HOMO–LUMO interactions between the 1s AO of He and the empty 2p( $\sigma$ ) AO of  $N^{2+}(^2P)$  and  $O^{2+}(^3P)$ , respectively (Figure 2). Since the energy level of the 2p $\sigma$  orbital decreases with increasing nuclear charge, stabilizing interactions also increase as is demonstrated by the IA values and interatomic distances given in Table VI. Unlike  $HeC^{2+}$ , the most favorable dissociation pathways of the ground states of  $HeN^{2+}$  and  $HeO^{2+}$  are the charge-separation reactions shown in Chart II. Due to the rather high second IE of N (29.601 eV<sup>29</sup>) and O (35.116 eV<sup>29</sup>) these dissociation reactions are highly exothermic by  $-69.7$  and  $-149.0$  kcal/mol (Table VI), respectively. In the same way the properties of the excited states of  $HeN^{2+}(^1\Sigma^-)$  and  $HeO^{2+}(^3\Pi)$  can be explained (Table VI). HOMO–SOMO interactions now involve the low-lying singly occupied 2s AO of  $X^{2+}$ . As a consequence, the bond lengths ( $D_e$  values) in these excited states are shorter (larger) than for the ground states. The  $r_e$  values decrease in the order  $X = C > N > O$ , while the calculated IA values increase in this order (Table VI). On the other hand, the dissociation reactions of  $HeN^{2+}(^4\Sigma^-)$  and  $HeO^{2+}(^3\Pi)$  are more exothermic (Chart II) than those of the corresponding ground states. All calculated states of  $HeN^{2+}$  and  $HeO^{2+}$  exhibit a dissociation behavior as schematically shown in Figure 5c.

$HeN^{2+}$  and  $HeO^{2+}$  have previously been studied at the Hartree–Fock level.<sup>10b,12c</sup> Cooper and Wilson<sup>10b</sup> (CW) report approximate bond lengths of 1.32 and 1.06 Å for  $(^2\Pi)$   $HeN^{2+}$  and  $(^3\Sigma^-)$   $HeO^{2+}$ , respectively. They also give the potential energy curves for  $HeN^{2+}$  and  $HeO^{2+}$  which are similar to that of  $HeC^{2+}$ , i.e., an energy minimum at the equilibrium geometry and an increase in energy at longer distances. Hence, the calculated potential energy curves do not refer to the most favorable dissociation reaction, i.e., the charge-separation reaction yielding  $He^+ + X^+$ . CW<sup>10b</sup> give approximate well depths for  $HeN^{2+}$  (40.0 kcal/mol) and  $HeO^{2+}$  (60.0 kcal/mol) which roughly agree with our calculated IA values for the ground states (Table VI). Thus, the calculated potential energy curve for  $HeN^{2+}(^2\Pi)$  and  $HeO^{2+}(^3\Sigma^-)$  at the Hartree–Fock level reported by CW leads to the wrong dissociation limit, namely, neutral He and  $X^{2+}$ . Similarly, Masse and Masse-Barlocher<sup>12c</sup> predict on the basis of Hartree–Fock calculations that the  $^3\Sigma^-$ ,  $^1D$ , and  $^1\Sigma^+$  states of  $HeO^{2+}$  are stable. Again, these authors only consider dissociation reactions which yield neutral He. All three electronic states are unstable toward dissociation into  $He^+ + O^+$ .

