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

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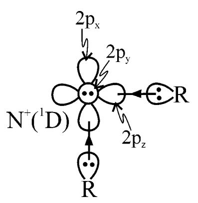
We present a high-level theoretical study of the interaction of the ground-state CH^+ cation with the noble gas, Ng = He to Xe, atoms. Considerably strong C−Ng bonds were detected in the ground-state singlet $HC(Ng)^+$ and $HC(Ng)_2^+$ species when Ng = Ar, Kr, and Xe. Bonding occurs in a Lewis acid−base fashion via dative bonds of $HC^+ \leftarrow$:Ng type, resembling the bonding nature of the recently isolated N_5^+ cation. Both closed-shell $HC(Ng)^+$ and $HC(Ng)_2^+$ 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 N_5^+ salts[1] and the mass-spectrometric detection of the cyclic N_5^- anion[2] (isoelectronic to the well-known $C_5H_5^-$ cyclopentadienyl anion) by Christe and co-workers, the gas-phase detection of N_4 and O_4 by Cacace and co-workers,[3,4] the synthesis and characterization of $N(CO)_2^+$ (isoelectronic to $N_5^+ = N(N_2)_2^+$) salts by Seppelt and co-workers,[5] and the matrix isolation and spectroscopic characterization of HNgX-type molecules, where Ng is a noble gas atom and X a group with large electron affinity, by Räsänen and co-workers.[6] Among the latter family of molecules stands HArF,[7a] which along with ArBeO[7b,7c] 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 HNgX family, HHeF, lies in a shallow minimum of 6.7 kcal/mol and thus might also be accessible experimentally.[8]

In a recent paper,[9] we attempted to clarify the bonding mechanism in the newly synthesized isoelectronic N_5^+ and $N(CO)_2^+$ species using highly correlated ab initio calculations. It was shown that the bonding occurs through a simple Lewis “acid−base” interaction with the N_2 or CO σ^2 electron pairs transferred to the central $N^+(^1D)$ cation and forming dative bonds according to the following valence-bond Lewis (vbL) diagram

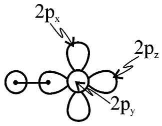


(1)

which also explicates the highly bent structure of these systems. Obviously, what is meant by this scheme is that the in situ central N^+ is in its first ^1D excited-state lying 1.888 eV above the ground ^3P state.[10] Our calculations showed that the simultaneous breaking of the two N−R (R = N_2, CO) bonds leads, indeed, to $N^+(^1D) + 2R(X\ ^1\Sigma_{(g)}^+)$.[9] It is clear that the ground $N^+(^3P)$ state could not be entailed in the formation of singlet NR_2^+ species due to spin angular momentum conservation.

In the same work[9] 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 $N(Ng)_n^+$ family, where Ng = He, Ne, Ar, and Kr and n = 1 or 2. For the NAr_2^+ and NKr_2^+ cations of $^1A_1$ 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 $NAr_2^+(^1A_1)$ and $NKr_2^+(^1A_1)$ are not ground states as in the case of $N(N_2)_2^+$ and $N(CO)_2^+$; the energy required to promote N^+ into its ^1D state is not efficiently counterbalanced by the formation of the two N−Ng bonds. The ground states here are triplets of the type $N(Ng)^+\cdots Ng$, where the second Ng atom is weakly bound electrostatically to the X $^3\Sigma^-$ ground state of the $N(Ng)^+$ diatomic.

At this point, it was natural to inquire about replacing the central N^+ cation by a molecular entity having the same electronic characteristics as $N^+(^1D)$ but being in its *ground state*. Such a candidate could be the molecular cation CH^+, isoelectronic and isovalent to $N^+(^1D)$, the ground state of which is accurately represented by eq 2.



$$= HC^+(X\ ^1\Sigma^+) \qquad (2)$$

Note that $CH^+(X\ ^1\Sigma^+)$ carries the same “binding sites” as the first excited ^1D state of N^+ (Scheme 1). The vantage point, as compared to $N^+(^1D)$, 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, $HC(Ng)_n^+$, n = 1 or 2. At this point, we should mention the very recent isolation and characterization of a salt containing a *sec*-alkyl ($-CH^+-$) cation by Bochmann and co-workers,[11] providing hope for observation and experimental study of the analogous $HC(Ng)_n^+$ species proposed here.

