

# Theoretical Investigation of Organo-Noble Gas Compounds, $\text{HC}(\text{Ng})_n^+$ , $n = 1, 2$ ; $\text{Ng} = \text{He}, \text{Ne}, \text{Ar}, \text{Kr}, \text{and Xe}$ . Evidence for Potentially Isolable $\text{HCAr}_n^+$ , $\text{HCKr}_n^+$ , and $\text{HCXe}_n^+$ Species

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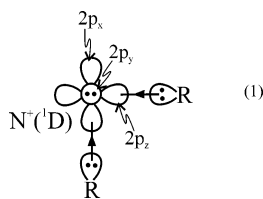
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We present a high-level theoretical study of the interaction of the ground-state  $\text{CH}^+$  cation with the noble gas,  $\text{Ng} = \text{He}$  to  $\text{Xe}$ , atoms. Considerably strong  $\text{C}-\text{Ng}$  bonds were detected in the ground-state singlet  $\text{HC}(\text{Ng})^+$  and  $\text{HC}(\text{Ng})_2^+$  species when  $\text{Ng} = \text{Ar}, \text{Kr}, \text{and Xe}$ . Bonding occurs in a Lewis acid–base fashion via dative bonds of  $\text{HC}^+ \leftarrow :\text{Ng}$  type, resembling the bonding nature of the recently isolated  $\text{N}_5^+$  cation. Both closed-shell  $\text{HC}(\text{Ng})^+$  and  $\text{HC}(\text{Ng})_2^+$  cations are likely to be isolable under appropriate experimental conditions.

## Introduction

The recent laboratory synthesis of novel nitrogen and noble gas containing compounds has stimulated a surge of interest in both experimental and theoretical studies of “exotic” molecules. Recent examples include the synthesis of stable  $\text{N}_5^+$  salts<sup>1</sup> and the mass-spectrometric detection of the cyclic  $\text{N}_5^-$  anion<sup>2</sup> (isoelectronic to the well-known  $\text{C}_5\text{H}_5^-$  cyclopentadienyl anion) by Christie and co-workers, the gas-phase detection of  $\text{N}_4$  and  $\text{O}_4$  by Cacace and co-workers,<sup>3,4</sup> the synthesis and characterization of  $\text{N}(\text{CO})_2^+$  (isoelectronic to  $\text{N}_5^+ = \text{N}(\text{N}_2)_2^+$ ) salts by Seppelt and co-workers,<sup>5</sup> and the matrix isolation and spectroscopic characterization of  $\text{HNgX}$ -type molecules, where  $\text{Ng}$  is a noble gas atom and  $\text{X}$  a group with large electron affinity, by Räsänen and co-workers.<sup>6</sup> Among the latter family of molecules stands  $\text{HArF}$ ,<sup>7a</sup> which along with  $\text{ArBeO}$ <sup>7b,7c</sup> are, to the best of our knowledge, the only argon-containing isolated (in an Ar matrix) neutral compounds. Wong has recently predicted via quantitative ab initio calculations that another member of the  $\text{HNgX}$  family,  $\text{HHeF}$ , lies in a shallow minimum of 6.7 kcal/mol and thus might also be accessible experimentally.<sup>8</sup>

In a recent paper,<sup>9</sup> we attempted to clarify the bonding mechanism in the newly synthesized isoelectronic  $\text{N}_5^+$  and  $\text{N}(\text{CO})_2^+$  species using highly correlated ab initio calculations. It was shown that the bonding occurs through a simple Lewis “acid–base” interaction with the  $\text{N}_2$  or  $\text{CO}$   $\sigma^2$  electron pairs transferred to the central  $\text{N}^+(\text{D})$  cation and forming dative bonds according to the following valence-bond Lewis (vbL) diagram

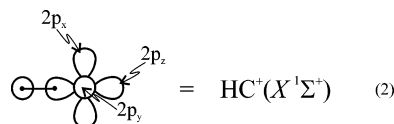


which also explicates the highly bent structure of these systems. Obviously, what is meant by this scheme is that the in situ

central  $\text{N}^+$  is in its first  $^1\text{D}$  excited-state lying 1.888 eV above the ground  $^3\text{P}$  state.<sup>10</sup> Our calculations showed that the simultaneous breaking of the two  $\text{N}-\text{R}$  ( $\text{R} = \text{N}_2, \text{CO}$ ) bonds leads, indeed, to  $\text{N}^+(\text{D}) + 2\text{R}(\text{X } ^1\Sigma_g^+)$ .<sup>9</sup> It is clear that the ground  $\text{N}^+(\text{D})$  state could not be entailed in the formation of singlet  $\text{NR}_2^+$  species due to spin angular momentum conservation.

