The high-energy band in the photoelectron spectrum of alkanes and its dependence on molecular structure

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In the model for the ionization energies of the C_{2s}-electrons in saturated hydrocarbons, put forward by Heilbronner *et al.*, the energy levels are calculated as eigenvalues of the line graph of the hydrogen-filled molecular graph. It is now shown that in the case of alkanes, these energy levels are related to the Laplacian eigenvalues of the molecular graph. A few rules are formulated, relating these ionization energies with molecular structure.

Key words: photoelectron spectrum (of alkanes), ionization energy, molecular graph, Laplacian eigenvalues.

In theoretical organic chemistry, graph spectra[1,2] are traditionally used for the description of π-electrons in unsaturated conjugated molecules.[3-5] Relatively recently, Heilbronner in collaboration with Bieri, Dill and Schmelzer[6,7] developed a model, based on graph spectra, capable of reproducing the experimental photoelectron spectra of saturated hydrocarbons.[8] The model is applicable to the photelectron spectra in the range 17–26 eV, the so-called high-energy band (HEB). In saturated hydrocarbons the HEB corresponds to the ionisation of electrons from the 2s-orbitals of the carbon atoms, so-called C_{2s}-electrons.

In what follows, this model by Heilbronner *et al.* will be referred to[9] as the BDHS model.

The BDHS model uses a Hamiltonian matrix **H** on the basis of the (localized) carbon-carbon and carbon-hydrogen bonding orbitals, having a Hückel-type form.[6]

$$\mathbf{H} = \alpha\,\mathbf{I} + \beta\,\mathbf{A}\,(L(G)) \qquad (1)$$

with **I** standing for the unit matrix and $\mathbf{A}\,(L(G))$ being the adjacency matrix[2] of the line graph[2,9–12] $L(G)$ of the molecular graph G of the corresponding hydrocarbon. Recall that, within the BDHS model, G is a hydrogen-filled molecular graph (sometimes called plerogram[13,14]), in which both the carbon and hydrogen atoms

are represented by vertices. For alkanes, the semiempirical parameters α and β in Eq. (1) were estimated as:[6]

$$\alpha = -16.10 \pm 0.08 \text{ eV}$$
$$\beta = -2.11 \pm 0.03 \text{ eV}$$

Eventually, the BDHS model found numerous applications and was further elaborated.[7,9,15–20] However, a detailed analysis of the dependence of the (calculated) features of the HEB on molecular structure has not been undertaken so far. The present work is a contribution towards filling this gap.

GRAPH THEORETICAL CONNECTIONS

As a direct consequence[3–5] of relation (1), the C_{2s}-electron energy levels are of the form

$$E_j = \alpha + \beta x_j \tag{2}$$

where x_j is an eigenvalue of $L(G)$. The (experimentally measurable) ionisation potentials are then calculated assuming the validity of the Koopmans theorem,[6] and are equal to $-\beta x_j$. As a result of the nature of the BDHS approximation, only the first few (largest) eigenvalues of $L(G)$ are relevant for the interpretation of the HEB. Anyway, physical meaning (may) have only those E_j-values which lie below the multiply degenerate[9] $\alpha - \beta$ manifold, *i.e.*, the energy levels for which $x_j > -1$.

The hydrogen-filled molecular graphs of propane and 2,3,5-trimethyl-hexane and the corresponding line graphs are depicted in Fig. 1. More about line graphs and their chemical applications can be found elsewhere.[9–12]
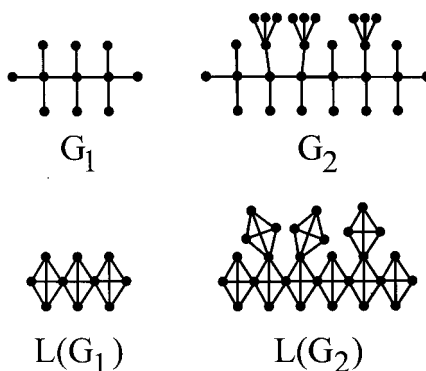

Fig. 1. The hydrogen-filled molecular graphs of propane (G_1) and 2,3,5-trimethyl-hexane (G_2) and their line graphs $L(G_1)$ and $L(G_2)$; observe the close formal resemblance of $L(G_1)$ and $L(G_2)$ to the van't Hoff tetrahedron models of the respective alkanes.

Now, in order to apply formula (2) to a given alkane, the eigenvalues of the line graph of the respective hydrogen-filled molecular graph (cf. Fig. 1) have to be determined. Of interest are the eigenvalues greater than -1.