An accurate theoretical description of the dissociation of doubly charged diatomics into singly charged fragments is a notoriously difficult problem because several states of different symmetry may cross.<sup>24,48,49</sup> Even multiconfiguration methods such as CASSCF have been questioned<sup>48</sup> as to whether they are adequate for a

quantitative treatment of the potential energy curves of dications. Although the dissociation of  $He^+$  may not pose such difficulties, the Hartree–Fock method is certainly insufficient to calculate the potential energy curve of  $HeX^{2+}$  since it yields the wrong dissociation products. We tried to locate a transition state for the dissociation reaction of some  $HeX^{2+}$  which dissociate into  $He^+ + X^+$ . We failed in several cases because of the reasons mentioned above. However, for  $(X^3\Sigma^-)$   $HeO^{2+}$  we did find a transition state for the dissociation into  $He^+(^2S) + O^+(^4S)$ . At the MP4-(SDTQ)/6-311G(2df,2pd)//MP2/6-31G(d,p) + ZPE level, the activation energy is calculated as 19.8 kcal/mol at a He,O distance of 1.574 Å. Thus,  $HeO^{2+}$  is predicted to be a metastable species that might be observable in the gas phase, for example, as the reaction product of  $\beta$ -decay of the tritium-containing cation  $OT^+$ .

**$HeF^{2+}$  and  $HeNe^{2+}$ .** The ground-state potential energy curves of  $HeF^{2+}(X^4\Sigma^-)$  and  $HeNe^{2+}(X^3\Pi)$  are calculated to be purely repulsive (Table VI). At first sight this is surprising especially in case of  $HeF^{2+}$  because the second IE of F is even slightly lower than the corresponding value of O (Table IV). Why do the interactions of  $F^{2+}$  with He not yield a bound ground-state minimum structure, while  $HeO^{2+}$  in its  $X^3\Sigma^-$  ground state exhibits a rather short (1.164 Å) bond length? The answer to this lies in the different orbital interactions between He and the atomic ions  $O^{2+}(^3P)$ ,  $F^{2+}(^4S)$ , and  $Ne^{2+}(^3P)$  (Figure 2).  $O^{2+}(^3P)$  has an empty p( $\sigma$ ) AO, while the ground states of  $F^{2+}$  and  $Ne^{2+}$  possess a singly occupied 2p( $\sigma$ ) orbital. HOMO–SOMO interactions with He do not suffice to yield a minimum-energy structure. Strong Coulomb repulsion in  $HeF^{2+}(X^4\Sigma^-)$  and  $HeNe^{2+}(X^3\Pi)$  prevents the formation of metastable species. However, those excited states of  $F^{2+}$  and  $Ne^{2+}$  which have an empty p( $\sigma$ ) AO, i.e., the  $^2D$  and  $^1D$  state (Figure 2), respectively, do form a minimum-energy structure with He ( $HeF^{2+}(^2\Pi)$  and  $HeNe^{2+}(^1\Sigma^+)$ ) due to strong HOMO–LUMO interactions similar to those in  $HeO^{2+}(X^3\Sigma^-)$  (Table 6). In agreement with this, the interatomic distances show the order  $HeO^{2+}(X^3\Sigma^-) > HeF^{2+}(^2\Pi) > HeNe^{2+}(^1\Sigma^+)$ . For the  $^1\Sigma^+$  state of  $HeNe^{2+}$ , the largest interaction energy, IA, is predicted of all cations investigated here. The ground states of  $HeF^{2+}$  and  $HeNe^{2+}$  are further examples for the situation shown in Figure 5d, while the respective excited states are represented by Figure 5c.

Our computed data for the  $^1\Sigma^+$  state of  $HeNe^{2+}$  are in excellent agreement with an SCF-CI study by Montabonel et al.<sup>16a</sup> of the potential energy curves of  $^1\Sigma^+$  states of  $HeNe^{2+}$ . From their data, an  $r_e$  value of ca. 1.111 Å and a negative dissociation energy of  $-209.8$  kcal/mol are predicted. However, the energy barrier for dissociation into  $He^+(^2S) + Ne^+(^2P)$  is calculated as just ca. 0.1 kcal/mol.<sup>16a</sup> This is an example where the potential energy curve is very flat, because the position of the curve crossing and the minimum energy distance of the  $X^{2+} + Y$  curve are not far apart.  $HeNe^{2+}$  in its  $^1\Sigma^+$  state is very unlikely to be detected in the gas phase.

