

## Theoretical prediction on the structures and stability of the noble-gas containing anions $\text{FNgCC}^-$ (Ng=He, Ar, Kr, and Xe)

Chia-Yu Peng, Chang-Yu Yang, Yi-Lun Sun, and Wei-Ping Hu

Citation: *J. Chem. Phys.* **137**, 194303 (2012); doi: 10.1063/1.4766326

View online: <http://dx.doi.org/10.1063/1.4766326>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v137/i19>

Published by the [American Institute of Physics](#).

---

### Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT



**ACCELERATE COMPUTATIONAL CHEMISTRY BY 5X.  
TRY IT ON A FREE, REMOTELY-HOSTED CLUSTER.**

[LEARN MORE](#)

# Theoretical prediction on the structures and stability of the noble-gas containing anions $\text{FNgCC}^-$ (Ng=He, Ar, Kr, and Xe)

Chia-Yu Peng, Chang-Yu Yang, Yi-Lun Sun, and Wei-Ping Hu<sup>a)</sup>*Department of Chemistry and Biochemistry, National Chung Cheng University, Chia-Yi 62102, Taiwan*

(Received 23 July 2012; accepted 23 October 2012; published online 21 November 2012)

We have made high-level theoretical study on a new type of noble-gas (Ng) containing anions  $\text{FNgCC}^-$ . The calculated short Ng–CC bond lengths of 1.13, 1.77, 1.89, and 2.04 Å for Ng=He, Ar, Kr, and Xe, respectively, and the electron density distributions indicated strong covalent interactions between the Ng and CC induced by the polarizing fluoride ion. Except for  $\text{FHeCC}^-$ , the structures of all other  $\text{FNgCC}^-$  were predicted to be linear. The intrinsic stability of the  $\text{FNgCC}^-$  was studied by calculating the energies of the three-body dissociation reaction:  $\text{FNgCC}^- \rightarrow \text{F}^- + \text{Ng} + \text{CC}$  and by calculating the energy barriers of the two-body dissociation reaction:  $\text{FNgCC}^- \rightarrow \text{Ng} + \text{FCC}^-$ . The results showed that  $\text{FNgCC}^-$  (Ng=Ar, Kr, Xe) could be kinetically stable in the gas phase with the three-body dissociation energies of 17, 37, and 64 kcal/mol and two body-dissociation barriers of 22, 31, and 42 kcal/mol, respectively, at the coupled-cluster single double (triple)/aug-cc-pVQZ level of theory. The structures and the stability were also confirmed using the multi-reference CASPT2 calculation. Future experimental identification of the  $\text{FNgCC}^-$  anions is expected under cryogenic conditions. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4766326>]

## I. INTRODUCTION

While the noble gases (Ng=He, Ne, Ar, Kr, Xe) were generally regarded as chemically “inert,” starting from 1962 the element xenon has been known to form many types of stable compounds such as  $\text{XePtF}_6$ .<sup>1</sup> In recent years, several new types of noble-gas molecules have been observed experimentally, including the various noble-gas hydrides  $\text{HNgY}$  (Y = electronegative chemical groups) notably by Räsänen and co-workers using the matrix photolysis/isolation techniques,<sup>2–7</sup> and the noble-gas noble-metal halide complexes  $\text{NgMX}$  by Gerry and co-workers using the laser ablation source.<sup>8–18</sup> The noble gas is also known to form ligands to transition-metal ions,<sup>19,20</sup> and to form actinide complexes with the CUO molecule.<sup>21–23</sup> In addition, the advent of computational chemistry has now made the accurate prediction of the structures and stability of small noble-gas molecule possible.<sup>24–36</sup> In particular, we have made prediction that the noble-gas containing anions  $\text{FNgO}^-$  (Ng=He, Ar, Kr, Xe) would have very compact structures and relatively strong charge induced Ng=O bonding.<sup>24</sup> It was even postulated that the fluoride ion can induce multiple Ng=O bonding simultaneously in  $\text{F}^-(\text{NgO})_n$  anions.<sup>27</sup> Following the prediction of  $\text{FNgO}^-$  and  $\text{FNgBO}^{25}$  molecules, Grandinetti and co-workers predicted that the anions  $\text{FNgBN}^-$  would also have strong F–Ng and Ng–B bonding and could be stable at cryogenic condition.<sup>30</sup> We have also recently predicted that the anions  $\text{NXeO}_2^-$  and  $\text{NXeO}_3^-$  could be stable and contain tentative Xe–N triple bonds.<sup>28</sup> Although somewhat unexpected, the noble gases do seem to have rich and interesting anionic chemistry after all.<sup>37</sup> In searching for other anionic noble-gas containing species computationally, we have recently noticed that the  $\text{FNgCC}^-$  anions (Ng=He, Ar, Kr, Xe) also contained

very short Ng–C bonds and could be a new type of potentially stable noble-gas containing species. In addition to the first predicted stable anions with Ng–C bonding, the  $\text{FNgCC}^-$  anions are interesting in several other ways. Firstly, while the  $\text{FNgCC}^-$  is isoelectronic to  $\text{FNgBO}$  and  $\text{FNgBN}^-$ , it is still somewhat surprising that a relatively stable Ng–C bond can be formed. It was thought that in  $\text{FNgBO}$  and  $\text{FNgBN}^-$  the electron-withdrawing or negatively charged fluorine atom could polarize the Ng–B bonds. Upon forming the Ng–B bond the Ng atom would donate partial electron charges toward the electron-poor boron atom. However, in the present case of  $\text{FNgCC}^-$ , the CC group is neither very electron deficient nor electron withdrawing. The nature of the Ng–C bonding should thus be different from that of the Ng–B bonding. Perhaps, it is more similar to  $\text{FNgO}^-$  where the fluoride ion polarizes the formation of the Ng=O bonds, and in the current case the Ng=C bonds. Secondly, while stable carbon-noble gas bonding has recently been predicted and experimentally observed in  $\text{HXeCN}$ ,<sup>38</sup>  $\text{HXeCCH}$ ,<sup>39</sup>  $\text{HXeCCXeH}$ ,<sup>39</sup>  $\text{HKrCCH}$ ,<sup>40</sup> and  $\text{FKrCCH}^4$  molecules, but, to our knowledge, no stable Ar–C bonds have been observed or predicted.<sup>26</sup> As will be seen in Secs. II–IV, the  $\text{FArCC}^-$  does seem to be a stable anion with significant dissociation barriers. Thirdly, since the ground state of CC is singlet,  $\text{FNgCC}^-$  anions would be less susceptible to dissociation through intersystem crossing to the triplet state, as in the case for  $\text{FNgO}^-$ .<sup>24</sup> In Secs. II–IV we will present the detailed theoretical study on the structures, stability, and the bonding nature of the new type noble-gas containing anions  $\text{FNgCC}^-$ .

