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Low-Lying Electronic States of HCF$^-$ and HCF

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The ground ($^1A'$) and low-lying excited states ($^1A''$, $^3A''$) of HCF and the ground ($^2A''$) and excited ($^2A'$) states of HCF$^-$ are examined via ab initio quantum-chemical methods. The anion is found to be stable relative to HCF by at least 21.7 kcal/mol. The $^2A'' \rightarrow {}^2A'$ electronic transition in HCF$^-$ is predicted to occur at ~18700 cm^{-1} which is at higher energy than the (observed) corresponding transition ($^1A' \rightarrow {}^1A''$) of neutral HCF.

Introduction

The primary goal of the work discussed in this paper is to estimate the relative stabilities of the $^2A''$ and $^2A'$ states of the fluorocarbene anion HCF$^-$ and the $^1A''$ and $^3A''$ states of HCF. Previous theoretical work has been done on the low-lying states of this neutral carbene ($^1A'$, $^3A''$) by Bauschlichter, Schaefer, and Bagus,[1] who described the triplet state with a single-determinant self-consistent field (SCF) wave functon and the singlet state with a two-configuration SCF wave function (because of the near degeneracy of the $(7a')^2$ and $(2a'')^2$ configurations which is common to most carbenes). Based upon past experience[1-6] in evaluating such energy differences via one- and two-configuration wave functions, the $^1A' \rightarrow {}^3A''$ splitting of 9.2 kcal/mol obtained in ref 1 is thought to be reasonably accurate (±5 kcal/mol).

In the present paper we present, for both the neutral and anionic states of this carbene, total electronic energies and electronically adiabatic energy splitting which have been obtained through configuration-interaction (CI) calculations involving ~2000 electronic configurations for each electronic state. The dominant configuration of the $^2A''$ state (ground state) of the anion is described by the orbital occupancy $(1a')^2 (2a')^2 (3a')^2 (4a')^2 (5a')^2 (6a')^2 (1a'')^2 (7a')^2\, 2a''$, where the 7a′ and 2a″ orbitals describe the σ and π "carbene center" orbitals on carbon. The Slater determinant corresponding to this orbital occupancy was found to have an expansion coefficient of 0.932 in our 1400-configuration CI wave function when the multiconfiguration SCF (MCSCF) orbitals described below were used to construct the configurations. The $^2A'$ excited state of the ion can be approximately described by the orbital occupancy $(1a')^2 (2a')^2 (3a')^2 (4a')^2 (5a')^2 (6a')^2 (1a'')^2 (2a'')^2\, 7a'$. The corresponding Slater determinant was found to possess an expansion coefficient of 0.947 in our 1943-configuration CI wave function which also employed MCSCF orbitals appropriate for this state. For the $^1A''$ and $^3A''$ states of HCF neutral, we also found the CI wave function to be dominated by single configurations having 2a″ 7a′ orbital occupancy, whereas the $^1A'$ ground state required, as expected,[1-6] two dominant configurations with $(2a'')^2$ and $(7a')^2$ occupancy.

The $^2A'' \rightarrow {}^2A'$ transition of the HCF$^-$ species was suggested by Andrews[7] to account for an observed transition[8] whose peak absorption occurs at 15400 ± 100 cm^{-1}. Our interest in HCF$^-$ was sparked by this observation, and we therefore decided to attempt to gain information which might permit us to verify or refute Andrews' prediction via quantum-chemical calculations. In so doing, we carried out calculations at the CI level (using ~1000–2000 configurations) on both of the anion states and on the three low-energy states of the neutral molecule. The calculations on the neutral molecule were undertaken to allow us to test our results against those of Baushlichter et al.[1] and make a prediction of the electron affinity of HCF. Our computational procedures and results are discussed below.

