

Theoretical study on the noble-gas anions $F^-(NgO)_n$ ($Ng = He, Ar, \text{ and } Kr$)

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Abstract

We have calculated the molecular geometries, association energies, and charge distribution of the noble-gas containing anions $F^-(NgO)_n$ ($Ng = He, Ar, Kr; n = 1-6$). The geometries of these anions were found to be highly symmetric. The predicted ranges of association energies were 19–39, 37–134, and 58–231 kcal/mol for $Ng = He, Ar, \text{ and } Kr$, respectively. The stability of these anions was due to the charge-induced formation of the $Ng-O$ bonds. As the size of the system increases, the charge separation along the $Ng-O$ bond decreases, while the fluorine atom remains fully charged.

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1. Introduction

The chemistry of noble gas (Ng) has received significant attention in recent years [1]. Experimentally, the noble gas elements were found to act as ligands to transition metals [2,3], and the light noble gas (Ar, Kr) were found to form neutral molecules of the type $HNgY$ [4–7] where Y is electronegative atoms or groups. Most of the noble-gas molecules studied to date are meta-stable species, and they were observed only at cryogenic conditions in noble-gas matrixes. Theoretical calculation plays a very important role in studying simple noble-gas molecules because the fingerprint IR peaks can be readily calculated and compared with experimental data. Furthermore, the stability of the noble-gas molecules can be justified or even predicted by high-level electronic structure calculation.

Recently, we predicted that noble gas elements can form very stable anions $FNgO^-$ [8]. The stability results from the charge-induced formation of $Ng-O$ bonds. Large singlet–triplet gaps were predicted at the optimized geometries of the singlet states, and significant energy barriers exist for

the unimolecular dissociation channels. Charge distribution analysis showed that the fluorine atoms stay almost fully charged in the anions. It is thus reasonable to speculate that the fluoride ion might be able to induce the formation of more than one $Ng-O$ bonds simultaneously. In this letter, we explore this possibility by performing correlated electronic structure calculation with extended basis sets on the anions of the type $F^-(NgO)_n$, ($Ng = He, Ar, Kr; n = 1-6$). The geometries, association energies, and the charge distribution as a function of n and the identity of the noble gas will be discussed.

2. Method

The geometries of $F^-(NgO)_n$, ($Ng = He, Ar, Kr; n = 1-6$) were calculated using the MP2 theory with the aug-cc-pVDZ basis set. Geometries were also calculated at MP2/aug-cc-pVTZ level for $n = 1-4$, and at CCSD(T)/aug-cc-pVTZ level for $Ng = He, Ar; n = 1-3$, and for $Ng = Kr; n = 1-2$. According to our calculation, the noble gas neon does not form similar anions. Single-point energy calculation at MP2/aug-cc-pVTZ levels was performed on the MP2/aug-cc-pVDZ geometries for $Ng = He, Ar; n = 5-6$. Single-point energy calculation at CCSD(T)/aug-cc-pVTZ levels was performed on the MP2/aug-cc-pVDZ geometries

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for Ng = He, $n = 4-6$, and for Ar, $n = 4$, and for Kr, $n = 3$, 4. The energies of electronic states with higher multiplicities ($2S + 1 = 3, 5, 7$) were calculated at the singlet state geometry to ascertain the singlet state is the ground state. The harmonic vibrational frequencies were calculated at MP2/aug-cc-pVDZ level. The atomic charges were calculated using the NBO method [9]. The electronic calculations were performed using the GAUSSIAN 03 program [10].

