Trapping of noble gases (He–Kr) by the aromatic H_3^+ and Li_3^+ species: a conceptual DFT approach

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The stability, reactivity and aromaticity of clusters of various noble gas atoms trapped in aromatic H_3^+ and Li_3^+ rings are studied at the B3LYP/6-311+G(d) and MP2/6-311+G(d) levels of theory. Electrophilicity, a gain in energy and nucleus-independent chemical shift values lend additional insights into the overall behavior of these clusters.

Introduction

The noble gases occupy a dominant position in the periodic table of the elements. Although they were earlier thought to hardly have any reactivity, and hence named inert, the jinx was broken for the first time by Bartlett[1] with the synthesis of $Xe^+[PtF_6]^-$. Since then, the unexplored chemistry of the noble gases has flourished in leaps and bounds, and motivated both synthetic and theoretical chemists in their work.[2] The recent discovery of noble gas insertion compounds having vital terrestrial applications,[2a,3] and experimental and theoretical studies of neutral van der Waals complexes of the noble gases with large and small molecular moieties[4] has further nourished the chemical aspects of these so-called inert systems. Pauzat and co-workers,[5] in their series of recent studies on the reactivity of the noble gases, have discussed the prospect of H_3^+ as a trap for these rare gases. On the other hand, it is well established that the seminal concept of aromaticity in conjugated organic systems is intensely related to their unusual stability compared to their open-chain analogs. Moreover, the existence of "all-metal aromaticity" in the purely inorganic Al_4^{2-} cluster proposed by Boldyrev *et al.*[6] further strengthened the correlation between the phenomenon of aromaticity and the stability of metallic as well as non-metallic clusters. The H_3^+ unit chosen by Pauzat *et al.*[5] as a catch for the noble gases, along with its another group compatriot Li_3^+, have recently been reported to possess σ-aromaticity in terms of ring current and nucleus-independent chemical shift (NICS)[7] measures. The Li_3^+ unit, however, does not show any ring current[8] but leads to a negative NICS value, the essential aromaticity criterion.

In this work, we intend to investigate the potential ability of the H_3^+ and Li_3^+ units as possible traps for the noble gases (He–Kr) from the viewpoint of conceptual density functional theory and aromaticity. The stability of these trapped noble gas complexes can be effectively elucidated under the paradigm of conceptual DFT[9] in association with its various global reactivity descriptors, such as electronegativity[10] (χ), hardness[11] (η), electrophilicity[12] (ω), and the local variants like atomic charges[13] (Q_k) and Fukui functions[14] (f_k). The aromaticity criterion for the H_3^+ and Li_3^+ trigonal rings in the noble gas complexes measured in terms of the NICS[7] will convey valuable insights into judging the stability of the noble gas complexes.

Theoretical background

Electrophilicity (ω) does play a vital role in quantifying the thermodynamic stability and reactivity of molecular systems. A minimum electrophilicity principle[15] (MEP) has been proposed for this purpose. In an N-electron system, the electronegativity[10] (χ) and hardness[11] (η) can be defined as follows:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \tag{1}$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} \tag{2}$$

Here, E is the total energy of the N-electron system and μ and $v(\vec{r})$ are its chemical potential and external potential, respectively. The electrophilicity[12] (ω) is defined as:

$$\omega = \mu^2/2\eta = \chi^2/2\eta \tag{3}$$

A finite difference approximation to eqn (1) and eqn (2) can be expressed as:

$$\chi = (I + A)/2 \tag{4}$$

and

$$\eta = I - A \tag{5}$$

where I and A represent the ionization potential and electron affinity of the system, respectively, and are computed in terms of the energies of the N and $N \pm 1$ electron systems. For an N-electron system with energy $E(N)$, they may be expressed as follows:

$$I = E(N-1) - E(N) \tag{6}$$

and

$$A = E(N) - E(N+1) \tag{7}$$

The local reactivity descriptor, Fukui function[14] (FF), measures the change in electron density at a given point when

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an electron is added to or removed from a system at constant $\nu(\vec{r})$. It may be written as:

$$f(\vec{r}) = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)_{\nu(\vec{r})} = \left(\frac{\delta\mu}{\delta v(\vec{r})}\right)_N \tag{8}$$

Table 1 The electronegativity (χ), hardness (η), and electrophilicity (ω) values for the noble gas atoms and the corresponding $H_3{}^+$-trapped clusters

Molecule	χ/eV	η/eV	ω/eV
He	1.770	46.310	0.034
Ne	7.609	28.384	1.020
Ar	6.450	18.800	1.106
Kr	6.216	16.008	1.207
$H_3{}^+$	19.928	27.380	7.252
$HeH_3{}^+$	18.126	24.060	6.828
$He_2H_3{}^+$	17.085	22.624	6.451
$He_3H_3{}^+$	16.354	22.218	6.018
$NeH_3{}^+$	16.918	21.962	6.516
$Ne_2H_3{}^+$	15.641	20.144	6.072
$Ne_3H_3{}^+$	14.912	19.652	5.658
$ArH_3{}^+$	13.985	17.530	5.578
$Ar_2H_3{}^+$	12.520	15.394	5.091
$Ar_3H_3{}^+$	11.781	14.828	4.680
$Ar_4H_3{}^+$	11.393	14.088	4.606
$Ar_5H_3{}^+$	11.079	13.510	4.543
$KrH_3{}^+$	13.389	16.144	5.552
$Kr_2H_3{}^+$	11.707	13.552	5.056
$Kr_3H_3{}^+$	10.785	13.286	4.377

Table 2 The electronegativity (χ), hardness (η), and electrophilicity (ω) values for the $Li_3{}^+$-trapped clusters of noble gas atoms

Molecule	χ/eV	η/eV	ω/eV
$Li_3{}^+$	7.345	6.444	4.186
$HeLi_3{}^+$	7.306	6.424	4.154
$He_2Li_3{}^+$	7.261	6.502	4.054
$He_3Li_3{}^+$	7.111	6.616	3.821
$NeLi_3{}^+$	7.290	6.422	4.136
$Ne_2Li_3{}^+$	7.209	6.448	4.029
$Ne_3Li_3{}^+$	7.093	6.562	3.833
$ArLi_3{}^+$	7.192	6.356	4.069
$Ar_2Li_3{}^+$	7.028	6.316	3.910
$Ar_3Li_3{}^+$	6.793	6.396	3.608

