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CNDO, INDO and RCNDO-CI Calculations on the Electronic Spectra of Saturated Hydrocarbons*

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CNDO, INDO and RCNDO (CNDO including higher (Rydberg) atomic orbitals in the basis) calculations completed by first order configuration interaction were performed on straight chain and branched chain paraffins.

The results interpret reasonably the main characteristics of the observed electronic spectra. The importance of outer atomic orbitals is stressed and it is found that the first singlet-singlet transition of highly branched paraffins leads to an excited state with considerable Rydberg character.

Rechnungen vom Typ CNDO, INDO und RCNDO (CNDO mit höheren (Rydberg) Atomorbitalen in der Basis) unter Einschluß von Konfigurationswechselwirkung 1. Ordnung wurden für unverzweigte und verzweigte gesättigte Kohlenwasserstoffe durchgeführt.

Die Resultate lassen eine Deutung der Hauptcharakteristika der beobachteten Elektronenspektren zu. Die Wichtigkeit der äußeren Atomorbitale ist zu betonen. Die ersten Singulett-Singulett-Übergänge der stark verzweigten Paraffine führen zu angeregten Zuständen mit beträchtlichem „Rydbergcharakter".

Des calculs CNDO, INDO et RCNDO (ayant des orbitales atomiques supérieures dans la base) ont été effectués sur les paraffines normales et ramifiées tenant compte de l'intéraction de configuration de premier ordre jusqu'à 30 configurations.

Les résultats interprêtent d'une manière raisonnable les spectres électroniques mesurés. L'importance des orbitales atomiques supérieures apparaît clairement. La première bande observée des hydrocarbures hautement ramifiés comme le néopentane ou l'isobutane est attribuée à une transition dont l'état excité possède un fort caractère Rydberg.

Introduction

The first Pariser-Parr-Pople-type calculations on the electronic spectra of paraffins (methane, ethane and propane) were carried out by Katagiri and Sandorfy [1]. This was a simple PPP aproach based on H 1*s* and C sp^3 orbitals only. It interpreted correctly, however, the symmetry of the first singlet excited state of methane (T_2 under T_d symmetry) and that of ethane (E) showing that the first singlet transition in ethane is a perpendicular transition in agreement with experiment [2]. It reflected also the bathochromic shift observed in the series methane → ethane → propane [3, 4], predicted the location of the first singlet-

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triplet transitions and the differences that can be expected between the electronic spectra of conformational isomers. Brown and Krishna [5] applied a somewhat different PPP-type method to cyclopropane and Imamura, Kodama, Tagashira and Nagata [6] still another to the peptide link. Several papers were devoted to the electronic spectra of molecules containing both σ and π-electrons. We shall not enumerate these but we mention the works of Del Bene and Jaffé [7–9] who adapted the CNDO method of Pople, Santry and Segal [10–12] to the calculation of the energy levels of certain conjugated molecules with the principal aim of gaining information on the effect of the σ electrons on the energy levels of the π-electrons.

All of these methods used a minimum basis set of valence-shell AO, and thus could not account for transitions which involve a change in principal quantum number. The use of extended basis sets in semi-empirical methods has received little attention. Kato, Konishi and Yonezawa [13], included outer orbitals in extended Hückel [14] calculations on ethylene, methyl chloride and some related molecules. Watson, Armstrong and Mc Glynn [15] studied valence and Rydberg transitions in mono-olefinic hydrocarbons also using Mulliken-Wolfsberg-Helmholtz [16, 17] parametrization, including C 3*s* orbitals in the basis.

Outline of the Work

The following molecules were studied: CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, i-C_4H_{10}, i-C_5H_{12}, neo-C_5H_{12}. Only the planar, all-trans conformers were studied except for ethane for which both the staggered and eclipsed forms were considered. All angles were taken as tetrahedral, C–H bond lengths as 1.09 Å, and C–C bond lengths as 1.54 Å.

Three separate calculations were made for each molecule; a CNDO calculation, an INDO [18, 19] calculation and an RCNDO calculation where R stands for Rydberg and excited atomic orbitals were included in the basis. These methods are described below.

1. The CNDO method is a variant of that of Del Bene and Jaffé [7]. Preliminary calculations showed that their parameters which were aimed at the π levels had to be modified to interpret correctly σ-electronic spectra. In [7] the resonance integrals were taken to be

$$\beta_{\mu\nu} = 1/2\,(\beta_A^0 + \beta_B^0)\,S_{\mu\nu}$$

for all except π-π interactions for which

$$\beta_{\mu\nu} = 1/2\,(\beta_A^0 + \beta_B^0)\,K S_{\mu\nu}$$

was used where β_A^0 was adjusted for each atom. Instead of this we used

$$\beta_{\mu\nu} = 1/2\,\beta_{AB}^0\,S_{\mu\nu}$$

with a separate β^0_{AB} for each *atom pair*. The values of β^0_{AB} used were $\beta^0_{H-H} = -9.5$ eV, $\beta^0_{C-H} = -11.0$ eV, and $\beta^0_{C-C} = -15.0$ eV.

2. In the INDO calculations the same parameters were used and the one center exchange integrals were taken from [18].

3. In the RCNDO method[1] we added to the basis H 2*s*, H 2*p*, C 3*s*, and C 3*p* Slater atomic orbitals. The approximations described below ensure that the method is invariant to the choice of internal axes.

