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TERM-VALUES AND VALENCE-RYDBERG MIXING IN CORE-EXCITED STATES: SiH_4 and PH_3

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Term-Values and Valence-Rydberg Mixing in Core-Excited States:

SiH_4 and PH_3

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Abstract

The controversial interpretations of the XUV spectra of PH_3 and Si H_4 have been examined experimentally and theoretically. An assignment consistent with measured 2p-absorption spectra of gaseous and solid Si H_4 and PH_3, and with CI calculations on core-excited states of Si H_4 is presented. The predictions of the Equivalent Ionic Core Virtual Orbital Model are confirmed. Term-values for core-excited states differ systematically from those for valence-excited states.

1. Introduction

The 2p core excitation spectra of the second row hydrides reported by Hayes and Brown [1] have raised some controversy in the literature. Three different assignments, summarized in Table 1, have been proposed for the broad bands and the adjoining sharp lines detected at the 2p threshold. Hayes and Brown [1] interpreted their spectra on the basis of a single center SCF calculation on Si H_4 by Deutsch and Kunz [2]. The assignment of Schwarz [3] is based on the Equivalent Ionic Core Virtual Orbital Model and LCAO-SCF calculations on all four hydride molecules and argon. Robin's assignment [4] results from a comparison with data on valence shell excitations.

The three assignments of the broad bands differ in three respects (Table 1):

1) Hayes and Brown [1] assume that all excited orbitals are of Rydberg character. According to Robin [4] the lowest empty orbital is of mixed valence-Rydberg type (σ^*-4s). Contrary to both, the SCF calculations of Schwarz [3] attribute predominant valence character to both the lowest empty orbitals and mixed character only to the lowest one in Si H_4.

2) Whereas Hayes and Brown and also Schwarz assign the high energy part of the broad bands to asymmetric final orbitals, Robin attributes it to a totally symmetric orbital (4s).

3) Hayes and Brown, and Robin assign a larger number of excitations to the broad band.

As a consequence of these discrepancies, the three interpretations also disagree in the higher energy range of the sharp lines. Robin assigns the first sharp strong line to 2p→4p transitions, although such transitions should be nearly forbidden especially in the case of the highly symmetric Si H_4 molecule. The assignments by Hayes and Brown and Schwarz question the validity of the "constancy of term values"+) on which Robin's interpretation is based. The assignment of Schwarz corresponds to rather unusual Rydberg quantum defects.

To clarify the situation the 2p spectra of solid PH_3 and Si H_4 have been measured. The absorption of molecules in the condensed phase forms an "operational yard stick" to judge the valence-Rydberg mixing [5]. Furthermore extensive CI calculations have been performed for the ground and seven core excited states of Si H_4.

+) Term value of final orbital = ionisation potential of initial orbital minus excitation energy. Constancy of term values: the final orbital term value does not vary with excitation from different initial orbitals.

2. Experimental Results

The 7.5 GeV electron synchrotron DESY served as a light source. The experimental setup has been described elsewhere [6]. Solid PH_3 and $Si\,H_4$ were prepared by condensation onto thin carbon films cooled to ~ 50 K. The absorption spectra of gaseous and solid $Si\,H_4$ and PH_3 are shown in Figs. 1-3.

Our gas phase spectra agree with those of Hayes and Brown [1]. However, the high energy shoulder of our broad band in the 2p region of $Si\,H_4$ at 103.8 eV (Fig. 2) is more pronounced. Due to our somewhat lower resolution not all details of the fine structure above 104.5 eV for $Si\,H_4$ and above 134 eV for PH_3 as reported by Hayes and Brown could be resolved. Therefore the gas phase fine structures of Hayes and Brown have been substituted in Figs. 2 and 3. The maxima at the Si 2s threshold (153.6 eV and 155.8 eV) have been observed for the first time (Fig. 1).

