223. Valence Ionization Energies of Hydrocarbons

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Summary

Experimental valence ionisation energies of 143 hydrocarbons, C_nH_m, have been determined from their He(II*a*) (40.80 eV) and He(I*a*) (21.22 eV) excited photoelectron spectra. Ionization energies, usually up to 26 eV are given in tabular form for 108 hydrocarbons with $n \leqslant 6$, together with their (tentative) assignment. The ionization energies up to approximately 25 eV, of 35 selected hydrocarbons with $7 \leqslant n \leqslant 10$, are presented by means of their He(II*a*) photoelectron spectra.

Introduction. - Following the pioneering work of *Price, Potts & Streets* [1] it has become a matter of considerable interest to obtain as many complete sets of valence ionization energies of small hydrocarbons C_nH_m as possible. These are the ionization energies which correspond, within the usual *Koopmans*'-Approximation [2] to the ejection of a photoelectron from one of the $2n+m/2$ occupied valence shell molecular orbitals. Within a LCAO formalism, these orbitals are adequately represented by linear combinations of carbon 2s, $2p_x$, $2p_y$, $2p_z$ and hydrogen 1s atomic orbitals. The contribution of the carbon 1s orbitals may safely be neglected, because of their low basis energy (−290 to −295 eV) [3], and for most practical applications the higher atomic orbitals and/or polarization functions need not to be taken into consideration.

For obvious reasons, such an extended set of data for closely related molecules, is of prime importance for developing and testing those theoretical models of varying degree of sophistication, which are currently used for the rationalization and prediction of ionization energies. (Some particular cases will be discussed in subsequent contributions, *e.g.* in [4].) In this respect, simple hydrocarbons are the compounds of choice, for the following reasons. To begin with, all valence ionization energies are found within an easily accessible region (~8 to ~26 eV), which is not the case for molecules containing one or more heteroatoms. Furthermore, for a given type of atomic orbital, *i.e.* 2p(C) or 2s(C) or 1s(H), the basis energy does not change from one atom to another, and therefore the resultant molecular σ-orbitals are usually spread more or less uniformly over the whole of the molecule, with rare, symmetry-conditioned exceptions. As a consequence the positive charge of the radical cation obtained by removing an electron from such a delocalized orbital will be evenly distributed over the molecular frame. This minimizes the effect of electron rearrangement in the radical cation, eliminating the complications arising when the photoelectron is removed from a spatially strongly localized molecular orbital (*e.g.* lone pair orbitals). Finally, semi-localized carbon-carbon π-orbitals of unsaturated hydrocarbons are by necessity the highest occupied orbitals (HOMO) of the particular molecule, and even when conjugated π-orbitals are present, the corresponding π-bands in the photoelectron spectrum of the system are easily identified.

Apart from these practical advantages of studying small hydrocarbons, a complete set of their valence shell ionization energies is of particular interest in connection with the application of *Woodward-Hoffmann* rules to orbitally controlled reactions [5], because these molecules provide obviously the most simple and transparent examples. Note, however, that the identification of negative ionization energies with orbital energies is sometimes less straightforward than usually assumed.

Guide to the Tables. - In the following *Tables* and *Figures* are presented experimental valence ionization energies of 143 hydrocarbons C_nH_m, obtained by the technique of photoelectron spectroscopy using He(Iα) (21.22 eV; $\lambda = 58.4$ nm) and/or He(IIα) (40.80 eV; $\lambda = 30.4$ nm) radiation for excitation. Ionization energies up to approximately 26 eV were measured for most hydrocarbons listed. With the exception of some of the more unusual polycyclic hydrocarbons, most of the systems C_nH_m with $n \leqslant 5$ are included, as well as a large number of hydrocarbons with $n = 6$. For $n > 6$ the bands in the photoelectron spectra tend to conglomerate, particularly when the molecular symmetry is low, and it becomes very difficult if not impossible to deconvolute the overlapping band systems into well defined individual bands, let alone to assign them unambiguously as can be done for the smaller molecules. Thus, the valence ionization energies of only some selected larger hydrocarbons with $7 \leqslant n \leqslant 10$ have been included. In these cases we have refrained from listing band positions in tabular form, but preferred to present the original spectra instead. This should give the reader an opportunity to judge for himself the precision with which such spectra can be interpreted. The spectra shown in *Fig. 4* to *8* were all obtained using He(IIα) photon excitation and the ionization energy scale was calibrated in the region of interest *i.e.* ~ 15 to 26 eV. Consequently, although the complete spectra are reproduced, the scale on the low ionization energy side, extending from ~ 7 to 12 eV, is to be taken only as a guideline, and can be in error by approximately ± 0.2 eV.

Ionization energies of the inner valence shell of hydrocarbons (the so-called C_{2s}-shell, according to *Price, Potts & Streets* [1]) have been recorded previously by other authors, using He(IIα) radiation. Thus, data are available for linear and branched saturated systems C_nH_{2n+2} [1] [6] [7], for cycloalkanes C_nH_{2n} with $n = 3$ to 8 [7], for some unsaturated hydrocarbons [8] [9] and in particular for benzene [10]. (A compilation can be found in [11]). Lately a few such ionization energies have also become available through excitation with monochromatized X-rays, *e.g.* for the *n*-alkanes [12]. For further details the reader is referred to the references given in the *Tables.*

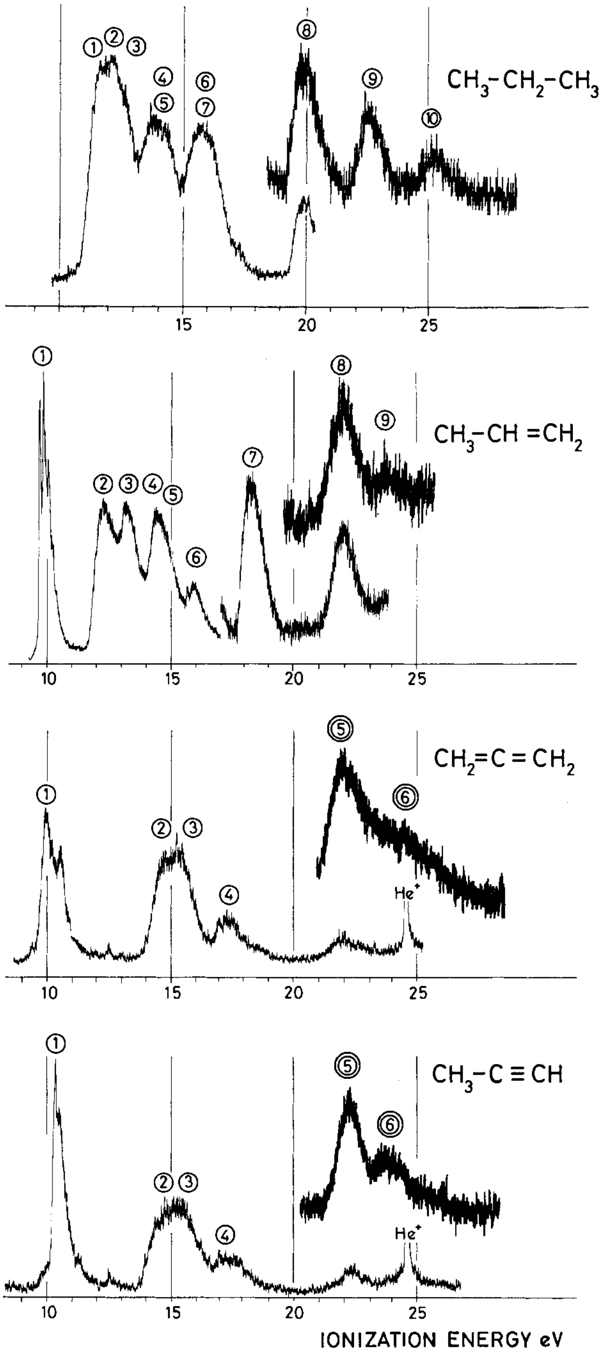


Fig. 1. *He(IIa) photoelectron spectra of propane, propene, allene and methylacetylene.* The upper curve in each spectrum was obtained by isolating the photon source from the ionization region by a thin polystyrene film (see Experimental Part).

In the present work we have tried to provide as complete a set of hydrocarbon valence shell ionization energies as possible for systems C_nH_m with $n \leqslant 6$ and for a few higher ones. However, in those cases where the profuse overlap in the He(Iα) region prevents deconvolution and an unambigous assignment, only the positions of the prominent, well defined maxima of the C_{2p}-band system and those of the bands in the C_{2s}-region, recorded with He(IIα) radiation, are tabulated. Ionization energies taken from published data are referenced in the *Tables.* For internal consistency, the values determined in this laboratory are listed in cases where the discrepancy with published data exceeded ±0.2 eV. This seems to be a conservative estimate of the error with which the position of the broad bands can be determined in the absence of strong overlap with other, close lying bands.