TABLE I: Gaussian Basis Set Used

atom	orbital type	exponent	contraction coeff
C	s	0.4233×10^4	0.2029×10^{-2}
		0.6349×10^3	0.1554×10^{-1}
		0.1461×10^3	0.7541×10^{-1}
		0.4250×10^2	0.2571
		0.1419×10^2	0.5966
		0.1967×10^2	0.2425
	s	0.5148×10^1	1.0
	s	0.4962	1.0
	s	0.1533	1.0
	p	0.1816×10^2	0.1853×10^{-1}
		0.3986×10	0.1154
		0.1143×10	0.3862
		0.3594	0.6401
	p	0.1146	1.0
	d	0.6769	1.0
H	s	0.1335×10^2	0.1308
		0.2013×10	0.9215
	s	0.1233	1.0
	s	0.4538	1.0
F	s	0.9995×10^4	0.2017×10^{-2}
		0.1506×10^4	0.1529×10^{-1}
		0.3503×10^3	0.7311×10^{-1}
		0.1041×10^3	0.2464
		0.3484×10^2	0.6126
		0.4369×10	0.2425
	s	0.1222×10^2	1.0
	s	0.1208×10	1.0
	s	0.3634	1.0
	p	0.4436×10^2	0.2087×10^{-1}
		0.1008×10^2	0.1301
		0.2996×10	0.3962
		0.9383	0.6204
	p	0.2733	1.0

Atomic Basis Sets

Except for the d orbital on the carbon atom, the basis sets used were taken from Dunning's tabulation of con-

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(1) C. W. Bauschlichter, Jr., H. F. Schaefer III, and P. S. Bagus, *J. Am. Chem. Soc.*, **99**, 7106 (1977).

(2) L. B. Harding and W. A. Goddard III, *Chem. Phys. Lett.*, **55**, 217 (1978), and references therein.

(3) S. Shih, S. D. Peyerimhoff, R. J. Buenker, and M. Peric, *Chem. Phys. Lett.*, **55**, 206 (1978), and references therein.

(4) C. W. Bauschlichter, Jr., and I. Shavitt, *J. Am. Chem. Soc.*, **100**, 739 (1978); L. B. Harding and W. A. Goddard III, *J. Chem. Phys.*, **67**, 1777 (1977); B. O. Roos and P. M. Siegbahn, *J. Am. Chem. Soc.*, **99**, 7716 (1977); R. R. Lucchese and H. F. Schaefer III, *ibid.*, **99**, 6766 (1977).

(5) For a reasonably extensive review of the situation on CH_2 prior to 1975, see J. F. Harrison, *Acc. Chem. Res.*, **7**, 378 (1974).

(6) J. W. Kenney III, J. Simons, G. D. Purvis, and R. J. Bartlett, *J. Am. Chem. Soc.*, **100**, 6930 (1978); R. Shepard, A. Banerjee, and J. Simons, *ibid.*, **101**, 6174 (1979).

(7) L. Andrews, private communication to J.S.

(8) L. Andrews and F. T. Prochaska, *J. Chem. Phys.*, **70**, 4714 (1979).

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TABLE II: Configuration Interaction Energies for HCF and HCF$^-$

state	R(CH), Å	R(CF), Å	θ, deg	E, hartree	no. of configurations
$^1A'$	1.161	1.325	102.2	−137.884 537	2128
$^1A'$	1.161	1.325	102.2	−137.799 569	2
$^1A'$	1.111	1.325	102.2	−137.802 72[a]	2
$^3A''$	1.077	1.321	120.4	−137.808 997	2296
$^3A''$	1.077	1.321	120.4	−137.788 13[a]	1
$^1A''$	1.077	1.321	120.4	−137.748 976	2296
$^1A''$	1.114	1.537	102.2	−137.858 228	1400
$^2A'$	1.080	1.480	115	−137.772 842	1943

[a] Bauschlichter et al., ref 1.

tracted Gaussians.[9] For the hydrogen-atom basis we used Dunning's 4s/3s contraction of Huzinaga's primitive set[10] (with a scale factor of 1.2); for fluorine and carbon we used his 9s5p/4s2p contractions of Huzinaga's primitive sets.

