TWO-PHOTON SPECTROSCOPY OF DIPOLE-FORBIDDEN TRANSITIONS. THE LOW-LYING SINGLET STATES OF ANTHRACENE

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The two-photon excitation spectrum of anthracene in solution is reported from 29000 to 47000 cm^{-1}. Two-photon allowed transitions to $1B_{3g}$(35800 cm^{-1}), $2A_g$ (38000 cm^{-1}) and $3A_g$ (43000 cm^{-1}) are assigned by polarization measurements. These results, with those from one-photon spectroscopy, agree with calculations. Theoretical data suggest assignment of a B_{3g} state to a shoulder at 39000 cm^{-1} in the two-photon spectrum.

1. Introduction

From the electronic excited singlet states up to an excitation energy of 50000 cm^{-1} only three (labelled $1L_a$, $1B_b$, and $1B_a$ in Platt's nomenclature [1,2]) are clearly identified in the UV spectrum of anthracene. A fourth excited singlet state ($1L_b$) is assumed to lie $\approx$30000 cm^{-1} above the ground state [3–5]. Up to seven additional excited singlet states are predicted from theoretical considerations in this energy range. Most of these states have g symmetry and therefore do not show in the UV spectrum Transitions to the g states are, however, allowed for two-photon excitation. An assignment of these transitions is greatly simplified if the polarization is observed as well [6]. In order to clarify location and assignment of the low-lying excited g states, we have measured the two-photon excitation spectrum at a precision equivalent to normal UV spectra and have also determined the two-photon polarization parameter. The results are compared with the early two-photon study of Bergman and Jortner [7] and with theory.

2. Experimental

Relative two-photon cross sections for circularly and linearly polarized light ($\delta_{\circlearrowright\circlearrowleft}$ and $\delta_{\uparrow\uparrow}$) have been measured by monitoring the fluorescence of a sample of anthracene ($\approx 10^{-3}$ M in ethanol) irradiated by a tunable pulsed dye laser. Experimental details have been described [8]. The spectral range from 400 to 700 nm laser wavelength has been measured in steps of 0.5 nm using 13 dyes.

From the cross sections $\delta_{\circlearrowright\circlearrowleft}$ and $\delta_{\uparrow\uparrow}$ the two-photon polarization parameter

$$\Omega = \delta_{\circlearrowright\circlearrowleft}/\delta_{\uparrow\uparrow}$$

is derived which serves as a symmetry indicator in many cases [6]. In point group D_{2h}, in which transitions from the ground state $1A_g$ to A_g and B_g states are two-photon allowed, the upper limit for Ω of 1.5 should be observed for B_g states, while A_g states usually lead to minima in $\Omega(\nu)$ with values down to 0.25 [6,9].

3. Calculations

In order to support our interpretation and assignment of the electronic spectra by comparison with theoretical predictions, two kinds of calculations have been performed. Both use the CNDO/S semi-empirical hamiltonian of Del Bene and Jaffé [10,11], which takes into account all valence electrons:

(a) A standard CNDO/S calculation (SCI), using 60 singly excited configurations and approximating electron repulsion by the Mataga–Nishimoto formula [12].

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(b) To account for correlation effects, the second calculation includes 200 singly and doubly excited energy-selected configurations (SDCI). In this case electron repulsion is best described by using the Pariser formula [13]. All other parameters are as in standard CNDO/S.

Calculations of type (b) yield not only better agreement with excitation energies, but also with two-photon cross sections [9]. The input geometry for both calculations has been taken from X-ray data [14].

4. Results and discussion

4.1. The two-photon excitation spectrum

The two-photon excitation spectrum of anthracene in ethanol solution is shown in fig. 1 together with the two-photon polarization parameter Ω. In fig. 2 the two-photon excitation spectrum is compared to the conventional UV spectrum.