Condensation of this Fukui function, $f(\vec{r})$, to an individual atomic site k in a molecule gives rise to the following expressions in terms of electron population,[16] q_k:

$$f_k^+ = q_k(N+1) - q_k(N) \text{ for nucleophilic attack} \tag{9a}$$

$$f_k^- = q_k(N) - q_k(N-1) \text{ for electrophilic attack} \tag{9b}$$

$$f_k^0 = [q_k(N+1) - q_k(N-1)]/2 \text{ for nucleophilic attack} \tag{9c}$$

Computational details

The geometry optimization of the molecular conformations of the trapped noble gas clusters and their subsequent frequency calculations were carried out at the B3LYP and MP2 levels of theory using the 6-311 + G(d) molecular basis set with the aid of the GAUSSIAN 03 program package.[17] The NIMAG values of all the optimized geometries were zero, thereby confirming their existence at minima on the potential energy surface (PES). Single point calculations were further performed to evaluate the energies of the $N \pm 1$ electron systems by adopting the geometries of the corresponding N-electron systems optimized at the B3LYP/6-311 + G(d) level of theory. The I and A values were calculated using a ΔSCF technique. It may be noted that the problem of negative electron affinity of a noble gas atom may be tackled by the method developed by Tozer *et al.*[18] or by using a suitable solvent and/or counterion.[19] The electrophilicity (ω) and hardness (η) were computed using eqn (3) and eqn (5), respectively. A Mulliken population analysis (MPA) scheme was adopted to calculate the atomic charges (Q_k) and Fukui functions ($f(\vec{r})$). NICS[7] values at the center (NICS(0)) of the trigonal $H_3{}^+$ and $Li_3{}^+$ rings, as well as at different distances perpendicular to the ring center, were calculated. Frontier molecular orbital pictures were obtained using the GAUSSVIEW 03 package.[17] BSSE and ZPE corrections were not taken into account in this work, which was expected not to alter the conceptual analysis of the noble gas-trapped $H_3{}^+$ and $Li_3{}^+$ clusters.

Results and discussion

The global reactivity descriptors like electronegativity (χ), hardness (η) and electrophilicity (ω) of the four noble gas

Table 3 The molecular point group (PG) and NICS values of $H_3{}^+$ and corresponding trapped noble gas clusters

Molecule	Point group (PG)	NICS(0)/ppm	NICS(1)/ppm	NICS(2)/ppm	NICS(3)/ppm	NICS(4)/ppm
$H_3{}^+$	D_{3h}	−30.66	−1.75	−0.03	−0.01	−0.00
$HeH_3{}^+$	C_{2v}	−30.58	−1.81	−0.07	−0.02	−0.01
$He_2H_3{}^+$	C_{2v}	−30.56	−1.86	−0.10	−0.04	−0.02
$He_3H_3{}^+$	C_s	−30.56	−1.91	−0.13	−0.06	−0.03
$NeH_3{}^+$	C_{2v}	−30.19	−1.84	−0.08	−0.03	−0.01
$Ne_2H_3{}^+$	C_{2v}	−29.94	−1.90	−0.12	−0.05	−0.02
$Ne_3H_3{}^+$	C_s	−29.74	−1.91	−0.15	−0.06	−0.03
$ArH_3{}^+$	C_{2v}	−24.79	−1.44	−0.05	−0.03	−0.01
$Ar_2H_3{}^+$	C_{2v}	−25.39	−1.39	−0.12	−0.07	−0.04
$Ar_3H_3{}^+$	C_1	−25.55	−1.40	−0.19	−0.11	−0.06
$Ar_4H_3{}^+$	C_1	−25.46	−1.38 (below the plane)	−0.18 (below the plane)	−0.11 (below the plane)	−0.06 (below the plane)
$Ar_5H_3{}^+$	C_1	−25.37	−1.30	−4.71	−88.36	−41.91
$KrH_3{}^+$	C_s	−20.28	−1.24	0.01	0.00	0.00
$Kr_2H_3{}^+$	C_{2v}	−22.16	−0.93	−0.02	−0.03	−0.01
$Kr_3H_3{}^+$	C_1	−22.82	−0.87	−0.09	−0.07	−0.04

atoms (He–Kr), H_3^+ and its trapped clusters, and that of Li_3^+ and its corresponding trapped cluster molecules are presented in Table 1 and Table 2, respectively. The molecular point groups (PG) and NICS values at different distances from the

Table 4 The molecular point group (PG) and NICS values of Li_3^+ and corresponding trapped noble gas clusters

Molecule	Point group (PG)	NICS(0)/ppm	NICS(1)/ppm	NICS(2)/ppm	NICS(3)/ppm	NICS(4)/ppm
Li_3^+	D_{3h}	−11.08	−6.78	−1.61	−0.10	0.04
$HeLi_3^+$	C_{2v}	−11.08	−6.79	−1.64	−0.12	0.03
$He_2Li_3^+$	C_{2v}	−11.09	−6.80	−1.66	−0.13	0.02
$He_3Li_3^+$	C_1	−11.05	−6.81	−1.71	−0.16	0.02
$NeLi_3^+$	C_{2v}	−11.11	−6.81	−1.64	−0.12	0.03
$Ne_2Li_3^+$	C_{2v}	−11.14	−6.83	−1.68	−0.14	0.02
$Ne_3Li_3^+$	C_1	−11.17	−6.86	−1.71	−0.16	0.01
$ArLi_3^+$	C_{2v}	−11.12	−6.83	−1.69	−0.16	0.01
$Ar_2Li_3^+$	C_{2v}	−11.15	−6.88	−1.77	−0.21	−0.02
$Ar_3Li_3^+$	C_1	−11.16	−6.92	−1.86	−0.27	−0.05

Table 5 Comparison of the Ng–H (Ng = Ne, Ar, Kr) bond lengths (Å) obtained from Pauzat's calculations and the present study

Molecule	Ng–H bond length/Å [Ng = Ne, Ar, Kr]	Pauzat's results[a] [BH&HLYP/cc-pVTZ]	Present study [B3LYP/6-311+G(d)]
NeH_3^+	Ne–H	1.723	1.769
$Ne_2H_3^+$	Ne–H	1.778	1.819
$Ne_3H_3^+$	Ne–H	1.817	1.855
ArH_3^+	Ar–H	1.791	1.709
$Ar_2H_3^+$	Ar–H	1.984	1.969
$Ar_3H_3^+$	Ar–H	2.082	2.088
$Ar_4H_3^+$	Ar–H	2.087	2.096
$Ar_5H_3^+$	Ar–H	2.094	2.098
KrH_3^+	Kr–H	1.799	1.665
$Kr_2H_3^+$	Kr–H	2.093	2.026
$Kr_3H_3^+$	Kr–H	2.211	2.190

[a] Values are taken from ref. 5*a–c*.

