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# Beryllium–helium cations: computational evidence for a large class of thermodynamically stable species

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Dedicated to Prof. Dr. Helmut Schwarz on the occasion of his 60th birthday.

## Abstract

Ab initio calculations, at the MP2, QCISD, CCSD, and CASSCF levels of theory, have been performed to investigate the structure, stability, and properties of a new class of thermodynamically stable cations containing helium. These species have general formula $XBeHe^+$ (X: monovalent group) and arise from the ligation of a helium atom to singlet ground state $BeX^+$. The presently investigated systems include prototype "inorganic" ions such as $HBeHe^+$, $FBeHe^+$, $ClBeHe^+$, $HOBeHe^+$, and $H_2NBeHe^+$, as well as "organic" species such as $H_3CBeHe^+$, $F_3CBeHe^+$, $HC_2BeHe^+$, $H_3C_2BeHe^+$, and $C_6H_5BeHe^+$. Irrespective of the substituent X, at any computational level, including the highly accurate Gaussian-3 (G3), the dissociation energies at 298.15 K of $XBeHe^+$ into singlet ground-state $BeX^+$ and He are predicted to be remarkably large and range from ca. 6 kcal mol$^{-1}$ for $C_6H_5BeHe^+$ to ca. 11 kcal mol$^{-1}$ for $FBeHe^+$. Thus, the electronic structure of the substituent X has an appreciable effect on the structure and stability of the $XBeHe^+$ cations. We have also briefly examined the implications of our theoretical calculations for future gas-phase experiments aimed at the experimental observation and characterization of members of this new class of thermodynamically stable species of the lightest noble gas.

*Keywords:* Ab initio calculations; Beryllium; G3 theory; Helium cations

## 1. Introduction

The adducts between helium atoms and positively-charged ions $M^{n+}$ ($n \geq 1$) are of central interest in many areas of gas-phase ion chemistry and physics, ranging from the solvation and clustering of positive ions [1–4] to the dynamics of the elastic and inelastic collisions between ionic projectiles and atomic targets [5,6]. The interaction with helium atoms is also important for evaluating the transport properties of cations in a bath of the inert gas, which is of consequence in understanding the mobility of ions in plasma discharges [7,8] and planetary atmospheres [9]. In the current years, the clusters of helium atoms with singly- and multiply-charged cations are investigated with renewed interest, stimulated by the possible use

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of ionic dopants as probes to investigate the superfluid properties of helium [10–12]. In addition, taking into account the reluctance of the lightest noble gas to form stable compounds in the condensed phase, the study of its gaseous ionic adducts is expected to provide telling information on the factors conceivably involved in the chemical fixation of this element [13]. It is therefore not surprising that, over the years, numerous research groups have employed various experimental techniques, including lasers, molecular ion beams, mass spectrometry, and molecular spectroscopy, to investigate the gaseous adducts and clusters of helium with a variety of monoatomic and polyatomic ions [2–4,14–25]. Pioneering observations include, for example, the reports by Tsong and coworkers on the ability of numerous transition metals to form mono- and dihelide cations [26,27]. The structure, stability, and properties of the adducts of helium with $M^{n+}$ ($n \geq 1$) have been also the focus of intensive theoretical work, performed not only to aid the interpretation of the experiments but also to independently disclose novel fascinating features of this chemistry [28–42].

Generally speaking, small-size multiply-charged ions $M^{n+}$ ($n \geq 2$) are able to fix helium with formation of $M^{n+}$–He complexes whose stability may be as large as some tens of $\mathrm{kcal\,mol^{-1}}$ [12,31,37,43–46]. On the other hand, apart from some remarkable exceptions such as the endohedral $C_{60}He^+$ cluster containing a helium atom "encapsulated" into the cage [17,32], or simple diatomic and triatomic species such as $HeNe^+$ and $HeH_2{}^+$, whose dissociation energies into $Ne^+$ and He and $H_2{}^+$ and He amount to ca. 18 $\mathrm{kcal\,mol^{-1}}$ [15] and ca. 8 $\mathrm{kcal\,mol^{-1}}$ [41], respectively, the adducts of He with monoatomic and simple polyatomic ions $M^+$ are usually characterized as extremely fragile complexes, which feature typical dissociation energies of less than 1 or 2 $\mathrm{kcal\,mol^{-1}}$ [1–4]. Thus, the identification of novel $M^+$–He adducts of appreciable thermodynamic stability is still posing stimulating questions of experimental and theoretical interest.

In the late 1980s, Frenking and coworkers [13,47] reported that the diatomic BeO, in its singlet ground state ${}^1\Sigma^+$, fixes the lightest noble gases with formation of OBeNg complexes (Ng = He, Ne, Ar, Kr, Xe), which are thermodynamically stable with respect to dissociation into BeO and Ng. The Obe–Ng bond energies were calculated to range from about 3 $\mathrm{kcal\,mol^{-1}}$ for Ng = He to about 13 $\mathrm{kcal\,mol^{-1}}$ for Ng = Xe, and the stability of the adducts was related with the small radius of the $Be^{2+}$ cation in the neutral BeO, which leads to an electric field large enough to trap even a helium atom. This suggestion is consistent with the older idea, supported by early theoretical calculations [48–51] and confirmed by more recent ones [31,37], that it is possible to use the $Be^{2+}$ dication to fix the unreactive helium. Stimulated by these findings, as part of our continuing interest in the chemistry of gaseous fluorinated cations [52–60], we have recently found that, in its singlet ground state ${}^1\Sigma^+$, the diatomic $BeF^+$, isoelectronic with BeO, forms thermochemically stable $FBeNg^+$ adducts (Ng = He, Ne, Ar) whose dissociation enthalpies (at 298.15 K) into $BeF^+$ and Ng are computed, at the Gaussian-3 (G3) level of theory, as large as 10.6 $\mathrm{kcal\,mol^{-1}}$ for Ng = He, 16.0 $\mathrm{kcal\,mol^{-1}}$ for Ng = Ne, and 34.5 $\mathrm{kcal\,mol^{-1}}$ for Ng = Ar [61]. The implications of these findings for the conceivable existence of stable salts of the lightest noble gases have been examined in our previous article [61]. In the present one, we wish to discuss the results of novel ab initio and density functional theory (DFT) calculations which indicate that $BeF^+$ is just a member of a large class of $BeX^+$ cations (X: monovalent group), which, in their singlet ground state, are able to fix helium with formation of thermodynamically stable $XBeHe^+$ adducts. The detailed investigation of a series of exemplary "inorganic" and "organic" species such as $HBeHe^+$, $FBeHe^+$, $ClBeHe^+$, $HOBeHe^+$, $H_2NBeHe^+$, $H_3CBeHe^+$, $F_3CBeHe^+$, $HC_2BeHe^+$, $H_3C_2BeHe^+$, and $C_6H_5BeHe^+$ indicate that the substituent X has appreciable effects on the structure, stability, and properties of these ions. In addition, we will briefly examine the implications of our calculations for future conceivable gas-phase experiments aimed at the experimental observation and characterization of members of this new class of beryllium–helium cations.