In the spectra of the solids the sharp 2p→Rydberg lines are completely smeared out (Figs. 2 and 3). There are only a broad hump at 105.3 eV for solid $Si\,H_4$ and a weak shoulder at 135 eV for solid PH_3. In contrast to this the broad bands at the 2p threshold are rather similar. Solidification mainly results in a broadening, especially for $Si\,H_4$. For PH_3 the third maximum shifts towards higher energies by 0.3 eV and two weak shoulders emerge at 133.2 and 134.2 eV.

3. CI-Calculations

3.1 The AO basis

For Si the (12s6p)/[6s4p] gaussian basis of Veillard [7] was used. In order to allow for the reorganization of the valence shell upon core excitation the 3s and 3p AO's were taken from P. This basis was augmented by one set of polarisation d-functions ($\zeta = 0.35$) [8] and also by two diffuse s ($\zeta = 0.035, 0.012$), one p ($\zeta = 0.015$) and one d-set ($\zeta = 0.015$) [9]. For H a (5s1p)/[2s1p] basis was chosen with the s-orbitals from Whitten [10] and $\zeta p = 0.74$. This amounts to a total of 55 AO's and yields a ground state SCF energy for $Si\,H_4$ (T_d symmetry, R(Si H) = $2.801 a_0$) of −291.2341 au (best literature value −291.2355 [11]).

3.2 CI-calculations

The calculations were performed with the MRD-CI package of Buenker, Peyerimhoff and Butscher [12]. We are interested in one-electron excitations from Si 2p t_2 to a_1, e and t_2 MO's, which give rise to the following symmetry species under T_d symmetry:

$$t_2 \rightarrow a_1 \; : \; {}^{1,3}T_2$$
$$t_2 \rightarrow e \; : \; {}^{1,3}T_2, \; {}^{1,3}T_1$$
$$t_2 \rightarrow t_2 \; : \; {}^{1,3}T_2, \; {}^{1,3}T_1, \; {}^{1,3}E, \; {}^{1,3}A_1$$

Only ${}^1T_2$ is optically accessible from the ${}^1A_1$ ground state. Our program system only takes account of abelian symmetry groups. The largest abelian subgroup of T_d is C_{2v}. Because of the following correlation of irreducible representations

$$\begin{array}{lllll} T_d \rightarrow C_{2v}: & A_1 \rightarrow A_1 & & & \\ & E \rightarrow A_1 & + A_2 & & \\ & T_1 \rightarrow A_1 & & + B_1 & + B_2 \\ & T_2 \rightarrow & A_2 & + B_1 & + B_2 \end{array}$$

the optically accessible states are no longer distinguished by symmetry under C_{2v}. Furthermore they are energetically nearly degenerate with all the other states of the same one-electron-excitation type. Therefore one has to bestow care on generating configurations with the correct transformation properties.

The calculations were performed in the following way: In a first calculation ground state SCF symmetry MO's were used. Up to ten reference configurations were chosen in an unbiased manner including both diffuse and nondiffuse states. From the corresponding CI wave function symmetry NO's were generated and used in the final calculation. Because of the strong reorganisation the latter orbitals differ appreciably from the ground state orbitals. According to test calculations the Si 1s and 2s orbitals could be kept fully occupied. The CI-dimensions ranged from 4000 to 6000. The problem of extracting the root corresponding to a special highly excited state from a large CI-matrix was solved with the diagonalisation routine of Butscher and Kammer [13].

3.3 Results

The ground state CI energy was -291.416 au covering 5 eV of correlation energy. In order to compare the calculated excitation energies with experiment, two points have to be taken into account.

First all calculated excitation energies will be shifted by a constant amount because of 2 reasons: 1. the basis does not contain angular correlation orbitals for the core shells (the GS E_{corr} of 5 eV mainly corresponds to correlation in the valence shell); 2. the 2p level is relativistically stabilized. Second the experimental excitation energies are split due to spin-orbit interaction. Within the range of reasonable exchange interactions, the statistically weighted mean experimental energy $(2\Delta E(p3/2) + \Delta E(p1/2))/3$ should correspond to the calculated singlet-triplet mean $(\Delta E(S) + \Delta E(T))/2$. Therefore the corresponding values are given in Table 2. Furthermore the lowest core excited state has been used as energy zero in order to cancel the energy shift mentioned above. r-expectation values and oscillator strengths from the CI wave functions and the Coulomb selfinteraction integrals for the excited NO's are also presented.