Table 6 The atomic charges (Q_k) and Fukui functions (f_k^+, f_k^-) of H_3^+ and corresponding trapped noble gas clusters computed under the MPA formulation

Molecule	Unit	Q_k	f_k^+	f_k^-
H_3^+	H, H, H	0.333, 0.333, 0.333	0.077, 0.462, 0.462	0.333, 0.333, 0.333
HeH_3^+	H, H, H He	0.296, 0.331, 0.331, 0.042	0.059, 0.462, 0.461, 0.018	0.027, 0.187, 0.187, 0.598
$He_2H_3^+$	H, H, H He, He	0.296, 0.329, 0.296, 0.040, 0.040	0.149, 0.681, 0.142, 0.014, 0.014	0.025, 0.130, 0.026, 0.467, 0.351
$He_3H_3^+$	H, H, H He, He, He	0.295, 0.295, 0.295, 0.038, 0.038, 0.038	0.220, 0.161, 0.593, 0.012, 0.000, 0.014	0.041, 0.041, 0.041, 0.292, 0.292, 0.292
NeH_3^+	H, H, H Ne	0.268, 0.331, 0.331, 0.069	0.066, 0.459, 0.443, 0.032	−0.062, 0.138, 0.139, 0.785
$Ne_2H_3^+$	H, H, H Ne, Ne	0.272, 0.331, 0.272, 0.062, 0.062	0.155, 0.675, 0.152, 0.009, 0.009	−0.007, 0.106, −0.007, 0.453, 0.454
$Ne_3H_3^+$	H, H, H Ne, Ne, Ne	0.273, 0.274, 0.273, 0.060, 0.060, 0.060	0.267, 0.144, 0.663, −0.081, −0.007, 0.014	0.022, 0.022, 0.021, 0.310, 0.311, 0.312
ArH_3^+	H, H, H Ar	0.247, 0.251, 0.251, 0.25	0.443, 0.216, 0.222, 0.118	−0.056, 0.091, 0.091, 0.875
$Ar_2H_3^+$	H, H, H Ar, Ar	0.222, 0.257, 0.222, 0.150, 0.150	0.401, 0.029, 0.401, 0.084, 0.084	−0.002, 0.072, −0.002, 0.466, 0.466
$Ar_3H_3^+$	H, H, H Ar, Ar, Ar	0.214, 0.214, 0.213, 0.121, 0.117, 0.120	0.203, 0.055, 0.483, 0.063, 0.103, 0.093	0.006, 0.005, 0.006, 0.324, 0.333, 0.326
$Ar_4H_3^+$	H, H, H Ar, Ar, Ar, Ar	0.213, 0.212, 0.213, −0.001, 0.120, 0.121, 0.12	−0.004, 0.430, 0.315, 0.014, 0.106, 0.062, 0.077	−0.008, −0.008, −0.003, 0.439, 0.195, 0.191, 0.194
$Ar_5H_3^+$	H, H, H Ar, Ar, Ar, Ar, Ar	0.212, 0.212, 0.212, −0.001, −0.001, 0.122, 0.122, 0.122	−0.014, 0.401, 0.353, 0.014, 0.013, 0.105, 0.061, 0.067	−0.015, −0.015, −0.015, 0.376, 0.383, 0.097, 0.101, 0.089
KrH_3^+	H, H, H Kr	0.238, 0.190, 0.190, 0.382	0.416, 0.147, 0.141, 0.295	−0.024, 0.085, 0.086, 0.852
$Kr_2H_3^+$	H, H, H Kr, Kr	0.200, 0.216, 0.200, 0.192, 0.192	0.336, 0.030, 0.336, 0.148, 0.148	0.000, 0.066, 0.000, 0.466, 0.468
$Kr_3H_3^+$	H, H, H Kr, Kr, Kr	0.193, 0.193, 0.193, 0.142, 0.139, 0.140	0.081, 0.130, 0.433, 0.117, 0.120, 0.119	0.000, 0.000, 0.000, 0.328, 0.337, 0.334

Table 7 The atomic charges (Q_k) and Fukui functions (f_k^+, f_k^-) of Li_3^+ and corresponding trapped noble gas clusters computed under the MPA formulation

Molecule	Unit	Q_k	f_k^+	f_k^-
Li_3^+	Li, Li, Li	0.333, 0.333, 0.333	0.209, 0.395, 0.395	0.333, 0.333, 0.333
$HeLi_3^+$	Li, Li, Li He	0.369, 0.215, 0.374, 0.041	0.341, 0.331, 0.322, 0.005	0.305, 0.386, 0.299, 0.01
$He_2Li_3^+$	Li, Li, Li He, He	0.258, 0.262, 0.407, 0.036, 0.037	0.303, 0.304, 0.384, 0.004, 0.005	0.354, 0.351, 0.276, 0.009, 0.009
$He_3Li_3^+$	Li, Li, Li He, He, He	0.295, 0.297, 0.282, 0.042, 0.042, 0.043	0.433, 0.104, 0.449, 0.006, 0.004, 0.004	0.320, 0.313, 0.333, 0.011, 0.011, 0.011
$NeLi_3^+$	Li, Li, Li Ne	0.329, 0.276, 0.329, 0.066	0.406, 0.200, 0.390, 0.003	0.352, 0.279, 0.354, 0.015
$Ne_2Li_3^+$	Li, Li, Li Ne, Ne	0.274, 0.273, 0.324, 0.064, 0.065	0.283, 0.240, 0.473, 0.002, 0.002	0.299, 0.300, 0.372, 0.014, 0.015
$Ne_3Li_3^+$	Li, Li, Li Ne, Ne, Ne	0.267, 0.267, 0.267, 0.066, 0.066, 0.066	0.444, 0.297, 0.263, 0.000, −0.010, 0.001	0.318, 0.319, 0.319, 0.015, 0.015, 0.015
$ArLi_3^+$	Li, Li, Li Ar	0.316, 0.248, 0.316, 0.119	0.427, 0.146, 0.413, 0.014	0.359, 0.237, 0.355, 0.049
$Ar_2Li_3^+$	Li, Li, Li Ar, Ar	0.239, 0.240, 0.306, 0.108, 0.108	0.234, 0.229, 0.514, 0.012, 0.012	0.262, 0.260, 0.378, 0.050, 0.050
$Ar_3Li_3^+$	Li, Li, Li Ar, Ar, Ar	0.225, 0.225, 0.225, 0.108, 0.108, 0.109	0.358, 0.356, 0.296, 0.010, −0.010, −0.010	0.283, 0.282, 0.280, 0.051, 0.051, 0.051

ring center for the H_3^+- and Li_3^+-trapped noble gas clusters are put forward in Table 3 and Table 4, respectively. A comparison of the N_g–H (N_g = Ne, Ar, Kr) bond distances (Å) obtained from Pauzat's calculations[5a–c] and from the present study are given in Table 5. A detailed population analysis under the Mulliken scheme (MPA), consisting of the atomic charges (Q_k) and Fukui functions (f_k^+, f_k^-) for all the atomic sites of the H_3^+- and Li_3^+-trapped noble gas clusters, are shown in Table 6 and Table 7 respectively. Table 8 and Table 9 depict some plausible complexation reactions that may occur during the trapping of the noble gas atoms by H_3^+ or Li_3^+, respectively. The feasibility of such reactions in real practice may be justified from their ΔH or $\Delta\omega$ values. Fig. 1 and Fig. 2 depict the stable molecular conformations of the H_3^+- and Li_3^+-trapped noble gas clusters, respectively. Fig. 3(a–d) and Fig. 4(a–c) illustrate the gain in energy (ΔE) computed at the B3LYP level and the electrophilicity (ω) of the different noble gas atomic assemblies trapped by the H_3^+ and Li_3^+ aromatic systems. Fig. 5 and Fig. 6 portray the important frontier molecular orbitals (FMOs) of the H_3^+- and Li_3^+-trapped noble gas clusters, respectively.

