Hydrogen substituted by Helium(+): Theoretical Investigations on the Structures and Stabilities of He_2O^{2+}, He_2N^{2+}, and He_2C^{2+}

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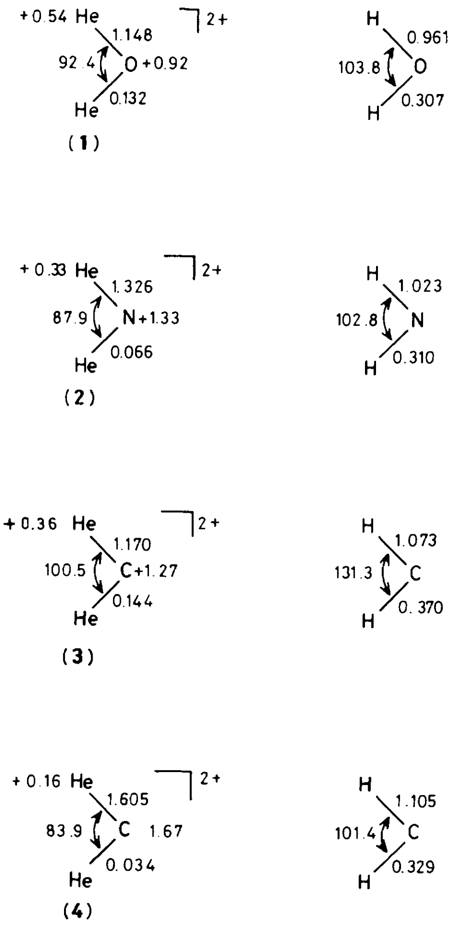
Theoretical studies of the structures and stabilities of the title compounds with respect to their dissociation reactions are reported at the MP4(SDTQ)/6-311G(2df,2pd)//MP2/6-31G(d,p) + zero point energy level of theory which shows that He_2O^{2+} ($^1A_1$) and He_2C^{2+} ($^3B_1$) exhibit short, strong bonds, while He_2N^{2+} ($^2B_1$) and He_2C^{2+} ($^1A_1$) are found to have comparatively long, weak bonds; He_2C^{2+} ($^1A_1$) is predicted to be stable towards dissociation, while the other three dicationic species are energetically unstable.

We report the results of the first *ab initio* investigations of the structures and stabilities of He_2X^{2+}, X = O, N, C. These dications are isoelectronic with water, NH_2, and methylene, respectively and an isoelectronic comparison is used to establish similarities between hydrogen and helium(+)-containing species. Theoretical investigations have been carried out with the CRAY version of GAUSSIAN 82.[1] The ground state minima for He_2O^{2+} (**1**), He_2N^{2+} (**2**), and He_2C^{2+} in its $^3B_1$ (**3**) and $^1A_1$ (**4**) states were optimized at the MP2/6-31G(d,p)[2] (full core) level of theory, and vibrational frequencies have been obtained with the harmonic approximation to determine zero-point energies (Z.P.E.). Additional single-point energy calculations were carried out at the MP4(SDTQ)/6-311G(2df,2pd) (frozen core) level.[2] At this level of theory, atomization energies can be expected to be reliable within a limit of ±5 kcal/mol^{-1}.†[2a]



Scheme 1. Optimized geometries, charge distribution, and overlap population obtained at the MP2/6-31G(d,p) level for structures (**1**)—(**4**) and for the neutral hydrogen compounds.

Table 1 exhibits the calculated total energies, and Scheme 1 shows the optimized geometries and results of the Mulliken population analysis.[3] The geometries of the respective isoelectronic hydrogen species optimized at MP2/6-31G(d,p) (full core) are also shown. The vibrational frequencies of (**1**)—(**4**) are listed in Table 2. Dications (**1**) and (**3**) are found to have rather short bonds, while (**2**) and especially (**4**) exhibit longer bonds. The overlap populations and frequencies of the stretching vibrations are clearly larger for (**1**) and (**3**) than for (**2**) and (**4**). All calculated data indicate stronger bonds for (**1**) and (**3**) compared with (**2**) and (**4**). The bond angles are smaller for the helium dications (**1**)—(**4**) relative to the isoelectronic hydrogen-containing molecules, which can be explained by the higher electronegativity of helium(+).

