Theoret. chim. Acta (Berl.) 22, 330–336 (1971)

Semi-Empirical MO–CI Calculations on Excited States

IV. Unsaturated Molecules*

D. R. SALAHUB**
Département de Chimie, Université de Montréal, Montréal, Québec, Canada

Received December 2, 1970

Results of semi-empirical all-valence-electron MO–CI calculations are presented for the electronic spectra of ethylene, the fluoroethylenes, a series of imines, and a series of aldehydes. These results are compared with the experimental spectra.

Die Ergebnisse semiempirischer Allvalenzelektronen-MO–CI-Rechnungen für die Elektronenspektren von Äthylen, Fluoräthylen, sowie einer Reihe von Iminen und Aldehyden werden mitgeteilt und mit den experimentellen Spektren verglichen.

Des calculs semi-empiriques tenant compte de tous les électrons de valence relatifs aux spectres électroniques de l'éthylène, des fluoroéthylènes, d'une série d'imines, et d'une série d'aldéhydes ont été effectués. On compare ces résultats aux spectres observés.

Introduction

In previous papers [1–3] we have given results of semi-empirical MO–CI calculations on the electronic spectra of saturated molecules. While these methods were primarily aimed at interpreting the spectra of σ-electronic systems and the parameters were chosen to this aim, we have also done calculations on several unsaturated molecules.

The invariance requirements of the CNDO and INDO methods greatly reduce their flexibility and, indeed, Del Bene and Jaffé [4] found a complete intermingling of σ and π levels in benzenoid hydrocarbons. They circumvented this by taking different bonding parameters for $\pi-\pi$ interactions. Jug [5] has recently given a critical apraisal of invariant procedures and suggests the use of different orbital exponents for σ and π orbitals.

While these modified methods generally give better agreement with experiment, we feel that they prejudice the outcome of a calculation to a large extent. If we wish to know about $\sigma-\pi$ interaction, or separability, or to be able to distinguish $\pi^*\leftarrow\pi$, $\pi\leftrightarrow\sigma$, and $\sigma^*\leftarrow\sigma$ transitions by a calculation then preliminary assumptions about the relative positions of these should be avoided. We have therefore retained the same methods of calculation as we used for the saturated molecules [1].

---

* Paper I: Salahub, D. R., Sandorfy, C.: Theoret. chim. Acta (Berl.) **20**, 227 (1971).
Paper II: Salahub, D. R., Sandorfy, C.: Chem. Physics Letters **8**, 71 (1971).
Paper III: Salahub, D. R.: Theoret. chim. Acta (Berl.) **22**, 325 (1971), preceding paper.

** Present address: School of Molecular Sciences, The University of Sussex, Brighton, BN1 9QJ, England.

We have studied ethylene, the fluoroethylene, a series of imines, and a series of aldehydes. As for the saturated molecules [3] because of the large number of molecules studied we limit ourselves to a brief discussion of the major results for electronic transitions. More extensive results, including charge distributions, lone-pair delocalization, ionization potentials, and singlet-singlet and singlet-triplet transitions are available on request, in the form of technical reports.

Results and Discussion

Ethylene

It is beyond the scope of the present work to enumerate all the references on the ethylene spectrum. We instead refer the reader to the review article of Merer and Mulliken [6]. A recent paper by Basch and McKoy [7] gives a good review of some of the non-empirical calculations on ethylene.

We have studied ethylene by all three of our methods, CNDO, INDO and RCNDO (including Rydberg atomic orbitals in the basis). The main results are gathered in Table 1. While we could not hope for a detailed interpretation of the ethylene spectrum, several features of the results are noteworthy.

i) In all methods there is at least one singlet $\sigma \leftarrow \pi$ transition predicted lower than the $V \leftarrow N(\pi^* \leftarrow \pi)$ band. While this is not in direct conflict with experiment since these are all forbidden or of low calculated intensity, and would be expected to be weak and possibly hidden under the long wavelength tail of the $V \leftarrow N$ band, there is no spectral evidence for their existence.

ii) The V state is, in all methods, composed mainly of the (π^*, π) configuration but also a non-negligible contribution from a higher $B_{1u}(\sigma^*, \sigma)$ configuration (14% for CNDO, 23% for INDO, and 35% for RCNDO). This type of configurational mixing was suggested by Basch and McKoy [7] as a means to correct the faulty prediction of open-shell Hartree-Fock calculations that the V state has a higher energy than the Rydberg state observed at 9.05 eV.