From Table 1 and Table 2, it transpires that H_3^+ serves as a better trap for noble gas atoms as it has the ability to hold any of them (He–Kr). For an $Ar_nH_3^+$ cluster, as many as five Ar atoms can be bound together by the H_3^+ trigonal ring. The situation is nevertheless not so encouraging with the Li_3^+ unit, as it can trap He, Ne and Ar atoms but not Kr. The hardness (η) and electrophilicity (ω) for the noble gas atoms follow the expected pattern with the gradual incrementing of the atomic size from He to Kr, and the hardness (η) falls as the atoms get softer, thereby encouraging an increment in the corresponding electrophilicity (ω) values. Thus, the noble gases are supposed to be more reactive as one moves down the periodic group from He to Kr. However, the hardness (η) and electrophilicity (ω) trends show some interesting outcomes for the trapped noble atomic clusters. For the Li_3^+-trapped clusters, it is observed from Table 2 that the η values more or less increase with increasing cluster size (n value) for the corresponding noble gas atoms, and is accompanied by a gradual decrease in their respective ω values. This signifies the sheer unwillingness of the larger Li_3^+-trapped noble atomic clusters towards chemical reactivity, a phenomenon in accordance with the MEP criterion. Of course, both the chemical and external potentials change drastically. Moreover, it is expected that a system would get softer with increasing size. The situation is, however, not so straightforward for the corresponding

Table 8 Some plausible reactions that could occur due to the attack of noble gas atoms onto the H_3^+ moiety

No.	Reactions	ΔH/a.u.	$\Delta\omega$/eV
1	$H_3^+ + He = HeH_3^+$	−0.445	−0.917
2	$HeH_3^+ + He = He_2H_3^+$	−0.541	−0.820
3	$He_2H_3^+ + He = He_3H_3^+$	−0.520	−0.933
4	$H_3^+ + Ne = NeH_3^+$	−1.488	−3.511
5	$NeH_3^+ + Ne = Ne_2H_3^+$	−1.389	−2.927
6	$Ne_2H_3^+ + Ne = Ne_3H_3^+$	−1.279	−2.870
7	$H_3^+ + Ar = ArH_3^+$	−9.570	−2.870
8	$ArH_3^+ + Ar = Ar_2H_3^+$	−3.027	−3.188
9	$Ar_2H_3^+ + Ar = Ar_3H_3^+$	−2.497	−3.035
10	$Ar_3H_3^+ + Ar = Ar_4H_3^+$	−0.240	−2.360
11	$Ar_4H_3^+ + Ar = Ar_5H_3^+$	−0.223	−2.340
12	$H_3^+ + Kr = KrH_3^+$	−17.866	−5.813
13	$KrH_3^+ + Kr = Kr_2H_3^+$	−2.946	−3.406
14	$Kr_2H_3^+ + Kr = Kr_3H_3^+$	−2.618	−3.773

Table 9 Some plausible reactions that could occur due to the attack of noble gas atoms onto the Li_3^+ moiety

No.	Reactions	ΔH/a.u.	$\Delta\omega$/eV
1	$Li_3^+ + He = HeLi_3^+$	−0.247	−0.131
2	$HeLi_3^+ + He = He_2Li_3^+$	−0.187	−0.268
3	$He_2Li_3^+ + He = He_3Li_3^+$	−0.111	−0.532
4	$Li_3^+ + Ne = NeLi_3^+$	−1.008	−2.138
5	$NeLi_3^+ + Ne = Ne_2Li_3^+$	−0.982	−2.254
6	$Ne_2Li_3^+ + Ne = Ne_3Li_3^+$	−0.982	−2.432
7	$Li_3^+ + Ar = ArLi_3^+$	−2.070	−2.446
8	$ArLi_3^+ + Ar = Ar_2Li_3^+$	−1.877	−2.531
9	$Ar_2Li_3^+ + Ar = Ar_3Li_3^+$	−1.782	−2.817

