Asian Journal of Chemistry Vol. 4, No. 4 (1992), 838-843

Molecular Rydberg Transitions in Carboxylic Acids by RINDO/S-CI Method

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Rydberg transitions in some carboxylic acids like acetic acid, propanoic acid and butanoic acid have been calculated using semi-empirical SCF-LCAO-MO-RINDO/S-CI method. The computed transition energies, oscillator strengths and percentage Rydberg character for singlet singlet (S → S) and singlet-triplet (S → T) transitions alogwith S → T splittings are in good agreement with the experimental values.

INTRODUCTION

The electronic spectra of saturated and unsaturated acids have been studied in the gas or condensed phase by Barnes *et. al.*[1], Salahub[2] and Derissen[3]. In the study of formic acid and acetic acid, Nagakura *et. al.*[4] assigned a band of $\pi \rightarrow \pi^*$ transition. Basch *et. al.*[5] studied the spectra of isoelectronic amides, acids and acryl fluorides held that the band observed by Nagakura *et. al.*[4] should be Rydberg transition of n → 3s series.

The RINDO/S-CI method[6-7] has been applied on various carboxylic acids to investigate their spectral properties. In the present paper, the main objective is to find out the transitions which are Rydberg in nature. Though valence transitions are also interpreted but emphasis is given to Rydberg transitions.

Calculation Procedure

In approximate MO method, Rydberg character C_R for i^{th} states is calculated by

$$C_R = \sum_p C_{ip}^2 \sum_r C_{ra}^2$$

where C_{ip} = CI coefficient of the p^{th} configuration in the i^{th} state

C_{ra} = coefficient of the Rydberg A. O'^{S} in the excited MO used to form p^{th} configuration.

The first summation is over all configuration considered in CI approach and the second is over the Rydberg A O'^{S}.

If $C_R = 1$, the contribution due to Rydberg transition is cent percent (pure Rydberg transition).

If $O_R = 0$ or very small, then the transition is valence type.

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If C_R = moderate, then the transition is a mixture of valence Rydberg (intra valence transition).

Electronic Transitions

The S → S transition energies, oscillator strengths (f) and percentage Rydberg character are collected in Table 1. The experimental transition energies cited therein are taken from Barnes *et. al.*[1], Hoshino *et. al.*[8] and Nilson[9]. The singlet-triplet (S → T) transition energies and the corresponding splits are collected in Table 2.

TABLE 1

THE LOWEST S → S TRANSITIONS IN CARBOXYLIC ACIDS (eV)

Molecule	Experimental		RINDO/S-CI			% Rydberg characters			
	△E	f	△E	f	Sym	H	C	O	T
1	2	3	4	5	6	7	8	9	10
CH_3COOH (C_s)	5·92[a]	6.63	5·01	0·00	$A''(n \rightarrow \pi^*)$	00	00	00	00
	7·19[a]		6·63	0·00	$A'(n \rightarrow \sigma^*)$	00	01	01	02
	7·78[a]		6·82	0·07	$A'(\pi_n \rightarrow \pi^*)$	01	03	01	05
	7·81[a]		6·98	0·00	$A''(\pi_n \rightarrow \sigma^*)$	00	00	00	00
	8·43[a]		7·32	0·01	$A'(\pi_n \rightarrow \pi^*)$	01	03	01	05
	9·05[a]		8·62	0·00	$A''(\pi_n \rightarrow \sigma^*)$	03	10	02	15
	9·23[a]		8·98	0·00	$A'\{n \rightarrow \sigma^*, n \rightarrow \sigma^*_R\}$	06	24	02	32
			9·32	0·18	$A''(\sigma \rightarrow \sigma^*)$	02	10	02	14
			9·68	0·00	$A''(\sigma \rightarrow \pi^*)$	02	18	04	24
			10·42	0·00	$A'\{n \rightarrow \sigma^*, n \rightarrow \sigma^*_R\}$	10	14	07	31
			10·68	0·00	$A''(\sigma \rightarrow \pi^*)$	00	00	00	00
			10·96	0·00	$A'\{n \rightarrow \sigma^*_R, n \rightarrow R_Y(p)\}$	24	30	23	77
			11·02	0·01	$A'\{n \rightarrow \sigma^*_R, n \rightarrow R_Y(p)\}$	18	62	12	92
C_2H_5COOH (C_s)	6·10[b]		5·96	0·00	$A''(n \rightarrow \pi^*)$	00	00	00	00
	6·56[b]		6.21	0·00	$A''(n \rightarrow \sigma^*)$	00	01	01	02
	7·00[c]	6·63	0·06		$A'(n \rightarrow \sigma^*)$	02	03	01	06
	8·00[c]	7·24	0·00		$A''(\pi_n \rightarrow \sigma^*)$	00	00	00	00
	8·40[c]	8·13	0·02		$A'(\pi_n \rightarrow \pi^*)$	02	04	01	07
		8·62	0·00		$A''(\pi_n \rightarrow \sigma^*)$	02	12	01	15

Table 1 (*Contd.*)

