TWO-PHOTON SPECTROSCOPY OF THE LOW-LYING SINGLET STATES OF NAPHTHALENE AND ACENAPHTHENE

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Two-photon excitation spectra of naphthalene and acenaphthene have been measured up to 50000 cm^{-1}. In naphthalene, three two-photon allowed states are observed for which the symmetry assignment is confirmed by polarization. The corresponding transitions are also seen in acenaphthene The experimental data are in excellent agreement with theoretical predictions

1. Introduction

In recent years it has been shown that two-photon excitation spectra (TPES) can provide valuable information on dipole forbidden transitions not observable in conventional UV absorption [1]. Of the limited number of molecules studied by this technique over a wide spectral range, naphthalene is the best investigated one. In addition to two TPES of lower resolution [2,3], one spectrum has been published with resolution comparable to that usually achieved in standard UV spectroscopy [4]. Unfortunately no polarization information has been included. All the assignments given are therefore tentative and have been questioned in later publications [5,6]. Thus even in naphthalene the assignment of the low-lying excited singlet states up to an excitation energy of ≈50000 cm^{-1} is not yet settled.

To provide as far as possible unambiguous assignments, we have reinvestigated the TPES of naphthalene including polarization measurements. The results obtained and those already known from one-photon spectroscopy are then compared to the results of theoretical calculations.

Naphthalene has a center of symmetry and therefore the principle of mutual exclusion holds for one- and two-photon allowed transitions. Small perturbations, as e.g. alkyl substituents, have little influence on the energetic position and intensity of allowed transitions in alternant hydrocarbons. The selection rules, however, may be drastically changed. Thus transitions appearing only in the one- *or* in the two-photon absorption spectrum of the unperturbed system may be detectable in both spectra in a slightly perturbed system. To realize such a double check in the case of naphthalene, we also studied acenaphthene (see fig. 1b), a system in which the molecular symmetry is reduced to C_{2v}, but a system which has a similar rigid skeleton to naphthalene itself.

The apparatus used for our measurements has been described in detail elsewhere [7,8]. Experimental conditions were the same as in our study on anthracene [9]. Naphthalene and acenapthene were measured in ethanol solution with concentrations ranging from 0.02 to 0.001 M.

2. Results and discussion

2.1. The two-photon excitation spectra

As seen from fig. 1a, the first band (I) in the two-photon excitation spectrum (TPES) of naphthalene shows pronounced vibrational structure, the most intense peak lying at 33250 cm^{-1}. The observed vibrational structure is in accord with the high-resolution work of Mikami and Ito [10] (naphthalene studied in a durene matrix). The first peak at 31700 cm^{-1} is very weak and coincides within experimental error with the