## 2. Computational details

All the presently reported calculations have been performed using the Unix versions of the GAUSSIAN 98 [62] and the MOLPRO 2000.1 [63] sets of programs installed on a Alphaserver 1200 and a DS20E Compaq machine.

The geometries of the $XBeHe^+$ ions and of their $BeX^+$ fragments have been optimized at various ab initio levels of theory, including the second-order Møller–Plesset with inclusion of the inner electrons, MP2(full) [64], the quadratic configuration interaction with single and double substitutions, QCISD [65], the coupled cluster with inclusion of the contribution from single and double substitutions and of an estimate of connected triples, CCSD(T) [66,67], and the multireference SCF, MC-SCF, based on active spaces including all the valence electrons distributed in all the valence orbitals (CASSCF) [68,69]. The optimizations were performed with basis sets of increasing size and flexibility, ranging from the smallest 6-31G(d) to the largest 6-311++G(2df,2pd) [70,71]. For comparative purposes, the geometry optimization were also performed at the DFT level of theory, using the B3LYP functional [72–74] in conjunction with the above mentioned basis sets.

All the $XBeHe^+$ ions were ascertained to be true energy minima on the potential energy surface by computing the corresponding MP2(full)/6-31G(d) analytical harmonic vibrational frequencies. In addition, accurate total energies of all the investigated species have been obtained, at the MP2(full)/6-31G(d) optimized geometries, using the G3 computational procedure by Pople and coworkers [75]. It consists of a sequence of well defined ab initio calculations used to calculate the total energy of a species according to an additivity scheme, the results of which are corrected by appending a small higher-level empirical term (HLC). The full details of the procedure are given in ref. [75], and we simply report here the expression used to calculate the G3 total energies (in hartrees) at 0 K, G3 (0 K), of polyatomic, closed-shell species like those investigated in the present article

$$\begin{aligned}
\mathrm{G3}\,(0\,\mathrm{K}) = {} & E[\mathrm{MP4(fc)/6\text{-}31+G(d)}] \\
& + E[\mathrm{MP4(fc)/6\text{-}31G(2df,p)}] \\
& + E[\mathrm{QCISD(T)/6\text{-}31G(d)}] \\
& - 2 \times E[\mathrm{MP4(fc)/6\text{-}31G(d)}] \\
& + E[\mathrm{MP2(full)/G3large}] \\
& - E[\mathrm{MP2(fc)/6\text{-}31G(2df,p)}] \\
& - E[\mathrm{MP2(fc)/6\text{-}31+G(d)}] \\
& + E[\mathrm{MP2(fc)/6\text{-}31G(d)}] \\
& - 0.006386 n_{\mathrm{val}} + \mathrm{ZPE}
\end{aligned}$$

Here, $n_{\mathrm{val}}$ is the number of valence electron pairs and ZPE is the zero-point energy calculated at the HF/6-31G(d) level and scaled by 0.8929 to take account of known deficiencies at this level [76]. The G3 total energies of the investigated species at 298.15 K, G3 (298.15 K), were calculated by adding to G3 (0 K) a thermal correction calculated by standard statistical mechanics formulas [77] using the MP2(full)/6-31G(d) harmonic frequencies and moments of inertia. The classical approximation was used to include translation, (3/2)RT, and rotation contribution (RT for linear species and (3/2)RT for non-linear species, respectively). The total entropies at 298.15 K of the investigated species have been obtained using their MP2(full)/6-31G(d) harmonic frequencies and moments of inertia.

The MP2(full), the QCISD, and the B3LYP geometry optimizations were performed using the GAUSSIAN 98, whereas the CCSD(T) and the CASSCF geometry optimizations were performed using the MOLPRO 2000.1 program package. To perform the G3 calculations, we used the 6-31G(d), 6-31+G(d), and 6-31G(2df,p) basis sets standard in GAUSSIAN 98, whereas the G3large basis set was downloaded from the website suggested in ref. [75]. The 6-31G(d), 6-31+G(d), and 6-31G(2df,p) basis sets use six Cartesian d-functions (6d), while the G3large basis set uses five “pure” d-functions (5d). Both the 6-31G(2df,p) and G3large basis sets use a set of “pure” 7f functions.

Chemical bonding analysis was based on the theory of atoms in molecules (AIM), using the implementation in GAUSSIAN 98 due to Cioslowski and coworkers [78–82]. In particular, we have calculated the QCISD/6-311G(d,p) charge density $\rho$ and the Laplacian of the charge density, $\nabla^2\rho$, at the bond critical points (BCP), intended as the points on the attractor interaction lines where $\nabla\rho = 0$.

## 3. Results and discussion

### 3.1. *Structure, stability, and properties of XBeHe$^+$ (X = H, F, Cl, OH, NH$_2$, CH$_3$)*

The geometries of the XBeHe$^+$ ions containing monoatomic and simple polyatomic substituents HBeHe$^+$, FBeHe$^+$, ClBeHe$^+$, HOBeHe$^+$, H$_2$NBeHe$^+$, and H$_3$CBeHe$^+$, in their singlet ground state, have been optimized, using various basis sets, at the B3LYP and at several ab initio levels of theory, including MP2, QCISD, and CCSD(T). The obtained parameters are collected in Tables 1 and 2, and the MP2(full)/6-31G(d) harmonic vibrational frequencies are listed in Table 3 together with those of the BeX$^+$ fragments.