Consider the hydrogen-filled molecular graph G of an alkane with n carbon atoms. This graph has $3n + 2$ vertices and $3n + 1$ edges. Consequently, $L(G)$ has $3n + 1$ vertices.[9–12]

Denote the eigenvalues of $L(G)$ by x_i, $i = 1,2,...,3n + 1$, and assume that

$$x_1 \geq x_2 \geq ... \geq x_{3n+1}$$

In the Appendix, it is demonstrated that in the case of alkanes, for $j = 1,2,...,3n +1$,

$$x_j = y_j - 2 \tag{3}$$

where $y_1, y_2,...,y_{3n+1}$ are the non-zero Laplacian eigenvalues of the molecular graph.

The importance of relations (3) is twofold. First, the calculation of the Laplacian eigenvalues of an alkane graph is somewhat easier than the calculation of the ordinary eigenvalues of the line graph of this graph.[21] Second, it is much simpler to envisage the dependence of y_i on molecular structure[22] than the dependence of x_i on molecular structure (which, however, must be precisely the same).

NUMERICAL WORK

The Laplacian eigenvalues of all alkanes with up to 10 carbon atoms (methane, ethane, propane, 2 butanes, 3 pentanes, 5 hexanes, 9 heptanes, 18 octanes, 35 nonanes and 75 decanes) were calculated. These are available from the authors upon request. The Laplacian eigenvalues, relevant for the HEB of some selected members of the decane family, are given in Table I.

TABLE I. The Laplacian eigenvalues of the hydrogen-filled molecular graphs of some decanes; only the eigenvalues greater than unity are given, because only these are relevant for the BDHS model of the photoelectron spectra

n-decane	6.032	6.098	5.776	5.363	4.892
	4.403	3.941	3.544	3.245	3.062
2-methyl nonane	6.331	6.126	5.745	5.229	4.791
	4.640	4.052	3.542	3.174	2.960
3-methyl nonane	6.353	6.108	5.672	5.309	4.959
	4.381	4.061	3.638	3.203	2.905
4-methyl nonane	6.365	6.070	5.716	5.345	4.724
	4.652	3.964	3.609	3.257	2.887
3,4-dimethyl octane	6.423	6.035	5.645	5.225	5.051
	4.352	4.162	3.646	3.275	2.737
3,6-dimethyl octane	6.390	6.127	5.523	5.293	5.041
	4.358	4.106	3.812	3.058	2.844
2,2,6-trimethyl heptane	6.421	6.175	5.533	4.791	4.791
	4.791	4.630	3.697	3.006	2.612
2,2,5,5-tetramethyl hexane	6.469	6.201	5.242	4.791	4.791
	4.791	4.791	4.000	2.719	2.545

TABLE I. Contd.

3,3-diethyl hexane	6.501	5.827	5.555	5.555	4.947
	4.384	3.859	3.859	3.527	2.462
3,4-diethyl hexane	6.459	5.913	5.555	5.555	4.921
	4.391	3.859	3.859	3.358	2.681
4-propyl heptane	6.399	5.880	5.880	5.363	4.678
	4.678	3.927	3.478	3.478	2.827
2,4-dimethyl,3-isopropyl pentane	6.500	5.842	5.842	4.791	4.791
	4.791	4.605	3.369	3.369	2.576
3,3-diethyl,4-methyl pentane	6.535	5.763	5.555	5.555	4.791
	4.639	3.859	3.859	3.498	2.380
2,2,3,4,4-pentamethyl pentane	6.554	6.054	5.309	4.791	4.791
	4.791	4.791	4.000	2.889	2.322
2,2,3,3,4-pentamethyl pentane	6.581	5.948	5.447	4.791	4.791
	4.791	4.791	3.812	3.133	2.189

Based on these calculations, a few general rules for the dependence of the HEB of alkanes on molecular structure were established. These are formulated in the subsequent section.

RESULTS AND DISCUSSION

The rules below were obtained by analyzing the calculated Laplacian eigenvalues, corresponding to alkanes. The rules are stated in terms of the C_{2s}-electron energies (E_j, Eq. (2)). They are strictly valid within the BDHS model, but, of course, have a direct correspondence to experimental photoelectron spectra.[8]

In the following, isomeric alkanes with the formula C_nH_{2n+2} will be referred to as C_n-alkanes.

Rule 1. Every C_n-alkane has exactly n C_{2s}-electron energy levels lying below the degenerate $\alpha - \beta$ manifold. [In other words, the respective hydrogen-filled molecular graph has exactly n Laplacian eigenvalues greater than $+1$.]