4. Discussion

4.1 Valence to Rydberg Character of the Broad Band

The persistence of the broad bands of $Si\ H_4$ and PH_3 upon solidification forms strong evidence for the core to valence character of the transitions involved. Also the considerable widths, which by far exceed those of the Rydberg transitions at higher energies, indicate that the final orbitals must incorporate a large amount of antibonding valence character. This is borne out by the CI calculations on $Si\ H_4$. The excited orbitals in the main configurations of the lowest two excited states are the antibonding counterparts (σ^*) of the Si-H σ-bonding MO's. However, due to considerable 4s admixture, the magnitude of the Coulomb integral of the lowest excited orbital (σ^*-4s) lies on the borderline between valence and Rydberg MO's; also the molecular $\langle r \rangle$ - value increases by 0.8 Å upon excitation (see Table 1). The second excited state is of pure core to valence character with small increase in $\langle r \rangle$ and large Coulomb integral.

4.2 Number, Symmetry and Intensity of the Core to Valence Excitations

Only two core-excitations are calculated in the energy region of the broad band. The corresponding deconvolution into four components is given in Figs. 2 and 3; it was performed subject to the following constraints: i) spin-orbit pairs are separated by the s-o splitting of the 2p orbital (0.6 eV for $Si\ H_4$, 0.8 eV for PH_3); ii) spin-orbit pairs have the same line shapes and widths. The resulting distance between the $2p \rightarrow \sigma^*4s$ and $2p \rightarrow \sigma^*(t_2)$ excitations of 1.0 eV (see Table 2) is in good agreement with the calculated value of 1.2 eV, which corroborates the assignment of the 103.8/104.4 eV doublet to a non-totally symmetric excited orbital.

In analogy to Robin's rule [5] for UV spectra one may extract the rule from experimental XUV spectra [14] that oscillator strengths of core to Rydberg transitions ($\Delta n > 1$) are smaller than $f \approx 0.005$ per degree of degeneracy, whereas core to valence transitions ($\Delta n = 1$) are usually more intense. The f-value of the $Si\ H_4\ 2p_{1/2} \rightarrow \sigma^*4s$ excitation clearly exceeds this value, whereas the strengths of the other transitions are near to the border region. The rather low $Si\ H_4\ 2p \rightarrow \sigma^*(t_2)$ intensity is caused by the large Si 3p component in the $\sigma^*(t_2)$-orbital.

The ratio of the oscillator strengths $2p3/2 \rightarrow \sigma^*4s$ to $2p1/2 \rightarrow \sigma^*4s$ for both $Si\ H_4$ (1:2) and PH_3 (1:1) considerably deviates from the statistical ratio of 2:1. This implies that the $2p$-σ^*4s exchange integral K is comparable to the 2p-spin-orbit coupling constant λ: $K = 0.2$ eV for $Si\ H_4$ and 0.15 eV for PH_3 [15]. It again demonstrates considerable valence character of the final orbital. The calculations on $Si\ H_4$ seem to overestimate the Rydberg character slightly (f too small; $K = 0.1$ eV).

4.3 Rydberg Transitions

According to their widths, intensities and their vanishing upon solidification, the sharp absorption lines at higher energies are assigned to $2p \rightarrow$ Rydberg transitions. The lowest Rydberg excitation in $Si\ H_4$ is predicted at ~ 104.5 eV, but due to its $2p \rightarrow 4p$ character the intensity is too low to be detectable. Our CI-calculations show that the first sharp line in $Si\ H_4$ is due to the $2p3/2 \rightarrow 5s$ excitation. The near-by $2p3/2 \rightarrow 3de$ excitation has negligible intensity.

