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Equilibrium C−F Bond Length and the Structure of Formyl Fluoride, Difluorocarbene, Monofluoromethylene, and Difluoromethane

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Highly correlated ab initio calculations with large basis sets are reported for formyl fluoride, OCHF; difluorocarbene, CF_2; monofluoromethylene, CHF, and difluoromethane, CH_2F_2. Based on CCSD(T)/cc-pVQZ results (including a correction for the effect of diffuse functions on fluorine and oxygen), equilibrium structures are derived. These structures are compared to experimental results, when available, and to those of similar molecules; and their accuracy is discussed.

Introduction

The determination of the experimental structure of a fluorine derivative is a difficult problem because there is only one stable isotope for fluorine, making studies of isotopic species impossible. In fact, very few accurate structures of such molecules have been determined so far. Furthermore, in some cases, the derived geometry is obviously inaccurate. The calculation of a reliable ab initio structure is further complicated by the fact that fluorine is a highly electronegative atom which requires very large basis sets and highly correlated methods. However, this problem is now tractable, at least for small molecules. Inconsistencies in the structure of formyl fluoride, O═CHF, prompted us to try to determine an accurate structure for this molecule. During the course of this work, we found it useful to redetermine the structure of a few simple fluorocarbons in order to check the accuracy and the capabability of the method used and to extend our knowledge of the C−F bond.

Many studies, both experimental and theoretical, have already been devoted to formyl fluoride because it is a small polyatomic molecule (4 atoms belonging to the first row of the periodic classification) and a fluorine substituted formaldehyde. Particularly, its reactivity has been studied in great detail (see for instance ref 1 and references therein). This prompted several theoretical studies of the potential energy surface.[1−3] These investigations pointed out a great uncertainty in the geometric structure of this molecule. The structure of formyl fluoride has indeed been determined by electron diffraction[4] but the resulting parameters are rather imprecise (for instance there is an uncertainty of 4° for the ∠(OCH) angle and 0.020 Å for the CH bond length); furthermore this structure is an r_g structure which is significantly different from the equilibrium structure.

The rotational spectrum of formyl fluoride has been studied in some detail leading to the determination of several effective structures (r_o).[5−7] But, again, these structures are inaccurate because they are calculated from the uncorrected ground-state rotational constants even though vibration−rotation effects are expected to be large for a molecule with such large rotational constants. Furthermore, no isotopic substitution is possible for fluorine and the carbon and hydrogen atoms are close to the *b*-principal axis. In conclusion, the coordinates of F, C, and H are not expected to be accurate. However the high resolution infrared spectra of all fundamental bands of OCHF were recently studied. First, Wong et al.[8] measured the ν_2 band using a combination of laser Stark and Fourier transform spectroscopies. Later, the same group analyzed the five remaining fundamental bands which were recorded with a Fourier transform spectrometer.[9] Thus, in principle, the equilibrium rotational constants of the parent species are available. But, as the molecule is planar, the three moments of inertia are not independent, and these experiments only give us two independent data points to determine five structural parameters.

However it is now well established that the equilibrium structure of a simple molecule can be accurately determined with high-level coupled cluster methods and large basis sets.[10−15] The goal of the present paper is to determine an ab initio structure for formyl fluoride and to try to estimate its accuracy. Whereas our prime interest was the determination of an accurate structure for formyl fluoride, we also calculated the structure of a few other simple fluorocarbons whose equilibrium structure is not yet firmly established: dicarbene, monofluoromethylene, and difluoromethane.

The transient species dicarbene (or difluoromethylene), CF_2 has been the subject of many studies (see refs 16−21, and references therein) because it is an important intermediate in fluorine chemistry (particularly in the dissociation of fluorocarbons) and it is one of the most stable gas-phase carbenes. Its electronic ground state is $\tilde{X}(^1A_1)$. The effective (r_o) structure was determined quite early[16] and an accurate average (r_z) structure was calculated in 1973.[17] Since that time, accurate ground-state rotational constants have been obtained from millimeterwave spectroscopy[18] and the rotational constants of the three excited fundamental vibrational states have been determined either by high-resolution Fourier transform spec-

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troscopy[19] or by infrared diode laser spectroscopy.[20] Thus, there is enough experimental information available to determine an equilibrium (r_e) structure, but, surprisingly, this does not seem to have been done. Many theoretical investigations have been reported for CF_2 (ref 21 and references therein). A paper particularly relevant to our work is that of Cameron et al.[21] where the geometry and harmonic force field have been calculated ab initio using the complete active space SCF method and Dunning's correlation-consistent polarized triple-ζ cc-pVTZ basis set.