The thermodynamic stability of the XBeHe$^+$ adducts has been evaluated by calculating, at various levels of theory and at the temperatures of 0 and 298.15 K, the energy ($\Delta E$), the enthalpy ($\Delta H$), and the free-energy ($\Delta G$) change of the reaction

$$\mathrm{XBeHe^+ \rightarrow BeX^+ + He} \quad (1)$$

In particular, the energy changes obtained at 0 K at any of the computational levels employed for the geometry optimizations are collected in Tables 1 and 2, and the values of $\Delta E$, $\Delta H$, and $\Delta G$ obtained at the G3 level of theory are listed in Table 4 together with the relevant absolute energies and total entropies of all the species involved in reaction (1).

None of the presently investigated XBeHe$^+$ ions has been experimentally observed, and only the parent HBeHe$^+$ has been the focus of previous theoretical work. In particular, Ikuta et al. [83] have so far performed HF/STO-6G calculations to investigate whether HBeHe$^+$ could remain bound following its formation from the $\beta^-$ decay of HBeT. It was found that, in its singlet ground state, HBeHe$^+$ actually resides in a potential well, stable with respect to

Table 1
Optimized geometries (Å and °) of linear XBeHe$^+$, and energy change $\Delta E$ at 0 K (kcal mol$^{-1}$) of the reaction XBeHe$^+ \rightarrow$ BeX$^+$ + He (X = H, F, Cl)

| Method | Basis set | HBeHe$^+$ | | | FBeHe$^+$ | | | ClBeHe$^+$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Be–H | Be–He | $\Delta E$ | Be–F | Be–He | $\Delta E$ | Be–Cl | Be–He | $\Delta E$ |
| B3LYP | 6-31G(d) | 1.311 | 1.546 | 6.8 | 1.331 | 1.499 | 10.5 | 1.725 | 1.501 | 9.3 |
| | 6-311G(d,p) | 1.304 | 1.535 | 7.6 | 1.326 | 1.491 | 11.5 | 1.720 | 1.487 | 10.0 |
| | 6-311++G(d,p) | 1.304 | 1.535 | 7.3 | 1.328 | 1.490 | 10.9 | 1.721 | 1.487 | 9.7 |
| | 6-311++G(2df,2pd) | 1.302 | 1.525 | 7.6 | 1.319 | 1.488 | 10.6 | 1.718 | 1.483 | 10.1 |
| MP2(full) | 6-31G(d) | 1.309 | 1.525 | 5.0 | 1.339 | 1.481 | 8.8 | 1.713 | 1.488 | 7.6 |
| | 6-311G(d,p) | 1.300 | 1.539 | 6.1 | 1.331 | 1.496 | 9.9 | 1.720 | 1.490 | 8.8 |
| | 6-311++G(d,p) | 1.300 | 1.539 | 6.2 | 1.335 | 1.496 | 9.7 | 1.720 | 1.490 | 8.8 |
| | 6-311++G(2df,2pd) | 1.294 | 1.519 | 6.8 | 1.324 | 1.490 | 9.5 | 1.723 | 1.491 | 9.6 |
| QCISD | 6-31G(d) | 1.316 | 1.534 | 4.8 | 1.341 | 1.482 | 9.2 | 1.718 | 1.492 | 7.8 |
| | 6-311G(d,p) | 1.306 | 1.548 | 5.9 | 1.331 | 1.500 | 10.0 | 1.723 | 1.498 | 8.7 |
| | 6-311++G(d,p) | 1.306 | 1.548 | 5.9 | 1.334 | 1.500 | 9.7 | 1.723 | 1.498 | 8.7 |
| | 6-311++G(2df,2pd) | 1.304 | 1.529 | 6.5 | 1.324 | 1.494 | 9.5 | 1.727 | 1.490 | 9.2 |
| CCSD(T) | 6-31G(d) | 1.315 | 1.532 | 4.8 | 1.341 | 1.481 | 9.2 | 1.720 | 1.491 | 7.8 |
| | 6-311G(d,p) | 1.306 | 1.547 | 5.9 | 1.332 | 1.497 | 10.0 | 1.724 | 1.496 | 8.7 |
| | 6-311++G(d,p) | 1.306 | 1.547 | 6.0 | 1.335 | 1.499 | 9.8 | 1.724 | 1.496 | 8.7 |
| | 6-311++G(2df,2pd) | 1.305 | 1.529 | 6.5 | 1.325 | 1.494 | 6.5 | 1.728 | 1.489 | 9.3 |

Table 2
Optimized geometries (Å and °) of $XBeHe^+$, and energy change $\Delta E$ at 0 K (kcal mol$^{-1}$) of the reaction $XBeHe^+ \rightarrow BeX^+ + He$ (X = OH, $NH_2$, $CH_3$)

| Method | Basis set | $HOBeHe^+$ ($C_{\infty v}$) | | | $H_2NBeHe^+$ ($C_{2v}$) | | | | $CH_3BeHe^+$ ($C_{3v}$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Be–O[a] | Be–He | $\Delta E$ | Be–N[b] | Be–He | Be–N–H | $\Delta E$ | Be–C[c] | Be–He | Be–C–H | $\Delta E$ |
| B3LYP | 6-31G(d) | 1.332 | 1.500 | 9.3 | 1.447 | 1.502 | 125.2 | 8.9 | 1.637 | 1.557 | 110.8 | 5.3 |
| | 6-311G(d,p) | 1.325 | 1.492 | 10.1 | 1.440 | 1.490 | 125.4 | 9.5 | 1.627 | 1.545 | 110.9 | 6.3 |
| | 6-311++G(d,p) | 1.327 | 1.492 | 9.6 | 1.442 | 1.490 | 125.4 | 9.2 | 1.627 | 1.545 | 110.9 | 6.0 |
| | 6-311++G(2df,2pd) | 1.323 | 1.490 | 9.4 | 1.439 | 1.489 | 125.5 | 9.1 | 1.625 | 1.538 | 110.9 | 6.2 |
| MP2(full) | 6-31G(d) | 1.335 | 1.487 | 7.7 | 1.453 | 1.492 | 125.0 | 7.1 | 1.640 | 1.535 | 110.5 | 3.8 |
| | 6-311G(d,p) | 1.329 | 1.500 | 8.6 | 1.449 | 1.499 | 125.1 | 8.0 | 1.638 | 1.551 | 110.3 | 4.9 |
| | 6-311++G(d,p) | 1.332 | 1.500 | 8.6 | 1.451 | 1.499 | 125.1 | 8.1 | 1.638 | 1.551 | 110.3 | 5.0 |
| | 6-311++G(2df,2pd) | 1.327 | 1.493 | 8.6 | 1.446 | 1.497 | 125.3 | 8.3 | 1.631 | 1.546 | 110.7 | 5.9 |
| QCISD | 6-31G(d) | 1.337 | 1.487 | 8.0 | 1.455 | 1.493 | 125.0 | 7.4 | 1.647 | 1.541 | 110.6 | 3.7 |
| | 6-311G(d,p) | 1.330 | 1.503 | 8.7 | 1.450 | 1.506 | 125.1 | 8.0 | 1.648 | 1.564 | 110.1 | 4.7 |
| | 6-311++G(d,p) | 1.332 | 1.503 | 8.6 | 1.452 | 1.505 | 125.1 | 8.1 | 1.648 | 1.564 | 110.1 | 4.7 |
| | 6-311++G(2df,2pd) | 1.327 | 1.497 | 8.5 | 1.448 | 1.497 | 125.3 | 8.1 | 1.642 | 1.545 | 110.5 | 5.5 |
| CCSD(T) | 6-31G(d) | 1.337 | 1.486 | 8.0 | 1.456 | 1.492 | 125.0 | 7.4 | 1.648 | 1.544 | 110.4 | 3.6 |
| | 6-311G(d,p) | 1.331 | 1.501 | 8.8 | 1.452 | 1.502 | 125.1 | 8.1 | 1.648 | 1.560 | 110.1 | 4.6 |
| | 6-311++G(d,p) | 1.333 | 1.502 | 8.7 | 1.454 | 1.503 | 125.1 | 8.2 | 1.648 | 1.562 | 110.1 | 4.6 |
| | 6-311++G(2df,2pd) | 1.328 | 1.494 | 8.6 | 1.450 | 1.496 | 125.3 | 8.2 | 1.642 | 1.547 | 110.5 | 5.4 |