1	2	3	4	5	6	7	8	9	10
		8·78	0·00		$A'\begin{cases} n \rightarrow \sigma^* \\ n \rightarrow \sigma_R^* \end{cases}$	07	23	01	31
		8·92	0·15		$A''\ (\sigma \rightarrow \sigma^*)$	03	11	03	17
		9·02	0·00		$A''\ (\sigma \rightarrow \pi^*)$	01	19	03	28
		9·41	0·00		$A'\begin{cases} n \rightarrow \sigma^* \\ n \rightarrow \sigma_R^* \end{cases}$	12	40	06	58
		9·68	0·00		$A''\ (\sigma \rightarrow \pi^*)$	00	00	00	00
		9·84	0·00		$A'\begin{cases} n \rightarrow \sigma_R^* \\ n \rightarrow R_Y\,(p) \end{cases}$	25	31	22	78
		10·62	0·02		$A'\begin{cases} n \rightarrow \sigma_R^* \\ n \rightarrow R_Y\,(p) \end{cases}$	20	60	14	94
C_3H_7COOH (C_s)	7·00[a]	6·01	0·00		$A''\ (n \rightarrow \pi^*)$	00	00	00	00
	8·00[a]	6·73	0·00		$A'\ (n \rightarrow \sigma^*)$	00	02	02	04
	8·40[a]	7·64	0·04		$A'\ (\pi_n \leftarrow \pi^*)$	03	03	03	09
		7·83	0·00		$A'\ (\pi_n \rightarrow \sigma^*)$	00	00	00	00
		8·02	0·03		$A'\ (\pi_n \rightarrow \pi^*)$	03	06	02	11
			8·35	0·00	$A''\ (\pi_n \rightarrow \sigma^*)$	02	10	02	14
			8·62	0·00	$A'\begin{cases} n \rightarrow \sigma^* \\ n \rightarrow \sigma_R^* \end{cases}$	08	25	02	35
			8·78	0·06	$A'\ (\sigma \rightarrow \sigma^*)$	04	10	02	16
			9.02	0·00	$A''\ (\sigma \rightarrow \pi^*)$	02	20	04	26
			9·21	0.00	$A''\begin{cases} n \rightarrow \sigma^* \\ n \rightarrow \sigma_R^* \end{cases}$	10	35	12	57
			9·43	0·00	$A''\ (\sigma \rightarrow \pi^*)$	00	00	00	00
			9·65	0·00	$A'\begin{cases} n \rightarrow \sigma_R^* \\ n \rightarrow R_Y\,(p) \end{cases}$	24	30	21	75
			9·98	0·01	$A'\begin{cases} n \rightarrow \sigma_R^* \\ n \rightarrow R_Y\,(p) \end{cases}$	22	62	14	98

a = Ref (1), b = Ref (8), c = Ref (9).

(*i*) *Acetic acid* : The most common bands in acetic acid predicted by Barnes *et. al.*[1] in the order

$$n \rightarrow \pi^* < n \rightarrow \sigma^* < n \rightarrow R_Y\,(s) < \pi \rightarrow \pi^* < n \rightarrow R_Y\,(p)$$

The present calculation predicts the first two lowest $S \rightarrow S$ transition

TABLE 2

THE LOWEST S → T TRANSITIONS IN CARBOXYLIC ACIDS (eV)

Molecule	RINDO/S-CI			% Rydberg character			
	ΔE	S–T split	Symmetry	H	C	O	T
CH_3COOH (C_s)	2.73	0.36	A'' (n → π*)	00	00	00	00
	3.86	0.64	A' (π → π*)	00	00	00	00
	4.65	0.83	A' (n → σ*)	02	02	01	05
C_2H_5COOH (C_s)	2.70	0.35	A'' (n — π*)	00	00	00	00
	3.81	0.61	A' (π — π*)	00	00	00	00
	4.50	0.79	A' (n — σ*)	03	03	03	09
C_3H_7COOH (C_s)	2.98	0.33	A'' (n — π*)	00	00	00	00
	3.95	1.02	A '(π — π*)	00	00	00	00
	4.67	1.31	A' (n — σ*)	01	01	01	03

energy in this order. But contrary to the blue-shift, the weak n → π* transition undergoes a red-shift with respect to the formic acid spectrum corresponds to Haque[10] and Prasad[11]. Acetic acid exhibits a number of valence shell transitions in the region from 5.01 to 8.62 eV. Beyond this region there appears a number of Rydberg series associated with percentage Rydberg character.

The lowest S → S transition energy calculated at 5.01 eV. is assigned as n → π* which is followed by another n → σ transition at 6.63 eV. These two bands are weak in nature owing to their oscillator strength (f = 0.00) and agrees well with the observed band at 5.92 eV. and 7.19 eV. by Barnes *et. al.*[1]. A $\pi_n \rightarrow \pi^*$ transition is observed at 6.82 eV. Since the originating MO for this excitation is a lone-pair π MO and the oscillator strength (f = .07) is too small, the band should be better labeled as $\pi_n \rightarrow \pi^*$, instead of $\pi \rightarrow \pi^*$. This is followed by another $\pi_n \rightarrow \pi^*$ transition (f = 0.01) at 7.32 eV. In between these a n → σ* transition at 6.98 eV. lies.

