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November 2004

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Gallup, Gordon A., "The structures of $c\text{-C}_4\text{F}_8$ and $c\text{-C}_4\text{F}_8^-$ and the adiabatic electron affinity of $c\text{-C}_4\text{F}_8$ " (2004). *Gordon Gallup Publications*. 41.
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The structures of $c\text{-C}_4\text{F}_8$ and $c\text{-C}_4\text{F}_8^-$ and the adiabatic electron affinity of $c\text{-C}_4\text{F}_8$

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Submitted August 2004; revised September 2004; available online October 22, 2004.

Abstract: Calculations at the 6311G(dps) level have been used to elucidate the structures of octafluorocyclobutane $c\text{-C}_4\text{F}_8$ and its negative ion $c\text{-C}_4\text{F}_8^-$. With no empirical adjustments, we obtain 0.640 eV for the adiabatic electron affinity of $c\text{-C}_4\text{F}_8$. This may be compared with an experimental value of 0.63 ± 0.05 eV from the FALP method. $c\text{-C}_4\text{F}_8$ has unusual features in that there is an increase in symmetry, D_{2d} to D_{4h} , in going from the neutral molecule to the negative ion, and the singly occupied molecular orbital in the ion has an unexpected nodal structure.

1. Introduction

Considerable interest in the properties of $c\text{-C}_4\text{F}_8$ exists because of its use as a feed stock in plasma processing, its reactions in the upper atmosphere, and its potential as an insulating gas for high voltages [1] and [2]. There is good experimental evidence that an adiabatically stable negative ion exists. Miller et al. [3] and [4] have made flowing-afterglow-Langmuir-probe studies and have arrived at an adiabatic electron affinity (AEA) of 0.63 ± 0.05 eV. Photo-detachment measurements have also been made by Miller and Lineberger for which the 0–0 transition has not been clearly identified¹. The observed threshold is nevertheless near 0.68 eV, consistent with the kinetic measurement.

It is perhaps surprising that such a relatively small saturated molecule, made entirely of elements from the second row of the periodic table, possesses a stable negative ion. It is the purpose of this article to examine $c\text{-C}_4\text{F}_8$ with a number of basis sets to show how this arises. The calculations are all done with the GAMESS [5] program suite. The theory also predicts that $c\text{-C}_4\text{F}_8$ exhibits a rather unusual symmetry change in forming $c\text{-C}_4\text{F}_8^-$.

This occurs in such a way as to make the negative ion of this molecule even more challenging for theory than such entities usually are.

2. Calculations

Molecular structure calculations normally proceed by carrying out some sort of self-consistent field calculations followed by a second step that introduces the electron correlation effects that are missing from the first step. During these steps decisions must be made as to how the geometry is to be optimized. It also known that successful negative ion calculations require large diffuse basis sets. For the ion we are considering, $c\text{-C}_4\text{F}_8^-$, these two requirements are in conflict to an extent, because calculations predict that the ion has a higher symmetry than the neutral molecule. This prediction does not arise directly, however, from a simple straightforward application of the procedures above. We first examine the symmetry question at the self-consistent field level.

We have performed calculations with three different basis sets, which we abbreviate A, B and C. These are 6-31G(d), 6-311G(d), and 6-311G(sp), respective-

ly. The energies are given in Table 1. With all three basis sets the optimized restricted closed-shell Hartree–Fock (RHF) geometry for $c\text{-C}_4\text{F}_8$ has a puckered ring D_{2d} symmetry, but for the optimized restricted open-shell Hartree–Fock (ROHF) geometry of $c\text{-C}_4\text{F}_8^-$ basis sets A and B give planar ring D_{4h} symmetry while C gives either a D_{2d} or a D_{4h} geometry depending upon the starting point for the search. This behavior for basis set A has already been seen by Miller et al. [4] who used the G3(MP2) procedure of Curtiss et al. [6] The basis set B results differ from those of A only in quantitative details. Calculations of the nuclear Hessians for the two ROHF geometries with basis set C show that these are both stable local minima. We therefore have here two different electronic states that will not interact (i.e., they may cross) for all geometries which satisfy subgroups of D_{4h} in which z is not a totally symmetric coordinate.

Basis set C also shows a ${}^2A_{2u}$ state symmetry for $c\text{-C}_4\text{F}_8^-$ in the D_{4h} geometry, as do the other two basis sets. The apparent D_{2d} geometry for $c\text{-C}_4\text{F}_8^-$ and basis set C has a state symmetry of 2A_1 . Examination of the orbitals here shows that without the diffuse s and p functions, basis sets A and B constrain the singly occupied molecular orbital (SOMO) to remain in the vicinity of the molecule, while C in D_{2d} symmetry allows this orbital to collapse into a continuum-like function. Starting the geometry optimization for C at larger bond lengths allows the more compact a_{2u} SOMO to form and the geometry to become more symmetric. For all basis sets the D_{4h} SOMO is bonding for the C–C bonds and antibonding for the C–F bonds, and in Table 2 we show how the MP2 bond lengths vary with basis set. For both the B and C basis sets, the bonding character of the SOMO is clearly shown by the changes in bond length upon formation of the ion.