5. Conclusions

The CI calculations in conjunction with a comparison of the absorption spectra of the molecules in the gaseous and solid state confirm the assignment of Schwarz [3] which was based on the Equivalent Ionic Core Virtual Orbital Model. On the other hand, the concept of transferring Rydberg term values from the UV to the XUV region (Robin [4]), which had proven successful in several other cases [5,16], failed here. In Table 3 Robin's Rydberg term values [4], which are consistent with valence excitation energies, are compared with those of Schwarz [3]. Evidently term values useful in the discussion of core-excited states are larger than those from the UV region. This is easily understood within the independent particle-frozen orbital approximation. There the term value for singlet to singlet excitations is given by

$$T^{1}(i \rightarrow R) = - \varepsilon_R + J_{iR} - 2K_{iR}$$

(ε = HF-orbital energy; J, K = Coulomb and exchange integrals). The Coulomb interaction of a diffuse Rydberg orbital with the much smaller valence or core orbital i is nearly independent of i and may be approximated by the nuclear attraction integral $\langle R|1/r|R\rangle$ (Z+1-analogy):

$$T^{1}(i \rightarrow R) \approx (-\varepsilon_R + \langle R|1/r|R\rangle) - 2K_{iR}$$

That is, the variation of the Rydberg term values with the initial orbital i is due to the exchange interaction. K_{iR} is rather small for initial core orbitals (i=c), but not for valence orbitals (i=v). Furthermore, the term $2K_{iR}$ is absent for singlet to triplet excitations. Thus we obtain the approximate relation

$$T^{1}(v \rightarrow R) + 2\,K_{vR} = T^{3}(v \rightarrow R) \approx T^{1,3}(c \rightarrow R).$$

Term values of core excited Rydberg states resemble those of ordinary triplet Rydberg states and are larger than those of valence to Rydberg singlet states.

The same should hold for excitations into empty valence orbitals v*. Consequently the relative position of v->v* to v->R excitations may differ from the relative position of c->v* to c->R excitations, resulting in different valence-Rydberg mixings [17] for core-excited and valence-excited states. What is to be expected qualitatively in this respect, is summarized in Table 4.

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Table 1. Different assignments of the final orbitals[a)] of 2p-core electron exitations in second row hydrides

molecule	HCl			H_2S			PH_3			SiH_4		
authors[b)]	H - B	Sch	Rob	H - B	Sch	Rob	H - B	Sch	Rob	H - B	Sch	Rob
broad band	4s 3d	σ^*	σ^*-4s 4s	4s 3d	$\sigma^*(a_1)$ $\sigma^*(b_2)$	σ^*-4s σ^*-4s 4s	4s 3d	$\sigma^*(a_1)$ $\sigma^*(e)$	σ^*-4s 4s	4s $3d(t_2)$ 3d(e)	σ^*-4s $\sigma^*(t_2)$	σ^*-4s 4s
first sharp lines	5s 4d 6s	4s 4p 5s, 3d	4p 4p' 3d	5s 4d	4p, 4s 3d	4p 3d	5s 4d	4s 3d	4p 3d	5s $4d(t_2)$	5s, 3d(e) $3d(t_2)$	4p 3d

a) σ^* : empty valence orbital, originating from the 3sp-shell of the heavy atom; σ^*-4s : mixed valence - Rydberg; 3d, 4s, 4p, etc. : Rydberg orbitals

b) H - B : Hayes and Brown [1], Sch : Schwarz [3], Rob : Robin [4]

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Table 2. Si 2p core excitations in Si H_4

	experimental data				CI calculations				
	p3/2 excitation energy in eV	p1/2 spin-orbit mate	relative energy in eV a)	total oscillator strength	main configuration	relative energy in eV a)	$\langle r \rangle$ b) in Å	J c) in a.u.	oscillator strength
ground state	-	-	-102.9±0.2	-	-	-104.4	4.37	-	-
first broad band	102.7±0.2	103.4±0.2	- 0 -	0.07	$2p \to \sigma^* 4s$	- 0 -	5.09	0.17	0.03
	103.8±0.2	104.4±0.3	1.0±0.2	~0.02	$2p \to \sigma^*(t_2)$	1.19	4.51	0.37	0.02
					$2p \to 4p$	1.90			
strong sharp lines	104.9±0.1	105.5±0.1	2.2±0.1	$\sim 0.01_5$	$2p \to 5s$	2.41			0.014
					$2p \to 3d(e)$	2.48	7.28	0.09	0.0005
	105.5±0.1	106.1±0.1	2.8±0.1		$2p \to 4d(t_2)$	3.05			
ion. limit	107.1	107.7	4.4±0.2		2p	4.04			

