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Non-Empirical LCAO-MO-SCF-CI Calculations on Organic Molecules with Gaussian Type Functions

Part II. Preliminary Investigations on Formyl Fluoride

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Non-empirical molecular quantum chemical calculations were performed on formyl fluoride (HCOF) in the LCAO–MO–SCF framework using Gaussian type functions as atomic orbitals. In the first half of this paper a quantitative correlation has been established between some of the calculable molecular properties of HCOF and the size of the basis set used. It is hoped that the basic conclusions are general enough to be applicable to calculations of similar type on different molecules. The second part consists of a preliminary SCF study of HCOF in its electronic ground state.

La molécule de fluorure de formyle (HCOF) a été calculée d'une manière non semi-empirique dans le cadre de la méthode LCAO–MO–SCF en utilisant des fonctions du type gaussien en tant qu'orbitales atomiques. Dans la première moitié de cet article une corrélation quantitative est établie entre certaines propriétés moléculaires de HCOF calculables et la dimension de la base utilisée. On espère que les conclusions fondamentales sont suffisamment générales pour pouvoir être appliquées à des calculs du même type sur des molécules différentes. La seconde partie consiste en une étude SCF préliminaire de HCOF dans son état fondamental.

Im Rahmen des LCAO–SCF–MO-Verfahrens werden nicht-empirische quantenchemische Rechnungen am Formylfluorid (HCOF) mit Gaußfunktionen als Atomfunktionen durchgeführt. In der ersten Hälfte der Arbeit wird eine quantitative Beziehung zwischen den berechenbaren molekularen Eigenschaften von HCOF und der Größe des benutzten Basissatzes aufgestellt. Man hofft, daß die grundlegenden Schlüsse allgemein genug sind, um bei Rechnungen ähnlicher Art an anderen Molekülen angewandt werden zu können. Der zweite Teil besteht aus einer vorläufigen SCF-Studie des Grundzustandes von HCOF.

1. Introduction

In the last few years a number of quantum mechanical computations have been performed on small chemical systems utilizing gaussian functions [*23, 24*] as atomic orbitals. Among the 10 electron hydrides HF, $(HO)^-$, H_2O, $(H_3O)^+$ (each of which contains one heavy atom, and possesses core, σ and n electrons), were investigated by Harrison and Moskowitz [*15, 21*] while the 16 electron ethylene (which contains two heavy atoms and possesses core, σ and π electrons*) was

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* In our phraseology "heavy atom" means elements from the second and third row of the periodic system (i.e. from Li to Cl). The approximate grouping of electrons [*3*] into classess "core", "σ", "π" and "n" (i.e. "K-shell", "σ", "π" and "nonbonding") electrons is used in the chemical sense, even when symmetry allows mixing within each other in the MO approach.

treated by Moskowitz and Harrison [*20*]. This paper will deal with the 24-electron formyl fluoride (which contains three different heavy atoms and exhibits the properties of both core, σ, π, and n electrons). The system is planar in its ground state, having no symmetry element other than the plane of the molecule. Because of its low symmetry it may be expected to provide quite an exacting test of the usefulness of gaussian functions. Any conclusions drawn from these calculations may, perhaps, have greater generality than any drawn from the results of calculations on more highly symmetric molecules.

Formly fluoride (HCOF), however, has not been chosen for generality only, but also because it exhibits a great variety of interesting physical and chemical features in spite of its small size.

1.1 Structural and Physical Properties of Formyl Fluoride

Tab. 1 summarizes the experimental structural parameters of HCOF, so far reported in the literature. Although the structure of this planar molecule is fairly well defined, the position of the hydrogen atom seems rather uncertain. The OCH angles reported are distributed over a range of approximately 20°. If the substituting oxygen and fluorine atoms on the carbon were identical in every respect the OCH angle would be 119° (reported values range between 110° and 129°). It was difficult to assess the reliability of the values reported, but intuitively it would seem likely that the hydrogen should be closer to the oxygen. Thus the values of Ref. [*10*] were preferred and used in the initial study. These values are shown in the first line of Tab. 1.

Fig. 1 shows the structure of the formyl fluoride molecule in relation to the x, y, z, right-handed coordinate system selected for the study. The z axis, which is

Table 1. *Experimental structural parameters of formyl fluoride*

Exp. Method	r(C–F)	r(C=O)	r(C–H)	∢FCO	∢HCO	∢HCF	Ref.
	Ångström			Degree			
Micro-Wave	1.345	1.185	1.082	121.9	110.2	127.9	[*10*]
Micro-Wave	1.338 ±0.005	1.181 ±0.005	1.095 ±0.008	122.8 ± 0.5	127.3 ± 3.0	109.9 ± 3.0	[*19*]
Micro-Wave	1.341	1.183	1.100	122.7	129	108	[*17*]
Micro-Wave	1.341 ±0.003	1.182 ±0.003	1.087 ±0.010	123.04 ± 0.002	123	114	[*9*]
Infra Red	1.3428	1.1857	(1.080)[a]	122.6			[*26*]
Micro-Wave	1.345	1.190	1.093	121.1	120.7	118.2	[*7*]
Electr. Diffr.	1.351 ±0.013	1.192 ±0.011		121.9 ± 0.9			[*16*]

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[a] Assigned.

not shown on the diagram, is perpendicular to, and points out of, the plane of the molecule. Since this molecule is conveniently considered as a general formyl derivative, both x and y axes of the major coordinate system were chosen to pass through the carbon atom, while the local coordinate axes (x_{SUB} and y_{SUB}) of the substituent were chosen so that y_{SUB} passed through the carbon atom. The axes of moment of inertia (a. b) used in microwave spectroscopy are also represented in Fig. 1. Dipole moment values measured on the basis of Stark effect by microwave spectroscopy are given with respect to this coordinate system (a, b). Since in the present calculation x and y axes are used as reference system, the dipole moment components μ_a, μ_b, were transformed to μ_x and μ_y. The values are shown in Tab. 2.

The near ultraviolet (1900—2900 Å) spectrum of formyl fluoride has been studied by several authors [*11*, *13*, *14*]. Two types of excitations were distinguished [*13*], a low intensity band ($\lambda_{\max} = 2100$ Å, $\varepsilon = 50$ cm$^{-1}\cdot$mol^{-1}) and an extremely weak band ($\lambda_{\max} = 2680$ Å, $\varepsilon = 0.01$ cm$^{-1}\cdot$mol^{-1}). It has been suggested [*8*] that the first one of these is a $\pi^* \leftarrow n$ (singlet-singlet) excitation with an origin at 37.500 cm^{-1} (2667 Å) while the second one remained unassigned. A Pople-Pariser-Parr semiempirical LCAO-MO-SCF calculation [*12*] agreed with the $\pi^* \leftarrow n$ assignment, since the energy difference obtained (4.72 eV before and 4.27 eV after CI) matched the experimental value of 5.3 eV reasonably well.

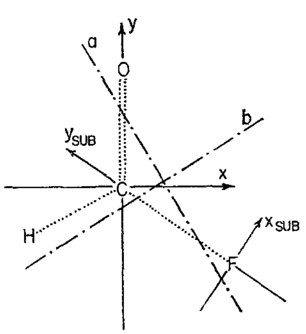


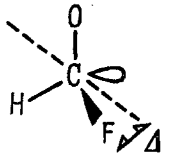
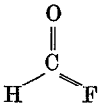
Fig. 1. Coordinate systems for the HCOF molecule

On the basis of vibrational analysis [*13*] the stereochemistry of the $\pi^* \leftarrow n$ excited state was found to be different from that of the ground state. Calculations of the excited state inertial constants predicted a pyramidal conformation, similar to that found for formaldehyde in its $\pi^* \leftarrow n$ excited state. Given in Tab. 3 are the predicted geometrical parameters of the formyl fluoride $\pi^* \leftarrow n$ excited state, including Δ, the acute angle between the plane of the HCO nuclei and CF axis [*13*]. The numbers given in parentheses are taken from LeBlanc et al. [*17*]. Although an appreciable deviation from planarity seems to be established, there seems to be no evidence of inversion of the pyramidal structure [*13*].