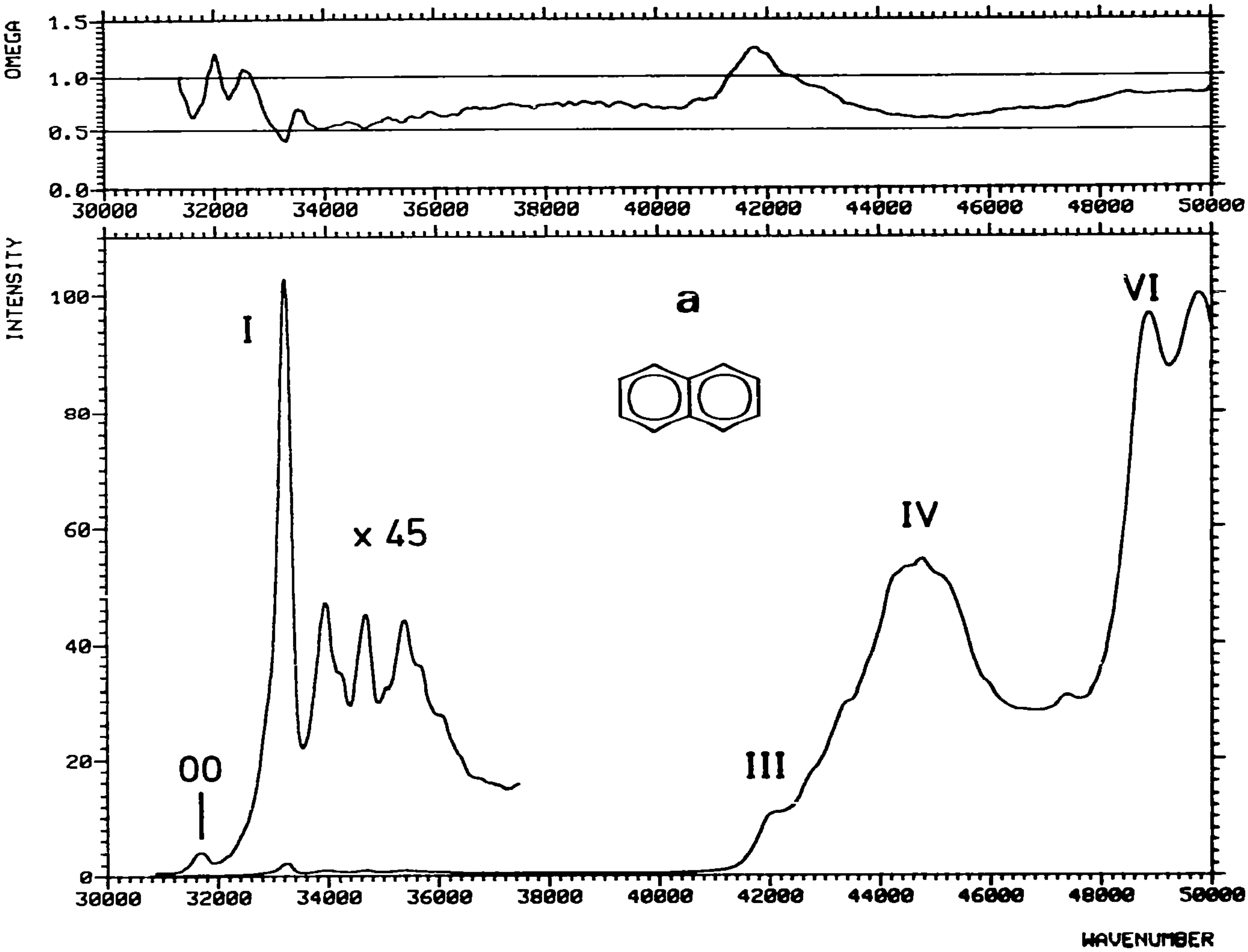

Fig 1a

0–0 transition of the $1B_{2u}$ (L_b) band of the UV spectrum. $1A_g \rightarrow 1B_{2u}$ transition is forbidden for direct two-photon absorption, it gains its intensity by vibronic coupling via b_{2u} modes, especially by a promoting mode of ≈ 1550 cm^{-1}. This is confirmed by our Ω spectrum which shows minima at the most prominent vibrational peaks indicating total A_g symmetry. The appearance of the 0–0 transition has been attributed to asymmetries in the solvent cage [4].

No significant TPA is found between 37000 and 40000 cm^{-1}. Above 41000 cm^{-1} a broad band is observed with a maximum at 44500 cm^{-1} (IV) and some additional structure (III) at the low-energy side of the maximum. The integrated intensity of this band is about two orders of magnitude higher than band I. Assuming the quantum efficiency of the fluorescence to be constant, this yields a lower limit for the ratio of the absolute two-photon cross section. The second band (III + IV) therefore most likely results from allowed two-photon transitions with final states of g symmetry.

On the basis of Pariser's π-electron calculation [11], Mikami and Ito have made a tentative assignment of the maximum IV to an A_g^- state and of the shoulder at