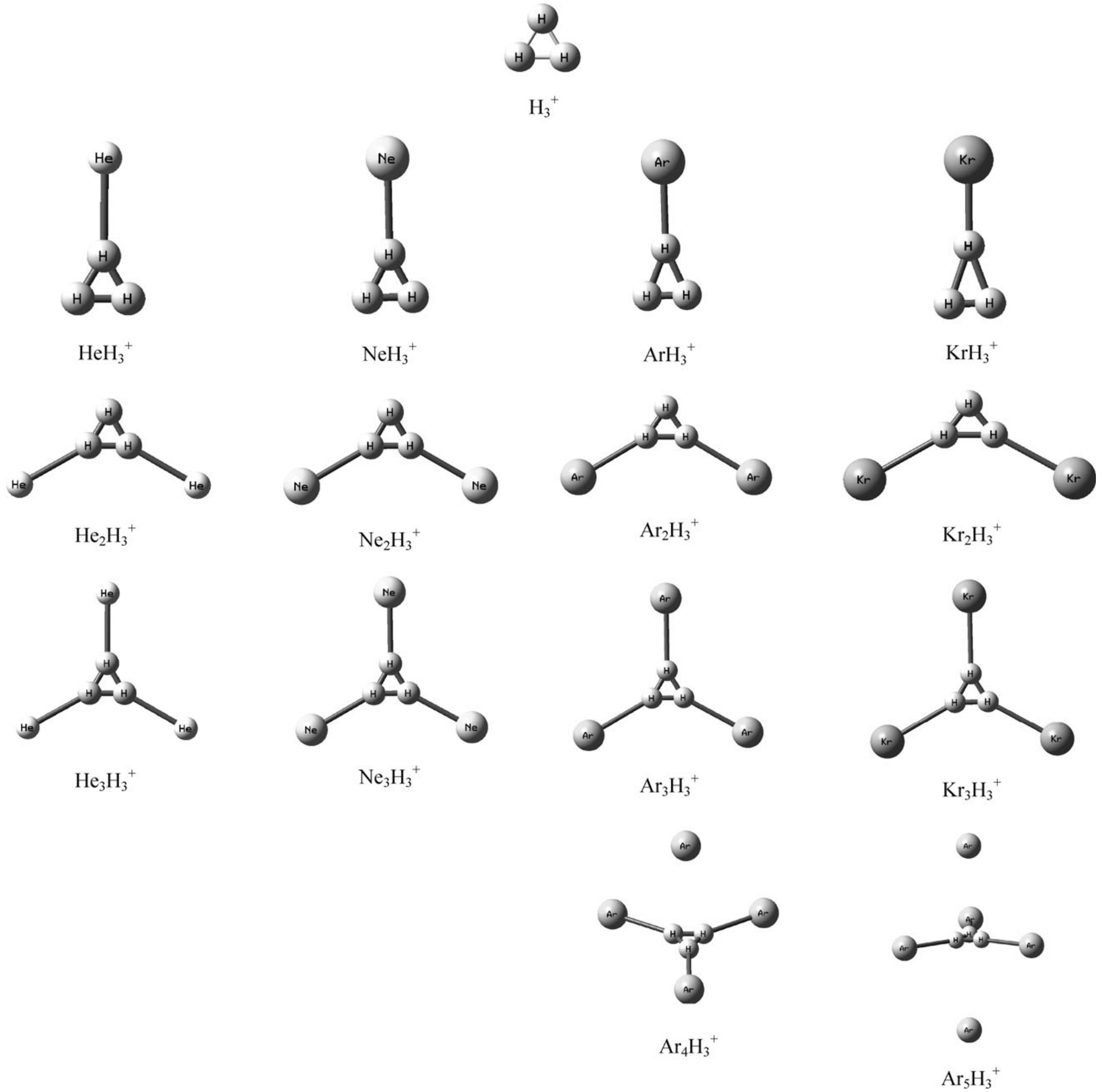
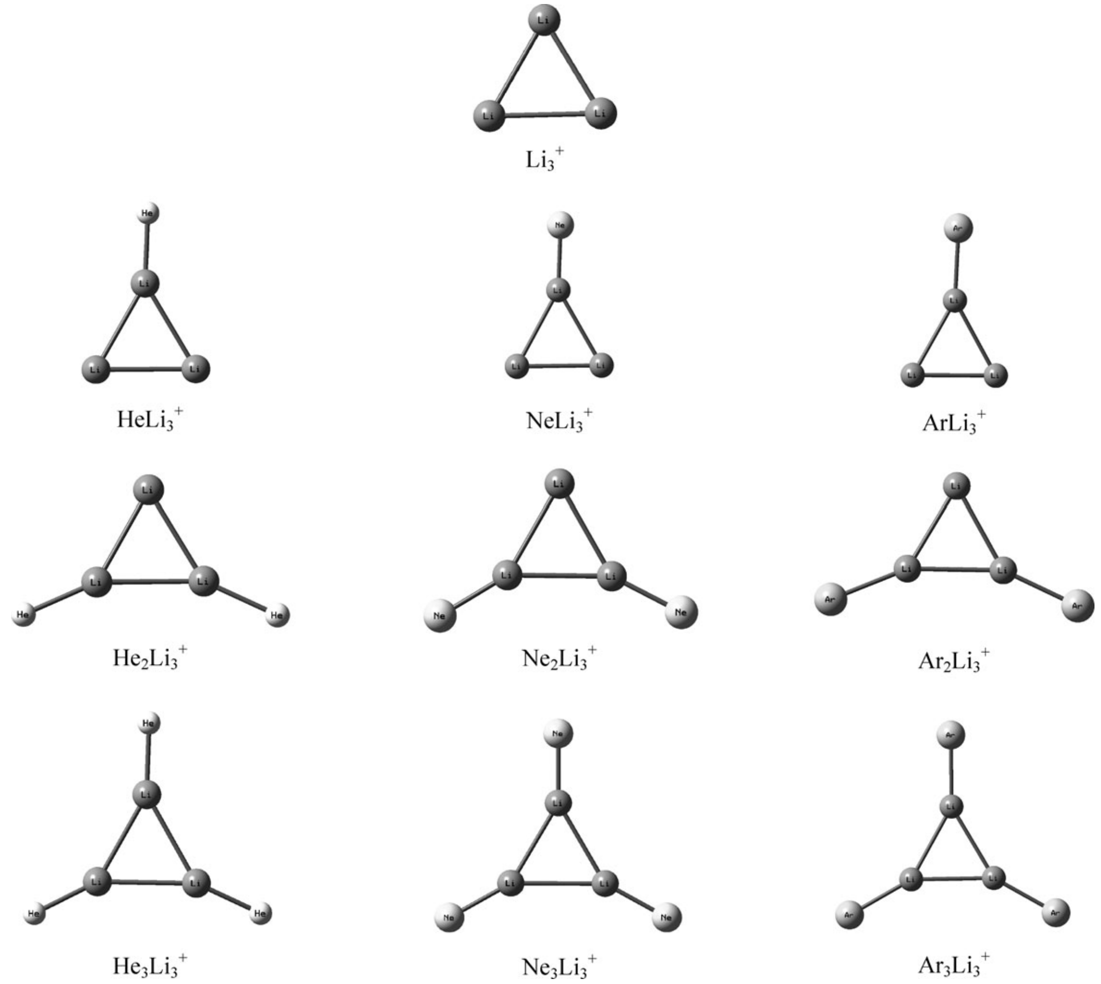


Fig. 1 Geometrical structures of H_3^+ and corresponding trapped noble gas clusters optimized at the B3LYP/6-311 + G(d) level of theory.

H_3^+-trapped noble gas clusters. Table 1 shows that for all the noble gas atoms, the η values decrease with increasing cluster size, which is a trademark of an increase in chemical reactivity. On the contrary, the ω values also show a hand-in-hand decreasing trend. From Table 3 and Table 4, it becomes relevant that both the H_3^+ and Li_3^+ rings in their free uncombined, as well as in their trapped, states show a highly negative NICS(0) value, a phenomenon pointing towards high stability of the molecular systems in terms of aromaticity.[7]

It can perhaps now be assured that although the η and ω trends for the H_3^+-trapped noble gas clusters show some anomalies, the stability of the H_3^+ unit upon trapping noble gas atoms, as many as five for Ar, is well established from the viewpoint of the aromaticity criterion in terms of NICS measurements. It was further noticed that the NICS values showed an obvious decrease as one moved away from the ring centers. The situation became rather interesting for the $Ar_5H_3^+$ cluster, where the NICS(3) and NICS(4) values were much more negative than the NICS(0) value. This trend became justified upon consideration of the trigonal bipyramidal arrangement of the five Ar atoms around the triangular H_3^+ unit, which, of course, deserves careful scrutiny. Qualitative trends remained same in both the levels. Close scrutiny of Table 5 reveals that the variation of the Ng–H (Ng = Ne, Ar, Kr) bond distances for the different noble gas-trapped clusters follows the same trend as that reported by Pauzat *et al.*[5] Moreover, it may be noted that the most stable structures among the several stationary points for the trapped clusters reported by Pauzat *et al.*[5] exactly correspond to the ones obtained in this study. From the information regarding the


Li_3^+

$HeLi_3^+$ $NeLi_3^+$ $ArLi_3^+$

$He_2Li_3^+$ $Ne_2Li_3^+$ $Ar_2Li_3^+$

$He_3Li_3^+$ $Ne_3Li_3^+$ $Ar_3Li_3^+$

Fig. 2 Geometrical structures of Li_3^+ and corresponding trapped noble gas clusters optimized at the B3LYP/6-311 + G(d) level of theory.

local parameters presented in Table 6 and Table 7, it is observed that the atomic charges (Q_k) for almost all of the atomic sites of the H_3^+- and Li_3^+-trapped clusters are positive. Although the Q_k values in all three atomic sites of H_3^+/Li_3^+ are the same due to symmetry, the same behavior is not observed in the corresponding f_k values, since the uniformity in the Q_k values is lost in the cases of the respective anions (*i.e.*, neutral H_3/Li_3), calculated using a single point method on the geometry of the corresponding *N*-electron species (H_3^+/Li_3^+).