## II. METHODS

The structures and energies of the  $\text{FNgCC}^-$  ion (Ng=He, Ar, Kr, Xe) were calculated using the MP2<sup>41</sup> and

<sup>a)</sup>E-mail: chewph@ccu.edu.tw.

coupled-cluster single double (triple) (CCSD(T))<sup>42</sup> methods and the hybrid density functionals B3LYP<sup>43–45</sup> and MPW1PW91<sup>46</sup> with Dunning's augmented correlation consistent basis sets (aug-cc-pVnZ,  $n = D, T, Q$ ).<sup>47–51</sup> For Ar the aug-cc-pV( $n+d$ )Z<sup>51</sup> basis sets were used, and for Xe the aug-cc-pVnZ-pp<sup>52</sup> basis sets were used. The “pp” means that a pseudopotential was used to replace the core electrons of the Xe atom. In the current study, 28 core electrons of Xe were replaced by the pseudopotential developed by Peterson *et al.*<sup>52</sup> For brevity, the basis sets will just be described as aug-cc-pVnZ for the rest of this article, and they are abbreviated as apnZ in all the tables. Additionally, the triplet state energies at the singlet-state geometry, the dissociation energies of (1) FNgCC<sup>-</sup> → F<sup>-</sup> + Ng + CC, (2) FNgCC<sup>-</sup> → F + Ng + CC<sup>-</sup>, (3) FNgCC<sup>-</sup> → FCC<sup>-</sup> + Ng, and the structures and energies of the transition states for the third dissociation channel were also calculated. The CASSCF<sup>53</sup> and CASPT2<sup>54,55</sup> calculations were also carried out to predict the FNgCC<sup>-</sup> structures and the dissociation barrier heights. All the valence electrons and orbitals except the *ns* electrons and orbitals of F, Ar, Kr, Xe were included in the active space. Thus, for FHeCC<sup>-</sup>, the active space consisted of 16 electrons in 12 orbitals (16,12), and for Ng=Ar, Kr, and Xe the active space consisted of 20 electrons in 14 orbitals (20,14). The ChelpG<sup>56</sup> and NBO<sup>57</sup> atomic charges and Laplacian of the electron density for FNgCC<sup>-</sup> were calculated at MP2/aug-cc-pVDZ level, and the harmonic vibrational frequencies and IR intensities were calculated at MP2/aug-cc-pVTZ level. The MP2, CCSD(T), and DFT calculation was performed using the GAUSSIAN 03 program,<sup>58</sup> and the CASSCF and CASPT2 calculation was performed using the MOLPRO 2009.1 program.<sup>59</sup> To supplement our earlier study on FNgO<sup>-</sup> (Ng=He, Ar, Kr),<sup>24</sup> the structures and energies of FXeO<sup>-</sup> were also calculated by MP2 and CCSD(T) theory with the aug-c-pVnZ basis sets. All the calculated structural parameters and relative energies of FNgO<sup>-</sup> (Ng=He, Ar, Kr, Xe) are included in the supplementary material.<sup>60</sup>

### III. RESULTS AND DISCUSSION

#### A. Structures

A schematic plot of a linear FNgCC<sup>-</sup> molecule was shown in Fig. 1. The calculated structures by various theoretical methods were listed in Table I. The FHeCC<sup>-</sup> anion was predicted to have a bent structure by all theoretical methods with He–C–C angle of ~137° by coupled cluster theory. The FArCC<sup>-</sup>, FKrCC<sup>-</sup> and FXeCC<sup>-</sup> anions were predicted to be linear by all methods. The FNeCC<sup>-</sup> anion was found not to be an energy minimum at all theoretical levels. The F–He distance in FHeCC<sup>-</sup> was predicted to be 1.62 Å at the CCSD(T)/aug-cc-pVQZ level. Unless specified otherwise, the structures and energies discussed below referred to the calculated results at this level. From Ar to Xe the F–Ng distances were predicted to be rather insensitive to the sizes of the Ng atoms, and the bond distances increased only slightly from 2.16 to 2.23 Å. This is consistent with the earlier study of FNgO<sup>-</sup><sup>24</sup> and with the picture of an ionic interaction be-

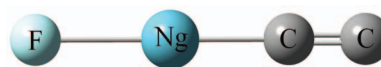


FIG. 1. Schematic plot of FNgCC<sup>-</sup>.

tween the fluoride ion and the NgCC unit. The He–CC distance was predicted to be only 1.13 Å, which was very short considering the predicted He–F distance in HHeF is 1.41 Å at the same level of theory.<sup>29</sup> From Ar to Xe the predicted Ng–CC distances were 1.77, 1.89, and 2.04 Å, respectively. The steady increases in bond distances reflected the covalent character of the Ng–C bonding, and the short distances seemed to suggest that the Ng–CC bonding might contain some double-bond character. The calculated C–C distances were all very similar from He to Xe, within 0.01 Å of a bond distance of 1.26 Å. In comparison, the calculated C–C distances in HCCH and C<sub>2</sub> molecules were 1.21 Å and 1.25 Å, respectively, at the same level of theory. The FNgCC<sup>-</sup>

TABLE I. Calculated bond lengths (Å) and bond angles (°) of FNgCC<sup>-</sup>.

Method	F–Ng	Ng–C	C–C	F–Ng–C	Ng–C–C
FHeCC <sup>-</sup>					
MP2/apdz	1.612	1.120	1.282	177.5	156.6
MP2/aptz	1.586	1.104	1.259	178.3	161.4
MPW1PW91/aptz	1.569	1.155	1.252	179.1	140.6
B3LYP/aptz	1.593	1.177	1.259	178.8	133.6
CCSD(T)/aptz	1.624	1.137	1.274	177.1	137.4
CCSD(T)/apqz	1.623	1.133	1.269	176.5	137.3
CASSCF/aptz	1.705	1.123	1.281	174.1	136.2
CASPT2/aptz	1.610	1.121	1.267	176.6	139.6
FArCC <sup>-</sup>					
MP2/apdz	2.187	1.782	1.290	180.0	180.0
MP2/aptz	2.146	1.737	1.265	180.0	180.0
MPW1PW91/aptz	2.174	1.895	1.243	180.0	180.0
B3LYP/aptz	2.209	1.930	1.245	180.0	180.0
CCSD(T)/aptz	2.175	1.782	1.263	180.0	180.0
CCSD(T)/apqz	2.164	1.767	1.258	180.0	180.0
CASSCF/aptz	2.302	1.822	1.273	180.0	180.0
CASPT2/aptz	2.130	1.900	1.272	180.0	180.0
FKrCC <sup>-</sup>					
MP2/apdz	2.214	1.919	1.288	180.0	180.0
MP2/aptz	2.180	1.879	1.265	180.0	180.0
MPW1PW91/aptz	2.174	1.894	1.243	180.0	180.0
B3LYP/aptz	2.209	1.930	1.245	180.0	180.0
CCSD(T)/aptz	2.203	1.905	1.261	180.0	180.0
CCSD(T)/apqz	2.186	1.893	1.257	180.0	180.0
CASSCF/aptz	2.279	1.921	1.269	180.0	180.0
CASPT2/aptz	2.117	1.965	1.268	180.0	180.0
FXeCC <sup>-</sup>					
MP2/apdz	2.264	2.080	1.285	180.0	180.0
MP2/aptz	2.239	2.041	1.264	180.0	180.0
MPW1PW91/aptz	2.234	2.054	1.244	180.0	180.0
B3LYP/aptz	2.266	2.081	1.245	180.0	180.0
CCSD(T)/aptz	2.249	2.057	1.261	180.0	180.0
CCSD(T)/apqz	2.232	2.044	1.256	180.0	180.0
CASSCF/aptz	2.279	2.078	1.268	180.0	180.0
CASPT2/aptz	2.244	2.077	1.264	180.0	180.0