In the same work<sup>9</sup> and within the same spirit, we examined the possibility for noble gas atoms to form a similar type of bonds. In particular, we studied the  $\text{N}(\text{Ng})_n^+$  family, where  $\text{Ng} = \text{He}, \text{Ne}, \text{Ar}, \text{and Kr}$  and  $n = 1$  or 2. For the  $\text{NAr}_2^+$  and  $\text{NKr}_2^+$  cations of  $^1\text{A}_1$  symmetry, significant atomization energies were obtained indicating that they could be isolated if combined with appropriate counteranions. However, this can prove to be a rather difficult task because  $\text{NAr}_2^+(\text{A}_1)$  and  $\text{NKr}_2^+(\text{A}_1)$  are not ground states as in the case of  $\text{N}(\text{N}_2)_2^+$  and  $\text{N}(\text{CO})_2^+$ ; the energy required to promote  $\text{N}^+$  into its  $^1\text{D}$  state is not efficiently counterbalanced by the formation of the two  $\text{N}-\text{Ng}$  bonds. The ground states here are triplets of the type  $\text{N}(\text{Ng})^+\cdots\text{Ng}$ , where the second  $\text{Ng}$  atom is weakly bound electrostatically to the  $\text{X } ^3\Sigma^-$  ground state of the  $\text{N}(\text{Ng})^+$  diatomic.

At this point, it was natural to inquire about replacing the central  $\text{N}^+$  cation by a molecular entity having the same electronic characteristics as  $\text{N}^+(\text{D})$  but being in its *ground state*. Such a candidate could be the molecular cation  $\text{CH}^+$ , isoelectronic and isovalent to  $\text{N}^+(\text{D})$ , the ground state of which is accurately represented by eq 2.



Note that  $\text{CH}^+(\text{X } ^1\Sigma^+)$  carries the same “binding sites” as the first excited  $^1\text{D}$  state of  $\text{N}^+$  (Scheme 1). The vantage point, as compared to  $\text{N}^+(\text{D})$ , is that its ground state is already prepared to act as a host for one or two electron pairs, that is, to form stable singlets,  $\text{HC}(\text{Ng})_n^+$ ,  $n = 1$  or 2. At this point, we should mention the very recent isolation and characterization of a salt containing a *sec*-alkyl ( $-\text{CH}^+-$ ) cation by Bochmann and co-workers,<sup>11</sup> providing hope for observation and experimental study of the analogous  $\text{HC}(\text{Ng})_n^+$  species proposed here.

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**TABLE 1: Total Energies,  $E$  (hartree), Bond Lengths ( $\text{\AA}$ ), Separation Energies,  $T_e$  ( $\text{cm}^{-1}$ ), of CH and  $\text{CH}^+$ , and Ionization Energies, IE (eV), of He, Ne, Ar, Kr, and Xe at the RCCSD(T)/cc-pVTZ Level of Theory<sup>a</sup>**

species	$-E$	$r_c^b$	$T_e^b$	IE
CH ( $X^2\Pi$ )	38.410 24	1.1224 (1.1199)	0	10.52 (10.64) <sup>b</sup>
$\text{CH}^+$ ( $X^1\Sigma^+$ )	38.023 62	1.1311 (1.1309)	0	
$\text{CH}^+$ ( $a^3\Pi$ )	37.980 10	1.1358 (1.1361)	9 550 (9200)	
$\text{CH}^+$ ( $b^3\Sigma^-$ )	37.847 60	1.2449 (1.2446)	39 661 (38200)	
He ( $^1S$ )	2.900 232			24.53 (24.59) <sup>c</sup>
He <sup>+</sup> ( $^2S$ )	1.998 921			
Ne ( $^1S$ )	128.802 45			21.30 (21.56) <sup>c</sup>
Ne <sup>+</sup> ( $^2P$ )	128.019 57			
Ar ( $^1S$ )	527.043 07			15.55 (15.76) <sup>c</sup>
Ar <sup>+</sup> ( $^2P$ )	526.471 63			
Kr ( $^1S$ )	2752.244 98			13.92 (14.00) <sup>c</sup>
Kr <sup>+</sup> ( $^2P$ )	2751.733 33			
Xe ( $^1S$ )	7232.307 12			12.25 (12.13) <sup>c</sup>
Xe <sup>+</sup> ( $^2P$ )	7231.856 85			

<sup>a</sup> Experimental values in parentheses. <sup>b</sup> Experimental values from ref 19. <sup>c</sup> Experimental values from ref 10.

In what follows, we attempt to investigate theoretically the possibility of formation of stable  $\text{HC}(\text{Ng})_n^+$  molecules, where  $\text{Ng} = \text{He, Ne, Ar, Kr, and Xe}$  and  $n = 1, 2$ , using coupled-cluster techniques and quantitative basis sets. We provide total energies, geometries, binding energies, and potential energy curves. Although, in general, noble gas containing cations have been studied in the past,<sup>12</sup> to the best of our knowledge, there exists only one previous theoretical study on the  $\text{HCHe}^+$  cation but in a completely different spirit.<sup>13</sup>

### Computational Outline

For all our calculations, the coupled cluster singles and doubles with a perturbative treatment of the triple excitations, CCSD(T), method was employed.<sup>14</sup> For the triplet states, the restricted variant based on a restricted open-shell Hartree–Fock reference, ROHF-RCCSD(T), method was used.<sup>15</sup> The CC-single-reference approach is ideal for describing purely dative bonds as in the present case. Indeed, full potential energy curves of  $\text{CH}^+ + n\text{Ng}$  have been constructed (vide infra) at the CCSD(T) level.