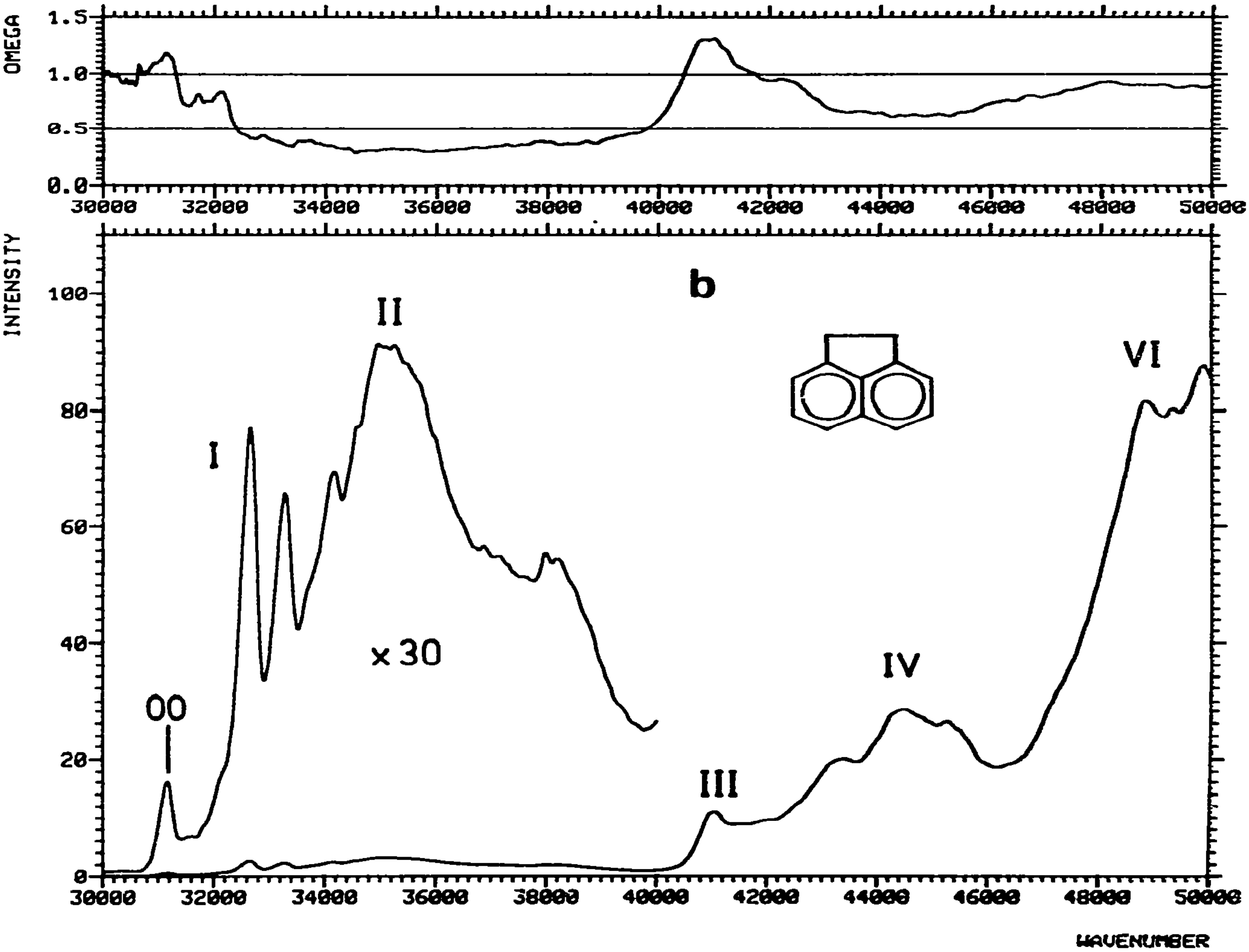

Fig 1 Two-photon excitation spectra for linearly polarized light ($\delta_{\uparrow\uparrow}$) and two-photon polarization parameter Ω. (a) Naphthalene, (b) acenaphthene.

42000 cm^{-1} to a B_{3g}^{+} state [4]. More elaborate π-electron calculations were used recently to make a different assignment (III = 1A_g^+, IV = 1B_{3g}^-) [5], an assignment supported by the fact that plus states within the PPP theory are forbidden for two-photon excitations [12]. The corresponding transitions are therefore expected to be weak. The Ω curve has a maximum in the region of the shoulder at 42100 cm^{-1}, clearly indicating B_g-type symmetry for this transition. In the range of the absorption maximum IV the Ω value drops down to a minimum characteristic for an A_g transition. Thus it has been confirmed that indeed two electronic transitions are responsible for the TPA between 41000 and 46000 cm^{-1} and that the tentative assignment by Mikami and Itō [4] is correct.