[a] The O–H bond distance ranges from 0.951 Å (QCISD/6-311++G(2df,2pd)) to 0.964 Å (MP2/6-31G(d)).
[b] The N–H bond distance ranges from 1.011 Å (QCISD/6-311++G(2df,2pd)) to 1.021 Å (CCSD(T)/6-31G(d)).
[c] The C–H bond distance ranges from 1.091 Å (MP2/6-311++G(2df,2pd)) to 1.100 Å (CCSD(T)/6-31G(d)).

Table 3
MP2(full)/6-31G(d) vibrational frequencies (cm$^{-1}$) of $BeX^+$ and $XBeHe^+$ (X = H, F, Cl, OH, $NH_2$, $CH_3$)

| | $BeH^+$ | $HBeHe^+$ | | $BeF^+$ | $FBeHe^+$ |
|---|---|---|---|---|---|
| $\nu$(Be–H) | 2284.8 (35.5) | 2349.5 (0.3) | $\nu$(Be–F) | 1448.7 (223.2) | 1503.8 (273.9) |
| $\nu$(Be–He) | | 642.9 (76.9) | $\nu$(Be–He) | | 673.2 (1.8) |
| $\delta$(H–Be–He) | | 278.3 (246.4) | $\delta$(F–Be–He) | | 184.0 (130.5) |
| | $BeCl^+$ | $ClBeHe^+$ | | $BeOH^+$ | $HOBeHe^+$ |
| $\nu$(Be–Cl) | 1055.3 (233.2) | 1156.4 (310.7) | $\nu$(Be–O) | 1579.6 (205.3) | 1612.2 (251.1) |
| $\nu$(Be–He) | | 587.6 (1.4) | $\nu$(O–H) | 3935.4 (580.8) | 3934.0 (585.3) |
| $\delta$(Cl–Be–He) | | 172.2 (58.4) | $\delta$(Be–O–H) | 476.4 (232.6) | 485.8 (228.1) |
| | | | $\nu$(Be–He) | | 653.0 (4.8) |
| | | | $\delta$(O–Be–He) | | 178.7 (34.9) |
| | $BeNH_2{}^+$ | $H_2NBeHe^+$ | | $BeCH_3{}^+$ | $H_3CBeHe^+$ |
| $\nu$(Be–N) | 1318.6 (101.9) | 1372.3 (134.1) | $\nu$(Be–C) | 886.0 (13.0) | 1035.1 (134.9) |
| $\nu_s$(N–H) | 3552.7 (190.0) | 3563.5 (188.2) | $\nu_s$(C–H) | 3091.5 (24.9) | 3094.6 (26.4) |
| $\nu_{as}$(N–H) | 3640.4 (163.4) | 3651.0 (151.7) | $\nu_{as}$(C–H) | 3203.2 (28.7) | 3193.3 (18.0) |
| $\delta$(H–N–H) | 1605.3 (99.0) | 1613.5 (122.5) | $\delta$(H–C–H) | 1234.4 (13.7) | 1296.4 (26.5) |
| $\delta$(Be–N–H) | 614.2 (189.2) | 627.4 (4.5) | $\delta$(H–C–H) | 1461.1 (1.7) | 1466.4 (2.0) |
| $\delta$(Be–N–H) | 671.3 (187.0) | 663.6 (180.1) | $\delta$(Be–C–H) | 718.7 (160.8) | 703.8 (168.6) |
| $\nu$(Be–He) | | 624.5 (209.9) | $\nu$(Be–He) | | 516.2 (14.7) |
| $\delta$(Be–N–He) | | 135.4 (30.7) | $\delta$(C–Be–He) | | 167.7 (32.4) |
| $\delta$(Be–N–He) | | 213.0 (29.0) | | | |

Intensities (km mol$^{-1}$) are given in parenthesis.