Table 1. *Experimental and calculated results for the ethylene spectrum* (eV)

Exptl.[a]		CNDO			INDO			RCNDO			% Ryd. char.		
ΔE	f	ΔE	f	Sym.	ΔE	f	Sym.	ΔE	f	Sym.	H	C	Tot.
7.1		7.50	0.00	$B_{2g}(\sigma^* \leftarrow \pi)$	7.76	0.00	$B_{2g}(\sigma^* \leftarrow \pi)$	5.84	0.00	$B_{2g}(\sigma^* \leftarrow \pi)$	1	1	2
$(3s \leftarrow \pi)$		7.57	0.00	$B_{1g}(\pi^* \leftarrow \sigma)$	8.27	0.00	$B_{1g}(\pi^* \leftarrow \sigma)$	7.03	0.08	$\left.\begin{matrix} B_{1u}(\pi^* \leftarrow \pi) \\ (\sigma^* \leftarrow \sigma) \end{matrix}\right\}$	1	0	1
7.45	0.00	8.27	0.00	$B_{3u}(\sigma^* \leftarrow \pi)$	8.46	0.00	$B_{3u}(\sigma^* \leftarrow \pi)$	7.15	0.00	$B_{1g}(\pi^* \leftarrow \sigma)$	1	0	1
7.6 $(\pi^* \leftarrow \pi)$	0.3	8.53	0.20	$\left.\begin{matrix} B_{1u}(\pi^* \leftarrow \pi) \\ (\sigma^* \leftarrow \sigma) \end{matrix}\right\}$	9.10	0.14	$\left.\begin{matrix} B_{1u}(\pi^* \leftarrow \pi) \\ (\sigma^* \leftarrow \sigma) \end{matrix}\right\}$	7.19	0.00	$B_{2g}(\pi^* \leftarrow \sigma)$	1	0	1
		8.83	0.00	$B_{2g}(\pi^* \leftarrow \sigma)$	9.19	0.30	$B_{2u}(\sigma^* \leftarrow \sigma)$	7.64	0.00	$\left.\begin{matrix} B_{3u}(\sigma^* \leftarrow \pi) \\ (3s \leftarrow \pi) \end{matrix}\right\}$	13	7	20
4.4 $^3(\pi^* \leftarrow \pi)$		6.19	—	$B_{1u}(\pi^* \leftarrow \pi)$	5.77	—	$B_{1u}(\pi^* \leftarrow \pi)$	4.69	—	$B_{1u}(\pi^* \leftarrow \pi)$	1	0	1

[a] Experimental values are given in Ref. [6]. States which have two assignments, joined by a curly bracket, receive large contributions from both configurations.

iii) The agreement with experiment even for the valence-shell transitions seems best for the RCNDO method. The bonding parameters used in this method may be more appropriate for π systems. We obtain quite good agreement for the V (7.03 eV vs. 7.6 eV), R (7.64 eV vs. 7.1 eV) and T (4.69 eV vs. 4.4 eV) states. The first Rydberg[1] p transition is found at 9.65 eV and gives a calculated quantum defect of 0.77. This is followed quite closely by transitions to other combinations of Rydberg orbitals which have different energies because of the loss of spherical symmetry in the molecule.

iv) The calculation yields B_{1g} and $B_{2g}\pi^* \leftarrow \sigma$ transitions at 7.15 and 7.19 eV respectively. We would tentatively assign the electric-dipole forbidden, electric-quadrupole allowed transition observed at 7.45 eV [8, 9] to one of these.

v) In all methods the lowest triplet state is predicted to be the T, $^3(\pi^*, \pi)$ state. This is, in all cases, nearly completely $\pi^* \leftarrow \pi$ in contrast to the V state which had considerable $\sigma^* \leftarrow \sigma$ character. The RCNDO method necessarily fails to predict a singlet-triplet split for $\pi \leftrightarrow \sigma$ transitions so that we can make no prediction as to the position of the triplet $3s \leftarrow \pi$ transition.