a) with respect to the mean of the lowest 2p3/2 and 2p1/2 excitation energies

b) $\langle r \rangle$ means $\langle \Psi | \sum r_i^2 | \Psi \rangle^{1/2}$

c) J is the Coulomb selfinteraction integral of the excited MO

Table 3. Rydberg term values of SiH_4 and PH_3, typical for valence excitations (Robin [4]) and for core excitations (Schwarz [3])

	SiH_4		PH_3	
MO	Robin	Schwarz	Robin	Schwarz
4s	3.6	4.3	3.9	5.1
4p	2.35	2.5	2.25	2.8
3d	1.65	1.8	1.65	2.0

Table 4. Valence - Rydberg mixing in core and valence excited states

relative energy position of final orbitals in valence excited states	case 1 $v^* \gg R$	case 2 $v^* > R$	case 3 $v^* \approx R$	case 4 $v^* < R$
character of lowest valence excitations	unperturbed Rydberg series	slightly perturbed Rydberg series	strongly mixed valence - Rydberg pair	valence transition below Rydberg series
character of corresponding core excitations	unperturbed Rydberg series	strongly mixed valence - Rydberg pair	valence transition below slightly perturbed Rydberg series	valence transition below Rydberg series

Figure captions

Fig. 1 Absolute absorption cross section of gaseous (solid line) and relative absorption cross section of solid (dashed line) SiH_4 in the energy range from 100 eV - 170 eV.

Fig. 2 Absolute absorption cross section of gaseous (solid line) and relative absorption cross section of solid SiH_4 (dashed line). The deconvolution of the broad band at threshold is indicated (dash-dotted lines). The assignment is included.

Fig. 3 Absolute absorption cross section of gaseous (solid line) and relative absorption cross section of solid (dashed line) PH_3. The deconvolution of the broad band at threshold is indicated (dash-dottes lines). The assignment is included.

