Cyclic Perfluorocarbon Radicals and Anions Having High Global Warming Potentials (GWPs): Structures, Electron Affinities, and Vibrational Frequencies

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Cyclic Perfluorocarbon Radicals and Anions Having High Global Warming Potentials (GWPs): Structures, Electron Affinities, and Vibrational Frequencies

Partha Pratim Bera, Ľuboš Horný, and Henry F. Schaefer III*

Contribution from the Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602

Received September 9, 2003; Revised Manuscript Received March 1, 2004; E-mail: hfs@uga.edu

Abstract: Adiabatic electron affinities, optimized molecular geometries, and IR-active vibrational frequencies have been predicted for small cyclic hydrocarbon radicals C_nH_{2n-1} ($n = 3-6$) and their perfluoro counterparts C_nF_{2n-1} ($n = 3-6$). Total energies and optimized geometries of the radicals and corresponding anions have been obtained using carefully calibrated (*Chem. Rev.* **2002**, *102*, 231) density functional methods, namely, the B3LYP, BLYP, and BP86 functionals in conjunction with the DZP++ basis set. The predicted electron affinities show that only the cyclopropyl radical tends to bind electrons among the hydrocarbon radicals studied. The trend for the perfluorocarbon (PFC) radicals is quite different. The electron affinities increase with expanding ring size until $n = 5$ and then slightly decrease at $n = 6$. Predicted electron affinities of the hydrocarbon radicals using the B3LYP hybrid functional are 0.24 eV ($C_3H_5/C_3H_5^-$), -0.19 eV ($C_4H_7/C_4H_7^-$), -0.15 eV ($C_5H_9/C_5H_9^-$), and -0.11 eV ($C_6H_{11}/C_6H_{11}^-$). Analogous electron affinities of the perflurocarbon radicals are 2.81 eV ($C_3F_5/C_3F_5^-$), 3.18 eV ($C_4F_7/C_4F_7^-$), 3.34 eV ($C_5F_9/C_5F_9^-$), and 3.21 eV ($C_6F_{11}/C_6F_{11}^-$).

Introduction

Cyclic hydrocarbons and perfluorocarbons (PFC) have drawn attention due to their effects on the environment, very high atmospheric stability, and lack of proper systematic study. Smaller (three−six C-atom rings) cyclic hydrocarbons and especially perfluorocarbons are exceptionally stable in the atmosphere (>3000 years).[1,2] This exceptionally high stability has earned them (cyclic perfluorocarbons) the dubious name "immortal molecules". Along with their very high atmospheric stability these PFCs are very potent greenhouse gases. The PFCs global warming potentials (GWPs) are 10^3-10^4 times as high as that of carbon dioxide. Although the present amount of PFCs in the atmosphere is not high enough to cause any immediate threat to the environment, concern over these molecules is serious because, unlike other PFCs (CF_4 and C_2F_6, controlled substances considered by the Kyoto Protocol,[3] United Nations, 1997), they are not controlled substances. However, cyclic PFCs due to their nontoxic nature, oxygen and carbon dioxide dissolving power, and high stability make them usable as blood plasma substitutes[4] (cyclic seven- and eight-membered rings). Also they are extensively used in rapidly developing high-density plasma (HDP) processes and atmospheric tracer studies.[5−7]

All these factors and the lack of sufficient experimental data for the hydrocarbon and pefluorocarbon radicals and anions make these types of molecules important and interesting for further study.

The cyclopropyl radical has been studied over the years both theoretically[8−16] and experimentally. Fessenden and Schuler[11] deduced the out-of-plane angle of the α-hydrogen to be 41° from ESR spectra. Ellinger et al.[12] in the 1970s carried out ab initio studies of the cyclopropyl radical and reported the hyperfine coupling properties. Dupuis and Pacansky[13] in early 1980s had predicted the eqillibrium structure and the vibrational properties of the cyclopropyl radical at the ab initio Hartree−Fock level, using the standard Pople "split valence" 4-31G basis. They estimated the total energy to be −116.2394 a.u. and the out of plane angle to be 39.3° at the equilibrium geometry which has C_s symmetry. However, no comprehensive study has been

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reported on the structure and energetics of the larger hydrocarbon radicals and anions. Schleyer, Spitznagel, and Chandrashekhar[17] in 1986 predicted the existence of cyclopropyl anion in the gas phase. They even predicted that the cyclopropyl anion should be more stable than other secondary carbanions. For example, Schleyer considered the cyclobutyl anion and concluded that C_4H_9 should have a negative electron affinitiy. The electron affinities estimated by them, at the MP2/6-31+G* level of theory, were 5.1 kcal/mol (0.22 eV) for C_3H_5 and -11.4 kcal/mol (-0.49 eV) for C_4H_7. Subsequently, Squires et al.[18] in the same year demonstrated the existence of the cyclopropyl anion produced by collision-induced decarboxylation in the gas phase. Seburg and Squires[19] in 1997 determined the electron affinity of C_3H_5 to be 0.397 ± 0.069 eV using gas-phase kinetic methods. Recent studies[20,21] by our group have shown that DFT methods generally reproduce the experimental electron affinities of the radicals and neutral molecules well, on average within 0.15 eV of definitive experimental values. Despite the controversies involving the HOMO energies of the anions and electron self-interaction, DFT functionals have been proved to predict the structures and electron affinities well.[22–35] Although the cyclopropyl radical and anion have been investigated over the years, very little research has been done on the corresponding cyclobutyl, cyclopentyl, and cyclohexyl counterparts, suggested by Schleyer, Spitznagel, and Chandrashekhar[17] to have negative (unfavorable) electron affinities. Although a lot of work has been done on the straight chain perfluorocarbons, the cyclic perfluorocarbons were neglected for a long time. In this work are presented optimized equilibrium geometries, total energies, and vibrational frequencies of the cyclic hydrocarbon as well as cyclic perfluorocarbon radicals and anions.

II. Theoretical Methods

Density functional theory (DFT) studies were performed on the cyclic hydrocarbon C_nH_{2n-1} ($n = 3-6$) radicals and corresponding anions, as well as the cyclic perfluorocarbon C_nF_{2n-1}($n = 3-6$) radicals and the corresponding anions. We report optimized equilibrium molecular geometries, harmonic vibrational frequencies, and electron affinities of the radicals using three well-known DFT functionals,[19] B3LYP, BLYP, and BP86. The radicals were initially simulated (theoretically)

by homolytically cleaving (pedagogically) a C–H bond for hydrocarbons or C–F bond in case of perfluorocarbons. The anions were examined by adding an electron to the radicals. All radical and anion molecular structures were fully optimized. Adiabatic electron affinities have been evaluated by subtracting the total energy of the anion from the total energy of the neutral radical. The optimized geometries of the molecules and anions and their harmonic vibrational frequencies are also reported.

Throughout this study, DZP++,[36–39] a standard[19] basis set of contracted double-ζ Gaussian functions, was used. This basis set is constructed by augmenting the Huzinaga–Dunning set of contracted double-ζ Gaussian functions with one set of p polarization functions (H) and one set of five d polarization functions (C, F). The basis set is completed by adding one even-tempered s diffuse function to each H atom and a set of even-tempered s and p diffuse functions to all the heavier atoms. The even-tempered orbital exponents were determined according to the recommendations made by Lee and Schaefer.[39] The s-type or p-type diffuse function exponent for a given atom is given by

$$\alpha_{\text{diffuse}} = \frac{1}{2}\left(\frac{\alpha_1}{\alpha_2} + \frac{\alpha_2}{\alpha_3}\right)\alpha_1$$

where α_1, α_2, and α_3 are, respectively, the first, second, and third smallest Gaussion orbital exponent of the s-type or p-type primitive functions of that atom.

Three different exchange-correlation density functionals were used in this study, namely, B3LYP, BLYP, and BP86. B3LYP is a hybrid Hartree–Fock/DFT functional which employs Becke's three-parameter HF/DFT hybrid exchange functional[40] (B3) coupled with the dynamical correlation functional of Lee, Yang, and Parr[41] (LYP). BLYP, a pure DFT functional, employs Becke's 1988[42] exchange functional (B) in conjunction with correlation functional of Lee, Yang, and Parr (LYP). BP86 uses Perdew's[43] correlation fuctional with Becke's exchange functional.

All the quantum chemical computations were conducted using the GAUSSIAN 94[44] set of DFT programs. Both radical and the anion geometries were fully optimized by the analytic gradient method. The harmonic vibrational frequencies were obtained analytically from the mass-weighted Hessian matrix.

