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CNDO/S-CI SCF MO Study of the Lower States of Perfluoroacetic Anhydride. Singlet-Singlet and Singlet-Triplet Electronic Transitions

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The CNDO/S-CI spectral parametrization has been used to elucidate the lower electronic states of perfluoroacetic anhydride. The $a_2(\pi^*)$ unoccupied molecular orbital lies predominantly on the carbonyl group, while the $b_1(n_0)$ is largely on the oxygen atoms. The lowest energy singlet excited state $1B_2$ is comprised almost entirely of the $n\pi^*$ configuration. Since the singlet and triplet $1B_2(n_0\pi^*)$, $1A_2(n_0\pi^*)$ result from a transition from molecular orbitals that are predominantly located on the oxygens to a molecular orbital containing about 80% C=O character, transitions to these states result in charge transfer from the oxygen to the carbon atom of the carbonyl group. Although the transition energies calculated in this study may not yield absolute comparisons with experimental values, it appears that the introduction of self-consistency, together with configuration interaction, leads to a fairly good interpretation of the singlet-singlet and singlet-triplet transitions. Various approximations were used to evaluate the two-center Coulomb repulsion integrals and the core Hamiltonian matrix elements.

INTRODUCTION

In previous papers a description was given of the ground state molecular orbitals (MO's) as well as a detailed analysis of the lower spectroscopic states associated with the singlet-singlet^{1a} and singlet-triplet^{1b} electronic transitions of perfluoromethyl oxalate (PFMO) and perfluorofluoroformate (PFMF) using the CNDO/S-CI methodology. Several approximations to the two-center Coulomb integrals γ_{AB} were used: Pariser-Parr (PP)², Nishimoto-Mataga (NM)³, and Ohno-Klopman (OK)⁴ integrals. In addition, different relationships were also used for evaluating the bond parameters $\beta_{\mu\nu}$: Del Bene-Jaffé (DBJ)⁵,

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Pople-Segal (PS)⁶, theoretical, and Mulliken (M)⁷. The aim of the present work is to extend these results to the study of the perfluoroacetic anhydride (PFA) in order to analyze the influence of the Mulliken and Del Bene-Jaffé approximations on the electronic spectra calculation.

METHOD OF COMPUTATION

Complete computational details are given in ref.^{1a}. Since no structural study of the PFA is available, the molecular geometry has been ascertained by comparison with related compounds⁸.

RESULTS AND DISCUSSION

A) GROUND STATE AND VIRTUAL ORBITALS CORRELATION

A look at the selected occupied and virtual eigenvectors that take part in the computed electronic transitions shows that the relative localization and symmetry pattern are virtually independent of the approximation used to calculate both the two-center Coulomb repulsion integrals γ_{AB} and bond parameters β_{uv} . Therefore, the present discussion is restricted to the results obtained with the NM, PP, M, and DBJ approximations to the calculation of the electron repulsion and bond parameters, as presented in Table I.

TABLE I

CNDO/S Eigenvectors and Relative Localization for Selected Eigenvalues of Perfluoroacetic Anhydride

(NM/DBJ) approximation

40 b_2 (π^*)	$C_{2,4}$ (0.36)	$O_{6,7}$ (0.14)
39 a_2 (π^*)	$C_{2,4}$ (0.31)	$O_{6,7}$ (0.18)
38 b_1 (σ)	$C_{2,4;3,5}$ (0.07)	$O_{6,7}$ (0.27)
37 a_1 (σ)	$O_{6,7}$ (0.28)	
36 b_2 (π)	O_1 (0.27)	$O_{6,7}$ (0.30)
34 a_1 (σ)	O_1 (0.37)	$O_{6,7}$ (0.37)
33 b_1 (σ)	$O_{6,7}$ (0.19)	