Fluoroethylenes

Recently Bélanger and Sandorfy [10] measured the spectra of the fluorine substituted ethylenes. They found an easily identifiable $\pi^* \leftarrow \pi$ band with its maximum between 7.28 and 7.81 eV for all but tetrafluoroethylene for which a large hypsochromic shift was observed, the band maximum being at 8.88 eV. This was preceded in several cases by a weaker band between 6.49 and 6.63 eV. Several of these have been interpreted as the first members of Rydbergs series [11].

In order to find these trends in the calculated results we were obliged, as in the case of the perfluoroalkanes [3], to take different values of $\beta^0_{\mathrm{C-C}}$ in our INDO method depending on the number of fluorine atoms in the molecule. The values used were -15 eV for mono- and di-, -17 eV for tri-, and -20 eV for tetra-substituted molecules. The results for the first $(\sigma^* \leftarrow \pi)$ transitions and the $\pi^* \leftarrow \pi$ transition are shown in Table 2.

In this way we find a relatively intense band of mainly $\pi^* \leftarrow \pi$ type which falls in the range 7.4 to 8.1 eV for all the molecules except C_2F_4 where it is found at 9.2 eV. This large hypsochromic shift occurs in spite of a decreased ionization potential ($I_{C_2HF_3} = 10.14_{\mathrm{expt.}}$ [12] $= 9.85_{\mathrm{calc.}}$; $I_{C_2F_4} = 10.11_{\mathrm{expt.}}$ [13] $= 9.59_{\mathrm{calc.}}$).

The effect of configuration interaction is very important for these molecules. Before CI the $\pi^* \leftarrow \pi$ transitions fall in the range 8.4 to 9.5 eV. For the partially fluorinated molecules these mix with higher $\sigma^* \leftarrow \sigma$ (C–C–H) configurations and are "pushed" to the red. In C_2F_4 there are no more C–H bonds and the σ^* (C–C–F) states come at much higher energies resulting in less interaction and little change in the $\pi^* \leftarrow \pi$ transition energy.

The first transition in all the molecules was found to be of the $\sigma^* \leftarrow \pi$ type at an energy in the range 5.4 to 7 eV.

---

[1] We have not used the concept of united-atom Rydberg states. See Ref. [1].

Table 2. *The first* $(\sigma^*\leftarrow\pi)$ *bands and* $\pi^*\leftarrow\pi$ *band of fluoroethylenes* (eV). *Experimental values are from Ref.* [9]

Molecule	Expt.		INDO		
	$\Delta E_{\max}$	ε	ΔE	f	Sym.
$CH_2=CHF(C_s)$	…	…	6.48	0.00	$A''(\sigma^*\leftarrow\pi)$
			7.67	0.00	$A''(\sigma^*\leftarrow\pi)$
	7.44	10000	8.17	0.06	$A'(\pi^*\leftarrow\pi)$
			(9.18)[a]		$(\sigma^*\leftarrow\sigma)$
$CH_2=CF_2(C_{2v})$	…	…	5.76	0.00	$B_1(\sigma^*\leftarrow\pi)$
			8.16	0.00	$B_1(\sigma^*\leftarrow\pi)$
			8.18	0.00	$A_2(\sigma^*\leftarrow\pi)$
	7.50	7900	8.19	0.12	$A_1(\pi^*\leftarrow\pi)$
			(8.92)[a]		$(\sigma^*\leftarrow\sigma)$
cis-$CHF=CHF(C_{2v})$	6.49	1680	5.62	0.00	$A_2(\sigma^*\leftarrow\pi)$
			6.63	0.00	$B_1(\sigma^*\leftarrow\pi)$
	7.81	7490	7.41	0.07	$B_2(\pi^*\leftarrow\pi)$
			(8.35)[a]		$(\sigma^*\leftarrow\sigma)$
trans-$CHF=CHF(C_{2h})$	6.63	780	5.43	0.00	$B_g(\sigma^*\leftarrow\pi)$
	7.28	5360	7.40	0.09	$B_u(\pi^*\leftarrow\pi)$
			(8.38)[a]		$(\sigma^*\leftarrow\sigma)$
$CHF=CF_2(C_s)$	6.50	1940	5.77	0.00	$A''(\sigma^*\leftarrow\pi)$
			7.80	0.00	$A''(\sigma^*\leftarrow\pi)$
	7.61	6800	8.17	0.17	$A'(\pi^*\leftarrow\pi)$
			(8.80)[a]		$(\sigma^*\leftarrow\sigma)$
$CF_2=CF_2(D_{2h})$	6.57	2475	7.17	0.00	$B_{2g}(\sigma^*\leftarrow\pi)$
			9.04	0.00	$B_{1g}(\sigma^*\leftarrow\pi)$
	8.88	11370	9.16	0.33	$B_{1u}(\pi^*\leftarrow\pi)$
			(9.49)[a]		