### Summary, Chemical Relevance, and Outlook

The systematic comparison of theoretical data for singly and doubly charged cations  $XeN^{n+}$  in their ground and excited states shows that their stability can be rationalized as the result of donor–acceptor interactions between neutral helium as the donor and the respective cationic fragment as the acceptor. The acceptor ability of a fragment is primarily determined by its electronic structure and not by its electronic charge or electronegativity. Knowing the properties of the LUMO of  $X^{n+}$ , qualitative predictions with regard to  $r_e$  and  $D_e$  of  $HeX^{n+}$  can be made. Even better predictions are possible by investigating the Laplace concentration of  $X^{n+}$ , which comprises the effects of all electrons and, therefore, provides reliable information on the holes in the valence shell of  $X^{n+}$  and the resulting acceptor ability. Donor–acceptor interactions between He and the ground state of  $X^{n+}$  lead to a van der Waals complex for singly charged  $X^+$  but to a covalently bonded ion for doubly charged  $X^{2+}$ . The excited states of  $HeX^{n+}$  investigated here are all covalently bonded due to increased donor–acceptor interactions. Analysis of electron density  $\rho(\mathbf{r})$  and energy density  $H(\mathbf{r})$  confirm this and provide additional insight

(48) (a) Wetmore, R. W.; LeRoy, R. J.; Boyd, R. K. *J. Phys. Chem.* **1984**, *88*, 6318. (b) Wetmore, R. W.; LeRoy, R. J.; Boyd, R. K. *Chem. Phys.* **1984**, *89*, 329.

(49) Taylor, P. R. *Mol. Phys.* **1983**, *49*, 1297.

CHART II: Dissociation Reactions of Ground and Excited States of Dications HeX<sup>2+</sup>: Calculated Dissociation Energies,  $D_0$  and  $D_e$ , Interaction Energies, IA, and Charge-Induced Dipole Interaction Energies,  $E_{ind}$  (in kcal/mol, at MP4(SDTQ)/6-311G(2df,2pd)//MP2/6-31G(d,p)

