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Optical Absorption of Benzene Vapour for Photon Energies from 6 eV to 35 eV

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Optical Absorption of Benzene Vapour for Photon Energies from 6 eV to 35 eV[+]

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The optical absorption of benzene vapour has been measured with the spectral continuous synchrotron radiation from the electron accelerator DESY within the photon energy range of 6 to 35 eV, where excitations of all but the C 1s-electrons are expected to occur. Besides the well known strong $\pi-\pi^*$ *transitions* $^1B_{1u}, {}^1E_{1u} \leftarrow {}^1A_{1g}$ *between 6 and 7 eV the observed structures superimposed on a broad continuum with its maximum at about 18 eV are discussed in terms of Rydberg transitions. The problem of an unequivocal assignment is pointed out.*

[+] Supported by the Deutsches Elektronen-Synchrotron DESY

The investigation of the electronic structure of the benzene molecule is of considerable interest for theoretical chemistry and, in particular, for the understanding of aromatic hydrocarbon molecules. The electronic structure of benzene has been discussed in detail by Jonsson and Lindholm[1]. Taking into account data on photoelectron spectroscopy, mass-spectroscopy, optical absorption, electron impact spectra, theoretical calculations and bonding properties of the different orbitals, they arrived at a special ordering of the 10 filled electron orbitals above the carbon 1s-shell. Quite a few conclusions were derived from the electron impact energy loss spectrum measured by Lassettre, Skerbele, Dillon and Ross[2] covering the energy range from 5 to 17 eV. This procedure is correct, provided the Born approximation for the inelastic electron scattering holds, since in this case electron loss spectra should give the same information as optical absorption. The relatively sharp structures of the electron impact spectra[2] were interpreted as Rydberg series.

More detailed information on the whole energy range, where excitations of all but the C 1s-electrons are expected to occur, may be derived from optical absorption measurements using a continuous light source and an improved resolution. Here we give measurements of the optical absorption of benzene vapour in the VUV-region for photon energies from 6 to 35 eV. The synchrotron radiation of the 7.5 GeV electron synchrotron DESY[3] imposed no restrictions on spectral continuity. The apparatus and experimental techniques have already been described[4]. Additionally, we used a 600 lines/mm grating blazed at 1200 Å and a closed absorption cell with a LiF-window for measurements up to 11.5 eV. The wavelength resolution was somewhat better than 1 Å and 4 Å depending on the grating used. This corresponds to 0.01 eV and 0.03 eV at 10 eV respectively. The absolute photon energies given by our results are correct within ±0.015 eV.

The absorption spectrum (Fig. 1) shows a broad and continuum like absorption starting above the strong $^1E_{1u} \leftarrow {}^1A_{1g}$ excitation at 6.9 eV with a maximum at about 17.8 eV, followed by a smooth decrease of the absorption cross section at higher energies, similar to the absorption spectra of the n-alkanes[4]. With the exception of additional details displayed here, the main features of the absorption spectrum are in good agreement with absolute cross section values as given in Ref. [5,6,7].

Figure 2 gives the region between 6 and 15 eV on an expanded scale. The spectral range up to 9.2 eV has been extensively discussed[8]. As regards the electronic structure, the very intense absorption at around 6.9 eV as well as the preceding absorption band with some diffuse vibrational structure starting at about 6.0 eV have been generally ascribed to $\pi-\pi^*$ transitions. The main peak is ascribed to an $^1E_{1u} \leftarrow {}^1A_{1g}$ transition and the preceding band to a $^1B_{1u} \leftarrow {}^1A_{1g}$ transition. In the energy range between 6.9 and 9.3 eV the main structures of the absorption, as measured with a higher resolution by Wilkinson[10] are reproduced. The Rydberg series R and R', as named by Wilkinson converging at the first ionization limit at 9.247 eV, are marked.

Indications for the group of bands in the range from 9.16 to 9.80 eV and from 10.40 to about 10.80 eV come from photographic plates taken by Price and Walsh[11]. The additional structure, as seen by Goto[12], between 9.6 and 10.40 eV is not confirmed by our spectra. The four bands starting at 10.40 eV as well as the general increase of the absorption with a maximum at about 11.0 eV shows up as autoionization structures in the mass spectroscopic study of photoionization by Dibeler and Reese[13] and by Brehm[14].