The correlation-consistent plain triple- $\zeta$  cc-pVTZ basis of Dunning<sup>16</sup> was used through all calculations of potential energy curves, geometries, and harmonic frequencies. The  $\text{HC}-(\text{Ng})_n^+$  binding energies obtained were, then, recalculated at the CCSD(T)/cc-pVQZ ( $n = 1, 2$ ) and CCSD(T)/aug-cc-pV5Z ( $n = 1$ ) levels of theory using the CCSD(T)/cc-pVTZ geometries. In the calculations involving xenon atoms, the well-tempered basis set (WTBS) of Huzinaga and co-workers<sup>17</sup> was used, augmented with 2p and 2f functions, (28s25p17d2f), and generally contracted to [10s9p6d2f].

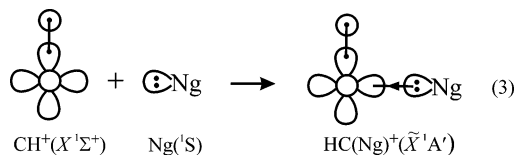
All our calculations were performed via the MOLPRO 2002.6 code.<sup>18</sup>

### Results and Discussion

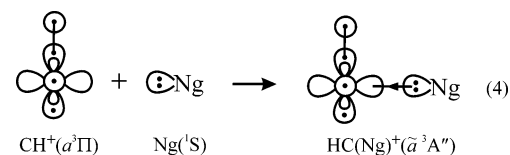
Table 1 lists pertinent characteristics of the CH,  $\text{CH}^+$ , Ng, and  $\text{Ng}^+$  species,  $\text{Ng} = \text{He, Ne, Ar, Kr, and Xe}$ , at the CCSD(T)/cc-pVTZ level. All calculated quantities are in good agreement with the corresponding experimental values. The ionization energies (IE) of all Ng atoms are larger than the IE of  $\text{CH}(X^2\Pi)$ ; therefore, the asymptotic fragments are  $\text{CH}^+(X^1\Sigma^+) + n\text{Ng}(^1S)$  in all cases.

**a.  $\text{HC}(\text{Ng})^+$ ,  $\text{Ng} = \text{He, Ne, Ar, Kr, and Xe}$ .** All our numerical results concerning the  $\text{HC}(\text{Ng})^+$  species are sum-

marized in Table 2. The binding process is described succinctly by the following vBL icon



leading naturally to bent singlet ( $^1A'$ ) states. To ensure that  $^1A'$  is the ground state of all  $\text{HC}(\text{Ng})^+$  molecules, we also studied the  $^3A''$  triplets. The latter correlate to  $\text{CH}^+(a^3\Pi) + \text{Ng}(^1S)$ , lying 9550  $\text{cm}^{-1}$  above the ground-state fragments  $\text{CH}^+(X^1\Sigma^+) + \text{Ng}(^1S)$ ; see Table 1. Reaction 4 below is self-explanatory, and it suggests strongly bent triplets.



For all Ng atoms and for both  $\tilde{X}^1A'$  and  $\tilde{a}^3A''$  states our calculations predict bent geometries in accordance with the above proposed binding mechanisms with the C–H bond length decreasing slightly as compared to the free  $\text{CH}^+(X^1\Sigma^+)$  bond length (Tables 1 and 2).

The binding energies ( $D_e$ ) of  $\text{HC}-\text{He}^+$  and  $\text{HC}-\text{Ne}^+$   $\tilde{X}^1A'$  states are quite small, 0.98 and 2.90 kcal/mol at the CCSD(T)/cc-pVTZ level, increasing to 1.52 and 3.02 kcal/mol at the CCSD(T)/aug-cc-pV5Z level of theory, see Table 2. Taking into account the harmonic zero-point energy corrections (ZPE) at the cc-pVTZ level, the above values reduce to  $D_0 = 0.15$  and 1.90 kcal/mol. A dramatic increase in  $\text{HC}-\text{Ng}^+ D_e$  is observed by moving to the Ar, Kr, and Xe analogues: at the highest level of calculation,  $D_e(D_0) = 20.4$  (18.3), 30.8 (28.6), and 44.7 (42.6) kcal/mol, respectively. According to reaction 3, the binding depends on the ability of the Ng atom to donate electrons to the empty  $2p_\sigma$  orbital of  $\text{CH}^+(X^1\Sigma^+)$ , which in turn depends, in essence, on the Ng polarizabilities ( $\alpha$ ). A plot of the  $\text{HC}-\text{Ng}^+ D_e$  values versus the (experimental)  $\alpha$ 's ( $\text{\AA}^3$ ) [ $\text{He}(0.205)$ ,  $\text{Ne}(0.395)$ ,  $\text{Ar}(1.641)$ ,  $\text{Kr}(2.48)$ ,  $\text{Xe}(4.04)$ ]<sup>20</sup> testifies to the correctness of this argument (Figure 1), in agreement also with the Hartree–Fock (HF) Mulliken atomic charges (Table 2). Extrapolating the  $D_e$  vs  $\alpha$  linear curve to the radon polarizability ( $\alpha = 5.3 \text{\AA}^3$ ),<sup>21</sup> a  $\text{HC}-\text{Rn}^+$  dissociation energy of 60 kcal/mol is obtained. Similar behavior of  $D_e$  as a function of  $\alpha$  has been recently observed in the  $\text{Li}-\text{Ng}$  ( $X^2\Sigma^+$ ,  $B^2\Sigma^+$ , and  $A^2\Pi$ ) states,  $\text{Ng} = \text{Ne to Kr}$  (see ref 22).