Besides the neglect of differential overlap we make the following approximations (the notation is as close as possible to that of Pople, Santry, and Segal):

The electron repulsion integrals $\gamma_{\mu\nu}$ depend only on the atoms to which μ and ν belong and on their principal quantum numbers.

$$\gamma_{\mu\nu} = \underset{\mathrm{A\,B}}{\gamma_{n_1 n_2}}$$

where μ is an AO on atom A with principal quantum number n_1, and ν is on atom B and has principal quantum number n_2.

Core integrals are taken as

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{\mathrm{B} \neq \mathrm{A}} (\mu | V_\mathrm{B} | \mu)$$

$$H_{\mu\nu} = U_{\mu\nu} - \sum_{\mathrm{B} \neq \mathrm{A}} (\mu | V_\mathrm{B} | \nu) \qquad \mu, \nu \text{ on A}$$

$$= \beta_{\mu\nu} \qquad \text{otherwise.}$$

$\beta_{\mu\nu}$ is chosen as:

$$\beta_{\mu\nu} = \underset{\mathrm{A\,B}}{\beta^0_{n_1 n_2}} S_{\mu\nu} .$$

The terms $(\mu | V_\mathrm{B} | \mu)$ are taken equal for all orbitals on the same atom with the same principal quantum number.

$$(\mu | V_\mathrm{B} | \mu) = \underset{\mathrm{AB}}{V_{n_1}} .$$

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[1] Excited states are often derived from molecular orbital calculations based on a minimum set of atomic orbitals, that is atomic orbitals corresponding to the atomic ground states of the respective atoms.

As Mulliken pointed out a long time ago (see, for example, J. chem. Physics **3**, 517 (1935)) excited orbitals, especially in the case of σ orbitals, can be approximated — for short internuclear distances — by Rydberg orbitals of the corresponding united atom. This assumption is justified by the applicability of formulas for Rydberg series to the interpretation of the spectra and it is useful in many respects. (Applicability of approximate atomic selection rules, the obtention of characteristic values of the quantum defects, etc.) It is widely used by both theoretical and experimental spectroscopists.

In the present paper this concept of united atom Rydberg states is not used. Rather we base our molecular orbitals on sets of atomic orbitals which include a certain number of atomically excited orbitals and take the weight of these atomic Rydberg orbitals in a given molecular orbital (averaged over all the participating configurations) as the measure of the Rydberg character of that state.

With this the elements of the Hartree-Fock (HF) matrix become:

$$F_{\mu\mu} = U_{\mu\mu} - \sum_{B \neq A} \underset{AB}{V_{n_1}} + (\underset{AA}{P_{n_1 n_1}} - 1/2 p_{\mu\mu}) \underset{AA}{\gamma_{n_1 n_1}} + \sum_{n_2 \neq n_1}^{A} \underset{AA}{P_{n_2 n_2}} \underset{AA}{\gamma_{n_1 n_2}} + \sum_{B \neq A} \sum_{n_2}^{B} \underset{BB}{P_{n_2 n_2}} \underset{AB}{\gamma_{n_1 n_2}}$$

$$F_{\mu\nu} = \underset{AB}{\beta^0_{n_1 n_2}} S_{\mu\nu} - \tfrac{1}{2} p_{\mu\nu} \underset{AB}{\gamma_{n_1 n_2}} \,.$$

The terms $\underset{AB}{V_{n_1}}$ represent the attraction of an electron in orbital $\underset{A}{\phi_{n_1}}$ for the core (nucleus and inner shell) B. We approximate this by a valence-shell electron distribution multiplied by the nuclear charge.

$$\underset{AB}{V_{n_1}} = Z_B \underset{AB}{\gamma_{n_1 n_v}}$$

where n_v is the principal quantum number of the valence-shell of atom B.

The terms $U_{\mu\mu}$ are treated in a manner similar to that of Pople and Segal [11] giving.

$$U_{\mu\mu} = -1/2(I_\mu + A_\mu) - (Z_A - 1) \underset{AA}{\gamma_{n_1 n_v}} - 1/2 \underset{AA}{\gamma_{n_1 n_1}} \,.$$

Thus the HF matrix elements become

$$F_{\mu\mu} = -1/2(I_\mu + A_\mu) + \sum_{n_2}^{A} \underset{AA}{P_{n_2 n_2}} \underset{AA}{\gamma_{n_1 n_2}} - 1/2(p_{\mu\mu} + 1) \underset{AA}{\gamma_{n_1 n_1}} + \underset{AA}{\gamma_{n_1 n_v}} + \sum_{B \neq A} \sum_{n_2}^{B} \underset{BB}{P_{n_2 n_2}} \underset{AB}{\gamma_{n_1 n_2}} - \sum_{B} Z_B \underset{AB}{\gamma_{n_1 n_v}}$$

$$F_{\mu\nu} = \underset{AB}{\beta^0_{n_1 n_2}} S_{\mu\nu} - \tfrac{1}{2} p_{\mu\nu} \underset{AB}{\gamma_{n_1 n_2}} \,.$$

The integrals were evaluated in the following way.

a) Overlap integrals were calculated with the formulas of Mulliken, Rieke, Orloff, and Orloff [20], using Slater exponents: except for H, where $\xi_{1s} = 1.2$ and $\xi_{2s} = \xi_{2p} = 0.6$.