The *Tables of ionization energies* are arranged in order of increasing number n of carbon atoms in the molecules C_nH_m. Within each set, characterized by n, molecules having the same connectivity, *i.e.* the same topological graph, are grouped together.

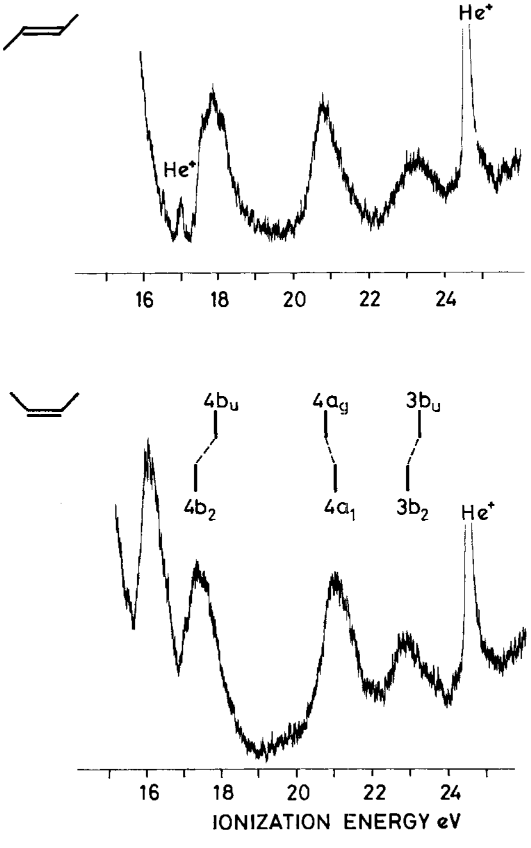


Fig. 2. *He(IIa) photoelectron spectra of* trans- *and* cis-*2-butene.* The labeled vertical lines correspond to the positions of the respective band maxima, thus allowing an assessment of the C_{2s}-band shifts, due to the change in configuration.

In the photoelectron spectra of the "linear" C_3 hydrocarbons shown in *Fig. 1*, the individual bands have been numbered to illustrate the assignment underlying the compilation. Within *Koopmans'* approximation, the bands correspond to the following molecular orbitals:

	$CH_3CH_2CH_3$	$CH_3{-}CH{=}CH_2$	$CH_2{=}C{=}CH_2$	$CH_3{-}C{\equiv}CH$
①	$4b_2$	$2a''(\pi)$	$2e(\pi)$	$2e(\pi)$
②	$6a_1$	$10a'$	$1e(\pi)$	$1e(\pi)$
③	$2b_1$	$9a'$	$3b_2$	$7a_1$
④	$1a_2$	$1a''(\pi)$	$4a_1$	$6a_1$
⑤	$3b_2$	$8a'$	$2b_2$	$5a_1$
⑥	$5a_1$	$7a'$	$3a_1$	$4a_1$
⑦	$1b_1$	$6a'$		
⑧	$4a_1$	$5a'$		
⑨	$2b_2$	$4a'$		
⑩	$3a_1$			

The second π-orbital of propene (band ④; $1a''(\pi)$), and the second degenerate π-orbital-pair in allene (band ②; $1e(\pi)$) and methylacetylene (band ② or ③; $1e(\pi)$), are dominantly π-orbitals of the hyperconjugating alkyl moieties, *i.e.* of the methyl- or methylene-groups.

Fig. 2 illustrates the precision with which relative band positions can be assessed in the photoelectron spectra of isomeric hydrocarbons, using *trans*- and *cis*-2-butene as an example. Although there are significant shifts in the C_{2s}-band system, going from one spectrum to the other, it is obvious that they are not large enough to allow, for example, the quantitative analysis of a mixture of such isomers.

As a third example, the complete spectrum of the linear C_4 hydrocarbon diacetylene is shown in *Fig. 3*. Here the part of the spectrum below 19 eV has been recorded with He(Iα) radiation, that above 19 eV with filtered He(IIα) radiation.

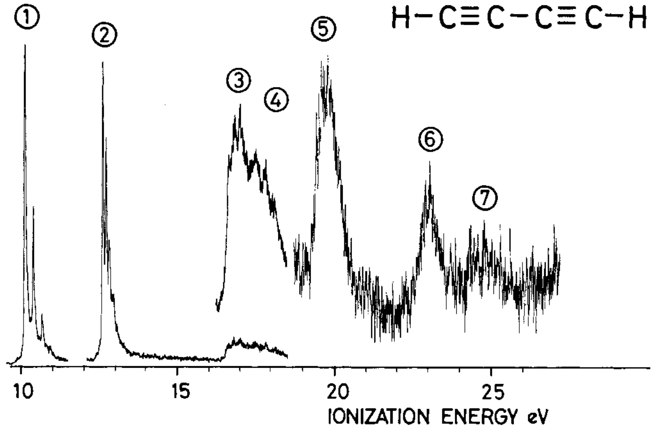


Fig. 3. *Complete valence shell photoelectron spectrum of diacetylene, excited by He(Iα) radiation* (below 19 eV) *and He(IIα) radiation* (above 19 eV). In the latter case the radiation has been filtered with a thin polystyrene film (see Experimental Part).

In those cases where the individual ionization energies are correlated with orbitals belonging to a given irreducible representation, assuming a conformation of appropriate symmetry, this correlation rests on STO-3G [13], SPINDO [14] and/or empirical calculations and parametrizations [9]. Whenever the ionization energies are separated by less than ~0.5 eV and/or if the bands overlap strongly an unambiguous assignment of the order of the radical cation states is of course not possible. Where such an assignment is given, it should be regarded as a working hypothesis at best.

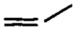
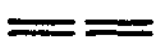
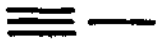
The ionization energies listed are the positions I_j^m of the band maxima. Within the experimental uncertainties and in view of the usually rather broad bands, they may be assumed to be equal to the vertical ionization energies I_j^v for all practical purposes. If given, adiabatic ionization energies I_j^a are printed in italics, and we estimate that these values are good to ±0.02 eV, whereas the onset values given in the footnotes are uncertain to ±0.1 eV (see legend to *Tab.*). The $I_j^m \approx I_j^v$ values have error limits of at least ±0.1 eV in most of the cases. For the positions I_j^m of the maxima above 23 eV in the C_{2s}-band system, the uncertainties are presumably equal or perhaps larger than ±0.2 eV, due to the weakness and spread of the bands.

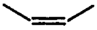
Tables
Valence Ionization Energies of Hydrocarbons

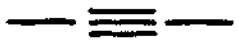
All ionization energies listed (in eV) refer to the position of the corresponding band maximum I_j^m in the photoelectron spectrum of the hydrocarbon with an accuracy of ±0.1 eV. For all practical purposes $I_j^m \approx I_j^v$ = vertical ionization energy. In those cases where the vibrational fine structure of the band can be resolved, adiabatic ionization energies I_j^a are given in italics or in the footnotes, with an estimated accuracy of ±0.02 eV. Numbers in square brackets are the references and a star in square brackets ([*]) indicates that these are new values determined in the course of this work. A given reference number is valid also for all successive values in the column until a new reference number appears. I_j^m-values in round brackets refer to strongly overlapped bands and are therefore uncertain. The accuracy of the band onset ionization energies given in the footnotes is taken to be ±0.1 eV.

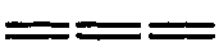
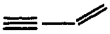
A) *Linear Hydrocarbons*

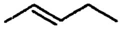
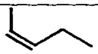
	CH_4		(T_d)	C_2H_6		(D_{3d})	C_2H_4		(D_{2h})	C_2H_2		$(D_{\infty h})$
	CH_4			H_3C-CH_3			$H_2C=CH_2$			$HC\equiv CH$		
π							$1b_{3u}$	*10.51*	[19]	$1\pi_u$	*11.40*	[20]
p	$1t_2$	$13.6^{a)}$ $14.4^{a)}$ $15.0^{a)}$	[17]	$3a_{1g}$	$12.1^{c)}$	[18]	$1b_{3g}$	12.5		$3\sigma_g$	16.7	
				$1e_g$	$12.7^{d)}$ $13.3^{d)}$		$3a_g$	14.8				
							$1b_{2u}$	15.9				
				$1e_u$	$15.0^{d)}$ $15.8^{d)}$							
s	$2a_1$	$22.9^{b)}$		$2a_{2u}$	20.4	[7]	$2b_{1u}$	19.1	[8]	$2\sigma_u$	18.7	[8]
				$2a_{1g}$	23.9		$2a_g$	23.7		$2\sigma_g$	23.5	

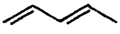
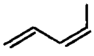
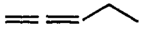
	C_3H_8	(C_{2v})		C_3H_6	(C_s)		C_3H_4	(D_{2d})		C_3H_4	(C_{3v})	
												