[a] Numbers in parentheses are the energies of the (π^*, π) configuration before CI.

Imines

The $C=N$ group is especially interesting (as is the $C=O$ group) in that its electronic spectrum should consist of all the general types of transitions: $\pi^*\leftarrow\pi$, $\pi^*\leftarrow n$, $\sigma^*\leftarrow n$, $\sigma^*\leftarrow\pi$, $\pi^*\leftarrow\sigma$, $\sigma^*\leftarrow\sigma$, as well as, possibly, Rydberg transitions. In a recent monograph Sandorfy [14] presented the far-ultraviolet spectra of $CH_3CH=N-C_3H_7$ and $(CH_3)_2CH-CH=N-C_2H_5$ taken in these laboratories by P. Sauvageau and the author. These consist of broad, structureless bands with wellpronounced maxima at about 7.3 eV and 8.0 eV. Many shoulders and inflections are also present, indicating that the bands are of a composite nature. Robin and Simpson [15], published the spectrum of $C_2H_5-CH=N-(CH_2)_3CH_3$ in an article on azo-dye prototypes and also found a weak band at about 42,000 cm^{-1}.

Unfortunately compounds (R′) (R) $C=N-R''$ where R, R′, and R″ are small alkyl groups are quite unstable. These could have possibly given spectra with finer detail and also have served as guides for calculations. We have used our INDO method to calculate the spectra of the models: $H_2C=N-H$ (I), $CH_3CH=N-CH_3$ (II) and $(CH_3)_2\,C=N-CH_3$. The main results are shown in Table 3.

Table 3. *The five lowest singlet-singlet transitions of imines by the* INDO–CI *method* (eV)

Molecule	ΔE	f	Type
$H_2C{=}N{-}H$	5.50	0.00	$\pi^* \leftarrow n$
	6.20	0.12	$\sigma^* \leftarrow n$
	6.87	0.10	$\sigma^* \leftarrow n$
	9.98	0.02	$\sigma^* \leftarrow n$
	10.01	0.02	$\sigma^* \leftarrow \pi$
$CH_3CH{=}N{-}CH_3$	4.86	0.00	$\pi^* \leftarrow n$
	5.84	0.00	$\sigma^* \leftarrow n$
	5.93	0.14	$\sigma^* \leftarrow n$
	7.10	0.02	$\sigma^* \leftarrow n$
	8.15	0.02	$\sigma^* \leftarrow \pi$
$(CH_3)_2C{=}N{-}CH_3$	4.72	0.00	$\pi^* \leftarrow n$
	5.66	0.10	$\sigma^* \leftarrow n$
	5.90	0.10	$\sigma^* \leftarrow n$
	6.76	0.04	$\sigma^* \leftarrow n$
	7.66	0.04	$\sigma^* \leftarrow \pi$

The first transition for all the molecules is of the $\pi^* \leftarrow n$ type and is found at about 5 eV, in reasonable agreement with the above mentioned weak band.