III. Results and Discussion

A. Hydrocarbons. The optimized molecular geometries of the ground-state cyclic hydrocarbon radicals and the corresponding anions are given in Figures 1–8. The hydrocarbon radicals were initially obtained by breaking one of the C–H bonds homolytically. The optimized C_s symmetry ground-state structures of the C_3H_5 (Figure 1) and C_4H_7 (Figure 3) radicals have $^2A'$ electronic ground states. The anions were obtained conceptually by adding one electron in the singly occupied radical HOMO orbitals. The ground electronic state of the anions

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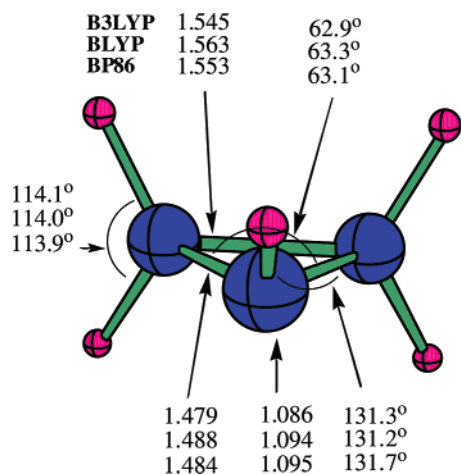
Figure 1. Optimized geometry of the C_3H_5 radical (C_s) in the $^2A'$ ground state. Bond lengths are in Å.
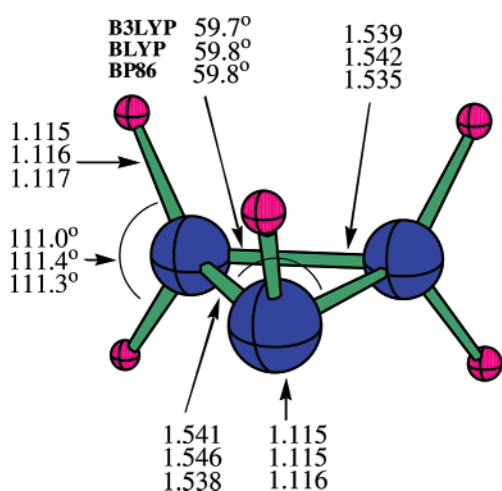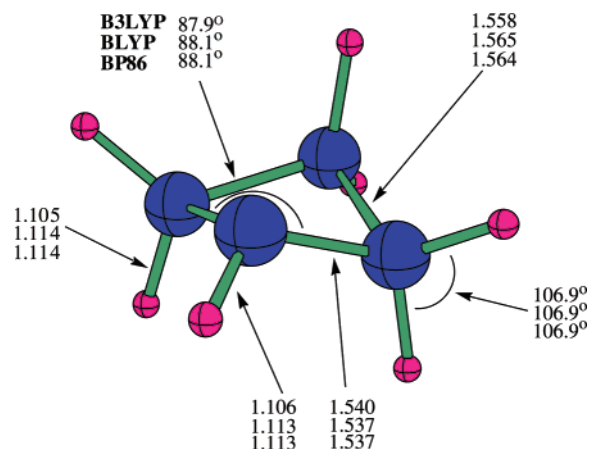

Figure 2. Optimized molecular geometry of the $C_3H_5^-$ anion in its $^1A'$ ground state. Bond lengths are in Å.
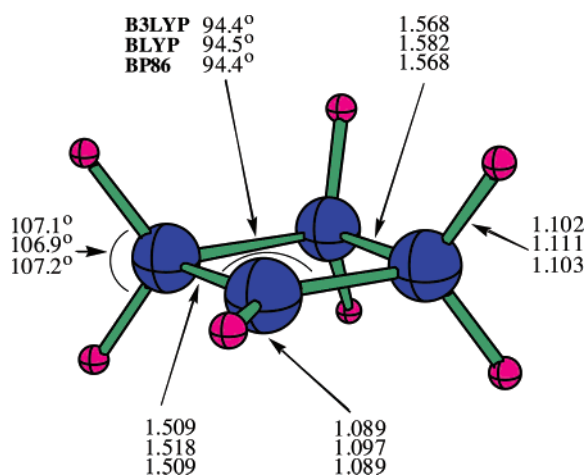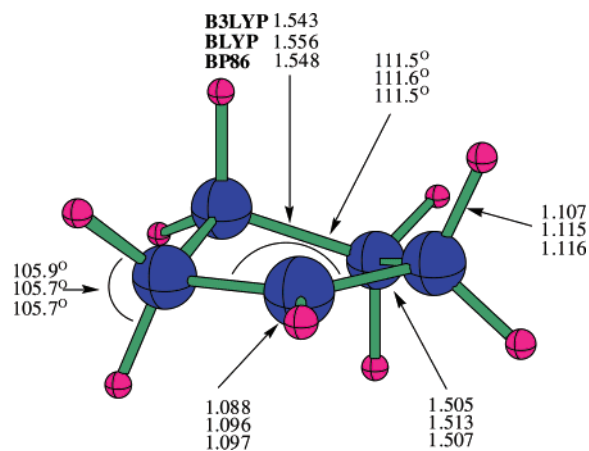

Figure 3. Optimized geometry of the C_4H_7 radical (C_s) in its $^2A'$ ground state. Bond lengths are in Å.

Figure 4. Optimized geometry of the $C_4H_7^-$ anion (C_s) in its $^1A'$ ground state. Bond angles are expressed in Å.

Figure 5. Optimized geometry of the C_5H_9 radical (C_2) in its ^2A ground state. Bond lengths are in Å.
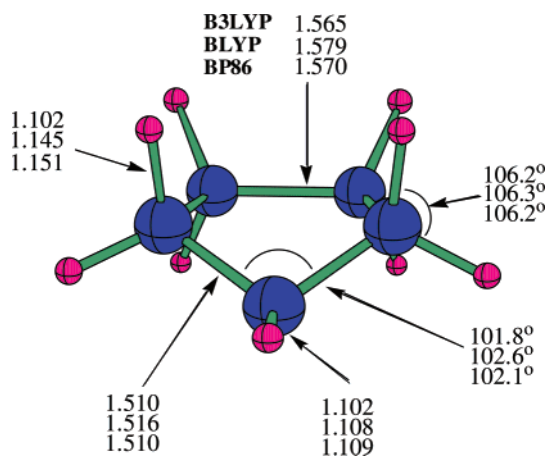
Figure 6. Optimized geometry of the $C_5H_9^-$ anion (C_s) in its $^1A'$ ground state. Bond lengths are in Å.

$C_3H_5^-$, $C_4H_7^-$, and $C_6H_{11}^-$ thus are of $^1A'$ symmetry, as expected. Interestingly, the C_5H_9 (Figure 5) radical is puckered and is most stable in C_2 symmetry whereas the corresponding anion $C_5H_9^-$ (Figure 6) has C_s symmetry in the ground state. The C_5H_9 radical in C_s geometry is found to represent a transition state with a single but significant (144i cm^{-1}) imaginary vibrational frequency.

The adiabatic electron affinity (AEA) is obtained by subtracting the energy of the optimized anion in the $^1A'$ state from the energy of the optimized radical in the $^2A'$ state. The total energies and adiabatic electron affinities (AEA) of the radicals and anions at their respective optimized ground-state geometries are listed in Table 1. Addition of one electron to the radical lowers the total energy of the anion $C_3H_5^-$ compared to the C_3H_5 radical. The positive (favorable) adiabatic electron affinity indicates that the C_3H_5 radical successfully binds an electron.

B3LYP 1.102
BLYP 1.120
BP86 1.111

1.501
1.508
1.503

106.9°
107.1°
107.0°

1.545
1.560
1.551

118.9° 1.090
119.0° 1.097
118.9° 1.099
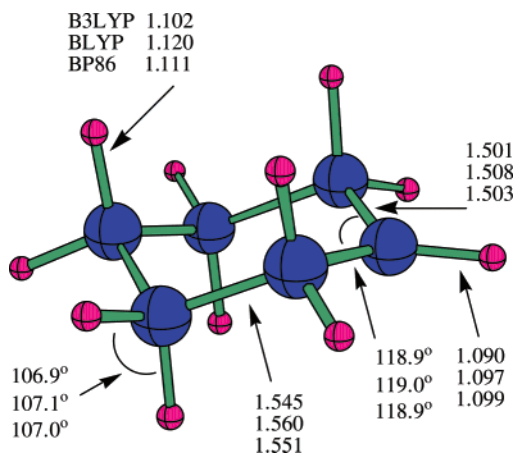
Figure 7. Optimized geometry of the C_6H_{11} radical (C_s) in its $^2A'$ ground state. Bond lengths are in Å.