In the energy range 29000–34000 cm^{-1} the very weak two-photon absorption shows pronounced vibrational structure. Two maxima are seen at 29300 cm^{-1} and 30800 cm^{-1}, each followed by a shoulder with roughly half the intensity of the corresponding maximum. This pattern is very similar to the well known vibrational structure of the L_a band (B_{1u}) (compare fig. 2). The polarization parameter Ω is nearly constant over this progression with a value of 0.8, indicating total A_g symmetry for this transition. Bergman and Jortner, who obtained only the peak at 31000 cm^{-1} in their spectrum [7], assigned it to the false origin of the $1A_g \rightarrow 1B_{2u}$ transition (L_b), the 0–0 transition of which is believed to lie at ≈ 30000

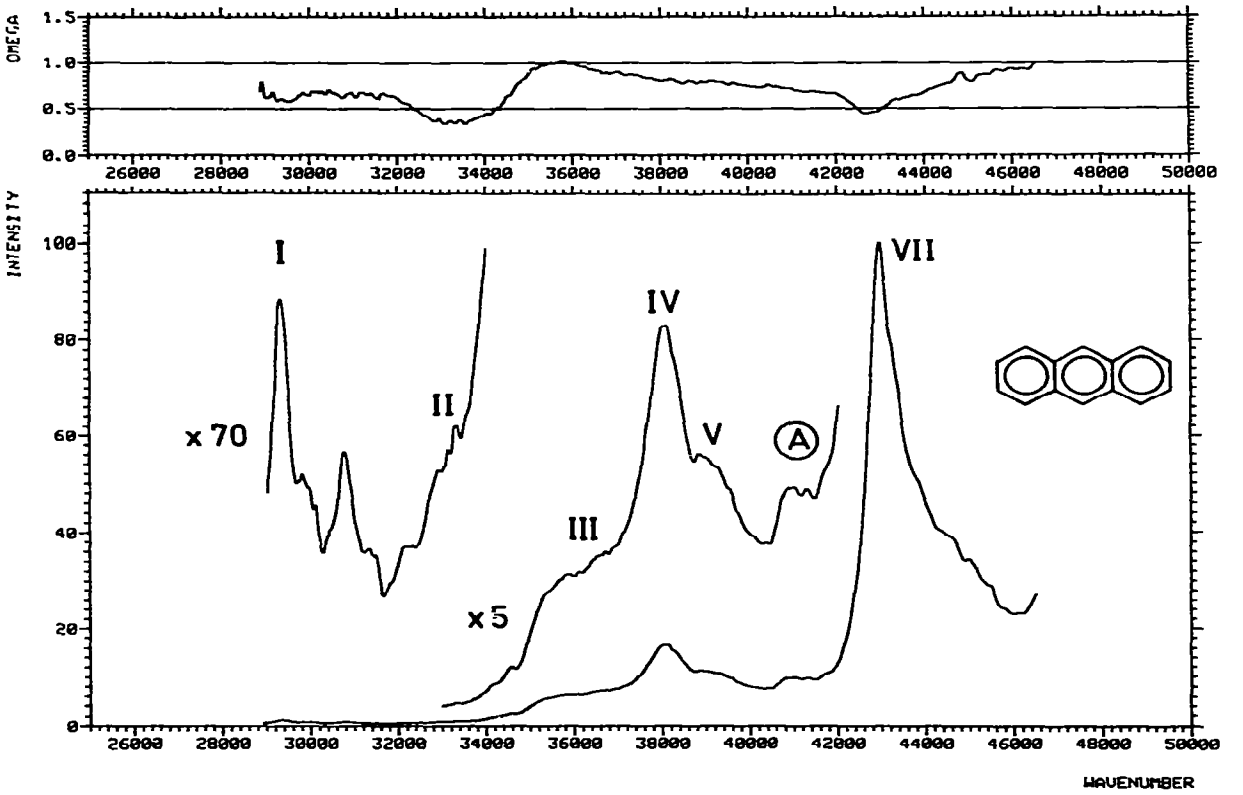

Fig. 1. Two-photon excitation spectrum of anthracene solution for linearly polarized light ($\delta_{\uparrow\uparrow}$) and two-photon polarization parameter Ω (upper part).