anions are isoelectronic to the FNgCC molecules. In the current study, the predicted F–Ng bond distances were  $\sim 0.2$  Å longer and the Ng–CC distances  $\sim 0.02$  Å shorter than those in FNgCC obtained from an earlier study.<sup>26</sup> The two MP2 and two DFT methods in Table I all predicted very consistent results with differences less than 0.05 Å in bond distances as compared to the CCSD(T)/aug-cc-pVQZ results. Overall speaking, the structures predicted by MPW1PW91/aug-cc-pVTZ method seemed to best match the CCSD(T)/aug-cc-pVQZ values. The CCSD(T)/aug-cc-pVTZ results were all within 0.01 Å of the CCSD(T)/aug-cc-pVQZ values, indicating converged structure calculation with respect to the size of the basis sets. We also calculated the geometry of FNgCC<sup>−</sup> using the CASSCF and CASPT2 theory with the aug-cc-pVTZ basis set to check the possible effects due to the multiconfigurational and multireference nature. Both methods confirmed that the FNgCC<sup>−</sup> anions were energy minima, and the calculated results were also shown in Table I. The structures predicted by CCSD(T)/aug-cc-pVTZ and CASPT2/aug-cc-pVTZ were very similar. The CASPT2 method predicted slightly shorter (0.01–0.09 Å) F–Ng (Ng=He–Xe) distances and longer (0.02–0.12 Å) Ng–C (Ng=Ar–Xe) distances. Comparing the CASSCF and CASPT2 structures, the inclusion of dynamic correlation caused significant decreases in the F–Ng distances and slight increases in the Ng–C distances for Ng=Ar and Kr.

## B. Relative energies

Table II shows the calculated singlet-triplet (S-T) energy gaps of FNgCC<sup>−</sup> and the energies of three sets of dissociation products relative to FNgCC<sup>−</sup> by various methods. The S-T gaps calculated using the singlet structures were all quite high, and were 67, 81, 91, and 98 kcal/mol for Ng=He, Ar, Kr, and Xe, respectively. The MPW1PW91/aug-cc-pVTZ method predicted S-T gaps very closely matched with the CCSD(T)/aug-cc-pVQZ values, while the MP2/aug-cc-pVTZ methods significantly overestimated the S-T gaps. The calculated dissociation energies of the first channel were −1, 17, 37, and 64 kcal/mol for Ng=He, Ar, Kr, and Xe, respectively. Thus, except for Ng=He, all other FNgCC<sup>−</sup> anions were predicted to be stable with respect to this dissociation pathway. The energy difference between the first and second sets of products corresponds to the difference in electron affinity (EA) between F atom and CC molecule. At the CCSD(T)/aug-cc-pVQZ level, the EA of F is 3.6 kcal/mol higher, and thus the dissociation energy of the first channel is 3.6 kcal/mol lower. The calculated difference in EA of the F atom and CC molecule was in good agreement with the experimental value of 2.9 kcal/mol.<sup>61</sup> This indicated that the relative energies calculated by the CCSD(T) method were quite reliable. The DFT methods were problematic in calculating the ground singlet state of CC molecule, resulting very large errors on the dissociation energies of the first channel. All calculations gave very similar results on the energies of the third dissociation pathway which were all highly exoergic. The dissociation energy barriers will be discussed next.

TABLE II. Calculated S-T gap and energies relative to FNgCC<sup>−</sup> (kcal/mol).

Method	S-T gap	F <sup>−</sup> + Ng + CC	F + Ng + CC <sup>−</sup>	Ng + FCC <sup>−</sup>
FHeCC <sup>−</sup>				
B3LYP/aptz	54.7	29.9	10.6	−100.3
MPW1PW91/aptz	61.8	31.8	5.9	−105.9
MP2/apdz	92.6	−10.8	−3.0	−108.8
MP2/aptz	108.5	−6.6	2.1	−110.9
CCSD(T)/aptz	65.9	−1.7	1.0	−106.7
CCSD(T)/apqz	66.7	−1.1	2.5	−106.8
FArCC <sup>−</sup>				
B3LYP/aptz	72.2	45.5	26.3	−84.7
MPW1PW91/aptz	82.3	50.9	25.0	−86.8
MP2/apdz	87.5	10.0	17.9	−87.9
MP2/aptz	100.0	17.5	26.2	−86.8
CCSD(T)/aptz	80.5	17.5	20.2	−87.4
CCSD(T)/apqz	81.3	17.1	20.7	−88.6
FKrCC <sup>−</sup>				
B3LYP/aptz	77.6	60.9	41.7	−69.2
MPW1PW91/aptz	85.7	67.4	41.5	−70.3
MP2/apdz	93.3	29.2	37.1	−68.7
MP2/aptz	103.7	37.6	46.3	−66.7
CCSD(T)/aptz	88.0	36.6	39.3	−68.3
CCSD(T)/apqz	91.1	37.1	40.7	−68.7
FXeCC <sup>−</sup>				
B3LYP/aptz	83.5	82.7	63.5	−47.5
MPW1PW91/aptz	89.7	90.1	64.2	−47.6
MP2/apdz	99.4	55.0	62.8	−43.0
MP2/aptz	107.3	63.5	72.2	−40.8
CCSD(T)/aptz	95.2	61.9	64.6	−43.0
CCSD(T)/apqz	97.7	63.8	67.4	−42.0

