ON THE STRUCTURE AND SPECTRA OF σ-ELECTRON SYSTEMS*

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Recent advances in the theories of saturated hydrocarbons are briefly reviewed. The problem of the non-additivity of certain ground state properties of these molecules is discussed as well as their electronic absorption spectra.

Introduction

The interest of quantum chemists in the properties of larger saturated organic molecules is relatively recent. The approximate additivity of certain physico-chemical quantities in the case of paraffins seemed to render calculations on these of no great interest. First attempts to treat σ-electron systems by approximative wave mechanical methods were based on group — or bond orbitals. These have been reviewed [1,2] and we shall refrain from doing this again. We prefer to take the attitude that localizability or additivity relationships, if these apply, should be a result of the calculations and not their starting point.

There are at least two properties of saturated molecules which exhibit a clear departure of additivity or localizability.

1) The heats of formation show a slight but well established default of additivity (Table I).

2) The first ionization potentials of normal-paraffins show an outspoken diminishing trend with increasing chain length (Table II). They drop from 13.17 ev for methane to 10.19 for n-decane.

Table I

Observed heats of formation of paraffins in units of resonance integral $\beta = -38.866$ kcal-M after subtracting the contributions of the C—H bonds. After KLOPMAN [6]

Methane	0
Ethane	2
Propane	4.06
Isobutane	6.20
Neopentane	8.34
Cyclohexane	12.43

Table II

Observed ionization potentials of paraffins in ev. After FUKUI, KATO and YONEZAWA [5] and KLOPMAN [6]

Methane	13.17
Ethane	11.76
Propane	11.21
n-Butane	10.80
n-Pentane	10.55
n-Hexane	10.43
n-Heptane	10.35
n-Octane	10.24
n-Decane	10.19
Isobutane	10.40
Neopentane	10.30
Cyclohexane	10.40

Any theory concerned with single bonded systems should be able to interpret these facts.

The first "individual electron" calculations on saturated hydrocarbons were made in 1954 by SÁNDORFY and DAUDEL [3] and by SANDORFY [4]. These works explored the possibility of applying the simple Hückel molecular orbital method in all-valence electron calculations.

Hückel-type methods similar to the above mentioned were extensively used and improved by FUKUI, KATO and YONEZAWA [5] and by KLOPMAN [6] with the main purpose of explaining the behavior of the ionization potentials and heats of formation in series of normal and branched paraffins. This was successfully achieved by these authors with a suitable choice of parameters. A number of problems relating to chemical reactivity have also been treated [7]. Then HOFFMAN [8] introduced the very simple WOLFSBERG—HELMHOLTZ [9] parametrization into σ-Hückel calculations thus providing them with the flexibility necessary to treat stereochemical problems. POPLE and SANTRY [10], in a more elaborate treatment, examined the causes of delocalization and non-additivity in paraffins.

The next stage in the evolution started in 1964 when the Pariser – Parr – Pople method was adapted to σ-electron problems. This has been done by several authors at almost the same time: KLOPMAN [11], POHL, REIN and APPEL [12], POPLE, SANTRY and SEGAL [13], KAUFMAN [14], KATAGIRI and SÁNDORFY [15], SKANCKE [16], YONEZAWA, YAMAGUCHI and KATO [17].

These methods use either the zero differential overlap approximation or MULLIKEN's approximation and differ mainly in the way of handling the interactions between electrons in orbitals on the same atom and by the extent in which atomic spectral data are used for obtaining parameters.

In the writer's opinion, the Hückel and Pariser—Parr – Pople methods have now attained the same degree of usefulness in σ-electron problems as they have in π-electron problems.

Delocalization and ground state properties

In the empirical methods, if hybrid orbitals are used, the interaction between electrons on the same atom but in different orbitals is represented by the resonance integral $m\beta$ where m is a number chosen to be much less than unity and β is the resonance integral for a C—C bond. It is immediately clear (Fig. 1) that the degree of delocalization depends on the value of m and that for $m = 0$ we obtain completely localized bonds.
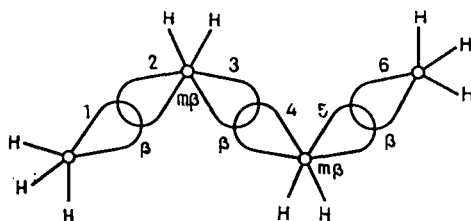

Fig. 1. Carbon hybridized sp^3 orbitals in n-butane

It is interesting in this respect to compare a chain of C—C bonds linked by sp^3 hybrid orbitals and a conjugated chain in which we consider the π—π bonds only.