A further strong band in the TPES is observed above 48000 cm^{-1} with a first maximum at 48800 cm^{-1} (VI). The corresponding Ω value is 0.8 indicating a final state of A_g symmetry. The maximum at 48800 cm^{-1} was also observed by Mikami and Ito [4], but due to its close coincidence with a band of the $T_1 \rightarrow T_n$ spectrum [13], they assigned it to a two-step process involving an intermediate triplet state. For such a two-step process, however, Ω should be 1.0 in liquid solution [8] and the measured value 0.8 is significantly different from 1.0. In addition, by a more detailed analysis of the two-step processes suggested by Mikami and Ito, it turns out that the transition rate of both should be negligible with respect to direct two-photon excitation under our experimental conditions [7].

In acenaphthene the main effect of the alicyclic ring is a reduction of symmetry from D_{2h} to C_{2v}. B_{2u} and B_{3g} representations become B_2 and B_{1u} and A_g become A_1. This change allows for mixing of states which cannot interact in the unperturbed system and it alters selection rules All $\pi \rightarrow \pi^*$ transitions are two-photon allowed in acenaphthene. For B_2 transitions the polarization parameter Ω is still fixed to 1.5 by symmetry. B_2 transitions should therefore lead to maxima in the Ω curve while A_1 transitions should lead to minima.

The vibrational structure of the first band (I) in the TPES of acenaphthene (fig. 1b) shows a pattern similar to naphthalene. The 0–0 transition is somewhat more intense than in naphthalene but the main intensity of band I still comes from vibronic coupling. This is also seen from the strong change of Ω from 1.20 at the 0–0 transition to 0.4 at the most prominent band. The electronic state is B_2, as expected, but the main intensity is borrowed from an A_1 transition via b_2 vibrations

Above 34000 cm^{-1} the vibrational structure of the first band is overlayed by a broad band of intermediate intensity with much less vibrational structure and a maximum at ≈35000 cm^{-1} (II) This band has no counterpart in the two-photon spectrum of naphthalene. Ω shows a constant value of 0.30 over the whole band.

At 41000 cm^{-1} a further band appears (III), with an intensity four times higher than that of II. Since the