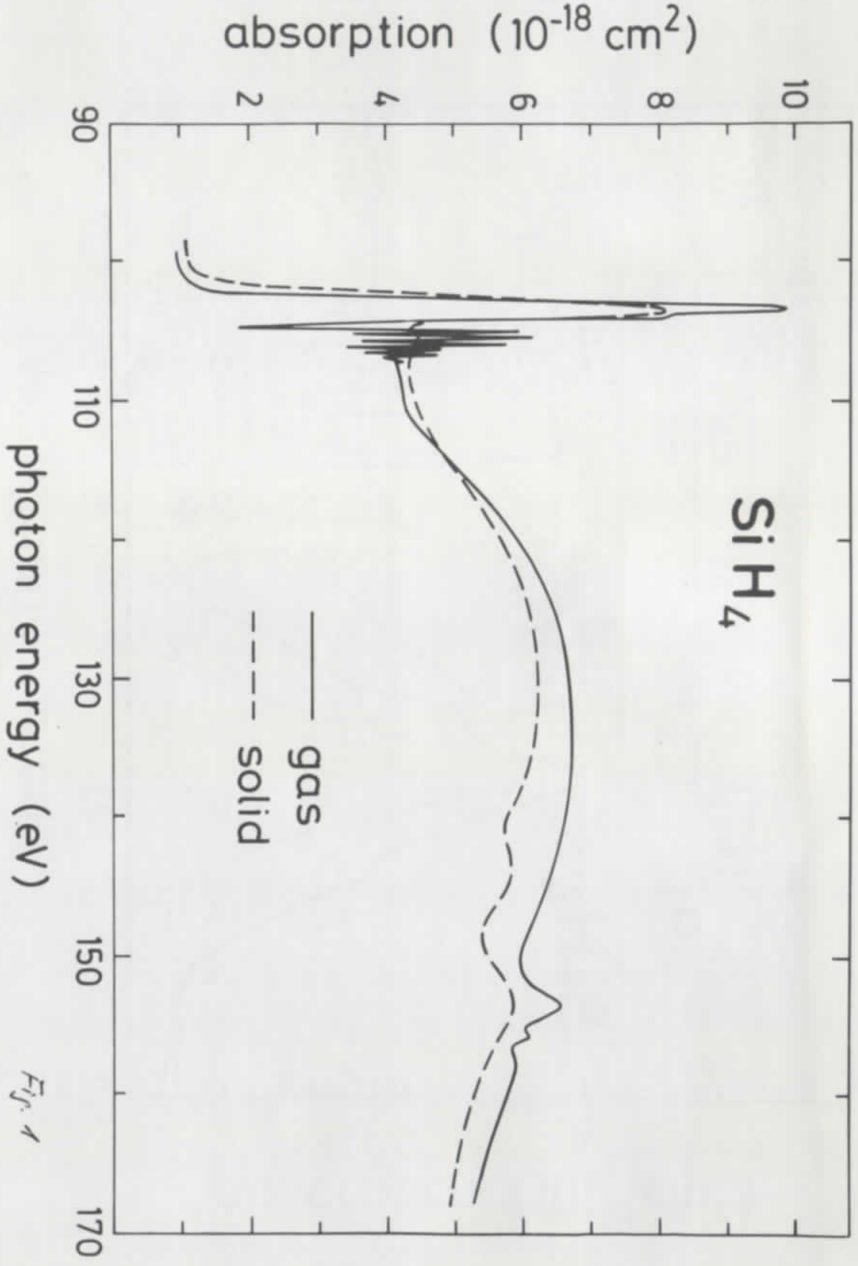

Fig. 1

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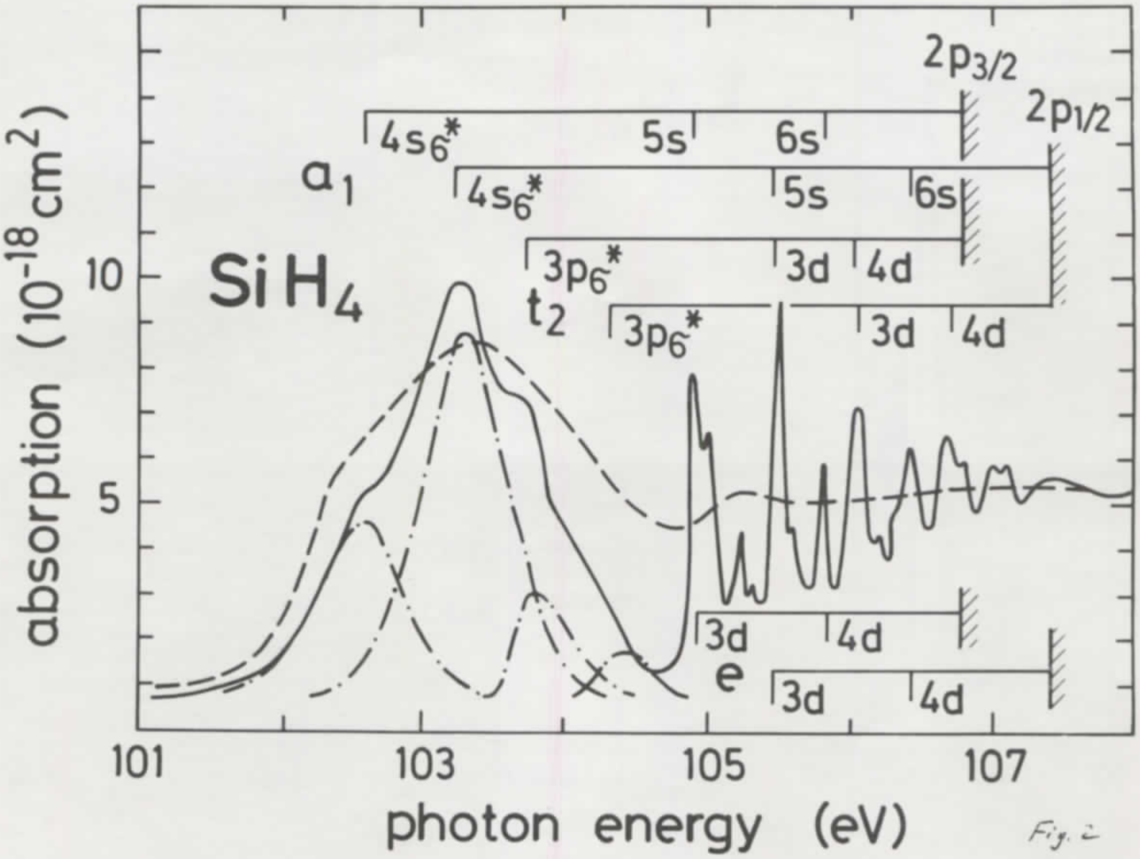