B3LYP 1.104
BLYP 1.111
BP86 1.113

111.1°
112.1°
111.6°

108.1°
108.2°
108.3°

1.546
1.559
1.551

1.101
1.107
1.108

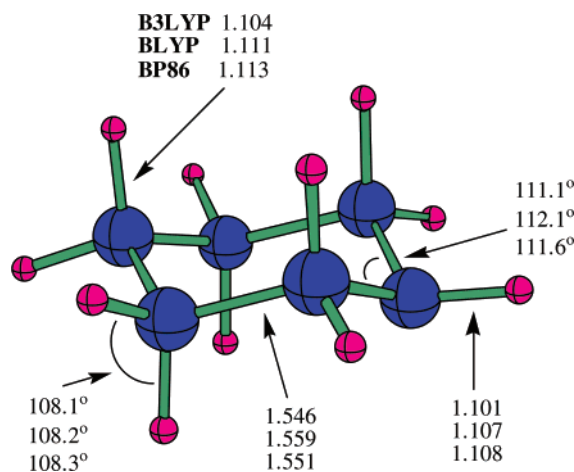**Figure 8.** Optimized geometry of the $C_6H_{11}^-$ anion (C_s) in its $^1A'$ ground state. Bond lengths are in Å.

Table 1. Ground-State Total Energies (Hartrees) and Adiabatic Electron Affinities (eV) of Hydrocarbon Radicals (C_nH_{2n-1}) and Anions ($C_nH_{2n-1}^-$), $n = 3–6$, Using the DFT Functionals B3LYP, BLYP, and BP86

| molecule/method	B3LYP	BLYP	BP86	expt
C_3H_5	−117.23306	−117.15972	−117.22738	
$C_3H_5^-$	−117.24199	−117.16822	−117.24127	
AEA ($C_3H_5/C_3H_5^-$)	0.24	0.23	0.38	0.397 ± 0.069[a]
C_4H_7	−156.57168	−156.46954	−156.563667	
$C_4H_7^-$	−156.56455	−156.46376	−156.563677	
AEA ($C_4H_7/C_4H_7^-$)	−0.19	−0.16	0.00	
C_5H_9	−195.92735	−195.79505	−195.91574	
$C_5H_9^-$	−195.91766	−195.78809	−195.91380	
AEA ($C_5H_9/C_5H_9^-$)	−0.26	−0.19	−0.05	
C_6H_{11}	−235.251815	−235.090917	−235.236120	
$C_6H_{11}^-$	−235.247951	−235.089898	−235.240896	
AEA (C_6H_{11}/C_6H_{11})	−0.11	−0.03	0.13	

^{a} Reference 35.

On the contrary, addition of one electron to the other hydrocarbon radicals studied does not stabilize the radical energetically. The total energies of the anions are thus higher than the energies of the respective radicals. Indeed, as predicted by Schleyer, Spitznagel, and Chandrashekhar,[17] the cyclobutyl and higher member cyclic hydrocarbon anions are not bound with respect to loss of an electron. This finding can be explained in two ways. It is clear from the HOMO of the cyclopropyl anion (Chart 1) that the anionic charge is delocalized to an extent

Chart 1
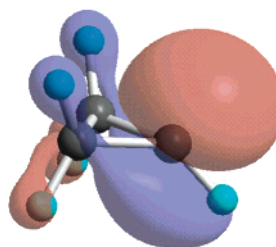
Chart 2
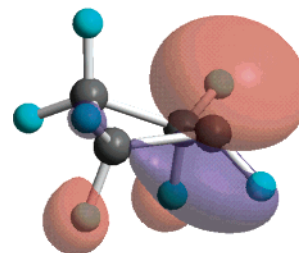
which is not visible in the HOMO of the cyclobutyl (Chart 2), cyclopentyl, and cyclohexyl anions. Second, due to the very small C−C−C bond angle (62.9°) in the cyclopropyl radical (Figure 1) the C−C bonds have a high degree of p character, and the orbital which the radical electron occupies has very high degree of s character. The extra electron in the anion goes to an s-rich orbital. In general, s orbitals are compact and hold the electrons tighter. However, in larger cyclic hydrocarbon radicals, angle strain is relieved and the degree of p character increases gradually on the orbital which "holds" the radical electron. Clearly the extra stability of the cyclopropyl anion accounts for the positive electron affinity of the cyclopropyl radical. For all three radicals, the AEA predicted by the BP86 DFT functional is higher than that predicted by the B3LYP and BLYP functionals. In the case of C_3H_5, the theoretically obtained electron affinities generally agree with the experimental electron affinity obtained using the kinetic method by Seburg and Squires.[19] The electron affinity predicted by BP86 (0.38 eV) DFT functional is in very good agreement with the experimentally reported electron affinity (0.40 ± 0.07 eV). Electron affinities predicted by B3LYP and BLYP methods are 0.24 and 0.23 eV, respectively.

The optimized ground state geometries for both the radicals and the anions are given in Figures 1−8. As predicted previously by Ellinger et al.[12] and by Dupuis and Pacanski,[13] the three C atoms and the H at the radical center of the cyclopropyl radical are not in plane. Due to the very small C−C−C bond angles, the orbitals used for C−C bonding have a large degree of p character. The orbital used for holding the radical's single electron has high s character. This s-rich orbital pushes the C−H bonding orbital by an angle of ∼39° from the C−C−C plane. The high electron density at the carbanion center (Chart 1) also makes the C−C−C bond angle smaller than 60° (deviation of 3.2° from the radical, Figure 2) on the anion. Table 4 summarizes the IR active harmonic vibrational frequencies along with their symmetries of the three hydrocarbon radicals and anions.

B. Perfluorocarbons. A similar approach has been taken for the study of geometries, total energies, and IR active harmonic vibrational frequencies of the four ($n = 3−6$) cyclic perfluo-

Table 2. Total Energies (Hartrees) and Adiabatic Electron Affinities (in eV) of the Cyclic Perfluorocarbon Radicals (C_nF_{2n-1}) and Anions ($C_nF_{2n-1}^-$), $n = 3-6$ Using the B3LYP, BLYP, and BP86 DFT Methods with the DZP++ Basis Set

| molecule/method	B3LYP	BLYP	BP86
C_3F_5	−613.541566	−613.480233	−613.548986
$C_3F_5^-$	−613.644657	−613.582968	−613.654864
AEA (in eV)	2.81	2.80	2.88
C_4F_7	−851.441657	−851.351393	−851.447499
$C_4F_7^-$	−851.558364	−851.467774	−851.566922
AEA (in eV)	3.18	3.17	3.25
C_5F_9	−1089.315798	−1089.198057	−1089.319689
$C_5F_9^-$	−1089.438622	−1089.32103	−1089.445400
AEA (in eV)	3.34	3.35	3.42
C_6F_{11}	−1327.171135	−1327.025864	−1327.173528
$C_6F_{11}^-$	−1327.288979	−1327.144246	−1327.294084
AEA (in eV)	3.21	3.22	3.28

Table 3. . Comparative Study of IR Intensities (in km/mol) of CO_2 and Perfluorocarbons Using B3LYP/DZP++

	cumulative IR intensity of all the vibrational modes (in km/mol)	cumulative IR intensity in the atmospheric IR "window" (in km/mol)	percent of IR intensity falling in the atmospheric IR "window"
CO_2	734		
C_3F_5	1149	979	85.2%
$C_3F_5^-$	2073	1502	72.5%
C_4F_7	1579	1116	70.6%
$C_4F_7^-$	2328	1900	81.6%
C_5F_9	1721	1295	75.2%
$C_5F_9^-$	3077	2091	67.9%
C_6F_{11}	1951	1466	75.1%
$C_6F_{11}^-$	2991	2252	75.3%