This pre-supposes a nucleophilic or radical attack at all the atomic centers. The gradual acceptance of neutral noble gas atoms by the H_3^+ and Li_3^+ units to form larger stable clusters further strengthens this point. Scrutiny of Table 8 and Table 9 reveals that the reaction enthalpy (ΔH) for the first phase trapping reactions between H_3^+ and Li_3^+ systems with a single noble gas atom becomes more favorable as one moves from He to Kr, thereby lending ample weight to the increasing reactivities of the noble gas atoms down their periodic group. Thus, the first phase trapping reactions of H_3^+ and Li_3^+ with noble gases are thermodynamically quite favorable.

However, for second phase and further higher order trapping reactions, the ΔH values relatively increase for the corresponding noble gas atoms. This may be attributed to the phenomenon of "steric crowding", which probably comes into play with increasing numbers of atoms around the trigonal H_3^+ and Li_3^+ rings. The reaction electrophilicity ($\Delta\omega$) values for the trapping reactions with the H_3^+ moiety follow a relatively similar pattern, as dictated by their corresponding ΔH values. However, for the Li_3^+ trapping reactions, the $\Delta\omega$ values markedly decrease with further trapping, thereby encouraging the process further. Thus, it may be inferred that although the H_3^+ or Li_3^+ units show the ability to trap a number of noble gas atoms, the corresponding trapped clusters, particularly those with heavier atoms, may exhibit kinetic stability and be of the "fleeting" type.[20] Fig. 3(a–d) pictorially demonstrate the variation of gain in energy (ΔE) and electrophilicity (ω) values for the H_3^+-trapped noble atomic clusters. Both of these descriptors show a decreasing trend upon gradual cluster growth of H_3^+ with noble atoms, as expected from the Table 8 and Table 9. The gain in energy (ΔE) values show a consistent falling trend, except for the pairs $Ar_4H_3^+$–$Ar_5H_3^+$, $Kr_2H_3^+$–$Kr_3H_3^+$ and $Ne_2Li_3^+$–$Ne_3Li_3^+$. Among the former H_3^+-trapped clusters, the values are quite comparable, whereas for the latter Li_3^+-trapped pair, the ΔE value shows a reverse trend. This may be attributed to a relatively smaller increase in the energy (E) of the system during higher order trapping. Fig. 4(a–c) describe the trends

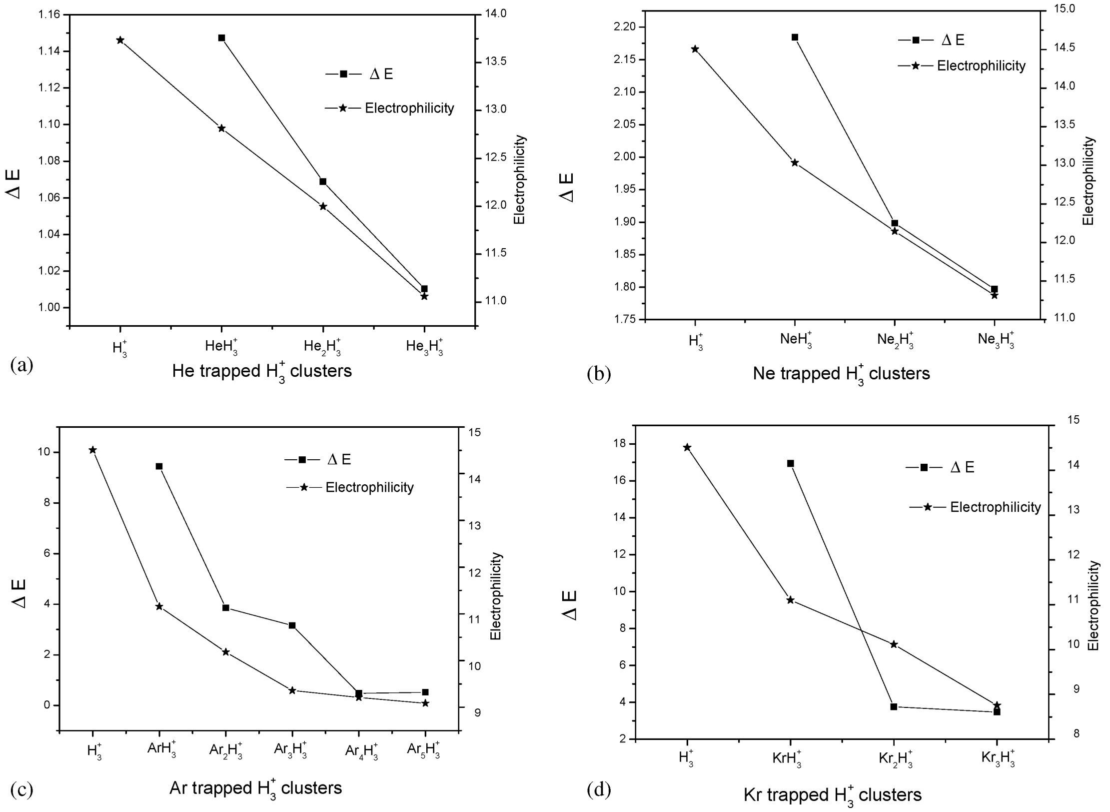


Fig. 3 Gain in energy for the formation of the complexes (ΔE/Kcal mol^{-1}) and electrophilicity (ω/eV) of the (a) He-trapped, (b) Ne-trapped, (c) Ar-trapped and (d) Kr-trapped H_3^+ clusters.