π				2a"	*9.73*	[22]	2e	*9.62*	[18]	2e	*10.37*	[18]
								10.2			*10.37*	
p	$4b_2$	$11.5^{e)}$	[21]	10a'	12.2	[*]	1e	*14.10*		1e	14.6	
	$6a_1$	12.1		9a'	13.1			14.9			14.6	
	$2b_1$	12.6		1a"	14.4		$3b_2$	15.5		$7a_1$	15.4	
	$1a_2$	13.5		8a'	14.4							
	$3b_2$	14.1		7a'	15.9							
	$5a_1$	15.2										
	$1b_1$	16.0										
s	$4a_1$	19.5	[*]	6a'	18.2	[8]	$4a_1$	17.4	[*]	$6a_1$	17.4	[*]
	$2b_2$	22.1	[7]	5a'	21.9		$2b_2$	22.0		$5a_1$	22.4	
	$3a_1$	24.7		4a'	23.7		$3a_1$	24.4		$4a_1$	23.9	

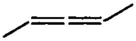
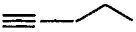
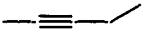
	C_4H_{10}	(C_{2h})		C_4H_8	(C_s)		C_4H_8	(C_{2h})		C_4H_8	(C_{2v})	
												
π				3a"	*9.63*	[22]	$2a_u$	*9.12*	[22]	$2b_1$	*9.12*	[22]
p	$7a_g$	$11.2^{f)}$	[*]	13a'	11.3	[*]	$7a_g$	11.8	[*]	$6b_2$	11.7	[23]
	$6a_g$	11.7		12a'	12.3		$6a_g$	12.7		$7a_1$	12.7	
	$2b_g$	(11.7)			13.2		$6b_u$	13.1		$5b_2$	13.5	
	$2a_u$	12.2			13.6		$1b_g$	14.0		$1a_2$	14.1	
	$6b_u$	12.7		10a'	14.8		$5b_u$	14.5		$6a_1$	14.1	
	$5b_u$	13.2		9a'	15.1		$1a_u$	15.0		$1b_1$	14.5	
	$1b_g$	14.3		1a"	16.0		$5a_g$	15.0		$5a_1$	16.1	
	$5a_g$	14.6										
	$1a_u$	16.0										
s	$4b_u$	18.8	[7]	8a'	18.2		$4b_u$	17.9	[*]	$4b_2$	17.5	[*]
	$4a_g$	20.7		7a'	20.5		$4a_g$	20.9		$4a_1$	21.2	
	$3b_u$	23.0		6a'	22.8		$3b_u$	23.1		$3b_2$	22.9	
	$3a_g$	24.7		5a'	-		$3a_g$	-		$3a_1$	-	

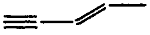
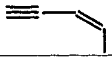
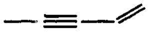
	C_4H_6	(C_s)		C_4H_6	(C_{2h})		C_4H_6	(C_s)		C_4H_6	(D_{3d})	
												
π	3a"	*9.33*	[24]	$1b_g$	*9.03*	[25]	3a"	*10.20*	[26]	$2e_u$	*9.59*	[27]
	12a'	*10.06*		$1a_u$	*11.46*		12a'	10.3				
p				$7a_g$	12.2			12.8	[*]	$5a_{1g}$	14.3	[*]
				$6b_u$	13.4			13.4		$1e_g$	14.9	
				$6a_g$	13.9			14.2				
				$5b_u$	15.5			15.8		$1e_u$	15.3	
				$5a_g$	15.5			15.8				
s				$4b_u$	18.1	[8]	8a'	17.2		$4a_{2u}$	16.3	
				$4a_g$	19.2		7a'	20.9		$4a_{1g}$	21.1	
				$3b_u$	22.6		6a'	22.9		$3a_{2u}$	23.6	
				$3a_g$	24.8		5a'	-		$3a_{1g}$	-	

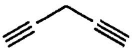
	C_4H_4	(D_{2h})		C_4H_4	(C_s)		C_4H_2	$(D_{\infty h})$	
									
π	$1b_{3g}$	*9.15*	[28]	2a"	*9.58*	[29]	$1\pi_u$	*10.17*	[20]
	$2b_{3u}$	*9.98*		12a'	*10.58*				
	$1b_{2u}$	*11.70*		1a"	12.0		$1\pi_g$	*12.62*	
p	$1b_{2g}$	14.2		11a'	13.2	[30]	$5\sigma_g$	17.0	
	$1b_{3u}$	15.0		10a'	15.2				
	$5a_g$	15.5		9a'	16.1				
s	$4b_{1u}$	16.5	[*]	8a'	17.4	[*]	$4\sigma_u$	17.5	[*]
	$4a_g$	20.6		7a'	19.7		$4\sigma_g$	20.0	
	$3b_{1u}$	23.0		6a'	22.9		$3\sigma_u$	23.3	
	$3a_g$	-		5a'			$3\sigma_g$	25.0	

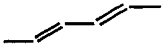
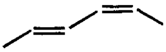
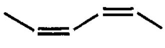
		C_5H_{12}	(C_{2v})		C_5H_{10}	(C_s)		C_5H_{10}	(C_s)		C_5H_{10}	(C_s)
												
π				4a"	*9.52*	[22]	4a"	*9.04*	[22]	4a"	*9.04*	[22]
p		10.9$^{g)}$	[*]									
		11.5										
s	$6a_1$	18.7	[8]	10a'	18.1	[*]	10a'	17.8	[*]	10a'	17.3	[*]
	$4b_2$	19.9		9a'	19.5		9a'	19.9		9a'	20.2	
	$5a_1$	21.7		8a'	21.7		8a'	21.8		8a'	21.8	
	$3b_2$	23.7		7a'	23.4		7a'	24.0		7a'	24.0	
	$4a_1$	24.8		6a'	-		6a'	-		6a'	-	

		C_5H_8	(C_s)		C_5H_8	(C_s)		C_5H_8	(C_{2v})		C_5H_8	(C_s)
												
π	3a"	*8.61*	[25]	3a"	*8.67*	[*]	$2a_u$	*9.62*	[31]		*9.25*	[*]
	2a"	11.1		2a"	11.1		$1b_g$	*10.12*			10.0	
p	16a'	11.9	[*]	16a'	11.7			12.0	[*]		12.1	
	15a'	12.5		15a'	12.8			12.5			12.7	
	14a'	13.1		14a'	13.2			13.4			(13.4)	
	13a'	13.9		13a'	13.9			14.4			14.6	
	1a"	14.8		1a"	14.9			14.6			?	
	12a'	14.8		12a'	14.9			15.5			15.1	
	11a'	15.6		11a'	15.9			16.0			15.8	
s	10a'	18.3		10a'	17.3		$6a_1$	18.1		10a'	16.8	
	9a'	18.6		9a'	18.9		$4b_2$	18.6		9a'	19.8	
	8a'	21.6		8a'	21.6		$5a_1$	21.5		8a'	21.8	
	7a'	23.2		7a'	22.9		$3b_2$	23.1		7a'	23.6	
	6a'	-		6a'	-		$4a_1$	-		6a'	-	

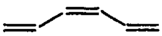
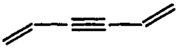
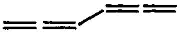
		C_5H_8	(D_2)		C_5H_8	(C_s)		C_5H_8	(C_s)		C_5H_6	(C_s)
												
π		*9.13*	[24]	4a"	*10.10*	[26]	4a"	*9.44*	[26]	3a"	*8.88*	[32]
		9.65								15a'	*10.04*	
										2a"	11.4	
p		12.7			12.0	[*]		12.4	[*]	14a'	12.5	
		13.0			12.7			(12.4)		13a'	13.9	
		13.7			(13.0)			13.0				
		14.2			14.2			13.9				
		14.6			14.8			14.3				
		15.7			15.8			15.2				
		16.6			16.2			15.2				
s				10a'	17.2		10a'	16.3				
				9a'	19.8		9a'	20.3				
				8a'	22.0		8a'	21.6				
				7a'	23.1		7a'	22.7				
				6a'	-		6a'	-				

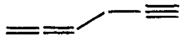
		C_5H_6	(C_s)		C_5H_6	(C_s)		C_5H_6	(C_s)		C_5H_4	(D_{2d})
												
π	3a"	*9.11*	[33]	3a"	*9.17*	[33]	3a"	*9.06*	[33]	3e	*8.67*	[34]
	15a'	*10.38*		15a'	*10.44*		15a'	*9.86*			9.2	
	2a"	*11.64*		2a"	*11.63*		2a"	*11.48*		2e	11.8	
p							14a'	12.8		1e	14.6	
							13a'	14.7				
							1a"	15.0		$5b_2$	15.8	

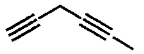
	C_5H_4 (C_{3v})	C_5H_4 (C_{2v})
		