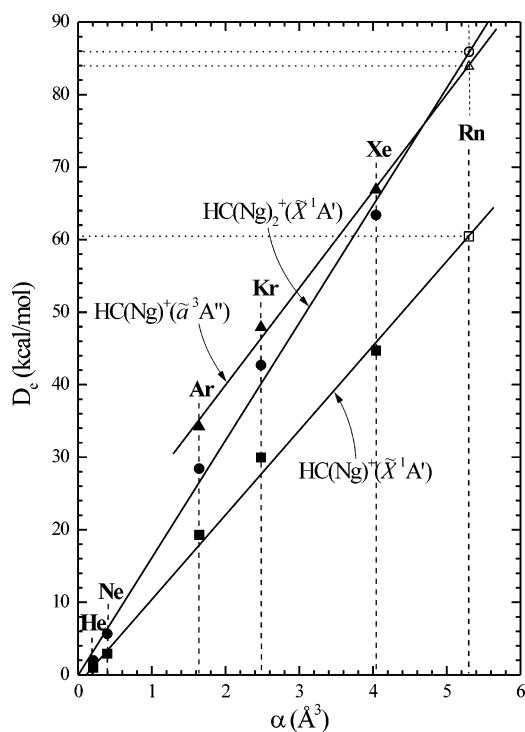
Notice that in the  $\text{HC}(\text{Ng})^+$  sequence,  $\text{Ng} = \text{He, Ne, Ar, and Kr}$ , the  $D_e$  values increase by less than 1 kcal/mol on going from the plain cc-pVTZ to the aug-cc-pV5Z basis set. Finally the  $\angle \text{HCNg}$  ( $\theta$ ) angle increases monotonically from 82° ( $\text{HCHe}^+$ ) to 96° ( $\text{HCXe}^+$ ) in conformity with reaction 3 suggesting  $\theta = 90^\circ$ .

Now, the triplet  $\text{HC}(\text{Ng})^+$  states of  $^3A''$  symmetry, as already described, trace their lineage to  $\text{CH}^+(a^3\Pi) + \text{Ng}(^1S)$ , reaction 4. The in situ carbon atom in the  $\text{CH}^+(a^3\Pi)$  state finds itself in the  $^4P(2s^12p^2; M_L = \pm 1)$  state; hence, the binding mode with the Ng atoms is identical to the previously discussed singlets, reaction 3. However, a stronger  $\text{HC}-\text{Ng}^+$  bond is expected on account of the semi-exposed carbon core; indeed, our RCCSD(T)/cc-pVTZ calculations predict strongly bent states, much higher binding  $\text{HC}-\text{Ng}^+$  energies, and bond distances much shorter than those in the corresponding singlets, see Table 2. A

**TABLE 2: Energies,  $E$  (hartree), Bond Lengths,  $r$  (Å), and Bond Angles,  $\theta$  ( $\angle\text{HCNg}$ ; deg), Energy Separations,  $T_e$  (kcal/mol), HC–Ng<sup>+</sup> Binding Energies,  $D_e$  and  $D_0$  (kcal/mol), and Net Mulliken Charges,  $q_C$ ,  $q_{\text{Ng}}$ , of HC(Ng)<sup>+</sup>( $\tilde{X}^1A'$  and  $\tilde{a}^3A''$ ) Species, Where Ng = He, Ne, Ar, Kr, and Xe, at the RCCSD(T)/cc-pVTZ, cc-pVQZ, and aug-cc-pV5Z Levels of Theory**