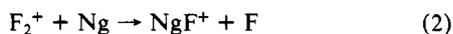
	$D_0$	$D_e$	IA	$E_{ind}$
HeBe <sup>2+</sup> (X <sup>1</sup> Σ <sup>+</sup> ) → He( <sup>1</sup> S) + Be <sup>2+</sup> ( <sup>1</sup> S)	+18.9	+20.1	+20.1	+30.5
HeB <sup>2+</sup> (X <sup>2</sup> Σ <sup>+</sup> ) → He( <sup>2</sup> S) + B <sup>+</sup> ( <sup>1</sup> S)	+15.2	+16.6		
HeB <sup>2+</sup> (X <sup>2</sup> Σ <sup>+</sup> ) → He( <sup>1</sup> S) + B <sup>2+</sup> ( <sup>2</sup> S)			+26.8	+42.3
HeB <sup>2+</sup> ( <sup>2</sup> Π) → He( <sup>2</sup> S) + B <sup>+</sup> ( <sup>3</sup> P)		+18.6		
HeB <sup>2+</sup> ( <sup>2</sup> Π) → He( <sup>1</sup> S) + B <sup>2+</sup> ( <sup>2</sup> P)			+64.5	+67.6
HeC <sup>2+</sup> (X <sup>1</sup> Σ <sup>+</sup> ) → He( <sup>1</sup> S) + C <sup>2+</sup> ( <sup>1</sup> S)	+16.8	+17.7	+17.7	+22.1
HeC <sup>2+</sup> ( <sup>3</sup> Π) → He( <sup>2</sup> S) + C <sup>+</sup> ( <sup>2</sup> P)	-76.2	-74.2		
HeC <sup>2+</sup> ( <sup>3</sup> Π) → He( <sup>1</sup> S) + C <sup>2+</sup> ( <sup>3</sup> P)			+67.0	+73.3
HeN <sup>2+</sup> (X <sup>2</sup> Π) → He( <sup>2</sup> S) + N <sup>+</sup> ( <sup>3</sup> P)	-69.7	-68.3		
HeN <sup>2+</sup> (X <sup>2</sup> Π) → He( <sup>1</sup> S) + N <sup>2+</sup> ( <sup>2</sup> P)			+48.2	+44.7
HeN <sup>2+</sup> ( <sup>4</sup> Σ <sup>-</sup> ) → He( <sup>2</sup> S) + N <sup>+</sup> ( <sup>3</sup> P)	-148.8	-146.2		
HeN <sup>2+</sup> ( <sup>4</sup> Σ <sup>-</sup> ) → He( <sup>1</sup> S) + N <sup>2+</sup> ( <sup>4</sup> P)			+127.9	+107.7
HeO <sup>2+</sup> (X <sup>3</sup> Σ <sup>-</sup> ) → He( <sup>2</sup> S) + O <sup>+</sup> ( <sup>4</sup> S)	-149.0	-146.6		
HeO <sup>2+</sup> (X <sup>3</sup> Σ <sup>-</sup> ) → He( <sup>1</sup> S) + O <sup>2+</sup> ( <sup>3</sup> P)			+98.4	+74.1
HeO <sup>2+</sup> ( <sup>3</sup> Π) → He( <sup>2</sup> S) + O <sup>+</sup> ( <sup>2</sup> D)		-288.2 <sup>a</sup>		
HeO <sup>2+</sup> ( <sup>3</sup> Π) → He( <sup>1</sup> S) + O <sup>2+</sup> ( <sup>3</sup> D)			+223.3 <sup>a</sup>	+134.4
HeF <sup>2+</sup> (X <sup>4</sup> Σ <sup>-</sup> ) → He( <sup>2</sup> S) + F <sup>+</sup> ( <sup>3</sup> P)				
HeF <sup>2+</sup> (X <sup>4</sup> Σ <sup>-</sup> ) → He( <sup>1</sup> S) + F <sup>2+</sup> ( <sup>4</sup> S)				
HeF <sup>2+</sup> ( <sup>2</sup> Π) → He( <sup>2</sup> S) + F <sup>+</sup> ( <sup>3</sup> P)	-193.5	-189.7		
HeF <sup>2+</sup> ( <sup>2</sup> Π) → He( <sup>1</sup> S) + F <sup>2+</sup> ( <sup>2</sup> D)			+143.0 <sup>a</sup>	+114.5
HeNe <sup>2+</sup> (X <sup>3</sup> Π) → He( <sup>2</sup> S) + Ne <sup>+</sup> ( <sup>2</sup> P)				
HeNe <sup>2+</sup> (X <sup>3</sup> Π) → He( <sup>1</sup> S) + Ne <sup>2+</sup> ( <sup>3</sup> P)				
HeNe <sup>2+</sup> ( <sup>1</sup> Σ <sup>+</sup> ) → He( <sup>2</sup> S) + Ne <sup>+</sup> ( <sup>2</sup> P)	-211.7	-209.3		
HeNe <sup>2+</sup> ( <sup>1</sup> Σ) → He( <sup>1</sup> S) + Ne <sup>2+</sup> ( <sup>1</sup> D)			+240.1 <sup>a</sup>	+123.1

<sup>a</sup>Calculated by using the atomic ground states and excitation energies shown in Table II.

into the strength of electrostatic or covalent interactions. This model of helium bonding correctly predicts trends in the bond strengths of weakly bound systems such as the ground states of HeX<sup>+</sup> monocations as well as the strongly and covalently bound excited states of HeX<sup>+</sup> and HeX<sup>2+</sup>.