rocarbon radicals (C_nF_{2n-1}) and the corresponding anions ($C_nF_{2n-1}^-$). Conceptually, the perfluorocarbon radicals are obtained by breaking one C−F bond homolytically. All the radicals have C_s symmetry and the HOMOs have a′ symmetry resulting in $^2A'$ electronic ground states. Anions are obtained by adding one electron to the half filled HOMO of the radicals and therefore have $^1A'$ electronic ground states. Adiabatic electron affinities (AEA) were evaluated by subtracting the total energy of the anion, in the $^1A'$ state, from the total energy of the radical in the $^2A'$ state. The total energies of the perfluorocarbon radicals and anions and the adiabatic electron affinities are shown in Table 2. The electron affinities of the radicals are in general gradually increasing with ring size ($n = 3-6$) in the case of perfluorocarbons. Fluorine, due to its high electronegativity and powerful electron-withdrawing inductive effect, pulls the bonding electrons toward itself from the C−F single bond, rendering the already electron deficient radical carbon even more electron deficient. Thus the electron binding ability of the perfluorocarbon radicals is much greater than that of analogous hydrocarbon radicals. With the increasing ring size ($n = 3-6$) more fluorine atoms are attached to the ring, which makes the ring and the radical center more electron deficient. The anions are stabilized due to delocalization of anionic charge by the negative hyperconjugative effect of F. Thus the electron affinities of the perfluorocarbons increase gradually with ring size. The adiabatic electron affinity reaches a maximum for C_5F_9. Fluorine atoms that are far away from the radical carbon atom do not have much influence on the electron affinity of the radical. The changes in electron affinity with increasing atomic number are shown in Chart 3.
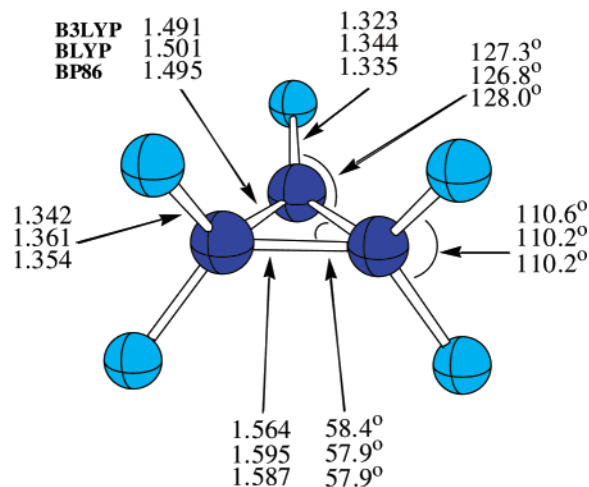
Figure 9. Optimized geometry of the C_3F_5 radical (C_s) in its $^2A'$ ground state. Bond lengths are in Å.
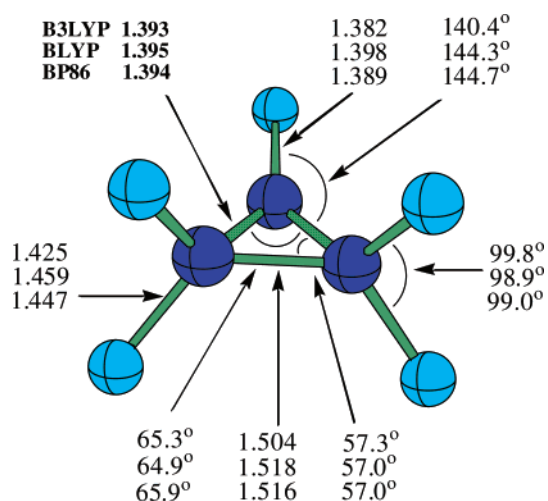
Figure 10. Optimized geometry of the $C_3F_5^-$ anion (C_s) in its $^1A'$ ground state. Bond lengths are in Å.

Chart 3

The optimized ground-state structures of the radicals and anions are shown in Figures 9−16. The C−C single bond distances increase in all PFC species when compared with the C−C distance on hydrocarbons. The fluorine atoms pull electron density toward themselves by negative hyperconjugative and inductive effects, making the C−C bonds weaker. Most of the structural features are the same as in the analogous hydrocar-
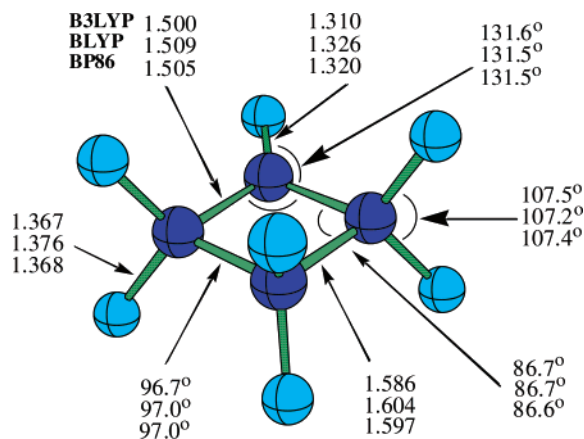
Figure 11. Optimized geometry of the C_4F_7 radical (C_s) in its $^2A'$ ground state. Bond lengths are in Å.
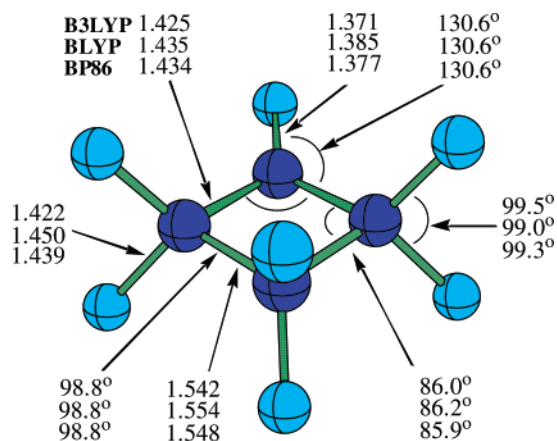
Figure 12. Optimized geometry of the $C_4F_7^-$ anion (C_s) in its $^1A'$ ground state. Bond lengths are in Å.
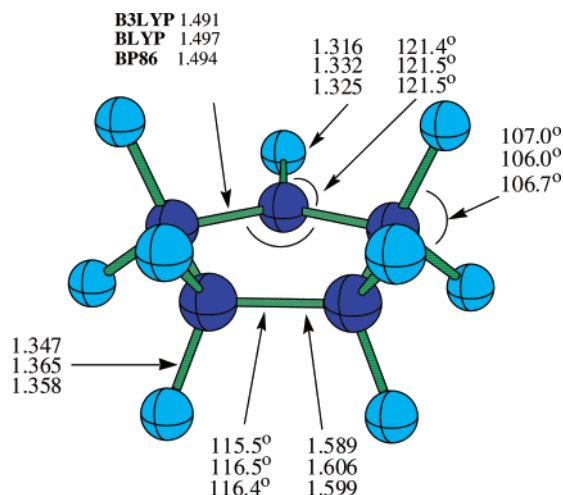
Figure 13. Optimized geometry of the C_5F_9 radical (C_s) in its $^2A'$ ground state. Bond lengths are in Å.

Figure 14. Optimized geometry of the $C_5F_9^-$ anion (C_s) in its $^1A'$ ground state. Bond lengths are in Å.
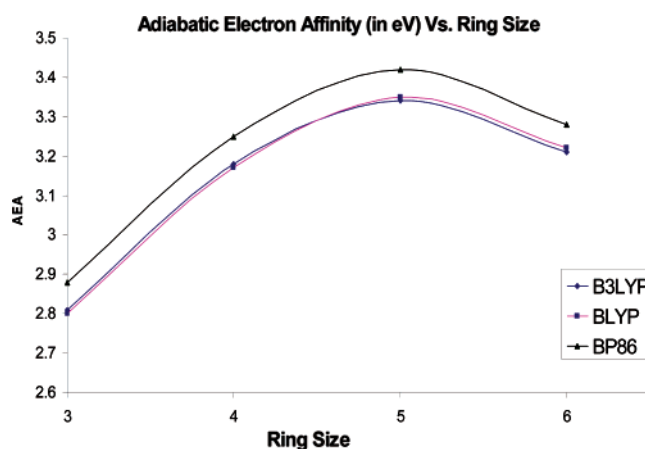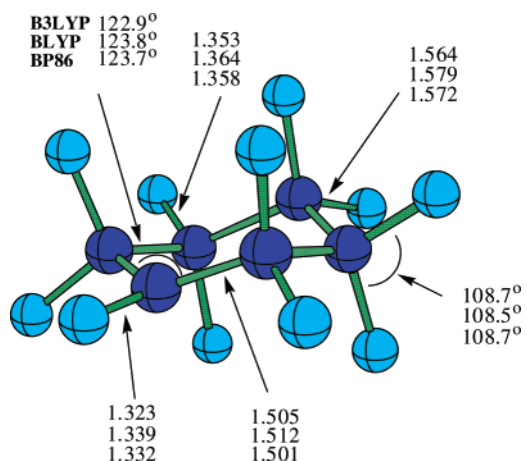

Figure 15. Optimized geometry of the C_6F_{11} radical (C_s) in its $^2A'$ ground state. Bond lengths are in Å.
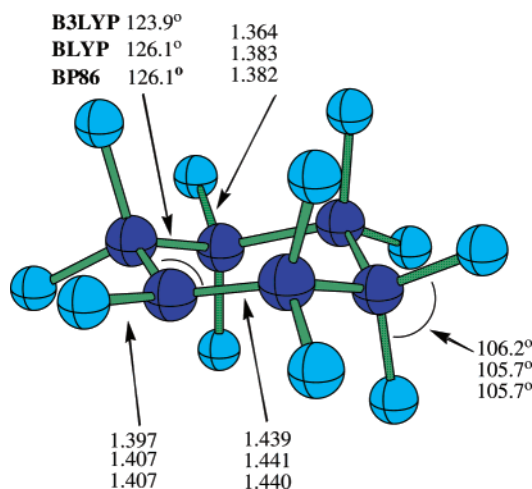
Figure 16. Optimized geometry of the $C_6F_{11}^-$ anion (C_s) in its $^1A'$ ground state. Bond lengths are in Å.

bons. The C_5F_9 radical has C_s symmetry in its ground state, unlike C_5H_9 which is of C_2 symmetry.