Table 4
Energy change ($\Delta E$), enthalpy change ($\Delta H$) and free energy change ($\Delta G$) (kcal mol$^{-1}$) of the dissociation $XBeHe^+ \rightarrow BeX^+ + He$, and G3 total energies (a.u.) and MP2(full)/6-31G(d) total entropies (cal mol$^{-1}$ K$^{-1}$) of the species involved in this process

| Species[a] | G3 (0 K) | TC | G3 (298.15 K) | $S$ | $\Delta E$ (0 K) | $\Delta H$ (298.15 K) | $\Delta G$ (298.15 K) |
|---|---|---|---|---|---|---|---|
| $HBeHe^+$ | −17.83963 | 0.00340 | −17.83624 | 48.8 | 7.0 | 7.8 | 1.2 |
| $FBeHe^+$ | −117.13906 | 0.00366 | −117.13540 | 55.0 | 10.2 | 10.9 | 4.1 |
| $ClBeHe^+$ | −477.38808 | 0.00376 | −477.38432 | 57.7 | 9.7 | 10.3 | 3.5 |
| $HOBeHe^+$ | −93.12981 | 0.00416 | −93.12565 | 56.5 | 9.3 | 10.0 | 3.2 |
| $H_2NBeHe^+$ | −73.23953 | 0.00447 | −73.23506 | 59.8 | 8.9 | 9.5 | 2.8 |
| $H_3CBeHe^+$ | −57.14613 | 0.00455 | −57.14158 | 60.2 | 5.9 | 6.5 | −0.2 |
| $F_3CBeHe^+$ | −354.72976 | 0.00628 | −354.72348 | 76.4 | 7.1 | 7.6 | 1.2 |
| $HC_2BeHe^+$ | −93.98466 | 0.00487 | −93.97979 | 61.8 | 8.9 | 9.6 | 2.7 |
| $H_3C_2BeHe^+$ | −95.19991 | 0.00518 | −95.19473 | 68.3 | 6.4 | 6.9 | 0.2 |
| $C_6H_5BeHe^+$ | −248.75101 | 0.00726 | −248.74375 | 81.9 | 5.4 | 6.0 | −0.7 |
| $HBe^+$ | −14.92620 | 0.00236 | −14.92384 | 40.7 | | | |
| $FBe^+$ | −114.22047 | 0.00237 | −114.21810 | 47.7 | | | |
| $ClBe^+$ | −474.47032 | 0.00239 | −474.46793 | 50.4 | | | |
| $HOBe^+$ | −90.21260 | 0.00285 | −90.20975 | 49.1 | | | |
| $H_2NBe^+$ | −70.32304 | 0.00312 | −70.31992 | 52.3 | | | |
| $H_3CBe^+$ | −54.23431 | 0.00313 | −54.23118 | 52.7 | | | |
| $F_3CBe^+$ | −351.81604 | 0.00466 | −351.81138 | 67.8 | | | |
| $HC_2Be^+$ | −91.06807 | 0.00351 | −91.06456 | 54.9 | | | |
| $H_3C_2Be^+$ | −92.28744 | 0.00373 | −92.28371 | 60.7 | | | |
| $C_6H_5Be^+$ | −245.84000 | 0.00578 | −245.83422 | 74.2 | | | |
| He | −2.90235 | 0.00142 | −2.90093 | 30.1 | | | |

dissociation into $BeH^+$ and He by 9.5 kcal mol$^{-1}$. In addition, the Be–H and the Be–He bond distances were estimated as 1.31 and 1.69 Å, respectively. Although the theoretical method employed so far is in principle rather poor, it is of interest to note that it correctly predicts the essential details of the structure and stability of $HBeHe^+$. Thus, in the present study, at any computational level and irrespective of the employed basis set, $HBeHe^+$ has been found to be a linear bound species which possesses a singlet ground state $^1\Sigma^+$. From Table 1, the MP2/6-311++G(2df,2pd) estimate of the Be–He bond distance, 1.519 Å, is quite similar to the value of 1.529 Å obtained, with the same basis set, at both the QCISD and CCSD(T) computational levels. We note also that, at any ab initio level, the estimates obtained with the largest 6-311++G(2df,2pd) basis set compare quite favourably with those based on the smallest 6-31G(d). In addition, irrespective of the employed computational level and basis set, the predicted values of the Be–H bond distance range around 1.300 Å. Positive evidence for the validity of a monodeterminantal description of the wave function of $HBeHe^+$ was obtained by repeating the geometry optimization of this ion at the CASSCF/6-311G(d,p) level of theory and finding a good agreement (Be–H = 1.309 Å and Be–He = 1.554 Å) with the geometry predicted at any ab initio level with the same basis set. Finally, it is of interest to note that, for any basis set, the less expensive B3LYP method predicts a geometry which is in good agreement with the ab initio estimates.

From Tables 1 and 2, at any ab initio level of theory and with the largest 6-311++G(2df,2p) basis set, the $\Delta E$ at 0 K of reaction (1) (X = H), with formation of singlet ground state $BeH^+$ [84], is calculated as ca. 6.5 kcal mol$^{-1}$. The G3 estimate at 0 K, 7.0 kcal mol$^{-1}$, is even larger, and corrects to a $\Delta H$ value of 7.8 kcal mol$^{-1}$ at 298.15 K. If one combines this enthalpy change with the experimental [85] enthalpy of formation of $BeH^+$, 266.1 kcal mol$^{-1}$, the enthalpy of formation of $HBeHe^+$ is estimated as 258.3 kcal mol$^{-1}$. In addition, using the total entropies reported in Table 4, the free energy change of reaction (1) ($X = H$) is predicted to be positive up to ca. 355 K. Thus, our calculations support the prediction that the $HBeHe^+$ ion is a thermodynamically stable species, in principle observable in a relatively large range of temperatures. In this perspective, taking into account the recent progress made in the spectroscopic characterization of gaseous adducts and clusters containing helium [3], we note from Table 3 that the two structurally-diagnostic frequencies of $HBeHe^+$, namely, the stretching of the Be–He bond at 643 $cm^{-1}$ and the degenerate bending at 278 $cm^{-1}$, are predicted to possess relatively large IR intensities.