This is followed by several $\sigma^* \leftarrow n$ and $\sigma^* \leftarrow \pi$ bands before the transition of highest $\pi^* \leftarrow \pi$ character which is calculated to be at 11.56, 8.63, and 8.50 eV for I, II, and III, respectively. These are highly mixed with other configurations and have 39, 38, and 78% contributions from the $\pi^* \leftarrow \pi$ configuration, respectively for I, II, and III.

The large number of transitions below 10 eV may be one of the causes for the diffuse nature of the observed spectra.

Aldehydes

Recently Lucazeau and Sandorfy [16] measured the far UV spectra of acetaldehyde, propionaldehyde, butyraldehyde, and several deuterated and halogenated derivatives. They find transitions which they assign as $\pi^* \leftarrow n$, $\sigma^* \leftarrow n$, $\pi^* \leftarrow \pi$, $\sigma^* \leftarrow \sigma$, and $R \leftarrow n$. The spectrum of formaldehyde has been extensively studied ([17], p. 518 and Refs. therein).

We have performed calculations on formaldehyde and acetaldehyde by the RCNDO method and formaldehyde, acetaldehyde, propionaldehyde and butyraldehyde by the INDO method. The results are shown in Table 4.

In all cases the transition of lowest energy is found to be of the $\pi^* \leftarrow n$ type, very weak and at around 4.5 eV by the INDO method and 3.5 eV by the RCNDO method. This is in all cases followed roughly 2 eV higher by a relatively strong $\sigma^* \leftarrow n$ transition.

The $\pi^* \leftarrow \pi$ transition is again found to contain appreciable contributions from higher (σ^*, n) and (σ^*, σ) configurations. This is in agreement with recent non-empirical CI calculations on formaldehyde performed by Whitten and Hackmeyer [18].

Table 4. *The five lowest singlet-singlet transitions of aldehydes* (eV). *The experimental results for formaldehyde are from Ref.* [16]; *all others are from Ref.* [15]

Molecule	Expt.		INDO			RCNDO			% Ryd. char.			
	ΔE_{0-0}	$\Delta E_{\max}$	ΔE	f	Type	ΔE	f	Type	C	O	H	Tot.
H_2CO	3.51		4.54	0.00	$\pi^* \leftarrow n$	3.25	0.00	$\pi^* \leftarrow n$	0	0	1	1
	7.08		6.03	0.14	$\sigma^* \leftarrow n$	5.75	0.04	$\sigma^* \leftarrow n$	1	5	1	7
	7.97		9.38	0.08	$\sigma^* \leftarrow n$	6.64	0.00	$\pi^* \leftarrow \sigma$	0	0	1	1
	8.13		9.56	0.00	$\pi^* \leftarrow \sigma$	7.69	0.00	$\sigma^* \leftarrow \pi$	1	1	0	2
	8.87		10.68	0.00	$\sigma^* \leftarrow \sigma$	7.73	0.08	$\pi^* \leftarrow \pi$	0	0	2	2
CH_3CHO	3.7	4.3	4.51	0.00	$\pi^* \leftarrow n$	3.53	0.00	$\pi^* \leftarrow n$	0	0	0	0
	6.8	6.8	6.16	0.20	$\sigma^* \leftarrow n$	5.39	0.12	$\sigma^* \leftarrow n$	3	1	3	7
	6.7		7.29	0.06	$\sigma^* \leftarrow n$	6.71	0.00	$\pi^* \leftarrow \sigma$	0	0	0	0
	7.5	7.5	8.93	0.02	$\sigma^* \leftarrow n$	7.05	0.00	$\sigma^* \leftarrow \pi$	2	0	1	3
	7.7	7.8	8.95	0.00	$\sigma^* \leftarrow \pi$	7.28	0.02	$\left.\begin{array}{l}\pi^* \leftarrow \pi \\ \sigma^* \leftarrow \sigma\end{array}\right\}$	3	0	3	6
C_2H_5CHO	3.6	4.3	4.47	0.00	$\pi^* \leftarrow n$							
	6.6	6.7	6.26	0.26	$\sigma^* \leftarrow n$							
	6.8	6.8	7.22	0.06	$\sigma^* \leftarrow n$							
	7.2	≈7.4	7.53	0.02	$\sigma^* \leftarrow n$							
	7.3	7.3	8.71	0.04	$\sigma^* \leftarrow \sigma$							
C_3H_7CHO	3.7	4.2	4.47	0.00	$\pi^* \leftarrow n$							
	—	6.7	6.23	0.30	$\sigma^* \leftarrow n$							
	6.8	6.8	7.18	0.06	$\sigma^* \leftarrow n$							
	7.3	7.3	7.67	0.06	$\sigma^* \leftarrow n$							
		7.4	8.48	0.18	$\sigma^* \leftarrow \sigma$							