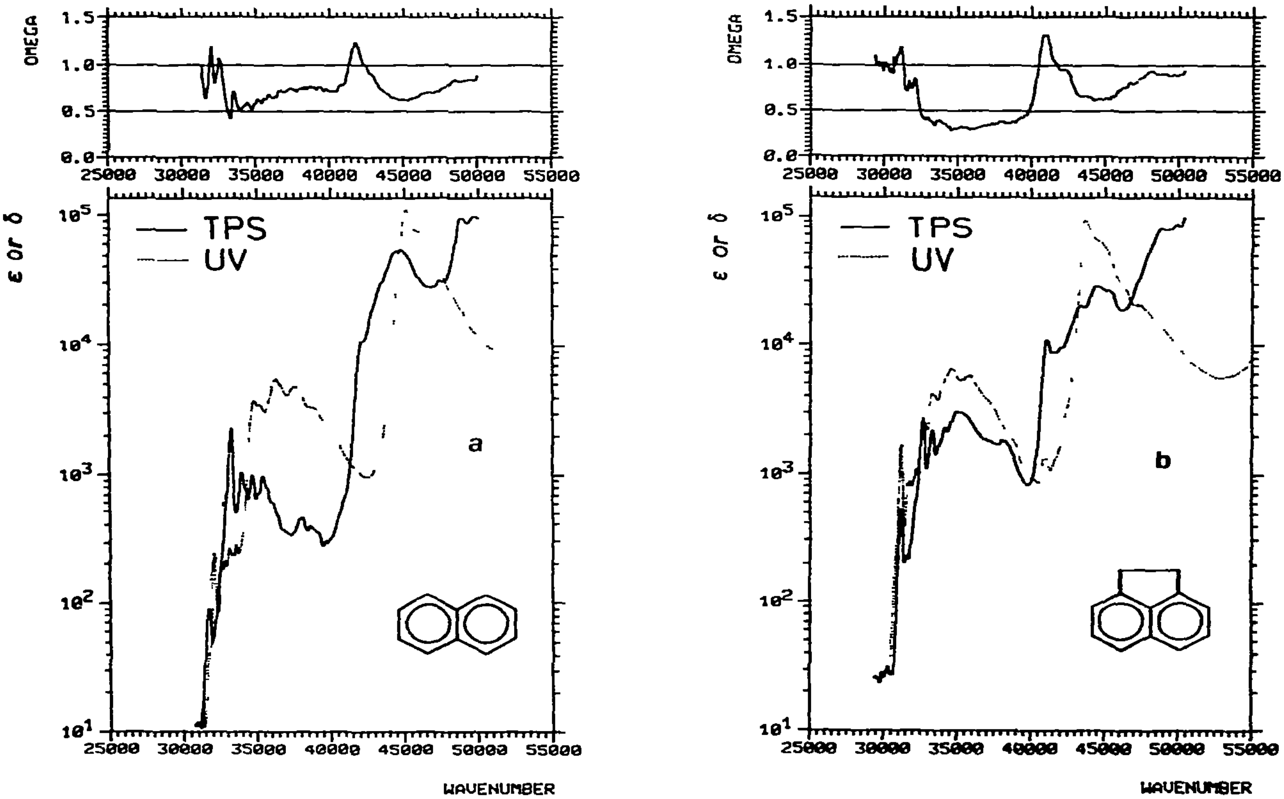

Fig. 2. Comparison of one-photon and two-photon spectra (a) Naphthalene, (b) acenaphthene. Scale for $\delta_{\uparrow\uparrow}$ is arbitrary, ϵ in $\ell\ mol^{-1}\ cm^{-1}$

polarization reaches a maximum (Ω = 1.30), in this range the symmetry of the corresponding state must be B_2. This state obviously corresponds to the state B_{3g} responsible for the structure labelled III in naphthalene.

In the energy range where we found the A_g band IV in naphthalene, a broad band is also seen in acenaphthene with maxima at 43400, 44500 and 45200 cm^{-1}. The polarization parameter indicates A_1 symmetry. Nevertheless, the broadening of the band and the additional maxima may be due to states which could not be observed in naphthalene. Finally the most intense transition (VI) is found at the same position and with nearly the same value for the polarization parameter as in naphthalene.

2.2. *Comparison with one-photon absorption*

The one-photon absorption spectra (OPAS) are compared to the corresponding two-photon excitation spectra in fig. 2. Excitation energies and intensities are collected in table 1, together with further data known from gas-phase and synchrotron-radiation studies.

In the near-UV spectrum of naphthalene three absorption bands are seen with maxima at 31800 (I), 36400 (II) and 45300 cm^{-1} (V) (in hexane solution). Following Platt's nomenclature [22], these bands are usually called L_b, L_a and B_b. They result from transitions to the states $1B_{2u}$, $1B_{1u}$ and $2B_{2u}$.

Corresponding bands are also seen in acenaphthene with similar intensity distribution and only slight redshifts caused by the alkyl substitution. There appears, however, an additional band at 41000 cm^{-1} in the OPAS which coincides with the feature III in the TPES. This feature has been assigned to a B_2 transition. In naphthalene itself, the corresponding feature was assigned to a B_{3g} state and consequently does not show up in the OPAS (fig. 2a). The L_a band which could not be seen in the TPES of naphthalene (where the

Table 1
Excitation energies ΔE (in 1000 cm^{-1}) and intensities of electronic excited singlet states in naphthalene and anthracene. f is the oscillator strength, ϵ the molar extinction coefficient in ℓ mol^{-1} cm^{-1}, and δ the two-photon cross sections in arbitrary units. All one-photon data are from ref. [14] unless otherwise indicated; the two-photon data are from this work