Table 2. *Experimental dipole moments of formyl fluoride*

Exp. Method	$\lvert\mu_a\rvert$ Debye	$\lvert\mu_b\rvert$	$\lvert\mu\rvert$	$\lvert\mu_x\rvert$	$\lvert\mu_y\rvert$	Ref.
Micro-Wave	0.595 ±0.006	1.934 ±0.020	2.02 ±0.02	1.149 ±0.012	1.666 ±0.015	[*17*]
Micro-Wave	0.58 ±0.02	1.91 ±0.03	1.99 ±0.03	1.17 ±0.04	1.62 ±0.03	[*8*]
Micro Wave	$\lvert\mu_a\rvert < \lvert\mu_b\rvert$		—	$\lvert\mu_x\rvert < \lvert\mu_y\rvert$		[*7*]

Table 3. *Experimental Structural parameters of formyl fluoride in the ground and lowest excited singlet states*

Electronic State	$r(C-F)$	$r(C-O)$	$r(C-H)$	$\sphericalangle FCO$	$\sphericalangle HCO$	Δ
	Ångström			Degree		
 $\pi^* \leftarrow n$ Excited State [*13*]	(1.34)	1.35—1.38	(1.10)	106—113	(129)	20
 Ground State [*17*]	1.34	1.18	1.10	122.7	129	0

2. Results and Discussion

In this paper we present the results of some calculations on formyl fluoride in its ground electronic state. In a later paper we shall present the results of calculations on the $\pi^* \leftarrow n$ and $\pi^* \leftarrow n$ excited singlet and triplet states. The physical properties of the molecule calculated were the electric dipole moment, the electron density, and the total, electronic, binding and orbital energies.

The initial investigations [*2, 4*] were performed with a small basis set (referred to as the "minimal" set), chosen in the light of some recently performed calculations on small molecules [*5, 15, 23, 24*]. The aim was to adjust and increase this basis set systematically until a satisfactory one was found. It was hoped that a systematic study would reveal in a quantitative manner the relationship between the size of the basis set (N) and the numerical accuracy of the results obtained.

2.1 Calculation with Minimal Basis Set

A set of atomic functions assembled from three *s*-type (3^s) and one *p*-type (1^p) gaussian functions on each of the heavy atoms and one *s*-type (1^s) gaussian function on the hydrogen atom was considered [*2*] to be a minimal gaussian basis set. The minimal gaussian basis set for formyl fluoride thus consists of 19 atomic gaussian type functions. Equivalent *p*-orbital exponents (scaled from the optimized nitrogen atom) were used [*24*] rather than those optimized individually for ammonia. The orbital exponents [*6*] are summarized in Tab. 4 for convenience. The SCF calculation gave an electronic energy of −266.883450 a.u. and a total energy of −199.596526 a.u. The coefficients of the molecular orbitals are given in Tab. 5 together with the corresponding orbital energies.

Electron density contour maps of some of the MO's are shown in Fig. 2 together with approximate assignments of their "chemical" nature, though it is clear from the maps that most molecular orbitals have an appreciable admixture of atomic orbitals from all the centres. The total electron density of the molecule (last picture in Fig. 2) is the sum of the twelve occupied orbital densities.

In addition to the fact that these electron density contours provide an approximate model for the electronic distribution in the system it is also hoped that the geometry of these orbital electron density maps will help in understanding the stereochemistry of "transition state" formation in chemical reactions [*3*].

The binding energy [*6*] was found to be 1.32202 a.u. (about 830 kcal/mole) as the difference of calculated total molecular (−199.59653 a.u.) and calculated total atomic (−198.27451 a.u.) energies [*25*]. No experimental binding energy is reported in the literature, but the value obtained (830 kcal/mole) seems to be unreasonably large. Estimates for the total binding energy were obtained using as a basis Pauling's rule for the additivity of bond energies corrected for the total zero point energy. The values obtained using different bond energies (Tab. 6) range between 348.5 and 413.9 kcal/mole.

Table 4. *Orbital exponents used for* HCOF *in the minimal basis set assembled from Gaussian type functions* (GTF)

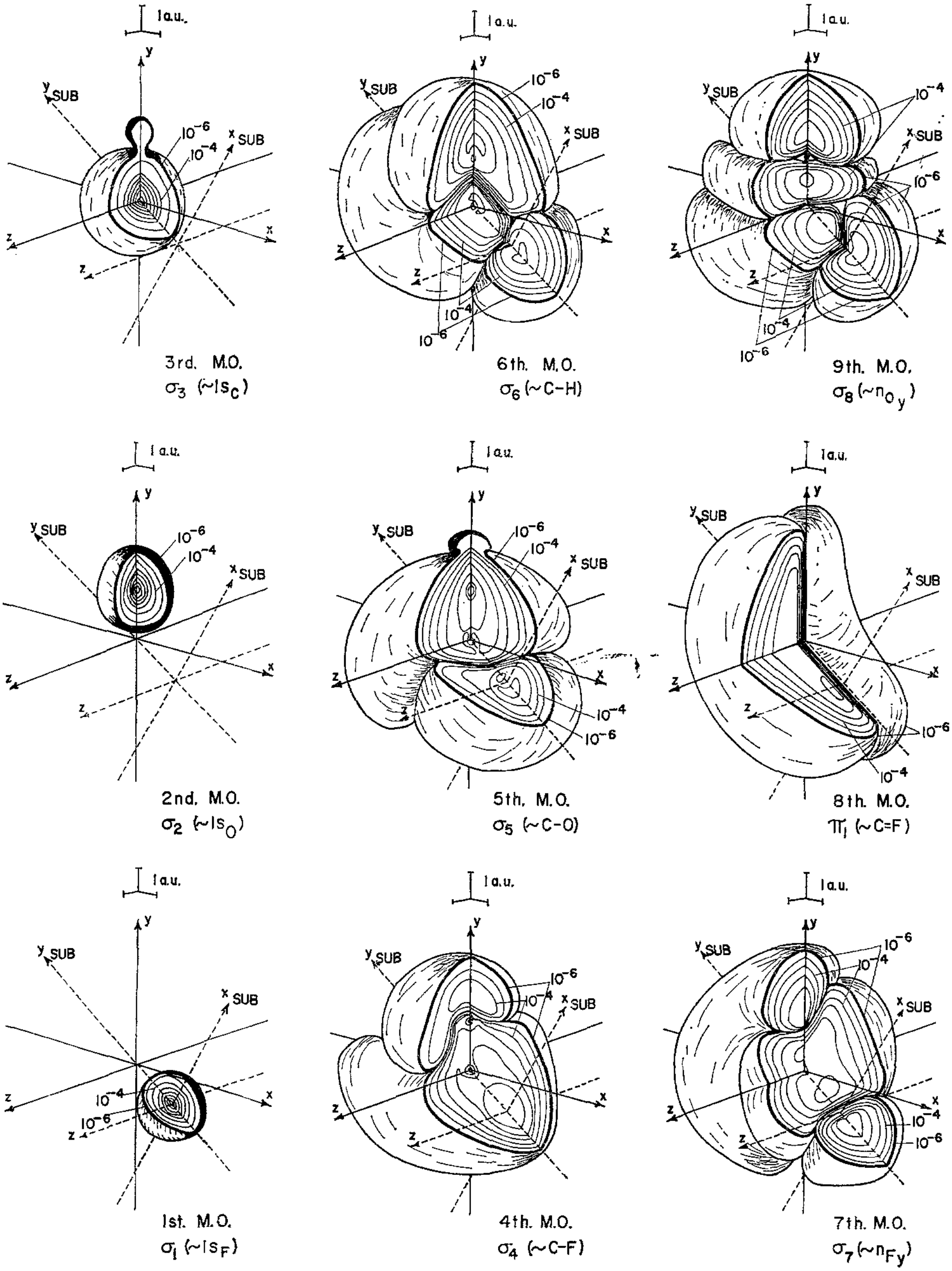
i	η_i	Centre	Orbital Exponent (α)	i	η_i	Centre	Orbital Exponent (α)
1	s	C	0.634	11	p_y	O	0.749
2	s	C	5.00	12	p_z	O	0.749
3	s	C	39.6	13	s	F	1.55
4	p_x	C	0.382	14	s	F	12.5
5	p_y	C	0.382	15	s	F	96.5
6	p_z	C	0.382	16	p_{SUBX}	F	0.978
7	s	O	1.20	17	p_{SUBY}	F	0.978
8	s	O	9.45	18	p_z	F	0.978
9	s	O	74.7	19	s	H	0.380
10	p_x	O	0.749				

The net atomic and overlap electron populations of atomic orbitals obtained by Mulliken's population analysis are given in Fig. 3 in square and round parentheses respectively. The net charges (δq) obtained indicate that O, F are partially positive and C and H are partially negative. This is directly opposite to the distribution expected from atomic electronegativities.