## C. Stability

The linear FNgCC<sup>−</sup> ion, as depicted in Fig. 1, can be viewed as an ion–dipole complex of F<sup>−</sup>...NgCC. However, the NgCC molecule is highly unstable, and only the XeCC has been observed by experiments.<sup>62,63</sup> The association energies of Ng + CC were calculated to be less than 1 kcal/mol for Ng=Ar and Kr, and  $\sim 5$  kcal/mol for Ng=Xe at the CCSD(T)/aug-cc-pVTZ level. These are compared to the dissociation energies of 17–64 kcal/mol to F<sup>−</sup> + Ng + CC listed in Table II. Apparently, the polarizing effects of the fluoride ion induced strong binding between Ng and CC. The intrinsic thermal stability of FNgCC<sup>−</sup> anions depends on the difficulty of undergoing unimolecular dissociation through the three channels mentioned above. Except for FHeCC<sup>−</sup>, dissociation through the first two channels was protected by high endoergic energies of reactions, as shown in Table II. For FHeCC<sup>−</sup> we were able to find the transition state (TS) corresponding to the first dissociation channel, and the classical barrier height was predicted to be 5.5 kcal/mol. The structural parameters of the TS were included in the supplementary material.<sup>60</sup> Since the third dissociation channel is highly exoergic, thermal stability of FNgCC<sup>−</sup> requires high energy barriers for the reaction of FNgCC<sup>−</sup> → Ng + FCC<sup>−</sup>. Figure 2 showed schematic plots of two possible TS geometries for the third dissociation channel. In TS1, the fluoride



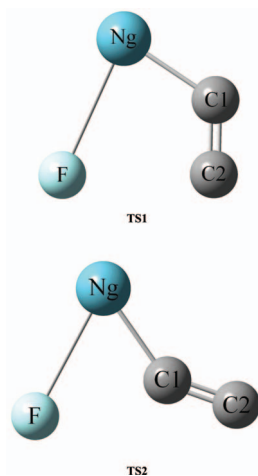


FIG. 2. Schematic plots of TS1 and TS2 structures.

ion approaches the terminal carbon atom (C2), while in TS2 the fluoride approaches the carbon next to the noble gas (C1). Table III listed the calculated structures of TS1 and TS2 and Table IV listed the predicted classical energy barriers. We were able to use MP2/aug-cc-pVTZ and MPW1PW91/aug-cc-pVTZ methods to locate the geometry of both TS. Full list of calculated geometry and energies of the TS are included in the supplementary material.<sup>60</sup> All the calculated TS1 and TS2

TABLE III. Calculated bond lengths (Å) and bond angles (°) of the transition states.

Method	F–Ng	Ng–C1	C1–C2	F–Ng–C1	Ng–C1–C2
<b>TS1</b>					
FHeCC <sup>−</sup>					
MP2/aptz	1.816	1.166	1.311	128.2	105.7
MPW1PW91/aptz	1.764	1.248	1.304	130.3	103.7
CCSD(T)/aptz	1.809	1.235	1.319	129.1	105.7
FArCC <sup>−</sup>					
MP2/aptz	2.553	1.816	1.293	86.0	123.9
MPW1PW91/aptz	2.646	2.017	1.293	101.4	113.3
FKrCC <sup>−</sup>					
MP2/aptz	2.605	1.918	1.294	80.7	122.3
MPW1PW91/aptz	2.644	1.988	1.286	90.9	119.7
FXeCC <sup>−</sup>					
MP2/aptz	2.632	2.058	1.296	75.3	119.4
MPW1PW91/aptz	2.616	2.108	1.281	80.5	122.2
<b>TS2</b>					
FHeCC <sup>−</sup>					
MP2/aptz	1.831	1.150	1.271	97.6	139.0
MPW1PW91/aptz	1.836	1.202	1.261	101.6	129.2
FArCC <sup>−</sup>					
MP2/aptz	2.468	1.840	1.278	70.6	147.9
MPW1PW91/aptz	2.517	1.849	1.257	78.9	139.2
FKrCC <sup>−</sup>					
MP2/aptz	2.514	1.955	1.277	62.8	144.7
MPW1PW91/aptz	2.543	1.974	1.254	68.2	140.0
FXeCC <sup>−</sup>					
MP2/aptz	2.561	2.124	1.277	55.9	142.6
MPW1PW91/aptz	2.583	2.155	1.251	58.1	140.7

TABLE IV. Calculated barrier heights (kcal/mol).

Method	FHeCC <sup>−</sup>			FArCC <sup>−</sup>		FKrCC <sup>−</sup>		FXeCC <sup>−</sup>	
	TS1	TS2	TS3	TS1	TS2	TS1	TS2	TS1	TS2
MP2/aptz	18.0	13.0	10.7	33.6	25.6	42.0	34.3	50.5	44.0
MPW1PW91/aptz	11.4	15.0		28.0	27.9	36.3	35.3	44.7	44.5
CCSD(T)/aptz <sup>a</sup>	10.0 <sup>b</sup>	11.2	5.0	22.1	21.4	31.4	30.3	41.1	41.1
CCSD(T)/apqz <sup>a</sup>	10.3 <sup>b</sup>	11.2	5.7	22.7	21.6	31.8	30.5	41.8	41.7
CASSCF/aptz <sup>c</sup>	10.3	11.6		23.7	24.9	36.1	27.9	43.1	41.0
CASPT2/aptz <sup>c</sup>	11.3	12.6		30.6	19.7	33.5	31.9	46.6	37.2

<sup>a</sup>Single-point energies calculated using MPW1PW91/aptz geometries except for TS1 of FHeCC<sup>−</sup>.

<sup>b</sup>Single-point energies calculated using CCSD(T)/aptz geometries.

<sup>c</sup>Single-point energies calculated using MP2/aptz geometries.

were confirmed to connect to FNgCC<sup>−</sup> and the dissociation products by calculating the reaction paths (the IRC calculation). The results of the IRC calculation were included in the supplementary material.<sup>60</sup> From FNgCC<sup>−</sup> to TS1 and TS2, the F–Ng distances increased by 0.1–0.2 Å for Ng=He, and by 0.4–0.5 Å for Ng=Ar, Kr, and Xe. The Ng–C1 distances increased less significantly (0.1–0.2 Å) from FNgCC<sup>−</sup> to TS for all noble gas atoms, and the C1–C2 distances decreased by 0.03–0.05 Å for TS1 and by only ~0.01 Å for TS2. The F–Ng–C1 angles in TS2 were ~20° smaller than in TS1, which was understandable since the fluoride ion was forming a chemical bond with C2 in TS1 and with C1 in TS2, respectively. The predicted barrier heights increased with the sizes of the noble gas atoms, from ~10 kcal/mol for Ng=He to ~33 kcal/mol for Ng=Xe. At MP2/aug-cc-pVTZ level, the energies of TS1 were significantly (5–8 kcal/mol) higher than those of TS2. However, the energies of the two TS were predicted to be similar by MPW1PW91 and CCSD(T) methods, with TS2 slightly lower than TS1. For Ng=Ar, Kr, and Xe, all the barrier heights for the FNgCC<sup>−</sup> → Ng + FCC<sup>−</sup> dissociation channel were found to be higher than 20 kcal/mol, and thus these FNgCC<sup>−</sup> were predicted to be kinetically stable. One important issue that needs to be addressed here is the reliability of the single-reference methods such as MP2 and CCSD(T) theory in predicting the barrier heights. We have performed the T1 diagnostics<sup>64</sup> calculation on FNgCC<sup>−</sup> and on TS1 and TS2. The calculated T1 values were listed in Table V. The T1 values for FNgCC<sup>−</sup> were below or slightly over the empirical threshold of 0.02. However, almost all the T1 values for TS were higher than 0.03. This suggested that the TS energies were less adequately modeled by the CCSD theory. As a result, we also calculated the barrier heights using the multi-reference CASPT2 method based on the CASSCF wavefunction. As also shown in Table IV, the CASPT2 results