π	$3e$ *9.51* [27] $2e$ *12.02*	$2b_1$ *10.27* [30] $6b_2$ *10.50* $8a_1$ *11.02* $1a_2$ 11.1
p	$11a_1$ 14.6 [*] $1e$ 15.5	15.4 16.0 16.0
s	$10a_1$ 16.8 $9a_1$ 19.2 $8a_1$ 22.7 $7a_1$ - $6a_1$ -	$6a_1$ 17.5 $4b_2$ 18.0 $5a_1$ 22.6 $3b_2$ (22.6) $4a_1$ -

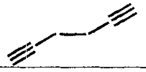
	C_6H_{14} (C_{2h})	C_6H_{10} (C_{2h})	C_6H_{10} (C_s)	C_6H_{10} (C_{2h})
				
π		$2b_g$ *8.22* [25] $2a_u$ 10.7	$4a''$ *8.25* [*] $3a''$ 10.7	$2b_g$ *8.18* [*] $2a_u$ 10.7
p			$19a''$ 11.7	11.3
s	$6b_u$ 18.7 [*] $6a_g$ 19.3 $5b_u$ 20.7 $5a_g$ 22.4 $4b_u$ - $4a_g$ -	$6b_u$ 17.8 [*] $6a_g$ 18.0 $5b_u$ 20.8 $5a_g$ 22.5 $4b_u$ - $4a_g$ -	$12a'$ 17.3 $11a'$ 18.2 $10a'$ 21.0 $9a'$ 22.5 $8a'$ - $7a'$ -	$6b_u$ 17.0 $6a_g$ 18.5 $5b_u$ 21.3 $5a_g$ 22.5 $4b_u$ (22.5) $4a_g$ -

	C_6H_{10} (C_s)	C_6H_{10} (C_s)	C_6H_{10} (C_s)	C_6H_{10} (C_{2h})
				
π	$3a''$ *8.53* [*] $2a''$ 11.1	*10.07* [26]	*9.37* [26]	*9.32* [26]
p				12.4
s	$12a'$ 18.1 $11a'$ 18.1 $10a'$ 20.3 $9a'$ 22.1 $8a'$ - $7a'$ -	$12a'$ 16.9 $11a'$ 19.1 $10a'$ 20.9 $9a'$ 22.4 $8a'$ 23.5 $7a'$ -		$6b_u$ - $6a_g$ (16.5) $5b_u$ 20.1 $5a_g$ 20.7 $4b_u$ (22.9) $4a_g$ -

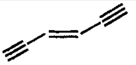
	C_6H_8 (C_{2h})	C_6H_8 (C_{2v})	C_6H_6 (C_{2h})	C_6H_6 (C_{2h})
				
π	$2a_u$ *8.29* [25] $1b_g$ *10.26* $1a_u$ 11.9	$2b_1$ *8.32* [25] $1a_2$ *10.27* $1b_1$ 11.9	$2a_u$ *8.50* [30] $9b_u$ 10.0 $1b_g$ *10.72* $1a_u$ 12.0	b_g *8.53* [32] a_g *9.78* b_u *10.32* a_u 11.3
p	$10a_g$ 11.6 $9b_u$ 12.6 $9a_g$ 13.3 $8a_g$ 13.9 $8b_u$ 14.5 $7b_u$ 15.2 $7a_g$ 15.9	$9b_2$ 11.5 $10a_1$ 12.6 $9a_1$ 13.4 $8b_2$ 13.5 $7b_2$ 14.5 $8a_1$ 15.2 $7a_1$ 16.0	12.9 13.2 14.9 (14.9) 16.0	
s	$6a_g$ 17.9 [*] $6b_u$ 18.1 $5b_u$ 19.3 $5a_g$ 22.1 $4b_u$ 23.5 $4a_g$ -	$6b_2$ 17.2 [*] $6a_1$ 18.6 $5b_2$ 19.1 $5a_1$ 22.1 $4b_2$ 23.5 $4a_1$ -	- [*] 18.8 19.8 22.5 - -	

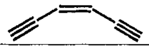
	C_6H_6	(C_s)	
			
π	a''	*9.65*	[32]
	a'	10.3	
	a'	10.5	
	a''	10.8	
p	a'	13.8	
s			

	C_6H_6	(C_s)	
			
π	$4a''$	*9.66*	[30]
	$17a'$	*9.91*	
	$16a'$	*10.61*	
	$3a''$	10.7	
p		*13.78*	
		15.2	
		15.2	
		15.5	
		15.5	
s	$12a'$	16.5	[*]
	$11a'$	17.5	
	$10a'$	21.5	
	$9a'$	22.5	
	$8a'$	-	
	$7a'$	-	

	C_6H_6	(C_{2h})	
			
π	$9a_g$	*9.90*	[30]
	$2a_u$	10.4	
	$2b_g$	10.6	
	$8b_u$	*10.88*	
p	$1b_g$	13.3	
	$8a_g$	14.0	
	$7a_g$	14.7	
	$7b_u$	16.0	
	$1a_u$	-	
s		-	[*]
		17.4	
		21.2	
		22.7	
		-	
		-	

	C_6H_6	(D_{3d})	
			
π	$2e_g$	*8.92*	[27]
	$2e_u$	*11.48*	
p	$7a_{1g}$	14.3	
	$1e_g$	14.5	
	$1e_u$	15.2	
s	$6a_{2u}$	15.7	[*]
	$6a_{1g}$	18.6	
	$5a_{2u}$	22.0	
	$5a_{1g}$	22.6	
	$4a_{2u}$	-	
	$4a_{1g}$	-	

	C_6H_4	(C_{2h})	
			
π	$2a_u$	*9.07*	[30]
	$9a_g$	*10.55*	
	$8b_u$	10.8	
	$1b_g$	*11.18*	
	$1a_u$	*12.43*	
p	$8a_g$	13.7	
	$7a_g$	15.7	
	$7b_u$	(15.7)	
s	$6b_u$	16.4	

	C_6H_4	(C_{2v})	
			
π	$2b_1$	*9.10*	[30]
	$9a_1$	*10.54*	
	$8b_2$	*10.78*	
	$1a_2$	*11.10*	
	$1b_1$	*12.39*	
p	$7b_2$	13.7	
	$8a_1$	15.7	
	$7a_1$	(15.7)	
s	$6b_2$	16.4	

	C_6H_2	$(D_{\infty h})$	
			
π	$2\pi_u$	*9.50*	[27]
	$1\pi_g$	*11.55*	
	$1\pi_u$	*12.89*	
p	$7\sigma_g$	16.5	[*]
s	$6\sigma_u$	17.0	
	$6\sigma_g$	18.8	
	$5\sigma_u$	20.3	
	$5\sigma_g$	22.8	
	$4\sigma_u$	23.5	
	$4\sigma_g$	-	

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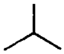
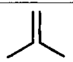
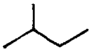
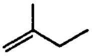
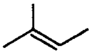
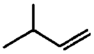
a) Band maxima of *Jahn-Teller* distorted ^2T_d-band. The adiabatic ionization potential is $I_1^a = 12.75$ eV. b) Adiabatic ionization energy $I_1^a = 22.39$ eV. c) Adiabatic ionization energy $I_1^a = 11.56$ eV. The sequence of the electronic states of the radical cation is uncertain. This work assumes that the radical cation ground state $\tilde{X}$ is a $^2A_{1g}$-state. d) Band maxima of *Jahn-Teller* distorted ^2E-band. e) Onset of first band = 10.9 eV. f) Onset of first band = 10.6 eV. g) Onset of first band = 10.2 eV.

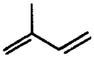
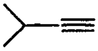
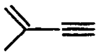
B) *Branched Hydrocarbons*

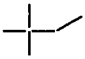
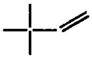
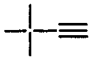
	C_4H_{10}	(C_{3v})	
			
π			
p	$5e$	11.0 a)	[21]
		11.6	
	$6a_1$	12.0	
	$1a_2$	12.9	
	$4e$	13.4	
		13.4	
	$3e$	14.9	
		14.9	
	$5a_1$	15.9	
s	$4a_1$	18.4	[7]
	$2e$	21.9	
		21.9	
	$3a_1$	24.8	

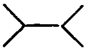
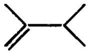
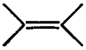
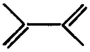
	C_4H_8	(C_{2v})	
			
π	$2b_1$	*9.24*	[22]
p	$5b_2$	11.8	[23]
	$8a_1$	12.9	
	$1a_2$	12.9	
	$4b_2$	13.6	
	$7a_1$	15.2	
	$3b_2$	15.2	
	$1b_1$	15.2	
s	$6a_1$	17.3	
	$5a_1$	21.5	
	$2b_2$	22.2	
	$4a_1$	-	