For a discussion of the absorption structures above the two π-π^* excitations as being due to Rydberg series converging at different ionization potentials we refer to Table 1. Column one contains information on the different ionization potentials as won by the convergence of Rydberg series[10,15] and by photoelectron spectroscopy[16–19]. Since the photoelectron spectra of Turner[18] show the best resolution the ionization potentials derived from them have been used throughout this work. Column two contains the assignment of these ionization potentials to the different orbitals, characterized by their group theoretical notation as given in Ref.[1] and[17]. The bonding properties of the orbitals have been taken from[1], won by symmetry considerations, e.g. the correlation diagram given by Herzberg[9] and the coefficients of the atomic functions in LCAO-calculations (e.g. Ref.[20]). The fourth column in Table 1 gives the symmetry allowed transitions from these orbitals to Rydberg levels of s, p and d-symmetry in the united atom limit. In addition to the quantum numbers ns, np and nd the symmetry of the particular Rydberg orbital in the group D_{6h} of the benzene molecule is indicated. The polarization direction as well as the character of the Rydberg levels with respect to the reflection σ_h at the molecular plane are also given in the column. We expect the transition probability and the quantum defect δ to decrease going from s to p and d[21]. As negative characters $\chi(\sigma_h)$ are equivalent to a nodal plane of the Rydberg orbital in the molecular plane, we expect these transitions to be much less prominent than transitions with $\chi(\sigma_h) > 0$ [1].

The break-up of the molecular ion only starts for photon energies above 13.8 eV[13,14]. It is, therefore, most probable that the allowed Rydberg states bound to ions below this energy are well defined states and should show up in the absorption spectra.

The last column indicates those photoelectron peaks for which vibrational structure has been observed[18,19]. The vibrational structure as measured by Turner[18] is given by the inserted parts of Fig. 2. We expect the corresponding vibrational structure for the Rydberg series converging at these particular ionization potentials. Our discussion will confirm this correspondence.

As regards the first ionization potential it should be noted that the peaks at 6.89 and 6.98 eV (the whole absorption structure in this energy range corresponds very nicely to the photodensiometric spectra taken by Wilkinson[20]) do not have a counterpart in Turner's photoelectron spectrum[18]. This corroborates the interpretation given for these peaks in[10] as being due to the underlying $\pi-\pi^{*}$ excitation. There is, as yet, no definit group theoretical assignment for Wilkinson's R and R' series[22,23], but there seems to be general agreement that the ionization potential at 9.25 eV is due to the removal of electrons from the $\pi-1e_{1g}$-orbital.

The good correspondence of the vibrational structure between the photoelectron spectrum for the second ionization potential at 11.49 eV and the groups of bands starting at 9.16 eV in the absorption spectrum confirms the assignment of this absorption structure as a first member of a Rydberg series converging at 11.45 eV. The second and third members of this series would then be the group of bands as indicated in Fig. 2 which approximately fit into a Rydberg formula with quantum defect $\delta = 0.47$. This series has been assigned in[1] to the npe_{1u} series converging at $3e_{2g}$. We note, however, that the vibrational structure of the second member is different from that of the first.

We assign the absorption structure in the range of 11.0 eV up to 13 eV, as in[1], to three Rydberg series as shown in Fig. 2, namely: $3e_{1u}^{4} \rightarrow nsa_{1g}$ ($\delta \approx 0.77$)

and $3e_{1u}^{4} \rightarrow nda_{1g}$, nde_{2g} ($\delta \approx 0.12$) (compare Table 1). In this way the steep increase of absorption near 11 eV is explained by the first member of a s-type Rydberg series. A s-series of similar strength should be expected to converge at the π-$1a_{2u}$ ionization limit (see Table 1).

It is still an open question as to how to assign the σ-$3e_{2g}$ and π-$1a_{2u}$ orbitals to the second (11.49) and third ionization potential (12.0 - 12.3 eV)[24]. In both cases a problem arises, which has not been discussed, when the electron energy loss spectra[2] have been interpreted[1,23]: if the ordering as given in Table 1 and the above assignment of the Rydberg series starting at 9.16 eV is correct, we see no clear indication for the expected s-type series leading to $1a_{2u}$ which we have indicated together with the possible d-type series by dashed lines in Fig. 2. Alternatively, if the order of the orbitals is reversed the observed series has to be assigned to an $1a_{2u} \rightarrow nsa_{1g}$ series. An argument for the second ionization potential being π-$1a_{2u}$ comes from photoelectron work of W.C. Price and D.G. Streets[13] on benzene and its fluorine derivatives. In this case, however, there is no clear indication for the expected $3e_{2g} \rightarrow npe_{1u}$ series.