TABLE V. Calculated T1 values at CCSD/aptz//MPW1PW91/aptz level.

Ng	FNgCC <sup>−</sup>	TS1	TS2
He	0.028	0.041	0.035
Ar	0.023	0.054	0.035
Kr	0.018	0.036	0.032
Xe	0.015	0.029	0.031

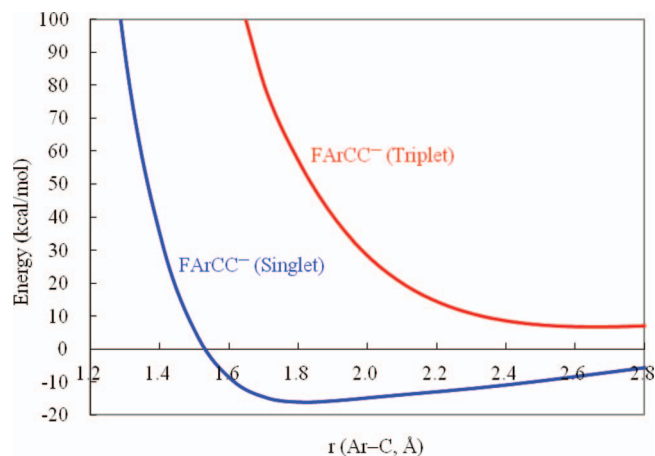


FIG. 3. Potential energy curve of  $\text{FArCC}^-$ . The energies were calculated at the CCSD(T)/aug-cc-pVTZ level. The  $\text{FArCC}^-$  energies are relative to  $\text{F}^- + \text{Ar} + \text{CC}(\text{S})$  with  $\text{F}-\text{Ar}$  distance fixed at 2.211 Å and  $\text{C}-\text{C}$  distance fixed at 1.292 Å.

were, within a few kcal/mol, consistent with the trends obtained by the CCSD(T) calculation. Thus, from the predicted energetics listed in Tables II and IV, the  $\text{FNgCC}^-$  anions ( $\text{Ng}=\text{Ar}$ ,  $\text{Kr}$ , and  $\text{Xe}$ ) seemed to be kinetically stable species on the ground-state singlet potential energy surface (PES) at cryogenic conditions. Another possible dissociation channel for  $\text{FNgCC}^-$  is via intersystem crossing to the repulsive triplet state, as discussed in previous study on the  $\text{FNgO}^-$  anion.<sup>24</sup> However, unlike the oxygen atom which has a triplet ground state, the  $\text{CC}$  molecule has a singlet ground state which is  $\sim 2$  kcal/mol lower than the lowest triplet state.<sup>65</sup> Thus, the  $\text{FNgCC}^-$  anion is stable against the dissociation channel to  $\text{F}^- + \text{Ng} + \text{CC}(\text{T})$  as shown in Fig. 3 where the singlet and triplet curves of  $\text{FArCC}^-$  never crossed along the  $\text{Ar}-\text{C1}$  coordinate. The curves for other noble gases (included in the supplementary material<sup>60</sup>) were found to be qualitatively similar.

#### D. Vibrational frequencies

The calculated harmonic vibrational frequencies and IR intensities of  $\text{FNgCC}^-$  were listed in Table VI. Since the  $\text{FHeCC}^-$  anion is nonlinear, it has one fewer mode (the degenerate bending) than other anions. In most cases, the calculated frequencies at CCSD(T)/aug-cc-pVTZ levels were a few tens of wavenumber smaller than the corresponding MP2/aug-cc-pVTZ values, except for the  $\text{He}-\text{C}-\text{C}$  and one of the  $\text{F}-\text{He}-\text{C}$  bending modes where the CCSD(T) result was  $\sim 30$   $\text{cm}^{-1}$  higher. The following discussion will be based on the frequencies calculated by the CCSD(T) theory and intensities calculated by the MP2 theory. Interestingly, the frequencies of all the  $\text{F}-\text{Ng}$  stretching modes were similar (270–350  $\text{cm}^{-1}$ ) despite the very large difference in the mass of the noble gases. This could be understood by the balancing effects of the atomic masses and the bonding strengths down the noble gas family. This mode, which has relatively strong IR intensity, can be used as the fingerprint for future experimental identification of the  $\text{FNgCC}^-$  anion. Except for  $\text{Ng}=\text{He}$ , all other  $\text{Ng}-\text{C}$  stretching frequencies were also very simi-

TABLE VI. Calculated harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) of  $\text{FNgCC}^-$ .

		MP2/aptz	CCSD(T)/aptz
$\text{FHeCC}^-$			
$\nu_1$	He–C–C	129 (17) <sup>a</sup>	154
$\nu_2$	He–F	378 (131)	353
$\nu_3$	F–He–C (1)	427 (101)	395
$\nu_4$	F–He–C (2)	465 (92)	493
$\nu_5$	He–C	1352 (272)	1288
$\nu_6$	C–C	2059 (313)	1890
$\text{FArCC}^-$			
$\nu_1$	Ar–C–C	80 (25)	9
$\nu_2$	F–Ar–C	225 (31)	188
$\nu_3$	Ar–F	306 (206)	266
$\nu_4$	Ar–C	471 (77)	404
$\nu_5$	C–C	1853 (63)	1870
$\text{FKrCC}^-$			
$\nu_1$	Kr–C–C	87 (31)	68
$\nu_2$	F–Kr–C	231 (21)	205
$\nu_3$	Kr–F	333 (248)	315
$\nu_4$	Kr–C	439 (82)	409
$\nu_5$	C–C	1864 (88)	1896
$\text{FXeCC}^-$			
$\nu_1$	Xe–C–C	91 (32)	82
$\nu_2$	F–Xe–C	230 (16)	216
$\nu_3$	Xe–F	350 (256)	339
$\nu_4$	Xe–C	437 (84)	421
$\nu_5$	C–C	1869 (109)	1906

<sup>a</sup>Values in parentheses are calculated IR intensities (in  $\text{Km/mol}$ ).

lar (440–470  $\text{cm}^{-1}$ ), while in  $\text{FHeCC}^-$  the  $\text{He}-\text{C}$  stretching mode was predicted to be as large as  $\sim 1300$   $\text{cm}^{-1}$ . All the  $\text{C}-\text{C}$  stretching frequencies were also very similar, in the range of 1870–1906  $\text{cm}^{-1}$ . In comparison the calculated values for  $\text{HCCH}$  and  $\text{C}_2$  molecule were 2004 and 1854  $\text{cm}^{-1}$ , respectively.