The appreciable thermodynamic stability of $HBeHe^+$ is indeed remarkable, if one thinks that, as already pointed out in the Introduction, the adducts of helium with monoatomic and simple polyatomic ions $M^+$ usually feature largest dissociation energies of ca. 1 or 2 kcal $mol^{-1}$. In particular, the bond dissociation energy of the diatomic $Be^+$–He adduct into ground state $Be^+$ ($^2\Sigma^+$) and He is theoretically predicted as low as ca. 0.4 kcal $mol^{-1}$ [4]. A reasonable explanation for this somewhat unexpected finding comes from the results of the AIM calculations presently performed to investigate the nature of the interaction between $BeH^+$ and He in the $HBeHe^+$ adduct. First, we found that at the QCISD/6-311G(d,p) level of theory, the Laplacian of the electron density $\nabla^2\rho$ at the bond critical point located on the attractor interaction line corresponding to the Be–He bond resulted positive and evaluated as +0.265 electron a.u.$^{-5}$, thus suggesting that the interaction between the Be atom of $BeH^+$ and He is essentially electrostatic. Consistently, the positive charge of the Be atom of $HBeHe^+$ resulted practically identical with free $BeH^+$ and evaluated as large as +1.708 electron. This is consistent with the results of previous theoretical investigations on simple $BeX^+$ cations, including $BeH^+$ [84,86–88], $BeF^+$ [89,90], and $BeOH^+$ [90], which invariably predict that, in keeping with simple qualitative arguments which assign a formal oxidation state of +2 to the less electronegative beryllium atom of $BeX^+$ ($X = H$, OH, F), the charge distribution of these ions in their singlet ground state closely resembles $Be^{2+}X^-$ rather than $Be^+X$. Therefore, any helium atom which approaches the beryllium atom of $BeX^+$ actually experiences a positive charge which is appreciably largest than +1, and, in the limiting case of a real positive charge on the beryllium atom of +2, the interaction energy should be similar to the binding energy of He the $Be^{2+}$ dication, so far theoretically estimated as 20.1 kcal $mol^{-1}$ at the MP4 level of theory [31] and more recently refined as 21.1 kcal $mol^{-1}$ at the QCISD(T) level of theory [37]. In order to find a more quantitative support to this qualitative argument, assuming that the energy change of reaction (1) calculated ab initio, $\Delta E_{\text{ab initio}}$, reflects essentially the electrostatic interaction energy $\Delta E_{\text{electr.}}$ between a $BeX^+$ ion and a helium atom, we decided to model the latter one using the following expression [4]:

$$\Delta E_{\text{ab initio}} = \Delta E_{\text{electr.}} = -\frac{1}{2}\left(\frac{q^2\alpha}{R^4}\right) + A\,e^{-bR} \quad (2a)$$

The first term is attractive and depends on the polarizability of the helium atom, $0.205 \times 10^{-24}$ $cm^3$ [91], and on the *effective* charge $q$ on the beryllium atom of $BeX^+$. The latter value should be critically affected by the electronic structure of X, and, in particular, it should increase for electron-withdrawing substituents and should decrease for electron releasing ones. The second term is repulsive and, if one assumes that the two parameters $A$ and $b$ are essentially independent on the nature of the substituent X, they can be determined by fitting Eq. (2a) to the interaction energies $\Delta E_{\text{electr.}}$ of He with a reference pair of $BeX^+$ cations, including the “naked” $Be^{2+}$ as the limiting case. Thus, taking $BeH^+$ and $Be^{2+}$ as the reference pair and using the ab initio QCISD/6-311G(d,p) energy data at 0 K (at this computational level, the interaction energy between $Be^{2+}$ and He at the equilibrium bond distance of 1.457 Å is calculated as 18.2 kcal $mol^{-1}$), the two terms $A$ and $b$ are evaluated as 27.4 kcal $mol^{-1}$ and 0.567 Å$^{-1}$, respectively. Therefore, if one expresses the charge $q$ in electronic units and the bond distance $R$ in Å, taking into account the proper conversion factors, the interaction energy between any $BeX^+$ cation and He is given by the following equation:

$$\Delta E_{\mathrm{electr.}}\,(\mathrm{kcal\,mol^{-1}}) = -\frac{1}{2}\left(\frac{q^2 \times 0.205}{R^4}\right) \times 331.5 + 27.4\,\mathrm{e}^{-0.567R} \tag{2b}$$

To appreciate the validity of Eq. (2b) in predicting the stability of the $XBeHe^+$ complexes according to a simple electrostatic model and also to perceive the variety of conceivably existent $XBeHe^+$ ions, we decided to investigate, at the same computational levels used for the parent $HBeHe^+$, the five prototype ionic species $FBeHe^+$, $ClBeHe^+$, $HOBeHe^+$, $H_2NBeHe^+$, and $H_3CBeHe^+$. From Tables 1 and 2, we first note that, for all these ions, the effects of changing the computational level and the basis set employed to perform the geometry optimization are quite similar to those already discussed for $HBeHe^+$. In particular, the MP2/6-311++G(2df,2pd) estimates of the Be–He bond distances, 1.490 Å ($FBeHe^+$), 1.491 Å ($ClBeHe^+$), 1.493 Å ($HOBeHe^+$), 1.497 Å ($H_2NBeHe^+$), and 1.546 Å ($H_3CBeHe^+$), are quite similar to the values obtained, with the same basis set, at both the QCISD and CCSD(T) computational levels. In addition, at any ab initio level, the estimates obtained with the largest basis set 6-311++G(2df,2pd) compare quite favourably with those derived using the smallest 6-31G(d) basis set. Finally, as already noted for $HBeHe^+$, the results of CASSCF/6-311G(d,p) geometry optimizations confirmed the existence, at the multiconfigurational level of theory, of bound $XBeHe^+$ species (X = F, Cl, OH, $NH_2$, $CH_3$) whose structures are quite similar to those obtained at any ab initio level with the same basis set. In addition, we note from Table 3 that all the $XBeHe^+$ ions possess structurally diagnostic vibrational frequencies, such as the stretching of the Be–He bond, whose IR intensity is probably large enough to be experimentally detected.