Table 1. "*Average*" *ionization potentials and electron affinities (eV) for carbon and hydrogen orbitals (0.0 values were assumed)*

Atom	Orbital	I	A
H	$1s$	13.605	0.747
	$2s$	3.399	0.0
	$2p$	3.399	0.0
C	$2s$	19.44	8.662
	$2p$	10.67	0.474
	$3s$	3.735	0.0
	$3p$	2.509	0.0

b) Ionization potentials and electron affinities for valence orbitals were taken from Pople and Segal [11]. For the outer orbitals average ionization potentials were calculated from atomic spectral data in a similar manner. The values are shown in Table 1. Electron affinities for these were neglected. They are expected to be small.

c) Two-electron integrals were chosen as follows.

i) One-orbital integrals:

$$(\mu\mu|\mu\mu) = \underset{AA}{\gamma_{n_1n_1}} = \underset{A}{I_{n_1}} - \underset{A}{A_{n_1}}\,.$$

The values for p electrons were taken, as Del Bene and Jaffé [7] did.

ii) Two-center integrals $\underset{AB}{\gamma_{n_1n_2}}$ were calculated using Pariser and Parr's [21, 22] uniformly charged sphere extrapolation technique.

iii) One-center, two orbital integrals:

$$\underset{AA}{\gamma_{n_1n_2}} = \tfrac{1}{2}\,(\underset{AA}{\gamma_{n_1n_1}} + \underset{AA}{\gamma_{n_2n_2}})\,.$$

d) Resonance Integrals.

Because of the size of the secular equations to be solved we did not vary these independently but rather used the expression

$$\underset{AB}{\beta^0_{n_1n_2}} = \eta(\underset{A}{I_{n_1}} + \underset{B}{I_{n_2}})$$

where $\underset{A}{I_{n_1}}$ is the average of n_1s and n_1p ionization potentials. η was taken as 0.4 for valence-valence interactions and as 0.05 for all others. This was necessary to keep the Rydberg orbitals from entering too strongly into the ground state.

In all the calculations the energy of the ground state was first minimized in the usual way. Then configuration interaction was applied including the lowest thirty singly excited configurations for both singlets and triplets.

The three methods described above were programmed in Fortran IV for the CDC 6400. The CNDO program was a slightly modified version of the program of Del Bene and Jaffé [7]. The INDO and RCNDO programs retained parts of this program and were written in a similar manner. Jacobi diagonalization iterations were continued until all off-diagonal elements were smaller than 10^{-4} a.u. and the SCF procedure was terminated when all eigenvalues agreed within 10^{-3} a.u. between succesive iterations.

Results

Table 2[2] contains the lower singlet-singlet excitation energies in electron volts, oscillator strengths and symmetries of the excited states as computed in the three different approximations described above. Experimental values are given in the first columns. These were taken from Lombos, Sauvageau, and Sandorfy [4].

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[2] In the program of Del Beye and Jaffé the oscillator strengths were calculated with simple product wave-functions. The values given here should, therefore, be multiplied by 2 in order to correspond to determinantal wave-functions.

Table 2. *Lowest singlet-singlet transitions in alkanes. All energies are in eV*

Molecule (symmetry)	Experimental transitions		Calculated values									% Rydberg character		
			CNDO			INDO			RCNDO					
	Energy of max.	f	Transition energy	f	Sym. of exc. state	Transition energy	f	Sym. of exc. state	Transition energy	f	Sym. of exc. state	H	C	Tot.
$CH_4(T_d)$	9.705	0.26	9.95	0.14	T_2	10.41	0.15	T_2	10.24	0.22	T_2	2	6	8
			12.17	0.00	$E+T_1$	12.42	0.00	T_1	13.08	0.00	T_2	44	45	89
						12.70	0.00	E						
			13.00	0.78	T_2	13.53	0.81	T_2	13.13	0.00	T_1	30	17	47
			…			…			…					
$C_2H_6(D_{3d})$	9.402	0.3	8.68	0.14	E_u	8.76	0.14	E_u	8.09	0.10	E_u	2	1	3
	(10.151)		9.06	0.00	E_g	9.27	0.00	E_g	8.85	0.23	A_{2u}	2	1	3
			10.02	0.05	A_{2u}	10.14	0.04	A_{2u}	9.43	0.00	A_{1g}	21	16	37
			…			…			9.64	0.00	E_g	23	19	42
$C_2H_6(D_{3h})$			8.67	0.15	E'	8.76	0.16	E'	8.02	0.10	E'	2	2	4
			8.96	0.00	E''	9.16	0.00	E''	8.89	0.24	A_2''	2	1	3
			10.03	0.04	A_2''	10.14	0.03	A_2''	9.41	0.00	A_1'	22	16	38
			…			…			9.51	0.00	E''	23	19	42
									…					
$C_3H_8(C_{2v})$	8.887	0.33	8.50	0.09	B_1	8.42	0.09	B_1	7.51	0.06	B_1	3	2	5
	9.648		8.89	0.00	A_2	8.73	0.08	B_2	7.52	0.19	B_2	3	2	5
	10.331		8.92	0.08	B_2	8.90	0.00	A_2	7.77	0.08	A_1	4	4	8
	10.574		9.05	0.05	A_1	8.91	0.09	A_1	8.67	0.00	A_2	9	12	21
			9.14	0.00	B_1	9.23	0.00	B_1	8.69	0.10	B_2	12	13	25
			9.37	0.00	B_2	9.42	0.02	B_2	8.73	0.05	A_1	10	12	22
			9.52	0.00	A_1	9.44	0.00	A_1	8.97	0.00	B_2	29	24	53
			9.73	0.06	B_2	9.63	0.08	B_2	9.40	0.00	B_1	32	28	60
			9.95	0.02	A_1	9.73	0.01	A_1	9.46	0.00	A_1	33	27	60
			10.35	0.00	A_2	10.29	0.00	A_2	9.78	0.01	B_2	27	22	49
			10.62	0.00	B_1	10.72	0.01	B_1	10.21	0.00	B_1	25	20	45
			10.69	0.25	A_1	10.76	0.25	A_1	10.25	0.00	A_1	25	19	44
			…			…			…					