Predicted IR active harmonic vibrational frequencies along with their intensities are also listed for all the radicals and anions in Table 5. The total infrared intensities of the perfluorocarbons show a growing trend on going from radicals to anions. The typical IR intensities of the perfluorocarbons are also higher than those of hydrocarbons for the same ring size. The radiation

spectrum of earth spans almost the entire IR and near-IR range of the electromagnetic spectra. However, molecules having high absorption intensities in the atmospheric IR "window" [45] ($\sim$800 to $\sim$1200 cm^{-1}) are likely to have high GWPs. Molecules that were once rare but are now being introduced in the atmosphere

(45) Sturges, W. T.; Wallington, T. J.; Hurley, M. D.; Shine, K. P.; Sihra, K.; Angel, A.; Oram, D. E.; Penkett, S. A.; Mulvaney, R.; Brenninkmeijer, C. A. M. *Science* **2000**, *289*, 611.

Table 4. IR Active Harmonic Vibrational Frequencies of Hydrocarbon Radicals and Anions (in cm^{-1}) and Their Intensities (in parentheses in km/mol)

			B3LYP	BLYP	BP86				B3LYP	BLYP	BP86
C_3H_5	C_s	A′	3215 (11)	3126 (16)	3143 (13)	$C_4H_7{}^-$	C_s	A′	3062 (80)	2980 (77)	2992 (76)
		A′	3181 (29)	3091 (34)	3103 (32)			A′	2966 (110)	2881 (40)	2892 (50)
		A″	3169 (0)	3078 (0)	3091 (0)			A′	2940 (280)	2864 (303)	2875 (307)
		A′	3097 (14)	3011 (17)	3021 (16)			A′	2930 (138)	2855 (45)	2866 (89)
		A″	3096 (24)	3010 (27)	3020 (26)			A′	2928 (12)	2854 (24)	2863 (27)
		A′	1476.3 (0.6)	1427 (0)	1423 (1)			A′	2672 (1444)	2559 (1191)	2561 (1230)
		A″	1442 (1.3)	1402 (1)	1391 (1)			A″	2639 (644)	2515 (969)	2514 (880)
		A′	1254 (1.1)	1211 (1)	1231 (1)			A′	1473 (8)	1424 (7)	1414 (4)
		A″	1146 (0)	1106 (0)	1106 (0)			A″	1450 (33)	1405 (50)	1394 (47)
		A′	1090 (3)	1054 (2)	1049 (3)			A′	1435 (1)	1391 (2)	1375 (3)
		A″	1070 (0.01)	1033 (0)	1036 (0)			A″	1247 (7)	1201 (10)	1207 (12)
		A″	1042 (2.6)	997 (3)	992 (3)			A′	1246 (7)	1198 (1)	1199 (1)
		A″	1010 (26)	968 (30)	967 (28)			A″	1225 (0)	1180 (1)	1175 (1)
		A″	922 (28)	887 (27)	902 (27)			A″	1204 (5)	1163 (2)	1157 (4)
		A″	839 (9)	798 (5)	821 (8)			A′	1162 (24)	1122 (29)	1123 (20)
		A″	765 (6)	742 (7)	739 (7)			A″	1108 (22)	1064 (15)	1067 (18)
		A′	762 (7)	729 (9)	736 (6)			A′	1070 (0)	1031 (0)	1035 (0)
		A′	564 (24)	530 (27)	529 (27)			A′	992 (19)	961 (23)	973 (72)
$C_3H_5{}^-$	C_s	A′	3010 (402)	2920 (41)	2927 (46)			A′	987 (45)	954 (55)	963 (24)
		A″	3005 (49)	2917 (480)	2926 (471)			A″	935 (0)	903 (3)	918 (2)
		A′	2958 (545)	2862 (635)	2878 (560)			A″	911 (5)	870 (3)	884 (7)
		A″	2930 (246)	2816 (340)	2827 (322)			A′	906 (0)	870 (6)	880 (0)
		A′	2891 (219)	2797 (409)	2813 (538)			A′	888 (12)	858 (15)	864 (24)
		A′	1471 (27)	1425 (25)	1420 (30)			A″	811 (1)	782 (1)	792 (2)
		A″	1452 (14)	1411 (21)	1402 (18)			A′	657 (140)	640 (99)	640 (173)
		A′	1185 (0)	1146 (0)	1161 (0)			A′	591 (624)	554 (789)	563 (786)
		A″	1175 (1)	1135 (2)	1131 (2)			A′	295 (38)	296 (33)	303 (24)
		A″	1085 (1)	1043 (5)	1041 (4)	C_5H_9	C_2		3201 (27)	3115 (32)	3128 (30)
		A′	1082 (17)	1030 (10)	1038 (12)				3101 (68)	3019 (74)	3032 (65)
		A″	987 (10)	947 (9)	941 (12)				3091 (42)	3008 (45)	3023 (42)
		A′	974 (6)	933 (9)	934 (6)				3044 (9)	2963 (91)	2973 (97)
		A′	877 (7)	848 (9)	848 (8)				3043 (106)	2962 (18)	2972 (13)
		A′	825 (14)	782 (7)	802 (14)				3028 (27)	2940 (18)	2954 (21)
		A″	779 (1)	752 (5)	768 (0)				3028 (24)	2938 (55)	2954 (38)
		A″	751 (14)	720 (6)	741 (11)				1950 (1)	2855 (0)	1869 (1)
		A′	695 (122)	654 (211)	656 (225)				2949 (98)	2854 (112)	2867 (107)
C_4H_7	C_s	A′	3190 (36)	3101 (44)	3113 (43)				1504 (1)	1462 (1)	1452 (2)
		A′	3127 (44)	3046 (47)	3058 (41)				1486 (5)	1447 (4)	1435 (5)
		A′	3070 (54)	2989 (50)	2999 (56)				1465 (6)	1424 (5)	1412 (6)
		A″	3022 (0)	2924 (0)	2940 (0)				1463 (0)	1422 (0)	1410 (1)
		A′	3018 (69)	2920 (81)	2935 (73)				1361 (0)	1316 (1)	1317 (1)
		A′	2993 (0)	2903 (0)	2913 (0)				1342 (0)	1297 (0)	1293 (0)
		A″	2990 (121)	2899 (139)	2910 (132)				1321 (0)	1276 (0)	1275 (1)
		A′	1491 (0)	1448 (0)	1439 (1)				1292 (0)	1251 (1)	1244 (0)
		A′	1455 (0)	1414 (0)	1403 (0)				1283 (0)	1234 (1)	1233 (1)
		A″	1448 (3)	1406 (2)	1394 (3)				1233 (0)	1187 (0)	1194 (1)
		A″	1308 (0)	1261 (0)	1269 (0)				1216 (0)	1174 (0)	1173 (0)
		A′	1277 (3)	1229 (3)	1230 (4)				1180 (0)	1136 (0)	1139 (0)
		A″	1237 (2)	1198 (2)	1118 (2)				1087 (0)	1053 (0)	1049 (1)
		A″	1207 (0)	1162 (0)	1165 (0)				1042 (0)	1011 (0)	1016 (0)
		A″	1204 (0)	1159 (0)	1163 (0)				1036 (0)	999 (0)	1011 (0)
		A′	1174 (0)	1132 (1)	1130 (0)				1003 (0)	972 (0)	968 (0)
		A′	1039 (0)	1003 (0)	1023 (1)				930 (2)	899 (2)	905 (3)
		A′	997 (0)	965 (0)	961 (0)				914 (2)	883 (2)	898 (1)
		A″	991 (0)	957 (0)	957 (0)				900 (2)	866 (1)	881 (2)
		A″	968 (0)	935 (0)	950 (0)				890 (0)	861 (0)	862 (0)
		A″	909 (2)	870 (2)	890 (3)				848 (1)	818 (1)	824 (1)
		A′	905 (3)	868 (3)	887 (3)				816 (0)	788 (0)	791 (0)
		A′	790 (0)	766 (0)	763 (0)				656 (0)	639 (0)	636 (0)
		A″	738 (0)	716 (1)	713 (1)				568 (0)	555 (0)	549 (0)
		A′	737 (1)	714 (0)	710 (0)				332 (33)	339 (33)	346 (34)
		A′	223 (41)	236 (42)	256 (43)				238 (0)	230 (0)	234 (0)
		A′	71 (2)	75 (1)	60 (1)				168 (1)	163 (1)	164 (1)