species	basis set	$-E$	$r_{\text{C-H}}$	$r_{\text{C-Ng}}$	$\theta$	$T_e$	$D_e$	$D_0^a$	$q_C^b$	$q_{\text{Ng}}^b$
HC–He <sup>+</sup> ( $\tilde{X}^1A'$ )	cc-pVTZ	40.925 42	1.130	2.212	81.6		0.98	0.15	+0.69	+0.03
HC–He <sup>+</sup> ( $\tilde{X}^1A'$ )	cc-pVQZ	40.934 62					1.33		+0.70	+0.03
HC–He <sup>+</sup> ( $\tilde{X}^1A'$ )	aug-cc-pV5Z	40.937 62					1.52		+0.55	+0.01
HC–He <sup>+</sup> ( $\tilde{a}^3A''$ )	cc-pVTZ	40.883 78	1.122	1.679	101.5	26.1	2.16		+0.63	+0.03
HC–Ne <sup>+</sup> ( $\tilde{X}^1A'$ )	cc-pVTZ	166.830 69	1.129	2.239	83.8		2.90	1.90	+0.69	+0.04
HC–Ne <sup>+</sup> ( $\tilde{X}^1A'$ )	cc-pVQZ	166.878 26					2.82		+0.70	+0.04
HC–Ne <sup>+</sup> ( $\tilde{X}^1A'$ )	aug-cc-pV5Z	166.896 64					3.02		+0.55	+0.02
HC–Ne <sup>+</sup> ( $\tilde{a}^3A''$ )	cc-pVTZ	166.790 16	1.121	1.915	102.9	25.4	4.77		+0.59	+0.08
HC–Ar <sup>+</sup> ( $\tilde{X}^1A'$ )	cc-pVTZ	565.097 46	1.121	2.034	92.7		19.3	17.2	+0.43	+0.33
HC–Ar <sup>+</sup> ( $\tilde{X}^1A'$ )	cc-pVQZ	565.134 65					19.9		+0.45	+0.32
HC–Ar <sup>+</sup> ( $\tilde{X}^1A'$ )	aug-cc-pV5Z	565.167 93					20.4		+0.28	+0.31
HC–Ar <sup>+</sup> ( $\tilde{a}^3A''$ )	cc-pVTZ	565.077 62	1.095	1.821	116.1	12.4	34.2		+0.26	+0.47
HC–Kr <sup>+</sup> ( $\tilde{X}^1A'$ )	cc-pVTZ	2790.316 33	1.120	2.109	94.5		30.0	27.8	+0.33	+0.44
HC–Kr <sup>+</sup> ( $\tilde{X}^1A'$ )	cc-pVQZ	2790.350 17					30.4		+0.34	+0.45
HC–Kr <sup>+</sup> ( $\tilde{X}^1A'$ )	aug-cc-pV5Z	2790.361 87					30.8		+0.13	+0.47
HC–Kr <sup>+</sup> ( $\tilde{a}^3A''$ )	cc-pVTZ	2790.301 36	1.093	1.927	119.1	9.40	47.9		+0.16	+0.58
HC–Xe <sup>+</sup> ( $\tilde{X}^1A'$ )	cc-pVTZ/WTBS <sup>c</sup>	7270.402 03	1.119	2.240	96.5		44.7	42.6	+0.21	+0.57
HC–Xe <sup>+</sup> ( $\tilde{a}^3A''$ )	cc-pVTZ/WTBS <sup>c</sup>	7270.393 14	1.090	2.075	123.1	5.58	66.5		+0.02	+0.73

<sup>a</sup>  $D_0$  = corrected  $D_e$  with respect to the zero-point energies (ZPE) of HC(Ng)<sup>+</sup> and CH<sup>+</sup>. <sup>b</sup> Hartree–Fock charges. <sup>c</sup> Well-tempered basis set on Xe, ref 17.



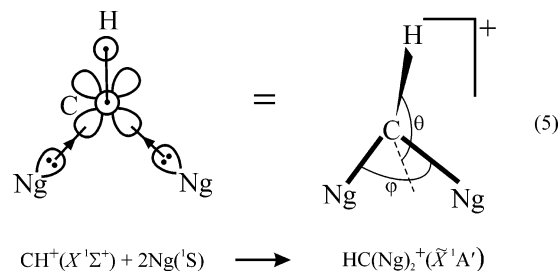
**Figure 1.** Plots of dissociation energies,  $D_e$ , of the  $\tilde{X}^1A'$ ,  $\tilde{a}^3A''$  HC–Ng<sup>+</sup> and the  $\tilde{X}^1A'$  HC–(Ng)<sub>2</sub><sup>+</sup> states as a function of the (experimental) polarizabilities of the Ng atoms at the RCCSD(T)/cc-pVTZ level. Open marks (Ng = Rn) obtained by extrapolation. See text.

plot of the HC–Ng<sup>+</sup>  $D_e$  values vs the (experimental) Ar, Kr, and Xe polarizabilities indicates practically a linear dependence similar to the singlets but with a steeper slope, Figure 1.

Despite the much higher (18 kcal/mol on the average) HC–Ng<sup>+</sup> binding energies of the triplets, Ng = Ar, Kr, and Xe cases, as compared to the corresponding singlets, these cannot compensate for the CH<sup>+</sup>( $a^3\Pi$ ) ← CH<sup>+</sup>( $X^1\Sigma^+$ ) energy separation of 9550 cm<sup>−1</sup> (27.3 kcal/mol); therefore, the singlets are clearly the ground states. However, because of the increasing differential binding energy between singlets and triplets as we move from Ar to Kr to Xe, the  $\tilde{a}^3A''$  ←  $\tilde{X}^1A'$  energy splitting decreases monotonically from 12.4 to 9.4 to 5.6 kcal/mol, respectively. In all three cases, HCAr<sup>+</sup>, HCKr<sup>+</sup>, and HCXe<sup>+</sup>,

the  $\tilde{a}^3A''$  states are bound with respect to the ground-state fragments CH<sup>+</sup>( $X^1\Sigma^+$ ) + Ng( $^1S$ ) by 6.86, 20.6, and 39.2 kcal/mol, respectively, at the RCCSD(T)/cc-pVTZ level of theory. The HC–Rn<sup>+</sup>  $\tilde{a}^3A''$  binding energy obtained as previously discussed by extrapolation is about 84 kcal/mol (Figure 1). Figures 2, 3, and 4 display potential energy curves of the  $\tilde{X}^1A'$  and  $\tilde{a}^3A''$  states along the HC–Ng<sup>+</sup> coordinate, Ng = Ar, Kr, and Xe.