If all the β were equal in the π calculation every π orbital would have two equivalent neighbors and it is this situation which we call "conjugation", (benzene, for example). In an open chain conjugated molecule like butadiene large β alternate with small ones. In saturated molecules the m value determined by YOSHIZUMI [18] is about 0.35.

Thus we can see that the difference between saturated and conjugated chains is less fundamental than it might appear at first sight. Propane, for example, becomes similar to butadiene. (SIMPSON [19] [20] was able to treat the electronic spectra of both by an excitonic approach that is, supposing localization in individual bonds in the ground state and forming combinations of wave functions excited in anyone bond for the excited states).

KLOPMAN has shown [21] by examining the secular determinants that the introducing of the 2—3 interaction in the Hückel type treatment is equivalent to introducing the nonneighbor 1—4 interaction (Fig. 1). This can be exploited in the treatment of stereochemical problems [22].

If we use pure atomic orbitals instead of hybridized ones in the σ-bond problem (like HOFFMANN [8] or POPLE and SANTRY [10] the relation between delocalization and interactions between orbitals on the same atom is no more evident.

POPLE and SANTRY who used perturbation calculations to establish the causes of delocalization in saturated hydrocarbons found that there are three

of these: the energy difference between $2s$ and $2p$ orbitals; the resonance integrals between chemically non-bonded atoms and the interactions between the $2p_z$ ($\equiv \pi$) orbitals. It is interesting to note that if the axes of the latter are parallel — as in the all-trans isomers — every π electron has two equivalent neighbors although, naturally, the distances between neighbors are now about 1.54 Å.

These considerations may help in the understanding of the behavior of ionization potentials and heats of formation in the paraffin series (cf. Tables I and II).
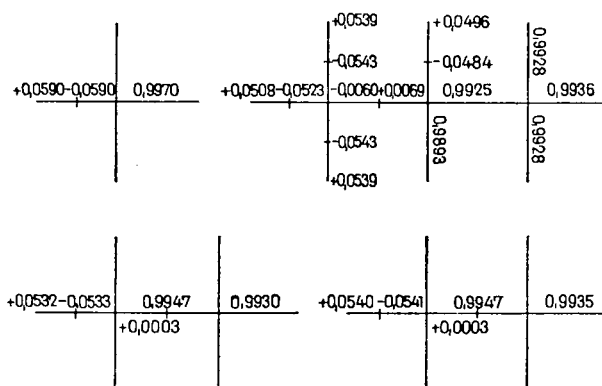
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                                          +0,0539    +0,0496
                                          -0,0543    -0,0484    0,9928

+0,0590 -0,0590   0,9970    +0,0508 -0,0523  -0,0060 +0,0069   0,9925    0,9936

                                          -0,0543    0,9939    0,9928

                                          +0,0539


+0,0532 -0,0533   0,9947   0,9930   +0,0540 -0,0541   0,9947    0,9935
          +0,0003                                      +0,0003
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Fig. 2. Effective orbital charges and bond charges in methane, staggered and eclipsed ethane and in propane

The following diagrams (Fig. 2) represent the distribution of electronic charge densities in methane, ethane and propane computed by the PPP-type approximation of KATAGIRI and SÁNDORFY [15]. The hydrogen atoms are seen to loose negative charges amounting to about 0.05 electronic charges. These are picked up essentially by the Csp^3 orbitals linked directly to the hydrogens. Hydrogens on secondary carbons loose slightly less charge than those on primary ones. Bond orders in both C—C and C—H bonds are close to 0.99. This distribution as well as the C—H bond dipole are seen to be in conformity with general chemical knowledge.

It is interesting to note that while delocalization causes an appreciable amount of non-additivity in ionization potentials and heats of formation it affects charge distribution only slightly.