An important question concerning our theoretical results is the experimental verification of the predicted data. What is the prospect of finding experimental evidence for HeX<sup>n+</sup> cations? What experiments can be suggested to verify the theoretical predictions? Up to now, direct experimental evidence for the existence of the He<sup>n+</sup> cations investigated here exists only for singly charged HeC<sup>+</sup><sup>42</sup> and HeNe<sup>+</sup>.<sup>15a</sup> Scattering experiments have given indirect information for the potential well of HeLi<sup>+</sup>.<sup>7</sup> Also, the observation of HeF<sup>+</sup> in a mass spectrometer has been reported,<sup>13b</sup> but the evidence has later been questioned.<sup>13a</sup> Detailed spectroscopic data are available for HeNe<sup>+</sup> only.<sup>15</sup>

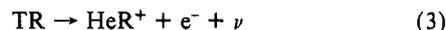
Most of the experimental evidence has been gained from discharge studies of mixtures of helium and an appropriate reaction partner. In case of HeNe<sup>+</sup>, a mixture of helium and neon was used, and several excited states were observed in addition to the <sup>2</sup>Σ<sup>+</sup> ground state. Since our calculations indicate fairly strong binding for the excited states of HeX<sup>+</sup> studied here, discharge experiments should principally be a way to produce HeX<sup>+</sup> cations. A successful experiment has been reported for HeC<sup>+</sup> by Young and Coggiola.<sup>42</sup> Surprisingly, attempts to observe HeF<sup>+</sup> failed,<sup>13a</sup> although our results predict very strong binding in the <sup>1</sup>Σ<sup>+</sup> excited state of HeF<sup>+</sup> (46.2 kcal/mol; Table I). In their experiments using techniques of charge-transfer reactions, Berkowitz and Chupka<sup>13a</sup> (BC) studied among others the following reaction (Ng denotes noble gas):



BC were able to observe KrF<sup>+</sup> and ArF<sup>+</sup> via reaction 2<sup>50</sup> but did not find any evidence for NeF<sup>+</sup> or HeF<sup>+</sup>. They speculated that the reason may either be a very low cross section for reaction 2 in the case of Ng = Ne and He or the absence of stable structures for HeF<sup>+</sup> and NeF<sup>+</sup>. We calculated ArF<sup>+</sup> and NeF<sup>+</sup> in addition to HeF<sup>+</sup> and found<sup>51</sup> that, unlike HeF<sup>+</sup> and NeF<sup>+</sup>, the strongly bound <sup>1</sup>Σ<sup>+</sup> state is the ground state for ArF<sup>+</sup>. However, the <sup>1</sup>Σ<sup>+</sup>

excited state of HeF<sup>+</sup> should still be observable unless a fast singlet-triplet conversion to the weakly bound X<sup>3</sup>Π state takes place which is unlikely for such a small molecule. It seems likely that a low cross section for reaction 2 is the reason that HeF<sup>+</sup> was not observed and that other reactions might be more likely to produce HeF<sup>+</sup>.

There is a completely different method to produce HeX<sup>+</sup> cations under controlled conditions. The β-decay of tritium leads to He<sup>+</sup> and a neutrino, and therefore, tritiated compounds may serve as precursors for helium cations via reaction 3:



Since this reaction has successfully been employed to observe<sup>52</sup> in low yield HeCH<sub>3</sub><sup>+</sup>, the analogous reaction using diatomic XT may be used to detect HeX<sup>+</sup> cations perhaps even in their weakly bound ground states. HeCH<sub>3</sub> was calculated<sup>53</sup> with a binding energy of only <0.3 kcal/mol and a He-C distance of 2.053 Å. The easily available TF might be used as a precursor for HeF<sup>+</sup>.