**b. HC(Ng)<sub>2</sub><sup>+</sup>, Ng = He, Ne, Ar, Kr, and Xe.** From reaction 3, it is clear that a second Ng atom, the same or different than the first one, can attach itself to the HC(Ng)<sup>+</sup> moiety exactly with the same mechanism as previously described, thus forming a tetratomic HC(Ng)<sub>2</sub><sup>+</sup> singlet species as shown in eq 5.



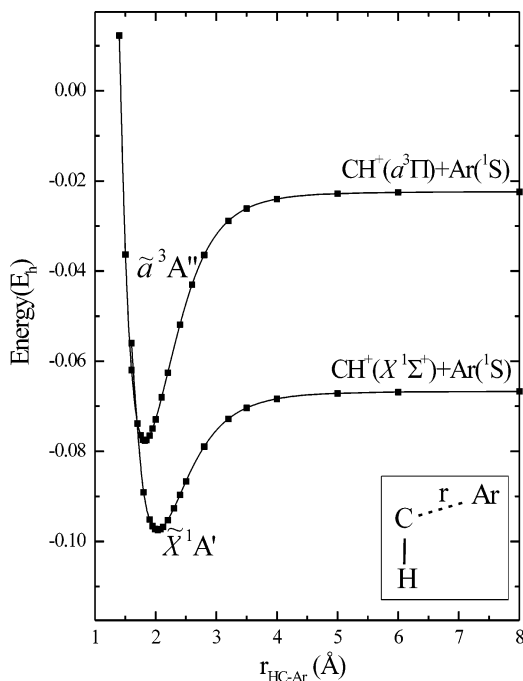
From the vbL diagram above, we expect closed-shell HC(Ng)<sub>2</sub><sup>+</sup> molecular cations of C<sub>s</sub> symmetry ( $^1A'$ ), angles  $\theta$  and  $\varphi$  of about 90°, and that the second Ng atom will enter with smaller binding energy ( $D_e$ ) as contrasted to HC–Ng<sup>+</sup> singlets, due of course to the partial neutralization of the in situ carbon atom after the entrance of the first Ng atom; a concomitant C–Ng bond length increase is also expected. The numerical results at the CCSD(T)/cc-pVTZ and cc-pVQZ levels listed in Table 3 confirm these thoughts. Indeed,  $\theta$  angles vary smoothly from 78° to 95° and  $\varphi$  angles from 81° to 105° for the entire series, while the mean  $D_e$  C–Ng values are 15, 22, and 32 kcal/mol for the –Ar, –Kr, and –Xe species, respectively, as compared to 20, 30, and 45 kcal/mol (Table 2) of the corresponding triatomic molecules at the cc-pVQZ level. In addition, C–Ng bond lengths increase by ~0.15 Å moving from HC(Ng)<sup>+</sup> to HC(Ng)<sub>2</sub><sup>+</sup>, Ng = Ar, Kr, and Xe.

Figure 1 shows again the linear relationship between the binding energies of both Ng atoms and their polarizabilities,

**TABLE 3:** Energies,  $E$  (hartree), Bond Lengths,  $r$  (Å), and Bond Angles,  $\varphi$  ( $\angle\text{NgCNg}$ )<sup>a</sup> and  $\theta$  (Angle of the C–H Bond with the  $\angle\text{NgCNg}$  Bisector)<sup>a</sup> (deg), Binding Energies,  $D_e$  and  $D_0$  (kcal/mol), and Net Mulliken Charges,  $q_C$  and  $q_{\text{Ng}}$ , of  $\text{HC}(\text{Ng})_2^+(\tilde{X}^1A')$  Species, Where Ng = He, Ne, Ar, Kr, and Xe, at the RCCSD(T)/cc-pVTZ and cc-pVQZ Levels of Theory

	$\text{HC}(\text{He})_2^+$		$\text{HC}(\text{Ne})_2^+$		$\text{HC}(\text{Ar})_2^+$		$\text{HC}(\text{Kr})_2^+$		$\text{HC}(\text{Xe})_2^+$
	cc-pVTZ	cc-pVQZ	cc-pVTZ	cc-pVQZ	cc-pVTZ	cc-pVQZ	cc-pVTZ	cc-pVQZ	cc-pVTZ/WTBS <sup>b</sup>
$-E$	43.827 25	43.839 17	295.637 53	295.726 12	1092.155 05	1092.223 25	5542.581 64	5542.643 52	14 502.738 83
$r_{\text{C-Ng}}$	2.210		2.272		2.187		2.265		2.390
$r_{\text{C-H}}$	1.129		1.127		1.118		1.117		1.117
$\varphi$	81.4		88.8		99.1		102.2		105.1
$\theta$	78.2		80.6		89.8		92.2		95.3
$D_e[\text{HC}(\text{Ng})-\text{Ng}]^c$	1.00	1.34	2.75	2.62	9.11	9.84	12.8	13.6	18.6
$D_0[\text{HC}(\text{Ng})-\text{Ng}]^d$	0.09		1.81		7.53		11.1		16.9
$D_e[\text{HC}-(\text{Ng})_2]^e$	1.98	2.67	5.65	5.44	28.4	29.7	42.8	44.0	63.3
$D_0[\text{HC}-(\text{Ng})_2]^f$	0.24		3.71		24.7		38.9		59.5
$q_C^g$	+0.65	+0.67	+0.66	+0.67	+0.32	+0.36	+0.18	+0.24	-0.03
$q_{\text{Ng}}^g$	+0.03	+0.03	+0.03	+0.04	+0.22	+0.21	+0.30	+0.29	+0.40

