

FIG. 1 Pi and gamma plots of hydrogen and deuterium loss from the molecule-ions of toluene and the deuterated toluenes.

from toluene- d_5 is well above any reasonable gamma line, the gamma factor for hydrogen loss from toluene- d_3 is below the gamma line, and the pi factor for deuterium loss from toluene- d_5 is lower than the pi plot line.

This difference between H loss from toluene- d_5 and D loss from toluene- d_3 means that the direct dissociation process is much more prominent in toluene- d_5 than in toluene- d_3 . Enhancement of the direct dissociation may be caused by the fact that the molecule-ion of toluene- d_5 contains hydrogen in the position which loses hydrogen in the direct process (methyl group of toluene or CH_2 group of cycloheptatriene) whereas toluene- d_3 contains deuterium in the corresponding position. Hydrogen loss in toluene- d_5 molecule-ion can compete with the isotope scrambling process, but deuterium loss in toluene- d_3 is enough slower that the isotope scrambling process predominates almost entirely.

¹ P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.* **79**, 842 (1957).

² H. M. Grubb and S. Meyerson in *Mass Spectrometry of Organic Ions*, edited by F. W. McLafferty (Academic Press Inc., New York, 1963), Chap. 10.

³ S. Meyerson and P. N. Rylander, *J. Chem. Phys.* **27**, 901 (1957).

⁴ J. G. Burr in *Tritium in the Physical and Biological Sciences* (International Atomic Energy Agency, Vienna, 1962), Vol. 1, p. 137.

⁵ F. H. Field and J. L. Franklin, *Electron Impact Phenomena* (Academic Press Inc., New York, 1957), pp. 211-212.

⁶ J. G. Burr, J. M. Scarborough, and R. H. Shudde, *J. Phys. Chem.* **64**, 1359 (1960).

⁷ (a) J. G. Burr, *J. Phys. Chem.* **61**, 1477 (1957); (b) R. A. Meyer and J. G. Burr (unpublished data).

Distribution of Electronic Levels in Alkanes

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IN a previous contribution a semiempirical LCAO-MO calculation on the normal alkanes through n -nonane was described.¹ The calculation showed the decrease in ionization potential as a function of n in C_nH_{2n+2} , but since the parameters were not chosen so as to match ionization potentials, these came out typically too large. The distribution of energy levels obtained in this calculation differs significantly from that calculated by the parametrized method of equivalent orbitals of Hall and Lennard-Jones² and if confirmed has interesting implications for the study of mass spectrometric ionization efficiencies.

Table I shows the calculated $3n+1$ bonding levels of a completely *trans*-staggered C_nH_{2n+2} for $n=1$ through 9. The levels fall into two bands: one of $2n+1$ levels with energies, for large n , between -12.3 and -17.0 eV, and the second of n levels, lying between -19.9 and -28.8 eV and composed entirely of levels symmetric with respect to reflection in the plane of the carbons. The levels in the latter lower band are largely but not entirely linear combinations of carbon $2s$ orbitals. Though there seems to be some grouping of symmetric and antisymmetric levels in the upper band, its only distinct feature is the increasing isolation of the top filled or first ionizing level.³ Whereas in the equivalent orbital method no decision could be made regarding the symmetry properties of this level,⁴ in this calculation it is symmetric for large n , with respect to the carbon plane, and for even n symmetric with respect to i in C_{2h} , for odd n antisymmetric with respect to σ' in C_{2v} . There is no noticeable grouping of levels in either band with respect to i or σ' .

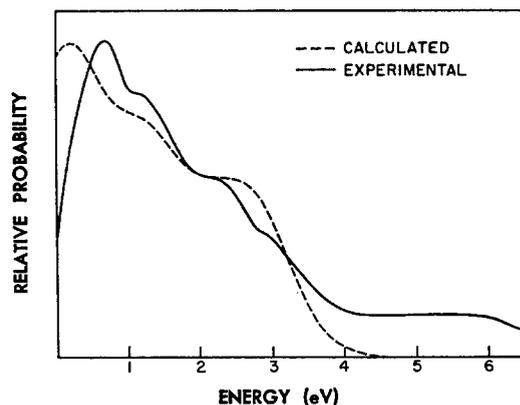


FIG. 1. Calculated and experimental (Ref. 5) ionization efficiency curves for propane. The calculated energy scale is relative to the computed ionizing level (13.42 eV). The relative intensity of each Gaussian is the same, with the first one centered at $\Delta E=0$.

TABLE I. Energy levels of the alkanes, $-E_i$ in eV. Starred levels are antisymmetric with respect to the plane containing the carbons.