		One photon		Two photon			Assignment	
		ΔE		ΔE	$\delta_{\uparrow\uparrow}$	Ω	symmetry	state
naphthalene	I	31.9 [a,b] 0–0 gas					$1B_{2u}$	L_b
		31.8 0–0 sol	f = 0.002 [c]	31.7 0–0	0.08	0.65		
		33.6 max	ϵ = 295	33.2 max	2.4	0.40		
	II	35.9 [a,b] 0–0 gas					$1B_{1u}$	L_a
		38.7 [d] max gas	f = 0.102 [c]					
		36.4 max sol	ϵ = 5.600					
	III			42.1	10.4	1.25	$1B_{3g}$	
	IV			44.5	54.9	0.65	$2A_g$	
	V	47.8 [a,e] max gas	f = 1.70 [c]				$2B_{2u}$	B_b
		45.3 max sol	ϵ = 117000					
	VI			48.8	100.0	0.80	$3A_g$	
	VII	52.5 [f]	ϵ = 10000				$3B_{2u}$	
	VIII	55.5 [g] $S_1 \rightarrow S_n$					$3B_{3g}$	
	IX	62.1 [e] max gas					$4B_{1u}$	
		59.8 [f] max sol	ϵ = 30000					
acenaphthene	I	31.1 0–0 sol	ϵ = 1700	31.1 0–0	0.66	1.20	$1B_2$	L_b
				32.6 max	3.1	0.40		
	II	34.6 max	ϵ = 6500	35.0 max	3.5	0.30	$2A_1$	L_a
	III	41.0	ϵ = 1400	41.0	13.8	1.30	$2B_2$	
	IV			43.4	24.6	0.65	$3A_1$	
				44.5	34.5	0.65		
	V	43.7	ϵ = 97000				$3B_2$	B_b
	VI			48.7	100.0	0.85	$5A_1$	

[a] Ref. [15]. [b] Ref. [16]. [c] Ref. [17]. [d] Ref. [18]. [e] Ref. [19]. [f] Ref. [20]. [g] Ref. [21].

Table 2
Calculated excitation energies ΔE (in 1000 cm^{-1}) and transition parameters. f is the oscillator strength, δ the two-photon cross section in 10^{-50} cm^4 s, Ω the two-photon polarization, and %D the percentage of doubly excited configurations. Below the horizontal line only states with $f > 0.1$ are shown. For details of calculation see text

Symmetry		S CI/M				SD CI/P					Exp.	
		ΔE	F	δ	Ω	ΔE	f	δ	Ω	%D		
naphthalene												
L_b	$1B_{2u}$		0.0082			33.7	0.0002			8.6	I	32.2
L_a	$1B_{1u}$	37.9	0.1696			37.8	0.0737			5.5	II	35.7
	$1B_{3g}$	46.8		6.4172	1.50	45.5		0.1329	1.50	13.2	III	42.1
	$2A_g$	46.0		19.2776	0.28	47.1		1.0992	0.26	11.6	IV	44.5
B_a	$2B_{1u}$	49.7	0.6854			49.5	0.3397			8.3		
B_b	$2B_{2u}$	45.9	1.8097			50.1	1.3061			5.1	V	47.2
	$3A_g$	56.6		190.506	1.27	50.8		5.8741	1.08	34.0	VI	48.8
	$2B_{3g}$	53.2		9.0786	1.50	51.0		0.3071	1.50	15.1		
	$3B_{2u}$	61.1	0.1119			56.2	0.0251			27.6	VII	52.5
	$3B_{3g}$					56.6		1.4533	1.50	25.2	VIII	55.5
	$3B_{1u}$	64.4	0.8721			62.7	0.0354			22.5		
	$4B_{1u}$					65.8	0.5256			13.2	IX	62.1
acenaphthene												
$L_b = 1B_2$		32.8	0.0323	0.1018	1.50	33.2	0.0073	0.0124	1.50	8.1	I	32.6
$L_a = 2A_1$		36.5	0.2095	0.2622	0.70	36.8	0.0944	0.1393	0.54	5.6	II	34.6
	$2B_2$	45.4	0.1896	5.2794	1.50	44.4	0.0002	0.1829	1.50	11.5	III	41.0
	$3A_1$	45.4	0.0235	18.3051	0.25	46.6	0.0075	0.8246	0.72	12.0	IV	43.4
$B_a = 4A_1$		48.5	0.6259	1.9923	0.26	48.8	0.2854	0.8888	0.53	9.0		
	$5A_1$	54.4	0.0025	201.59	1.24	49.3	0.0359	5.9305	1.12	29.6	VI	46.7
$B_b = 3B_2$		45.8	1.6233	1.0812	1.50	49.5	1.2757	0.0652	1.50	5.6	V	45.7
	$4B_2$	51.4	0.0129	11.349	1.50	50.5	0.0001	0.3247	1.50	15.2		
	$5B_2$	59.2	0.0001	20.526	1.50	55.3	0.0187	0.0043	1.50	26.0		
	$6B_2$	59.7	0.1063	0.8947	1.50	56.1	0.0009	1.0228	1.50	24.1		
	A_1					64.8	0.1248	36.0215	0.25	20.6		
	A_1	62.1	0.7576			65.7	0.4158	5.0976	0.44	17.5		