Turning to the stability of $XBeHe^+$, we first note from Tables 1, 2 and 4 that the nature of the substituent X has an appreciable influence on the thermodynamics of reaction (1). In particular, the G3 enthalpy changes $\Delta H$ at 298.15 K range from a minimum value of 6.5 kcal mol$^{-1}$ for X = $CH_3$ to a maximum value of 10.9 kcal mol$^{-1}$ for X = F, and pass through 9.5 (X = $NH_2$), 10.0 (X = OH), and 10.3 (X = Cl). In addition, we note that this observed trend supports the validity of an electrostatic model to discuss the stability of the $XBeHe^+$ complexes. In fact, one expects that replacing the H atom of $HBeHe^+$ with more electronegative substituents such as F or Cl, in principle able to increase the net positive charge on the beryllium atom, the stability of the complex should increase. On the other hand, electron-releasing substituents such as $CH_3$ are predicted to decrease the net positive charge on the beryllium atom, and, therefore, to be less efficient than H in stabilizing the $XBeHe^+$ adduct. To appreciate the validity of Eq. (2b) to quantitatively estimate the interaction energy of He with $BeX^+$ (X = F, Cl, OH, $NH_2$, $CH_3$), we have first confirmed the electrostatic nature of the $XBeHe^+$ adducts by performing AIM calculations, at the QCISD/6-311G(d,p) level of theory, and finding positive values of ca. +0.3 electron a.u.$^{-5}$ for the Laplacian of the electron density $\nabla^2\rho$ at the bond critical points located on the attractor interaction lines corresponding to the Be–He bond of the various $XBeHe^+$ adducts. Based on these findings, we have used the QCISD/6-311G(d,p) AIM atomic charges of the free $BeX^+$ ions (+1.816 for X = F, +1.759 for X = Cl, +1.778 for X = OH, +1.754 for X = $NH_2$, and +1.667 for X = $CH_3$), and the QCISD/6-311G(d,p) bond distances of the $XBeHe^+$ complexes reported in Tables 1 and 2, to calculate the interaction energies $\Delta E_{\mathrm{electr.}}$ between $BeX^+$ and He according to Eq. (2b). The obtained values of 10.4 (X = F), 9.2 (X = Cl), 9.4 (X = OH), 8.6 (X = $NH_2$), and 4.5 (X = $CH_3$), together with the estimates of the interaction energies in the $HBeHe^+$ and $Be^{2+}$–He adducts, have been compared with the ab initio estimates obtained at 0 K at the QCISD/6-311G(d,p) level of theory. The very good agreement between the two sets of data, graphically shown in Fig. 1 ($r^2 = 0.994$), confirms the expectation that a simple electrostatic model should be adequate to describe the interaction between $BeX^+$ ions and helium atoms, and provides simple qualitative arguments to predict the effect of

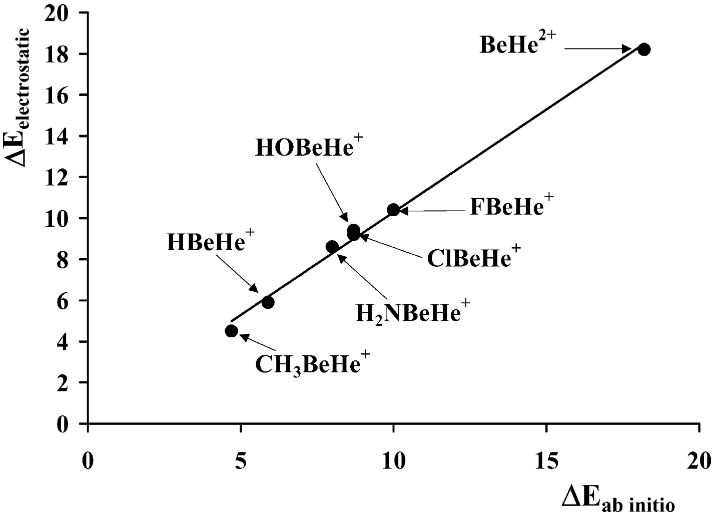

Fig. 1. Energy changes (kcal mol$^{-1}$) of the dissociation $XBeHe^+ \rightarrow BeX^+ + He$ calculated according to an electrostatic model, $\Delta E_{electr.}$ (Eq. (2b)), and at the QCISD/6-311G(d,p) ab initio level of theory, $\Delta E_{ab\,initio}$.

the substituent X on the stability of the $XBeHe^+$ adducts.

If one combines the experimentally available enthalpies of formation of $BeF^+$, 170.0 kcal mol$^{-1}$, and $BeCl^+$, 233.6 kcal mol$^{-1}$, with the G3 (298.15 K) enthalpy changes of reaction (1) for X = F, 10.9 kcal mol$^{-1}$, and X = Cl, 10.3 kcal mol$^{-1}$, the enthalpies of formation of $FBeHe^+$ and $ClBeHe^+$ at 298.15 K are theoretically evaluated as 159.1 and 223.3 kcal mol$^{-1}$, respectively. In addition, from Table 4, taking into account the contribution to reaction (1) of the entropy term, ions like $FBeHe^+$, $ClBeHe^+$, $HOBeHe^+$, and $H_2NBeHe^+$ are predicted to be thermodynamically stable up to temperatures of ca. 150–200 °C.

### 3.2. Structure, stability, and properties of organic $XBeHe^+$ ($R = CF_3$, $C_2H$, $C_2H_3$, $C_6H_5$)

The results concerning the simplest $XBeHe^+$ ions suggest that the electronic structure of the substituent X critically affects the stability of the $XBeHe^+$ complexes. In this respect, the organic substituents are in principle ideally suited to modulate the positive charge on the beryllium atom so to increase or decrease the thermodynamic stability of the $XBeHe^+$ complexes. Thus, based on the positive evidence for a stable prototype “organic” complex $H_3CBeHe^+$, we decided to investigate the structure and stability of $F_3CBeHe^+$, $HC_2BeHe^+$, $H_3C_2BeHe^+$, and $C_6H_5BeHe^+$ as exemplary cases of the influence of organic substituents on the stability of the $XBeHe^+$ cations. The conceivable existence of these species is also of interest in the context of the organometallic chemistry of the noble gases. This research area emerged first in 1975, when Perutz and Turner obtained spectroscopic evidence for the formation, in low-temperature matrices, of adducts between $M(CO)_5$ (M = Cr, Mo, W) and neon, argon, krypton, and xenon [92]. Over the years, the structure, properties, and reactivity of these and other organometallic complexes of the heaviest noble gases have been investigated with considerable experimental and theoretical interest [93–96]. On the other hand, analogous species containing the less polarizable helium have not yet been observed under any experimental condition. This is actually not surprising if one thinks, for example, that the M–Xe bond dissociation energies of the $M(CO)_5Xe$ adducts (M = Cr, Mo, W) have been measured as 8 kcal mol$^{-1}$, and that upper limits of ca. 6 and ca.

3 kcal mol$^{-1}$, respectively, have been estimated for the W–Kr and W–Ar bond dissociation energies of $W(CO)_5Kr$ and $W(CO)_5Ar$. Thus, the organometallic chemistry of the lightest rare-gas atoms, especially helium, still remains an essentially unexplored area, and any theoretical evidence for stable $XBeHe^+$ ions containing organic moieties could stimulate novel experimental work along this direction.

The relevant geometric parameters of $F_3CBeHe^+$, $HC_2BeHe^+$, $H_3C_2BeHe^+$, and $C_6H_5BeHe^+$, optimized at both the MP2(full) and the B3LYP level of theory in conjunction with the 6-31G(d) basis set, are shown in Fig. 2.