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

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

[a] Experimental values in parentheses. [b] Experimental values from ref 19. [c] Experimental values from ref 10.

In what follows, we attempt to investigate theoretically the possibility of formation of stable HC(Ng)$_n^+$ molecules, where Ng = 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,[12] to the best of our knowledge, there exists only one previous theoretical study on the HCHe$^+$ cation but in a completely different spirit.[13]

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.[14] For the triplet states, the restricted variant based on a restricted open-shell Hartree−Fock reference, ROHF-RCCSD(T), method was used.[15] The CC-single-reference approach is ideal for describing purely dative bonds as in the present case. Indeed, full potential energy curves of CH$^+$ + nNg have been constructed (vide infra) at the CCSD(T) level.

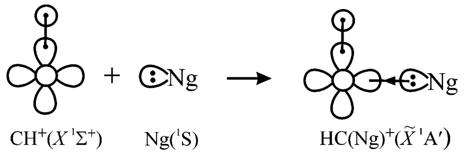
The correlation-consistent plain triple-ζ cc-pVTZ basis of Dunning[16] was used through all calculations of potential energy curves, geometries, and harmonic frequencies. The HC−(Ng)$_n^+$ binding energies obtained were, then, recalculated at the CCSD(T)/cc-pVQZ (n = 1, 2) and CCSD(T)/aug-cc-pV5Z (n = 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[17] 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.[18]

Results and Discussion

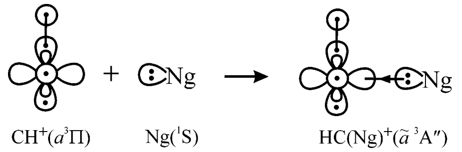
Table 1 lists pertinent characteristics of the CH, CH$^+$, Ng, and Ng$^+$ species, Ng = He, Ne, Ar, Kr, and Xe, at theCCSD(T)/cc-pVTZ level. All calculated quantities are in good agreement with the corresponding experimental values. The ionization energies (IE) of all Ng atoms are larger than the IE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

a. HC(Ng)$^+$, Ng = He, Ne, Ar, Kr, and Xe. All our numerical results concerning the HC(Ng)$^+$ species are summarized in Table 2. The binding process is described succinctly by the following vbL icon



(3)

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



(4)

For all Ng atoms and for both X̃ ^{1}A′ and ã ^{3}A″ 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 CH$^+$(X $^1\Sigma^+$) bond length (Tables 1 and 2).

The binding energies (D_e) of HC−He$^+$ and HC−Ne$^+$ X̃ ^{1}A′ 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 HC−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 CH$^+$(X $^1\Sigma^+$), which in turn depends, in essence, on the Ng polarizabilities (α). A plot of the HC−Ng$^+$ D_e values versus the (experimental) α's (Å^3) [He(0.205), Ne(0.395), Ar(1.641), Kr(2.48), Xe(4.04)][20] 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 α linear curve to the radon polarizability (α = 5.3 Å^3),[21] a HC−Rn$^+$ dissociation energy of 60 kcal/mol is obtained. Similar behavior of D_e as a function of α has been recently observed in the Li−Ng (X $^2\Sigma^+$, B $^2\Sigma^+$, and A $^2\Pi$) states, Ng = Ne to Kr (see ref 22).

Notice that in the HC(Ng)$^+$ sequence, Ng = 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 ∠HCNg (θ) angle increases monotonically from 82° (HCHe$^+$) to 96° (HCXe$^+$) in conformity with reaction 3 suggesting θ = 90°.