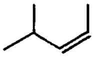
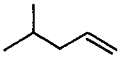
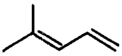
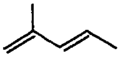
	C_5H_{12}	(T_d)	
			
p	$4t_2$	10.9 b)	[21]
		(11.2)	
		11.5	
	$1t_1$	12.4	
		12.4	
		12.4	
	$1e$	14.0	
		14.0	
	$3t_2$	15.2	
		15.2	
		15.2	
s	$4a_1$	17.8	[7]
	$2t_2$	21.9	
		21.9	
		21.9	
	$3a_1$	25.1	

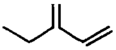
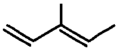
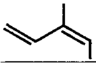
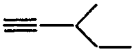
	C_5H_{12}	(C_s)		C_5H_{10}	(C_s)		C_5H_{10}	(C_s)		C_5H_{10}	(C_s)	
												
π				4a"	*9.15*	[22]	4a"	*8.68*	[22]		9.53	[22]
p		$11.0^{c)}$	[*]				16a'	11.3	[*]			
							15a'	12.4				
s	8a'	18.3	[7]	10a'	17.0	[*]	10a'	16.9		8a'	17.8	[*]
	7a'	20.4		9a'	20.3		9a'	20.4		7a'	19.6	
	2a"	22.0		8a'	22.6		8a'	22.2		2a"	22.0	
	6a'	23.3		7a'	23.1		7a'	23.0		6a'	(23.0)	
	5a'	24.9		6a'	-		6a'	-		5a'	-	

	C_5H_8	(C_s)		C_5H_8	(C_{2v})		C_5H_8	(C_{2v})		C_5H_6	(C_s)	
												
π	3a"	*8.85*	[25]		*8.95*	[24]		*10.05*	[26]	3a"	*9.27*	[33]
	2a"	10.9			9.9					15a'	*10.43*	[*]
										2a"	*11.44*	[33]
p	16a'	11.9	[*]		12.5			12.2	[*]	14a'	12.7	[*]
	15a'	12.9						12.7		13a'	13.5	
	14a'	13.4						13.1		1a"	14.8	
	13a'	13.9						13.8		12a'	14.8	
	1a"	( )						14.4		11a'	16.0	
	12a'	15.3						15.5				
	11a'	15.7						16.1				
s	10a'	17.2		$8a_1$	16.4	[*]	$8a_1$	17.0	[*]	10a'	16.9	
	9a'	19.1		$7a_1$	20.1		$7a_1$	20.0		9a'	19.2	
	8a'	22.0		$2b_2$	22.3		$6a_1$	22.3		8a'	22.0	
	7a'	22.7		$6a_1$	(23.3)		$2b_2$	22.3		7a'	22.5	
	6a'	-		$5a_1$	-		$5a_1$	-		6a'	-	

	C_6H_{14}	(C_s)		C_6H_{12}	(C_s)		C_6H_{10}	(C_{3v})	
									
π					*9.45*	[22]		*9.92*	[26]
p								11.7	[*]
s	10a'	17.6	[*]				$8a_1$	-	
	9a'	20.2					$7a_1$	19.3	
	8a'	21.9					$2e$	22.1	
	2a"	21.9						22.1	
	7a'	(23.2)					$6a_1$	(23.5)	
	6a'	-					$5a_1$	-	

	C_6H_{14}	(C_{2h})		C_6H_{12}	(C_s)		C_6H_{12}	(D_{2h})		C_6H_{10}	(C_{2h})	
												
π					*9.07*	[22]	$2b_{3u}$	*8.27*	[22]	$2b_g$	*8.62*	[25]
										$2a_u$	10.2	
p							$4b_{3g}$	11.0		$10a_g$	11.3	
							$6a_g$	12.2				
s	$4b_u$	17.9	[*]				$1b_{3u}$	-		$6b_u$	-	
	$4a_g$	19.8					$4a_g$	19.8	[*]	$6a_g$	18.8	[*]
	$2a_u$	21.9					$2b_{3g}$	21.5		$5a_g$	21.8	
	$2b_g$	21.9					$2b_{2u}$	22.2		$5b_u$	21.8	
	$3b_u$	23.5					$3b_{1u}$	23.4		$4b_u$	23.3	
	$3a_g$	-					$3a_g$	-		$4a_g$	-	

	C_6H_{12} (C_s)	C_6H_{12} (C_s)	C_6H_{10} (C_s)	C_6H_{10} (C_s)
				
π	8.98 [22]	9.45 [22]	4a" 8.28 [25] 3a" 10.8	4a" 8.47 [*] 3a" 10.5
p			11.4	11.5
s			17.1 18.2 21.2 22.0 (23.4) -	17.2 18.3 21.7 21.7 23.2 -

	C_6H_{10} (C_s)	C_6H_{10} (C_s)	C_6H_{10} (C_s)	C_6H_{10}
				
π	4a" 8.79 [*] 3a" 10.8	4a" 8.39 3a" 10.6		9.98 [26] -
p	11.5	11.4		
s	16.8 18.8 20.3 22.2 - -	16.9 18.3 21.1 22.6 - -	16.6 18.8 20.9 22.8 - -	

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a) Band maxima of *Jahn-Teller* distorted ^2E-band. Onset of first band = 10.3 eV.

b) Band maxima of *Jahn-Teller* distorted $^2T_2$-band. Onset of first band = 10.2 eV.

c) Onset of first band = 10.3 eV.

C) *Monocyclic Hydrocarbons*

	C_3H_6 (D_{3h})	C_3H_4 (C_{2v})	C_4H_8 (D_{2d})	C_4H_6 (C_{2v})
				
π		$2b_1$ 9.70 [35]		$2b_1$ 9.43 [35]
p	$3e'$ 10.6$^{a)b)}$ [18] 11.3 $1e''$ 13.0 13.0 $3a_1'$ 15.7 $1a_2''$ 16.6	$3b_2$ 11.0 [36] $6a_1$ 12.7 $1b_1$ 15.1 $5a_1$ 16.7	$4e$ 10.7$^{a)c)}$ [37] 11.3 $4a_1$ 11.7 $1b_1$ 12.5 $3e$ 13.4$^{a)}$ 13.6 $3a_1$ 15.9 $3b_2$ 16.2	$5b_2$ 11.0 [23] $7a_1$ 11.8 $1a_2$ 12.8 $6a_1$ 13.4 $1b_1$ 15.5 $5a_1$ 16.4
s	$2e'$ 19.5 [7] 19.5 $2a_1'$ 26.5	$2b_2$ 18.3 $4a_1$ 19.6 $3a_1$ -	$2b_2$ 18.2 [7] $2e$ 21.0 21.0 $2a_1$ 25.5	$4b_2$ 17.2 $3b_2$ 20.7 - -

	C_5H_{10}	(D_{5h})		C_5H_8	(C_s)		C_5H_6	(C_{2v})	
									
π				$12a'$	*9.01*	[35]	$1a_2$	*8.58*	[38]
							$2b_1$	*10.62*	
	$3e'_2$	$10.7^{a)d)}$	[*]	$7a''$	11.6	[23]	$6b_2$	12.3	
		11.3							
				$11a'$	12.0		$9a_1$	12.6	
	$3e'_1$	11.8							
		11.8		$6a''$	12.2		$8a_1$	13.2	
p	$1e''_2$	12.0		$10a'$	12.6		$5b_2$	13.8	
		12.0							
				$9a'$	13.1		$1b_1$	14.8	
	$1e''_1$	14.0							
		14.0		$5a''$	14.0		$7a_1$	16.4	
	$3a'_1$	16.0		$8a'$	15.8				
	$1a''_2$	16.5							
				$7a'$	16.1				
	$2e'_2$	18.3	[7]	$4a''$	17.3		$4b_2$	17.5	
		18.3							
				$6a'$	19.0		$6a_1$	18.4	
s	$2e'_1$	22.2							
		22.2		$3a''$	22.0		$5a_1$	22.0	
	$2a_1$	–		$5a'$	22.0		$3b_2$	22.3	
				$4a'$	–		$4a_1$	–	

	C_6H_{12}	(D_{3d})			C_6H_{10}	(C_2)		C_6H_8	(C_{2v})		C_6H_8	(D_{2h})	
													
π					*8.94*	[35]	$2a_2$	*8.25*	[*]	$2b_{1u}$	*8.82*	[*]
							$2b_1$	10.7		$1b_{3g}$	*9.88*	
	$4e_g$	$10.3^{a)e)}$	[39]		10.7	[*]		11.3			11.0	
		10.9										
					11.3			11.8			12.0	
	$4a_{1g}$	11.4										
					11.7			12.7			12.0	
	$4e_u$	11.9										
		11.9			12.8			(13.0)			13.3	
	$1a_{1u}$	(12.2)			13.2			13.5			13.7	
p	$3e_u$	12.9			13.2			14.0			13.7	
		12.9										
					13.8			14.9			14.7	
	$3e_g$	14.6										
		14.6			14.5			16.4			16.6	
	$3a_{2u}$	15.0			15.2							
	$3a_{1g}$	16.2			16.3							
	$2a_{2u}$	18.1	[7]		16.7	[8]		16.4	[8]		16.6	[8]
	$2e_g$	19.5			19.3			18.8			18.6	
		19.5			19.8			19.9			20.2	
s	$2e_u$	23.1			22.8			23.1			23.0	
		23.1			23.5			23.9			–	
	$2a_{1g}$	25.7			–			–			–	

	C_6H_6		(D_{6h})
			
π	$1e_{1g}$	9.25 9.25	[18]
p	$1a_{2u}$	12.4	
	$3e_{2g}$	11.49 11.49	
	$3e_{1u}$	14.0 14.0	
	$1b_{2u}$	14.8	
	$3a_{1g}$	16.84	
s	$2b_{1u}$	15.45	[8]
	$2e_{2g}$	19.0 19.0	
	$2e_{2u}$	23.0 23.0	
	$2a_{1g}$	25.9	

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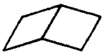
[a] Band maxima of *Jahn-Teller* distorted ^2E band.
[b] Onset of first band = 9.8 eV.
[c] Onset of first band = 9.6 eV.
[d] Onset of first band = 10.3 eV.
[e] Adiabatic ionization potential $I_1^a = 9.88$ eV.

