

Ab Initio Calculations on the Lowest π State of Difluorocarbene Radical Cation

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Abstract: Ab initio calculations have been performed on the lowest π state of difluorocarbene radical cation, which is isoelectronic with the allyl radical. π MCSCF calculations on this state of CF_2^+ give broken symmetry solutions at C_{2v} geometries, unless C_{2v} symmetry is imposed on the orbitals. The tendency of the π MCSCF wave function to localize, even at C_{2v} geometries, provides evidence for the relative unimportance of resonance in this allylic radical. CI calculations that include correlation between σ and π electrons do not exhibit symmetry breaking at C_{2v} geometries, but they do predict the dissociation of the lowest π state of CF_2^+ into CF^+ and a fluorine atom. Additional CI calculations, including all single and double excitations and the Davidson correction for the effect of quadruples, indicate that the dissociation of this state of CF_2^+ is exothermic by 59 kcal/mol. The computed exothermicity is compared to an experimental estimate, and the reason for the favorability of C-F bond breaking is discussed.

We have shown that the importance of resonance in allylic radicals is greatly diminished when there is a large difference in electronegativity between the central and terminal atoms.¹ In order to further test the generality of this result, we have performed ab initio calculations on the lowest π state (2A_2) of difluorocarbene radical cation (CF_2^+). This state of CF_2^+ is isoelectronic with the lowest state of the allyl radical, but the nuclear structure of CF_2^+ results in a very large electronegativity difference between the central and terminal atoms. Consequently, allylic resonance is expected to be rather unimportant in CF_2^+ .

Results

Calculations were performed with the Dunning (9s/5p) \rightarrow (3s/2p) split-valence basis set, augmented by a set of d orbitals on each atom.² The optimal C_{2v} geometry for CF_2^+ was found with an MCSCF wave function consisting of the four 2A_2 spin-adapted configurations that arise from all possible assignments of the three π electrons to the three lowest molecular orbitals. The geometry optimization and subsequent MCSCF calculations were carried out with use of GAMESS.³

The optimal FCF bond angle in CF_2^+ was found to be 95.1° , which is nearly 10° smaller than the experimentally measured bond angle of 104.8° in neutral CF_2 .⁴ The predicted bond angle contraction on removal of an electron from the $1a_2$ π MO is consistent with the F-F antibonding character of this orbital. A similar bond angle contraction on going from four to three π electrons is evident in the photoelectron spectrum of the allyl anion.⁵

At the MCSCF level of theory the C-F bond length in the radical cation was found to be 1.356 Å. This is considerably longer than the experimental bond length of 1.304 Å in neutral CF_2 .⁴ Thus, despite the fact that the $1a_2$ MO is essentially nonbonding between fluorine and carbon, the removal of an electron from this orbital is calculated to have a significant effect on the C-F bond length.

Although the d_{xy} orbital on carbon does have a_2 symmetry, its coefficient in the $1a_2$ MO is only 0.02. Since the $1a_2$ MO is almost entirely localized on fluorine, creation of a hole in this orbital results in increased electron localization on fluorine in other molecular orbitals (e.g., in the $1b_1$ π MO, which is bonding between carbon and fluorine). The consequent reduction in net C-F bonding is presumably responsible for the lengthening of the bonds in CF_2^+ compared to CF_2 .

The π MCSCF calculations at the optimal C_{2v} geometry of CF_2^+ gave a computed energy of -236.1517 hartrees. However, when the calculations were repeated at the same C_{2v} geometry, but with only C_s symmetry imposed on the wave function, the energy of the eight configuration, C_s wave function was found to be lower than that of the four configuration, C_{2v} wave function by more than 0.003 hartree.

This tendency of the wave function to break symmetry is *not* an example of the well-known doublet instability of allylic π systems,⁶ which is eliminated with wave functions that provide correlation for the π electrons.⁷ Instead, the symmetry breaking in the π MCSCF wave function is indicative of an allylic resonance energy in CF_2^+ which is so small that electron localization occurs, even when π correlation is provided. Symmetry breaking at the π MCSCF level is not observed in other allylic radicals with smaller electronegativity differences between the central and terminal atoms.^{1,8}

Symmetry breaking occurs in the π MCSCF wave function for CF_2^+ because this wave function provides no correlation between the σ and π electrons. In the absence of such correlation, σ electrons tend to favor localized π wave functions in charged molecules.^{7c,e,9} In order to provide such correlation for CF_2^+ , we performed CI calculations that included all single σ excitations from all four (eight in C_s symmetry) of the spin-adapted configurations that arise from occupation of the three lowest π MO's by three electrons. Modification of the π MO's upon inclusion of σ - π correlation was allowed by simultaneously permitting single excitations in the π space.