(NM/M) approximation

41 b_1 (σ^*)	$C_{2,4}$ (0.10)	$C_{3,5}$ (0.18)	O_1 (0.16)
40 b_2 (π^*)	$C_{2,4}$ (0.15)	$C_{3,5}$ (0.12)	$O_{6,7}$ (0.10)
39 a_2 (π^*)	$C_{2,4}$ (0.19)	$O_{6,6}$ (0.18)	
38 b_2 (π)	O_1 (0.34)	$O_{6,7}$ (0.29)	
37 b_1 (σ)	$O_{6,7}$ (0.32)		
36 a_2 (σ)	$O_{6,7}$ (0.36)		
34 a_1 (σ)	O_1 (0.21)	$O_{6,7}$ (0.31)	
29 b_1 (σ)	$O_{6,7}$ (0.34)		

(PP/DBJ) approximation:

42 b_1 (σ^*)	$C_{2,4}$ (0.22)	$C_{3,5}$ (0.22)
41 a_1 (σ^*)	$C_{2,4}$ (0.21)	$C_{3,5}$ (0.22)
40 b_2 (π^*)	$C_{2,4}$ (0.32)	$O_{6,7}$ (0.16)
39 a_2 (π^*)	$C_{2,4}$ (0.33)	$O_{6,7}$ (0.16)
38 b_1 (σ)	$O_{6,7}$ (0.28)	
37 a_1 (σ)	$O_{6,7}$ (0.30)	
36 b_2 (π)	O_1 (0.27)	$O_{6,7}$ (0.31)
35 a_1 (σ)	O_1 (0.33)	$O_{6,7}$ (0.17)
34 a_2 (π)	$C_{2,4}$ (0.15)	$O_{6,7}$ (0.32)
33 b_1 (σ)	$O_{6,7}$ (0.19)	$C_{2,4}$ (0.08)

(PP/M) approximation:

41 $b_1(\sigma^*)$	$C_{2,4}$ (0.11)	$C_{3,5}$ (0.17)	
40 $b_2(\pi^*)$	$C_{2,4}$ (0.16)	$C_{3,5}$ (0.12)	$O_{6,7}$ (0.09)
39 $a_2(\pi^*)$	$C_{2,4}$ (0.21)	$O_{6,7}$ (0.18)	
38 $b_1(\sigma)$	$O_{6,7}$ (0.31)	O_1 (0.08)	
36 $a_1(\sigma)$	$O_{6,7}$ (0.31)		
35 $a_1(\sigma)$	O_1 (0.18)	$O_{6,7}$ (0.32)	
34 $a_2(\pi)$	$C_{2,4}$ (0.14)	$O_{6,7}$ (0.23)	
33 $b_1(\sigma)$	$O_{6,7}$ (0.26)		
31 $b_1(\sigma)$	$O_{6,7}$ (0.15)	$F_{9,10,11,12,13}$ (0.13)	

(NM/DBJ): Nishimoto-Mataga/Del Bene-Jaffé

(NM/M): Nishimoto-Mataga/Mulliken

(PPP/DBJ): Pariser-Parr/Del Bene-Jaffé

(PPP/M): Pariser-Parr/Mulliken

In discussing the MO's resulting from these computations it is convenient to consider the molecule as divided between a carbonyl portion and a donor portion attached to the carbonyl group, in this case the lone pair electrons on the oxygens (n_0).

The MO's that important in the computed transitions are the lowest unoccupied MO $a_2(\pi^*)$ and the highest occupied MO of symmetry $b_1(n_0)$ according to the molecular symmetry group (Figure 1).

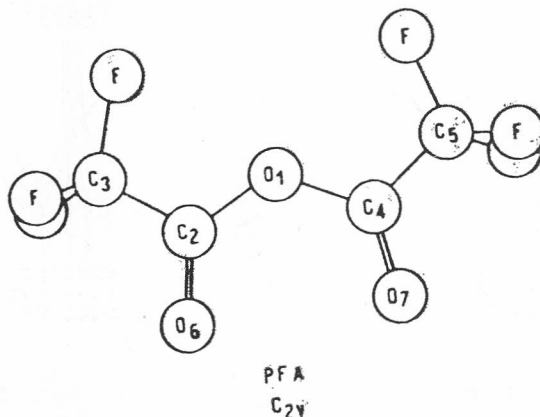


Figure 1. Numbering scheme of perfluoroacetic anhydride (PFA). Molecular symmetry group is C_{2v} .

