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THEORETICAL CALCULATION OF THE SINGLET-SINGLET ELECTRONIC TRANSITION AND PHOTOCHEMICAL REACTIVITY IN FLUOROXYTRIFLUOROMETHANE,FLUOROPEROXYTRIFLUOROMETHANE,BIS-(TRIFLUOROMETHYL)PEROXIDE AND BIS-(TRIFLUOROMETHYL)TRIOXIDE

Emilce OTTAVIANELLI and Eduardo A. CASTRO*
División Química Teórica,INIFTA,suc.4 c.c.16,La Plata (1900)
(Argentina)
Alicia H. JUBERT
QUINOR,Facultad de Ciencias Exactas,Universidad Nacional de La Plata,
47 y 115, La Plata (1900) (Argentina)

SUMMARY

Molecular properties following electronic excitation and calculation of the singlet-singlet electronic transitions in fluoroxytrifluoromethane,fluoroperoxytrifluoromethane,bis-(trifluoromethyl) peroxide and bis-(trifluoromethyl)trioxide were performed by means of the CNDO/S-CI method. Various approximations were used to evaluate the two-center Coulomb repulsion integrals and the core Hamiltonian matrix elements.

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* Author to whom correspondence should be addressed

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INTRODUCTION

Few papers have been devoted to the theoretical investigation of compounds such as the highly fluorinated hypofluorite, peroxide and trioxide compounds as fluoroxytrifluoromethane (CF_3OF),fluoroperoxytrifluoromethane (CF_3OOF),bis-(trifluoromethyl)peroxide (CF_3OOCF_3) and bis-(trifluoromethyl)trioxide (CF_3OOOCF_3).These molecules are of great chemical interest due to their photochemical reactivity.

In order to elucidate their photochemical behaviour we studied,from a theoretical point of view, their molecular properties following electronic excitation,by means of the semiempirical method CNDO/S-CI.

We studied,also,the effect on the calculations of the lower spectroscopic states associated with the singlet-singlet electronic transitions of several approximations to the two-center Coulomb repulsion integrals γ_{AB} and the core Hamiltonian matrix elements $\beta_{\mu\nu}$.

We feel that the calculations proposed would be a good tool for experimentalists in order to have a complementary insight on the photochemical and spectroscopic properties of the molecules considered .

METHOD OF COMPUTATION

We used the CNDO/S-CI method with the parametrization due to Del-Bene and Jaffe [1,2]. The computational program was run on an IBM 4361 computer.The source program was modified to suit local input-output requirements . Excited state wave functions were generated from the occupied ground state and virtual orbitals through a configuration interaction procedure among the 40 lowest energy single excited states.It was felt that inclusion of more Slater determinants would not alter the present findings qualitatively.The program provides for the choice of several approximations such as those of Nishimoto-Mataga (NM)[3],Ohno-Klopman (OK)[4] integrals to the two-center Coulomb integrals as well as the theoretical (T) option for the same calculations.In addition,several relationships have been proposed for evaluating the bond parameters,all of which take account of the dependence of $\beta_{\mu\nu}$ on bond length.In the present work we used the following approximations: Del Bene-Jaffe (DBJ)[2],Pople-Segal-Santry (PSS)[5] and Mulliken (M)[6].

The geometrical parameters for the calculations were taken from the literature [7-10] and the absortion spectra of the compounds from different references,as shown in Table 4.

The properties of the excited states can be rationalized by analyzing the charge densities in the various spectroscopic states.In the virtual orbital approximation to the excited states wave functions the atomic charge densities in the excited states are given by [2]:

$$q(A)_i^{*} = q(A)^{\circ} + \sum_{m=1}^{\ell} \sum_{r=1}^{n} C'^{2}_{im} \left(C^{2}_{k'r} - C^{2}_{jr} \right)$$

$q(A)^{\circ}$ is the ground state charge density,C'_{im} is the CI coefficient for the contribution to the <u>ith</u> state of the <u>mth</u> electronic configuration resulting from the excitation of an electron from orbital j to virtual k' and C_{jr} and $C_{k'r}$ are the coefficients of the <u>rth</u> orbital on atom A in molecular orbitals j and k',respectively.

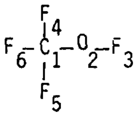
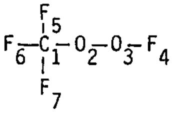
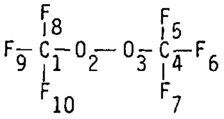
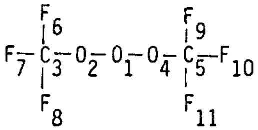
RESULTS AND DISCUSSION

A look at the selected occupied and virtual eigenvectors that take part in the computed electronic transitions shows that the relative localization and symmetry patterns are virtually independent of the approximation used to calculate both the two-center Coulomb repulsion integrals γ_{AB} and bond parameters $\beta_{\mu\nu}$ .Therefore,the present discussion is restricted to the results obtained with NM and M approximations to the calculation of γ_{AB} and $\beta_{\mu\nu}$,respectively,as presented in Table 1,although calculations were performed also with different approximations.