$C_4H_{10}(C_{2h})$	8.793	0.5	8.52	0.11	B_u	8.26	0.13	B_u	6.96	0.26	B_u	3	2	5
	9.287		8.56	0.12	A_u	8.41	0.12	A_u	7.35	0.08	A_u	3	2	5
	(10.018)		8.88	0.00	B_g	8.66	0.00	B_g	7.65	0.09	B_u	5	6	11
	(10.310)		8.89	0.00	A_g	8.78	0.00	A_g	7.78	0.00	A_g	5	3	8
	10.688		9.08	0.06	B_u	8.88	0.05	B_u	8.05	0.00	B_g	2	1	3
			9.11	0.00	A_u	9.02	0.00	A_u	8.31	0.00	A_g	43	40	83
			9.38	0.06	B_u	9.20	0.08	B_u	8.45	0.00	A_g	4	3	7
			9.42	0.00	B_g	9.41	0.00	A_g	8.59	0.07	B_u	21	28	49
			9.52	0.00	A_g	9.49	0.00	B_g	9.10	0.01	A_u	18	24	42
			9.75	0.00	A_g	9.62	0.00	A_g	9.20	0.00	A_g	46	42	88
			9.82	0.00	A_u	9.68	0.00	A_u	9.25	0.00	B_g	45	42	87
			9.93	0.08	B_u	9.79	0.07	B_u	9.40	0.09	B_u	22	29	51
			10.20	0.00	A_g	10.09	0.00	A_g	9.45	0.00	A_g	12	4	16
			10.65	0.00	B_g	10.17	0.00	B_g	9.51	0.00	A_u	45	50	95
			10.68	0.31	B_u	10.59	0.00	B_g	9.67	0.00	B_u	29	34	63
			…			10.73	0.30	B_u	…					
						…								
$C_5H_{12}(C_{2v})$	8.762	0.6	8.27	0.12	B_2	7.94	0.14	B_2	6.59	0.32	B_2	4	4	8
	9.218		8.62	0.14	B_1	8.44	0.15	B_1	7.46	0.06	B_1	5	5	10
			8.77	0.00	A_2	8.52	0.01	A_1	7.52	0.00	B_2	35	40	75
			8.86	0.01	A_1	8.64	0.00	A_2	7.55	0.03	A_1	14	17	31
			8.98	0.02	B_2	8.67	0.03	B_1	7.76	0.07	A_1	10	13	23
			9.23	0.01	B_1	8.89	0.03	B_2	7.82	0.00	B_2	18	20	38
			9.43	0.00	A_2	9.01	0.08	A_1	7.82	0.00	A_2	9	11	20
			9.45	0.05	A_1	9.23	0.05	B_2	8.30	0.01	B_2	18	19	37
			9.53	0.00	A_1	9.27	0.00	A_2	8.58	0.03	A_1	15	21	36
			9.56	0.00	A_2	9.33	0.04	A_1	8.87	0.00	A_1	40	45	85
			9.57	0.07	B_2	9.36	0.00	A_2	8.96	0.00	B_1	37	41	78
			9.61	0.00	B_1	9.51	0.01	B_2	8.98	0.00	A_2	44	52	96
			9.66	0.00	B_2	9.66	0.02	B_1	9.06	0.00	B_1	25	27	52
			10.32	0.00	A_2	9.75	0.02	A_1	9.22	0.00	B_2	23	23	46
			10.46	0.03	B_1	9.78	0.00	A_2	9.32	0.00	B_2	14	15	29
			10.50	0.00	A_1	9.99	0.04	B_2	9.47	0.02	B_2	17	20	37
			10.68	0.00	B_2	10.32	0.01	B_1	9.53	0.00	A_1	23	22	45
			10.79	0.00	B_2	10.45	0.04	B_1	9.58	0.00	A_2	37	43	80
			10.80	0.39	A_1	10.74	0.06	A_1	9.58	0.02	B_2	15	12	27
			10.86	0.47	B_2	10.82	0.21	A_1	9.87	0.00	A_2	15	18	33
			…			…			…					

The last columns of Table 2 contain the percentage Rydberg character of the states, defined as (% Rydberg character)$_i = \sum_p C_{ip}^2 \sum_r c_{ra}^2$ for state i where the first summation is over all configurations, C_{ip} is the contribution of the p^{th} configuration to the i^{th} state; the second summation is over all Rydberg atomic orbitals and c_{ra} is the LCAO coefficient for the upper molecular orbital in the p^{th} configuration. Table 3 shows transition energies, symmetries and percentage Rydberg characters of the three lowest singlet-triplet transitions of each molecule. Not all of the molecules were treated by the RCNDO method in this case.

Fig. 1 and Table 4 contain results relating to ground state properties. The diagrams of Fig. 1 contain the "atomic charges", that is the sum of the orbital charges on any given atom minus the nuclear charges. Table 4 gives the Koopmans theorem [23] ionization potentials and the corresponding orbital symmetries. The experimental values are the photoionization ionization potentials listed by Watanabe [24].

Discussion

The normal paraffins show generally diffuse bands which undergo a bathochromic shift and an increase in intensity as the length of the chain increases [3, 4]. The ethane spectrum is the only one to show vibrational fine structure at the resolution used.