As indicated in Table I the deepest MO's involved in the electronic transitions show the same character as far as the relative localization and atomic orbital composition is concerned. The $a_2(\pi^*)$ unoccupied MO lies predominantly on the carbonyl group, while the $b_1(n_0)$ is largely on the oxygens. The $a_1(\sigma)$, $b_1(\sigma)$ and $b_2(\pi)$ occupied MO's lie predominantly on the oxygens. However, the contribution, as shown in Table I, is not too large and thus the CNDO/S description of the electron lone pairs in this study is in general agreement with many previous all valence electron SCF calculations which have predicted the electron lone pairs to be partially delocalized through the molecule^{5,9-12}.

The first ionization potential is predicted to be $b_1(n_0)$, mainly localized on the oxygens. Thus, according to Koopman's theorem, this ionization is of σ symmetry.

B) EXCITED STATES CORRELATION

The correlation of the excited singlet and triplet states of PFA, involving different approximations to the calculation of the two-center Coulomb repulsion integrals γ_{AB} and bond parameters β_{lv} is given in Figures 2 and 3.

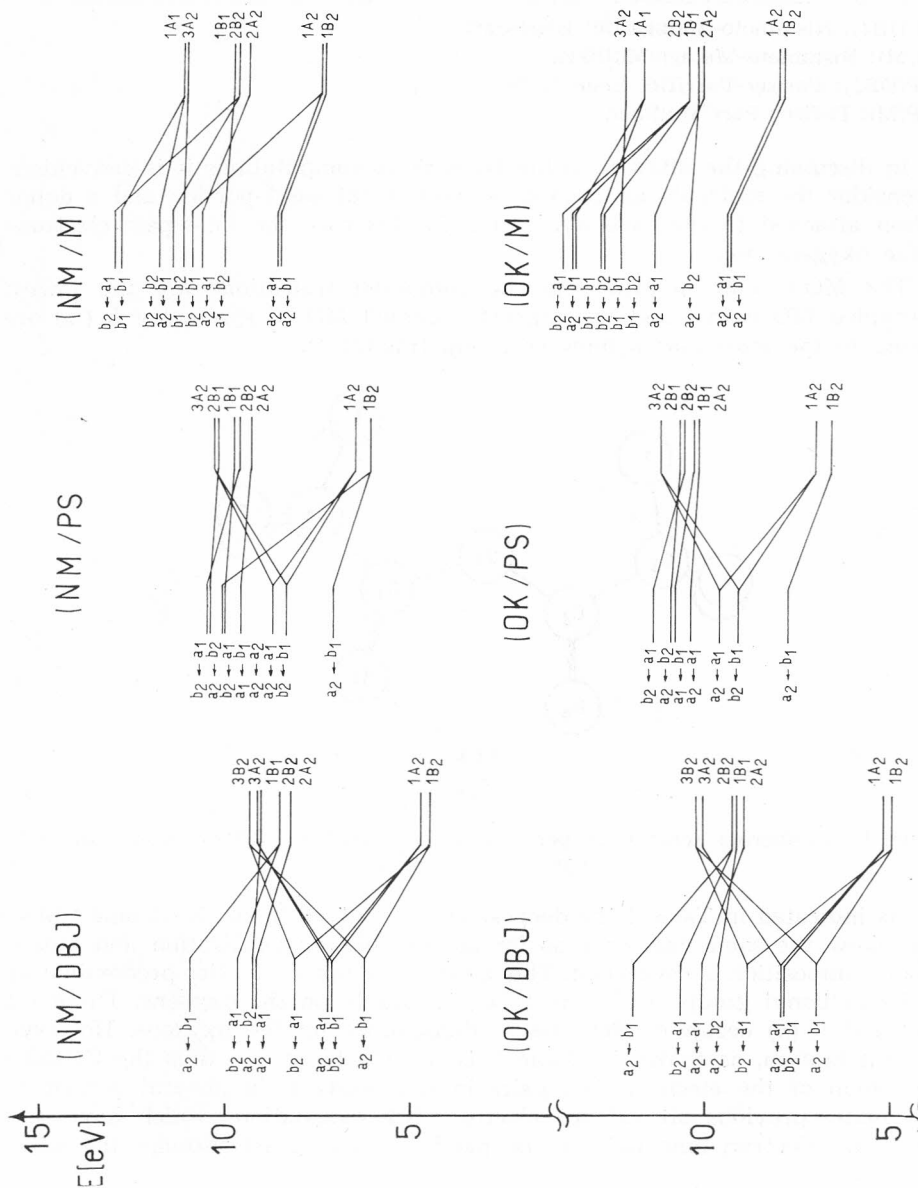


Figure 2. continued on next page

A certain quasidegeneracy can be observed of 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 three- and four-center integrals are neglected as they are 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 state $1B_2$ is comprised almost entirely of the $n\pi^*$ configuration. The singlet electronic transition between 4.17 and

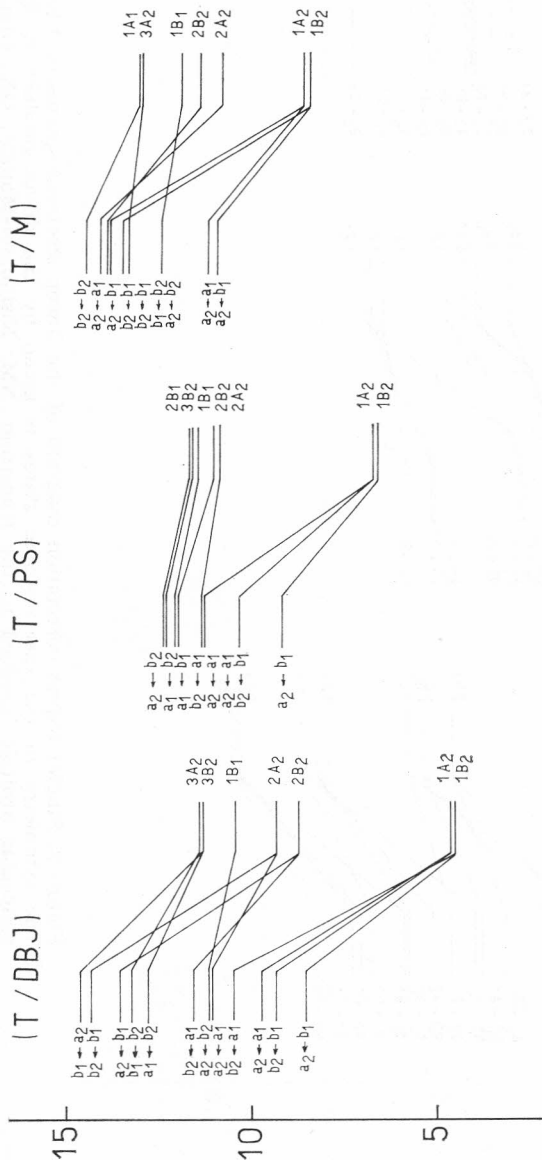


Figure 2. Singlet-singlet correlation diagram of the lower electronic states of PFA. The symmetry of the spectroscopic states is given by the direct product of the spectroscopic states is given by the direct product of the molecular orbitals involved in the transition. NM: Nishimoto-Mataga; OK: Ohno-Klopman; T: Theoretical; DBJ: Del Bene-Jaffé; PS: Pople-Segal; M: Mulliken.