Now, the triplet HC(Ng)$^+$ states of ^{3}A″ symmetry, as already described, trace their lineage to CH$^+$(a $^3\Pi$) + Ng(^{1}S), reaction 4. The in situ carbon atom in the CH$^+$ a $^3\Pi$ state finds itself in the ^{4}P(2s^{1}2p^2; M_L = ±1) state; hence, the binding mode with the Ng atoms is identical to the previously discussed singlets, reaction 3. However, a stronger HC−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 HC−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, θ (∠HCNg; deg), Energy Separations, T_e (kcal/mol), HC−Ng$^+$ Binding Energies, D_e and D_0 (kcal/mol), and Net Mulliken Charges, q_C, q_{Ng}, of HC(Ng)$^+$($\tilde{X}$ ^{1}A′ and ã ^{3}A″) 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_{C-H}	r_{C-Ng}	θ	T_e	D_e	D_0[a]	q_C[b]	q_{Ng}[b]
HC−He$^+$($\tilde{X}$ ^{1}A′)	cc-pVTZ	40.925 42	1.130	2.212	81.6		0.98	0.15	+0.69	+0.03
HC−He$^+$($\tilde{X}$ ^{1}A′)	cc-pVQZ	40.934 62					1.33		+0.70	+0.03
HC−He$^+$($\tilde{X}$ ^{1}A′)	aug-cc-pV5Z	40.937 62					1.52		+0.55	+0.01
HC−He$^+$(ã ^{3}A″)	cc-pVTZ	40.883 78	1.122	1.679	101.5	26.1	2.16		+0.63	+0.03
HC−Ne$^+$($\tilde{X}$ ^{1}A′)	cc-pVTZ	166.830 69	1.129	2.239	83.8		2.90	1.90	+0.69	+0.04
HC−Ne$^+$($\tilde{X}$ ^{1}A′)	cc-pVQZ	166.878 26					2.82		+0.70	+0.04
HC−Ne$^+$($\tilde{X}$ ^{1}A′)	aug-cc-pV5Z	166.896 64					3.02		+0.55	+0.02
HC−Ne$^+$(ã ^{3}A″)	cc-pVTZ	166.790 16	1.121	1.915	102.9	25.4	4.77		+0.59	+0.08
HC−Ar$^+$($\tilde{X}$ ^{1}A′)	cc-pVTZ	565.097 46	1.121	2.034	92.7		19.3	17.2	+0.43	+0.33
HC−Ar$^+$($\tilde{X}$ ^{1}A′)	cc-pVQZ	565.134 65					19.9		+0.45	+0.32
HC−Ar$^+$($\tilde{X}$ ^{1}A′)	aug-cc-pV5Z	565.167 93					20.4		+0.28	+0.31
HC−Ar$^+$(ã ^{3}A″)	cc-pVTZ	565.077 62	1.095	1.821	116.1	12.4	34.2		+0.26	+0.47
HC−Kr$^+$($\tilde{X}$ ^{1}A′)	cc-pVTZ	2790.316 33	1.120	2.109	94.5		30.0	27.8	+0.33	+0.44
HC−Kr$^+$($\tilde{X}$ ^{1}A′)	cc-pVQZ	2790.350 17					30.4		+0.34	+0.45
HC−Kr$^+$($\tilde{X}$ ^{1}A′)	aug-cc-pV5Z	2790.361 87					30.8		+0.13	+0.47
HC−Kr$^+$(ã ^{3}A″)	cc-pVTZ	2790.301 36	1.093	1.927	119.1	9.40	47.9		+0.16	+0.58
HC−Xe$^+$($\tilde{X}$ ^{1}A′)	cc-pVTZ/WTBS[c]	7270.402 03	1.119	2.240	96.5		44.7	42.6	+0.21	+0.57
HC−Xe$^+$(ã ^{3}A″)	cc-pVTZ/WTBS[c]	7270.393 14	1.090	2.075	123.1	5.58	66.5		+0.02	+0.73