Table 1. Calculated total energies (in Hartrees) at MP2/6-31G(d,p) level optimized geometries.

Structure	State	MP2/6-31G(d,p)	MP4(SDTQ)/ 6-311G(2df,2pd)
He_2O^{2+} (**1**)	$^1A_1$	−79.00502	−79.14250
He_2N^{2+} (**2**)	$^2B_1$	−58.72464	−58.82244
He_2C^{2+} (**3**)	$^3B_1$	−42.16297	−42.22003
He_2C^{2+} (**4**)	$^1A_1$	−42.24327	−42.31740
HeO^+	$^2\Pi$	−77.15174	−77.25868
HeN^+	$^3\Sigma^-$	−56.81431	−56.87972
HeC^{2+}	$^1\Sigma^+$	−39.34548	−39.39672
O^+	^4S	−74.40617	−74.47513
N^+	^3P	−53.92927	−53.97549
C^{2+}	^1S	−36.44374	−36.47096
C^+	^2P	−37.33107	−37.36239
He^+	^2S	−1.99362	−1.99814
He	^1S	−2.88064	−2.89721

Table 2. Vibrational frequencies (in cm^{-1}) obtained at the MP2/6-31G(d,p) level.

Structure	Mode	Symmetry	ν
(**1**)	He–O str.	B_2	1497
	He–O str.	A_1	1385
	Bend	A_1	1002
(**2**)	He–N str.	B_2	1022
	He–N str.	A_1	1008
	Bend	A_1	670
(**3**)	He–C str.	B_2	1502
	He–C str.	A_1	1382
	Bend	A_1	801
(**4**)	He–C str.	A_1	619
	He–C str.	B_2	560
	Bend	A_1	336

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† 1 kcal = 4.184 kJ.

$$\underset{(\mathbf{1})}{He_2O^{2+}} \longrightarrow He^+ + HeO^+ \qquad -71.7 \quad (1a)$$

$$He_2O^{2+} \longrightarrow He^+ + He + O^+ \qquad -148.5 \quad (1b)$$

$$\underset{(\mathbf{2})}{He_2N^{2+}} \longrightarrow He^+ + HeN^+ \qquad -38.3 \quad (2a)$$

$$He_2N^{2+} \longrightarrow He^+ + He + N^+ \qquad -34.3 \quad (2b)$$

$$\underset{(\mathbf{3})}{He_2C^{2+}} \longrightarrow He + HeC^{2+} \qquad -50.7 \quad (3a)$$

$$He_2C^{2+} \longrightarrow 2He + C^{2+} \qquad -33.7 \quad (3b)$$

$$He_2C^{2+} \longrightarrow He^+ + He + C^+ \qquad -28.9 \quad (3c)$$

$$\underset{(\mathbf{4})}{He_2C^{2+}} \longrightarrow He + HeC^{2+} \qquad +13.4 \quad (4a)$$

$$He_2C^{2+} \longrightarrow 2He + C^{2+} \qquad +30.4 \quad (4b)$$

$$He_2C^{2+} \longrightarrow He^+ + He + C^+ \qquad +35.3 \quad (4c)$$

Scheme 2. Energies of reaction for the most favourable dissociation reactions of dications (**1**)—(**4**) calculated at the MP4(SDTQ)/6-311G(2df,2pd)//MP2/6-31G(d,p) + Z.P.E. level. The energy for equation (1a) was calculated without Z.P.E. § Energies are in kcal mol^{-1}.