We attribute the structure near 14.6 eV to the transition $3a_{1g} \rightarrow 3pe_{1u}$ with the same quantum defect $\delta \approx 0.47$ as for $3e_{2g} \rightarrow npe_{1u}$. However, we are not able to confirm without doubt the vibrational structure reported in Ref.[15] and seen with the same spacing in the corresponding photoelectron peak. This is due to our experimental conditions: since the absorption is very high vapour pressure in the windowless absorption cell must be kept very low. Because of the photoelectric registration used a possible vibrational structure is, in this case, difficult to distinguish from noise arising from pressure fluctuations.

As Table 1 shows Rydberg series are possible to occur at higher energies. Since for these energies processes like ionization, dissociation and predicssociation as well as possible N - V transitions of the σ-electrons most probably contribute more strongly than at lower energies to the total absorption cross section, it seems impossible to interpret the broad continuum like structures in our spectra at 16.00 and 17.80 eV unequivocally.

Acknowledgment

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Table 1 Electronic properties of benzene

Figure Captions

Fig. 1 Absorption spectrum of benzene vapour from 6 to 35 eV.

Fig. 2 Absorption spectrum of benzene vapour from 6 to 15 eV. Ionization potentials and inserts are taken from photoelectron spectra from Turner (Ref.[18]). Indicated Rydberg series have been calculated using the given quantum defects.

IONIZATION ENERGY (eV)					ORBITAL	BONDING PROPERTIES	GROUPTHEORETICALLY ALLOWED RYDBERG SERIES									VIBRATIONAL STRUCTURE OBSERVED IN PHOTOELECTRON SPECTRA (e)
							s			p			d			
(a)	(b)	(c)	(d)	(e)	(d)(f)	(f)(g)	SYMME-TRY	POL	$\chi(\sigma_h)$	SYMME-TRY	POL	$\chi(\sigma_h)$	SYMME-TRY	POL	$\chi(\sigma_h)$	
9.247	9.248	9.248	9.3	9.247	$1e_{1g}^4$	weakly CC-bonding π-type				npe_{1u} npa_{2u}	⊥ ∥	+2 -1				yes
	11.489	11.5	11.45	11.49	$3e_{2g}^4$	weakly CC-bonding weakly CH-bonding tr-type				npe_{1u}	∥	+2				yes
			12.15	12.0-12.3	$1a_{2u}^2$	strongly CC-bonding π-type	nsa_{1g}	⊥	+1				nda_{1g} nde_{1g}	⊥ ∥	+1 -2	no
		13.9	13.85	13.8	$3e_{1u}^4$	strongly CH-bonding CC-non-bonding r-type	nsa_{1g}	∥	+1				nda_{1g} nde_{2g} nde_{1g}	∥ ∥ ⊥	+1 +2 -2	no
			14.65	14.5-14.7	$1b_{2u}^2$	strongly CC-bonding CH-non-bonding t-type							nde_{2g}	∥	+2	no
		15.5	15.40	15.2-15.4	$2b_{1u}^2$	CC-anti-bonding strongly CH-bonding s-type							nde_{2g}	∥	+2	no
16.84			16.85	16.84	$3a_{1g}^2$	weakly CC-bonding strongly CH-bonding r-type				npe_{1u} npa_{2u}	∥ ⊥	+2 -1				yes
			18.6-19.2	18.7-19.2	$2e_{2g}^4$	weakly CH-bonding weakly CC-anti-bonding s-type				like for orbital $3e_{2g}$						no
			22.0-22.8		$2e_{1u}^4$	CC-bonding s-type				like for orbital $3e_{1u}$						no
			28.7		$2a_{1g}^2$	CC-bonding s-type				like for orbital $3a_{1g}$						no