Isopentane has a spectrum very similar to that of normal pentane except that it is shifted slightly to the red and is more intense. Isobutane and neo-pentane both show

Table 2 (continued)

Molecule (symmetry)	Experimental transitions		Calculated values									% Rydberg character		
			CNDO			INDO			RCNDO					
	Energy of max.	f	Transition energy	f	Sym. of exc. state	Transition energy	f	Sym. of exc. state	Transition energy	f	Sym. of exc. state	H	C	Tot.
i-$C_4H_{10}(C_{3v})$	(7.947)		8.64	0.13	E	8.37	0.22	E	6.97	0.28	E	14	16	30
	(8.234)		8.71	0.07	A_1	8.43	0.07	A_1	7.17	0.06	A_1	15	17	32
	8.580		9.11	0.01	E	8.93	0.00	A_2	8.25	0.17	E	24	24	48
	(8.984)		9.21	0.00	A_2	8.94	0.02	E	8.35	0.00	A_2	21	26	47
	9.218		9.27	0.00	A_1	9.10	0.00	A_2	8.57	0.03	E	31	30	61
			9.36	0.05	E	9.18	0.05	E	8.58	0.02	A_1	20	24	44
			9.51	0.04	E	9.37	0.05	E	8.77	0.08	E	24	28	52
			9.83	0.06	A_1	9.89	0.09	A_1	8.94	0.00	A_1	35	30	65
			10.61	0.03	E	10.27	0.00	A_2	9.51	0.00	A_2	16	19	35
			10.76	0.00	A_2	10.67	0.00	E	9.60	0.00	E	16	11	27
			…			…			…					

i-$C_5H_{12}(C_1)$	8.405	8.30	0.13	A	8.02	0.13	A	6.57	0.21	A	8	7	15
	8.984	8.52	0.11	A	8.22	0.12	A	6.80	0.12	A	9	7	16
	9.686	8.65	0.04	A	8.34	0.01	A	7.15	0.07	A	8	7	15
		8.79	0.00	A	8.42	0.04	A	7.43	0.03	A	17	18	35
		8.84	0.07	A	8.58	0.06	A	7.63	0.00	A	40	37	77
		9.08	0.03	A	8.74	0.04	A	7.71	0.02	A	20	21	41
		9.14	0.03	A	8.90	0.01	A	7.94	0.00	A	36	35	71
		9.15	0.00	A	8.92	0.01	A	8.07	0.00	A	13	13	26
		9.26	0.03	A	9.05	0.03	A	8.22	0.06	A	20	22	42
		9.36	0.01	A	9.19	0.00	A	8.49	0.03	A	18	20	38
		9.44	0.00	A	9.21	0.02	A	8.57	0.00	A	43	40	83
		9.55	0.00	A	9.32	0.03	A	8.78	0.01	A	22	27	49
		9.65	0.04	A	9.45	0.06	A	8.91	0.07	A	13	15	28
		9.86	0.03	A	9.69	0.02	A	9.04	0.00	A	20	24	44
		10.15	0.02	A	9.90	0.01	A	9.13	0.00	A	34	39	73
		10.26	0.02	A	10.04	0.03	A	9.24	0.02	A	21	23	44
		10.50	0.07	A	10.15	0.02	A	9.26	0.00	A	11	13	24
		10.56	0.00	A	10.39	0.02	A	9.30	0.01	A	18	22	40
		10.73	0.16	A	10.47	0.05	A	9.41	0.00	A	24	25	49
		…			…			…					
neo-$C_5H_{12}(T_d)$	(7.560)	8.40	0.44	T_2	8.05	0.39	T_2	6.52	0.36	T_2	26	22	48
	7.897	9.02	0.08	T_2	8.79	0.06	T_2	7.83	0.03	T_2	25	23	48
	(8.434)	9.04	0.00	A_1	8.80	0.00	A_1	8.22	0.47	T_2	19	20	39
	9.183	9.22	0.00	T_1	8.83	0.12	T_2	8.36	0.00	T_1	18	20	38
	(9.801)	9.40	0.00	E	8.88	0.00	E	8.40	0.00	E	17	20	37
		10.29	0.04	T_2	10.17	0.00	T_1	8.51	0.00	A_1	20	24	44
		…			…			…					

Table 3. *The three lowest singlet-triplet transitions in alkanes. All energies are in eV*