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

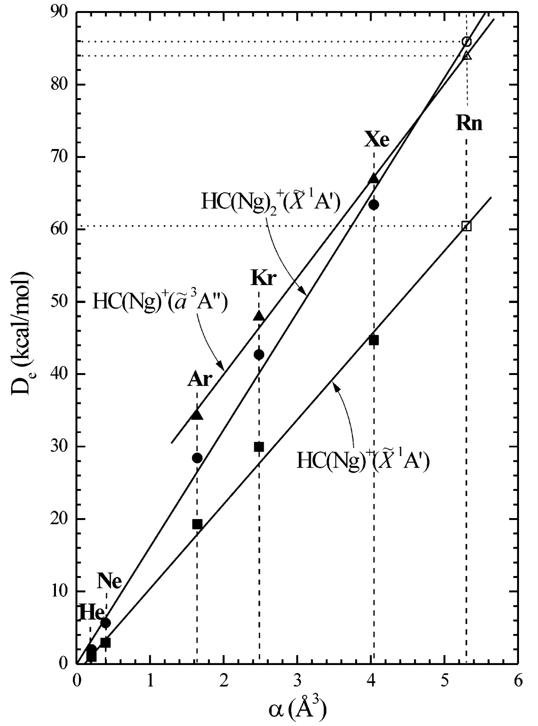
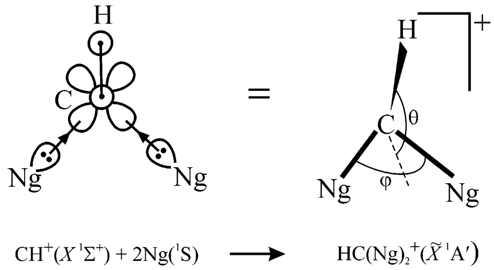


Figure 1. Plots of dissociation energies, D_e, of the $\tilde{X}$ ^{1}A′, ã ^{3}A″ HC−Ng$^+$ and the $\tilde{X}$ ^{1}A′ HC−(Ng)$_2$$^+$ states as a function of the (experimental) polarizabilities of the Ng atoms at the RCCSD(T)/cc-pVTZ level. Open marks (Ng = Rn) obtained by extrapolation. See text.

plot of the HC−Ng$^+$ 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$^+$ binding energies of the triplets, Ng = Ar, Kr, and Xe cases, as compared to the corresponding singlets, these cannot compensate for the CH$^+$(a $^3\Pi$) ← CH$^+$(X $^1\Sigma^+$) energy separation of 9550 cm^{-1} (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 ã ^{3}A″ ← $\tilde{X}$ ^{1}A′ energy splitting decreases monotonically from 12.4 to 9.4 to 5.6 kcal/mol, respectively. In all three cases, HCAr$^+$, HCKr$^+$, and HCXe$^+$, the ã ^{3}A″ states are bound with respect to the ground-state fragments CH$^+$(X $^1\Sigma^+$) + Ng(^{1}S) by 6.86, 20.6, and 39.2 kcal/mol, respectively, at the RCCSD(T)/cc-pVTZ level of theory. The HC−Rn$^+$ ^{3}A″ 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 $\tilde{X}$ ^{1}A′ and ã ^{3}A″ states along the HC−Ng$^+$ coordinate, Ng = Ar, Kr, and Xe.

b. HC(Ng)$_2$$^+$, Ng = He, Ne, Ar, Kr, and Xe. From reaction 3, it is clear that a second Ng atom, the same or different than the first one, can attach itself to the HC(Ng)$^+$ moiety exactly with the same mechanism as previously described, thus forming a tetratomic HC(Ng)$_2$$^+$ singlet species as shown in eq 5.



(5)

From the vbL diagram above, we expect closed-shell HC(Ng)$_2$$^+$ molecular cations of C_s symmetry (^{1}A′), angles θ and φ of about 90°, and that the second Ng atom will enter with smaller binding energy (D_e) as contrasted to HC−Ng$^+$ singlets, due of course to the partial neutralization of the in situ carbon atom after the entrance of the first Ng atom; a concomitant C−Ng bond length increase is also expected. The numerical results at the CCSD(T)/cc-pVTZ and cc-pVQZ levels listed in Table 3 confirm these thoughts. Indeed, θ angles vary smoothly from 78° to 95° and φ angles from 81° to 105° for the entire series, while the mean $\bar{D}_e$ C−Ng values are 15, 22, and 32 kcal/mol for the −Ar, −Kr, and −Xe species, respectively, as compared to 20, 30, and 45 kcal/mol (Table 2) of the corresponding triatomic molecules at the cc-pVQZ level. In addition, C−Ng bond lengths increase by ~0.15 Å moving from HC(Ng)$^+$ to HC(Ng)$_2$$^+$, 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, *φ* (∠NgCNg)[a] and *θ* (Angle of the C−H Bond with the ∠NgCNg Bisector)[a] (deg), Binding Energies, D_e and D_0 (kcal/mol), and Net Mulliken Charges, q_C and q_{Ng}, of $HC(Ng)_2^+$(X̃ $^1A'$) Species, Where Ng = He, Ne, Ar, Kr, and Xe, at the RCCSD(T)/cc-pVTZ and cc-pVQZ Levels of Theory