3. Results and discussion

Fig. 1 depicts the calculated structures (MP2/aug-cc-pVDZ level) of $F^-(NgO)_n$ as represented by $F^-(ArO)_n$. The optimized structures have high symmetry and belong to the point groups indicated in the Figure with the exception of $F^-(HeO)_5$ where the lowest energy structure was found to have the D_{3h} symmetry. In fact, for the three noble gas elements with $n = 5$, the C_{4v} (square pyramidal) and the D_{3h} (trigonal bipyramidal) structures are all very close in energy (within 0.1 kcal/mol). The parts of potential energy surface regarding the spatial arrangement of the NgO units for $n = 5$ are quite flat. This is similar to many cases for coordination compounds of transition metals with coordination number 5 [11]. Table 1 lists the calculated F–Ng and Ng–O distances at three theoretical levels. The F–Ng distance increases as the number of the NgO unit increases due to the Pauli and nuclear repulsion. For example, in $F^-(HeO)_n$ the F–He distances increases by 0.04–0.08 Å for every additional HeO unit in the MP2 cal-

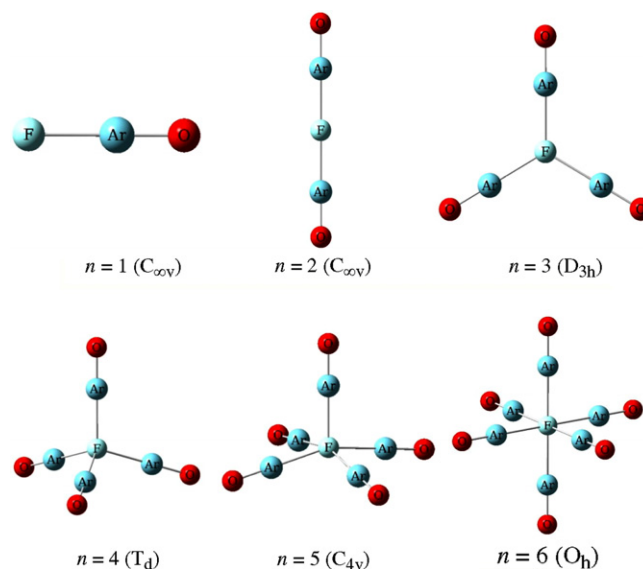


Fig. 1. Calculated structures of $F^-(NgO)_n$ at the MP2/aug-cc-pVDZ level as represented by $F^-(ArO)_n$. The only exception is $F^-(HeO)_5$ which has a trigonal bipyramidal (D_{3h}) structure.

ulation and by 0.08–0.09 Å in the CCSD(T) calculation. The trend is very similar for $F^-(ArO)_n$ and $F^-(KrO)_n$ with larger increase in F–Ng in distance (~ 0.10 Å per NgO in the CCSD(T) calculation). For $n = 1-3$, the calculated F–Ng distances at the MP2/aug-cc-pVDZ level are reasonably close to the CCSD(T)/aug-cc-pVTZ values.

Table 1
Calculated F–Ng and Ng–O bond lengths (in Å) in $F^-(NgO)_n$

n	1	2	3	4	5	6
<i>Ng = He</i>						
MP2/aug-cc-pVDZ	1.637 (1.054) ^a	1.721 (1.061)	1.795 (1.071)	1.857 (1.082)	1.923, 1.942 ^b (1.096), (1.100)	1.983 (1.109)
MP2/aug-cc-pVTZ	1.606 (1.043)	1.687 (1.047)	1.766 (1.055)	1.835 (1.066)		
CCSD(T)/aug-cc-pVTZ	1.626 (1.110)	1.713 (1.108)	1.793 (1.118)			
<i>Ng = Ar</i>						
MP2/aug-cc-pVDZ	2.271 (1.729)	2.360 (1.730)	2.437 (1.733)	2.499 (1.737)	2.573, 2.547 ^c (1.744), (1.742)	2.615 (1.748)
MP2/aug-cc-pVTZ	2.214 (1.685)	2.313 (1.682)	2.397 (1.682)	2.462 (1.683)		
CCSD(T)/aug-cc-pVTZ	2.241 (1.781)	2.344 (1.768)	2.431 (1.766)			
<i>Ng = Kr</i>						
MP2/aug-cc-pVDZ	2.250 (1.817)	2.375 (1.808)	2.466 (1.803)	2.534 (1.802)	2.633, 2.587 ^c (1.803), (1.801)	2.679 (1.803)
MP2/aug-cc-pVTZ	2.211 (1.786)	2.334 (1.772)	2.428 (1.766)	2.498 (1.763)		
CCSD(T)/aug-cc-pVTZ	2.259 (1.854)	2.372 (1.836)				

^a Values in parentheses are calculated Ng–O bond lengths.