#### E. Bonding and charge distribution

Figure 4 showed the iso-electron density plots of  $\text{FNgCC}^-$  calculated by the MP2/aug-cc-pVDZ method. The concentric electron density distribution around F atom clearly

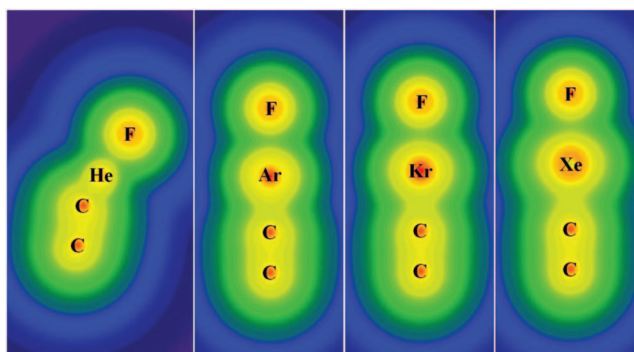


FIG. 4. Contour plots of the calculated electron density (MP2/aug-cc-pVDZ) of  $\text{FHeCC}^-$ ,  $\text{FArCC}^-$ ,  $\text{FKrCC}^-$ , and  $\text{FXeCC}^-$ .

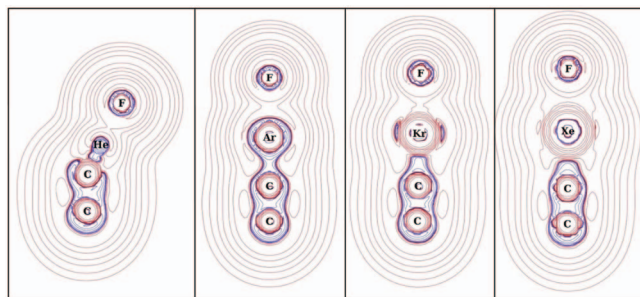


FIG. 5. Contour plots of the calculated Laplacian of electron density (MP2/aug-cc-pVDZ) for  $\text{FNgCC}^-$  in which the blue contour lines are in regions of electron concentration and the red contour lines are in regions of electron depletion.

suggested that it primarily existed as a fluoride ion in  $\text{FNgCC}^-$ . This picture was consistent with the ion-induced dipole interaction mentioned earlier in this section. Covalent-type electron sharing was also obvious between Ng and CC. Plots using the density obtained from MPW1PW91/aug-cc-pVTZ calculation gave very similar results, which were included in the supplementary material.<sup>60</sup> However (as was also pointed out by one of the reviewers), the electron density distribution mentioned above was not inconsistent with strongly polarized electrostatic Ng–C bonds. To further analyze the bonding types, the Laplacian of the electron density was calculated at MP2/aug-cc-pVDZ level and was shown in Fig. 5. Significant charge concentration (negative values of the Laplacian) was observed between the noble gas atom and the CC unit for Ng=Ar, Kr, and Xe. The calculated values of Laplacian at the Ng–C bond critical points were 0.11,  $-0.14$ ,  $-0.13$ , and  $-0.08$  (atomic units) for Ng=He, Ar, Kr, and Xe, respectively. This result thus also suggested important covalent characters<sup>25,66,67</sup> of the Ng–C bonding in  $\text{FNgCC}^-$  anions except for Ng=He. Table VII listed the calculated atomic charges by the Mullikan, ChelpG, and NBO methods. All methods predicted highly negative partial charges on F atom, as expected, and substantial positive partial charges on Ng,

TABLE VII. Calculated atomic charges.<sup>a</sup>

	F	Ng	C1	C2
		Mullikan		
FHeCC <sup>-</sup>	-0.858	0.190	0.185	-0.518
FArCC <sup>-</sup>	-0.856	0.486	-0.230	-0.399
FKrCC <sup>-</sup>	-0.812	0.712	-0.292	-0.608
FXeCC <sup>-</sup>	-0.749	1.009	-0.314	-0.946
		ChelpG		
FHeCC <sup>-</sup>	-0.914	0.597	-0.122	-0.561
FArCC <sup>-</sup>	-0.815	0.460	-0.010	-0.635
FKrCC <sup>-</sup>	-0.740	0.460	-0.011	-0.708
FXeCC <sup>-</sup>	-0.646	0.398	-0.005	-0.747
		NBO		
FHeCC <sup>-</sup>	-0.903	0.444	-0.239	-0.301
FArCC <sup>-</sup>	-0.885	0.623	-0.422	-0.317
FKrCC <sup>-</sup>	-0.845	0.761	-0.586	-0.331
FXeCC <sup>-</sup>	-0.824	0.912	-0.749	-0.339

<sup>a</sup>Atomic charges calculated at MP2/aug-cc-pVDZ level, in atomic unit, e.

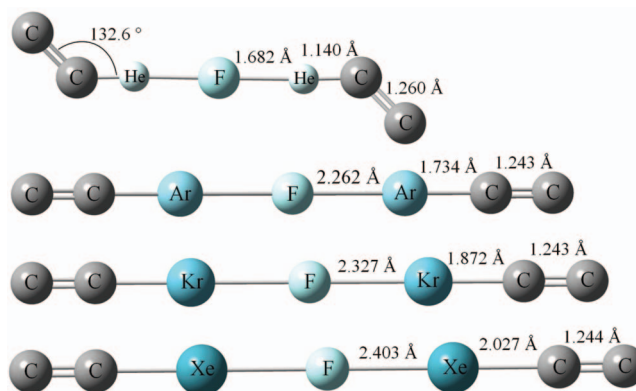


FIG. 6. The calculated structure of  $\text{F}^-\dots(\text{NgCC})_2$  at MPW1PW91/aug-cc-pVTZ level. The point group symmetry is  $\text{C}_{2h}$  for Ng=He, and is  $\text{D}_{\infty h}$  for Ng=Ar, Kr, and Xe.

suggesting important electron density transfer from the noble gas atom to the CC unit. The predicted atomic charges on the two carbon atoms, however, were quite different by different charge models. As seen in Table VII, the ChelpG method, which was based on the calculated electrostatic potential, predicted an almost neutral C1 atom and a highly negatively charged C2 atom. The NBO method, which was based on natural orbital population, gave more balanced charge distribution on C1 and C2. The commonly used Mullikan model gave results which are, in most cases, intermediate between the two models mentioned above on the two carbon atoms. Based on Fig. 4, it was difficult to perceive very significant differences in electron density distribution between the two carbon atoms.