The differences in the geometries between (**3**) and (**4**) are striking. The C–He interatomic distance in (**3**) is only 0.10 Å larger compared to triplet methylene, while that of (**4**) is much longer. There are six valence electrons in the molecular plane of (**4**), but only five in (**3**). The electronic structure of (**3**) is similar to a CH_2 group with a π-bonded carbon atom. In fact, helium has been found to be more strongly bound to unsaturated than saturated carbon.[4] Note that the ($^1A_1$) singlet structure (**4**) is lower in energy than the ($^3B_1$) triplet (**3**), which is opposite to that found for isoelectronic methylene.‡

Scheme 2 shows the energies of reaction for the energetically most favourable dissociation reactions of (**1**)—(**4**) obtained at the MP4(SDTQ)/6-311G(2df,2pd)//MP2/6-31G(d,p) + Z.P.E. level of theory.§ For (**1**) and (**2**), the primary products are the monocations HeX^+ and He^+, while for (**3**) and (**4**) HeC^{2+} and He are formed. HeO^+ was calculated to have a rather short (1.191 Å) bond, while HeN^+ and HeC^{2+} have long interatomic distances of 1.749 and 1.575 Å, respectively [MP2/6-31G(d,p)]. These data are in agreement with earlier S.C.F. and C.I. investigations.[4b,5]

The calculated energies of reaction for (**1**)—(**4**) clearly show an increase in thermochemical stability of the He_2X^{2+} ground states with respect to the dissociation reaction with decreasing electronegativity of X, *i.e.* $He_2O < He_2N < He_2C$. Dication (**4**) is even stable with respect to its decomposition and thus, is potentially observable in the gas phase. In fact, experiments which have been prompted by our theoretical results led to the first observation of an ion in the gas phase containing a carbon–helium bond.[6] Whether (**1**), (**2**), and (**3**) are metastable will depend on the activation barriers for reactions (1), (2), and (3).¶ A theoretical determination of the potential curves of these reactions will require a multiconfiguration study.

$$H_2O^{2+} \; (^3B_1) \longrightarrow OH^+ + H^+ \qquad -132.3^a$$

$$H_2O^{2+} \; (^1A_1) \longrightarrow OH^+ + H^+ \qquad -200.7^a$$

$$NH_2^{2+} \; (^2\Pi_u) \longrightarrow NH^+ + H^+ \qquad -108.1^b$$

$$CH_2^{2+} \; (^1\Sigma_g^+) \longrightarrow CH^+ + H^+ \qquad -71.4^c$$

Scheme 3. Energies of reaction (in kcal mol^{-1}) for the most favourable dissociation reactions of the hydrogen-containing dications. [a] MP4(SDTQ)/6-311++G(d,p)//MP2/6-31G(d,p) + Z.P.E. (ref. 7a). [b] MP4(SDTQ)/6-311++G(3df,3pd)//MP2/6-31G(p,d) + Z.P.E. (ref. 7b). [c] MP4(SDTQ)/6-311G(d,p)//6-31G(d,p) + Z.P.E. (ref. 7c).

The stabilities of (**1**)—(**4**) may be compared with the respective hydrogen-containing dications, which have already been studied.[7] The results for the hydrogen dication dissociation reactions are shown in Scheme 3. By analogy with reactions (1)—(4), the deprotonation reactions of H_2X^{2+} become increasingly exothermic with increasing electronegativity of X. However, the heats of reaction are much more negative compared to the reactions (1a)—(4a). We conclude that helium-containing dications may be more stable than the respective doubly charged cations containing hydrogen.

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‡ We also calculated the ($^1B_1$) singlet state of He_2C^{2+}. Although the geometry was similar to the ($^3B_1$) triplet structure (**3**) (r = 1.143 Å, angle = 104.1°), it was much higher (45.6 kcal mol^{-1}) in energy compared to (**3**); all data were obtained at the MP2/6-31G(d,p) (full core) level.

§ The vibrational frequencies for HeC^{2+} and HeN^+ at the MP2/6-31G(d,p) (full core) level are 655 and 269 cm^{-1}, respectively. For HeO^+, the frequency could not be determined owing to difficulties in the numerical calculation of the second derivative.

¶ Note that reactions (3a) and (3b) are spin-symmetry forbidden.