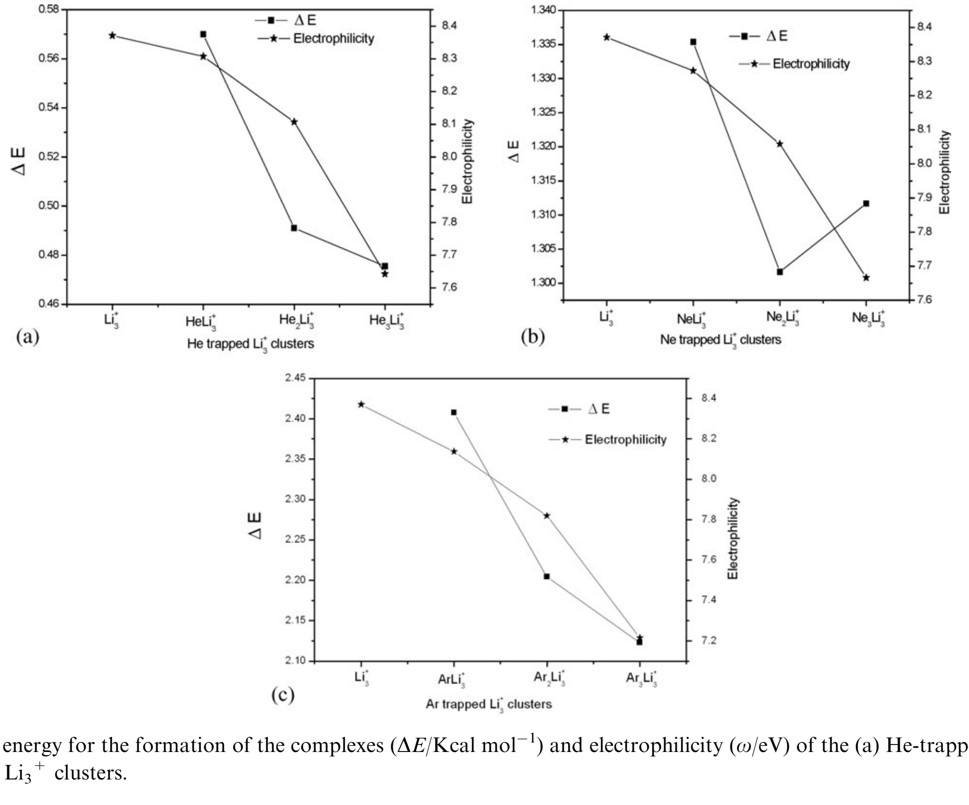


Fig. 4 (a) Gain in energy for the formation of the complexes (ΔE/Kcal mol^{-1}) and electrophilicity (ω/eV) of the (a) He-trapped, (b) Ne-trapped and (c) Ar-trapped Li_3^+ clusters.

of the energy gain (ΔE) and electrophilicity (ω) values upon trapping Li_3^+ with He, Ne and Ar, respectively. As discussed earlier, the Li_3^+-bound noble gas clusters are found to obey the minimum electrophilicity principle (MEP).

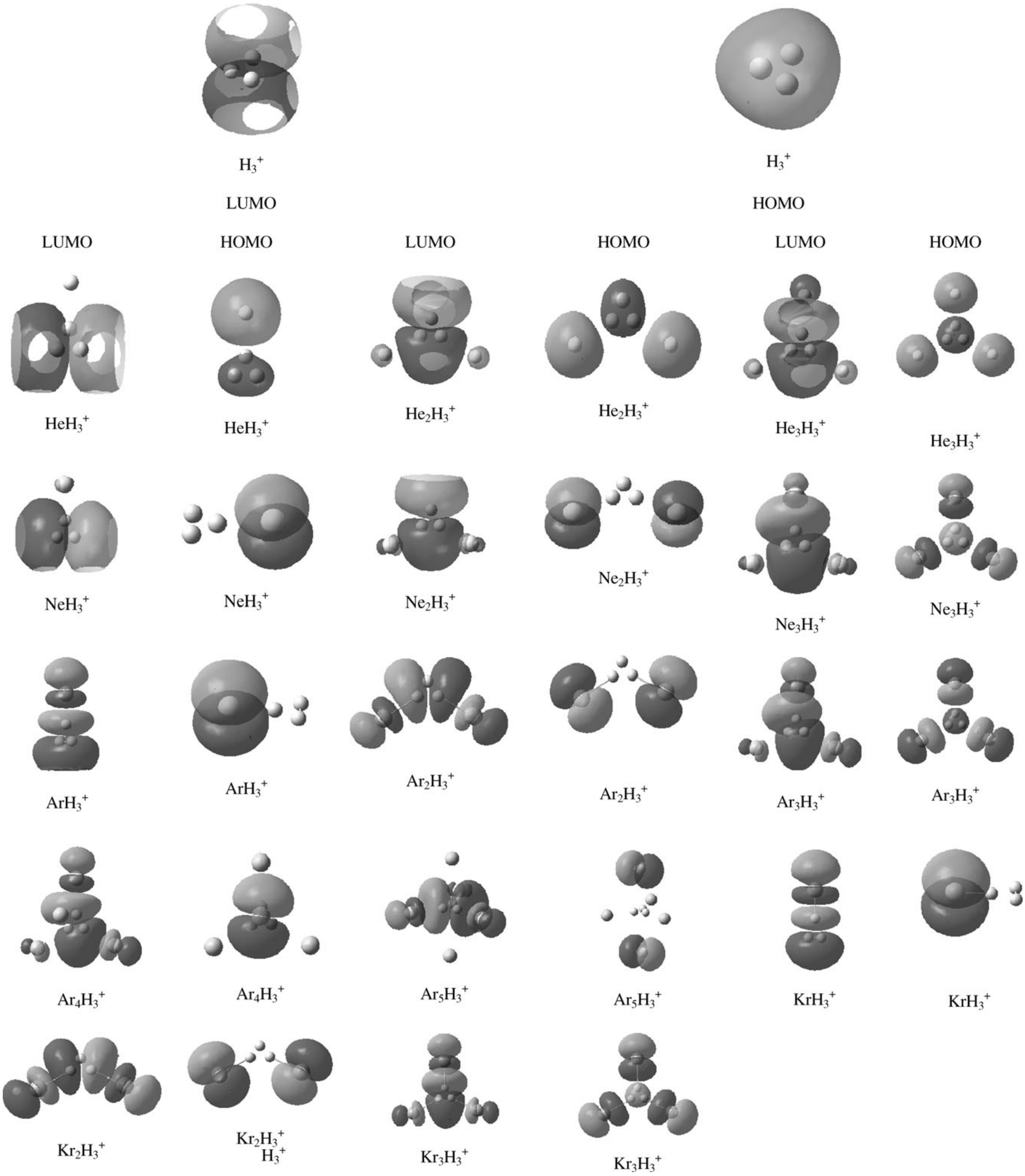


Fig. 5 The frontier molecular orbitals (LUMO, HOMO) of H_3^+ and corresponding trapped noble gas clusters optimized at the B3LYP/6-311+G(d) level of theory.

As shown in Fig. 5 and Fig. 6, the essential σ-symmetry in the frontier molecular orbitals of the H_3^+ and Li_3^+ trigonal rings is retained in most of the Li_3^+-trapped noble atomic clusters, whereas for the H_3^+-trapped clusters, additional π-symmetry is introduced.

An overall assessment of the relative responses of the H_3^+ and Li_3^+ systems towards the gradual trapping of the noble gases (He–Kr) can now be performed in the light of conceptual density functional theory (DFT)-based global and local reactivity descriptors, nucleus-independent chemical shift (NICS), an essential aromaticity criterion, and from scrutiny of the ΔH and $\Delta\omega$ values. Both the trigonal H_3^+ and Li_3^+ units possess σ-aromaticity and can serve as consistently fair trapping materials for noble gases. However, a detailed analysis of the