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Table 1

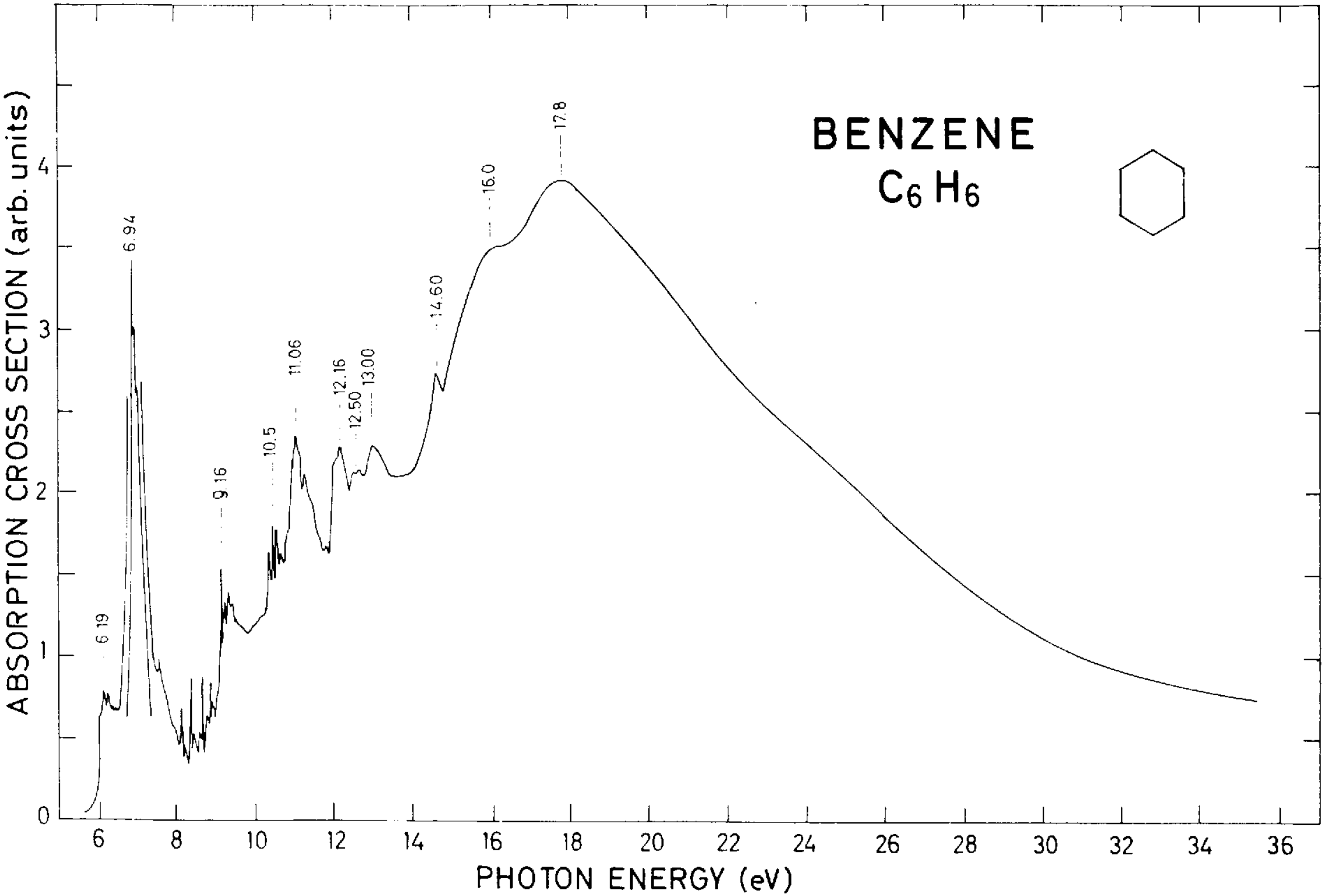
BENZENE
C_6H_6
ABSORPTION CROSS SECTION (arb. units)
PHOTON ENERGY (eV)
0
1
2
3
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
6.19
6.94
9.16
10.5
11.06
12.16
12.50
13.00
14.60
16.0
17.8