In the case of the HeX<sup>2+</sup> dications, two different methods seem to be possible. One takes advantage of reaction 3, using XT<sup>+</sup> cations as precursors. The other way might be charge-stripping<sup>54</sup> experiments using singly charged HeX<sup>+</sup> cations as starting material. Analogous experiments have recently been performed<sup>55</sup> for diatomic noble-gas ions NgX<sup>n+</sup> (X = C, N, O; n = 1, 2) for Ng = Xe, Kr, Ar, and Ne, but not for He. For neon, the singly charged cations NeC<sup>+</sup>, NeN<sup>+</sup>, and NeO<sup>+</sup> could be produced as precursor ions via discharge experiments.<sup>55</sup> Of the respective doubly charged cations NeN<sup>2+</sup> was detected, but not NeC<sup>2+</sup> and NeO<sup>2+</sup>.<sup>56</sup> We suggest performing analogous experiments for the helium ions.

The results presented in this paper show that the ion chemistry of helium is rich and diverse. It comprises many interesting aspects on bonding in noble-gas compounds that can be analyzed in a

(52) (a) Snell, A. H.; Pleasonton, F. *J. Phys. Chem.* **1958**, *62*, 1377. (b) Cacace, F. *Adv. Phys. Org. Chem.* **1970**, *8*, 79.

(53) Wong, M. W.; Nobes, R. H.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1987**, 233.

(54) For details of the experimental techniques, see: Ast, T. *Adv. Mass Spectrom.* **1985**, *10A*, 471.

(55) Jonathan, P.; Boyd, R. K.; Brenton, A. G.; Beynon, J. H. *Chem. Phys.* **1986**, *110*, 239.

(56) A possible explanation for this finding has been given in: Frenking, G.; Koch, W. *Int. J. Mass Spectrom. Ion Processes* **1988**, *82*, 335.

(50) Using a different ion-molecule reaction, XeF<sup>+</sup> was also observed.<sup>13a</sup> XeF<sup>+</sup> is also a "common" noble-gas-containing ion; cf. ref. 4.

(51) (a) Frenking, G.; Koch, W.; Deakne, C.; Liebman, J. F.; Bartlett, N. *J. Am. Chem. Soc.* **1989**, *111*, 31. (b) Frenking, G.; Koch, W.; Gauss, J.; Cremer, D.; Liebman, J. F. *J. Phys. Chem.*, following paper in this issue.

systematic manner with the aid of frontier orbital theory and the Laplace concentration.

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**Registry No.** He, 7440-59-7; Li<sup>+</sup>, 17341-24-1; Be<sup>+</sup>, 14701-08-7; B<sup>+</sup>, 14594-80-0; C<sup>+</sup>, 14067-05-1; N<sup>+</sup>, 14158-23-7; O<sup>+</sup>, 14581-93-2; F<sup>+</sup>, 14701-13-4; Ne<sup>+</sup>, 14782-23-1; BHe<sup>2+</sup>, 74891-40-0; CHE<sup>2+</sup>, 53262-54-7; HeN<sup>2+</sup>, 80896-02-2; HeO<sup>2+</sup>, 12269-22-6; HeF<sup>2+</sup>, 119455-36-6; HeNe<sup>2+</sup>, 57143-65-4.

## Neon and Argon Bonding in First-Row Cations NeX<sup>+</sup> and ArX<sup>+</sup> (X = Li-Ne)<sup>1</sup>

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Theoretically determined equilibrium distances, vibrational frequencies, and dissociation energies for the first-row diatomic cations NeX<sup>+</sup> and ArX<sup>+</sup> (X = Li-Ne) in their ground and selected excited states are reported at the MP4(SDTQ)/6-311G(2df,2pd)//MP2/6-31G(d,p) level and compared with the results for HeX<sup>+</sup>. The dissociation energies  $D_e$  for the electronic ground states increase for a given X in the order HeX<sup>+</sup> < NeX<sup>+</sup> < ArX<sup>+</sup>, with the exception of X = Ne. The differences in  $D_e$  values between NeX<sup>+</sup> and ArX<sup>+</sup> are significantly larger than between HeX<sup>+</sup> and NeX<sup>+</sup>. The binding energies for NeX<sup>+</sup> and ArX<sup>+</sup> show a distinct maximum for X = N. The trends in the calculated dissociation energies are rationalized by invoking donor-acceptor interactions between the weak electron donors Ne and Ar, respectively, and the electron acceptor X<sup>+</sup>. For this purpose, both frontier orbitals, electron density, energy density, and Laplace concentration are investigated. The analysis of the electronic structure shows that, in the case of the relatively weak acceptors Li<sup>+</sup>, Be<sup>+</sup>, and B<sup>+</sup>, the stability of the corresponding NeX<sup>+</sup> and ArX<sup>+</sup> ions in the ground state is solely due to charge-induced dipole interactions. Covalent bonding, however, is predicted for the ground state of NeN<sup>+</sup>, ArC<sup>+</sup>, ArN<sup>+</sup>, ArF<sup>+</sup>, and possibly NeNe<sup>+</sup>, as well as for most excited states of NeX<sup>+</sup> and ArX<sup>+</sup>.