^b The structure has D_{3h} symmetry, and the first values are the bond lengths on the trigonal plane, and the second values are the bond lengths on the C_3 axis.

^c The structure has C_{4v} symmetry, and the first values are the bond lengths on the square plane, and the second values are the bond lengths on the C_4 axis.

The calculated Ng–O distances are significantly shorter than the F–Ng distances, and they are almost constants for a particular Ng in the MP2 calculation (in most cases, changes are less than 0.01 Å for every additional NgO). The available CCSD(T) results however suggest the Ng–O distances would decrease slightly from $n = 1$ to 2. The F–Ng and Ng–O distances predicted by MP2/aug-cc-pVTZ calculation are significantly shorter than MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ values. This is due to the significant overestimation of the association energies as will be discussed below.

Table 2 and Fig. 2 show the calculated association energies of $F^-(NgO)_n$ which are defined as the energy changes for the process: $F^-(NgO)_n \rightarrow F^- + n Ng + n O$ on the singlet-state potential energy surface. Table 2 shows that the results are sensitive to both theory and basis-set sizes. Compared to the CCSD(T) results, the MP2 theory significantly overestimates the association energies in all cases. As shown in Fig. 2, approximately the overestimation is proportional to the sizes (or n). This is consistent with our recent finding that MP2 theory significantly overestimates the bond energies of noble-gas molecules [12]. It is also shown in Table 2 that calculation with larger basis sets predicts larger association energies. Thus, MP2 calculation with large basis sets should be avoided in predicting bond energies of noble-gas molecules and ions due to the accumulation of errors. For Ng = He, as n increases the association energies calculated at CCSD(T)/aug-cc-pVTZ level increase only gradually and reach a maximum at $n = 4$. The maximum association energy (39 kcal/mol) is only twice the value for $n = 1$. For Ng = Ar and Kr, the association energies increases more significantly as n increases. For example, at CCSD(T)/aug-cc-pVTZ level the association energies of $F^-(ArO)_n$ increases from 37 kcal/mol for $n = 1$ to 109 kcal/mol for $n = 4$. At the same level, the association energies of $F^-(KrO)_n$ increases from 58 kcal/mol

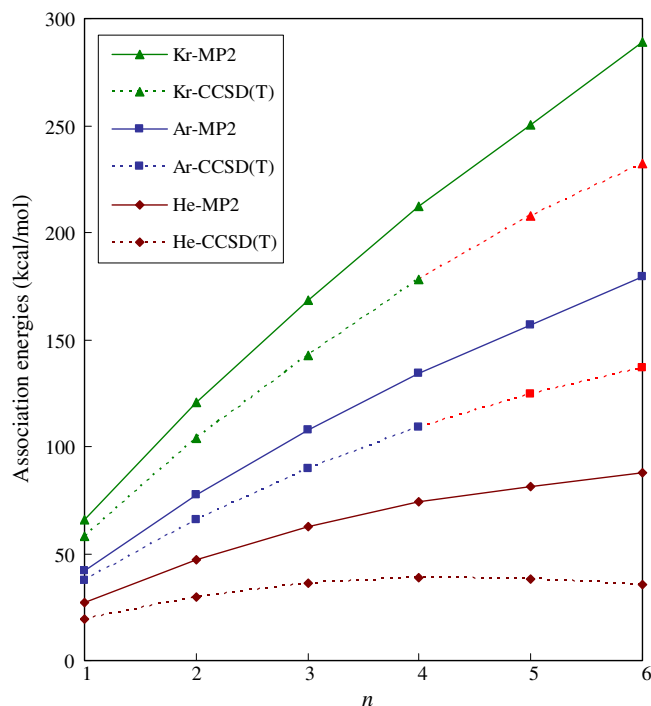


Fig. 2. The calculated association energies of $F^-(NgO)_n$ (Ng = He, Ar, Kr) at MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ levels as functions of n . The symbols in red represent the extrapolated values. (For interpretation of the reference in color in this figure legend, the reader is referred to the web version of this article.)