Monofluoromethylene, HCF, has also received much attention from a spectroscopic point of view. But, as it is less stable and less symmetric (C_s instead of C_{2v}) than CF_2, there is not enough experimental information to determine an equilibrium structure and only an r_0 structure was obtained from the ground state rotational constants of CHF and CDF.[22] This structure, involving the substitution of hydrogen by deuterium, is not expected to be accurate.[23] Many ab initio calculations have been carried out on HCF. One of the most recent reports a CCSD(T)/6−311++G** structure.[24]

Many spectroscopic studies have also been devoted to difluoromethane, CH_2F_2. Accurate ground-state rotational constants have been determined by millimeterwave spectroscopy.[25] The microwave spectra of several excited states have been analyzed by Hirota[26] who deduced a cubic force field and an approximate r_e structure.[27] The infrared spectrum has also been analyzed in great detail, particularly to assign submillimeter emissions.[28] Many ab initio calculations have also been dedicated to CH_2F_2. Particularly relevant to this work, a MP2/6-31G** quartic force field was recently calculated.[29] This study showed a rather large discrepancy between the ab initio structure and the experimental r_e structure of Hirota:[27] 0.0067 Å for the CH bond, 0.0154 Å for the CF bond, and 0.9° for the ∠(HCH) angle. These deviations are much too large and justify a new study.

Computational Details

The calculations with all electrons correlated were performed with the ACES II program[30] whereas for the frozen core approximation the Gaussian 94 program[31] was used.

To obtain good accuracy (i.e., about 0.001 Å for bond lengths and 0.2° for angles) it is sufficient to use the coupled-cluster theory with single and double excitations[32] augmented by a perturbational estimate of triple excitation effects: CCSD(T).[33] A higher level of theory in which the triple excitations are included exactly does not bring much gain in accuracy[34] which is fortunate because such a method is computationally demanding. On the other hand, very large basis sets of at least quadruple-ζ quality are required, particularly in the case of a fluorine compound as was recently shown on methyl fluoride, CH_3F.[35] The well-known Dunning's correlation-consistent polarized valence basis sets labeled cc-pVnZ (with n = D, T, Q) were employed.[36]

The calculations have been carried out with all electrons correlated. In principle, to correctly calculate the core correlation, it is necessary to use a core-valence cc-pCVnZ basis set[37,38] because the valence cc-pVnZ basis sets overestimate the core-correlation effect. This is important only for distances because the effect of core-correlation is almost negligible for angles. Furthermore this effect of core-correlation is almost constant for a given bond and can be corrected, if necessary, if it has already been rigorously calculated on a structurally similar molecule. This is lucky because the calculations are much easier with the cc-pVQZ basis set than with the huge cc-pCVQZ basis set. Furthermore, the cc-pVQZ basis set with all electrons correlated gives results which are closer to the equilibrium values than does the frozen core approximation.[12,34] Finally, the overestimation of the core-correlation is small and it is important to point out that the CCSD(T)/cc-pVQZ method with all electrons correlated gives bond lengths between first row atoms that lie within 0.002 Å of experimental values, the error being almost systematic for a given bond.[12,34]

TABLE 1: Influence of Diffuse Functions on the ab initio Structure: Comparison of the CCSD(T) and MP2 Methods (Distances in Å and Angles in Degrees)[a]

		CCSD(T)			MP2		
		AUG	N	diff.	AUG	N	diff.
CO	r(CO)	1.1318	1.1314	0.0004	1.1352	1.1346	0.0006
HF	r(HF)	0.9177	0.9162	0.0015	0.9186	0.9174	0.0012
NH_3	r(NH)	1.0128	1.0124	0.0004	1.0101	1.0098	0.0003
H_2O	r(OH)	0.9589	0.9579	0.0011	0.9588	0.9577	0.0011
CH_3F	r(CF)	1.3855	1.3824	0.0031	1.3854	1.3820	0.0034
CHF	r(CF)	1.3067	1.3052	0.0015	1.3062	1.3042	0.0020
NH_3	∠(HNH)	106.52	106.18	0.34	106.87	106.47	0.40
H_2O	∠(HOH)	104.36	104.12	0.24	104.26	104.02	0.24
CH_3F	∠(HCH)	110.22	110.03	0.19	110.22	110.03	0.19
CHF	∠(CHF)	102.33	102.42	−0.09	102.24	102.32	−0.09
FNO	∠(FNO)	109.86	110.16	−0.30	110.15	110.43	−0.28

[a] The cc-pVQZ basis set was used: AUG = aug-cc-pVQZ; N = cc-pVQZ.

TABLE 2: Computed Equilibrium Geometry of OCHF (Distances in Å and Angles in Degrees)[a]

	r(C=O)	r(C−H)	r(C−F)	∠(OCH)	∠(OCF)
CCSD(T)/cc-pVDZ (ae)	1.1901	1.1072	1.3486	127.562	123.116
CCSD(T)/cc-pVTZ (ae)	1.1806	1.0865	1.3372	127.476	122.972
CCSD(T)/cc-pVQZ (ae)	1.1779	1.0890	1.3368	127.605	122.823
MP2/cc-pVDZ (ae)	1.1903	1.1042	1.3494	127.800	123.228
MP2/pVDZ (ae)+aug(F,O)	1.1931	1.1015	1.3706	128.578	122.763
MP2/cc-pVTZ (ae)	1.1812	1.0848	1.3393	127.720	123.087
MP2/pVTZ (ae)+aug(F,O)	1.1815	1.0867	1.3433	128.037	122.849
MP2/cc-pVQZ (ae)	1.1789	1.0867	1.3392	127.846	122.943
MP2/cc-pVQZ (fc)	1.1811	1.0891	1.3425	127.926	122.920
MP2/pVQZ (fc)+aug(F,O)	1.1816	1.0892	1.3445	128.049	122.815
best estimate, see text	1.1773	1.0900	1.3385	127.719	122.710

[a] ae = all electrons correlated, fc = frozen core approximation.