The MOs that are significant in the computed transitions are the lowest unoccupied MO(LUMO) and the highest occupied MO(HOMO). The HOMO

TABLE 1

Eigenvectors and relative localization for selected eigenvalues

Molecule	Molecular symmetry	Eigenvectors	Localization
 $F_6-\overset{F_4}{\underset{F_5}{C_1}}-O_2-F_3$	C_s	HOMO a"(n)	$O_2=0.64$ $F_3=0.25$ $F_4=F_5=0.05$
		LUMO a'(π^*)	$C_1=0.32$ $O_2=0.25$ $F_3=0.22$ $F_5=0.07$
 $F_6-\overset{F_5}{\underset{F_7}{C_1}}-O_2-O_3-F_4$	C_1	HOMO a(n)	$O_2=0.23$ $O_3=0.51$ $F_4=0.15$
		LUMO a(π^*)	$C_1=0.39$ $O_2=0.12$ $O_3=0.20$ $F_6=0.09$
 $F_9-\overset{F_8}{\underset{F_{10}}{C_1}}-O_2-O_3-\overset{F_5}{\underset{F_7}{C_4}}-F_6$	C_s	HOMO a"(n)	$O_2=O_3=0.43$
		LUMO a'(π^*)	$C_1=C_4=0.19$ $O_2=O_3=0.18$
 $F_7-\overset{F_6}{\underset{F_8}{C_3}}-O_2-O_1-O_4-\overset{F_9}{\underset{F_{11}}{C_5}}-F_{10}$	C_1	HOMO a(n)	$O_1=0.48$ $O_2=0.12$ $O_4=0.30$
		LUMO a(π^*)	$O_1=0.33$ $O_2=0.13$ $O_4=0.11$ $C_3=0.11$ $C_5=0.12$

lies predominantly on the oxygens while the LUMO are localized on the C-O bonds for the different molecules,except in the bis-(trifluoromethyl)trioxide where the LUMO is localized on the oxygens.

The correlation of the excited singlet states for the different molecules involving NM/M approximation to the calculation of γ_{AB} and $\beta_{\mu\nu}$ is given in Table 2. Although calculations were also performed with different approximations.

A certain quasi degeneracy can be observed for some spectroscopic levels of equal or different symmetry which must be traced to the molecular Coulomb and exchange integrals.

In fact,it is quite possible that when the three and four-center integrals are neglected as in this method,it is impossible for the one and two-center integrals to distinguish sufficiently between the different electronic states and split them accordingly.

The lowest energy singlet excited states: $^1A''$ for CF_3OF and CF_3OOCF_3 and ^1A for CF_3OOF and CF_3OOOCF_3 comprise almost entirely the $n\pi^*$ configuration. The lowest singlet electronic transitions result from the transitions $a' \leftarrow\!\!-\!- a''$ in CF_3OF and CF_3OOCF_3 and $a \leftarrow\!\!-\!- a$ in CF_3OOF and CF_3OOOCF_3.

The results of the CNDO/S-CI atomic density differences for excited singlets from ground state of the atoms involved in intramolecular charge transfer are shown in Table 3.The discussion is restricted to the NM/M approximations,nevertheless the same tendency is shown in the results obtained with the other options . It can be seen that within the series CF_3OF,CF_3OOF,CF_3OOCF_3 and CF_3OOOCF_3 the carbon atoms become more basic in the excited state .In bis-(trifluoromethyl)peroxide an unequal difference of density is found on the carbon atoms when NM/DBJ and OK/DBJ approximations were used and on the oxygens atoms when T/DBJ and OK/DBJ options were considered. In bis-(trifluoromethyl)trioxide the difference of density is nearly zero for the carbon atoms because the electron densities on these atoms are not involved in the electronic transition.

In table 4 the experimental and calculated (by means of all the γ_{AB} and $\beta_{\mu\nu}$ approximations) values of the lowest $n \dashrightarrow \pi^*$ transitions for all the molecules are shown. As there are no experimental values

TABLE 2

CNDO/S singlet-singlet correlation of the lowest electronic states with NM/M approximations

Molecule	E before CI	Nature	State transition symmetry	E after CI
CF_3OF				
	9.1425	$a'' \rightarrow a'$	A''	7.5960
	10.7634	$a' \rightarrow a'$	A'	9.1031
	14.4700	$a'' \rightarrow a'$	$2A''$	12.7782
	14.2221	$a' \rightarrow a'$	$2A'$	12.9407
CF_3OOF				
	10.5462	$a \rightarrow a$	A	7.7369
	11.5792	$a \rightarrow a$	2A	9.9844
	11.7181	$a \rightarrow a$	3A	11.3871
	12.4798	$a \rightarrow a$	4A	11.9546
	13.1036	$a \rightarrow a$		
CF_3OOCF_3				
	8.0839	$a'' \rightarrow a'$	A''	7.4630
	10.5323	$a' \rightarrow a'$	A'	9.9921
	14.1186	$a'' \rightarrow a'$	$2A''$	12.7875
	14.1994	$a'' \rightarrow a'$	$3A''$	12.9454
CF_3OOOCF_3				
	9.6199	$a \rightarrow a$	A	8.1456
	10.5451	$a \rightarrow a$	2A	9.3778
	11.0050	$a \rightarrow a$	3A	9.6758
	11.9393	$a \rightarrow a$	4A	10.7554