D) *Bicyclic Hydrocarbons*

	C_4H_6		(C_{2v})
			
p			
s	$4a_1$	-	
	$2b_1$	19.1	[*]
	$2b_2$	22.2	
	$3a_1$	-	

	C_5H_8		(C_s)
			
p		$9.5^{a)}$	[*]
		10.4	
		11.5	
		11.9	
		13.0	
		14.8	
		(15.2)	
		16.8	
s	4a"	17.5	
	6a'	19.2	
	3a"	20.9	
	5a'	22.9	
	4a'	-	

	C_6H_{10}		(C_{2h})	C_6H_8		(C_s)	C_6H_6		(C_{2v})
									
π				13a'	$9.4^{c)}$	[40]	$5b_2$	$9.4^{d)}$	[41]
							$8a_1$	9.7	
p	$4a_2$	$9.6^{b)}$	[40]	9a"	10.3		$7a_1$	10.9	
	$6b_1$	10.2		12a'	10.8		$3a_2$	11.5	
	$8a_1$	10.8		8a'	11.4		$5b_1$	12.2	
	$3a_2$	11.5		11a'	12.4		$4b_2$	13.2	
	$5b_2$	12.3			12.9		$6a_1$	14.2	
		(12.3)			(12.9)		$3b_2$	15.9	
		13.2			15.1		$5a_1$	(16.6)	
		14.0			15.5				
		15.1		7a'	16.7				
		(15.5)							
		16.6							
s	$4b_2$	16.6	[*]	6a"	16.3	[*]	$4b_1$	(16.2)	[*]
	$2a_2$	19.3		5a"	18.5		$2a_2$	17.9	
	$4a_1$	19.9		6a'	19.9		$4a_1$	19.8	
	$3b_1$	21.5		4a"	21.2		$3b_1$	20.3	
	$2b_2$	23.4		5a'	23.2		$2b_2$	22.6	
	$3a_1$	-		4a'	-		$3a_1$	-	

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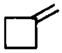
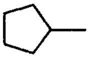
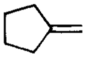
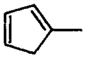
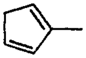
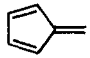
[a] Onset of first band = 8.7 eV.
[b][c][d] Onset of first band = 9.0 eV.

E) *Cyclic Hydrocarbons with Sidechains*

		C_4H_6	(C_{2v})		C_6H_6	(D_{3h})		C_5H_8	(C_{2v})		C_6H_6	(C_{2v})
												
	$2b_1$	9.6	[18]	1e"	*8.94*	[42]	$2b_1$	*9.19*	[18]	$2b_1$	*8.80*	[43]
π										$1a_2$	*9.44*	
				$1a_2''$	13.0					$1b_1$	12.3	
	$4b_2$	10.5		5e'	10.7[a]		$4b_2$	10.5			11.5	
	$8a_1$	11.3			11.6		$8a_1$	11.3			13.3	
p	$1a_2$	13.1		$(1a_2')$	14.1		$1a_2$	13.1			14.1	
	$3b_2$	14.5					$3b_2$	14.5			(15.2)	
	$7a_1$	15.7					$1b_1$	(16.0)			(16.0)	
	$1b_1$	(16.0)										
							$7a_1$	15.7	[23]			
	$6a_1$	17.4	[23]				$6a_1$	17.4				
s	$2b_2$	19.7					$2b_2$	19.7				
	$5a_1$	22.2					$5a_1$	22.2				
	$4a_1$	-					$4a_1$	-				

		C_6H_{12}	(C_{2v})		C_6H_{10}	(C_2)		C_6H_8	(C_s)		C_6H_8	(C_s)
												
π				10b	*8.96*	[18]	4a"	*8.40*	[44]	4a"	*8.45*	[44]
							3a"	*10.60*		3a"	*10.36*	
				9b	11.1	[22]	18a'	11.7		18a'	11.8	
				13a	11.4		17a'	12.2		17a'	12.2	
p				8b	11.9		16a'	12.8		16a'	12.6	
				12a	(12.2)		15a'	13.4		15a'	13.4	
				11a	(12.6)		2a"	13.4		2a"	13.4	
				7b	13.4		14a'	13.9		14a'	13.9	
				6b	14.1		1a"	14.9		1a'	14.7	
				10a	(14.5)		13a"	15.9		13a'	15.9	
				9a	15.8							
				5b	(15.8)							
s	$8a_1$	18.3	[*]	8a	17.1		12a'	16.9		12a'	16.6	
	$4b_2$	18.3		4b	18.8		11a'	17.7		11a'	17.8	
	$7a_1$	20.9		7a	20.5							
	$3b_2$	22.3		3b	22.7							
	$6a_1$	23.2		6a	-							
	$5a_1$	-		5a	-							

		C_6H_6	(C_{2v})
			
	$1a_2$	*8.36*	[43]
π	$2b_1$	*9.54*	
	$1b_1$	12.8	
p	$7b_2$	12.1	
	$9a_1$	(12.8)	
	$6b_2$	13.6	
	$8a_1$	(13.6)	

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[a] Band maxima of *Jahn-Teller* distorted $^2E'$-band.

Experimental Part

The photoelectron spectra have been recorded with two *Turner*-type spectrometers [15] fitted with $\pi/\sqrt{2}$ cylindrical condenser analysers of 10 cm and 5 cm radius respectively. The He(IIα) photon source was a modified version of the one described previously [16]. The modifications included tubular, water-cooled anodes and more efficient boron-nitride insulators to reduce considerably the usual sputtering. These changes allowed a continuous daily operation of the source with a 160 mA discharge current for several months in between each cleaning.

Most of the He(IIα) excited spectra of the smaller hydrocarbons were accumulated on-line with a PDP-9 computer, interfaced to act as a multichannel analyser with a display being provided by a Tektronix screen. The electron kinetic energy was repetively scanned with a frequency of $1\ \mathrm{s}^{-1}$ by applying to the analyser plates a symmetrical saw-tooth ramp voltage, generated by a $10^4\ \mathrm{s}^{-1}$ quartz clock driven D/A converter. The latter unit also provided synchronization with the computer by means of a start pulse to each cycle and pulses of 2000 or $5000\ \mathrm{s}^{-1}$ during the cycle to advance the pointer of the channel register in the memory of the computer. The number of channels and the voltage scan range were preselected, depending on the type of information required.