As the molecules investigated contain highly electronegative atoms, F and O, the aug-cc-pVnZ basis sets on F and O were also used.[39] The combination of an aug-cc-pVnZ basis set on F and of a cc-pVnZ basis set on the other atoms is denoted as: cc-pVnZ + aug(F). To estimate the correction due to the diffuse functions, in most cases (i.e., when single reference methods are adequate) it is enough to use the second-order Møller−Plesset perturbation theory (MP2).[40] This significantly reduces the complexity (time and memory) of the calculations whereas it gives a corrrection nearly identical to the CCSD(T) method. Table 1 shows the results for a few molecules for which the calculations were made with both the CCSD(T) and MP2 methods. It appears that the correction due to diffuse functions can be accurately calculated at the MP2 level for bond lengths as well as bond angles. The quadruple-ζ basis set results alone are given because the aug-ccpVTZ basis set is biased toward the diffuse functions and the description of long-distance effects whereas the problem disappears with the aug-cc-pVQZ basis set.[41]

Results and Discussion

Formyl Fluoride. *Results.* The results of the ab initio calculations are gathered in Table 2. Improvement of the basis set often leads to a decrease in the computed bond lengths. This trend is observed for the C═O and C−F bonds which are shortened by 0.0122 and 0.0118 Å, respectively (going from n = D to n = Q). The situation for the C−H bond is different: going from n = D to n = T, there is indeed a shortening by 0.0207 Å but, going from n = T to n = Q causes a lengthening by 0.0025 Å. The variation of the ∠(OCH) angle is erratic, paralleling the variation of the CH bond length. This angle only decreases by 0.09° from D to T but increases by 0.13° from T to Q. But taking into account the correction due to the diffuse functions allows us to obtain a monotonic variation. An extrapolation to infinite basis size was made using the following empirical exponential function

$$\theta(n) = \theta_\infty + b e^{-cn} \qquad (1)$$

where n is an index associated with each basis set, 2 = DZ, 3 = TZ, 4 = QZ. The parameters θ_∞, b, and c are determined from a nonlinear least-squares fit. The fit gives ∠(OCH) = 127.719°, to be compared with the CCSD(T)/cc-pVQZ+aug(O,F) value, 127.728°. The difference is almost negligible, hence the proposed best estimate: 127.72°. Basis set enlargements cause a monotonic decrease of the ∠(OCF) angle. Going from T to Q, there is still a change of 0.15° indicating that the equilibrium ∠(OCF) angle is probably slightly smaller than the cc-pVQZ value, 122.823°. If the effect of the diffuse functions on O and F is taken into account, the value is 122.718°. This is probably near the equilibrium value but it is difficult to estimate the accuracy. This situation is paradoxical because there is a large documented evidence which shows that ab initio angles are quite close to the equilibrium values. Thus, in principle, no correction is necessary. But, in the case of OCHF, it is obvious that the basis set limit is not fully attained. However, when the effect of diffuse functions is taken into account, the variation of ∠(OCF) is no longer monotonic with basis set enlargement. On the other hand, the variation of the ∠(HCF) angle is monotonic (taking into account the effect of diffuse functions) and an extrapolation to infinite basis size gives 109.57°. Thus, we find ∠(OCF) = 122.71°. This value is very close to the CCSD(T)/cc-pVQZ+aug(O,F) value but the extrapolation is purely empirical and there is no assurance that it will give the exact solution. If the difference between the extrapolated value and the cc-pVQZ+aug(O, F) value is used to estimate the accuracy of the angles, it seems to be better than 0.1°. If we also take into account the small effect of the core correlation which was calculated at the MP2/cc-pVQZ level (Table 2), the final accuracy is still better than 0.2°.

TABLE 3: Comparison of the Experimental and ab initio[a] *r*(C−F) Bond Lengths (in Å)

			CCSD(T)/cc-pVTZ		CCSD(T)/cc-pVQZ	
molecule	exp.	ref	calc.	e. − c.	calc.	e. − c.
CH_3F	1.3826	35	1.3816	0.0010	1.3824	0.0002
CHF_3	1.3284	52	1.3336	−0.0052		
HC≡CF	1.2768	53	1.2818	−0.0050	1.2791	−0.0023
FC≡N	1.2641	54	1.2701	−0.0060	1.2669	−0.0028
FCO^+	1.2014	55	1.2058	−0.0044		
FCH[b]	1.3050	22	1.3107	−0.0057		
FC≡CF	1.2835	56	1.2886	−0.0051	1.2859	−0.0024
CF_4	1.3151	57	1.3192	−0.0041		
CF_2	1.2975	this work	1.3024	−0.0050		
median				−0.0050		−0.0023
mean				−0.0044		−0.0018
σ^c				0.0023		0.0014

[a] All calculations were made with the frozen core approximation. [b] r_0 value. [c] Standard deviation.