Fig. 2

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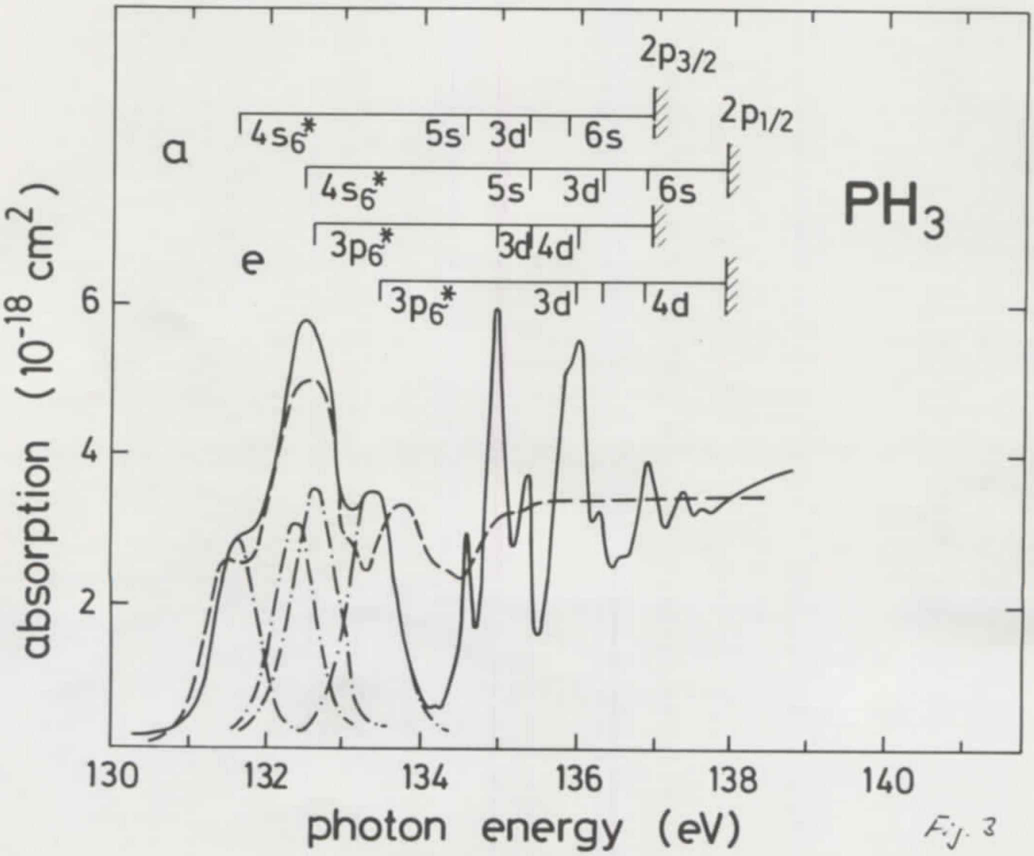

Fig. 3