As expected, the incorrect electron population, is also reflected in the electric dipole moment. The absolute value of the calculated dipole moment ($|\mu| = 2.3440$ Debye) is reasonably close to the experimental value (Tab. 2) but the actual components calculated ($\mu_x = +2.2930$, $\mu_y = -0.4867$ Debye) given a direction about 100° from the experimental one (Fig. 3). All these facts indicate that only a qualitative picture can be obtained from a calculation with a minimal number of gaussian type functions, and for numerical accuracy it is desirable to use more extensive basis sets.

2.2 Variation of Basis Sets

The basis set was varied simply by increasing its size and altering the way in which the orbitals were distributed among the centres. The orbital exponents for



3rd. M.O.
σ_3 ($\sim 1s_C$)

6th. M.O.
σ_6 ($\sim$C-H)

9th. M.O.
σ_8 ($\sim n_{O_y}$)

2nd. M.O.
σ_2 ($\sim 1s_O$)

5th. M.O.
σ_5 ($\sim$C-O)

8th. M.O.
π_1 ($\sim$C=F)

1st. M.O.
σ_1 ($\sim 1s_F$)

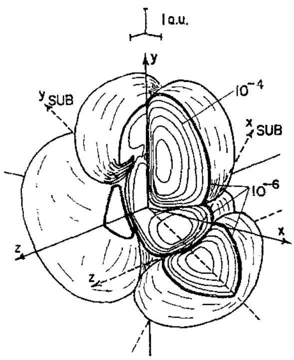
4th. M.O.
σ_4 ($\sim$C-F)

7th. M.O.
σ_7 ($\sim n_{F_y}$)

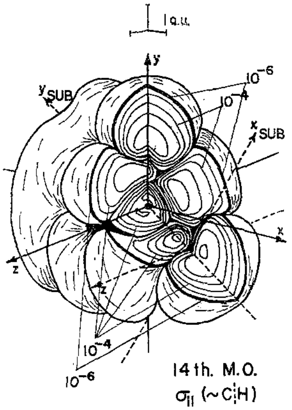
Fig. 2. Three dimensional orbital and total electron density contour models

the basic functions were found using the scaling rules of Part I on the exponents obtained from a careful calculation on the neon [*6*].

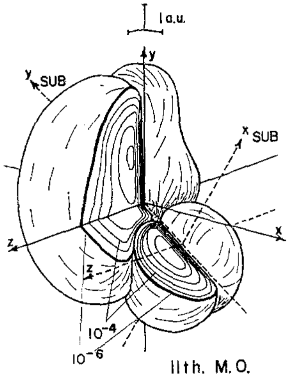
The problem is now given the maximum number of functions N that it is possible to use in a calculation (a number determined by the computational



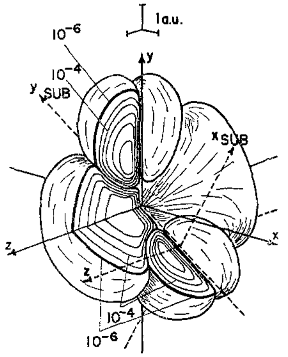
12th. M.O.
σ_{10} (~n_{O_x})



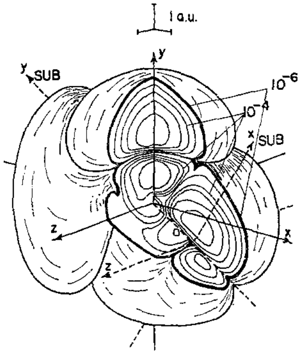
14th. M.O.
σ_{11} (~C¦H)



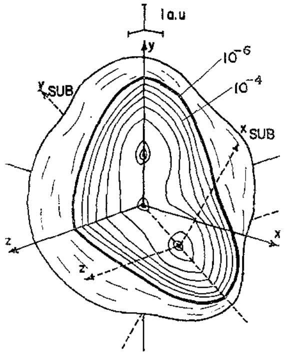
11th. M.O.
π_2 (~C=O)



13th. M.O.
π_3^* (~C¦O)



10th. M O.
σ_9 (~n_{F_x})



TOTAL ELECTRON DENSITY

machinery and time available), how should the functions be distributed among the centres to give the best results. This problem is peculiar to completely unsymmetrical molecules like the one studied here. The only *a priori* limitation is that there must be sufficient functions to describe the molecular electrons. In a

Table 5. *The optimum coefficient matrix* (Y_{ri}) *and orbital energies* (ε_r) *calculated with the minimal Gaussian basis set on* HCOF

Mol. Orbital		Centre	η_s	η_s	η_s	η_{px}	η_{py}	η_{pz}	Orbital Energy (a.u.)
		C	Y_{r1}	Y_{r2}	Y_{r3}	Y_{r4}	Y_{r5}	Y_{r6}	
r	ϕ_r	O	Y_{r7}	Y_{r8}	Y_{r9}	Y_{r10}	Y_{r11}	Y_{r12}	ε_r
		F	Y_{r13}	Y_{r14}	Y_{r15}	Y_{r16}	Y_{r17}	Y_{r18}	
		H	Y_{r19}						
1	σ_1	C	−0.000358	0.000208	−0.000024	−0.001275	0.000607	0.	
	$(1s_F)$	O	−0.000211	0.000047	−0.000001	0.000268	0.000116	0.	−25.825500
		F	0.034178	0.796156	0.303952	0.000032	0.001081	0.	
		H	−0.000481						
2	σ_2	C	0.001143	−0.000372	0.000027	0.000086	0.001259	0.	
	$(1s_O)$	O	−0.033113	−0.794018	−0.307608	−0.000064	0.001812	0.	−20.105600
		F	0.000113	−0.000029	−0.000002	−0.000123	0.000049	0.	
		H	0.000203						
3	σ_3	C	−0.027471	−0.788624	−0.318353	−0.000286	0.000351	−0.	
	$(1s_C)$	O	−0.000206	0.000555	0.000145	0.000050	0.002229	−0.	−11.004700
		F	0.000494	−0.000051	0.000023	−0.000027	−0.000070	−0.	
		H	−0.000151						
4	σ_4	C	0.249173	−0.119748	−0.027231	0.381635	−0.160464	−0.	
	(C–F)	O	0.073045	−0.021203	−0.004074	−0.027129	−0.057045	−0.	− 1.365700
		F	0.877862	−0.389209	−0.089196	−0.000758	0.002285	−0.	
		H	0.164377						
5	σ_5	C	0.407906	−0.188209	−0.043511	0.011297	0.410699	0.	
	(C–O)	O	0.676267	−0.324213	−0.075846	−0.001443	−0.060068	0.	− 1.229000
		F	−0.101819	0.050266	0.011964	0.006561	0.071057	0.	
		H	0.151989						
6	σ_6	C	0.424108	−0.217543	−0.054067	−0.180442	−0.283624	−0.	
	(C–H)	O	−0.333076	0.155409	0.036467	−0.067619	−0.247618	−0.	− 0.656700
		F	−0.253788	0.103917	0.023604	−0.075499	0.238987	−0.	
		H	0.402852						
7	σ_7	C	−0.176385	0.068606	0.017038	−0.402485	−0.026741	0.	
	(n_{F_y})	O	0.222690	−0.088349	−0.019949	−0.293375	0.193567	0.	− 0.407400
		F	0.399035	−0.150421	−0.033382	−0.184693	−0.439184	0.	
		H	0.272295						
8	π_1	C	−0.	0.	−0.	0.	−0.	−0.670677	
	(C=F)	O	0.	−0.	0.	−0.	−0.	−0.355241	− 0.333900
		F	−0.	0.	−0.	0.	−0.	−0.473958	
		H	0.						
9	σ_8	C	0.035562	0.010349	0.005723	0.069490	−0.259072	0.	
	(n_{O_y})	O	0.456520	−0.168297	−0.037527	0.070817	0.647543	0,	− 0.257700
		F	−0.185161	0.067738	0.015008	−0.289185	0.375320	0.	
		H	0.078579						