TABLE 4: Comparison of the Experimental and ab initio CCSD(T)/cc-pVQZ[a] *r*(C−F) Bond Lengths (in Å) with the Effect of the Diffuse Functions on F Taken into Account

	exp.	ref.	calc.	e. − c.[b]	aug. corr.[c]	e. − c.[d]
HC≡CF	1.2768	53	1.2762	0.0006	0.0010	−0.0004
FC≡N	1.2641	54	1.2639	0.0002	0.0006	−0.0004
FC≡CF	1.2835	56	1.2831	0.0004	0.0005	−0.0001
CH_3F	1.3826	35	1.3792	0.0034	0.0031	0.0003
HCF	1.3062	*e*	1.3052	0.0010	0.0011	−0.0001
CF_2	1.2975	*e*	1.2963	0.0011	0.0010	0.0002
CH_2F_2	1.3529	*e*	1.3511	0.0018	0.0019	−0.0001
OCHF	1.3385	*e*	1.3368	0.0017	0.0020	−0.0003
median				0.0011		−0.0001
mean				0.0013		−0.0001
range				0.0032		0.0007
σ				0.0010		0.0003

[a] All electrons correlated. [b] residuals: Exp. − CCSD(T)/cc-p-VQZ. [c] Correction due to the diffuse functions: aug-cc-pVQZ − cc-pVQZ at the MP2 level. [d] Residuals with the effect of the diffuse functions taken into account. [e] This work.

At the CCSD(T)/cc-pVQZ level (all electrons correlated), the discrepancy from experimental bond lengths is only 0.0011 Å on average although the basis set limit is not reached and the core correlation is not properly taken into account.[34] It is still possible to improve the accuracy of the calculated distances by estimating the possible remaining errors with the help of structurally similar molecules whose equilibrium structures are accurately known. It is enough to calculate the structure of these molecules at the same level of theory. It is indeed well established that the error ($\delta r = r$[exp.] − r[CCSD(T)/cc-pVnZ] with n = T, Q) is almost constant for a given bond[15] and can thus be used as an offset to correct the ab initio values. The C−F bond length is however a conspicuous exception to this rule, at least at first sight. Table 3 reports the equilibrium and ab initio CCSD(T)/cc-pVTZ bond lengths for a few molecules whose structures are accurately known. If methyl fluoride were not in the table, the offset would indeed be almost constant. Using the larger cc-pVQZ basis set reduces the discrepancy only slightly. But, the abnormal behavior of CH_3F may be rationalized by using an aug-cc-pVQZ basis set on the highly electronegative F atom (and the standard cc-pVQZ basis set on the remaining atoms). It is observed that the effect of diffuse functions on the C−F bond length is about 0.001 Å, at the quadruple-ζ level for most of the molecules of Table 3 except for CH_3F where it is three times as large: 0.0031 Å. When this effect is properly taken into account, the offset becomes extremely small: −0.0001 Å (mean value) and almost constant, the range of variation of residuals being four times smaller, see Table 4. This is particularly important for OCHF because the effect of diffuse functions on the C−F bond is 0.002 Å, i.e., similar to that of CH_3F. Neglecting this correction would lead to a systematic error of about 0.002 Å. This negligible offset is an interesting example of compensation of errors. At the quadruple-ζ level, the basis set convergence is not yet fully achieved, the overestimation of the C−F bond length being slightly less than 0.001 Å. We checked on CH_3F and HC≡CF that correlating all the electrons with the valence cc-pVQZ basis set overestimates the (negative) core-correlation effect by 0.001 Å. Thus, these two errors nearly compensate for each other. This is not completely satisfactory but it is no more empirical than the extrapolation to infinite basis size which is not always suitable.

The effect of diffuse functions on the C═O bond is not negligible either but much smaller than in formaldehyde: 0.0005 Å instead of 0.0012 Å. The offset values for the C═O and C−H bonds are estimated from formaldehyde and are given in Table

TABLE 5: Determination of the Offsets for the ab initio Structure (Distances in Å and Angles in Degrees)

molecule	ref.	parameter	exp.	ab initio[a]	aug corr.[b]	total corr.[c]
H_2CO	58	r(C═O)	1.2030	1.2042	0.0012	−0.0024
		r(C−H)	1.1006	1.0996	−0.0002	0.0013
		∠(OCH)	121.648	121.778	−0.092	−0.038
CO_2	62	r(C═O)	1.1600	1.1601	0.0006	−0.0007
CO	63	r(C═O)	1.1282	1.1289	0.0004	−0.0011
CH_3F	35	r(C−H)	1.0872	1.0863	−0.0001	0.0010

[a] CCSD(T)/cc-pVQZ, all electrons correlated. [b] Correction due to the diffuse functions: aug-cc-pVQZ − cc-pVQZ at the MP2 level. [c] Total correction: exp. − (ab initio + aug. corr.) = offset.