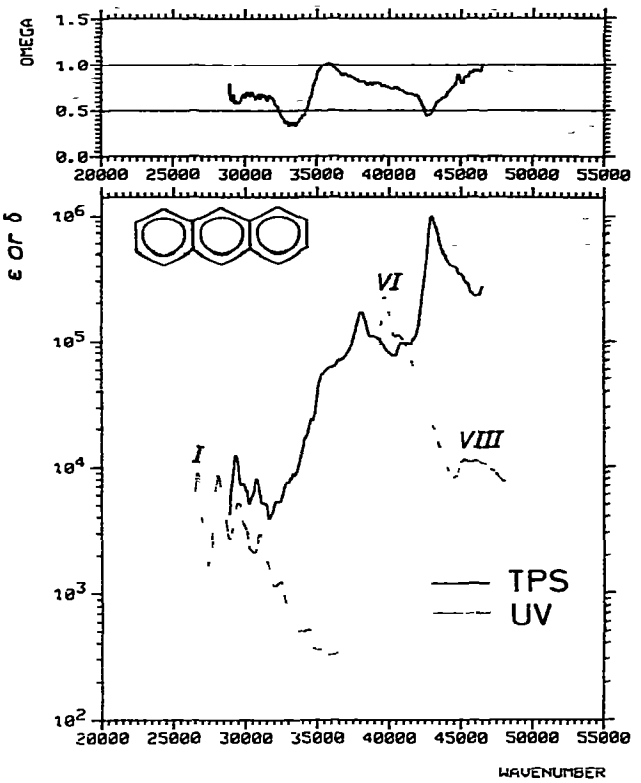

Fig. 2 Comparison of one-photon and two-photon spectra of anthracene. Scale for δ in arbitrary units, ε in ℓ mol^{-1} cm^{-1}.

cm^{-1} [3–5]. This would lead to a similar situation as in naphthalene, where only the $1A_g \rightarrow 1B_{2u}$ transition is observed in the two-photon spectrum due to vibronic coupling, whereas the $1A_g \rightarrow 1B_{1u}$ transition, though much stronger in one-photon absorption, is completely missing [15,16].

On the basis of our results, the above assignment is questioned. If the 0–0 energy of the L_b band really lies at ≈30000 cm^{-1}, the bands at 29300 and 30800 cm^{-1} cannot belong to a progression piling up on a false origin of this band. In addition the great similarity of the vibrational structure found in two-photon absorption with the one seen in the UV spectrum makes it most probable that the structure found between 29000 and 32000 cm^{-1} results from the L_a band. It can, however, not completely be ruled out that the 0–0 transition of the $1B_{2u}$ state lies at an energy considerably lower than 30000 cm^{-1}. While the vibronic progression monotonically decreases in intensity with increasing energy, the two-photon absorption rapidly increases above 32000 cm^{-1}, indicating the onset of a new transition. A small shoulder (II) is seen at 33500 cm^{-1}, which corresponds to a pronounced minimum of the Ω curve, indicating A_g symmetry for this transition. This feature can therefore not belong to a two-photon allowed B_{3g} transition, as suggested by Bergman and Jortner [7]. The intensity is nearly the same as for the 30800 cm^{-1} vibronic band; thus the transition seems not to be two-photon allowed.

Above 34000 cm^{-1} the two-photon absorption strongly rises in intensity. We therefore suggest that this part of the two-photon spectrum is dominated by two-photon allowed transitions. The first feature observed in this region is a broad shoulder at ≈36000 cm^{-1} (III) well separated from a sharp, intense maximum (IV) at 38000 cm^{-1}. While the shoulder corresponds to a maximum in Ω, the value drops down to 0.8 at 38000 cm^{-1}. This behavior of the Ω curve suggests the assignment of the shoulder to a B_{3g}, and of the peak to an A_g state. On the high-energy side of IV a second shoulder (V) appears at ≈39000 cm^{-1}. The Ω value of 0.8 again indicates, that the main intensity in this shoulder results from an A_g transition. From the experimental data it is not obvious whether V is a vibrational structure belonging to band IV or an individual electronic transition.