Molecule	CNDO			INDO			RCNDO			% Rydberg Character		
(symmetry)	Transition energy	Split	Sym. of exc. state	Transition energy	Split	Sym. of exc. state	Transition energy	Split	Sym. of exc. state	H	C	Tot.
$CH_4(T_d)$	9.10	0.85	T_2	8.46	1.95	T_2	9.49	0.75	T_2	2	6	8
	10.99	3.50	A_1	10.33	3.94	A_1	12.88	0.25	T_1	28	14	42
	11.53	2.47	T_2	11.49	2.04	T_2	13.07	0.01	T_2	45	47	92
$C_2H_6(D_{3d})$	7.94	0.74	E_u	7.37	1.39	E_u	7.61	1.24	A_{2u}	2	1	3
	8.34	0.72	E_g	8.00	1.27	E_g	7.75	0.34	E_u	2	1	3
	9.45	0.57	A_{2u}	8.63	1.51	A_{2u}	9.20	0.23	A_{1g}	20	15	35
$C_2H_6(D_{3h})$	7.88	0.79	E'	7.32	1.44	E'	7.63	1.26	A''_2	2	2	4
	8.22	0.74	E''	7.89	1.27	E''	7.68	0.34	E'	2	2	4
	9.40	0.63	A''_2	8.65	1.49	A''_2	9.11	0.40	E''	21	15	36
$C_3H_8(C_{2v})$	7.80	0.70	B_1	7.24	1.18	B_1	6.68	0.83	B_2	3	2	5
	8.40	0.49	A_2	7.68	1.05	B_2	7.10	0.41	B_1	3	2	5
	8.44	0.48	B_2	7.70	1.20	A_2	7.16	0.61	A_1	3	2	5
$C_4H_{10}(D_{2h})$	7.76	0.80	A_u	7.23	1.18	A_u						
	8.09	0.43	B_u	7.25	1.01	B_u						
	8.28	0.60	B_g	7.80	1.08	B_u						
$C_5H_{12}(C_{2v})$	7.83	0.79	B_1	7.04	0.90	B_2						
	8.00	0.27	B_2	7.29	1.15	B_1						
	8.08	0.69	A_2	7.60	1.04	A_2						
i-$C_4H_{10}(C_{3v})$	8.03	0.68	A_1	7.31	1.06	E	6.23	0.74	E	14	17	31
	8.16	0.48	E	7.46	0.97	A_1	6.67	0.50	A_1	14	17	31
	8.69	0.52	A_2	8.12	0.82	A_2	7.80	0.55	A_2	23	28	51
i-$C_5H_{12}(C_1)$	7.86	0.44	A	6.99	1.03	A	5.83	0.74	A	8	7	15
	7.88	0.64	A	7.21	1.01	A	6.20	0.60	A	9	7	16
	8.21	0.44	A	7.42	1.51	A	6.68	0.47	A	8	8	16
neo-$C_5H_{12}(T_d)$	7.93	0.47	T_2	7.01	1.04	T_2						
	8.73	0.27	A_1	8.10	0.70	A_1						
	8.90	0.12	T_2	8.24	0.55	T_2						

bands to the long wavelength side of the first band of the corresponding straight-chain isomer.

The bathochromic trend of the normal-alkanes has been successfully interpreted by both Raymonda and Simpson [3] who used a bond exciton independent systems model and by the PPP calculations of Katagiri and Sandorfy [1]. As to the extra bands of iso-butane and neo-pentane Raymonda and Simpson assigned them to charge-transfer around a C–C–C branch point. We will give a different interpretation to these bands.

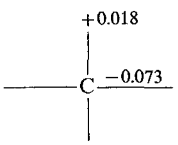
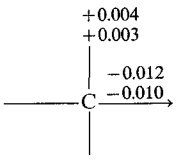
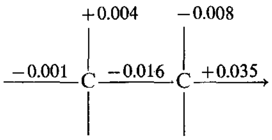
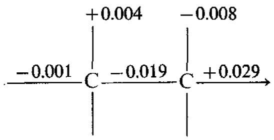
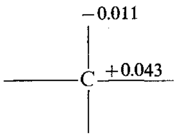
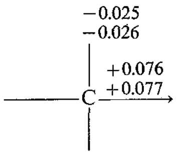
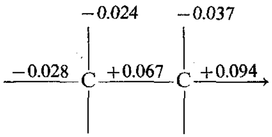
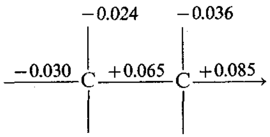
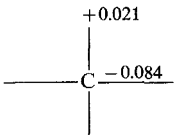
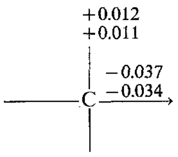
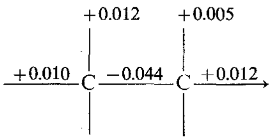
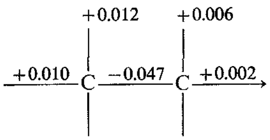
We may summarize our observations as follows.

1. The bathochromic shift in the series of the normal alkanes is correctly interpreted in all three of the approximations we used.

2. The RCNDO results indicate that the first singlet-singlet and singlet-triplet transition for the *n*-alkanes is almost entirely a valence-shell transition.

Table 4. *The five lowest ionization potentials of alkanes (in eV). The experimental values are from Ref.* [24]