Table 5 (Continued)

Mol. Orbital	Centre	η_s	η_s	η_s	η_{px}	η_{py}	η_{px}	Orbital Energy (a.u.)
10 σ_9	C	0.095813	−0.030410	−0.007426	−0.079005	−0.049680	−0.	
(n_{Fx})	O	0.005956	0.000778	0.000657	0.029654	−0.332345	−0.	− 0.135200
	F	0.014758	−0.004556	−0.000970	−0.880996	−0.044408	−0.	
	H	−0.401734						
11 π_2	C	−0.	0.	−0.	0.	−0.	0.212403	
(C O)	O	0.	−0.	0.	−0.	−0.	0.538610	− 0.071700
	F	−0.	0.	−0.	0.	−0.	−0.808653	
	H	0.						
12 σ_{10}	C	0.094957	−0.016969	−0.002856	−0.048173	−0.019533	−0.	
(n_{Ox})	O	0.017215	−0.005962	−0.001347	−0.883143	−0.021008	−0.	− 0.070600
	F	0.013192	−0.004700	−0.000843	0.092391	0.326895	−0.	
	H	−0.397877						
13 π_3^*	C	−0.	0.	−0.	0.	−0.	−0.766912	
(C¦O)	O	0.	−0.	0.	−0.	−0.	0.805303	0.566800
	F	−0.	0.	−0.	0.	−0.	0.373726	
	H	0.						
14 σ_{11}^*	C	0.969977	−0.318431	−0.068837	−0.522408	−0.537890	−0.	
(C¦H)	O	0.167863	−0.036478	−0.006689	0.156920	0.149855	−0.	0.768400
	F	−0.068558	0.031657	0.007399	0.243483	−0.397383	−0.	
	H	−0.958705						
15 σ_{12}^*	C	0.254078	−0.117831	−0.027735	1.111229	0.186975	0.	
	O	−0.256702	0.085809	0.018618	−0.423251	0.327361	0.	1.099800
	F	−0.514013	0.173432	0.037561	−0.183189	−0.684484	0.	
	H	0.634587						
16 σ_{13}^*	C	−0.602593	0.188636	0.039602	0.337041	−1.035286	0.	
	O	0.869776	−0.265335	−0.056383	−0.117817	−0.820481	0.	1.369700
	F	−0.343408	0.107068	0.022711	0.170538	−0.275906	0.	
	H	0.125458						
17 σ_{14}^*	C	0.385836	−1.011711	1.125666	−0.033925	0.022960	−0.	
	O	−0.054776	0.007344	0.013710	0.004641	0.070756	−0.	30.516500
	F	−0.010371	0.002847	0.002883	−0.000645	−0.035131	−0.	
	H	−0.083463						
18 σ_{15}^*	C	−0.053745	0.033465	−0.016743	−0.004336	−0.096301	0.	
	O	0.359735	−0.994752	1.128295	0.000384	−0.051879	0.	57.350300
	F	−0.009327	−0.001753	0.005360	0.010810	−0.007729	0.	
	H	−0.014308						
19 σ_{16}^*	C	0.005657	−0.007311	0.003485	0.059165	−0.029778	0.	
	O	0.013683	−0.008097	0.005882	−0.013318	−0.008547	0.	73.675599
	F	−0.327577	0.983116	−1.128492	−0.000592	−0.022963	0.	
	H	0.024234						

Table 6. *The predicted total binding energy of* HCOF *from experimental and empirically correlated dissociation energies*

	Experimental Pauling [*22*]	Empirical McKelvie [*18*]
C=O	142.	181.5
C–F	107.	118.5
C–H	87.3	101.7
Total dissociation energy (Kcal/mole)	336.3	401.7
Total zero point energy[a] (Kcal/mole)	12.2	12.2
Total binding energy (Kcal/mole)	348.5	413.9

---

[a] The total zero point energy has been estimated from IR frequencies [*26*] with the following formula $E_{\text{z.p.}} = 1.44 \times 10^{13} \times \times \frac{1}{2} \text{hc} \sum_{i=1}^{6} \tilde{\nu}_i = 1.43 \times 10^{-3} \sum_{i=1}^{6} \tilde{\nu}_i = 1.43 \times 19^{-3} \times (2981.0 + + 1836.9 + 1342.5 + 1067.8 + 662.5 + 1000.0) = 12.71$ Kcal/mole. The value $\tilde{\nu}_6 = 1000 \text{ cm}^{-1}$ is an estimated figure from the deuterium isotope spectrum.

more symmetrical molecule, such as ethylene [*20*], the problem does not appear so acute as the distribution of functions is dictated almost entirely by symmetry considerations.

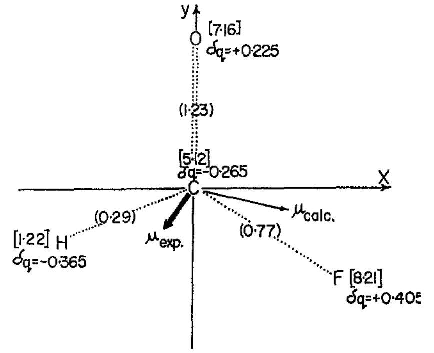


Fig. 3. Dipole moment, gross overlap electron populations, not atomic electron populations and net charges (q) of HCOF obtained from the minimal Gaussian basis set

In the present work three series of calculations were performed in an attempt to obtain at least partial and preliminary solutions to the distribution problem.

In the first series, equal numbers of functions were placed on each of the heavy atoms *(symmetrical improvement)*. In the second series, new functions were added to one centre only *(unsymmetrical improvement)*. In both these series of calculations the number of functions on the hydrogen atom was kept constant, as it was felt that, to a first approximation, the physical properties of the molecule would be determined mainly by the heavy atoms. In a third series of calculations the effects of varying the number of basis functions on the hydrogen atom was examined *(hydrogen improvement)*.

As well as the calculations on the molecules, calculations on the separated atoms were performed using the same basis sets as in the molecular calculations. This provided a "comparable" set of separated atom energies from which binding energies were calculated (cf. Section 2.3 of Ref. [*6*]).

2.2.1 *Symmetrical Improvement*

In the symmetrical improvement of the basis set either the number of s-type function was increased by two or the number of p-type function was increase by one (i.e. one in every direction: p_x, p_y, p_z); or both, from one discrete set to another. All the combinations within the given range ($3^s \leqq x^s \leqq 7^s$ and $1^p \leqq y^p \leqq 3^p$) gave nine distinct basis sets with minimum number of 19 and a maximum number of 49 atomic functions.

The total and orbital energies for some of the symmetrically improved basis sets are given in Tab. 7 for the various basis sets. Simple exponential function were fitted to the values for fixed s and p basis sets, and extrapolated to give total energy contours as a function of the changing basis size (Fig. 4). Exponential extrapolations were performed on the separated atoms also. The E values for all the extrapolations are summarized in Tab. 8. It is expected [*5*] that the enlargement of the basis set along the diagonal ($N = 19$, 34, 49) improved the wave function towards the Hartree-Fock limit as far as possible with scaled orbital exponents used.