The CI calculations were performed with the MELD package of ab initio programs.¹⁰ The calculations involved 16 627 spin-adapted configurations with C_{2v} symmetry imposed on the wave function and 33 255 with C_s symmetry. At C_{2v} geometries, starting with either RHF or MCSCF MO's, the CI calculations with C_{2v} symmetry orbitals gave lower energies by 0.0027 hartree than the corresponding CI calculations with broken symmetry C_s orbitals. At the CI level, starting with C_{2v} MCSCF MO's, the energy was computed to be -236.3252 hartrees at an optimal C-F bond length of 1.382 Å. The C_{2v} RHF MO's gave an energy 0.0014 hartree higher.

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The change in the energy of CF_2^+ on asymmetric distortion of the C–F bond lengths from equality was investigated at both the MCSCF and CI levels of theory. It was anticipated that such a distortion would be found to be favorable at the MCSCF level, since the π MCSCF wave function does not have C_{2v} symmetry, unless this symmetry is imposed upon it. However, attempts to optimize a C_s geometry at the π MCSCF level led not to an equilibrium geometry with slightly unequal C–F bond lengths but to complete dissociation of CF_2^+ to CF^+ and a fluorine atom.

This π MCSCF result was confirmed by CI calculations which included all single excitations from the eight configurations that arise from distributing three π electrons among the three lowest π MOs. As discussed above, this type of CI wave function, unlike the π MCSCF wave function, does not exhibit symmetry breaking. Therefore, in principle, the CI wave function could have found a C_{2v} equilibrium geometry for CF_2^+ . Nevertheless, CI calculations, performed with either RHF or MCSCF MOs, also showed a monotonic decrease in the energy on asymmetric distortion of the C–F bond lengths from those at the optimal C_{2v} geometry.

In order to verify that dissociation of the lowest π state of CF_2^+ to CF^+ and a fluorine atom is, indeed, energetically favorable, a different type of CI calculation was performed for CF_2^+ and its dissociation products. All single and double (SD) excitations were allowed from the Hartree–Fock configuration at both the optimized C_{2v} geometry and at a linear geometry for the dissociation products with one C–F bond length optimized for CF^+ and the other set at 20 Å. The calculation at the C_{2v} geometry involved 25 421 spin-adapted configurations. The calculation at the linear geometry for the dissociation products was also carried out in C_{2v} symmetry, with the C_2 axis passing through the three atoms. The latter SD–CI calculation involved 26 400 spin-adapted configurations.

An optimal CF^+ bond length of 1.146 Å was found at the SCF level, and 1.169 Å was obtained from SD–CI calculations on this fragment. An experimentally determined bond length of 1.148 Å has been reported for CF^+ .¹¹ At the SD–CI level of theory the energy of CF^+ was -137.1307 hartrees and that of a fluorine atom -99.5246 hartrees. The sum of these SD–CI energies (-236.6553 hartrees) is lower by 0.0165 hartree than the SD–CI energy of -236.6388 hartrees computed for the dissociation products when they are treated as a linear supermolecule.

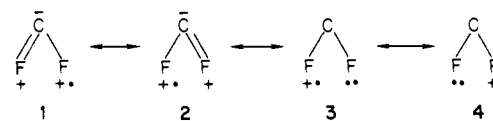
The energy difference between the two calculations on the dissociation products arises from the fact that performing individual SD–CI calculations on each of the fragments is tantamount to allowing some quadruple excitations in the CI calculation on the dissociation products when they are treated as a linear supermolecule.¹² It was precisely because of this size-consistency problem that SD–CI calculations were performed on the linear supermolecule, so that comparison of the energy of CF_2^+ with that of its fragmentation products would not be spuriously biased toward favoring the latter.