The strongest transition in the two-photon excitation spectrum of anthracene below 47000 cm^{-1} is the sharp peak at 43000 cm^{-1} (VII). The polarization parameter Ω shows a minimum at this energy; thus the only possible assignment is to an A_g transition. The bandshape closely resembles the pattern known from the strongest band in the one-photon absorption spectrum which has its maximum at 39700 cm^{-1} (fig. 2). In the low-energy tail of this transition an additional structure is observed near 41000 cm^{-1}, marked "A" in fig. 1.

In summary, seven bands are seen in the two-photon spectrum of anthracene up to 47000 cm^{-1}. Of these, two (IV and VII) can be assigned to A_g states and one (III) to a B_{3g} state by means of the polarization parameter Ω. To some extent these assignments do not agree with those derived from the low-resolution measurements of Bergman and Jortner [7].

(a) The 31000 cm^{-1} transition is not a false origin and belongs most probably to the $1B_{1u}$ and not to the $1B_{2u}$ state.

(b) The transition at 33200 cm^{-1} cannot have B_{3g} symmetry.

(c) The state at 38000 cm^{-1} clearly has A_g and not B_{3g} symmetry.

(d) No maximum assignable to an A_g state is found at 40000 cm^{-1}.

4.2. Comparison with one-photon absorption

The results obtained from the two-photon spectrum (TPS) are collected in table 1 together with those already known from one-photon spectroscopy. In the UV spectrum four bands (I, VI, VIII, X) are seen which all undergo considerable solvent shifts. We therefore give the position of the maxima in the gas phase [17–19] and in hexane solution [20]. No counterparts to the two-photon allowed transitions III, IV and VII are seen in the UV spectrum in accordance with the one-photon forbidden character (g→g) of these transitions. From $S_1 \rightarrow S_n$ spectroscopy, however, a state is known [21] ≈50000 cm^{-1} above the ground state which most probably has g symmetry.

The assignment of transitions I, VI and VIII to the states L_a ($1B_{1u}$), B_b ($2B_{2u}$) and B_a (nB_{1u}) is generally accepted. X is short-axis polarized as I and VIII, thus the final state must also have B_{1u} symmetry. The possible connection between the feature labeled I in the TPS and the L_a state has been discussed above. The L_b transition, expected for all aromatic systems, is believed to be hidden under the strong L_a band. From polarization measurements [3] and studies of linear [4] and circular dichroism [5] its 0–0 transition is assumed to lie near 30000 cm^{-1}. Possibly the shoulder II in the TPS is connected with this state. Vibronic coupling via a b_{2u} vibration as promoting mode would allow intensity borrowing from the strong two-photon allowed transitions IV and VII. The minimum found in the Ω curve in the region of II supports this interpretation.

4.3. Comparison with calculations

The results of both the SCI and the SDCI calculation are given in table 2. A comparison with experi-

Table 1
Excitation energies $\tilde{\nu}$ (in 1000 cm^{-1}) and intensities of electronic excited states in anthracene as derived from one-photon and two-photon spectra. f = oscillator strength, ϵ = molar extinction coefficient in $\ell\ mol^{-1}\ cm^{-1}$. Two-photon cross sections δ in arbitrary units. Pol. Polarization relative to fluorescence

State	One-photon			pol.	Two-photon			Assignment
	$\tilde{\nu}$				$\tilde{\nu}$	δ	Ω	
I	27 6	0–0 gas	ϵ = 8500	∥	(29.4)	1.3	0.75	$1B_{1u} = L_a$
	26.7	0–0 sol	f = 0.1 [b]					
II	30.0 [a,c,d]	P		⊥	33.5 [?]	0 8	0.35	$1B_{2u} = L_b$
III					35.8	6.3	1.00	$1B_{3g}$
IV					38.0	16.6	0.80	$2A_g$
V					39.0	11.1	0.80	$2B_{3g}$
VI	42.3 [e,f,g]	gas	ϵ = 220000	⊥	A 41 0	10.0	0.70	$2B_{2u} = B_b$
	39.7	sol	f = 2.3 [b]					
VII	42.0? [g]				43 0	100.0	0.45	$3A_g$
VIII	46.8 [e]	gas	ϵ = 11400	∥				$3B_{1u} = B_a$
	45 3 [i]	sol	f = 0.23 [h]					
IX	50.0 [k]	S_1–S_n						$4A_g$
X	55.7 [e]	gas	ϵ = 32000	∥				$5B_{1u}$
	53.7 [i]	sol	f = 0 65 [h]					