Table 7. *The orbital and total energies of* HCOF *as obtained from "symmetrically improved" basis sets*

	No. of Orbs. on C. O. F.	$3^s + 1^p$	$5^s + 2^p$	$7^s + 3^p$
	Size of Basis Set	19	34	49
Orbital Energies	σ_{11}^*	+ 0.7684	+ 0.3896	+ 0.3102
	π_3^*	+ 0.5668	+ 0.2079	+ 0.1332
	σ_{10}	− 0.0706	− 0.4319	− 0.4956
	π_2	− 0.0717	− 0.4803	− 0.5482
	σ_9	− 0.1352	− 0.5426	− 0.6289
	σ_8	− 0.2577	− 0.6458	− 0.7269
	π_1	− 0.3339	− 0.6582	− 0.7374
	σ_7	− 0.4074	− 0.7311	− 0.8028
	σ_6	− 0.6567	− 0.8632	− 0.9061
	σ_5	− 1.2290	− 1.4737	− 1.4915
	σ_4	− 1.3657	− 1.6836	− 1.7123
	σ_3	− 11.0047	− 11.4622	− 11.4766
	σ_2	− 20.1056	− 20.6537	− 20.6072
	σ_1	− 25.8255	− 26.4306	− 26.3895
	Total Energy	−199.596526	−210.433417	−212.113905

The values obtained for some of the binding energies are given in Tab. 9. As can be seen, as the basis set increases from $3^s + 1^p$ to $7^s + 3^p$ on each heavy atom the binding energy charges from 1.32202 a.u. (830 kcal/mole) to about 0.289 a.u. (181.4 kcal/mole). The binding energy obtained from the smallest basis set was this considerably larger than the estimated value. As the basis set was improved however, the value decrease and eventually fell below the estimated value (Fig. 5). Since the binding energy is calculated as the difference of the expectation values of the energy of two approximate wavefunctions there is no reason to believe that the calculated values must approximate the accurate binding energy in an "assymptotic" manner as the wave functions gradually improved. A similar behaviour for derivative properties of hydrogen fluoride has been discussed previously [*6*].

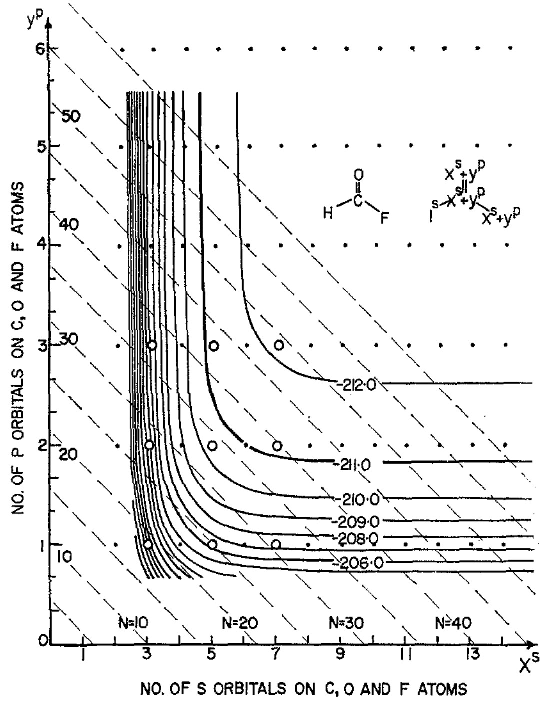


Fig. 4. Energy contours of the HCOF total energy for various "symmetrically improved" basis sets

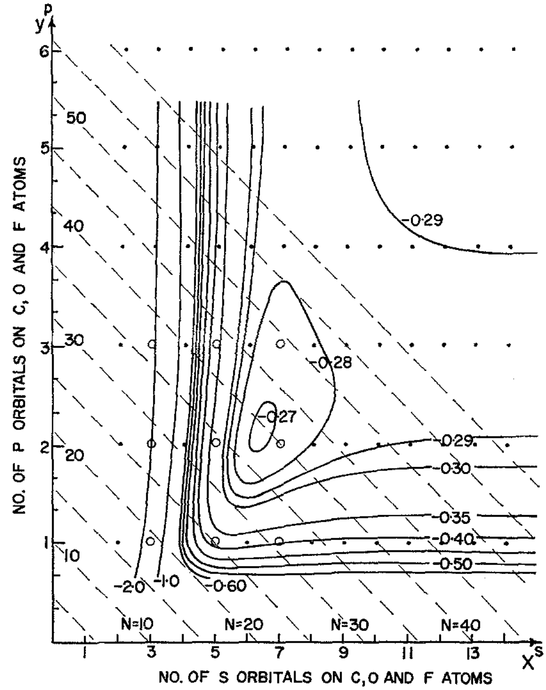


Fig. 5. Energy contours of the HCOF binding energy for various "symmetrically improved" basis sets

Table 8. *Exponential parameters (E_∞, E_0, β) of the orbital and total energies obtained by fitting an exponential ($E = E_\infty + E_0\, e^{-\beta q}$) along the diagonal ($q$)*

ϕ_r	E_∞	E_0	β
σ_{11}^*	$+\ 0.2891$	2.2864	0.4334
π_3^*	$+\ 0.1136$	2.1776	0.4353
σ_{10}	$-\ 0.5092$	2.4879	0.4814
π_2	$-\ 0.5617$	2.9489	0.4978
σ_9	$-\ 0.6521$	2.4401	0.4304
σ_8	$-\ 0.7483$	2.3479	0.4342
π_1	$-\ 0.7630$	1.7570	0.3910
σ_7	$-\ 0.8202$	1.8772	0.4181
σ_6	$-\ 0.9174$	1.2546	0.4358
σ_5	$-\ 1.4929$	3.6278	0.7270
σ_4	$-\ 1.7152$	3.8707	0.6670
σ_3	$-\ 11.4771$	15.0075	0.9592
σ_2	Not Exponential		
σ_1	Not Exponential		
Total Energy	-212.42233	82.70920	0.51695

The exact binding energy of the molecule ΔE_{exact} may be written as the sum of the following terms

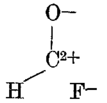
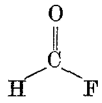
$$\Delta E_{\text{exact}} = \Delta E_{\text{H.F.}} + \Delta E_{\text{corr}} + \Delta E_{\text{rel}}\,.$$

The correlation energy ΔE_{corr} represents a systematic error in the wave function due to the fact that an SCF function, while taking care at least partially of correlation between electrons of parallel spin, does not take care at all of correlation between electrons of anti-parallel spin. $\Delta E_{\text{H.F.}}$ is simply the energy obtained in the Hartree-Fock limit. While ΔE_{rel} is that part of the energy that arises from relativistic effects. In a recent paper CLEMENTI suggested [*1*] that for first row atoms ΔE_{rel} should be rather small, while ΔE_{corr} could be estimated by summing the correlation energies per new electron pair created in the process of forming a molecule from the atoms. In HCOF four new electron pairs are created in forming the molecule, and if the correlation energy for each of these pairs can be determined, ΔE_{corr} can be estimated. In this work the total correlation correction was estimated making three different assumptions about the nature of the pairs formed. The resulting three values of ΔE_{corr} are shown in Tab. 10, and their close agreement encourages the hope that the estimates are meaningful. The preferred value of ΔE_{corr} is 0.263 a.u.

Table 9. *Sample binding energies of* HCOF *obtained from "symmetrically improved" basis sets as the difference of the total molecular energy and the sum of atomic energies*

No. of Orbs. on C, O, F atoms	$3^s + 1^p$	$5^s + 2^p$	$7^s + 3^p$
Size of Basis Set	19	34	49
Binding Energy	-1.32202	-0.30673	-0.28912

Table 10. *Estimation of the electronic correlation correction for the binding energy of Formyl fluoride*[a]

Classical Model	Ionic Model		Covalent Model	
4 Equivalent σ Bonds				
	2 σ bonds	0.130	C=O	0.111
4 × 0.065	O → O⁻	0.071	C–F	0.100
	F → F⁻	0.075	C–H	0.052
0.260		0.276		0.263

---

[a] The values of the components were kindly furnished by Dr. E. Clementi, to whom the authors are most grateful.