In our initial calculations on HCF$^-$, we explored decreasing the exponent of the most diffuse carbon s function (making it more diffuse) by a factor of 3, but this yielded a higher energy than with the original basis and was therefore not pursued further. After carrying out geometry variations on both states of the anion at the SCF (UHF) level, we added a d atomic basis function with exponent 0.6769[6] to the carbon atom. This d function, which has been found to be important in most studies of such carbenes,[1-6] was used in all of the subsequent unitary CI (UCI) calculations discussed below. Our final basis is listed in Table I.

Geometry Optimization

To obtain starting geometries for all five states, we used the optimal geometries found by Bauschlichter et al. in their calculations on the $^1A'$ and $^3A''$ states of the neutral molecule. For the $^2A'$ anion state we started with Bauschlichter's $^3A''$ geometry, since both species have the 7a′ orbital singly occupied, and for the $^2A''$ state we started with the $^1A'$ geometry of ref 1. For the $^1A''$ state of HCF we used the same geometry as for the $^3A''$ since both states have identical orbital occupancy (but different spin couplings). In our calculations on the neutral molecule, we varied (at the CI level) the bond lengths R(CH) and R(CF) and the HCF angle θ in the neighborhood of Bauschlichter's geometries. For the ionic states, we varied the same geometrical parameters first at the UHF level (without the d function on carbon) and subsequently at the UCI level after addition of the d function to the carbon atom. These geometry variations were not carried out with the aid of a gradient program. They were done simply by varying one geometrical parameter at a time. These optimized geometries are listed in Table II.

State Energy Calculations and Configuration Selection

Our initial anion calculations were done at the UHF level in order to consider the effects of geometry variations on the anion state energies. Once these roughly optimized geometries were determined, the following sequence of calculations was performed (on all states). We first carried out single-configuration restricted Hartree–Fock (RHF) calculations on each state as a first step toward obtaining decent molecular orbitals. We then performed small "configuration selection" CI calculations which were designed to find the *few* most important configurations for each state. Such configuration selections generated singly and doubly excited configurations from the one configuration which had been used to perform the RHF calculation. The state energy lowerings attributed to each of these configurations were used to choose the most important such configurations.

MCSCF calculations were then performed by using the five most dominant configurations for each state as determined by the configuration selections discussed above. The primary purpose of these MCSCF calculations was to improve the molecular orbitals used to construct the determinants because the initial RHF orbitals are known to be particularly poor for use in CI calculations (especially for the $^1A'$ state of the neutral carbene which requires a two-configuration wave function for even a qualitatively correct treatment).

Further configuration selection CI calculations were then carried out to determine the few most important configurations arising with the improved (MCSCF) molecular orbitals. Not surprisingly, the MCSCF orbital optimization caused more doubly excited configurations to become important in each of the resultant five CI reference wave functions. For each state, the five most dominant configurations as determined in these selections were then used to generate new MCSCF orbitals for use in the graphical unitary group CI (UCI) calculations which represent our final and most extensive set of calculations. The UCI configuration envelope, as described by the distinct row table (DRT) discussed in ref 11, was constructed so as to permit excitations to occur out of the few most important configurations of each state. The maximum level of the excitation and the number of MCSCF orbitals into which excitations were permitted to occur were determined by the space limitations of our computer. This final DRT configuration construction procedure resulted, for the $^1A'$, $^1A''$, $^3A''$, $^2A''$, and $^2A'$ species, in 2128, 2296, 2296, 1400, and 1976 configurations, respectively. Given the configuration lists, in terms of MCSCF orbitals, thus determined, we proceeded to carry out the geometry optimizations discussed above.

In performing the geometry variations for each of the states at the UCI level, the following computational sequence was used. First, an RHF calculation was carried out at the geometry whose energy was to be determined. Secondly, a five-configuration MCSCF calculation was done by using configurations chosen by our selection scheme for the preceding geometry. Next, a UCI calculation was performed by using the same configuration list (DRT) as was employed for the preceding geometry. The results of such geometry searching permit us to report, in Table II, our estimates of the total (electronic plus nuclear repulsion) energies of these five states at their respective minimum-energy geometries.