The electronic spectra of σ-electron systems

The electronic spectra of saturated hydrocarbons are located in the far ultraviolet and this is probably the reason why, until recently, they received so little attention. Methane seems to be the only exception. The most complete

works relating to this molecule are those of DITCHBURN [23] and SUN and WEISSLER [24], who also summarized the previous literature. More general works on aliphatic hydrocarbons started appearing four or five years ago. Among these we have to mention those of OKABE and BECKER [25], PARTRIDGE [26], SCHOEN [27] and RAYMONDA and SIMPSON [20]. The absorption spectra of a number of gaseous normal and branched paraffins were measured in the author's laboratory on a McPherson model 225 vacuum ultraviolet monochromator under approximately 0.2 Å resolution from 2000 to 1150 Å using a double beam attachment, a hydrogen light-source and photoelectric recording. Our discussion will be based on these spectra [28] [29].
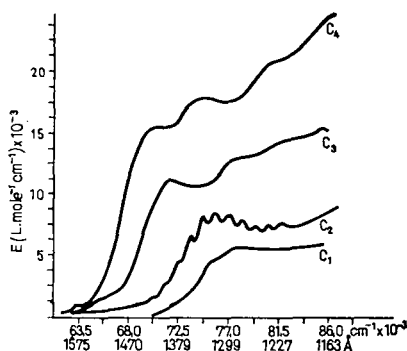

Fig. 3. Far ultraviolet absorption spectra of methane, ethane, propane and n-butane. Molecular extinction coefficients — against wavenumbers

Although a number of theoretical works are now available on ground state properties of saturated hydrocarbons we know only four concerning their electronic spectra. These are: MULLIKEN's united atom treatment [30] [31], the Pariser—Parr—Pople type calculations of KATAGIRI and SÁNDORFY [15] and of BROWN and KRISHNA [32] and the excitonic approach of RAYMONDA and SIMPSON [20].

The following observations can be made.

a) The bands are usually diffuse and no vibrational structure is observed. Ethane is a significant exception to this.

b) There seem to be one or two weak bands, or at least a pronounced inflection between 1630 and 1575 Å, in all the spectra except that of methane. These shift gradually to longer wavelengths.

c) At shorter wavelengths strong bands follow with molecular extinction coefficients in the 10^3—10^4 range. The bands exhibit much larger shifts toward lower frequencies, amounting to 4200 cm^{-1} from ethane to propane for the first strong band, then becoming gradually less and reaching an approximate limit of about 1420 Å for n-pentane. At the same time the intensities increase gradually (Table III), (Fig. 3).

Table III

The wavelengths and molecular extinction coefficients of the first two strong bands of normal paraffins

Compound	I		II	
	λ (Å)	ε(1. mole⁻¹cm⁻¹)	λ (Å)	ε(1. mole⁻¹cm⁻¹)
Methane	1277	5 839		
Ethane	1318	8 751		
Propane	1395	11 240	1285	13 010
n-Butane	1410	15 420	1335	17 950
n-Pentane	1415	17 330	1345	20 360
n-Hexane	1425	19 560	1335	24 080
n-Heptane	1430	20 950	1340	25 980
n-Octane	1415	24 550	1340	28 960

According to MULLIKEN, the united atom configuration of CH_4 is, omitting carbon $1s$ orbitals:

$$[sa_1]^2[pf_2]^6 \; {}^1A_1 \,,$$

where a_1 and f_2 are the usual group theoretical symbols under T_d symmetry. The lowest excited orbitals then would be Rydberg-type, large atomic orbitals $3s$, $3p$, $3d$ ... with $3s$ lowest. MULLIKEN pointed out, however, that anti-bonding localized C—H orbitals are qualitatively very similar to those of $3s$ and $3p$ orbitals of an atom. Thus in this united atom approach the first excited state of methane would have configuration $[sa_1]^2 \; [pf_2]^5 \; [3sa_1]^1 F_2$ and the corresponding transition would be of type

$${}^1F_2 \longleftarrow {}^1A_1 \quad \text{and allowed} \,.$$

The observed intensity ($\varepsilon = 5800$, oscillator strength $f = 0.26$) seems to justify this assignment although the possibility that the band is a forbidden one borrowing intensity from a stronger transition at higher frequencies is not ruled out. In fact we know from SCHOEN's [27] work that the 1277 Å band of methane is followed by even stronger bands.