Although the above equation holds strictly only for energies calculated in the Hartree-Fock limit, the ($7^s + 3^p$) calculation reported here is probably sufficiently near this limit [5] to make a reasonable estimate of ΔE_{exact}. The value of the binding energy obtained using the ($7^s + 3^p$) results is 0.552 a.u. (346.5 kcal/mole) which is quite close to the empirically predicted one shown in Tab. 6.

The change of dipole moment (μ) and the x and y components (μ_x, μ_y) were also studied in relation to the symmetric improvement of the basis set. With $5^s + 2^p$ functions on the heavy atoms the calculated dipole moment vectors agreed fairly closely with the experimentally determined ones, both in magnitude and direction (Tab. 11 and Fig. 6). However, when more p orbitals were added ($5^s + 3^p$ and $7^s + 3^p$) the dipole moment vector rotated beyond the experimental direction, shifting towards the hydrogen atom. This is probably due to the fact that the H-atom is very poorly represented by a single s-type (1^s) function. Evidence for this view is presented later.

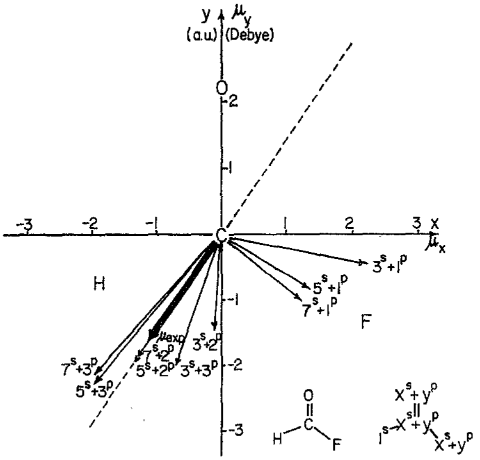


Fig. 6. Variation of the dipole moment vector of HCOF as a function of the "symmetrically improved" basis set

Table 11. *The calculated dipole moment*[a] *(in* Debye*) of* HCOF *as a function of the "symmetrically improved" basis set*

No. of Orbs. on C, O, F	$3^s + 1^p$	$5^s + 2^p$	$7^s + 3^p$
Size of Basis Set	19	34	49
μ_x	+2.2930	−1.3329	−1.9410
μ_y	−0.4867	−1.9394	−2.1546
$\|\mu\|$	2.3440	2.3533	2.9000

---

[a] The z component is always zero whenever the molecule is planar.

2.2.2. *Unsymmetrical Improvement*

The fluorine atom was chosen as the site for local improvement because much of the interest in the formyl series centres around possible substituents. It was hoped that local properties associated with this centre could calculated with greater accuracy from an unsymmetrical wave function.

In performing the unsymmetrical improvement the basis for the formyl portion of the molecule was kept fixed with 1^s on the hydrogen and $3^s + 2^p$ functions on the carbon and oxygen atoms. The number of functions of F was varied in the range $3^s \leq x^s \leq 7^s$, $1^p \leq y^p \leq 3^p$ so that again nine calculations were performed. Some orbital and total energy values are shown in Tab. 12, and total energy contours are given in Fig. 7. In Tab. 13 the binding energy values are given.

As may be seen the total energy obtained in each case is worse than the total energy obtained for a comparable number of functions in the symmetrically improved case. The extrapolated value of the electronic energy, −208.005417 a.u. is some 4 a.u. higher than the extrapolated value obtained using the symmetrically improved basis set. Comparison of the orbital energies indicates that only a few

Table 12. *The orbital and total energies of* HCOF *as obtained from "F-improved" basis sets*

No. of Orbs. on F		$3^s + 1^p$	$5^s + 2^p$	$7^s + 3^p$
Size of Basis Set		25	30	35
Orbital Energies	σ_{11}^*	+ 0.7168	+ 0.5789	+ 0.4929
	π_3	+ 0.3432	+ 0.2247	+ 0.1983
	σ_{10}	− 0.2808	− 0.4122	− 0.4371
	π_2	− 0.2534	− 0.4677	− 0.5097
	σ_9	− 0.3148	− 0.5222	− 0.5632
	σ_8	− 0.4083	− 0.5879	− 0.6649
	π_1	− 0.4954	− 0.6389	− 0.7130
	σ_7	− 0.5764	− 0.7142	− 0.7662
	σ_6	− 0.7121	− 0.8058	− 0.8476
	σ_5	− 1.1843	− 1.3089	− 1.3408
	σ_4	− 1.5982	− 1.6555	− 1.6868
	σ_3	− 10.8656	− 11.0076	− 11.0503
	σ_2	− 19.6032	− 19.7881	− 19.8174
	σ_1	− 26.1319	− 26.3964	− 26.3577
Total Energy		−201.68025	−206.95166	−207.82986

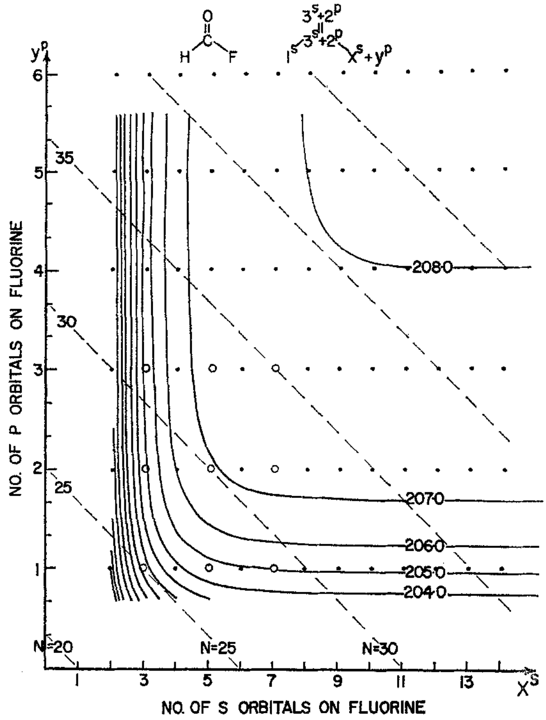


Fig. 7. Energy contours of the HCOF total energy as a function of "F-improved" basis sets

are lower in this case than in the symmetrical case. In particular the energy of the orbital σ_4 which can perhaps be associated with the C–F bond is invariably higher in this case than in the symmetrically improved case, although the energy of the orbital σ_1 associated chiefly with the fluroine core electrons is sometimes lower.

The tendency of the dipole moment vector to change direction as the basis set size is increased (Tab. 14 and Fig. 8) seems to indicate some part of "repulsive" effect caused by more orbitals being located on the fluorine centre.

The overall impression given by these results is that unsymmetrical improvement is not a successful policy. Once a certain part of the molecule is "frozen" the final outcome is limited by the crudely represented portion regardless of how well the remainder of the molecule is improved. This conclusion seems to apply not only to the case discussed but also to the case of "freezing" all the *s* orbitals while increasing only the number of *p* orbitals and *vice versa*, as was done when examining the effects of symmetrical improvement (see Tab. 7).

Table 13. *The binding energies of* HCOF *obtained from "F-improved" basis sets as the difference of total molecular energy and the sum of atomic energies*

No. of Orbs. on F atom	$3^s + 1^p$	$5^s + 2^p$	$7^s + 3^p$
Size of Basis Set	25	30	35
Binding Energy	−1.84422	−1.38636	−1.38543

Table 14. *The calculated dipole moment*[a] *(in* Debye*) of* HCOF *as a function of the "*F*-improved" basis set*

No. of Orbs. on F Size of Basis Set	$3^s + 1^p$ 25	$5^s + 2^p$ 30	$7^s + 3^p$ 35
μ_x	+0.3253	−0.8764	−1.5208
μ_y	−4.1039	−0.8970	−0.3454
$\lvert\mu\rvert$	4.1168	1.2540	1.5596

[a] The z component is always zero whenever the molecule is planar.