5. Correcting the CCSD(T)/cc-pVQZ+aug(F, O) value gives r(C═O) equal to 1.1760 Å. However, if the offsets are derived from either CO or from CO_2, slightly different results are obtained, the maximal difference however being smaller than 0.002 Å and the derived distance always being smaller than 1.178 Å. It may be argued that this small discrepancy is not surprising because bonding is extremely different in these three molecules and this indicates that the method used is only approximate for the C═O bond. However, Botschwina[42] performed a CCSD(T)/cc-pCVQZ calculation with all electrons correlated and proposes 1.2043 Å for the equilibrium value of r(C═O) instead of our value of 1.20296 Å.[58] If we adopt the value of Botschwina, the discrepancy disappears and gives our preferred value for r(C═O) in OCHF, 1.1773 Å, this last solution being in much better agreement with the experimental equilibrium moments of inertia, see below. This slight discrepancy would justify a systematic study of the C═O bond.

Discussion. To estimate the accuracy of the results, the moments of inertia were calculated from the ab initio structure with offset correction (last line of Table 2) and compared to the experimental equilibrium values. The ground-state rotational constants and the experimental rotation−vibration interaction constants α_i^g ($g = a, b, c$ and $i = 1, ..., 6$) are given in Table 6. The experimental rotational constants were also corrected for a small centrifugal distortion contribution[43] and for electronic contribution. This correction is due to the fact that the distribution of electrons contributes to the moments of inertia because an atom in a molecule is not a mass point and the center of mass of the electrons in an atom generally does not coincide with the position of the nucleus. The electronic contribution is related to the molecular g-factor by the relation[43]

$$B_{\mathrm{corr}}^{\alpha} = \frac{B_{\mathrm{exp}}^{\alpha}}{1 + \frac{\mathrm{m}}{\mathrm{M_p}} g_{\alpha\alpha}} \qquad (2)$$

where $g_{\alpha\alpha}$ is expressed in units of the nuclear magneton, m is the electron mass, M_p the proton mass, and $\alpha = a, b, c$. The g-factor has been obtained experimentally from the analysis of the Zeeman effect on the rotational spectrum.[44] The comparison of experimental and calculated moments of inertia shows that the ab initio structure is rather accurate. Furthermore, the equilibrium experimental inertial defect, Δ_e is equal to −0.0043 (2) uÅ^2 although much smaller than the ground-state inertial defect, Δ_o which equals +0.09215 uÅ^2, and Δ_e is significantly different from zero indicating that there is still a small systematic error in the experimental vibration−rotation interaction constants. This is not surprising because it is well established that, for a polyatomic molecule, it is extremely difficult to obtain reliable equilibrium rotational constants from experimental data alone.[45] This is particularly true for OCHF where several excited vibrational states interact. For instance, the sextic constants of the ν_1 state are very different from the ground state constants, indicating the possible existence of an interaction which is not taken into account. Nevertheless, it might be worth noting that a slightly longer C═O or C−F bond would give better agreement with experimental rotational constants.

There is another way to check the accuracy of some parameters. There is an empirical correlation between the r_e(C−H) distance and the isolated C−H bond stretching frequencies.[23,46] Using a value for ν(C−H) of 2981.2408 cm^{-1}, we obtain an r_e(C−H) value of 1.087 Å.[9] This value is slightly lower than our derived equilibrium value but, as said above, it is not obvious that the ν_1 state is well isolated. Furthermore, ab initio calculations using very different basis sets (from 6-31G* to cc-pVQZ) and different methods (MP2 and CCSD(T)) all give the same value after offset correction, attesting the accuracy of the C−H bond length.

The r_z(C−F) value has been determined by Huisman et al.[4] by combining electron diffraction and rotational spectroscopy results. This r_z value can be converted into an approximate r_e value either using an empirical correlation[47] or the well-known formula of Kuchitsu[48]

$$r_z = r_e + \frac{3}{2} a u^2 - K \qquad (3)$$

In this formula u^2 is the mean square amplitude for the bond concerned, and K the mean square perpendicular amplitude correction, both calculated from the harmonic force field, while a is the Morse anharmonicity parameter. This a parameter is generally assumed to be equal to the corresponding parameter for the diatomic molecule. The value of a for the C−F bond is 2.357 Å^{-1}.[49] Both methods give r_e(C−F) =1.339 (2) Å in extremely good agreement with our value. But it could be quite by chance because, on the other hand, for the C═O bond, using eq 3, we should have $r_z - r_e \approx 0.003$ Å whereas we find 0.009 Å.[50] However, calculations with smaller basis sets and the MP2 method give results which are fully consistent with our CCSD(T)/cc-pVQZ calculation.[50] Furthermore, if we compare in Table 7 the variation of the r(C═O) bond length in the two series OCH_nX_{2-n} (with X = F, Cl and $n = 0, 1, 2$), we see that r(C═O) in OCHF should be significantly lower than 1.182 Å, confirming the validity of our calculated structure.