Fig.1

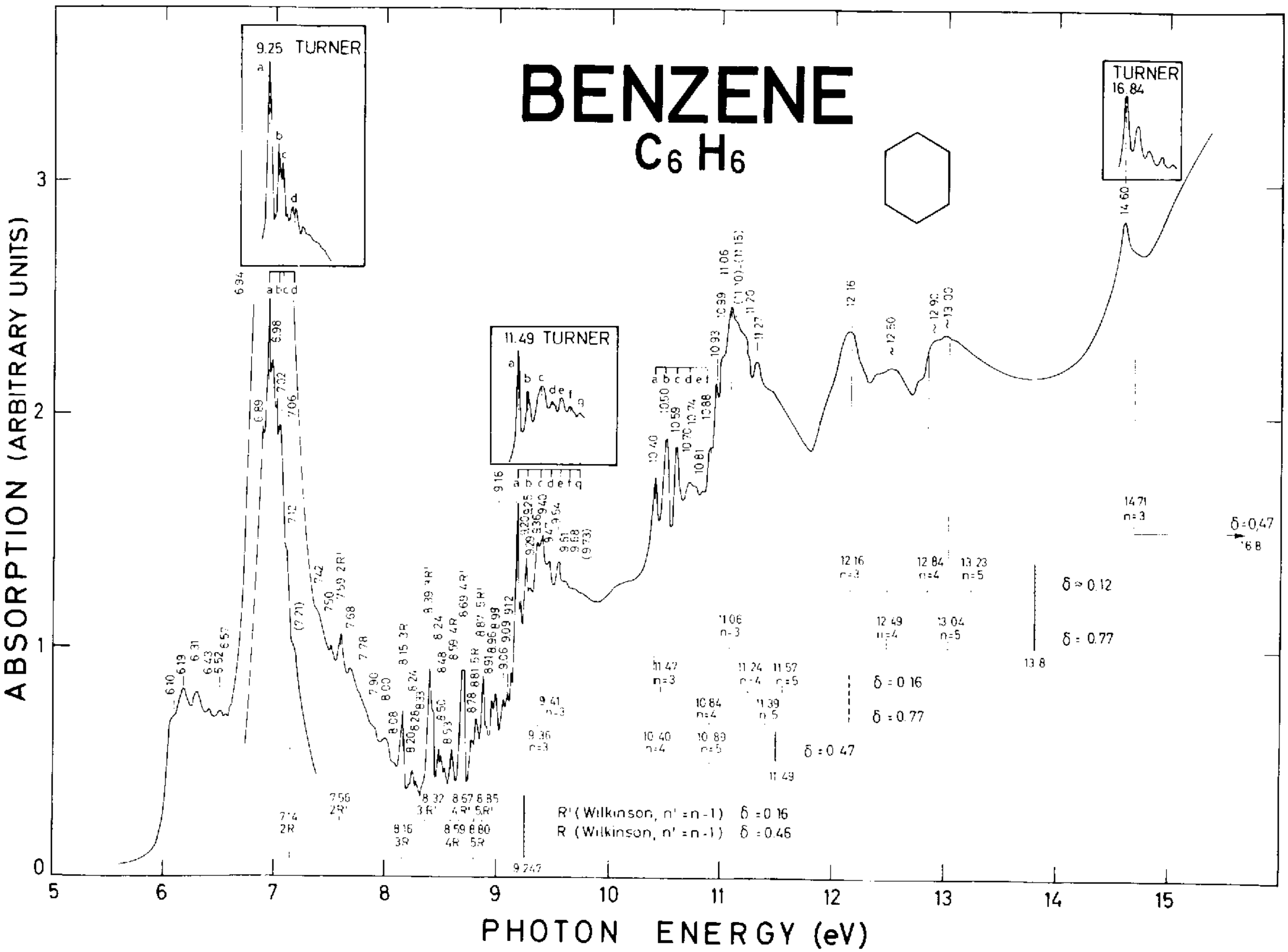
BENZENE
C_6H_6
9.25 TURNER
11.49 TURNER
TURNER 16.84
R' (Wilkinson, n' = n - 1) δ = 0.16
R (Wilkinson, n' = n - 1) δ = 0.46
δ = 0.47
δ = 0.16
δ = 0.77
δ ≈ 0.12
δ = 0.77
δ = 0.47
ABSORPTION (ARBITRARY UNITS)
PHOTON ENERGY (eV)
0
1
2
3
5
6
7
8
9
10
11
12
13
14
15

Fig. 2