The SD–CI energy computed for CF_2^+ at the optimized C_{2v} geometry was -236.5245 hartrees, fully 0.1143 hartree (71.7 kcal/mol) higher than that of the dissociated supermolecule. Because electron correlation is more important in CF_2^+ than in the fragmentation products, applying the Davidson correction for quadruple excitations¹² to the individual SD–CI energies reduces the energy difference to 0.096 hartree (59.1 kcal/mol). Thus, despite the fact that the lowest π state of CF_2^+ is isoelectronic with the allyl radical, our computational results unequivocally predict that in the lowest 2A_2 state CF_2^+ will dissociate.

Discussion

The reason that the lowest π state of CF_2^+ is computed to be dissociative is essentially the same as the reason that allylic resonance is expected to be relatively unimportant in this radical. The greater electronegativity of fluorine compared to carbon is responsible for the unimportance of resonance structures like **1** and **2**, whose analogues provide stabilization for allyl. This

difference in electronegativity also favors rupturing the C–F bond to the positively charged fluorine, so that, as this fluorine atom departs with the electron pair from the bond, the positive hole is transferred from fluorine to carbon.¹³



The photoelectron spectrum of CF_2 ¹⁴ provides evidence for the energetic favorability of creating a positive hole on carbon rather than on fluorine. The lowest energy ionization corresponds to the removal of an electron from the lone pair ($6a_1$) orbital, localized largely on carbon. The adiabatic ionization potential of an electron from this orbital is 11.4 eV. The band corresponding to vertical ionization from the $1a_2$ MO, which, as discussed above, is essentially a nonbonding combination of π orbitals on fluorine, is observed at 17.4 eV. The resulting difference in ionization potentials (6.0 eV) corresponds to 138 kcal/mol.

Unlike the ionization from $6a_1$, no vibrational structure is visible in the ionization from $1a_2$. The lack of vibrational structure is consistent with the predicted dissociation of the lowest π state of CF_2^+ , which is formed by this ionization. On the basis of our computational results, ionization from $1a_2$ is expected to lead adiabatically to the formation of CF^+ and a fluorine atom; so no vibrational structure is expected.

Additional evidence for the correctness of the predicted dissociation of the lowest π state of CF_2^+ also can be obtained from the photoelectron spectrum of CF_2 . Because the 2P state of the fluorine atom is triply degenerate, both the ground state (2A_1) and the lowest π state (2A_2) of CF_2^+ correlate with CF^+ and a 2P fluorine atom. Therefore, the difference in the C–F bond dissociation energies between the two states is equal to the difference between the energies of these two states. If the latter difference is taken from the photoelectron spectrum as 138 kcal/mol, dissociation of the lowest π state of CF_2^+ is predicted, unless the C–F bond dissociation energy of the ground state exceeds this value.

In fact, thermodynamic estimates of the C–F bond dissociation energy of the ground state of CF_2^+ are barely half this amount. Taking the bond dissociation energy of ground-state CF_2^+ as 72 kcal/mol,¹⁵ the π state, at the geometry of neutral CF_2 , is expected to undergo loss of a fluorine atom with an exothermicity of 66 kcal/mol.¹⁶

Our SDQ–CI computed value of 59 kcal/mol for the exothermicity of bond dissociation in the lowest π state of CF_2^+ compares reasonably well with the value estimated from experimental data. Moreover, it should be noted that our computed value is based on the energy of this state at its optimal C_{2v} geometry, whereas the experimental value is based on the energy at the geometry of neutral CF_2 . Since for the lowest π state of CF_2^+ the latter geometry is higher in energy than the C_{2v} geometry at which we performed the calculation, repeating our C_{2v} calculation at the geometry of neutral CF_2 would raise the computed exothermicity of bond dissociation and presumably bring it into even closer agreement with experiment.¹⁷

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Registry No. Difluorocarbene radical cation, 54250-40-7.

(13) The formally empty orbitals on carbon in CF^+ are stabilized by delocalization of the π lone pairs on fluorine. This accounts for the short bond length in CF^+ , which is close to that in CO , with which CF^+ is isoelectronic.

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(16) The same argument can be used to show that the 2B_2 σ state of CF_2^+ , which in the PE spectrum of CF_2 appears about 1.0 eV below the lowest π state, will dissociate to CF^+ and a fluorine atom with an exothermicity of 43 kcal/mol.

(17) An accurate comparison of the computed and experimental values would also require correction for the difference in zero-point vibrational energies between the lowest π state of CF_2^+ and CF^+ .

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