TABLE 3

CNDO/S-CI electron density difference for the lowest excited singlet from ground state in CF_3OF , CF_3OOF , CF_3OOCF_3 and CF_3OOOCF_3 calculated with NM/M approximations

Molecule	CF_3OF	CF_3OOF	CF_3OOCF_3	CF_3OOOCF_3
State	$^1A''$	^1A	$^1A''$	^1A
	C_1:0.32337	C_1:0.31985	C_1:0.16747	O_1:-0.17509
	O_2:-0.36749	O_2:-0.13509	O_2:-0.20690	O_2:-0.02022
	F_3:-0.06919	O_3:-0.24623	O_3:-0.20941	C_3:0.10195
	F_4:0.01992	F_4:-0.02059	C_4:0.16705	O_4:-0.15318
	F_5:0.07337	F_5:0.00897	F_5:-0.00609	C_5:-0.15942
	F_6:0.01992	F_6:0.02936	F_6:0.04986	F_6:0.03274
		F_7:0.04349	F_7:-0.00609	F_7:0.00869
			F_8:-0.00864	F_8:0.00081
			F_9:0.06038	F_9:0.06851
			F_{10}:-0.00864	F_{10}:-0.01135
				F_{11}:-0.01282

of the maximum absorption of the lowest $n \rightarrow \pi^*$ electronic transitions we have to use another criteria in order to discriminate the best calculated values. If we consider the electronegativities' of the different groups attached to CF_3O we have on the Huheey *[11-12] scale values for OF:12.95;$OOCF_3$; 12.30;F:12.18 and OCF_3:11.75.If we correlate the electronegativity of the substituent with the position of the band corresponding to the lowest $n \rightarrow \pi^*$ transition we will expect an energy order $\nu_{CF_3OOF} < \nu_{CF_3OOOCF_3} < \nu_{CF_3OF} < \nu_{CF_3OOCF_3}$.

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* Electronegativity values within a)Huheey's scale: H=7.17 ,F=12.18 , Cl=9.38 ,Br=8.40 ;b)Pauling's scale: H=2.1 ,F=4.0 ,Cl=3.0 ,Br=2.8 .

TABLE 4

The lowest experimental and calculated $n \rightarrow \pi^*$ electron transition[nm]

Molecule	E^{exp}	E^{calc}								
		Method of calculation								
		NM/DBJ	NM/PSS	NM/M	T/DBJ	T/PSS	T/M	OK/DBJ	OK/PSS	OK/M
CF_3OF	absorption from 340[a]	95.6	150.7	163.2	92.5	148.0	—	91.4	147.7	161.0
CF_3OOF	--	92.2	158.4	160.2	88.9	152.3	153.3	88.9	161.0	161.0
CF_3OOCF_3	--	96.5	165.4	166.1	89.5	156.5	142.1	91.9	161.2	162.0
CF_3OOOCF_3	absorption from 260[b]	137.3	273.5	152.2	131.5	253.9	138.7	139.2	279.8	154.8

[a] M.Blesa and P.Aymonino,Anal.Asoc.Quim.Argentina,56(1968)101

[b] P.Thompson,J.Am.Chem.Soc.,89(1967)4316

An inspection of the values in table 4 indicates that those calculated for the CF_3OOOCF_3 with the PSS approximation are out of the range of the absorption that begins at 260 nm and results on the difference of density calculated for the CF_3OOCF_3 with the DBJ option gives an unequal value for both carbon and oxygen atoms. In the light of the previous statements we considered that M would be the best approximation for the $\beta_{\mu\nu}$ calculation. As stated in [13] the value of γ_{AB} calculated theoretically is overestimated below R=2.0A . So NM or OK would be the recomnended options for evaluating γ_{AB} .

CONCLUSIONS

The photochemical behaviour of the molecules that follows the absorption of light corresponds to the lowest electronic transition. We can conclude that in CF_3OOF,CF_3OF and CF_3OOCF_3 the intramolecular charge transfer from the oxygen to the carbon atom will cause a lengthening of the C-O bond distance due to the excitation of the lone pair electron to the π^*_{C-O} orbital,while in CF_3OOOCF_3 the charge transfer occurs from the central oxygen atom O_1 to the oxygen O_2 and carbon atom C_3 and from the oxygen atom O_4 to the carbon atom C_5 so,we can expect that a lengthening of the O_1-O_4 bond will occur.

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