for $n = 1$ to 178 kcal/mol for $n = 4$. The CCSD(T)/aug-cc-pVTZ association energies for Ng = Ar, Kr; $n = 5, 6$ in Fig. 2 are extrapolated based on the values for $n = 1–4$. In all cases the singlet electronic states of $F^-(NgO)_n$ are found to be the ground state and are lower in energy than the lowest excited states by at least 61, 32, and 53 kcal/mol for Ng = He, Ar, and Kr, respectively.

Table 2

Calculated association energies^a (in kcal/mol) of $F^-(NgO)_n$

n	1	2	3	4	5	6
<i>Ng = He</i>						
MP2/aug-cc-pVDZ	26.8	47.0	62.4	74.3	81.4	87.7
MP2/aug-cc-pVTZ	31.8	56.5	75.7	90.9	100.7 ^b	109.6 ^b
CCSD(T)/aug-cc-pVDZ ^b	13.0	19.0	21.0	20.0	15.2	9.7
CCSD(T)/aug-cc-pVTZ	19.2	30.6	37.4	39.0 ^b	37.9 ^b	35.7 ^b
<i>Ng = Ar</i>						
MP2/aug-cc-pVDZ	41.9	77.3	107.5	134.2	157.0	179.1
MP2/aug-cc-pVTZ	51.4	95.2	133.3	167.6	194.5 ^b	222.8 ^b
CCSD(T)/aug-cc-pVDZ ^b	28.2	49.6	66.1	79.6	89.5	98.9
CCSD(T)/aug-cc-pVTZ	37.1	65.8	89.7	109.1 ^b		
<i>Ng = Kr</i>						
MP2/aug-cc-pVDZ	66.0	120.6	168.6	212.3	250.6	288.9
MP2/aug-cc-pVTZ	76.0	139.6	196.1	248.5		
CCSD(T)/aug-cc-pVDZ ^b	50.3	86.6	118.2	145.8		
CCSD(T)/aug-cc-pVTZ	58.1	103.9	142.7 ^b	178.0 ^b		

^a Born–Oppenheimer energies, not including vibrational zero-point energies.

^b Single-point energies calculated on MP2/aug-cc-pVDZ geometries.

Table 3

Calculated NBO atomic charges (in e) for $F^-(NgO)_n$

n		F	Ng	O
1	He	−0.91	0.57	−0.66
	Ar	−0.94	0.86	−0.92
	Kr	−0.85	0.86	−1.01
2	He	−0.89	0.33	−0.39
	Ar	−0.89	0.67	−0.72
	Kr	−0.84	0.83	−0.91
3	He	−0.89	0.25	−0.29
	Ar	−0.88	0.65	−0.69
	Kr	−0.84	0.81	−0.87
4	He	−0.89	0.21	−0.24
	Ar	−0.88	0.63	−0.66
	Kr	−0.85	0.80	−0.83
5	He	−0.90	0.18	−0.20
	Ar	−0.89	0.60	−0.63
	Kr	−0.86	0.78	−0.81
6	He	−0.91	0.16	−0.18
	Ar	−0.89	0.58	−0.61
	Kr	−0.87	0.76	−0.79