	$HC(He)_2^+$		$HC(Ne)_2^+$		$HC(Ar)_2^+$		$HC(Kr)_2^+$		$HC(Xe)_2^+$
	cc-pVTZ	cc-pVQZ	cc-pVTZ	cc-pVQZ	cc-pVTZ	cc-pVQZ	cc-pVTZ	cc-pVQZ	cc-pVTZ/WTBS[b]
$-E$	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_{C-Ng}	2.210		2.272		2.187		2.265		2.390
r_{C-H}	1.129		1.127		1.118		1.117		1.117
φ	81.4		88.8		99.1		102.2		105.1
θ	78.2		80.6		89.8		92.2		95.3
D_e[HC(Ng)−Ng][c]	1.00	1.34	2.75	2.62	9.11	9.84	12.8	13.6	18.6
D_0[HC(Ng)−Ng][d]	0.09		1.81		7.53		11.1		16.9
D_e[HC−$(Ng)_2$][e]	1.98	2.67	5.65	5.44	28.4	29.7	42.8	44.0	63.3
D_0[HC−$(Ng)_2$][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_{Ng}[g]	+0.03	+0.03	+0.03	+0.04	+0.22	+0.21	+0.30	+0.29	+0.40

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

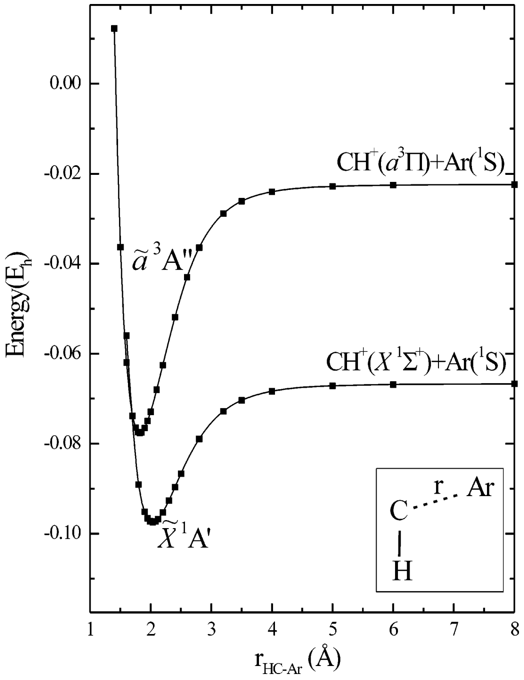


Figure 2. Potential energy curves of the X̃ $^1A'$ and ã $^3A''$ states of the $HCAr^+$ along the HC−Ar^+ coordinate at the RCCSD(T)/cc-pVTZ level. All energies are shifted by $+565.0E_h$.

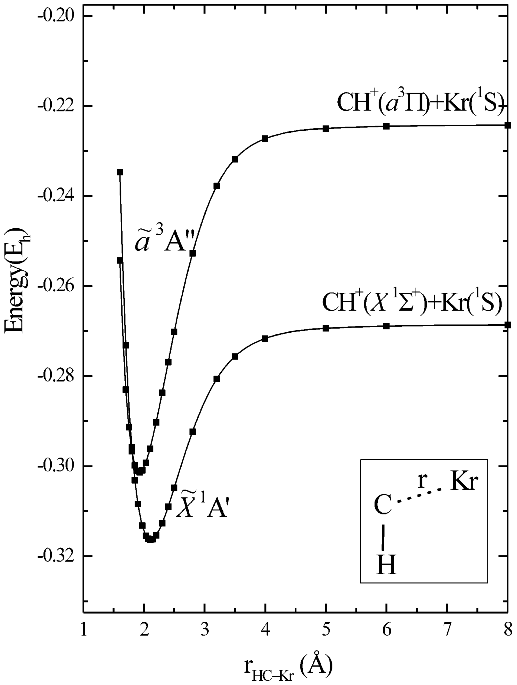


Figure 3. Potential energy curves of the X̃ $^1A'$ and ã $^3A''$ states of the $HCKr^+$ along the HC−Kr^+ coordinate at the RCCSD(T)/cc-pVTZ level. All energies are shifted by $+2790.0E_h$.