In conclusion our calculated structure should be fairly reliable although estimating its accuracy is extremely difficult.

Difluorocarbene and Monofluoromethylene. Another way to strengthen the reliability of our method is to apply it to other molecules. CF_2 is very favorable because it is possible to obtain an accurate r_e structure using only experimental information. The equilibrium rotational constants were determined using the rotation−vibration interaction constants listed in Table 8. The equilibrium inertial defect, Δ_e, is only −0.0048 uÅ^2 whereas the corresponding ground-state value, Δ_o, is 0.1032 uÅ^2. This relatively small value for Δ_e indicates that the equilibrium rotational constants are not far from their true value as was the case for OCHF. Using A_e and B_e to calculate the structure, we find r_e(C−F) = 1.2975 Å and $\angle_e$(FCF) of 104.81°. It is difficult to estimate the accuracy of this structure precisely because the errors due to the method (neglecting anharmonic resonances, neglecting magnetic correction, approximation of the Coriolis resonances, ...) are usually at least 1 order of magnitude larger than the statistical standard deviations of the rotational constants. However, it is possible to assess the accuracy of this structure indirectly because a highly reliable r_z structure is available.[17] For the bond angle, we should have $\angle_e(\mathrm{FCF}) \approx \angle_z(\mathrm{FCF}) =$ 104.78(2)°. For the bond distance, it is necessary to use eq 3 to

TABLE 6: Experimental Rotational Constants and Vibrational Corrections for Formyl Fluoride (in cm^{-1})

g	A	B	C	ref
B_g ($v = 0$)	3.040 655 50(73)	0.392 280 004(88)	0.346 795 677(79)	8
α_1	0.016 954 6(59)	0.000 076 9(13)	0.000 343 88(76)	9
α_2	0.013 109 6(20)	0.001 462 86(44)	0.001 257 01(46)	8
α_3	0.012 163 2(25)	−0.001 671 46(56)	0.000 311 09(44)	9
α_4	0.008 084(39)	0.002 957 78(48)	0.002 471 29(13)	9
α_5	−0.023 065 23(97)	0.000 441 94(14)	0.001 037 10(13)	9
α_6	0.008 830(39)	0.001 123 12(53)	−0.000 115 91(45)	9
magn.[a]	−0.000 014 1	−0.000 002 6	−0.000 001 2	
cd[b]	−0.000 001 7	−0.000 005 5	0.000 006 3	
B_g ($v = $ e)	3.059 396(28)	0.394 486 7(12)	0.349 461 3(11)	
I_e(exp)[c]	5.510 117(50)	42.733 08(13)	48.238 90(14)	
I_e(calc)[c]	5.4958	42.7203	48.2161	
e − c[c]	0.0143	0.0128	0.0228	
e − c (%)	0.26%	0.03%	0.05%	

[a] Magnetic correction, see text. [b] Centrifugal distortion correction, see text. [c] In uÅ^2.

TABLE 7: Structures of OCHF and Related Molecules (Distances in Å and Angles in Degrees)

molecule	$O{=}CH_2$	$O{=}CHF$			$O{=}CF_2$	$O{=}CHCl$	$O{=}CCl_2$
reference	58	7	4	this work	59	60	61
structure	r_e	r_o	r_z	r_e	r_e	r_e	r_e
r(C=O)	1.202 96	1.181 (5)	1.186 (1)	1.1773	1.170 (2)	1.182	1.176 (2)
r(C−H)	1.100 64	1.095 (8)	1.096 (4)	1.0900		1.090	
r(C−F)		1.338 (5)	1.345 (1)	1.3385	1.311 (2)		
r(C−Cl)						1.765	1.738 (2)
∠(OCH)	121.648	127.3 (30)	130 (1)	127.72		126.49	
∠(OCF)		122.8 (5)	122.3 (1)	122.71	126.2 (4)		
∠(OCCl)						123.07	124.11(12)

TABLE 8: Experimental Rotational Constants and Vibrational Corrections for CF$_2$ (in MHz)

g	A	B	C	ref.
B_g ($v = 0$)	88 355.0879 (61)	12 507.7303 (12)	10 932.2216 (12)	18
α_1	−278.28 (19)	67.926 (90)	58.443 (33)	19
α_2	−787.30 (24)	32.134 (18)	48.113 (18)	20
α_3	1265.76 (16)	53.344 (90)	65.420 (15)	19
A_e	88 455.18 (35)	12 584.43 (13)	11 018.209 (40)	
I_e (exp.)[a]	5.713 391 (22)	40.159 06 (41)	45.867 62 (17)	
I_e (calc.)[a,b]	5.705 52	40.1668	45.8723	
I(e − c) %	0.14	−0.02	−0.01	

[a] In uÅ^2. [b] Calculated with the best theoretical estimate from Table 9.