Molecule (symmetry)	Experimental ionization potential	Calculated values					
		CNDO		INDO		RCNDO	
		I.P.	Sym. of orbital	*I.P.*	Sym. of orbital	*I.P.*	Sym. of orbital
$CH_4(T_d)$	13.12	15.81	t_2	15.58	t_2	16.04	t_2
		28.86	a_1	29.34	a_1	29.82	a_1
$C_2H_6(D_{3d})$	11.65	13.33	e_g	13.21	e_g	13.70	e_g
		15.04	a_{1g}	14.67	a_{1g}	14.13	a_{1g}
		18.62	e_u	18.37	e_u	18.57	e_u
		24.21	a_{2u}	24.56	a_{2u}	24.82	a_{2u}
		33.13	a_{1g}	33.67	a_{1g}	33.11	a_{1g}
$C_2H_6(D_{3h})$		13.26	e''	13.14	e''	13.61	e''
		15.04	a'_1	14.68	a'_1	14.13	a'_1
		18.66	e'	18.42	e'	18.63	e'
		24.18	a''_2	24.54	a''_2	24.79	a''_2
		33.13	a'_1	33.67	a'_1	33.12	a'_1
$C_3H_8(C_{2v})$	11.21	12.72	b_1	12.65	b_1	12.75	b_2
		13.10	b_2	12.83	b_2	13.13	b_1
		13.38	a_1	13.20	a_1	13.19	a_1
		15.22	a_2	15.05	a_2	15.40	a_2
		16.49	b_2	16.21	b_2	16.13	b_2
$C_4H_{10}(C_{2h})$	10.63	12.39	a_g	12.09	a_g	12.01	a_g
		12.54	b_g	12.50	b_g	12.94	a_g
		13.34	a_g	13.14	a_g	12.96	b_g
		13.72	a_u	13.60	a_u	14.03	a_u
		14.67	b_u	14.50	b_u	14.64	b_u
$C_5H_{12}(C_{2v})$	10.35	11.97	b_2	11.61	b_2	11.51	b_2
		12.48	b_1	12.46	b_1	12.82	a_1
		13.07	a_2	12.98	a_2	12.90	b_1
		13.13	a_1	12.99	a_1	13.42	a_2
		14.16	b_2	13.94	b_2	13.87	b_2
i-$C_4H_{10}(C_{3v})$	10.57	12.66	a_1	12.44	e	12.38	e
		12.68	e	12.59	a_1	12.80	a_1
		14.28	a_2	14.15	a_2	14.53	a_2
		15.41	e	15.25	e	15.54	e
		18.22	e	18.01	e	17.88	e
i-$C_5H_{12}(C_1)$	10.32	12.12	a	11.86	a	11.80	a
		12.32	a	12.12	a	12.11	a
		12.64	a	12.57	a	12.72	a
		13.69	a	13.56	a	13.85	a
		14.39	a	14.23	a	14.30	a
neo-$C_5H_{12}(T_d)$	10.35	12.39	t_2	12.18	t_2	12.14	t_2
		14.31	t_1	14.20	t_1	14.57	t_1
		16.26	e	16.10	e	16.37	e
		19.13	t_2	18.98	t_2	18.80	t_2
		21.17	a_1	21.37	a_1	20.61	a_1

Mole- cule→	$CH_4(T_d)$	$C_2H_6\left(\substack{D_{3h}\\D_{3d}}\right)$	$C_3H_8(C_{2v})$	$C_4H_{10}(D_{2h})$
CNDO				
INDO				
RCNDO				

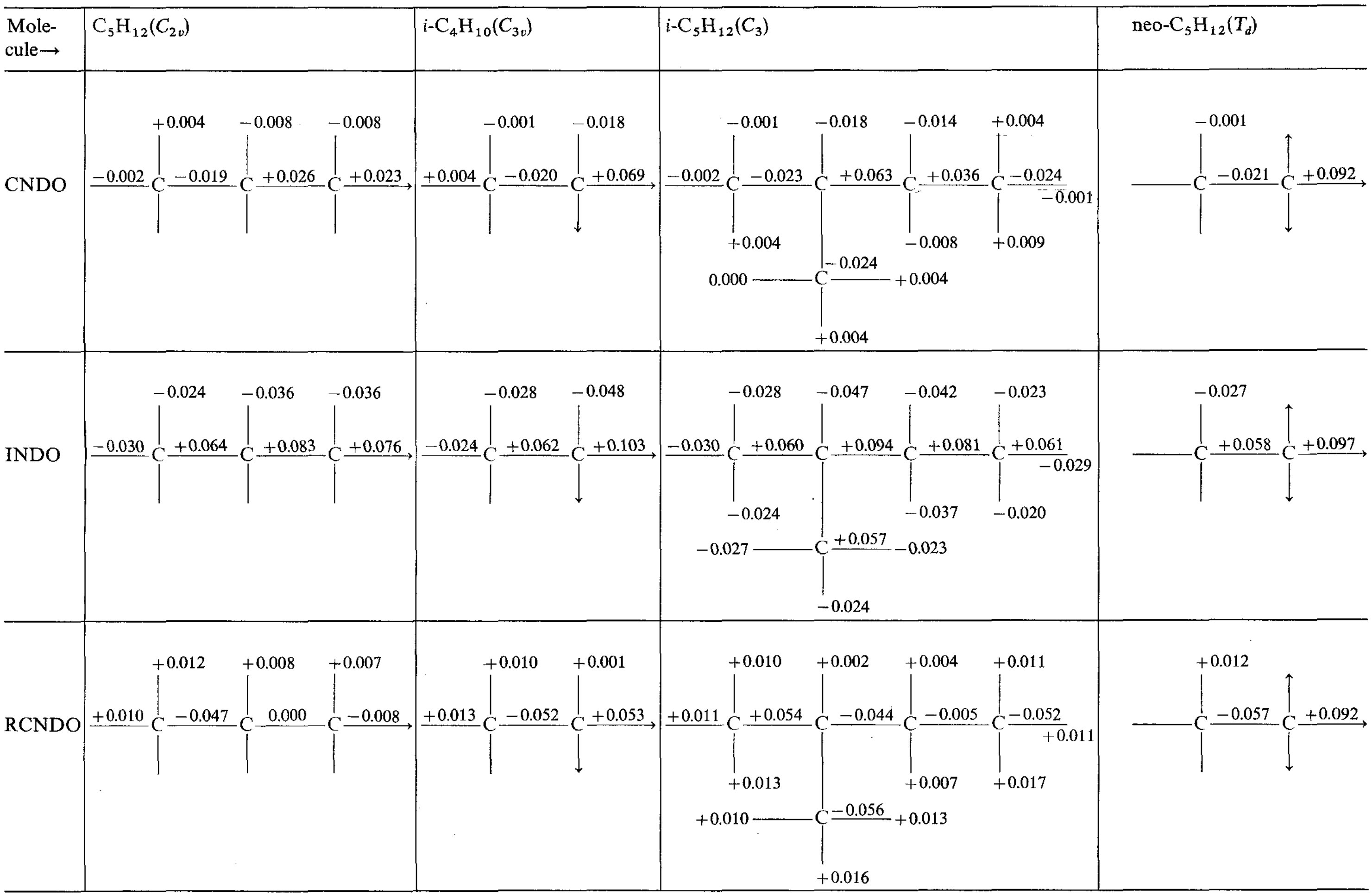


Fig. 1 Net atomic charges in alkanes. Arrows indicate attachment to part of the molecule related by symmetry to the part shown