## F. $\text{F}^-(\text{NgCC})_2$ anion

In our previous study of  $\text{F}^-(\text{NgO})_n$ ,<sup>27</sup> we have shown that up to six NgO units can be attached to a single fluoride ion with significant increases in association energies as  $n$  increased. Here, we also explored the possibility of attaching the fluoride ion with two NgCC units. Figure 6 showed the calculated structures of  $\text{F}^-(\text{NgCC})_2$  anions at MPW1PW91/aug-cc-pVTZ level. The structures of  $\text{F}^-(\text{ArCC})_2$ ,  $\text{F}^-(\text{KrCC})_2$ , and  $\text{F}^-(\text{XeCC})_2$  were all found to have the expected  $\text{D}_{\infty h}$  symmetry, while the  $\text{F}^-(\text{HeCC})_2$  was predicted to have the  $\text{C}_{2h}$  symmetry. The F–Ng distances increased by 0.1–0.2 Å and the Ng–C distances decrease slightly by 0.02–0.03 Å compared with the distances in  $\text{FNgCC}^-$ . The association energies relative to  $\text{F}^- + 2 \text{Ng} + 2 \text{CC}$  were predicted to be 18, 52, and 95 kcal/mol, for Ng=Ar, Kr, and Xe, respectively, at the CCSD(T)/aug-cc-pVTZ//MPW1PW91/aug-cc-pVTZ level. This translated to 8%, 43%, and 54% increase in the association energies than in  $\text{FNgCC}^-$ . For Ng=He, the additional HeCC unit was found to actually decrease the association energy, which was probably due to the Pauli repulsion. Attaching more than two NgCC units to the fluoride ions with important increase in association energies for Ng=Kr and Xe certainly seemed possible and will be explored in a future study.



#### IV. SUMMARY

We have made theoretical prediction on the structures and stability of the  $\text{FNgCC}^-$  ( $\text{Ng}=\text{He, Ar, Kr, and Xe}$ ) anions with a variety of electronic structure theory and atomic basis sets. The calculated results suggested that the tightly bonded structures of  $\text{FNgCC}^-$  can be formed by ion-induced dipole interaction with association energies of 17–64 kcal/mol for  $\text{Ng}=\text{Ar, Kr, and Xe}$ . These anions were also predicted to be stable with respect to the three possible unimolecular dissociation channels and to the intersystem crossing to the repulsive triplet states at low temperature. Our calculation also suggested that more than one  $\text{NgCC}$  unit could be attached to the fluoride ions with significant increase in association energies for  $\text{Ng}=\text{Kr and Xe}$ . The calculated vibrational frequencies, in particular, of the  $\text{F}-\text{Ng}$  and  $\text{Ng}-\text{C}$  stretching modes, can be used in future experimental identification of the  $\text{FNgCC}^-$  anions.

#### ACKNOWLEDGMENTS

This work is supported by the National Science Council of Taiwan, Grant No. NSC-100-2113-M-194-007. We are grateful to the National Center for High-Performance Computing (NCHC) for providing part of computing resources.