The samples were introduced into the instrument from a balloon reservoir and the spectra were recorded, at most, up to 24 h at one time. The ionization energies were calibrated relative to the peaks

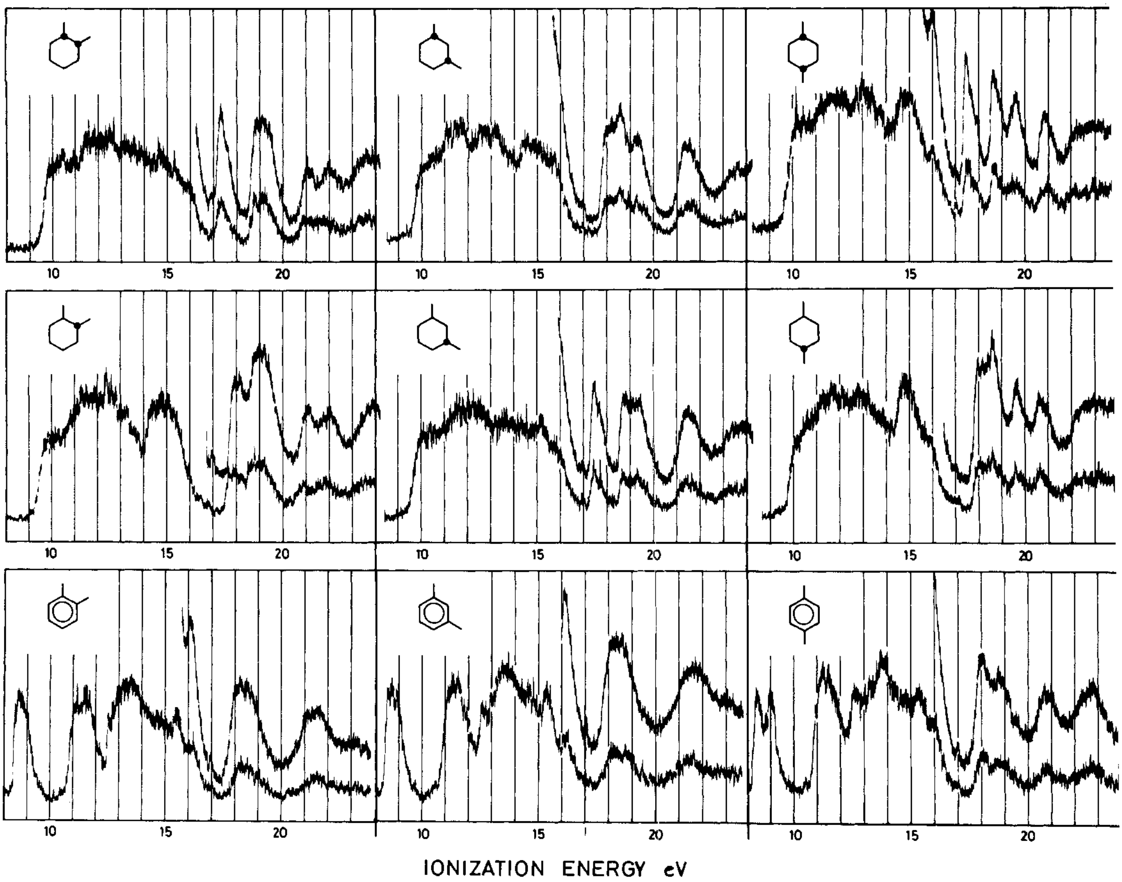

Fig. 4. *He(IIα) photoelectron spectra of* cis- *and* trans-*1,2-dimethylcyclohexane,* cis- *and* trans-*1,3-dimethylcyclohexane,* cis- *and* trans-*1,4-dimethylcyclohexane and of* o-, m-, *and* p-*xylene*

at 24.58 eV and 17.02 eV, which are due to the ionization of helium by the He(II*α*) (40.80 eV) and the He(II*β*) (48.37 eV) radiation. When it was felt desirable to eliminate these peaks, a thin (~200 nm) polystyrene film was used to physically isolate the lamp from the ionization chamber. Thin carbon (~40 nm) and aluminium (~100 nm) films supported on a fine mesh were also tried; however the polystyrene films which were used originally by *Potts, Williams & Price* [6] were found to be the most satisfactory and convenient. A transmission of ~30 to 50 percent for He(II*α*) radiation could usually

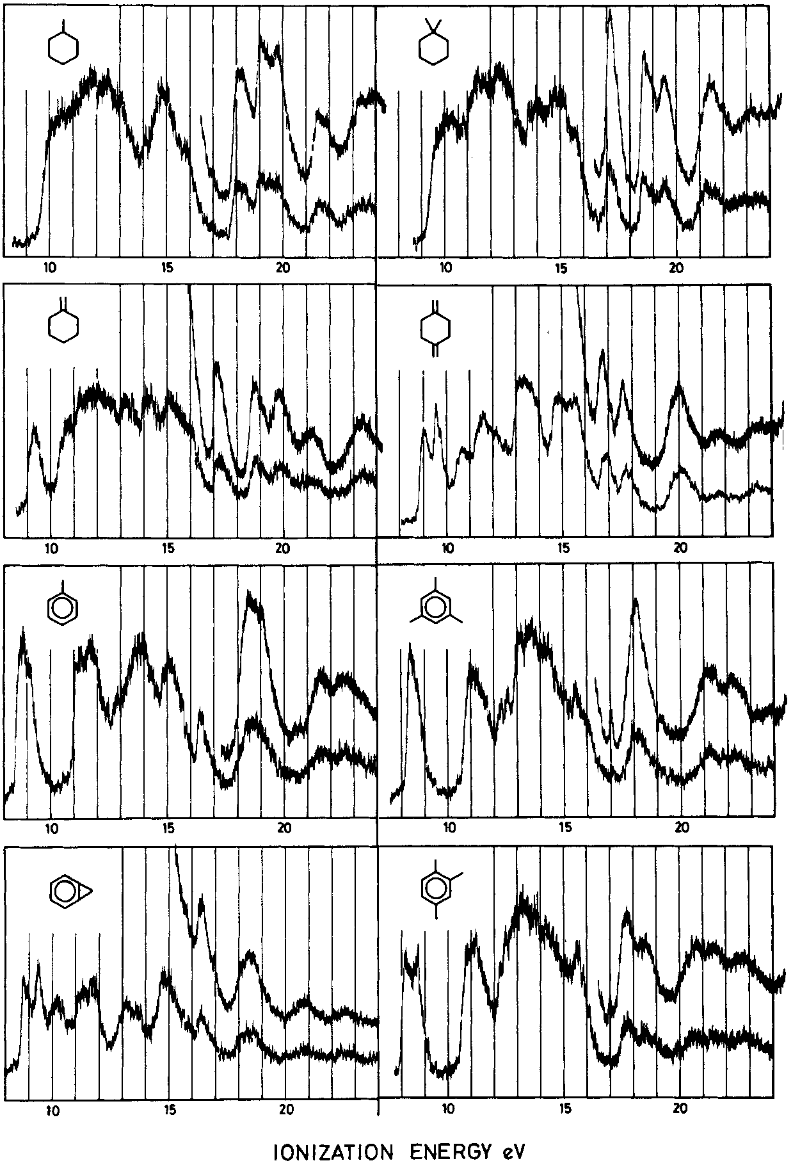

Fig. 5. *He(IIa) photoelectron spectra of methylcyclohexane, 1,1-dimethylcyclohexane, 1-methylidenecyclohexane, 1,4-dimethylidenecyclohexane, toluene, 1,3,5-trimethylbenzene, cyclopropenobenzene and 1,2,4-trimethylbenzene*

be achieved and the helium peaks were then absent. The films were prepared by letting a solution of polystyrene pellets in ethyl-benzoate evaporate from the surface of distilled water and by picking up the film neat on an insert. The latter fitted just below the entrance slit of the analyser, cut in the withdrawable target chamber which passed through a vacuum lock. This arrangement enabled films to be changed within minutes without disrupting the main chamber vacuum. Such films were found to remain intact for many hours. The use of polystyrene films allowed ionization energies to be determined up to 19.6 eV above the first one, because the He(Iβ, γ,....) lines converging to the ionization limit of helium at 24.58 eV, were sufficiently attenuated. In the absence of a thin film, the He(IIα) excited spectra were undisturbed by the He(Iα, β, γ....) lines up to 16.2 eV above the first adiabatic ionization energy (*cf. Fig. 1* to *3*).

A considerable handicap, which arises in the detection of the bands associated with the removal of an electron from the deep lying valence orbitals, is that these bands are broad, typically 2 eV, and very weak due to the unfavourable photoionization cross-section with the He(IIα) photons. The situation is further complicated by the occurrence of similarly weak bands in this ionization energy region arising by simultaneous electron excitation accompanying the photoionization process (shake-up bands). Consequently the deepest valence ionization energies are only given for the smaller hydrocarbons. In some cases these ionization energies have also been obtained by X-ray excitation, and in such photoelectron spectra shake-up bands are often apparent.