TABLE 9: Computed Equilibrium Geometry of CF$_2$ (Distances in Å and Angles in Degrees)[a]

	r(C−F)	∠(FCF)
CCSD(T)/cc-pVDZ (ae)	1.3140	104.617
CCSD(T)/cc-pVTZ (ae)	1.2985	105.032
CCSD(T)/cc-pVQZ (ae)	1.2963	104.939
MP2/cc-pVDZ (fc)	1.3101	104.708
MP2/pVDZ (fc)+aug(F)	1.3245	103.793
MP2/cc-pVTZ (fc)	1.2993	104.966
MP2/pVTZ(fc)+aug(F)	1.3022	104.708
MP2/cc-pVQZ (fc)	1.2969	104.945
MP2/pVQZ (fc)+aug(F)	1.2979	104.854
best estimate, see text	1.2972	104.858

[a] ae = all electrons correlated, fc = frozen core approximation.

correct the r_z value. This gives a value of r_e(C−F) of 1.297(2) Å. These values are in perfect agreement with the experimental r_e structure.

The results of the ab initio calculations on CF$_2$ are given in Table 9. The CCSD(T)/cc-pVQZ values corrected for the effect of diffuse functions on F gives: r_e(C−F) = 1.2972 Å and $\angle_e$(FCF) = 104.85°, in perfect agreement with the experimental values. If we extrapolate the angles using eq 1, we get $\angle_e$(FCF) = 104.858°. This confirms the accuracy of the CCSD(T)/cc-pVQZ ab initio calculations, provided the effect of the diffuse functions on fluorine is taken into account. It may however be noted that this effect is small in the particular case of CF$_2$.

TABLE 10: Computed Equilibrium Geometry of CHF (Distances in Å and Angles in Degrees)[a]

	r(C−H)	r(C−F)	∠(HCF)
CCSD(T)/cc-pVDZ (ae)	1.1406	1.3210	101.867
CCSD(T)/cc-pVTZ (ae)	1.1153	1.3070	102.444
CCSD(T)/cc-pVQZ (ae)	1.1175	1.3052	102.420
CCSD(T)/cc-pVDZ(ae)+aug(C,F)	1.1364	1.3392	101.428
CCSD(T)/cc-pVTZ(ae)+aug(C,F)	1.1164	1.3081	102.378
CCSD(T)/cc-pVQZ(ae)+aug(C,F)	1.1176	1.3063	102.407
best estimate, see text	1.116	1.306	102.41

[a] ae = all electrons correlated, fc = frozen core approximation.

It is also interesting to compare the experimental equilibrium moments of inertia with those calculated from the ab initio structure, see Table 8. It appears that the moments of inertia are quite sensitive to small structural changes and that the difference I(exp) − I(calc) is much greater than the uncertainty of I(exp) as was also the case for OCHF. The main source of error comes from the experimental determination of the vibrational correction because it is extremely difficult to obtain unperturbed rotational constants for excited states which are in interaction (which is rather common). Furthermore, in the case of CF$_2$, the magnetic correction could not be taken into account because the molecular g-factor is not known.

This success prompts us to try to calculate the structure of the structurally similar molecule CHF for which no r_e structure is known. The results of the ab initio computations are in Table 10. One may note that the angle has almost the same value at the cc-pVTZ and cc-pVQZ levels indicating that convergence is almost achieved. Taking into account the small effect of the diffuse functions, one finds: $\angle_e$(HCF) = 102.41°, to be compared with the effective value, $\angle_o$(HCF) = 104.1(5)°.[22] Our result is also in good agreement with the previous ab initio calculation made at the CCSD(T)/6-311+G** level, 102.0°.[24] Our calculation should be more accurate because a much larger

TABLE 11: Equilibrium Geometry of CH_2F_2 (Distances in Å and Angles in Degrees)[a]

	r(C−H)	r(C−F)	∠(HCH)	∠(FCF)
CCSD(T)/cc-pVDZ (ae)	1.1042	1.3603	112.264	108.886
CCSD(T)/cc-pVTZ (ae)	1.0854	1.3518	112.864	108.666
CCSD(T)/cc-pVQZ (ae)	1.0861	1.3511	113.088	108.503
MP2/cc-pVDZ (fc)	1.1012	1.3598	112.392	108.960
MP2/pVDZ (fc)+aug(F)	1.0985	1.3779	114.495	108.049
MP2/cc-pVTZ (fc)	1.0865	1.3454	113.028	108.713
MP2/pVTZ (fc)+aug(F)	1.0863	1.3592	113.722	108.337
MP2/cc-pVQZ (fc)	1.0853	1.3541	113.312	108.561
MP2/pVQZ (fc)+aug(F)	1.0854	1.3560	113.577	108.408
best estimate, see text	1.0872	1.3529	113.283	108.364
experimental, set I[b]	1.087 (3)	1.3514 (5)	113.1 (3)	108.43 (6)
experimental, set III[b,c]	1.084 (3)	1.3508 (5)	112.8 (3)	108.49 (6)

[a] ae = all electrons correlated, fc = frozen core approximation. [b] Reference 27. [c] Preferred value, see reference 27.

basis set has been used. The extrapolation (with diffuse functions included) at infinite basis size gives 102.41°, whereas the value is 102.42° when the diffuse functions are neglected.