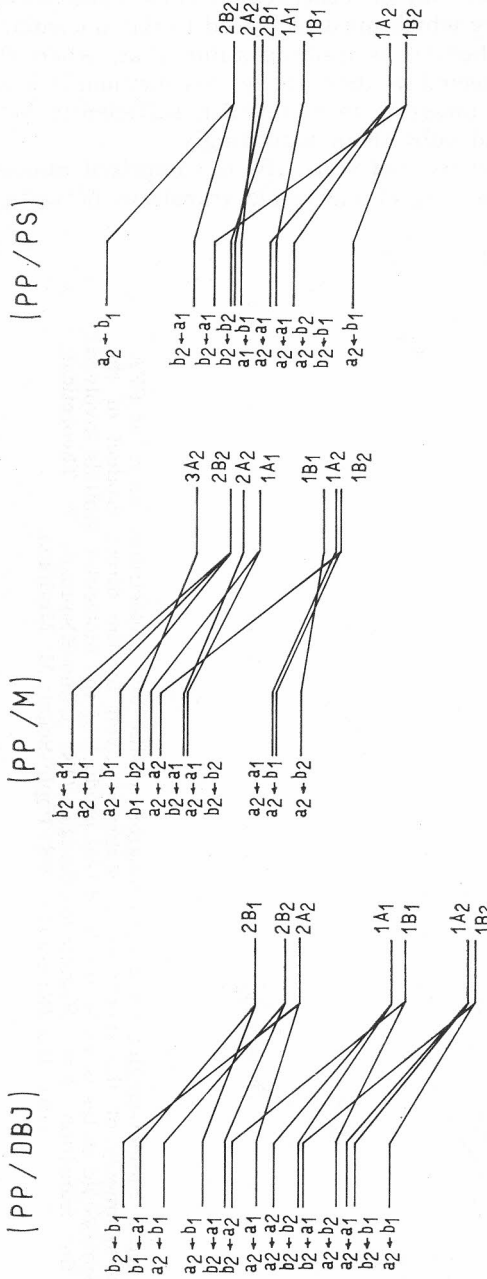


Figure 3. Singlet-triplet correlation diagram of the lower electronic states of PFA. The symmetry of the spectroscopic states is given by the direct product of the molecular orbitals involved in the transition. NM: Nishimoto-Mataga; OK: Ohno-Klopman; T: Theoretical; DBJ: Del Dene-Jaffé; PS: Pople-Ssegal; M: Mulliken.

7.67 eV (predicted with theoretical/DBJ and theoretical/M calculations respectively) results from the transition $a_2 \leftarrow b_1$. This electronic transition is expected to be of low and rather small intensity compared with the $\pi^* \leftarrow \pi$ transition because of the large difference between the charge distribution in the ground state and the $n\pi^*$ excited states. That is, the n orbital lies in the molecular plane, whereas the nodal plane of the π orbital is the molecular plane (the oscillator strengths of the $n\pi^*$ transitions are computed to be almost zero in the CNDO approximation).

It should be noted that the ε_{π^*} unoccupied orbital energies and the corresponding eigenvectors ψ_{π^*} responsible for the $n\pi^*$ transitions are not the same as the corresponding ones for the $\pi\pi^*$ transitions. This circumstance arises from the nonbonding orbital, i. e., the carbonylic oxygens become very electronegative in the $n\pi^*$ excited state. This change of the core Hamiltonian matrix elements leads to a value of ε_{π} which is lower than that of the $\pi\pi^*$ transition.