The inclusion of doubly-excited configurations in the CI basis does not change any of these features [19].

Rydberg transitions for formaldehyde and acetaldehyde are calculated somewhat too high, mainly because of an over-estimation of the ionization potential. Calculated quantum defects are, however, in reasonable agreement with experiment.

Conclusions

Results of semi-empirical MO–CI calculations on the electronic spectra of some unsaturated molecules have been presented. While our methods are of a very approximate nature, they nevertheless give reasonable results in most cases, and we feel that they are very useful aids in the interpretation of electronic spectra.

As a final remark we would like to emphasize that chemical concepts such as "lone-pair", $\pi^* \leftarrow \pi$ transition, etc., often become somewhat blurred with the CI wave functions used here. These should be considered as only very approximate measures of the character of an electronic state.

Acknowledgements. The author would like to thank Professor C. Sandorfy who sponsored this research and read the manuscript.

The calculations were performed at the Centre de Calcul de l'Université de Montréal, the staff of which we thank for their cooperation.

The award of a 1967 Science Scholarship from the National Research Council of Canada is gratefully acknowledged.

References

1. Salahub, D. R., Sandorfy, C.: Theoret. chim. Acta (Berl.) **20**, 227 (1971).
2. — — Chem. Physics Letters **8**, 71 (1971).
3. — Theoret. chim. Acta (Berl.) **22**, 325 (1971), preceding paper.
4. Del Bene, J., Jaffé, H. H.: J. chem. Physics **48**, 1807 (1968).
5. Jug, K.: Int. J. quant. Chemistry 3S, 241 (1969).
6. Merer, A. J., Mulliken, R. S.: Chem. Revs. **1969**, 639.
7. Basch, H., McKoy, V.: J. chem. Physics **53**, 1628 (1970).
8. Yaris, M., Moscowitz, A., Berry, R. S.: J. chem. Physics **49**, 3150 (1968).
9. Ross, K. J., Lassettre, E. N.: J. chem. Physics **44**, 4633 (1966).
10. Bélanger, G., Sandorfy, C.: Chem. Physics Letters **3**, 661 (1969).
11. — Ph. D. Thesis, Université de Montréal, (1970).
12. Bralsford, R., Harris, P. V., Price, W. C.: Proc. Roy. Soc. (London) A **258**, 459 (1960).
13. Robin, M. B.: Personal communication (1970).
14. Sandorfy, C.: in The chemistry of the carbon-nitrogen double bond, Ed. by S. Patai. New York: Interscience Publishers 1970.
15. Robin, M. B., Simpson, W. T.: J. chem. Physics **36**, 580 (1962).
16. Lucazeau, G., Sandorfy, C.: J. molecular Spectroscopy **35**, 214 (1970).
17. Herzberg, G.: Molecular spectra and molecular structure, III: Electronic spectra and electronic structure of polyatomic molecules. Princeton: D. Van Nostrand Company Inc. 1966.
18. Whitten, J. L., Hackmeyer, M.: J. chem. Physics **51**, 5584 (1969).
19. Brabant, C., Salahub, D. R.: Theoret. chim. Acta (Berl.), in press.

Dr. D. R. Salahub
Department of Chemistry
University of Montreal
Montreal, Quebec, Canada