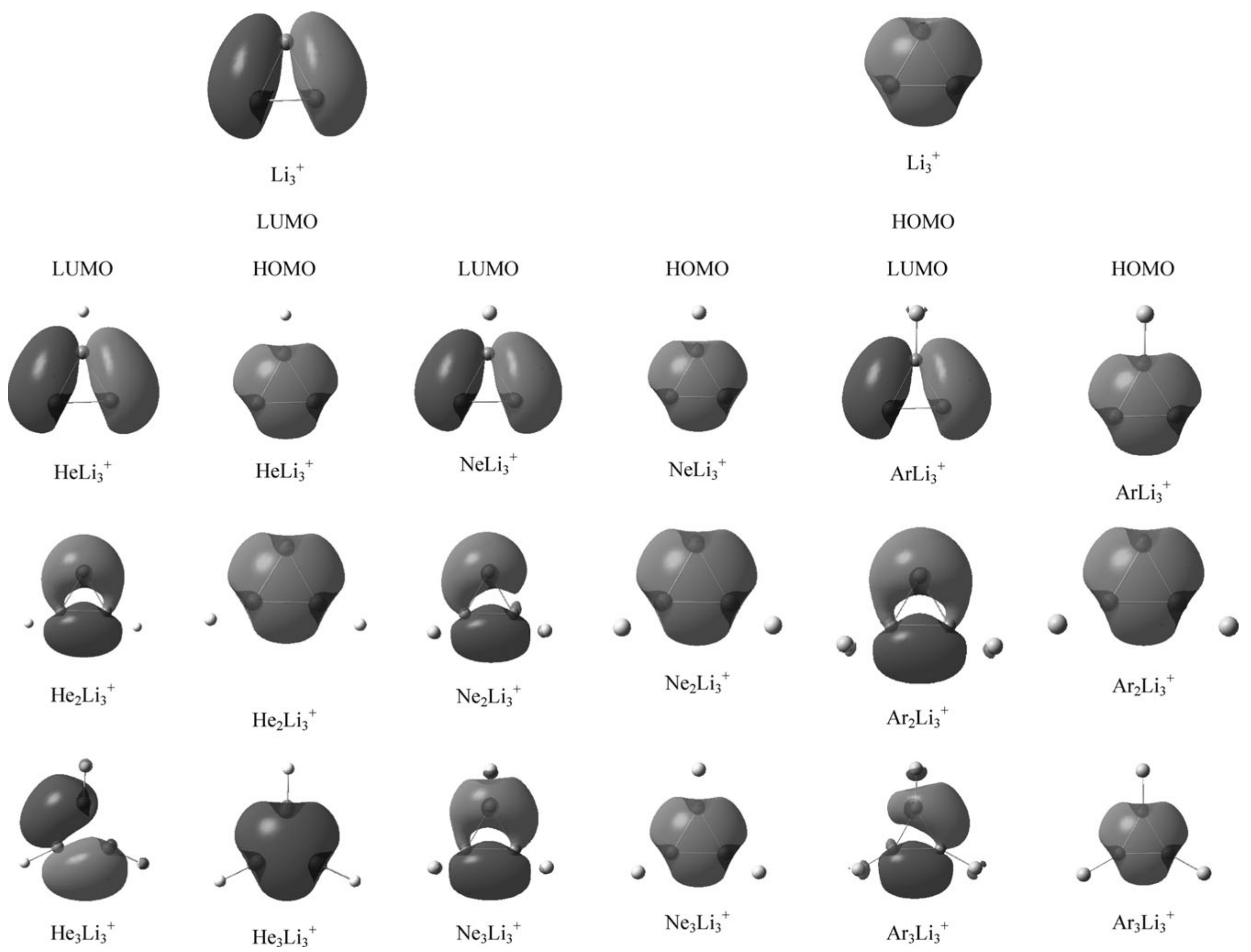


Fig. 6 The frontier molecular orbitals (LUMO, HOMO) of Li_3^+ and corresponding trapped noble gas clusters optimized at the B3LYP/6-311+G(d) level of theory.

relative capability of binding the inert gas atoms in multiple numbers to produce larger, and hence stable, cluster molecules presents some intriguing facts worthy of comparison. The Li_3^+-trapped noble gas clusters show an increasing trend in their η values upon cluster growth, which gradually mitigates the reactivity of the Li_3^+ system towards further trapping. On the other hand, the H_3^+ system, upon gradual binding with the noble gas atoms, illustrates a decrease in the corresponding η values, which justifies its ability to trap Kr and five Ar atoms as well. Thus, H_3^+ might serve as a marginally better "noble gas trap" compared to Li_3^+. This becomes more important as H_3^+ is lighter than Li_3^+. The uniformly decreasing ω values for the Li_3^+-trapped noble gas systems also point towards a diminishing reactivity of Li_3^+ towards further higher order trapping. The NICS(0) values for the H_3^+-trapped noble gas clusters range between -22.16 and -30.58. Alternatively, for the Li_3^+-bound systems, a very slender variance (-11.05 to -11.17) in the NICS(0) value is seen. The highly aromatic nature of H_3^+ is probably the driving force behind its more extensive trapping of noble gas atoms. The "all-metal" Li_3^+ system exhibits a comparatively lower NICS(0) value (-11.08), owing to which a larger stability of its trapped clusters in terms of aromaticity upon gradual cluster growth is not envisaged. The Li_3^+ unit therefore restricts itself to Ar trapping only. The decrease in η values, and hence an enhancement in the chemical response for the noble gas atoms upon travelling from He to Kr, is well elucidated from a thermodynamic viewpoint. The ΔH values for the first order trapping reactions for the H_3^+ and Li_3^+ moieties show a consistent decreasing trend. However, if the magnitudes are considered, it is again H_3^+ that takes the lead. The ΔH values for the H_3^+-trapped clusters are more negative compared to their corresponding Li_3^+ counterparts. This may again be attributed to much higher NICS values for the H_3^+-trapped systems, which perhaps affirms some additional stability in terms of a more effective diatropic ring current being sustained in the trigonal H_3^+ ring. The involvement of steric interactions among the incoming noble gas atoms upon increasing the cluster size is nevertheless a common incidence for both the H_3^+- and Li_3^+-trapped systems. All of these reactions being exothermic, and their $\Delta\omega$ values being negative (vide MEP), are thus thermodynamically favorable. The corresponding BSSE corrections and ZPE calculations for the H_3^+- and Li_3^+-trapped noble gas systems are being performed at several higher levels of theory (MP2, CCSD and CCSD(T)) using the 6-311+G(d) basis set to gain a better understanding of the bonding and energetics of these trapped clusters. The NIMAG values of the systems were confirmed as zero, meaning that they correspond to minima on the potential energy surface (PES). Alkali metal complexes of trigonal aromatic systems, X_3^{2-} (X $\equiv$ Be, Mg, Ca) can be used as traps for H_2 (to appear).

Conclusions

A study of the trapping of noble gas atoms (He–Kr) by trigonal H_3^+ and Li_3^+ systems within a conceptual density functional theory framework has revealed that a considerable amount of stability could be assured for the so-called inert gas atoms upon forming small- to medium-sized cationic clusters. This stability could further be justified by the aromaticity criterion defined in terms of NICS measurements. Further efforts to rationalize the stability of H_3^+- and Li_3^+-bound noble atomic clusters from thermodynamic perspective was also attempted from a study of the reaction enthalpy (ΔH) and reaction electrophilicity ($\Delta\omega$) values of plausible step-wise trapping reactions. In a nutshell, we have outlined that, unlike the first phase trapping steps, second and higher phase trapping processes may be marginally favorable. The stability of the medium-sized trapped clusters may however be somewhat compromised by steric crowding.

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