a) Ref. [22]. b) Ref. [23]. c) Ref. [24]. d) Ref. [3]. e) Ref. [17]. f) Ref. [18]. g) Ref. [19]. h) Ref. [26].
i) Ref [27]. k) Ref. [21]. ℓ) Ref. [25].

Table 2
Calculated excitation energies ΔE (in 1000 cm^{-1}) and transition parameters. f = oscillator strenth, δ = two-photon cross section in 10^{-50} cm^4 s, Ω = two-photon polarization, %D = percentage of doubly excited configurations. SCI/M: standard CNDO/S calculation with 60 singly excited configurations and Nishimoto–Mataga integrals. SCDI/P: CNDO/S calculation including 200 singly and doubly excited configurations of total $\pi\pi^*$ symmetry [9]. Electron repulsion approximated by the Pariser formula. Below the broken line only states with f greater than 0.1 are shown

Sym.	SCI/M				SDCI/P						Exp.
	ΔE	f	δ	Ω	ΔE	f	δ	Ω	%D		
$L_a = 1B_{1u}$	29 2	0.2602			29.7	0 1173			7.6	I	27.6
$L_b = 1B_{2u}$	28.9	0 0187			30.5	0.0014			6.1	II	30 0?
$1B_{3g}$	37 6		20.9236	1.50	38.6		1.1606	1.50	13.2	III	35.8
$2A_g$	40 3		37.7100	0 28	40.0		2 2454	0.90	43.0	IV	38.0
$2B_{3g}$	41.2		42.1651	1.50	41.7		1.7449	1.50	15.0	V	39.0
$2B_{1u}$	43.0	0 0023			42 6	0.0049			13 0		
$B_b = 2B_{2u}$	40 1	2.7892			45 3	2.2510			4.6	VI	42.3
$3A_g$	49.2		595.63	1.24	45.4		25.7725	0.39	21.2	VII	43.0
$B_a = 3B_{1u}$	47 0	0.3833			46.5	0 1081			8.7	VIII	46.8
$3B_{2u}$	48 1	0 0125			48.8	0.0011			36.9		
$4A_g$	52.7		61 3151	0.34	50 2		29.5027	1 03	61.2	IX	50.0
$4A_{1u}$	51.7	0.1259			51.2	0.0849			12.3		
$5B_{1u}$	57 4	0.9838			59.3	0 7776			21.0	X	55.7

mental data is shown in the correlation diagram of fig. 3. Correlation lines are drawn to the gas-phase energies of the dipole-allowed transitions, since in solution these transitions are heavily red-shifted.

The assignment of I (L_a), VI (B_b) and VIII (B_a) to the states $1B_{1u}$, $2B_{2u}$ and $3B_{1u}$ is obvious in both calculations with respect to energy as well as to oscillator strength. For X the state $4B_{1u}$ or $5B_{1u}$ might be responsible. Since the measured intensity is about three times that of the B_a band, and since calculated energies are higher than the experimental ones in all other cases, we prefer the latter assignment. The other u states ($1B_{2u}$, $2B_{1u}$ and $4B_{1u}$) are not observed in the UV spectrum in agreement with their predicted low oscillator strengths. The calculated energy of the $1B_{2u}(L_b)$ state is, however, very close to the position where it is placed by most authors through indirect observations [3–5].