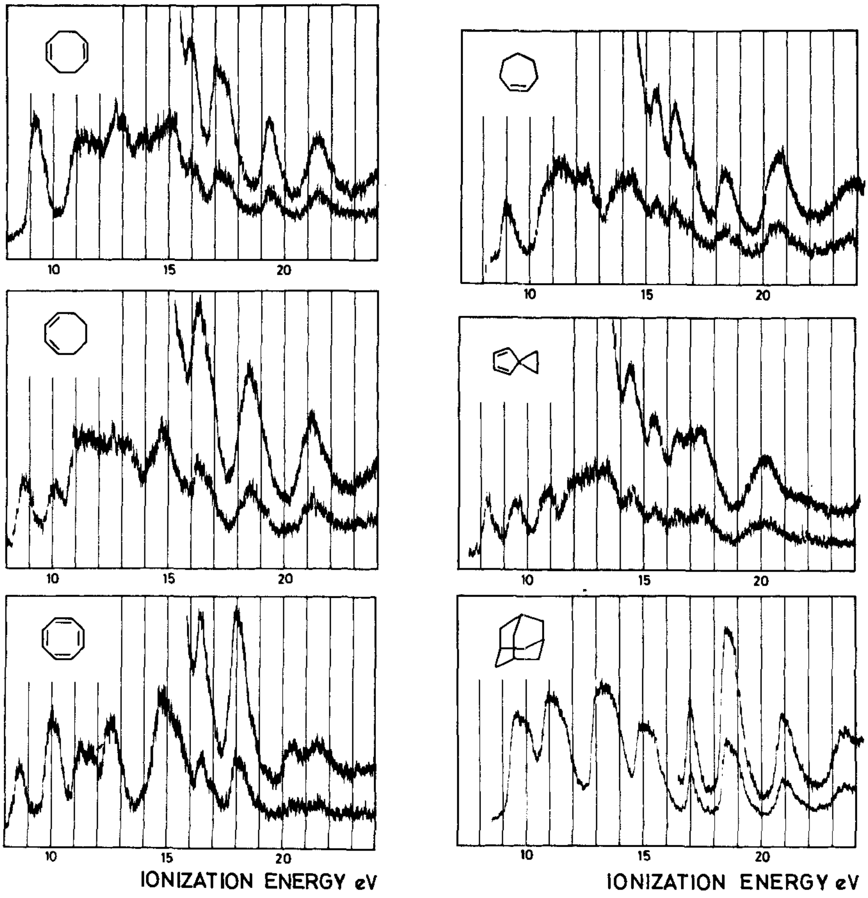

Fig. 6. *He(IIα) photoelectron spectra of 1,5-cyclooctadiene, 1,3-cyclooctadiene, cyclooctatetraene, cycloheptene, spiro-[2.4]hepta-4,6-diene* (= homofulvene) *and adamantane*

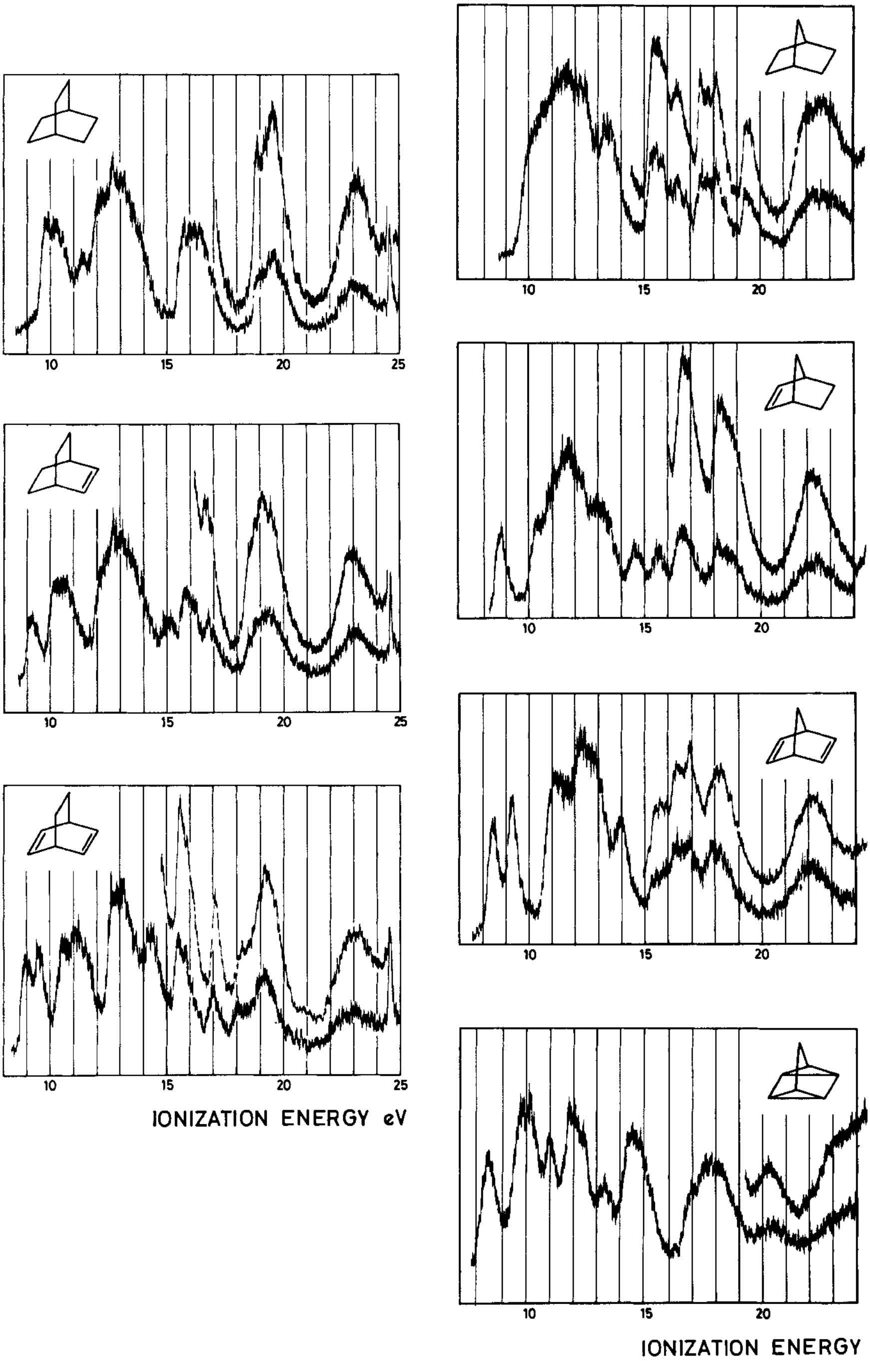

Fig. 7. *He(IIa) photoelectron spectra of bicyclo[2.2.1]-heptane* (= norbornane), *bicyclo[2.2.1]heptene* (= norbornene), *bicyclo[2.2.1]heptadiene* (= norbornadiene), *bicyclo[2.2.2]-octane, bicyclo[2.2.2]octene, bicyclo[2.2.2]octadiene and of tetracyclo*$[2.2.1.0^{2,6}0^{3,5}]$*heptane* (= quadricyclane)

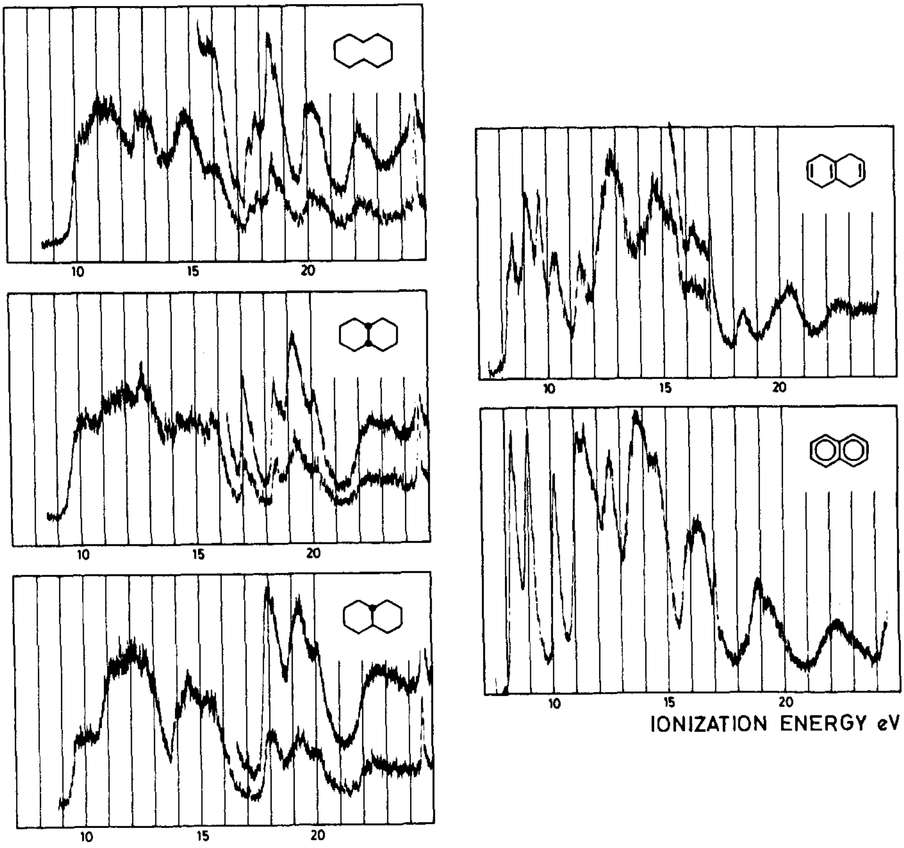

Fig. 8. *He(IIα) photoelectron spectra of cyclodecane,* cis- *and* trans*-decalin, 1,4,5,8-tetrahydronaphthalene and of naphthalene*

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