Examination of Table 1 shows that in spite of the geometry change $c\text{-C}_4\text{F}_8^-$ is not calculated at the R(O)HF level to be stable for any of the basis sets.

When MP2 calculations are carried out, providing correlation, we see that basis set C shows a positive AEA. Further geometry optimizations were carried out and all bond lengths increased in length as expected. Thus, as is usually the case, $c\text{-C}_4\text{F}_8^-$ attains its adiabatic stability through a combination of electron correlation effects and geometry relaxation. The behavior here is somewhat unusual in that the geometry change involves an *increase* in symmetry. The smaller bases provide a geometry change, but do not have enough electron correlation. Our final energies using this scheme are shown in the last column of Table 1. With the zero-point energies corresponding to the R(O)HF structures of basis set C, we obtain an AEA of 0.640 eV with no empirical corrections. The conventional ZPE correction (89% of the calculated value) gives 0.620 eV.

3. Orbital symmetry

The apparent ${}^2A_{2u}$ state symmetry of $c\text{-C}_4\text{F}_8^-$ is somewhat unusual for doublet negative ions, since we expect them to have as few nodes as possible in their SOMO. The upper part of Fig. 1 shows the SOMO obtained with an ROHF treatment using basis set C. It is seen to have a nodal plane at the C-atom plane. As can be seen from the lower part of Fig. 1, the upper orbital drawing is indistinguishable from that of the RHF LUMO, which represents the Koopmans' theorem (KT) [7] approximation to the SOMO.

When occupied in the ion, the SOMO contributes bonding character to C–C bonds and antibonding character to the C–F bonds. This is evident qualitatively from Fig. 1 and, quantitatively, from the change in bond distances shown in Table 2. The overall effect when forming the ion is an increase of ≈ 0.2 Å in the calculated non-bonded F–F distance that reduces the tendency for ring-puckering. An idea of what an a_{1g} orbital might look like can be obtained using the KT approximation

Table 1
The total energies (a.u.) of $c\text{-C}_4\text{F}_8$ and $c\text{-C}_4\text{F}_8^-$ for various bases and geometries

| | | A: 6-31G(d) | B: 6-311G(d) | C: 6-311G(sp) |
|--|----------|--------------------------|--------------------------|--------------------------|
| RHF | D_{2d} | –946.923762 | –947.179769 | –947.199913 |
| RHF + MP2 | D_{2d} | –948.774009 ^a | –949.375179 ^b | –949.417614 ^b |
| ROHF | D_{4h} | –946.863033 | –947.130848 | –947.166403 |
| ROHF + MP2 | D_{4h} | –948.755303 ^a | –949.366354 ^b | –949.454267 ^b |
| ROHF | D_{2d} | | | –947.131604 |
| ROHF + MP2 | D_{2d} | | | –949.360802 |
| $\Delta\text{ZPE}(\text{ROHF} - \text{RHF})$ | | | –0.006877 | |
| AEA | | 0.011829 | 0.0019547 | –0.023530 ^c |

^a R(O)HF optimized geometry.

^b Geometry optimized at the full R(O)HF – MP2 level for the basis.

^c –0.0228 if the conventional 0.89 scaling factor for vibrational frequencies is applied.

Table 2
Optimized bond lengths in angstroms using MP2 energies for the different basis sets

| Basis set | $c\text{-C}_4\text{F}_8$ | | | $c\text{-C}_4\text{F}_8^-$ | |
|-----------|--------------------------|------------------|------------------|----------------------------|-------|
| | C-C | C-F ₁ | C-F ₂ | C-C | C-F |
| A | 1.552 | 1.342 | 1.353 | — | — |
| B | 1.557 | 1.333 | 1.343 | 1.499 | 1.407 |
| C | 1.561 | 1.332 | 1.343 | 1.502 | 1.405 |

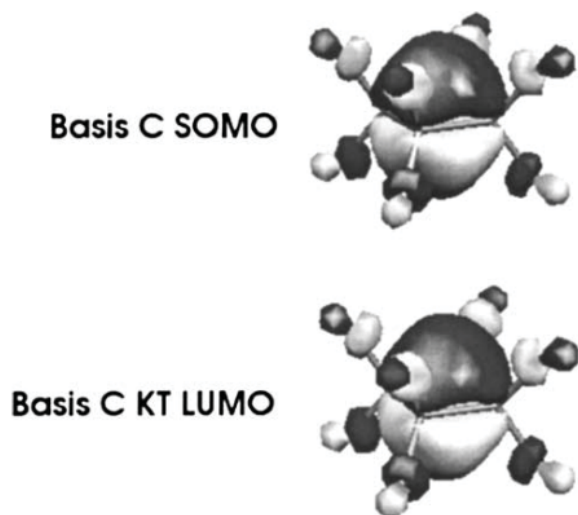


Fig. 1. The actual and the Koopmans' theorem representation of the a_{2u} SOMO using basis set C.