final state is B_{1u}) shows considerable intensity in the TPES of acenaphthene (where the final state is A_1). It is interesting to note that especially those transitions gain intensity which in the reduced symmetry can correlate to the most intense transition of the corresponding spectrum.

Above 50000 cm^{-1} three further states are known from one-photon spectroscopy, located at ≈52500 (VII), 55500 (VIII) and 60000 cm^{-1} (IX). Transitions VII and IX are one-photon allowed [20], but their polarization is not known. Since state VIII was detected in $S_1 \rightarrow S_n$ spectroscopy [21], it most probably has g symmetry.

2.3. Comparison with calculations

For both molecules, CNDO-CI calculations with 60 singly excited configurations and 200 singly and doubly excited configurations have been performed, according to our procedures S CI/M(60) and SD CI/P (200nr*) [6,7]. The results are given in table 2. Correlation to the experimental data is shown in fig. 3.

For naphthalene, both calculations give the states L_b, L_a and B_b with the correct order and intensity distribution. SD CI also puts the states $1B_{3g}$ and $2A_g$ at the right positions and yields a good approximation of the observed relative two-photon cross sections, while

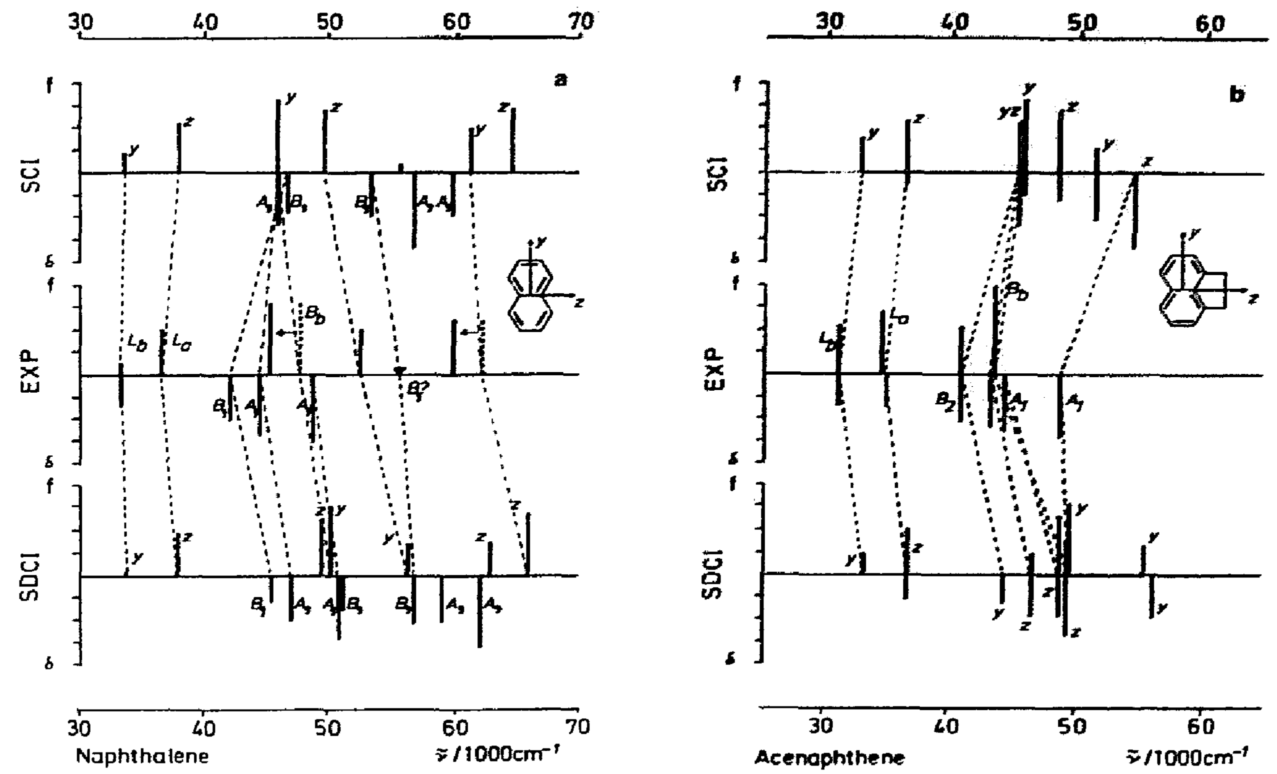

Fig. 3. Comparison of experimental data (EXP) with the results of S CI and SD CI calculations. The length of the upper bars corresponds to $\log f + 3$ (or $\log \epsilon - 1$ respectively), that of the lower bars to $\log \delta_{rel}$. Correlation lines indicate assignments, arrows indicate solvent shift. z: short-axis polarized (B_{1u} respectively A_1); y: long-axis polarized (B_{2u} respectively B_2).

S CI fails to predict these states below the B_b state and yields the false order $2A_g < 1B_{3g}$. The $3A_g$ state is predicted above but very close to the B_b state by SD CI, in good agreement with experiment. In S CI $3A_g$ lies more than 10000 cm^{-1} higher than B_b. Thus the inclusion of doubly excited configurations is essential in order to predict the energies of g states.