### Introduction

In the preceding paper<sup>2</sup> (henceforth called I), we investigated the binding interactions in first-row cations HeX<sup>+</sup>. After having established a theoretical model for helium binding<sup>2-5</sup> we now present an extension of our studies to neon and argon. We report our results of a "first-row sweep" of diatomic cations NeX<sup>+</sup> and ArX<sup>+</sup> (X = Li-Ne) and compare them with the data for the helium analogues HeX<sup>+</sup>. The aim of this study is to find out if the donor-acceptor model, which has been proven to be very helpful in explaining He chemistry,<sup>2-5</sup> can also be used to rationalize the trends calculated for Ne and Ar compounds.

There are two major differences between He and the heavier analogues Ne and Ar. One is that, unlike helium, neon and argon have (filled) p orbitals in their valence shells. Therefore,  $\pi$ -orbital interactions with first-row elements Li-Ne in NgX<sup>+</sup> (Ng = noble-gas element) are possible for Ng = Ne and Ar, but not He. A second difference is that the donor ability increases from He < Ne < Ar because the ionization energies (IE) become smaller (IE(He) = 24.587 eV, IE(Ne) = 21.564 eV, IE(Ar) = 15.759 eV).<sup>6</sup> While the latter effect should yield stronger bonding for

Ar > Ne > He, the effect of  $\pi$ -orbital interactions will depend on the occupancy of the  $\pi$  orbitals of the binding partner X in NgX<sup>+</sup>. If X has occupied  $\pi$  orbitals, there will be additional  $\pi$ - $\pi$  repulsion in NgX<sup>+</sup> for Ng = Ne or Ar. If X has empty  $\pi$  orbitals, donor-acceptor interactions should be stronger. Our study will show that binding in most (but not all!) ground states of NgX<sup>+</sup> (Ng = He, Ne, Ar) is caused largely by long-range forces with the dominant contribution at the equilibrium distance arising from charge-induced dipole interactions. It will be seen below that the

(1) Parts of this research have been reported in: (a) Frenking, G.; Koch, W. *Int. J. Mass Spectrom. Ion Processes* **1986**, *82*, 335. (b) Frenking, G.; Koch, W.; Deakynne, C.; Liebman, J. F.; Bartlett, N. J. *Am. Chem. Soc.* **1989**, *111*, 31.

(2) Frenking, G.; Koch, W.; Gauss, J.; Cremer, D.; Liebman, J. J. *J. Phys. Chem.*, preceding paper in this issue.

(3) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D.; Collins, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5917.

(4) Frenking, G.; Koch, W.; Liebman, J. F. In *Molecular Structure and Energetics: Isoelectronic and Plemioelectronic Reasoning*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1989; p 1697.

(5) (a) Koch, W.; Collins, J.; Frenking, G. *Chem. Phys. Lett.* **1986**, *132*, 330. (b) Frenking, G.; Koch, W.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1988**, *110*, 8007.

(6) Moore, C. E. *Analyses of Optical Spectra*; National Bureau of Standards; U.S. Government Printing Office: Washington, DC, 1970; NSRDS-NBS 34.

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