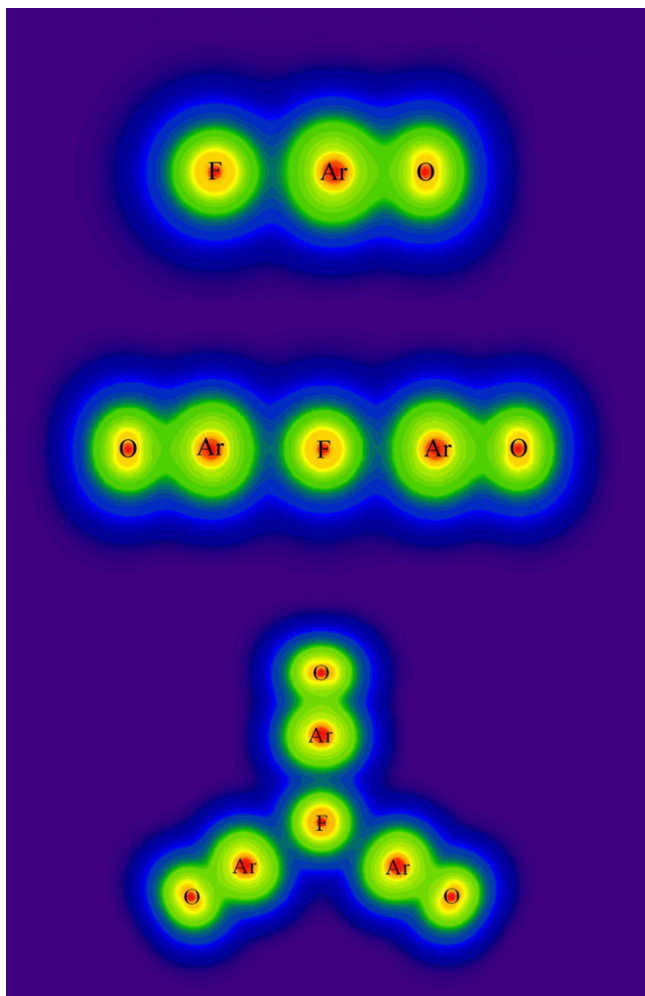


Fig. 3. Contour plot of the electron density (MP2/aug-cc-pVDZ) for $F^-(ArO)_n$ ($n = 1-3$).

Table 3 lists the calculated NBO atomic charges calculated at MP2/aug-cc-pVDZ level. As seen in the table, the fluorine atom remains almost fully charged ($\sim -0.9 e$) in all cases. The charge separations on the NgO units however, show significant variations. For the same n , the charge separations increase as the mass of the noble gas increases. This is in fact expected based on the ionization potentials of the noble gas atoms. Except for $n = 1$, the charge separations are relatively small on the HeO units. As n increases, the charge separation on the NgO units decrease gradually. This is probably because as the systems become more crowded, the F–Ng distances increase, and

thus charge separations on the NgO units induced by the fluoride ion become less significant. This is consistent with the results shown in Tables 1 and 2. Fig. 3 shows the contour plots of the electron density for $F^-(ArO)_n$ ($n = 1-3$). Clearly, the electron density around the fluoride ion show very little distortion while the highly distorted density distribution around the ArO units is similar to that of polar covalent bonds. This picture is consistent with the results shown in Table 3, although the effects of sizes (or n) are difficult to tell from the figure.

The vibrational frequency calculation suggests that some of the asymmetric F–Ng and Ng–O stretching modes of $F^-(NgO)_n$ have relatively strong IR intensities. For example, the predicted F–Ng absorption is around $190-330 \text{ cm}^{-1}$, $200-290 \text{ cm}^{-1}$, and $220-300 \text{ cm}^{-1}$ for Ng = He, Ar, and Kr, respectively. The predicted Ng–O absorption is around $1220-1660 \text{ cm}^{-1}$, $600-700 \text{ cm}^{-1}$, and $670-700 \text{ cm}^{-1}$ for Ng = He, Ar, and Kr, respectively. These IR fingerprints might be useful for future experimental identification of these noble-gas containing anions.

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