

Use of the INDO method in spectroscopy : alkenes

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1. INTRODUCTION

The CNDO method as developed by Pople and coworkers¹ results in a complete intermingling of σ and π levels in benzenoid hydrocarbons². To overcome this difficulty Del Bene and Jaffe used different bonding parameters for π,π and σ,σ interactions². Jug suggests the use of different orbital exponents for σ and π orbitals³.

As these modifications prejudice the preconceived ideas regarding σ - π separability, Salahub and Sandorfy opine that σ and π electrons should be treated on equal footing in order to distinguish $\pi^* \leftarrow \pi$, $\pi \leftarrow \sigma$ and $\sigma^* \leftarrow \sigma$ transitions from one another in unsaturated molecules⁴. So, they use the same bonding parameters β_{AB}^0 for both π,π and σ,σ interactions in their valence shell (CNDO and INDO) and extended basis set (RCNDO) calculations.

Before the suitability of these methods to interpret the electronic spectra of simple molecules is established, we require an extensive application of these methods. The present paper is one in this direction.

We have also observed that the RCNDO method, in its original parametrization, gives somewhat less satisfactory description of the ground state as well as the triplet excited state⁵. We have, therefore, changed the bonding parameters slightly and have also considered the atomic exchange integrals.

2. THEORY

The elements of the INDO HF (Hartee-Fock) matrix F

$$F_{pp} = U_{pp} + \sum_{\gamma}^A p_{\gamma\gamma} [(pp/\gamma\gamma) - (\frac{1}{2}) (p\gamma/p\gamma)] + \sum_{B \neq A} (P_{BB} - Z_B) \gamma_{AB}, \quad p \text{ on A}$$

$$F_{pq} = p_{pq} [(\frac{3}{2}) (pq/pq) - (\frac{1}{2}) (pp/qq)], \quad p \neq q \text{ both on A}$$

$$F_{pq} = \beta_{AB}^0 S_{pq} - (\frac{1}{2}) p_{pq} \gamma_{AB}, \quad p \text{ on A, } q \text{ on B}$$

and

$$U_{pp} = -(\frac{1}{2}) (I_p + A_p) - [Z_A - (\frac{1}{2})] \gamma_A$$

The F matrix under the RANDO approximations⁵ are

$$F_{pp} = U_{pp} + \sum_{\gamma}^{A, n_1} p_{\gamma\gamma} [(pp/\gamma\gamma) - (\frac{1}{2} (p\gamma/p\gamma))] \\ + \sum_{n_2 \neq n_1}^A P_{n_2 n_2}^A \gamma_{n_1 n_2}^A \\ + \sum_{B \neq A} \left[\sum_{n_2}^B P_{n_2 n_2}^B \gamma_{n_1 n_2}^B - Z_B \gamma_{n_1 n_2}^B \right], \quad p \text{ on } A_{n_1}$$

$$F_{pq} = p_{pq} \left[(3/2) (pq/pq) - (\frac{1}{2}) (pp/qq) \right], \quad p \neq q \text{ both on } A_{n_1}$$

$$F_{pq} = \beta_{n_1 n_2}^{AB} S_{pq} - (\frac{1}{2}) p_{pq} \gamma_{n_1 n_1}^{AB}, \quad p \text{ on } A_{n_1} \text{ and } q \text{ on } B_{n_2}$$

where the symbol $p_{on} A$ stands for atomic orbital Φ_p on atom A and belongs

to the principal quantum number n_1 , and

$$U_{pp} = - (\frac{1}{2}) (I_p + A_p) - (Z_A - 1) \gamma_{n_1 n_2}^{AA} - (\frac{1}{2}) \gamma_{n_1 n_1}^{AA}$$

where the symbols have their usual meanings⁵.

Using such F matrices the Hartree-Fock-Roothaan equation⁶

$$FC = \epsilon SC$$

were first solved and the excitation energies were computed in the so-called virtual orbital approximation. This was followed by a configuration interaction procedure for the lowest thirty singly excited configurations. The details of the procedure are given elsewhere⁵.