C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄	C ₇ H ₁₆	C ₈ H ₁₈	C ₉ H ₂₀
13.05	12.83	12.67	12.56	12.47	12.41
13.36*	13.32*	13.32*	13.26*	13.24*	13.24*
13.65	13.47*	13.33*	13.32*	13.31*	13.26*
13.82*	13.60	13.60	13.58*	13.44*	13.33
14.16	13.88	13.72	13.59	13.52	13.40*
15.14	14.42*	13.89*	13.67	13.60	13.60
15.24*	14.55	14.17	13.81	13.68	13.63
15.40	14.82	14.29	14.03	13.85	13.65*
16.53*	15.57	14.93*	14.34*	13.93*	13.77
20.23	15.69*	15.21	14.67	14.36	14.12
22.10	16.67*	15.44	15.20	14.72	14.30*
25.43	20.12	16.00*	15.33*	14.75*	14.47
27.97	20.99	16.75*	15.42	15.17	14.67
	23.62	20.10	16.22*	15.45	15.09*
	26.35	20.43	16.81*	15.63	15.33
C ₃ H ₈	28.23	22.26	20.10	16.37*	15.36
13.42*		24.76	20.18	16.85*	15.86*
13.42	C ₂ H ₆	26.95	21.33	20.07	16.49*
13.69		28.39	23.42	20.10	16.88*
14.55*	13.76*		25.60	20.73	20.03
14.79	13.76	CH ₄	27.38	22.36	20.10
15.68	14.11		28.50	24.36	20.39
16.30*	15.86*	14.98*		26.22	21.56
20.59	15.86	14.98		27.67	23.29
23.98	21.82	14.98		28.58	25.10
27.52	26.67	24.87			26.69
					27.89
					28.63

Several workers have attempted interpretation of differential ionization efficiency curves, regarded as largely reflecting internal energy distributions, in terms of the equivalent orbital level scheme.^{5,6} To compare with experimental curves Gaussian band shapes with $\sigma=0.5$ eV were used to broaden the calculated lines. Though such band shapes are not realistic, they suffice for purposes of comparison: Fig. 1 shows the calculated curve from the *top band only* of propane along with the experimental results of Chupka and Kaminsky.⁵ Considering the approximations, the correspondence is good. It is only fair for *n*-butane. The implication of this result is that ionization efficiency measurements in the range studied so far ($\lesssim 6$ eV above I_p) refer to ionization from $2n+1$ energy levels and not all $3n+1$ as one would conclude from equivalent orbital studies. Correspondingly, ionization from the lower band should occur at still higher energies (~ 12 eV above I_p). Such states are detected but have usually been attributed to multiple excitation processes. Since ionization efficiency measurements become increasingly unreliable at higher energies, there will be difficulties in studying higher processes.

There are two other implications from this calculation. One is that width of the energy distribution does not increase greatly with *n* for large alkanes; there have been some arguments advanced which would contradict this view.⁶ The second deals with the increasing isolation of the ionizing level. The experimental evidence is lacking, but this hypothesis offers an alternative explanation

for the dips at low energies in the ionization efficiency curves of Steiner, Giese, and Inghram⁷; these authors have attributed the dips to missing metastables.

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¹ R. Hoffmann, J. Chem. Phys. **39**, 1397 (1963). This is a calculation of the extended Hückel type, with $H_{ij}=0.5KS_{ij}(H_{ii}+H_{jj})$; $H_{ii}(C2s)=-21.40$ eV, $H_{ii}(C2p)=-11.40$ eV, $H_{ii}(H1s)=-13.60$ eV.

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³ We can compare the charge distribution in the ionizing level with that calculated by J. Lennard-Jones and G. G. Hall, Trans. Faraday Soc. **48**, 581 (1952). For *n*-octane our calculated electron density is distributed as follows: C₁, 0.108; C₂, 0.203; C₃, 0.308; C₄, 0.349; all H, 0.032. Overlap populations are: C₁-C₂, 0.0166; C₂-C₃, 0.0444; C₃-C₄, 0.0494; C₄-C_{4'}, 0.0543; qualitatively similar to the corresponding *bond* electron densities of Lennard-Jones and Hall: 0.0343, 0.1170, 0.1997, 0.2340. A change in $H_{ii}(C2p)$ from -11.4 to -9.1 eV gives ionization potentials which agree well with those obtained from photo-ionization measurements by S. Watanabe, J. Chem. Phys. **26**, 542 (1957), which, however, are not the vertical ionization potentials needed for a proper comparison. The new parametrization is not presented here since it yields a very similar level scheme, but with the 2s band at higher energies relative to ionization.

⁴ G. G. Hall, Trans. Faraday Soc. **50**, 319 (1954).

⁵ W. A. Chupka and M. Kaminsky, J. Chem. Phys. **35**, 1991 (1961), and references therein.

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On the Signs of the Hard Sphere Virial Coefficients*

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THE question, whether or not a central hard potential will give any negative virial coefficients, is an unsettled problem. Temperley¹ has calculated virial coefficients B_n for hyperdimensional hard cubes (angle-dependent potential). He found that B_4 in five dimensions and B_5 in four dimensions are negative for these systems. He then conjectured that a hard "three-dimensional gas" would give negative B_6 or B_7 . At that time there was no evidence that B_n for spheres and cubes could differ in sign. In fact, as suggested by Zwanzig,² inequalities which apply to individual integrals can be used to bound certain sphere integrals in terms of cube integrals. Unfortunately, these inequalities are so weak that they cannot be used to determine the signs of any of the B_n 's for $n>3$. By now it is known that sphere and cube virial coefficients *do* differ in sign as well as in magnitude. B_6 is positive for hard spheres,³ while, in support of Temperley's conjecture, B_6 is negative for hard cubes.⁴ Furthermore, two approximate