2.2.3 Hydrogen Improvement

In all the above calculations the hydrogen was represented by a single s-type function. In the third series of calculations the number of s-type functions on the hydrogen atom was increased, while the number of functions on the heavy atoms was kept constant at $3^s + 2^p$.

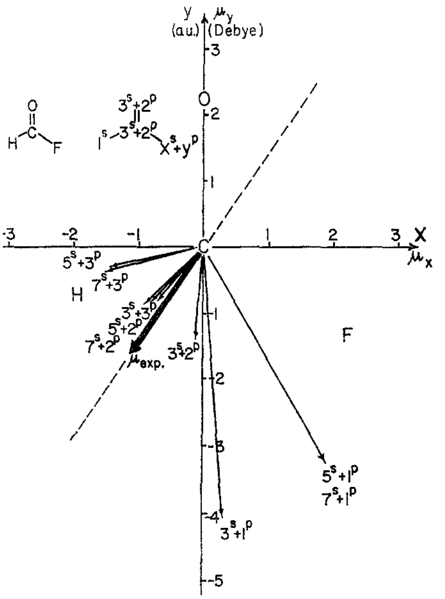


Fig. 8

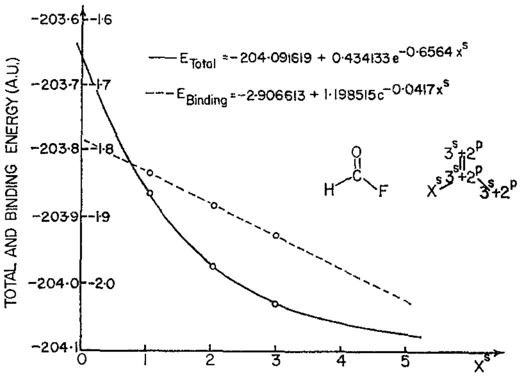


Fig. 9

Fig. 8. Variation of the dipole moment vector of HCOF as a function of the "F-improved" basis sets

Fig. 9. Variation of the total and binding energies of HCOF as a function of the "H-improved" basis set

The total orbital and binding energies are in Tab. 15 and Fig. 9. The decrease in energy with increase in the number of functions is seen to be quite small as expected, but it is interesting to note that the increase has a marked effect on the dipole moment vector direction (Tab. 16). Here there appears to be another "repulsive" effect, but this time pushing the dipole moment towards the fluorine atom (Fig. 10). This tendency of the dipole moment vector to change direction perhaps indicates a reason for the slightly tilted dipole moment vector obtained using the two largest symmetrically improved basis sets. The addition of one or two more s-functions to the hydrogens in these cases could possibly correct the defect in the dipole moment direction.

Table 15. *The orbital-, total- and binding-energies of* HCOF *for various "*H*-improved" basis sets*

No. of Orbitals on H Size of Basis Set (n)	1^s 28	2^s 29	3^s 30
	Orbital Energies in a.u.		
π_3^*	+ 0.2431	+ 0.2332	+ 0.2239
σ_{10}	− 0.3923	− 0.4100	− 0.4215
π_2	− 0.4415	− 0.4515	− 0.4629
σ_9	− 0.4964	− 0.5134	− 0.5261
σ_8	− 0.5665	− 0.5701	− 0.5901
π_1	− 0.6265	− 0.6333	− 0.6449
σ_7	− 0.6672	− 0.6768	− 0.6901
σ_6	− 0.7776	− 0.7955	− 0.8038
σ_5	− 1.2811	− 1.2954	− 1.3077
σ_4	− 1.3528	− 1.3716	− 1.3905
σ_3	− 10.9932	− 11.0101	− 11.0267
σ_2	− 19.7389	− 19.7687	− 19.7881
σ_1	− 25.2642	− 25.2732	− 25.2905
Total Molecular Energy	−203.86643	−203.97481	−204.03103
Total Atomic Energies	202.02935	202.09075	202.10191
Binding Energy	− 1.83708	− 1.88406	− 1.92912

2.3 The Structure of HCOF in its Electronic Ground State

In the light of the results given above a basis set must be chosen with which to perform the structural investigations. The results of the H-improved basis set calculations suggests that 2^s orbitals on the hydrogen represent on appreciable improvement over the single s-type function, and so two s type functions on the hydrogen were included throughout the structural calculations. The possible basis sets for the heavy atoms in order of preference $7^s + 3^p$, $5^s + 3^p$, $5^s + 2^p$, $3^s + 2^p$ and $3^s + 1^p$. Unfortunately use of the first three sets was ruled out on economic grounds. The calculations were therefore performed using $3^s + 2^p$ on the heavy atoms.

The structure of HCOF in its ground state was investigated by varying the bond lengths R(C–H), R(C=O) and R(C–F), the OCH angle and the out of plane

Table 16. *The calculated dipole moments (in* Debye*) of* HCOF *as a function of various "*H*-improved" basis sets*

No. of Orbs. on H Site of Basis Set	1^s 28	2^s 29	3^s 30
μ_x	−0.1058	+0.0662	+0.3877
μ_y	−1.4702	−1.4182	−1.3456
$\lvert \mu \rvert$	1.4740	1.4198	1.4004

---

[a] The z component is always zero whenever the molecule is planar.

angle Δ. For the bond length variations Δ was set at 0° (planar configuration) and OCH at the preferred angle (section 1.1) of 110° 2′. All the bond lengths except the one actually being investigated were held constant at their experimental values while the variation was performed. In determining the angle OCH, Δ was set at 0° (planar configuration), and R(C–O) and R(C–F) were given their experimental values, while R(C–H) was set at 1.024 Å, a distance somewhat longer than the best calculated one but shorter than the experimental value. To find the angular variation all the three substituting atoms O, F, H were bent out of the original plane of the molecule, keeping all interatomic distances at their experimental values.

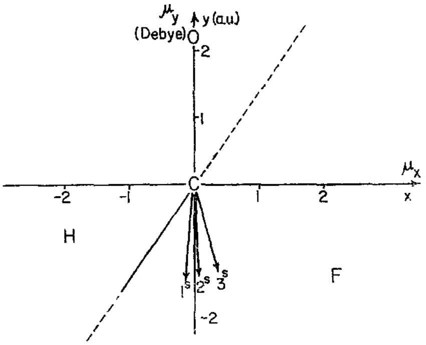


Fig. 10. Variation of the dipole moment vector of HCOF as a function of the "H-improved" basis set

The results of these calculations are shown in Tabs. 17 through 22 and in Figs. 11 through 13.

Table 17. *The electronic-, nuclear- and total-energy of* HCOF *as a function of* C–H *bond length*

R(C–H) (Å)	Electronic (a.u.)	Nuclear (a.u.)	Total (a.u.)
0.800	−272.875374	+68.893668	−203.981706
0.950	−271.960945	+67.949896	−204.011049
1.024	−271.557632	+67.562797	−203.994835
1.150	−270.936611	+66.989966	−203.946645

Table 18. *The electronic-, nuclear- and total-energy of* HCOF *as a of* C=O *bond lenth*

R(C=O) (Å)	Electronic (a.u.)	Nuclear (a.u.)	Total (a.u.)
0.900	−280.319298	+76.479465	−203.839833
1.185	−271.261734	+67.286924	−203.974810
1.300	−268.413754	+64.539234	−203.874520
1.400	−266.219219	+62.451923	−203.767296

Table 19. *The electronic-, nuclear- and total-energy of* HCOF *as a function of* C–F *bond length*

R(C–F) (Å)	Electronic (a.u.)	Nuclear (a.u.)	Total (a.u.)
1.000	−281.738712	+77.689701	−204.049011
1.150	−276.629047	+72.531646	−204.097401
1.250	−273.723854	+69.672979	−204.050875
1.345	−271.261734	+67.286924	−203.974810

Table 20. *The characteristic constants of parabolic stretching potential curves*

Stretching Mode of Motion	E_0 a.u.	R_0 Å	a a.u./Å^2
C=O	−203.996677	1.1125	3.474083
C–F	−204.099195	1.1262	3.151932
C–H	−204.011957	0.9278	1.851534