Table 4 (Continued)

|			B3LYP	BLYP	BP86				B3LYP	BLYP	BP86
$C_5H_9{}^-$	C_s	A′	3054 (95)	2972 (86)	2982 (87)			A′	1102 (0)	1067 (0)	1063 (0)
		A″	3032 (17)	2949 (14)	2961 (15)			A″	1085 (1)	1054 (1)	1049 (1)
		A′	3007 (92)	2941 (139)	2952 (128)			A″	1060 (0)	1025 (0)	1036 (0)
		A′	2998 (27)	2924 (2)	2934 (4)			A′	1033 (0)	996 (0)	1007 (0)
		A″	2996 (55)	2919 (13)	2931 (36)			A′	1006 (3)	970 (3)	971 (3)
		A′	2982 (262)	2893 (209)	2902 (246)			A″	917 (1)	890 (0)	884 (0)
		A″	2964 (104)	2877 (127)	2885 (131)			A′	878 (2)	847 (2)	862 (2)
		A′	2590 (1475)	2491 (1404)	2495 (1320)			A″	876 (1)	840 (1)	856 (2)
		A″	2551 (604)	2452 (767)	2453 (759)			A′	847 (3)	822 (3)	817 (4)
		A′	1476 (7)	1431 (3)	1417 (9)			A′	807 (0)	777 (1)	792 (0)
		A″	1456 (1)	1413 (1)	1399 (0)			A″	776 (0)	754 (0)	749 (0)
		A′	1446 (8)	1402 (14)	1388 (8)			A′	603 (2)	582 (2)	578 (3)
		A″	1444 (10)	1400 (16)	1387 (16)			A′	453 (3)	400 (3)	437 (3)
		A″	1319 (3)	1275 (4)	1273 (2)			A″	432 (0)	421 (0)	417 (0)
		A′	1311 (7)	1266 (2)	1263 (3)			A′	383 (14)	371 (12)	372 (13)
		A′	1279 (1)	1236 (0)	1234 (0)			A′	318 (6)	300 (8)	302 (7)
		A″	1272 (0)	1235 (0)	1225 (21)			A″	206 (0)	199 (0)	198 (0)
		A″	1264 (24)	1224 (24)	1219 (12)			A′	172 (1)	161 (2)	160 (2)
		A″	1196 (69)	1153 (110)	1155 (89)	$C_6H_{11}{}^-$	C_s	A′	3037 (86)	2960 (78)	2967 (72)
		A′	1187 (11)	1143 (15)	1147 (16)			A′	3030 (0)	2952 (118)	2961 (139)
		A″	1165 (1)	1124 (4)	1028 (18)			A″	3020 (146)	2947 (1)	2955 (1)
		A′	1130 (16)	1094 (13)	1093 (19)			A′	3005 (21)	2923 (15)	2934 (35)
		A′	1039 (7)	999 (9)	1011 (8)			A″	2998 (60)	2919 (2)	2930 (41)
		A″	1029 (6)	998 (6)	1001 (4)			A′	2997 (16)	2918 (22)	2930 (3)
		A″	1010 (15)	974 (16)	972 (23)			A′	2979 (134)	2897 (86)	2902 (102)
		A′	954 (1)	922 (6)	928 (10)			A″	2934 (323)	2839 (395)	2853 (424)
		A′	910 (86)	882 (73)	895 (83)			A′	2930 (101)	2836 (119)	2849 (137)
		A″	899 (0)	865 (0)	880 (0)			A′	2590 (1442)	2501 (1416)	2501 (1320)
		A′	877 (3)	840 (6)	856 (83)			A″	2553 (594)	2466 (684)	2462 (770)
		A′	843 (19)	816 (26)	817 (24)			A′	1479 (2)	1438 (1)	1423 (2)
		A′	812 (38)	779 (22)	783 (32)			A′	1456 (22)	1414 (17)	1398 (31)
		A′	693 (273)	666 (213)	671 (269)			A″	1451 (2)	1408 (1)	1392 (4)
		A″	611 (0)	595 (0)	593 (0)			A″	1433 (1)	1388 (3)	1375 (5)
		A′	523 (434)	492 (498)	502 (455)			A′	1428 (9)	1383 (13)	1368 (9)
		A′	345 (14)	335 (13)	337 (14)			A″	1364 (4)	1320 (6)	1314 (3)
		A″	164 (1)	161 (2)	162 (1)			A″	1356 (0)	1311 (1)	1309 (4)
C_6H_{11}	C_s	A′	3172 (39)	3090 (42)	3101 (40)			A′	1348 (2)	1306 (3)	1298 (3)
		A′	3073 (95)	2089 (108)	3002 (93)			A′	1335 (10)	1289 (4)	1288 (3)
		A″	3067 (27)	2984 (17)	2998 (25)			A″	1315 (1)	1277 (1)	1270 (27)
		A′	3064 (18)	2981 (6)	2995 (9)			A″	1303 (42)	1259 (50)	1259 (22)
		A″	3062 (92)	2980 (108)	1994 (92)			A′	1268 (14)	1227 (15)	1228 (21)
		A′	3061 (69)	2977 (83)	2991 (75)			A″	1260 (70)	1223 (93)	1215 (113)
		A′	3022 (35)	2941 (34)	2950 (40)			A′	1224 (4)	1186 (7)	1179 (10)
		A″	3021 (31)	2941 (38)	2949 (37)			A″	1139 (42)	1095 (64)	1116 (49)
		A′	3009 (31)	2929 (33)	2936 (34)			A″	1095 (9)	1066 (14)	1059 (26)
		A′	2916 (86)	2823 (99)	2838 (93)			A′	1090 (18)	1055 (24)	1050 (18)
		A″	2911 (23)	2817 (28)	2833 (30)			A″	1078 (37)	1047 (64)	1040 (51)
		A′	1494 (2)	1453 (2)	1440 (2)			A″	1044 (15)	1011 (14)	1022 (18)
		A′	1481 (8)	1441 (8)	1428 (10)			A′	1021 (16)	987 (17)	996 (20)
		A″	1479 (6)	1438 (5)	1425 (6)			A′	1017 (0)	981 (4)	981 (4)
		A′	1464 (5)	1423 (4)	1411 (5)			A″	931 (2)	898 (1)	894 (4)
		A″	1459 (2)	1418 (3)	1405 (3)			A′	874 (25)	845 (25)	859 (34)
		A″	1389 (1)	1342 (1)	1346 (0)			A″	862 (2)	829 (3)	843 (6)
		A′	1378 (0)	1334 (2)	1328 (0)			A′	837 (23)	809 (15)	807 (19)
		A″	1374 (0)	1326 (1)	1324 (0)			A′	801 (10)	775 (13)	785 (31)
		A′	1349 (2)	1297 (3)	1296 (3)			A″	800 (28)	769 (31)	771 (15)
		A″	1341 (0)	1293 (0)	1292 (0)			A′	646 (236)	614 (161)	618 (214)
		A″	1330 (0)	1286 (0)	1278 (0)			A′	521 (119)	498 (129)	498 (117)
		A′	1284 (0)	1243 (0)	1244 (0)			A″	440 (1)	430 (0)	427 (1)
		A″	1270 (3)	1231 (4)	1227 (3)			A′	425 (52)	410 (55)	410 (43)
		A′	1242 (0)	1203 (0)	1198 (0)			A′	385 (100)	371 (109)	368 (117)
		A″	1157 (0)	1109 (0)	1123 (0)			A″	259 (3)	248 (4)	252 (3)
		A″	1123 (0)	1093 (0)	1093 (0)			A′	244 (4)	237 (3)	237 (4)

Table 5. IR Active Harmonic Vibrational Frequencies of Perfluorocarbon Radicals and Anions (in cm^{-1}) and Their Intensities (in km/mol)