3. RESULTS AND DISCUSSION

We summarise the results of our INDO calculations on the S-S-transitions in alkenes in table 1. The lowest singlet-singlet transitions in ethylene is $\pi \rightarrow \sigma^*$ that is followed by $\sigma \rightarrow \pi^*$. The lowest S-S transition of the alkyl derivatives of ethylene is also found to be $\pi \rightarrow \sigma^*$. RINDO and RCNDO calculations⁵ on ethylene indicate that these are valence-shell transitions

Table 1. Singlet—Singlet transitions in alkenes

Molecule	Experimental Values			INDO-CI		sym.	Type
	$\Delta E_{0,0}$ (ev)	ΔE_{max} (ev)	f	ΔE	f		
$\text{CH}_2=\text{CH}_2$ (D_{2h})	7.6 ^a	7.58 ^b	0.3 ^a	7.76 ^a	0.00	B_{2g}	$\pi \rightarrow \sigma^*$
	($\pi \rightarrow \pi^*$)						
	8.75 ^c	7.1 ^a		8.27 ^a	0.00	B_{1g}	$\sigma \rightarrow \pi^*$
	8.96 ^c (R^{n-2})	($\pi \rightarrow 3s$)		8.46 ^a	0.00	B_{3u}	$\pi \rightarrow \sigma^*$
	9.62 ^c	7.45 ^a	0.6 ^a	9.10 ^a	0.14	B_{1u}	$\left\{ \begin{array}{l} \pi \rightarrow \pi^* \\ \sigma \rightarrow \sigma^* \end{array} \right.$
$\text{CH}_2=\text{CHCH}_3$ (C_s)	6.72 ^b	7.15 ^b	0.32 ^b	6.90	0.00		$\pi \rightarrow \sigma^*$
	($\text{R} \leftarrow \text{N}$)	($\text{V} \leftarrow \text{N}$)					
		7.1 ^d		7.84	0.01	A''	$\pi \rightarrow \sigma^*$
		8.24 ^d		8.07	0.00	A''	$\sigma \rightarrow \pi^*$
		8.82 ^d		8.27	0.01	A''	$\pi \rightarrow \sigma^*$
			8.37	0.15	A'	$\left\{ \begin{array}{l} \pi \rightarrow \pi^* \\ \sigma \rightarrow \sigma^* \end{array} \right.$	
$\text{CH}_2=\text{CHC}_2\text{H}_5$ (C_s)	6.62 ^e	7.04 ^f	0.36 ^f	6.97	0.01	A''	$\pi \rightarrow \sigma^*$
	($\text{R} \leftarrow \text{N}$)	($\text{V} \leftarrow \text{N}$)					
		0.36		7.77	0.05	A''	$\pi \rightarrow \sigma^*$
				7.94	0.00	A''	$\sigma \rightarrow \pi^*$
				8.28	0.02	A''	$\pi \rightarrow \sigma^*$
			8.34	0.08	A'	$\left\{ \begin{array}{l} \pi \rightarrow \pi^* \\ \sigma \rightarrow \sigma^* \end{array} \right.$	
Cis- $\text{CH}_3\text{CH}=\text{CHCH}_3$	6.03 ^{b,e,g}	7.10 ^b	0.59 ^e	6.48	0.00	A_2	$\pi \rightarrow \sigma^*$
	($\text{R} \leftarrow \text{N}$)	($\text{V} \leftarrow \text{N}$)					
	7.7 ^b			6.95	0.05	B_2	$\pi \rightarrow \sigma^*$
				7.52	0.01	B_2	$\pi \rightarrow \sigma^*$
			7.61	0.29	B_1	$\left\{ \begin{array}{l} \pi \rightarrow \pi^* \\ \sigma \rightarrow \sigma^* \end{array} \right.$	
$\text{CH}_2=\text{CHC}_3\text{H}_7$ (C_s)	6.57 ^h	7.01 ^h	0.38	7.08	0.01		$\pi \rightarrow \sigma^*$
	($\text{R} \leftarrow \text{N}$)	($\text{V} \leftarrow \text{N}$)					
				7.92	0.06	A''	$\pi \rightarrow \sigma$
				8.17	0.00	A''	$\sigma \rightarrow \pi$
			8.23	0.32	A'	$\left\{ \begin{array}{l} \sigma \rightarrow \sigma \\ \sigma \rightarrow \pi \end{array} \right.$	