Results and Discussion

For the $^1A'$ state of HCF we obtained a UCI energy of −137.884 537 au by using 2128 configurations, which is considerably below ref 1's two-configuration energy of −137.802 72 au. For this species, our optimum geometry differed from Bauschlichter's only in the C–H bond length, ours being longer by 0.05 Å. For the $^3A''$ HCF, our 2296-configuration energy is −137.808 997 au, and for this state our optimum geometry was identical with that of Bauschlichter, who obtained a one-configuration energy of −137.788 13 au. When one makes direct use of our UCI energies, the resulting $^1A' \rightarrow {}^3A''$ splitting of HCF is predicted to be 47.4 kcal/mol, which is not at all in agreement with the splitting of only 9.2 kcal/mol found in ref 1. Since

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(9) T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).

(10) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).

(11) I. Shavitt, *Int. J. Quantum Chem.*, **S11**, 131 (1977).

we have good reason to believe that the 9.2 kcal/mol value is more nearly correct, this large discrepancy in the splitting most probably arises from a unequal treatment of the correlation in the $^1A'$ and $^3A''$ states in our larger UCI calculations. As can be seen from Table II, our UCI energy for the $^1A'$ state is lower than our (or that of ref 1) two-configuration energy for the same state by ~4 times the energy difference between our UCI $^3A''$ energy and Bauschlichter's one-configuration $^3A''$ energy. The fact that our $^1A'$ and $^3A''$ geometries are really identical with those of ref 1 and that our basis yields a two-configuration $^1A'$ energy within 0.003 au of Bauschlichter's energy leads us to believe that neither basis-set difference nor geometry difference can account for the discrepancy in the computed splittings. It is our belief that in constructing distinct row tables for use in generating configurations for the CI calculations the emphasis placed on single and double excitations (to the exclusion of triple excitations) biased the DRTs toward the $^1A'$ state of HCF. At our UCI level of calculation the closed-shell, $^1A'$ species thus seems to be lowered with respect to all the other species. The factor which distinguishes $^1A'$ HCF from $^1A''$ and $^3A''$ HCF and $^2A'$ and $^2A''$ HCF⁻ is the presence of the "empty" low-energy valence orbital of a″ symmetry. In all four of the other species, this orbital is occupied, and hence the electron correlations, which are most commonly described in terms of "exciting" two occupied orbitals into "virtual" or "unoccupied orbitals", no longer have this empty 2a″ orbital to use as a virtual orbital. Hence, it is likely that all states except the $^1A'$ require triple excitations (which involve excitation of the occupied 2a″ orbital and some other orbitals) to achieve a description which is comparable to that reached for the $^1A'$ with a single- and double-CI wave function. On the basis of this belief that our $^1A'$ state energy is "too low", we decided to shift all of the other four state energies ($^1A''$, $^3A''$, $^2A'$, $^2A''$) down by an amount (13 370 cm^{-1}) which would make our $^1A' \rightarrow {}^3A''$ splitting agree with Bauschlichter's small-CI result.

As an independent check on this "energy shifting" idea, we decided to compute the $^1A' \rightarrow {}^1A''$ energy splitting whose 0 → 0 transition energy is known from gas-phase spectroscopic measurements[12] to be 17 287 cm^{-1}. Our CI-computed $^1A''$ state energy is −137.748 976, which, if we were to use our original $^1A'$ CI energy, would yield a splitting of 29 756 cm^{-1}. If, however, we use the $^1A'$ energy which has been shifted by the previously mentioned 13 370 cm^{-1}, we obtain a $^1A' \rightarrow {}^1A''$ splitting of 16 400 cm^{-1}, which is in quite good agreement with the experimental result of 17 287 cm^{-1}. It therefore seems that it is the unequal lowering of the closed-shell $^1A'$ state of HCF with respect to all other states (in our larger CIs) which causes the discrepancies in state splittings involving the $^1A'$ state.