corroborated also by the atomic HF Mulliken distributions (Table 3), while Figure 5 depicts energy profiles of $HC(Ng)_2^+$-(X̃ $^1A'$), 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 θ and φ angles and the C−H bond lengths at their equilibrium values.

In Table 3 we also report D_0 values, that is

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

$$= D_e - \{ZPE[HC(Ng)_2{}^+] - ZPE(CH^+)\}$$

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

Conclusions

For the series of molecular cations $HC(Ng)_n^+$, 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-ζ 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 X̃ $^1A'$ 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 $HC(Ng)^+$ triplets (ã $^3A''$) have much higher binding energies and much shorter HC−Ng bond distances as compared to the corresponding singlets. (d) For the X̃ $^1A'$ $HC(Ng)^+$ states, Ng = Ar, Kr, and Xe, significantly higher HC−Ng binding energies are obtained, the result of strong C ← 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

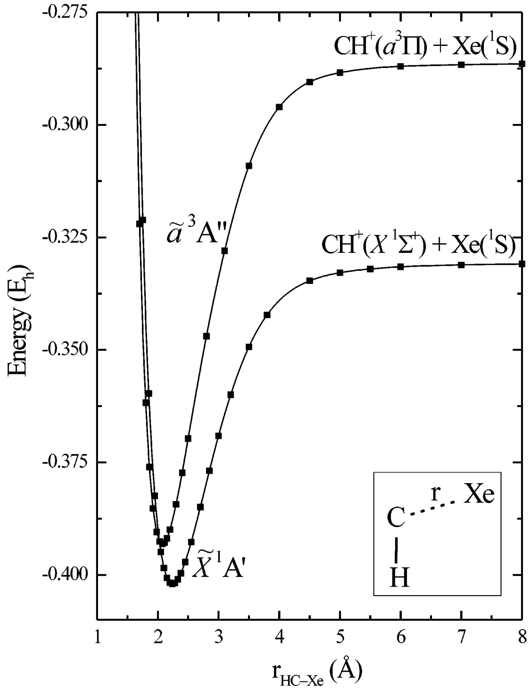


Figure 4. Potential energy curves of the $\tilde{X}\,^1A'$ and $\tilde{a}\,^3A''$ states of the $HCXe^+$ along the $HC-Xe^+$ coordinate at the RCCSD(T)/cc-pVTZ level. All energies are shifted by $+7270.0E_h$.

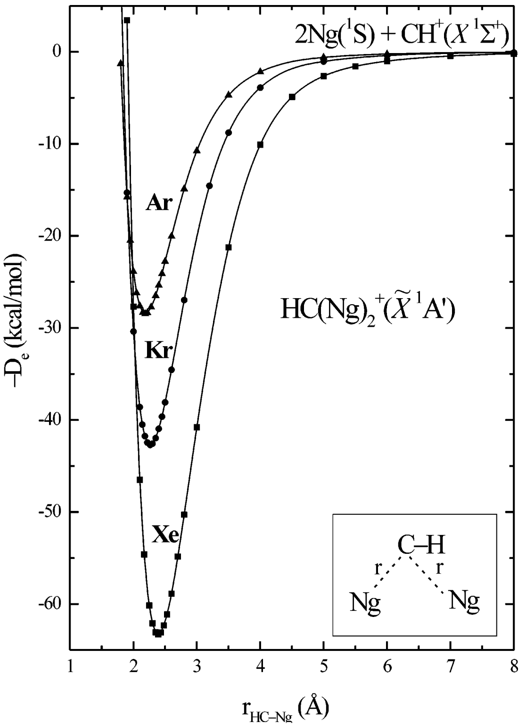


Figure 5. Potential energy profiles of the symmetric (C_s) dissociation of the $\tilde{X}\,^1A'$ $HC-(Ng)_2^+$ states, Ng = Ar, Kr, and Xe, at the RCCSD(T)/cc-pVTZ (WTBS for Xe) level of theory. Geometrical parameters θ, φ, and C−H distance (see eq 5) were kept constant at their equilibrium values.