<sup>a</sup> See eq 5. <sup>b</sup> Well-tempered basis set on Xe, ref 17. <sup>c</sup> With respect to  $\text{HC}(\text{Ng})^+(\tilde{X}^1A') + \text{Ng}(^1S)$ . <sup>d</sup> Zero-point energy corrected  $D_e[\text{HC}(\text{Ng})-\text{Ng}]$  values. <sup>e</sup> With respect to  $\text{CH}^+(X^1\Sigma^+) + 2\text{Ng}(^1S)$ . <sup>f</sup> Zero-point energy corrected  $D_e[\text{HC}-(\text{Ng})_2]$  values. <sup>g</sup> Hartree–Fock charges.

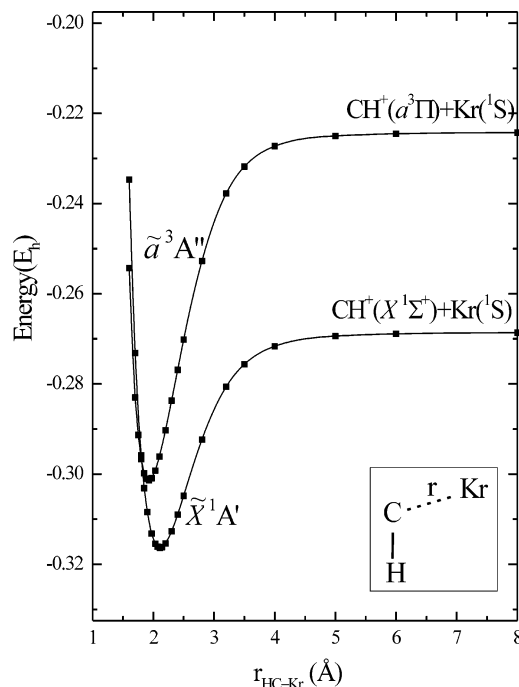
**Figure 2.** Potential energy curves of the  $\tilde{X}^1A'$  and  $\tilde{a}^3A''$  states of the  $\text{HCAr}^+$  along the  $\text{HC}-\text{Ar}^+$  coordinate at the RCCSD(T)/cc-pVTZ level. All energies are shifted by  $+565.0E_h$ .

corroborated also by the atomic HF Mulliken distributions (Table 3), while Figure 5 depicts energy profiles of  $\text{HC}(\text{Ng})_2^+(\tilde{X}^1A')$ , Ng = Ar, Kr, and Xe, as a function of the C–Ng bond distance, by pulling apart both Ng atoms under  $C_s$  symmetry while keeping the  $\theta$  and  $\varphi$  angles and the C–H bond lengths at their equilibrium values.

In Table 3 we also report  $D_0$  values, that is

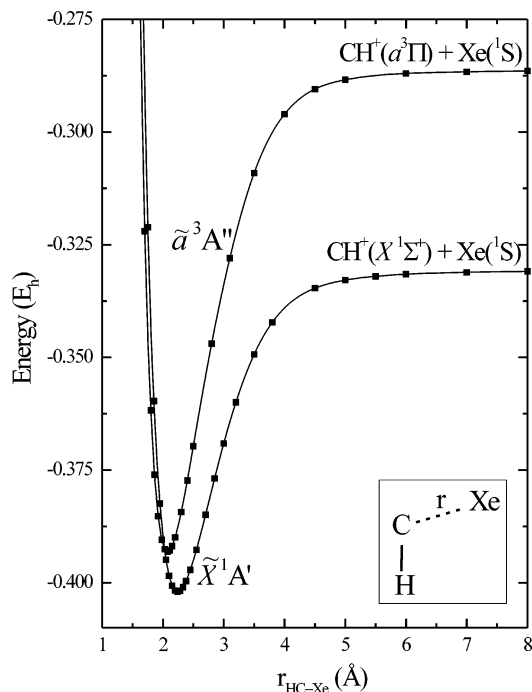
$$D_0 = E[\text{CH}^+; X^1\Sigma^+] + 2E(\text{Ng}; ^1S) - E[\text{HC}(\text{Ng})_2^+; \tilde{X}^1A'] - \left\{ \sum_{i=1}^6 \frac{\hbar\omega_i}{2} - \frac{\hbar\omega}{2} \right\} = D_e - \{ \text{ZPE}[\text{HC}(\text{Ng})_2^+] - \text{ZPE}(\text{CH}^+) \}$$

where  $\{\omega_i\}$  and  $\omega$  are the harmonic frequencies of  $\text{HC}(\text{Ng})_2^+$  and  $\text{CH}^+$ , respectively, at the CCSD(T)/cc-pVTZ level of theory. (Harmonic frequencies  $\{\omega_i\}$  for the  $\tilde{X}^1A'$   $\text{HC}(\text{Ng})_n^+$ ,  $n = 1, 2$  and Ng = He, Ne, Ar, Kr, and Xe, are available upon request).