For the states VII, VIII and IX no experimental symmetry information is available, so an assignment is only possible on the basis of energy and intensity predictions. While SCI suggests the assignment to the states $2B_{1u}$ (= B_a), $2B_{3g}$ and $3B_{2u}$, SD CI indicates the sequence $3B_{2u}$, $3B_{3g}$, and $4B_{1u}$. Until an experimental determination of the polarization of transitions VII and IX allows an unambiguous symmetry assignment, we prefer the SD CI result, since it gave the more reasonable results for the other transitions. There remains however one problem: SD CI predicts the B_a state ($2B_{1u}$) at a somewhat lower energy than the B_b state. If this is true, the B_b band should overlap the B_a band. This SD CI result is not in accord with the usual assumption of a separate B_a band on the high-energy side of the B_b band. It is known, however, from analysis of the UV spectra of annulenes [23], that these two bands may indeed lie in the same energy region. A recent interpretation of the MCD spectrum of naphthalene is also in line with this idea [24].

A further hint that the states B_a and B_b lie close together results from the analysis of the acenaphthene data: The results of the calculations for the states L_b ($1B_2$), L_a ($2A_1$), $2B_2$, $3A_1$, B_b ($3B_2$) and $5A_1$ are similar to those of the corresponding states in naphthalene (compare table 2). The B_a ($4A_1$) transition, however, which is calculated to be close to the $3A_1$ transition, has nearly the same two-photon cross section as the latter one. This yields a satisfying explanation for the broadening and the appearance of new maxima observed in band IV of the TPES of acenaphthene, compared to naphthalene. On the other hand, the shoulder appearing on the high-energy side of the B_b band in the OPAS of acenaphthene at ≈47000 cm^{-1} is probably due to a small amount of one-photon intensity gained by the $5A_1$ transition.

3. Summary

From the combined information obtained from one- and two-photon absorption spectra of naphthalene and acenaphthene, six excited states can be unambiquously assigned in the energy range up to 50000 cm^{-1} Most likely two further excited states occur in the energy range between 45000 and 50000 cm^{-1}. Above 50000 cm^{-1} a tentative assignment has been made for three further excited states. The experimental findings are in good agreement with the results of CDNO/SD CI calculations, if doubly excited configurations are included

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