Rule 2. The energy gap between the degenerate $\alpha - \beta$ manifold and the next lower energy level is remarkably large and in all cases studied (*i.e.*, for all alkanes C_nH_{2n+2} with $n \leq 10$) exceeds $1.2\ |\beta|$. This energy gap is a decreasing function of n and also decreases with increasing extent of branching of the molecular skeleton.

Rule 3. The width of the high-energy band in the photoelectron spectra of the C_n-alkanes increases with the increasing extent of branching of the molecular skeleton. The minimal bandwidth is found in the normal (unbranched) alkane, whereas the maximal bandwidth is observed in the most branched alkane isomer.

Rule 3 is illustrated by the data given in Table II.

Some particular numbers frequently occur among the Laplacian eigenvalues of alkanes and can be directly related with certain structural features thereof.

TABLE II. Extremel values of the Laplacian eigenvalues y_1 and y_n of hydrogen-filled molecular graphs of alkanes C_nH_{2n+2}, minimal y_1 and maximal y_n correspond to the normal (unbranched) alkane; maximal y_1 and minimaly y_n correspond to the maximally branched alkane whose structure is indicated; note that y_n is the smallest Laplacian eigenvalue being greater than 1

n	min y_1	max y_n	max y_1	min y_n	max. branched alkane
4	6.071	3.340	6.133	3.140	2-methyl propane
5	6.155	3.228	6.303	2.697	2,2-dimethyl propane
6	6.209	3.163	6.362	2.629	2,2-dimethyl butane
7	6.245	3.122	6.435	2.507	2,2,3-trimethyl butane
8	670	3.095	6.519	2.268	2,2,3,3-tetramethyl butane
9	6.289	3.075	6.545	2.241	2,2,3,3-tetramethyl pentane
10	6.302	3.062	6.581	2.189	2,2,3,3,4-pentamethyl pentane

Rule 4. (a) The energy level $\alpha + 2.791 \beta$ occurs whenever a $C(CH_3)_2$ fragment is present in the molecule.

(b) The energy levels $\alpha + 3.555 \beta$ and $\alpha + 1.859 \beta$ occur whenever a $C(CH_2CH_3)_2$ fragment is present in the molecule.

(c) The energy levels $\alpha + 3.880 \beta$, $\alpha + 2.678 \beta$ and $\alpha + 1.478 \beta$ occur whenever a $C(CH_2CH_2CH_3)_2$ fragment is present in the molecule.

(d) The energy levels $\alpha + 3.842 \beta$, $\alpha + 2.791 \beta$ and $\alpha + 1.369 \beta$ occur whenever a $C[CH(CH_3)_2]_2$ fragment is present in the molecule.

An inspection of the Laplacian spectra of alkanes (see, for instance the data given in Table I) shows that degenerate eigenvalues occur quite frequently. The structural origin of such degeneracies are easily recognized:

Rule 5. Degenerate C_{2s}-electron energy levels occur whenever either three equal fragments (*e.g.*, methyl, ethyl,..) are attached to the same carbon atom, or there are two carbon atoms to each of which two equal fragments are attached.

Numerous examples illustrating Rules 4 and 5 are found in Table I.

It should be noted that mathematical results tantamount to Rule 5 were recently reported by Sciriha[23] and one of the present authors.[24] When these considerations are applied to the eigenvalues of the alkane graphs, it can be shown that the Laplacian eigenvalue 4.791, indicating the presence of $C(CH_3)_2$ fragments, is one of the solutions of the equation $x^2 - 5x + 1 = 0$. Similarly, the eigenvalues 5.555 and 3.859, indicating the presence of $C(C_2H_5)_2$ fragments, are solution of the equation $x^4 - 10x^3 + 27 x^2 - 13x + 1 = 0$.

И З В О Д

ВИСОКОЕНЕРГЕТСКА ТРАКА У ФОТОЕЛЕКТРОНСКОМ СПЕКТРУ АЛКАНА И ЊЕНА ЗАВИСНОСТ ОД МОЛЕКУЛСКЕ СТРУКТУРЕ

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У моделу за енергију јонизације C_{2s}-електрона у засићеним угљоводоницима, који су предложили Хајлбронер и сарадници, енергетски нивои се рачунају из сопствених вредности графа гране молекулског графа конструисаног тако да су сви атоми (угљеника и водоника) представљени чворовима. Показано је да у случају алкана ови енергетски нивои одговарају Лапласовим сопственим вредностима молекулског графа. Формулисано је неколико правила о зависности енергија јонизације од молекулске структуре.