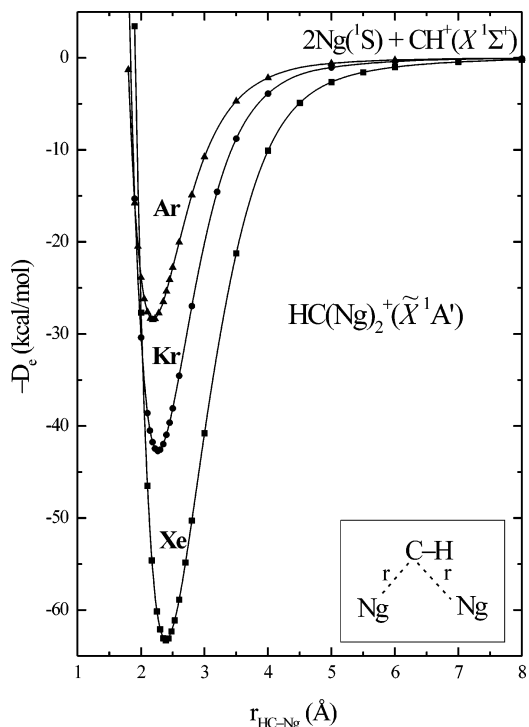
**Figure 3.** Potential energy curves of the  $\tilde{X}^1A'$  and  $\tilde{a}^3A''$  states of the  $\text{HCKr}^+$  along the  $\text{HC}-\text{Kr}^+$  coordinate at the RCCSD(T)/cc-pVTZ level. All energies are shifted by  $+2790.0E_h$ .

## Conclusions

For the series of molecular cations  $\text{HC}(\text{Ng})_n^+$ , where Ng = He, Ne, Ar, Kr, and Xe and  $n = 1, 2$ , we have performed CCSD(T) calculations coupled with triple, quadruple, and, for the  $n = 1$  case, augmented quintuple- $\zeta$  correlation-consistent basis sets. We report geometries, binding energies, and potential energy profiles. Our conclusions can be summarized as follows. (a) All species studied have ground states of  $\tilde{X}^1A'$  symmetry. (b) The He and Ne containing cations have very low C–Ng binding energies due, in essence, to the small polarizabilities of the He and Ne atoms. (c) The  $\text{HC}(\text{Ng})^+$  triplets ( $\tilde{a}^3A''$ ) have much higher binding energies and much shorter HC–Ng bond distances as compared to the corresponding singlets. (d) For the  $\tilde{X}^1A'$   $\text{HC}(\text{Ng})^+$  states, Ng = Ar, Kr, and Xe, significantly higher HC–Ng binding energies are obtained, the result of strong C  $\leftarrow$  Ng dative bonds. Moving from Ar to Kr to Xe, the C–Ng binding energies increase monotonically showing a practically linear dependence on the Ng atom static polarizabilities. At the CCSD(T)/cc-pVQZ level for Ng = Ar and Kr and CCSD(T)/cc-pVTZ-WTBS for Ng = Xe, the following



**Figure 4.** Potential energy curves of the  $\tilde{X}^1A'$  and  $\tilde{a}^3A''$  states of the  $HCXe^+$  along the  $HC-Xe^+$  coordinate at the RCCSD(T)/cc-pVTZ level. All energies are shifted by  $+7270.0E_h$ .



**Figure 5.** Potential energy profiles of the symmetric ( $C_2$ ) dissociation of the  $\tilde{X}^1A'$   $HC-(Ng)_2^+$  states,  $Ng = Ar, Kr,$  and  $Xe$ , at the RCCSD(T)/cc-pVTZ (WTBS for  $Xe$ ) level of theory. Geometrical parameters  $\theta$ ,  $\varphi$ , and  $C-H$  distance (see eq 5) were kept constant at their equilibrium values.

$C-Ng$  binding energies,  $D_e$ , and mean binding energies,  $\bar{D}_e$  (in kcal/mol), are obtained with respect to the ground-state fragments  $CH^+(X^1\Sigma^+) + nNg(¹S)$ :  $HC(Ng)^+(\tilde{X}^1A')$ ,  $D_e = 19.9$  (Ar),  $30.4$  (Kr), and  $44.7$  (Xe);  $HC(Ng)_2^+(\tilde{X}^1A')$ ,  $\bar{D}_e = 15$  (Ar),  $22$  (Kr), and  $32$  (Xe). (e) Using the (theoretical) polarizability of the Rn atom, we estimate the  $D_e$  and  $\bar{D}_e$   $HC-Rn^+$  and  $HC-(Rn)_2^+$  values of the singlets ( $\tilde{X}^1A'$ ) and the corresponding  $D_e$

value of the triplet  $\tilde{a}^3A''$  state to be 60, 43, and 84 kcal/mol, respectively.

We believe that all the molecular systems presently studied,  $HC(Ng)_n^+$ ,  $n = 1, 2$ , of either singlet or triplet ( $n = 1$ ) symmetry can be with no doubt observable in the gas phase. What is fascinating, however, is the plausibility of the singlets, especially the  $-Kr$  and  $-Xe$  ones, to be isolable in the solid phase under proper experimental conditions combined with appropriate counteranions.

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