In our 1400-configuration calculation on the $^2A''$ ground state of the HCF⁻ anion, we obtained an energy of −137.858 228 au, whereas our 1943-configuration energy for the $^2A'$ state of the ion is −137.772 842 au. These results produce a $^2A'' \rightarrow {}^2A'$ splitting of 18 742 cm^{-1}, which is substantially larger than the energy difference giving rise to the peak at 15 400 ± 100 cm^{-1} speculated by Andrews[7] to be due to the $^2A' \rightarrow {}^2A''$ transition of HCF⁻. Perhaps more importantly, we predict the spectroscopically allowed $^2A'' \rightarrow {}^1A'$ anion transition energy to be larger than the corresponding $^1A' \rightarrow {}^1A''$ allowed transition in HCF neutral. Both transitions involve a 7a′ → 2a″ orbital excitation, but in the anion transition the 2a″ orbital has an electron in it before the transition occurs. Thus, it is probably the repulsion energy arising from the two electrons in the 2a″ orbital of the $^2A'$ anion which gives rise to the increased transition energy. In order to attribute the $^2A'' \rightarrow {}^2A'$ transition to the observed 15 400-cm^{-1} absorption, one would have to claim that the $^2A''$ state has been preferentially solvated by 3300 cm^{-1} in Andrews experiment.[8]

The electron affinity of CHF is determined by the $^1A' \rightarrow {}^2A''$ energy difference. Again, by using our original CI energies for both of these states we would predict that there exists no stable anion for this carbene; this prediction is clearly in error. If we continue with the postulate, however, that the $^1A'$ state is preferentially lowered by ~13 400 cm^{-1} and therefore raise the $^1A'$ state by that amount, we obtain an electron-affinity estimate of 21.7 kcal/mol for HCF. The corresponding ($^2B_1 \rightarrow {}^1A_1$) electron affinity of CH_2 was found in ref 3 to be ~24.4 kcal/mol. However, to obtain this value Shih et al. had to assume, based upon their experience with similar basis sets and configuration lists for anions, that the correlation energy of the CH_2^- anion states is underestimated by ~0.24 eV. If we were to make this same assumption, our computed electron affinity would increase to 27.3 kcal/mol. Thus we feel that 21.7 kcal/mol is a lower limit to the electron affinity of HCF.

Summary

We have found that, by shifting the $^1A'$ state of HCF by 13 370 cm^{-1} relative to the other four states of HCF ($^1A''$, $^3A''$) and HCF⁻ ($^2A''$, $^2A'$), we are able to achieve a reasonably accurate value for the $^1A' \rightarrow {}^1A''$ transition energy[13] in HCF (which is experimentally known). This fact then lends support to the $^1A' \rightarrow {}^3A''$ splitting of 9.2 kcal/mol reported by Bauschlichter et al. We also predict that $^2A''$ HCF⁻ should be stable relative to $^1A'$ HCF by at least 21.7 kcal/mol and that the gas-phase $^2A'' \rightarrow {}^2A'$ energy difference in HCF⁻ should be 18 742 cm^{-1}. This latter fact leads us to conclude that the absorption *maximum* reported by Andrews at 15 400 cm^{-1} (the 0 → 0 transition, which should be compared with our number, would then occur at *lower* energy) is not likely to be due to the $^2A'' \rightarrow {}^2A'$ HCF⁻ transition unless solvation were to preferentially stabilize the $^2A''$ state by more than 3000 cm^{-1}.

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[12] A. J. Merer and D. N. Travis, *Can. J. Phys.*, 44, 1541 (1966).

[13] We could have chosen to shift the $^1A'$ state to give agreement with this $^1A' \rightarrow {}^1A''$ transition energy instead. This would increase our predicted $^1A' \rightarrow {}^3A''$ splitting by 2.6 kcal/mol and would decrease our electron affinity of HCF by this same amount. The accuracy of our calculations is no better than this uncertainty.