The first Rydberg band in acetic acid is observed at 8.98 eV. assigned as $n \rightarrow \sigma_R^*$ involves mainly the excitation of a lone-pair electron to the ($^3S_C + {}^3S_O + {}^3S_O + {}^2S_H + {}^2S_H$) Rydberg MO. The quantum defects (δ) is calculated about 0.86 and thus forms the ns Rydberg series. The other Rydberg transitions of n → 3s series is predicted at 10.42 and

10.68 eV. The $\sigma \rightarrow \sigma^*$ transition calculated at 9.32 eV. occurs just after the first Rydberg transition. The transition may be expected to share a common band involves with the first Rydberg band possible because of its nature of mix up with $n \rightarrow \sigma_R^*$ configuration. This can tentatively be assigned and Q band of Basch *et. al.*[5].

The other Rydberg band observed at 10.96 and 11.02 eV. by this method implies δ value about 0.60 and 0.68 and this can be compared with experimental $\delta \simeq 0.66$ for these band of Barnes *et. al.*[1]. This forms the np Rydberg series and is followed by several closely spaced transition of $n \rightarrow R_Y$ (p) type.

The lowest energy $S \rightarrow T$ transition is $^3(n \rightarrow \pi^*)_1$ predicted at 2.73 eV. with $S \rightarrow T$ split is 0.36 eV. This is followed by $^3(\pi \rightarrow \pi^*)_1$ transition at 3.86 eV. with about 0.64 eV. split. The another $S \rightarrow T$ transition is observed at 4.65 eV. and corresponding split is 0.83 eV. This is assigned as $^3(n \rightarrow \sigma^*)_1$ band.

(*ii*) *Propanoic acid* : The calculated spectra of this molecule is quite similar to those of acetic acid. The lowest $S \rightarrow S$ $(n \rightarrow \pi^*)$ band is weak in nature predicted at 5.96 eV. This is followed by $n \rightarrow \sigma^*$ band observed at 6.21 eV. The former transition, however undergoes a slight hyperchromic shift on alkylation. This is in qualitative agreement with experimental value observed by Barnes *et. al.*[1]. There are two $(\pi_n \rightarrow \pi^*)$ transitions found at 6.63 and 8.13 eV. and another two $(\pi_n \rightarrow \sigma^*)$ transitions at 7.24 and 8.62 eV. are valence shell type transition which appears before Rydberg excitation. These involves the excitation of a lone-pair electron from π MO.

The first Rydberg transition of $n \rightarrow 3s$ series is calculated at 8.78 eV. and implied $\delta \simeq 0.86$. The another Rydberg $n \rightarrow 3s$ series is predicted at 9.41 eV. with $\delta \simeq 0.81$. An intense band $(\sigma \rightarrow \sigma^*)$ is predicted at 8.92 eV. ($f = 0.15$) and may be correspond to the observed Q band of Basch *et. al.*[5] The band predicted at 9.84 and 10.62 eV. by this method with the calculated value of $\delta \simeq 0.65$ has been assigned as the Rydberg transition of $n \rightarrow R_Y$ (p) type and it forms the first member of np series.

The lowest energy $S \rightarrow T$ is predicted at 2.70 eV. The corresponding $S \rightarrow T$ split is 0·35 eV. However, the $S \rightarrow T$ splits of propanoic acid lie in the region from 0.61 to 0.8 eV.

(*iii*) *Butanoic acid* : The lower $(n \rightarrow \pi^*)$ transition is observed at 6.01 eV. which is followed by a number of valence shell type transition in the energy region from 6.73 to 7.64 eV. corresponds to Barnes *et. al.*[1] band. Before appearing Rydberg transition three more valence transitions are predicted at 7.83, 8.02 and 8.35 eV. and assigned as $\pi_n \rightarrow \pi^*$ and $\pi_n \rightarrow \sigma^*$ respectively.

The first Rydberg transition $(n \rightarrow \sigma_R^*)$ is calculated at 8.68 eV. ($\delta \simeq 0.83$) to form ns Rydberg series. The another band of this series is predicted

at 9.21, 9.65 and 9.98 eV. by this method. A strong ($\sigma \rightarrow \sigma^*$) transition is calculated 8.78 eV. which is most intense band having f = 0.06.

The Rydberg transition predicted at 9.65 eV. is assigned as the first member of $n \rightarrow R_Y(p)$ transition which is followed by another member of this transition calculated at 9.98 eV. These are closely spaced transition mixed with other Rydberg.

Below 4.67 eV, we predict two valence shell type $S \rightarrow T$ transitions. The first band is $^3(n \rightarrow \pi^*)_1$ in nature at 2.98 eV. shows corresponding $S \rightarrow T$ split at about 0.33 eV. This is followed by $^3(\pi \rightarrow \pi^*)_1$ transition at 3.95 eV. with $S \rightarrow T$ split at about 1.02 eV. by this method.

ACKNOWLEDGEMENT

One of the authors (R. P. Sinha) is grateful to U.G.C. for providing financial assistance in the form of Teacher Fellowship.

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[*Received*: 7 March 1991; *Accepted*: 2 August 1991] AJC-360