In KATAGIRI and SÁNDORFY's scheme (Fig. 4) which is based on the C2s, C2p and H1s orbitals only, the molecular orbitals are, in order of increasing energy, a_1, f_2, a_1, f_2 so that the transition of lowest energy is $a_1 \leftarrow f_2$, that is again ${}^1F_2 \leftarrow {}^1A_1$. The sequence of the excited orbitals, however, depends in a delicate way on the choice of certain parameters. If the order was a_1, f_2, f_2, a_1 the first transition would be $f_2 \leftarrow f_2$ yielding $F_2 \times F_2 = A_1 + E + F_1 + F_2$ the transition to F_2 being allowed and the others forbidden. The latter could be made allowed by vibronic interactions and the band we observed may be
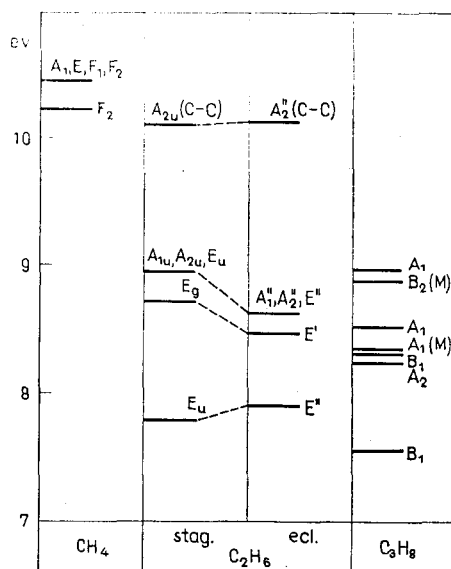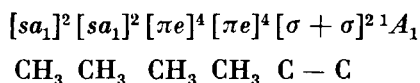
Fig. 4. Energies of the lower singlet—singlet electronic levels of methane, ethane and propane. C—C means that the orbital from which the transition departs (in absorption) has a high population in the C—C bonds; M (mixed) that it has a fairly large population in the C—C bonds. If the state is unmarked then all the charge is in C—H bonds in the orbital of departure.
After KATAGIRI and SÁNDORFY[15]

due to these. It is also possible that the shoulder at 1425 Å represents a separate electronic band due to one of these forbidden transitions. We have no means of checking upon these tentative assignments, however.

The ground state of ethane in MULLIKEN's united atom treatment had the following configuration:

$$[sa_1]^2 \, [sa_1]^2 \, [\pi e]^4 \, [\pi e]^4 \, [\sigma + \sigma]^2 \, {}^1A_1$$
$$\text{CH}_3 \;\; \text{CH}_3 \;\; \text{CH}_3 \;\; \text{CH}_3 \;\; \text{C} - \text{C}$$

Here the two methyl groups are treated as two separate united atoms except that a C—C molecular orbital is formed for the two $2p\sigma$ electrons forming that bond. This yields $[\sigma \pm \sigma]$ the plus sign applying to the orbital of lower energy. For the lowest excited state an electron would go to an orbital formed by the two carbon 3s atomic orbitals, $[3s + 3s]$. Then we obtain the configuration $[sa_1]^2 \, [sa_1]^2 \, [\pi e]^4 \, [\pi e]^4 \, [\sigma + \sigma] \, [3s + 3s] \, {}^1A_1$ if the electron is taken from the C—C bond. The transition to this state would be ${}^1A_1 \leftarrow {}^1A_1$ and forbidden. From considerations based on ionization potentials MULLIKEN predicted that the corresponding band should be at about 1600 Å. No such band was known at the time but we are now making the tentative suggestion that the weak band we find in the spectrum of ethane corresponds to this transition.

The first strong band would then be due to the transition of an electron in a C—H bond to the same excited orbital:

$$[sa_1]^2 [sa_1]^2 [\pi e]^4 [\pi e]^3 [\sigma + \sigma]^2 [3s + 3s] \, ^1E.$$

The $^1E \leftarrow \, ^1A$ transition is allowed.

In KATAGIRI and SÁNDORFY's Pariser and Parr type calculations the first transition is of the $^1E \leftarrow \, ^1A$ type but we find no equivalent for MULLIKEN's low lying $^1A_1 \leftarrow \, ^1A_1$ transition.

More extended $3s + 3s + 3s + \ldots$ type orbitals may account for the bathochromic shift which is observed when the number of carbon atoms increases.

More elaborate calculations using a basis of atomic orbitals including excited ones will probably be needed before we can pass the speculative stage in the interpretation of these spectra.