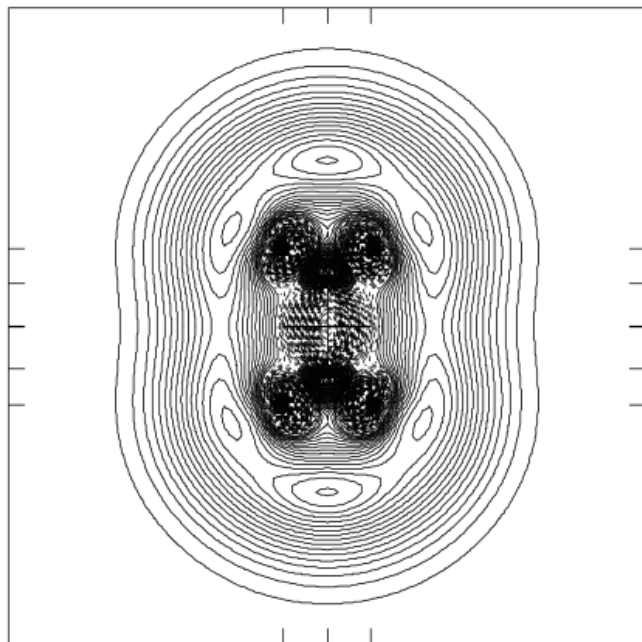


Fig. 2. A contour plot of the a_{1g} LUMO + 1 using basis set C. The contour is in a plane ($x-z$) containing 2 C and 4 F atoms at opposite corners of the molecule. The border around the contours is $16 \times 16 \text{ \AA}$, and the outside contour represents a probability amplitude of $0.001 (\text{bohr})^{-3/2}$.

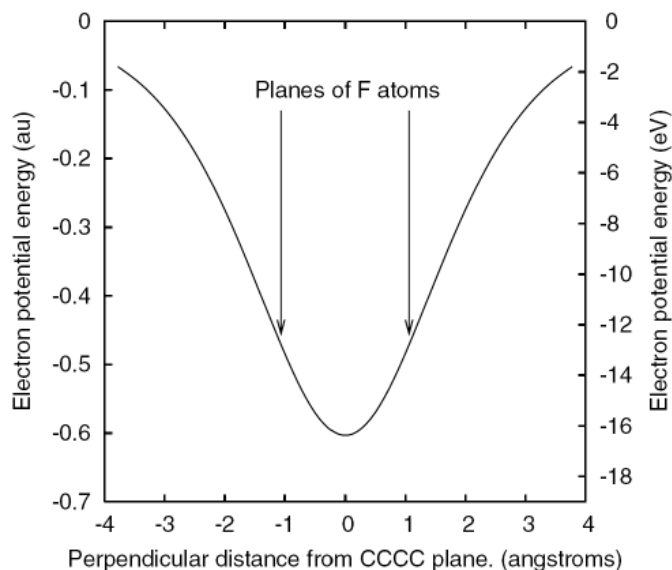


Fig. 3. The electron potential energy on a line perpendicular to the C-atom plane ($c\text{-C}_4\text{F}_8^-$ geometry) and going through the centre of the square. The places where the line intersects the planes of F-atoms are marked with arrows.

and the RHF LUMO + 1. Unfortunately, the software used to obtain Fig. 1 [8] cannot deal with such a diffuse orbital, and we instead show a contour plot in Fig. 2. As seen, it extends out to nearly 8.0 \AA and has a relatively small involvement in the vicinity of the atoms.

The electronegativities of C and F are quite different and are expected to produce a fairly large bond dipole. Since there are eight of them pointing roughly toward the center, it is not surprising that there is a fairly large positive electrical potential there. Fig. 3 shows the electron potential energy due to this potential along the z -axis of the D_{4h} symmetry constrained neutral molecule. The actual value of the potential at the origin is 0.6033 (a.u.), which, if such a model were to be used, would require a positive charge of $0.574|e|$ at the position of each C-atom with corresponding negative charges to produce electric neutrality at each F-atom.

As far as the state of the negative ion is concerned, we can only conjecture that a fairly delicate balance be-

tween the Pauli exclusion principal and the coulombic attraction yields an a_{2u} SOMO with one horizontal node.

4. Summary

Calculations of the energies of $c\text{-C}_4\text{F}_8$ and $c\text{-C}_4\text{F}_8^-$ with a 6311G(sp) basis at the R(O)HF – MP2 level at geometries optimized with a 6311G(d) basis at the R(O)HF – MP2 level yield an AEA of 0.640 eV. When the conventional correction to calculated vibrational frequencies of 0.89 is used the calculated AEA is reduced to 0.620 eV. This number is certainly in satisfactory agreement with the experimental FALP value of 0.63 ± 0.05 eV [4]. $c\text{-C}_4\text{F}_8^-$ is a somewhat unusual molecular negative ion whose stability can be attributed to the accumulated positive fields resulting from the eight C–F bond dipoles oriented with their positive ends near the center of the molecule.

Acknowledgement

The author wishes to thank the reviewer for a very useful comment.

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