In Tabs. 17, 18, and 19, the results of the bond length variation calculations are shown, while in Tab. 20 and Fig. 11, the results of fitting parabolas:

$$E = E_0 + a(R - R_0)^2$$

to these data are given. It is observed that the best calculated values for the bond lengths are appreciably shorter than the experimentally determined lengths. Using the parabolas fitted to the bond length variation data, force constants for bond stretching were obtained and these are shown in Tab. 21. The calculated force constants are several orders of magnitude larger than these estimated from the IR frequencies [*26*]. No doubt part of this error is due to the fact that the calculated force constants were not for proper normal modes of the molecule, but it seems likely that the error in this and in the bond lengths is mostly due to the defficiencies in the basis set. Comparable calculations on hydrogen fluoride [*6*]

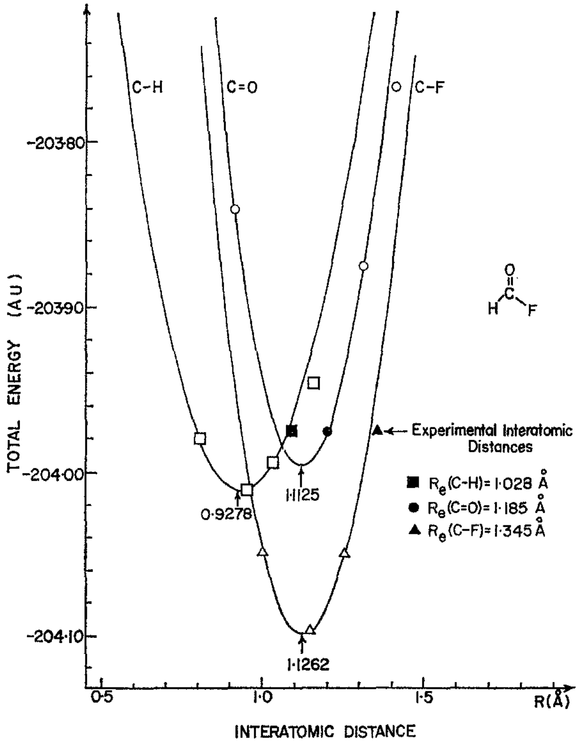
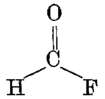
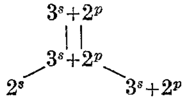


Fig. 11. Parabolic potential curves of HCOF as a function of the bond lengths

Table 21. *Interatomic distances and approximate stretching force constants of formyl fluoride* (HCOF)





Stretching Mode of Motion	Bond Distance			Force Constant		
	R^0_{exp} (Å)	R^0_{calc} (Å)	ΔR (%)	k_{exp} mdyn/Å	k_{calc} mdyn/Å	Δk (%)
C=O	1.1850	1.1125	6.08	13.6267	108.1649	693.8
C–F	1.3450	1.1262	16.28	4.9114	98.1359	1898
C–H	1.0820	0.9278	14.23	4.8647	57.6400	1085

indicate that bond lengths and force constants are fairly sensitive functions of basis set size, and that good results for them can be obtained only with fairly large basis sets. As can be seen from Tab. 22 and Fig. 12, the asymmetric potential curve for the OCH angle variation possesses a shallow but noticable double minimum. The lowest minimum (closer to oxygen) is at 105°, with higher shoulder (closer to fluorine) at 140°. The energy difference between these two is 0.004 a.u. (2.5 kcal/mole) which, though small, is felt to be important. However, for the reasons outlined before, it is not possible to give the value of this energy difference

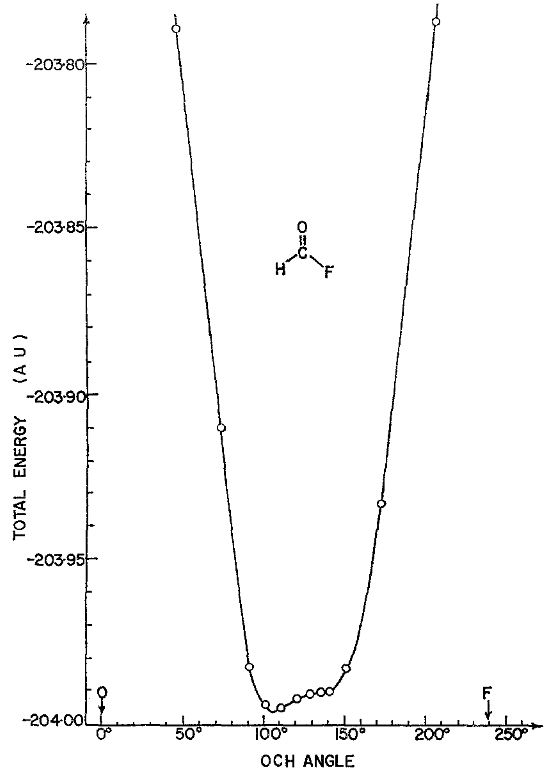


Fig. 12. Potential curve of HCOF as a function of the OCH angle

Table 22. *The electronic-, nuclear- and total-energy values of* HCOF *as a function of* OCH *angle*

OCH Angle	Electronic Attraction	Nuclear Repulsion	Total Energy
40.0°	−274.314526	+70.525656	−203.788870
70.0°	−272.251091	+68.340642	−203.919449
90.0°	−271.771332	+67.788714	−203.982618
100.0°	−271.637253	+67.643152	−203.994101
110.2°	−271.551632	+67.562797	−203.994835
120.0°	−271.535786	+67.543697	−203.992089
127.3°	−271.555923	+67.565392	−203.990531
135.0°	−271.611748	+67.622003	−203.989745
140.0°	−271.571423	+67.581155	−203.990268
150.0°	−271.826134	+67.843435	−203.982699
170.0°	−272.373440	+68.440558	−203.932882
200.0°	−274.463699	+70.675989	−203.787710

quantitative significance. It is believed to have physical significance which would certainly account for the variations in the experimentally measured OCH angles. It should perhaps be noted that the distance O ... H at ∢ OCH = 105° and F ... H at ∢ OCH = 140° are almost identical, which might be taken to indicate the presence of "pseudo" hydrogen bonding [*27*].

Calculations at out of plane conformations were made with Δ = 10°, 20°, 30° and 40°. The variation of energy is shown in Fig. 13. There seems to be no indication of a double minimum in this case, so it may be concluded that the calculation is in agreement with experiment in predicting a planar ground state for the system.

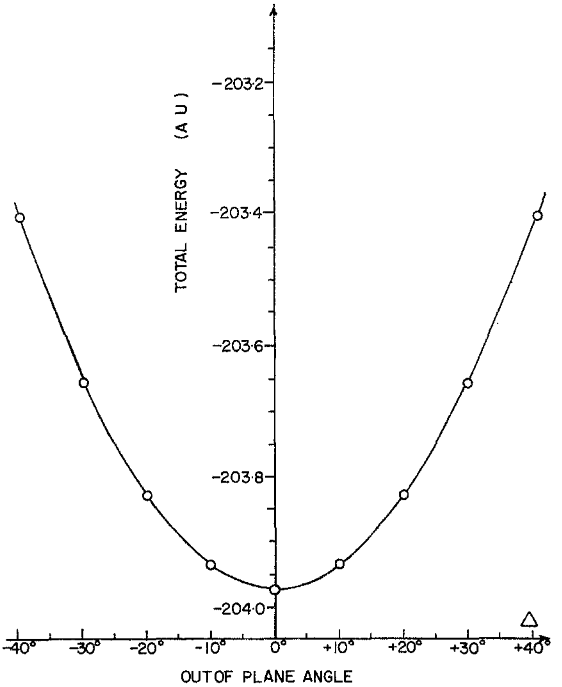


Fig. 13. Potential curve of HCOF as a function of the out of plane distortion

In a later paper we shall discuss the structure of HCOF in its excited state using a wave function obtained by a configuration interaction method. There we shall also consider the effect of CI on the ground state structure.

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