In compounds containing two carbonyl groups bonded by an oxygen atom, such as in PFA, the π MO's of the conjugated system may be considered as being formed by interaction of the π MO's of the two carbonyl groups and the oxygen atom. Thus, the lower energy of the lowest spectroscopic state of PFA compared with PFMO and PFMF is due to a conjugative interaction which operates fully since the C=O groups and the oxygen atom are coplanar. Hence, the separation between the antibonding π MO's and that between the bonding π MO's should become maximum, in agreement with previous calculations performed on PFMO¹. It should be also pointed out that the decrease of energy by admitting CI is higher when the DBJ approximation is used. Worth of mention is the fact that the Mulliken approximation seemed to be the most adequate to describe the lower singlet excited electronic states of PFMF.

The computed triplet transitions $1B_1$ and $1A_2$ lie in the range 6.23—8.56 eV and 4.74—7.70 eV respectively, and result from transitions from $b_2(\pi)$; $b_1(n_0)$, $a_1(n_0)$ to the $a_2(\pi^*)$; $b_2(\pi^*)$, $a_2(\pi^*)$. The triplet transitions $1A_1$, $2A_2$, $2B_2$ result from transitions to the $b_2(\pi^*)$, $a_2(\pi^*)$ which arise from transitions from the $b_2(\pi)$, $a_1(n_0)$ MO's.

For energies higher than 6.5 eV, it is observed that the introduction of a limited CI gives rise to a mixture of spectroscopic states of different symmetry, regardless of the approximation used, which complicates the assignment of theoretical bands in this spectral region.

Since the singlet and triplet $1B_2(n_0\pi^*)$, $1A_2(n_0\pi^*)$ result from a transition from MO's that are predominantly on the oxygen to a MO containing about 80% C=O character, transitions to these states result in charge transfer from oxygen to the carbon atom of the carbonyl group.

These excited state properties can be rationalized by analyzing the charge densities in the various spectroscopic states. In the virtual orbital approximation to the excited wavefunctions the atomic charge densities in the excited states are given by

$$q(A)_i^* = q(A)^0 + \sum_{m=1}^1 \sum_{\Gamma=1}^n c'_{im}{}^2 (c_{k\Gamma}{}^2 - c_{j\Gamma}{}^2)$$

where $q(A)^0$ is the ground state charge density; c_{im} is the CI coefficient for the contribution to the i th state of the m th 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 r th orbital on atom A in MO's j and k' respectively.

The results of the CNDO/S atomic electron density differences for excited singlets and triplets from ground state of the atoms involved in intramolecular charge transfer are compared in Table II.

TABLE II

CNDO/S-CI Electron Density Difference for Excited Singlets and Triplets From Ground State in Perfluoroacetic Anhydride

SINGLETs- (NM/DBJ) approximation:

Atom	State					
	1^1B_2	1^1A_2	2^1A_2	2^1B_2	1^1B_1	3^1A_2
O_1	-0.0243	-0.0117	-0.2635	-0.1974	-0.2621	-0.0012
$C_{2,4}$	0.2769	0.2689	0.2597	0.2566	0.2580	0.2697
$C_{3,5}$	-0.0625	-0.0671	-0.0232	-0.0245	0.0044	-0.0703
$O_{6,7}$	-0.1571	-0.1311	-0.0044	-0.0198	-0.1294	-0.1398

TRIPLETs- (PP/DBJ) approximation

Atom	State					
	1^3B_2	1^3A_2	1^3B_1	1^3A_1	2^3A_2	2^3B_2
O_1	-0.0233	-0.0107	-0.1739	-0.1109	-0.2311	-0.1587
$C_{2,4}$	0.2833	0.2826	0.2552	0.2385	0.2783	0.2749
$C_{3,5}$	-0.689	-0.0667	-0.0004	-0.0005	-0.0233	-0.0229
$O_{6,7}$	-0.1428	-0.1485	-0.1647	-0.1783	-0.0314	-0.0449

(NM/DBJ): Nishimoto-Mataga/Del Bene-Jaffé

(PP/DBJ): Pariser-Parr/Del Bene-Jaffé

The O_1 is predicted to be more basic in the ground state than in the excited states. A significant acidic character was found in the $2A_2$, $2B_2$, and $1B_1$ excited states. On the other hand, the carbonylic carbon atoms become more basic in these excited states, which supports the idea of intramolecular charge transfer from the oxygen to the carbon atom of the carbonyl group.