It is a matter of some interest to know if the first ionization leaves the "hole" in the C—C bonds or in the C—H bonds or if it is distributed over both. In MULLIKEN's united atom scheme the highest orbital filled in the ground state is of C—C character in ethane. The Hückel-type calculations of FUKUI, KATO and YONEZAWA [7], KLOPMAN [6] [21] and HOFFMANN [8] all seem to favor the C—C.

RAYMONDA and SIMPSON [20] assume that, in first approximation, the C—C electrons can be treated separately (like the π electrons in conjugated systems but with less justification) so that the first ionization is again C—C in their method. However, the Pariser—Parr—Pople type calculations of KATAGIRI and SÁNDORFY [15] yield electron densities mainly concentrated in the C—H bonds in the uppermost occupied orbitals, for at least ethane and propane.

From their photoelectron spectra AL-JOBOURY and TURNER [33] also concluded to the involvement of C—H rather than C—C bonds. Their bands were broad, however, and they have allowed for the possibility that they result from ionization from more than one close-lying orbital.

The matter does not seem to be definitely settled. Changes from C—H to C—C might occur in going from one paraffin molecule to the other and, in particular, between isomers with different degrees of branching.

The diffuse character of the bands in the spectra of the saturated hydrocarbons is usually attributed to dissociation or predissociation in the excited states which are indeed very probable in view of the high excitation energies which are involved. In relatively small molecules where the states are not very crowded the chances for predissociation are expected to be lower and this may be the reason why ethane [6] exhibits some vibrational fine structure.

Despite of the important role plaid by dissociation we should be cautious in attributing all the diffuseness what is observed to these phenomena. We have

to remember in this respect that because of rotational isomerism our spectra are actually spectra of mixtures and that the number of rotational isomers as well as the number of totally symmetrical vibrations increase rapidly with the increase in the number of atoms in the molecules.

There are some significant differences between the spectra of the branched chain paraffins, especially those of the highly branched ones, and those of the normal paraffins.

A typical example is shown in Fig. 5. The first bands are much stronger than in the spectra of the normal paraffin and they are followed by a fairly
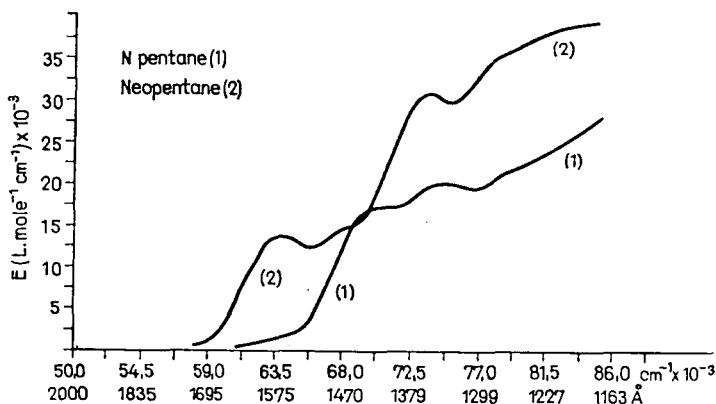
Fig. 5. Far ultraviolet absorption spectra of n-pentane and neopentane. Molecular extinction coefficients against wavenumbers

deep minimum toward higher frequencies. We have no quantum chemical calculations available to help in the interpretation of these spectra. It is possible that in this case the first bands correlate to the first *strong* bands of the normal paraffins. This would again mean that there has been a change in the order of the highest occupied molecular orbitals in the ground state.

All electronic transitions mentioned in this communication were singlet — singlet. The first singlet — triplet transitions were predicted by KATAGIRI and SÁNDORFY [15] to lie by about 1ev to lower frequencies from the first singlet — singlet bands. None of them has been found up to the present time.

We conclude by saying that much remains to be done. The solid theoretical basis for the discussion of σ-electron spectra is yet to be created.

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О СТРУКТУРЕ И СПЕКТРЕ σ-ЭЛЕКТРОННЫХ СИСТЕМ

Ц. ШАНДОРФИ

Резюме

В первой части работы дается краткий обзор новейших исследований по теоретической химии, касающихся насыщенных углеводородов. Во второй части рассматриваются расхождение некоторых относящиеся к основному состоянию физико-химических свойств от аддитивности и переходы σ-электронов (далекий ультрафиолетовый спектр).