The contribution of Rydberg orbitals to the next lowest excited states is moderate but much stronger Rydberg contributions come into play at higher energies. (Methane is a special case, the second and third calculated transitions having high Rydberg character.) The first transitions with a high Rydberg character also show a bathochromic shift which is more rapid than the corresponding shifting of the first bands (see Table 2).

3. The first singlet-triplet transition is predicted to lie at about 0.5 to 2.0 eV at the low frequency side of the first singlet-singlet band. As expected, the INDO method gives usually the higher values. These bands have not been observed as yet in absorption or emission but they were measured recently by Brongersma and Oosterhoff [25] with a low energy electron impact method for methane, ethane and a few cyclic paraffins and were found to be about 1 eV below the corresponding singlet-singlet transitions.

4. On examination of the wave functions we can see that the orbital of departure for the first singlet-singlet transition is mainly populated in the C–H bands for methane, ethane and propane but mainly in the C–C bonds for *n*-butane and *n*-pentane. This is in agreement with the calculations of Katagiri and Sandorfy and the experimental results of Pearson and Innes [2] on ethane but it is in contradiction with Raymonda and Simpson's assumption that the first transition in ethane is essentially C–C. The first singlet-triplet transition departs from a mainly C–H bonding orbital for all the normal alkanes. For the branched compounds the orbital of departure is of mixed C–C and C–H character.

5. In ethane (both staggered and eclipsed) the first singlet-singlet transition is allowed and polarized perpendicularly to the C–C bond axis. In propane it is polarized perpendicularly to the plane defined by the plane of the carbon atoms and in *n*-butane and *n*-pentane in that plane. In the case of ethane this has been confirmed by the high resolution work of Pearson and Innes [2].

The first singlet-triplet transitions are polarized perpendicular to the skeletal plane. (Except for *n*-pentane in the INDO method.)

6. The density of states is very great except for the smallest molecules. This is usually accentuated by the intervention of the Rydberg orbitals. We believe that this is a very important characteristic of the spectra of σ-electron systems and it is likely to be one of the causes of the diffuse character of the bands. Since many of these states are expected to be repulsive the opportunities for predissociation must be very frequent. The crowding is less for the first singlet-singlet transition in the smaller molecules and this is in line with the observed vibrational fine structure of ethane [2–4]. The same is, in general, true of the singlet-triplet bands.

7. The differences between corresponding transition energies of staggered and eclipsed ethane are of the order of 0.1 eV or less. This may be one of the reasons for the apparent broadening of the bands. It should become more important for the larger molecules.

8. Concerning the first band of the highly branched paraffins isobutane and neopentane, these could not be accounted for in any of the calculations using only valence shell atomic orbitals. The inclusion of Rydberg AO, however, shows that the corresponding first excited states have a high Rydberg character, about 30% for iso-butane and 50% for neo-pentane. No such state comes in for the straight chain molecules. This is linked to the fact that combinations of Rydberg

atomic orbitals have lower energies for the branched geometries than for the straight chain or slightly branched molecules. (If we make a simple Hückel calculation taking one AO on each carbon the lowest MO energies are: 1.618 β for *n*-butane, 1.732 for iso-butane; 1.732 for *n*-pentane, 1.848 for iso-pentane and 2.000 for neopentane.)

9. Hydrogen Rydberg AO play as important a part in the molecular wave functions as do the carbon Rydberg AO.

10. As to ground state properties, as usual, ionization potentials turn out to be about 2 eV too high in all three approximations. The decreasing trend with increasing chain length in the case of the *n*-paraffins is well accounted for by the calculations. The branched chain molecules also show the correct ordering among themselves but are slightly displaced with respect to the *n*-paraffins. As for the first singlet-singlet transitions the departing electron is taken from a molecular orbital mainly populated in the C–H bonds for methane, ethane and propane (except for propane in the RCNDO method, where the orbital of departure is predicted to be mainly in the C–C bonds) but from mainly C–C populated ones for *n*-butane and the longer chains. For the branched isomers, the orbital of departure is of mixed C–C and C–H character.

As to the charges the CNDO and RCNDO methods give values in conformity with chemical intuition while the INDO method puts small negative charges on the hydrogens and positive charges on the carbons. All methods predict the relative positive charge on various carbons in the order $CH_4 <$ primary $<$ secondary $<$ tertiary $<$ quaternary.

Conclusions

The authors of this paper have no delusions as to the approximate character of their calculations. This concerns especially the inclusion of the large Rydberg orbitals in the AO basis. Theoretical justification for this is clearly needed. The results of these calculations seem to be in agreement with and interpret correctly so many experimental facts, however, that we feel that this deeper justification will be forthcoming. There is a great need of theoretical investigations of the Rydberg states of polyatomic molecules.

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