CONCLUSIONS

This study has shown that CNDO/S calculations provide a quantitative basis for the understanding of various ground and excited singlet and triplet state properties of PFA.

The nature of the low lying singlet and triplet states were further elucidated by a detailed study of the calculated CI wavefunctions, thus providing an excellent opportunity to examine the nature of the lone pair electrons in these excited states. The first conclusion to be drawn is that the $1B_2$ band is correlated pictorially with a single electron jump between n_0 and π^* orbitals.

Thus, depending on the approximation used to calculate the two-center Coulomb integrals and bond parameters, a low intensity transition to the $1B_2(n_0 \pi^*)$ state is predicted to occur at 4.17—7.67 eV. The $\pi\pi^*$ electronic transition, on the other hand, is calculated to occur in the energy range 6.23—9.53 eV.

Worth of mention is the fact that within the CNDO/S approximation, the DBJ approximation to evaluate the core Hamiltonian matrix elements would seem to be the most appropriate to describe the lower singlet and triplet excited electronic states in the PFA (B_2 states) and PFMO (A_u, B_g states), while the Mulliken approximation would seem to be the most adequate to describe the lower singlet and triplet excited states of PFMF (A'' states).

The differences pointed out must be analyzed in the light of the approximations involved in the parametrization of the resonance integrals. The term $1/2 (\beta_A^0 + \beta_B^0) S_{\mu\nu}$ in the Fock matrix elements $F_{\mu\nu}$ plays the role of the resonance integral $\beta_{\mu\nu}$ of most MO methods and represents a measure of the bonding energy between the orbitals μ and ν . In the Mulliken approximation (6a, b), β_A^0 and β_B^0 are parameters characteristic of the atoms A and B. The use of this formulation led to complete intermingling of σ and π MO's.

DBJ approximation easily distinguishes the $\beta_{\mu\nu}$, where μ and ν are σ orbitals, from those where μ and ν are π orbitals, by introducing a new empirical parameter⁵. Thus, from the present and previous results¹ it is concluded that for PFA and PFMO (where the degree of conjugation is greater than in PFMF) the DBJ approximation gives better estimates of the electronic transitions than the Mulliken approximation, which must be attributed to the σ — π separation involved in the former.

Finally, although the transition energies calculated in this study may not yield an absolute comparison with experimental values, it appears that the introduction of self-consistency together with configuration interaction, leads to a fairly good interpretation of the singlet-singlet and singlet-triplet transitions. It was further found that transitions to the π^* states result in intramolecular charge transfer from the oxygen to the carbon atom of the carbonyl group. This probably causes a lengthening of the C=O bond distance due to the excitation of the lone pair electron to the $\pi_{C=O}^*$ orbital.

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SAŽETAK

Razmatranje nižih pobuđenih stanja anhidrida perfluoroctene kiseline s pomoću metode CNDO/S-CI SCF MO. Elektronski prijelazi između singulet-singulet i singulet-triplet stanja

Alicia Haydee Jubert i Horacio Grinberg

Elektronski prijelazi između osnovnog i nižih pobuđenih stanja anhidrida perfluoroctene kiseline proučavani su primjenom semiempirijske CNDO/S-CI metode. Računi pokazuju da je prazna molekulska orbitala $a_2(\pi^*)$ simetrije lokalizirana na CO-skupini, dok se $b_1(n_0)$ proteže preko kisikovih atoma. Utvrđeno je da pri elektronskim prijelazima singulet-singulet i singulet-triplet dolazi do preraspodjele naboja pri čemu se elektronska gustoća pomiče s kisikovih atoma na ugljik u karbonilnoj skupini. Energije prijelaza dosta se dobro slažu s eksperimentalnim vrijednostima.