Five two-photon allowed states are predicted up to $\approx$50000 cm^{-1} in both calculations. The first three are found close together with sequence $1B_{3g}$, A_g and $2B_{3g}$. The $1B_{3g}$ and $2A_g$ states compare very well with shoulder III and maximum IV in the two-photon spectrum. The shoulder V at 39000 cm^{-1} is, therefore, most probably due to the state $2B_{3g}$. The low Ω value found for this band is most likely due to an overlap with the stronger A_g band at 38000 cm^{-1}. While both calculations predict the same sequence, only in SDCI do all three states lie below the B_b state. The main effect of the doubly excited configurations is, therefore, a shift of all two-photon allowed states to lower energies. This is also seen with the $3A_g$ state corresponding to the strongest absorption band (VII) in the two-photon spectrum. While SDCI locates this state close to the B_b state in full agreement with experiment, SCI yields a position even higher than the B_a state.

The calculated cross sections both compare well with the experimental relative intensities. Absolute cross sections are, however, by a factor of 10 larger in SCI than in SDCI. From estimates of absolute experimental values the SDCI results are believed to give the right order of magnitude [9]. A further indication that SDCI is more reliable than SCI may be seen from the calculated Ω values of the two A_g transitions. While SCI yields 0.28 and 1.24, SDCI gives 0.90 and 0.39 in good agreement with the experimental values 0.80 and 0.45.

The fifth two-photon allowed state $4A_g$ is already calculated in an energy range not accessible by direct two-photon excitation spectroscopy, since the laser wavelength required overlaps with the fluorescence of

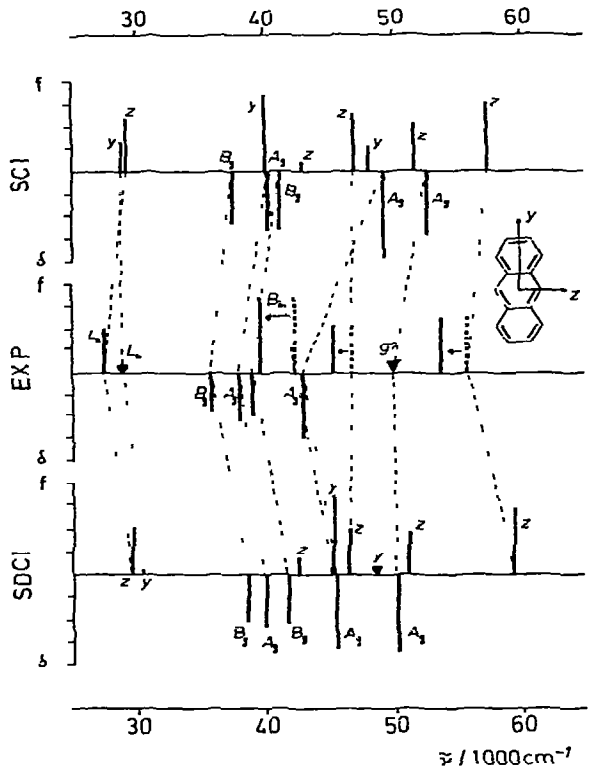

Fig. 3 Comparison of experimental data (EXP) with the results of SCI and SDCI calculations The length of the upper bars corresponds with log f, that of the lower bars to log δ ↑↑ Correlation lines indicate assignment Arrows indicate solvent shift z short-axis polarized (B_{1u}), y long-axis polarized (B_{2u})

anthracene. It fits, however, very well with the state (IX) near 50000 cm^{-1} known from $S_1 \rightarrow S_n$ spectroscopy. Since there is no further two-photon allowed transition predicted between $1B_{3g}$ and $3A_g$, we do not believe that the feature labelled A in the TPS belongs to a separate electronic transition. Its close coincidence with the first vibronic band of the B_b transition in the UV spectrum makes it much more probable that A belongs to the B_b transition, getting its intensity via vibronic coupling.

5. Conclusion

Including our new results from two-photon spectroscopy, we now have experimental evidence for ten excited singlet states up to an energy of ≈53000 cm^{-1}. Seven of them are unambiguously assigned (I, III, IV, VI, VII, VIII, X) and the other three (II, V, IX) highly probable. The experimental data are in excellent agreement with the results of CNDO/S SDCI calculations. The calculations predict two further transitions below 50000 cm^{-1} ($2B_{1u}$ and $3B_{2u}$) with very low oscillator strengths.

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