We first note that, for any of the investigated species, the two sets of optimized parameters are indeed in very good agreement, thus suggesting that the less expensive DFT method should be in principle adequate to investigate the structure of $XBeHe^+$ ions which are actually too large to be treated at the ab initio level of theory.

To appreciate the thermochemical stability of our investigated $XBeHe^+$ ions, invariably characterized as true minima on the singlet potential energy surface, we have calculated, at the G3 level of theory, the $\Delta E$, $\Delta H$, and $\Delta G$ of reaction (1) for $X = CF_3$, $C_2H$, $C_2H_3$, and $C_6H_5$. The obtained values, listed in Table 4, indicate that the effect of the organic substituents on the thermochemistry of the $XBeHe^+$ ions is in line with the qualitative arguments outlined in the previous paragraphs. Thus, the $\Delta H$ at 298.15 K of reaction (1) for $R = CF_3$, 7.6 kcal mol$^{-1}$, is larger than $R = CH_3$, 6.5 kcal mol$^{-1}$, thus confirming a stabilizing effect resulting by replacing the hydrogen atoms of $CH_3$ with three electron-withdrawing fluorine atoms. On the other hand, the replacement of a methyl group with a phenyl one results in a slight destabilization of the $XBeHe^+$ complex, which probably reflects the larger donor ability toward the positively charged beryllium atom of the aromatic ring with respect to $CH_3$. In this respect, a vinyl group is expected to be less efficient

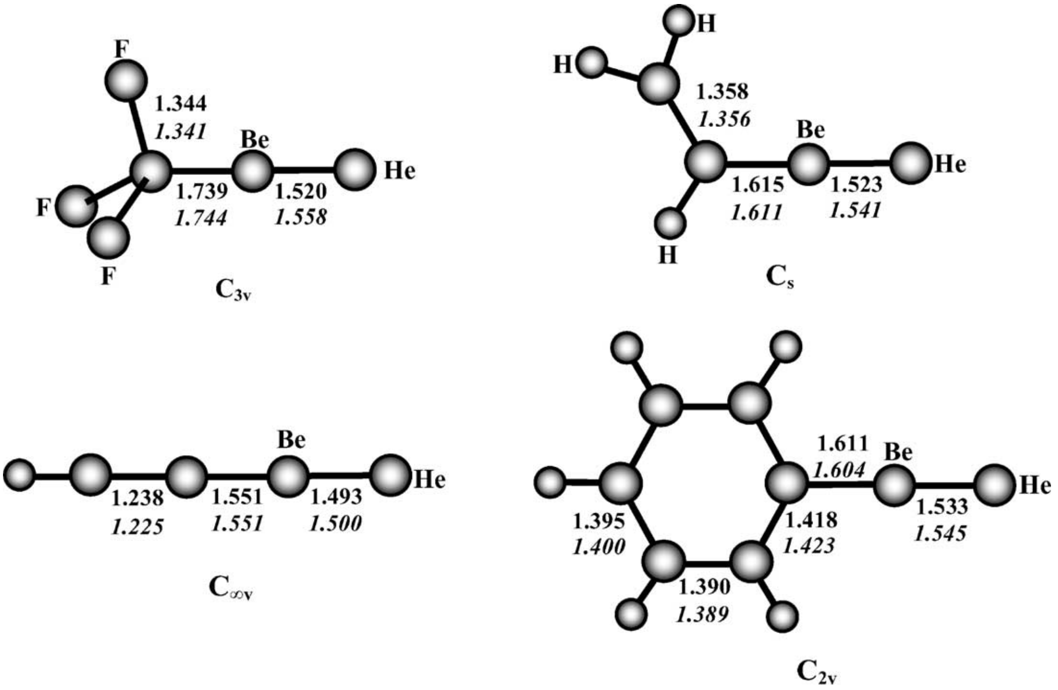

Fig. 2. MP2(full)/6-31G(d) and B3LYP/6-31G(d) (italic) optimized bond lengths (Å) of $F_3CBeHe^+$, $HC_2BeHe^+$, $H_3C_2BeHe^+$, and $C_6H_5BeHe^+$ (largest and smallest unlabelled circles are carbon and hydrogen atoms, respectively).

than a phenyl one, and, in fact, replacing the H atom of $HBeHe^+$ with a $C_2H_3$ group results in a thermochemical destabilization which is comparable with that observed passing from $HBeHe^+$ to $H_3CBeHe^+$. On the other hand, with respect to the H atom, groups containing triple bonds, such as $HC_2$, are expected to exert an appreciable stabilizing effect on the $XBeHe^+$ complex, since a formally sp-hybidized carbon atom has in principle a relatively large electronegativity. Consistently, from Table 4, the $\Delta H$ of reaction (1) for $X = C_2H$ is computed as large as $9.6\,\text{kcal mol}^{-1}$. Although our calculations concern just a few number of exemplary cases, they suggest that the thermodynamic stability of the $XBeHe^+$ ions should be appreciably affected by the nature of the organic substituent, and stimulate further computational work to search for the most effective ones in stabilizing the $XBeHe^+$ complexes.

## 4. Conclusions

The advances made recently in the mass spectrometric and spectroscopic investigation of fragile ionic complexes of the lightest noble gases, particularly helium, stimulate the theoretical investigation of still unexplored species which could be in principle experimentally investigated and characterized. In the present study, we have obtained evidence for a new large class of thermodynamically stable beryllium–helium cations. Although our calculations concern just a few number of "inorganic" and "organic" $XBeHe^+$ exemplary species, they suggest that the thermodynamic stability of these ions should be appreciably affected by the nature of the substituent X and stimulate further computational work to search for the most effective ones. From the experimental point of view, the results of our calculations could encourage future work aimed at the observation and structural characterization of these novel beryllium–helium cations. In this perspective, it is of interest to note, for example, that simple $XBe^+$ precursor ions such as $CH_3Be^+$, $C_2H_3Be^+$, $C_2H_5Be^+$, and $C_6H_5Be^+$ can be easily obtained from the electron-impact ionization of viable neutral precursors such as $R_2Be$ ($R = CH_3$, $C_2H_5$, $C_6H_5$) [97,98]. Thus, searching for stable organoberyllium ions containing helium could reveal an attractive challenge for future gas-phase experiments.

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