- <sup>1</sup>N. Bartlett, *Proc. Chem. Soc.* **1962**, 218.
- <sup>2</sup>M. Pettersson, J. Lundell, and M. Räsänen, *Eur. J. Inorg. Chem.* **1999**, 729.
- <sup>3</sup>L. Khriachtchev, M. Räsänen, and R. B. Gerber, *Acc. Chem. Res.* **42**, 183 (2009).
- <sup>4</sup>L. Khriachtchev, A. Domanskaya, J. Lundell, A. Akimov, M. Räsänen, and E. Misochko, *J. Phys. Chem. A* **114**, 4181 (2010).
- <sup>5</sup>L. Khriachtchev, S. Tapio, A. V. Domanskaya, M. Räsänen, and K. Isokoski, *J. Chem. Phys.* **134**, 124307 (2011).
- <sup>6</sup>W. Grochala, L. Khriachtchev, and M. Räsänen, in *Physics and Chemistry at Low Temperatures*, edited by L. Khriachtchev (CRC, 2011), Chap. 13, pp. 419.
- <sup>7</sup>T. Arppe, L. Khriachtchev, A. Lignell, A. V. Domanskaya, and M. Räsänen, *Inorg. Chem.* **51**, 4398 (2012).
- <sup>8</sup>C. J. Evans, A. Lesarri, and M. C. L. Gerry, *J. Am. Chem. Soc.* **122**, 6100 (2000).
- <sup>9</sup>C. J. Evans and M. C. L. Gerry, *J. Chem. Phys.* **112**, 1321 (2000).
- <sup>10</sup>C. J. Evans and M. C. L. Gerry, *J. Chem. Phys.* **112**, 9363 (2000).
- <sup>11</sup>C. J. Evans, D. S. Rubinoff, and M. C. L. Gerry, *Phys. Chem. Chem. Phys.* **2**, 3943 (2000).
- <sup>12</sup>L. M. Reynard, C. J. Evans, and M. C. L. Gerry, *J. Mol. Spectrosc.* **206**, 33 (2001).
- <sup>13</sup>N. R. Walker, L. M. Reynard, and M. C. L. Gerry, *J. Mol. Struct.* **612**, 109 (2002).
- <sup>14</sup>J. M. Thomas, N. R. Walker, S. A. Cooke, and M. C. L. Gerry, *J. Am. Chem. Soc.* **126**, 1235 (2004).
- <sup>15</sup>S. A. Cooke and M. C. L. Gerry, *J. Am. Chem. Soc.* **126**, 17000 (2004).
- <sup>16</sup>J. M. Michaud, S. A. Cooke, and M. C. L. Gerry, *Inorg. Chem.* **43**, 3871 (2004).
- <sup>17</sup>S. A. Cooke and M. C. L. Gerry, *Phys. Chem. Chem. Phys.* **6**, 3248 (2004).
- <sup>18</sup>J. M. Michaud and M. C. L. Gerry, *J. Am. Chem. Soc.* **128**, 7613 (2006).
- <sup>19</sup>S. Seidel and K. Seppelt, *Science* **290**, 117 (2000).
- <sup>20</sup>W.-P. Hu and C.-H. Huang, *J. Am. Chem. Soc.* **123**, 2340 (2001).
- <sup>21</sup>J. Li, B. E. Bursten, B. Liang, and L. Andrews, *Science* **295**, 2242 (2002).
- <sup>22</sup>L. Andrews, B. Liang, J. Li, and B. E. Bursten, *J. Am. Chem. Soc.* **125**, 3126 (2003).
- <sup>23</sup>B. Liang, L. Andrews, J. Li, and B. E. Bursten, *Inorg. Chem.* **43**, 882 (2004).
- <sup>24</sup>T.-H. Li, C.-H. Mou, H.-R. Chen, and W.-P. Hu, *J. Am. Chem. Soc.* **127**, 9241 (2005).
- <sup>25</sup>T.-Y. Lin, J.-B. Hsu, and W.-P. Hu, *Chem. Phys. Lett.* **402**, 514 (2005).
- <sup>26</sup>T.-H. Li, Y.-L. Liu, R.-J. Lin, T.-Y. Yeh, and W.-P. Hu, *Chem. Phys. Lett.* **434**, 38 (2007).
- <sup>27</sup>Y.-L. Liu, Y.-H. Chang, T.-H. Li, H.-R. Chen, and W.-P. Hu, *Chem. Phys. Lett.* **439**, 14 (2007).
- <sup>28</sup>Y.-L. Sun, J.-T. Hong, and W.-P. Hu, *J. Phys. Chem. A* **114**, 9359 (2010).
- <sup>29</sup>T.-Y. Lai, C.-Y. Yang, H.-J. Lin, C.-Y. Yang, and W.-P. Hu, *J. Chem. Phys.* **134**, 244110 (2011).
- <sup>30</sup>P. Antonietti, S. Borocci, N. Bronzolino, P. Cecchi, and F. Grandinetti, *J. Phys. Chem. A* **111**, 10144 (2007).
- <sup>31</sup>S. Borocci, N. Bronzolino, M. Giordani, and F. Grandinetti, *J. Phys. Chem. A* **114**, 7382 (2010).
- <sup>32</sup>A. Cohen, J. Lundell, and R. B. Gerber, *J. Chem. Phys.* **119**, 6415 (2003).
- <sup>33</sup>L. A. Mück, A. Y. Timoshkin, M. von Hopffgarten, and G. Frenking, *J. Am. Chem. Soc.* **131**, 3942 (2009).
- <sup>34</sup>L. Belpassi, I. Infante, F. Tarantelli, and L. Visscher, *J. Am. Chem. Soc.* **130**, 1048 (2008).
- <sup>35</sup>C.-H. Mou and H. A. Witek, *J. Chem. Phys.* **129**, 244310 (2008).
- <sup>36</sup>W. L. Zou, Y. Liu, and J. E. Boggs, *Dalton Trans.* **39**, 2023 (2010).
- <sup>37</sup>F. Grandinetti, *Eur. J. Mass Spectrom.* **17**, 423 (2011).
- <sup>38</sup>M. Pettersson, J. Lundell, L. Khriachtchev, and M. Räsänen, *J. Chem. Phys.* **109**, 618 (1998).
- <sup>39</sup>L. Khriachtchev, H. Tanskanen, J. Lundell, M. Pettersson, H. Kiljunen, and M. Räsänen, *J. Am. Chem. Soc.* **125**, 4696 (2003).
- <sup>40</sup>L. Khriachtchev, H. Tanskanen, A. Cohen, R. B. Gerber, J. Lundell, M. Pettersson, H. Kiljunen, and M. Räsänen, *J. Am. Chem. Soc.* **125**, 6876 (2003).
- <sup>41</sup>C. Møller and M. S. Plesset, *Phys. Rev.* **46**, 618 (1934).
- <sup>42</sup>J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).
- <sup>43</sup>A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- <sup>44</sup>C. T. Lee, W. T. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- <sup>45</sup>P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.* **98**, 11623 (1994).
- <sup>46</sup>C. Adamo and V. Barone, *J. Chem. Phys.* **108**, 664 (1998).
- <sup>47</sup>T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- <sup>48</sup>R. A. Kendall and T. H. Dunning, Jr., *J. Chem. Phys.* **96**, 6796 (1992).
- <sup>49</sup>D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **98**, 1358 (1993).
- <sup>50</sup>A. K. Wilson, D. E. Woon, K. A. Peterson, and T. H. Dunning, Jr., *J. Chem. Phys.* **110**, 7667 (1999).
- <sup>51</sup>T. H. Dunning, Jr., K. A. Peterson, and A. K. Wilson, *J. Chem. Phys.* **114**, 9244 (2001).
- <sup>52</sup>K. A. Peterson, D. Figgen, E. Goll, H. Stoll, and M. Dolg, *J. Chem. Phys.* **119**, 11113 (2003).
- <sup>53</sup>B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, *Chem. Phys.* **48**, 157 (1980).
- <sup>54</sup>H.-J. Werner, *Mol. Phys.* **89**, 645 (1996).
- <sup>55</sup>P. Celani and H.-J. Werner, *J. Chem. Phys.* **112**, 5546 (2000).
- <sup>56</sup>C. M. Breneman and K. B. Wiberg, *J. Comput. Chem.* **11**, 361 (1990).
- <sup>57</sup>J. E. Carpenter and F. Weinhold, *J. Mol. Struct.: THEOCHEM* **169**, 41 (1988).
- <sup>58</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision E.01, Gaussian, Inc., Wallingford, CT, 2004.
- <sup>59</sup>H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2009.1, a package of *ab initio* programs, 2009.
- <sup>60</sup>See supplementary material at <http://dx.doi.org/10.1063/1.4766326> for tables of optimized geometry and relative energies of the  $\text{FNgCC}^-$  and  $\text{FNgO}^-$  ( $\text{Ng}=\text{He, Ar, Kr, Xe}$ ) systems at various theoretical levels, results of IRC calculation, plots of electron density, and figures of potential energy curves.
- <sup>61</sup>See <http://webbook.nist.gov/chemistry/> for values of electron affinity.
- <sup>62</sup>G. Maier and C. Lutz, *Eur. J. Org. Chem.* **1998**, 769.
- <sup>63</sup>M. Frankowski, A. M. Smith-Gicklhorn, and V. E. Bondybey, *Can. J. Chem.* **82**, 837 (2004).
- <sup>64</sup>T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem.* **36**(S23), 199 (1989).
- <sup>65</sup>K. A. Peterson, *J. Chem. Phys.* **102**, 262 (1995).
- <sup>66</sup>W. Koch, G. Frenking, J. Gauss, D. Cremer, and J. R. Collins, *J. Am. Chem. Soc.* **109**, 5917 (1987).
- <sup>67</sup>M. W. Wong, *J. Am. Chem. Soc.* **122**, 6289 (2000).