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.

References and Notes

(1) (a) Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2004. (b) Vij, A.; Wilson, W. W.; Vij, V.; Tham, F. S.; Sheehy, J. A.; Christe, K. O. *J. Am. Chem. Soc.* **2001**, *123*, 6308.

(2) Vij, A.; Pavlovich, J. G.; Wilson, W. W.; Vij, V.; Christe, K. O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3051.

(3) Cacace, F.; de Petris, G.; Troiani, A. *Science* **2002**, *295*, 480.

(4) Cacace, F.; de Petris, G.; Troiani, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4062.

(5) Bernhardi, I.; Drews, T.; Seppelt, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 2232.

(6) Pettersson, M.; Khriachtchev, L.; Lignell, A.; Räsänen, M.; Bihary, Z.; Gerber, R. B. *J. Chem. Phys.* **2002**, *116*, 2508 and references therein.

(7) (a) Khriachtchev, L.; Pettersson, M.; Runenberg, N.; Lundell, J.; Räsänen, M. *Nature* **2000**, *406*, 874. (b) Thompson, C. A. T.; Andrews, L. *J. Am. Chem. Soc.* **1994**, *116*, 423. (c) Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1994**, *226*, 11.

(8) Wong, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6289.

(9) Kerkines, I. S. K.; Papakondylis, A.; Mavridis, A. *J. Phys. Chem. A* **2002**, *106*, 4453.

(10) Moore, C. E. *Atomic Energy Levels*; NRSDS−NBS, Circular No.35, U.S. GPO: Washington, DC, 1971.

(11) Schormann, M.; Garrattt, S.; Hughes, D. L.; Green, J. C.; Bochmann, M. *J. Am. Chem. Soc.* **2002**, *124*, 11266.

(12) See, for instance: (a) Frenking, G.; Cremer, D. *Struct. Bonding* **1990,** *73*, 17. (b) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D.; Collins, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5917. (c) Frenking, G.; Koch, W.; Cremer, D.; Gauss, J.; Liebman, J. F. *J. Phys. Chem.* **1989**, *93*, 3397. (d) Frenking, G.; Koch, W.; Cremer, D.; Gauss, J.; Liebman, J. F. *J. Phys. Chem.* **1989**, *93*, 3410.

(13) Hughes, J. M.; von Nagy-Felsobuki, E. I. *Chem. Phys. Lett.* **1997**, *272*, 313.

(14) (a) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479. (b) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513. (c) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *167*, 609E.

(15) (a) Knowles, P. J.; Hampel, C.; Werner H.-J. *J. Chem. Phys.* **1993**, *99*, 5219. (b) Knowles, P. J.; Hampel, C.; Werner H.-J. *J. Chem. Phys.* **2000**, *112*, 3106E.

(16) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 2975. (c) Wilson, A. K.; Woon, D. E.; Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1999**, *110*, 7667.

(17) (a) Huzinaga, S.; Miguel, B. *Chem. Phys. Lett.* **1990**, *175*, 289. (b) Huzinaga, S.; Klobukowski, M. *Chem. Phys. Lett.* **1993**, *212*, 260.

(18) MOLPRO is a package of ab initio programs designed by Werner, H.-J. and Knowles, P. J. Version 2002.6. Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Knowles, P. J.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Werner, H.-J.

(19) Huber, K. P.; Herzberg, G. H. *Molecular Spectra and Molecular Structure, vol. IV, Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

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

(21) Doolen, G. D. Unpublished theoretical results as cited in: *CRC Handbook of Chemistry and Physics*, 83rd ed.; Lide, D. R., Editor-in-chief; CRC Press: Boca Raton, FL, 2003.

(22) Kerkines, I. S. K.; Mavridis, A. *J. Chem. Phys.* **2002**, *116*, 9305.