			B3LYP	BLYP	BP86
C_3F_5	C_s	A′	1526 (20)	1417 (17)	1459 (16)
		A″	1281 (117)	1194 (123)	1223 (129)
		A′	1233 (494)	1136 (483)	1165 (493)
		A′	1225 (275)	1112 (318)	1145 (316)
		A″	1196 (53)	1097 (53)	1126 (48)
		A″	857 (118)	811 (115)	830 (115)
		A′	824 (39)	753 (17)	766 (21)
		A′	760 (2)	707 (2)	722 (1)
		A″	741 (1)	699 (3)	711 (2)
		A′	567 (1)	529 (0)	533 (0)
		A″	539 (17)	515 (13)	521 (14)
		A′	437 (3)	418 (2)	421 (2)
		A″	434 (1)	406 (0)	410 (0)
		A′	254 (0)	232 (1)	236 (0)
		A″	245 (1)	231 (0)	234 (1)
		A′	183 (5)	174 (4)	171 (3)
		A″	166 (0)	161 (0)	161 (0)
		A′	124 (2)	122 (2)	116 (3)
$C_3F_5^-$	C_s	A′	1663 (71)	1636 (25)	1665 (24)
		A″	1262 (289)	1235 (295)	1260 (303)
		A′	1111 (268)	1012 (396)	1044 (417)
		A′	846 (223)	796 (204)	815 (191)
		A″	819 (654)	746 (3)	756 (3)
		A′	808 (68)	699 (648)	735 (652)
		A″	785 (158)	689 (330)	718 (287)
		A″	722 (146)	635 (92)	668 (118)
		A′	672 (0)	608 (3)	624 (2)
		A″	529 (10)	495 (4)	505 (6)
		A′	521 (9)	471 (11)	482 (6)
		A″	444 (3)	417 (2)	426 (1)
		A′	440 (5)	492 (0)	415 (1)
		A′	237 (0)	220 (0)	224 (0)
		A″	232 (0)	217 (0)	221 (0)
		A′	181 (3)	171 (4)	175 (4)
		A″	164 (1)	146 (0)	149 (0)
		A′	86 (14)	56 (6)	58 (5)
C_4F_7	C_s	A′	1544 (46)	1455 (49)	1483 (52)
		A′	1336 (143)	1239 (147)	1266 (156)
		A″	1324 (197)	1236 (176)	1263 (186)
		A′	1252 (2)	1173 (4)	1191 (3)
		A′	1229 (123)	1137 (126)	1167 (146)
		A′	1166 (516)	1069 (495)	1100 (478)
		A″	1107 (0)	1004 (0)	1039 (0)
		A″	1044 (26)	967 (57)	987 (55)
		A′	976 (222)	925 (204)	941 (198)
		A″	935 (226)	873 (205)	892 (198)
		A″	848 (1)	806 (1)	814 (1)
		A′	686 (4)	649 (4)	660 (4)
		A′	636 (6)	606 (6)	613 (5)
		A	586 (0)	557 (0)	565 (0)
		A″	550 (31)	523 (26)	529 (27)
		A′	458 (2)	436 (2)	443 (2)
		A	433 (7)	414 (6)	418 (6)
		A′	407 (0)	385 (0)	388 (0)
		A′	355 (0)	340 (0)	342 (0)
		A′	281 (20)	264 (2)	268 (2)
		A″	271 (1)	255 (1)	258 (1)
		A″	235 (1)	225 (1)	226 (1)
		A″	222 (0)	209 (0)	210 (0)
		A″	206 (0)	194 (0)	194 (0)
		A′	198 (2)	189 (2)	189 (2)
		A′	72 (0)	79 (0)	89 (0)
		A′	35 (1)	41 (0)	40 (0)

			B3LYP	BLYP	BP86
$C_4F_7^-$	C_s	A′	1559 (10)	1490 (15)	1513 (15)
		A″	1346 (460)	1293 (433)	1315 (445)
		A′	1278 (300)	1185 (307)	1213 (324)
		A″	1140 (37)	1053 (40)	1076 (40)
		A′	1086 (14)	1015 (13)	1031 (14)
		A′	1051 (160)	947 (134)	976 (152)
		A′	934 (315)	876 (319)	895 (306)
		A′	888 (604)	813 (30)	832 (586)
		A″	861 (61)	802 (597)	823 (44)
		A″	789 (709)	722 (754)	750 (705)
		A″	788 (1)	685 (0)	726 (0)
		A′	653 (6)	613 (4)	626 (4)
		A′	613 (5)	577 (2)	588 (2)
		A″	546 (28)	513 (16)	522 (21)
		A′	533 (10)	489 (17)	504 (12)
		A′	468 (15)	438 (25)	448 (18)
		A″	456 (0)	426 (0)	435 (0)
		A′	447 (3)	425 (3)	431 (3)
		A′	369 (0)	351 (0)	355 (0)
		A′	271 (0)	255 (0)	259 (0)
		A″	266 (1)	251 (1)	254 (1)
		A″	234 (0)	223 (0)	225 (0)
		A″	223 (0)	208 (0)	210 (0)
		A″	197 (0)	183 (0)	186 (0)
		A′	194 (2)	182 (2)	184 (2)
		A′	133 (1)	131 (1)	136 (1)
		A′	52 (0)	53 (1)	53 (1)
C_5F_9	C_s	A′	1484 (69)	1403 (68)	1430 (73)
		A″	1342 (98)	1270 (69)	1292 (80)
		A′	1309 (81)	1218 (83)	1244 (90)
		A″	1291 (95)	1199 (101)	1224 (102)
		A′	1259 (12)	1165 (5)	1189 (7)
		A″	1224 (0)	1133 (0)	1161 (0)
		A′	1212 (403)	1122 (391)	1155 (403)
		A′	1131 (305)	1033 (11)	1063 (294)
		A″	1111 (10)	1030 (305)	1054 (12)
		A″	1087 (0)	994 (109)	1026 (0)
		A′	1056 (75)	993 (3)	1013 (94)
		A′	993 (212)	933 (157)	951 (162)
		A″	968 (290)	911 (302)	929 (290)
		A″	871 (0)	832 (1)	839 (1)
		A′	658 (2)	621 (3)	632 (3)
		A″	625 (2)	595 (3)	602 (3)
		A′	607 (6)	574 (10)	581 (10)
		A′	600 (8)	568 (1)	575 (2)
		A″	577 (6)	543 (4)	550 (4)
		A″	550 (31)	524 (28)	530 (29)
		A′	439 (1)	411 (1)	417 (1)
		A′	408 (5)	392 (5)	395 (5)
		A″	385 (1)	366 (0)	369 (0)
		A′	346 (0)	329 (0)	332 (0)
		A′	326 (0)	310 (0)	313 (0)
		A″	315 (2)	301 (2)	303 (2)
		A″	310 (0)	294 (0)	297 (0)
		A′	298 (3)	285 (3)	287 (3)
		A′	280 (0)	268 (0)	271 (0)
		A″	254 (0)	245 (0)	245 (0)
		A″	246 (0)	237 (0)	238 (0)
		A″	244 (0)	232 (0)	233 (0)
		A′	227 (3)	218 (2)	219 (2)
		A′	115 (1)	113 (1)	117 (0)
		A′	34 (0)	23 (1)	23 (0)
		A′	−39 (0)	−40 (0)	−39 (0)

Table 5. (Continued)