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21. The adjacency matrix of the hydrogen-filled molecular graph of an alkane C_nH_{2n+2} has $6n+2$ non-zero entries, whereas the number of non-zero entries in the adjacency matrix of the respective line graph is $12n$, hence almost twice as large. Therefore, computer-aided manipulations of a molecular graph are easier than the analogous manipulations of a line graph.
22. The dependence of the coefficients of the Laplacian characteristic polynomial $\psi(G,x)$ (defined in the Appendix) on the structure of the underlying graph G is fully determined by the well-known Kel'mans theorem (see, for instance, chapter 1.5 of the book[1]).
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APPENDIX
A RELATION BETWEEN GRAPH EIGENVALUES AND
LAPLACIAN GRAPH EIGENVALUES

Let G be a graph and υ_1, $\upsilon_2,...,\upsilon_N$ be its vertices. The adjacency matric $\mathbf{A}(G) = \|A_{ij}\|$ of this graph is a square matrix of order N, defined *via*

$$A_{ij} = \begin{cases} 1 & \text{if the vertices } \upsilon_i \text{ and } \upsilon_j \text{ are adjacent} \\ 0 & \text{otherwise} \end{cases}$$

Then the eigenvalues of the matrix $\mathbf{A}(G)$ are said to be the (ordinary) eigenvalues of the graph G.[1] These will be denoted by $x_1(G) \geq x_2(G) \geq ... \geq x_N(G)$. The eigenvalues of G are the zeros of the characteristic polynomial[1]

$$\phi(G,x) = \det [x\, \mathbf{I} - \mathbf{A}(G)]$$

The degree d_i of the vertex υ_i is the number of first neighbors of this vertex. Clearly

$$d_i = \sum_{j=1}^{N} A_{ij}$$

The matrix whose diagonal elements are $d_1, d_2,....,d_N$ and whose off-diagonal elements are zero, will be denoted by $\mathbf{D}\,(G)$. Then $\mathbf{C}(G) = \mathbf{D}(G) - \mathbf{A}(G)$ is the Laplacian matrix (or matrix of admittance) of the graph G.[1] Its eigenvalues, $y_1(G) \geq y_2(G) \geq ... \geq y_N(G)$, are the Laplacian eigenvalues of G. These are just the zeros of the Laplacian characteristic polynomial[2]

$$\psi(G,x) = \det [x\, \mathbf{I} - \mathbf{C}(G)]$$

For all N-vertex graphs y_N is 0, and for all connected graphs (and thus for all molecular graphs), $y_{N-1} > 0$.

For trees (= acyclic and connected graphs) there is a simple relation between the Laplacian and ordinary eigenvalues. Recall that the molecular graphs of alkanes are trees.

Let T be a tree with N vertices. Then T has $N - 1$ edges and, consequently, its line graph $L(T)$ has $N - 1$ vertices. Therefore $L(T)$ has $N - 1$ ordinary eigenvalues, whereas T has N Laplacian eigenvalues of which $N - 1$ are non-zero.

Lemma. For T being a tree with N vertices, the equality $x_i\,(L(T)) = y_i(T) - 2$ holds for $i = 1,2,...,N-1$.

Proof. Denote the vertices of T by υ_1, $\upsilon_2,....,\upsilon_N$ and its edges by $e_1, e_2,...,e_{N-1}$. Color the vertices of T in two colors, say black and white, so that no two vertices of the same color are adjacent. Direct the edges of T so that they all start at a black and end at a white vertex.

Define the matrix $\mathbf{Q} = \|Q_{ij}\|$ as follows:

$$Q_{ij} = \begin{cases} +1 & \text{if the edge } e_j \text{ starts at vertex } \upsilon_i \\ -1 & \text{if the edge } e_j \text{ ends at vertex } \upsilon_j \\ 0 & \text{otherwise} \end{cases}$$

Then

$$\mathbf{QQ}^t = \mathbf{C}(G)$$

$$\mathbf{Q}^t\mathbf{Q} = 2\,\mathbf{I} + \mathbf{A}(L(G))$$

where $\mathbf{M}^t$ stands for the transpose of the matrix $\mathbf{M}$. It is known from Linear Algebra that for any matrix $\mathbf{M}$, the non-zero eigenvalues of $\mathbf{MM}^t$ and $\mathbf{M}^t\mathbf{M}$ coincide. Therefore

$$\det[x\, \mathbf{I} - \mathbf{QQ}^t] = x \det [x\, \mathbf{I} - \mathbf{Q}^t\mathbf{Q}]$$

i.e.,

$\det[x\,\mathbf{I} - \mathbf{C}(G)] = x\,\det[x\,\mathbf{I} - 2\,\mathbf{I} - \mathbf{A}(L(G))]$

i.e.,

$\psi(G,x) = x\,\phi(\mathbf{L(G)},x-2)$

from which the Lemma straightforwardly follows.