For the C−F bond length, the CCSD(T)/cc-pVQZ+aug(C, F) value is 1.3063 Å, slightly larger than the experimental r_o value, 1.305(2) Å, although the difference lies within the experimental uncertainty. It may be noted that, for the CF bond length, basis set convergence is perhaps not fully achieved at the cc-pVQZ level. At infinite basis size, the length should be slightly smaller, assuming a monotonic variation. Furthermore, since the influence of the diffuse functions decreases as the basis size increases, this should further decrease the bond length. To solve this problem, we have calculated the structure of CHF at the CCSD(T) level using the cc-pVnZ+aug(C,F) basis sets with n = D, T, Q. The extrapolation to infinite basis size using eq 1 gives r(C−F) = 1.3061 Å whereas the same extrapolation, neglecting the diffuse functions, gives 1.3040 Å. This is in rather good agreement with our previous result and confirms the importance of diffuse functions in this particular case. The nonextrapolated value is preferred because the overestimation of the bond length at the quadruple-ζ level is 0.001 Å, which is fully compensated by the (negative) overestimation of the core-correlation (see discussion on OCHF). The CCSD(T)/cc-pVQZ r(C−H) bond length is about 0.001 Å shorter than the true equilibrium bond length, see Table 5. Thus, in principle, the equilibrium C−H bond length, should be r_e(C−H), 1.116 Å. But, as the bonding in CHF is very different from the other hydrocarbons, it is not possible to affirm that the offset is still valid for CHF and the true equilibrium value could be slightly different.

Difluoromethane. To complete the series of simple fluorine compounds, the structure of difluoromethane was also calculated. The results are given in Table 11 together with the previous experimental r_e structure of Hirota.[27] The variation of angles with the size of the basis set is monotonic; thus it is possible to extrapolate them to infinite basis size using eq 1. This gives an angle ∠(HCH) of 113.28° and an angle ∠(FCF) of 108.36° whereas, if the effect of the diffuse functions on F is neglected, one finds that ∠(HCH) equals 113.22° and ∠(FCF) equals 108.10°. In conclusion, as expected, the effect of the diffuse functions significantly broadens the angle ∠(FCF) but has almost no effect on the angle ∠(HCH). The computed value for ∠(HCH) is slightly larger than the preferred experimental value (set III), 112.8(3)°. The computed value of the r(C−F) bond length, after correction (see Table 4), 1.3529 Å is also larger than the preferred experimental value, 1.3508 (5) Å. Likewise, the computed value of the r(C−H) bond length, after correction (see Table 4), 1.0872 Å, is also larger than the preferred experimental value, 1.084 (3), although the large uncertainty does not allow us to draw any firm conclusion for this bond length. In conclusion, it seems that the experimental r_e structure calculated using the simple valence cubic force field (set I) is more accurate than the one obtained from the advanced force field (set III). To check that point, we have calculated the equilibrium rotational constants using the experimental ground-state constants and the rovibrational corrections calculated at the MP2/6-31G** level.[29] This gives (in MHz) $A_e = 49707$, $B_e = 10669$, and $C_e = 9321$, in excellent agreement with the values obtained from the computed structure: $A_e = 49709$; $B_e = 10664$; and $C_e = 9319$. This indicates that the ab initio force field is likely to be more accurate than the experimental one which is not surprising because it is known that ab initio methods are able to furnish with good accuracy cubic and quartic force constants.[51] This is further strengthened by the fact that our C−H bond length is in perfect agreement with the value estimated either from the isolated ν(C−H) stretching frequency or from the MP2/6-31G** calculation.[23]

Finally, it may be noted that r(C−F) is much smaller in CH_2F_2 than in CH_3F, see Table 4. This supports the well-documented observation that the C−F bond length decreases with increasing substitution. On the other hand, the variation of the C−H bond length from CH_3F to CH_2F_2 is negligible.

Conclusions

The equilibrium geometries of a few simple fluorine compounds (formyl fluoride, difluorocarbene, monofluoromethylene, and difluoromethane) have been computed using the coupled cluster correlation method with basis sets up to quadruple-ζ quality. The effects of diffuse functions on the electronegative atoms have been included. It is found that the CCSD(T)/cc-pVQZ+aug(F) method with all electrons correlated nicely reproduces the experimental equilibrium C−F bond length with a standard deviation of 0.0003 Å. The ab initio C−H bond bond length, calculated at the same level of theory, is 0.001 Å too short. The lack of monotonic convergence which was observed for some parameters with basis set enlargment might be due to an artifact of the cc-pVnZ basis sets (this behavior is observed with all electrons correlated as well as with the frozen core approximation). The use of the appropriate cc-pCVnZ basis sets might overcome this difficulty.

The theoretical predictions of bond lengths and bond angles are in good agreement with the available experimental data. However, a small discrepancy (0.0014 Å) is found for the C═O bond length in formaldehyde. This would justify a similar systematic study of the C═O bond.

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