			B3LYP	BLYP	BP86				B3LYP	BLYP	BP86
$C_5F_9^-$	C_s	A″	1455 (266)	1409 (280)	1428 (278)			A″	356 (0)	339 (0)	342 (0)
		A′	1459 (50)	1398 (61)	1419 (63)			A′	352 (2)	336 (2)	339 (2)
		A″	1250 (302)	1162 (256)	1186 (231)			A′	324 (0)	309 (0)	311 (0)
		A′	1257 (229)	1158 (211)	1186 (272)			A″	323 (1)	309 (1)	311 (0)
		A′	1229 (1)	1144 (40)	1169 (41)			A″	302 (4)	290 (3)	291 (4)
		A″	1114 (0)	1012 (0)	1039 (0)			A′	296 (7)	282 (6)	284 (6)
		A′	1101 (381)	996 (370)	1028 (380)			A″	281 (1)	271 (0)	270 (0)
		A″	1048 (0)	978 (4)	995 (4)			A′	280 (0)	270 (0)	269 (0)
		A′	1026 (72)	972 (110)	992 (103)			A′	273 (0)	265 (0)	264 (0)
		A′	947 (291)	880 (274)	899 (267)			A″	250 (0)	239 (0)	238 (0)
		A″	882 (258)	832 (76)	843 (120)			A″	239 (0)	229 (0)	229 (0)
		A′	874 (453)	786 (427)	817 (425)			A″	236 (0)	227 (1)	227 (1)
		A″	851 (246)	753 (870)	779 (801)			A′	174 (0)	168 (0)	167 (0)
		A″	799 (390)	722 (0)	760 (0)			A″	171 (1)	164 (1)	163 (0)
		A′	638 (16)	599 (16)	611 (15)			A′	128 (1)	125 (1)	124 (1)
		A″	617 (39)	582 (67)	591 (45)			A′	103 (0)	97 (0)	99 (0)
		A′	595 (13)	560 (6)	570 (9)			A″	59 (0)	55 (0)	56 (0)
		A″	553 (20)	519 (24)	528 (33)			A″	52 (1)	48 (0)	47 (0)
		A′	556 (5)	508 (20)	521 (12)	$C_6F_{11}^-$	C_s	A″	1423 (184)	1391 (231)	1410 (222)
		A″	534 (20)	490 (0)	506 (0)			A′	1365 (37)	1310 (44)	1331 (47)
		A′	433 (9)	407 (1)	411 (1)			A′	1295 (126)	1195 (139)	1222 (167)
		A″	427 (4)	404 (0)	411 (0)			A′	1264 (184)	1181 (27)	1207 (9)
		A′	421 (5)	402 (15)	410 (12)			A″	1264 (0)	1177 (121)	1202 (126)
		A′	364 (0)	344 (0)	348 (0)			A″	1215 (236)	1126 (257)	1151 (271)
		A′	326 (0)	310 (0)	313 (0)			A′	1162 (92)	1076 (10)	1095 (66)
		A″	323 (7)	309 (6)	311 (5)			A′	1159 (359)	1064 (254)	1093 (344)
		A″	303 (3)	288 (4)	291 (4)			A′	1137 (76)	1048 (239)	1074 (106)
		A′	292 (1)	276 (0)	279 (0)			A″	1113 (31)	1009 (8)	1040 (16)
		A′	285 (0)	272 (0)	275 (0)			A′	1010 (15)	953 (30)	974 (28)
		A″	260 (0)	246 (0)	249 (0)			A″	1010 (9)	943 (46)	961 (36)
		A″	248 (2)	242 (3)	241 (2)			A′	950 (406)	890 (374)	909 (364)
		A″	231 (0)	217 (0)	219 (0)			A″	924 (418)	844 (480)	865 (471)
		A′	227 (2)	215 (2)	217 (2)			A″	858 (21)	807 (10)	818 (0)
		A′	144 (2)	142 (1)	145 (1)			A′	852 (405)	761 (353)	791 (363)
		A′	26 (0)	18 (1)	17 (1)			A″	769 (230)	683 (226)	713 (239)
		A″	−26 (0)	−30 (0)	−30 (0)			A′	657 (14)	620 (7)	630 (10)
C_6F_{11}	C_s	A′	1422 (62)	1341 (60)	1369 (65)			A′	651 (4)	605 (14)	618 (11)
		A″	1334 (12)	1257 (15)	1280 (18)			A″	614 (3)	568 (5)	576 (5)
		A′	1318 (62)	1229 (69)	1256 (72)			A′	603 (7)	556 (30)	571 (15)
		A′	1297 (32)	1206 (22)	1230 (23)			A′	580 (3)	543 (0)	552 (0)
		A″	1293 (231)	1202 (217)	1229 (225)			A″	554 (2)	501 (5)	520 (4)
		A′	1245 (202)	1160 (135)	1184 (198)			A′	510 (21)	477 (22)	483 (21)
		A′	1220 (31)	1129 (40)	1157 (41)			A″	452 (73)	408 (112)	424 (94)
		A″	1205 (1)	1120 (0)	1144 (0)			A′	424 (1)	403 (2)	407 (2)
		A′	1186 (350)	1104 (380)	1133 (325)			A′	389 (7)	365 (11)	370 (9)
		A″	1174 (29)	1083 (22)	1114 (26)			A″	385 (0)	365 (2)	369 (0)
		A′	1107 (223)	1013 (17)	1037 (185)			A′	364 (0)	347 (0)	351 (0)
		A″	1097 (3)	1008 (0)	1034 (1)			A′	331 (0)	315 (1)	316 (1)
		A′	1073 (13)	1003 (224)	1031 (48)			A″	325 (12)	310 (13)	313 (10)
		A″	1056 (7)	973 (14)	1002 (9)			A″	308 (0)	295 (0)	296 (0)
		A′	989 (313)	937 (289)	951 (280)			A′	298 (2)	283 (2)	285 (2)
		A″	966 (294)	913 (297)	929 (287)			A″	285 (0)	273 (0)	274 (0)
		A″	847 (0)	809 (1)	815 (0)			A′	282 (1)	273 (1)	273 (0)
		A′	686 (0)	646 (1)	657 (1)			A″	267 (0)	258 (4)	258 (3)
		A′	666 (5)	633 (5)	641 (5)			A″	250 (0)	240 (0)	240 (0)
		A′	638 (9)	602 (8)	609 (7)			A′	244 (1)	235 (1)	235 (1)
		A″	618 (19)	586 (16)	593 (17)			A″	236 (4)	222 (8)	223 (5)
		A′	592 (2)	562 (1)	567 (2)			A″	193 (1)	186 (2)	186 (2)
		A″	580 (3)	550 (2)	556 (2)			A′	173 (2)	168 (2)	167 (2)
		A′	521 (5)	494 (4)	499 (4)			A′	138 (4)	137 (3)	137 (3)
		A″	467 (18)	445 (16)	448 (16)			A′	94 (0)	89 (0)	89 (0)
		A′	424 (6)	404 (5)	408 (5)			A″	62 (0)	55 (0)	54 (0)
		A′	385 (0)	365 (0)	369 (0)			A′	55 (0)	54 (0)	53 (0)

Chart 4
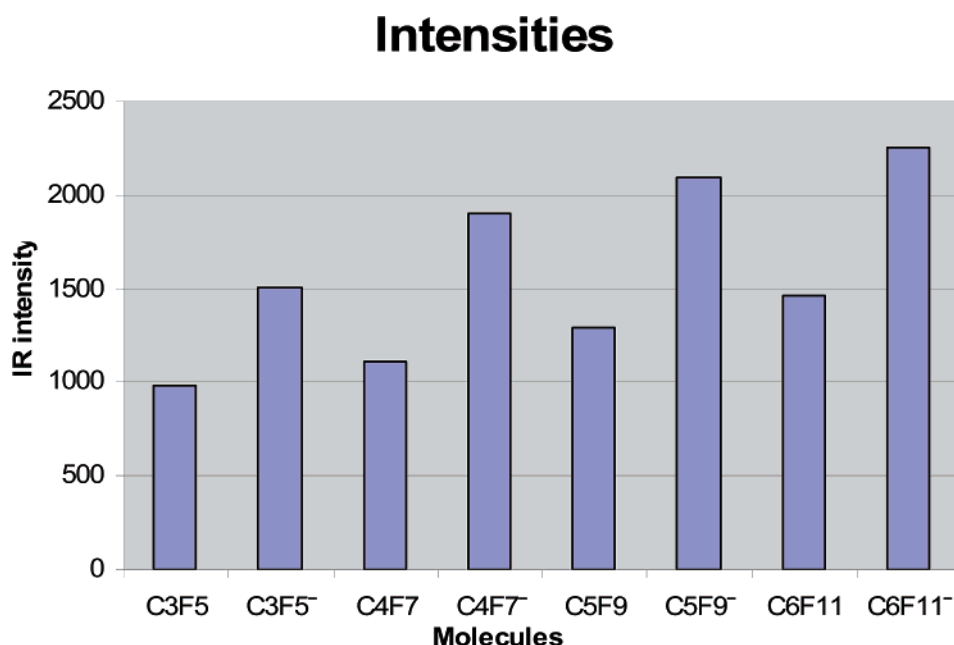
Intensities

can occupy new regions of the radiation spectrum emitted from the earth. From Table 5 it is evident that there are several vibrational modes available for each of the perfluorocarbons in this region. The total IR intensities (including CO_2) and the IR intensities in the atmospheric IR "window" are tabulated in Table 3. The predicted IR absorption lines are strong and 70–85% of the total IR intensities fall on the atmospheric IR "window" of the electromagnetic spectrum. Chart 4 depicts the cumulative intensities of all the vibrational modes, for each perfluorocarbon radical and anion, in the same region ($\sim$ 800 to $\sim$1200 cm^{-1}).

IV. Conclusions

Since not a great deal of experimental data is available for the molecules studied, we are convinced that this work on the cyclic hydrocarbon and perfluorocarbon radicals should be very helpful in the future in providing valuable information about the vibrational frequencies and electron affinities of these small perfluorocarbon radicals. However, there is no way of knowing with absolute certainty which DFT functional performs best in predicting the structures, energetics, and vibrational frequencies for a particular molecular system. Taken more positively, the scatter of the results from the three DFT methods gives us a good idea of the reliability of these methods. Using the same DZP++ basis set for all three DFT functionals we see that BP86 predicts the electron affinities (AEA) for all the radicals higher than those predicted by the other two DFT functionals, which are close to each other. BP86 performs very well in predicting the electron affinity of the C_3H_5 radical. Absolute error from experimentally known electron affinity of C_3H_5, reported by Seburg et al., are 0.16 eV (B3LYP), 0.17 eV (BLYP), and 0.02 eV (BP86).

We conclude that the ground electronic states of all the radicals are $^2A'$ except for C_5H_9 (which is ^2A) and that all the anions have $^1A'$ symmetry. The ground-state geometries of the radicals are C_s except for C_5H_9 which is C_2. The C_s structure of the C_3H_5 radical is a transition state. The unsubstituted cyclopropyl radical binds an electron while the cyclobutyl and cyclopentyl radicals do not. This observation is explained by the presence of "extended anionic charge delocalization" in $C_3H_5^-$ and absence of the same in $C_4H_7^-$, $C_5H_9^-$, and $C_6H_{11}^-$. The lack of a positive (favorable) electron affinity indicates that the cyclobutyl, and cyclohexyl radicals can exist in the atmosphere independently without fear of electron attachment.

In the case of perfluorocarbons, however, all the radicals strongly bind an electron because of the stabilization obtained from the delocalization of excess charge by the electron-withdrawing inductive and negative hyperconjugative effects of fluorine. The high electron affinities of radicals suggest that anions may have substantial lifetimes as independent species under atmospheric conditions. Cyclic perfluorocarbon radicals are likely to be short-lived in the atmosphere. However, the fact that the anions are very stable in the atmosphere and they absorb, with very high intensities, in the atmospheric IR "window" region makes them potentially very potent greenhouse gases.