a : Ref. 7 ; b : Ref. 8 ; c : Ref. 9 ; d : Ref. 10 ; e : Ref. 11 ; f : Ref. 12 ; g : Ref. 13 ; h : Ref. 14.

Transition $\pi \rightarrow \pi^*$ in alkenes usually undergoes red-shift that is accompanied by a decrease in intensity. However, we also find a blue-shift in the case of 1-pentene and an increase in intensity for cis-2-butene. The explanation of these effects is as follows:—Transitions $\sigma \rightarrow \sigma^*$ generally appear later than $\pi \rightarrow \pi^*$ transitions. The former transitions are associated with larger intensity as compared to the latter. Also the latter transitions are usually mixed with with the former as a result of configuration interactions.

The singlet-triplet transitions as obtained by INDO and RINDO methods are summarised in table 2. The first two transitions are found to consist essentially of a single configuration and the S-T splitting decreases upon alkylation.

Table 2. Singlet—Triplet transitions in alkenes

Molecule	Experimental			Theoretical		Type
	ΔE	S-T splitting	Method	$E\Delta$	S-T splitting	symmetry
$\text{CH}_2=\text{CH}_2$ (D_{2h})	4.6 ^a	3.0 ^a	INDO-CI	5.77 ^b	3.33	B_{1u} ($\pi \rightarrow \pi^*$)
	6.6 ^c	1.42 ^a		6.53 ^b	1.23	B_{2g} ($\pi \rightarrow \sigma^*$)
			RINDO-CI	4.60	3.38	B_{1u} ($\pi \rightarrow \pi^*$)
				5.32	1.42	B_{2g} ($\pi \rightarrow \sigma^*$)
				7.64	1.39	B_{3u} ($\sigma \rightarrow \sigma^*$)
$\text{CH}_2=\text{CHCH}_3$ (C_{2v})		2.96 ^d	INDO-CI	5.53	2.84	A' ($\pi \rightarrow \pi^*$)
		1.23 ^a		5.85	1.05	A'' ($\pi \rightarrow \sigma^*$)
				7.09	0.75	A'' ($\pi \rightarrow \sigma^*$)
$\text{CH}_2=\text{CHC}_2\text{H}_5$ (C_{2v})			INDO-CI	5.75	2.59	A' ($\pi \rightarrow \pi^*$)
				5.97	1.00	A'' ($\pi \rightarrow \sigma^*$)
				7.05	0.72	A'' ($\pi \rightarrow \sigma^*$)
Cis- $\text{CH}_3\text{CH}=\text{CHCH}_3$ (C_{2h})		3.39 ^e	INDO-CI	5.16	2.45	B_1 ($\pi \rightarrow \pi^*$)
		0.70 ^a		5.66	0.82	A_2 ($\pi \rightarrow \sigma^*$)
				6.57	0.38	B_2 ($\pi \rightarrow \sigma^*$)
$\text{CH}_2=\text{CHC}_3\text{H}_7$			INDO-CI	5.96	2.27	A' ($\pi \rightarrow \pi^*$)
				6.15	0.93	A'' ($\pi \rightarrow \sigma^*$)
				7.19	0.73	A'' ($\pi \rightarrow \sigma^*$)

a : Ref. 15 ; b. Ref. 7 c : Ref. 9 ; d : Ref. 16 ; e : Ref.

We remark that the extended basis set calculations (RINDO & RCNDO) describe the excited states of ethylene and higher alkenes better than valence basis (INDO) calculation. However, the INDO calculation, would assume better role in interpreting the spectra of larger molecules where the former cannot simply be carried out.

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