Chemical Physics 94 (1985) 131–145
North-Holland, Amsterdam

TWO-PHOTON SPECTROSCOPY OF THE BIPHENYL CHROMOPHORE. THE ELECTRONIC EXCITED STATES OF BIPHENYL AND FLUORENE BELOW 50000 cm^{-1}

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Received 6 September 1984

The two-photon excitation spectra of biphenyl and fluorene in dilute solution have been measured up to 50000 cm^{-1}. Both spectra exhibit a medium intense band system in the range 32000–42000 cm^{-1}, and a strong band above 45000 cm^{-1}. The lowest frequency feature is assigned to a B_3 symmetry transition in biphenyl and the corresponding B_2 transition in fluorene. The polarization of the higher bands leads to the assignment of two A states at 38000 and 47000 cm^{-1}. The origin of the electronically excited states of the biphenyl chromophore is discussed by simple composite molecule considerations as well as CNDO CI calculations. The latter give a semiquantitative picture of transition energies and transition probabilities for one- and two-photon allowed excitations. A compilation of one-photon spectra and calculations from the literature is included in the analysis to provide a consistent picture of the electronically excited states of the biphenyl chromophore up to 50000 cm^{-1}

1. Introduction

In a recent publication [1] we reported on the two-photon absorption (TPA) of stilbene in the energy range 29000–51000 cm^{-1}. Four low-lying excited states of symmetry A have been detected, of which at least two had not been expected at such low energies. Since the low-lying excited A states in stilbene evolve mainly from excitations localized in the phenyl rings, unusually low-lying A states are likely to appear in biphenyl, too. At least some of these states should be detectable in TPA due to the selection rules applying to this kind of spectroscopy [2–5].

The first wide range two-photon spectra of biphenyl and fluorene have been obtained by Drucker and McClain [6–8]. Regarding the structural similarity of these compounds, the conclusions of these authors seem contradictory. Their interpretation did not consider the possible existence of low-lying "covalent" states [9] just being realized at this time [10–13]. Appropriate semi-empirical calculations to aid the interpretation of two-photon spectra were not yet available. In addition, seveal early spectra of Drucker and McClain differed from our more recent and better resolved spectra [14–16]. Therefore, we believed a reinvestigation was justified. As demonstrated for the molecule pair naphthalene/acenaphthene [15], the investigation of two molecules with similar chromophores but different symmetry can be extremely helpful in reaching definite assignments.

To arrive at a consistent interpretation of the low-lying excited states we compared our experimental data with the results of calculations and with other spectroscopic studies. The biphenyl chromophore has been treated theoretically numerous times and with a variety of different methods [17–43]. This interest is due in part to the fact that the geometry of biphenyl strongly depends on the surroundings: In the crystal, biphenyl is planar at room temperatures [44–46] but phase transitions at 40 and 16 K have been interpreted as due to the appearance of slightly twisted conformers ($\phi \approx 10°$) [46,47]. Biphenyl is twisted around the central C–C bond in solution ($\phi = 20°–35°$)

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0301-0104/85/$03.30

[22,45,48–50] and in gas phase ($\phi = 40°–50°$) [51,52]. The twist angle ϕ also depends on substitution, especially in the o-position [18,22,24,53]. Often, biphenyl has been treated theoretically as a nearly ideal test case for all types of composite molecule methods [17,30,54–60], since the spectrum of the subsystem benzene, from which the molecule is composed, is believed to be well understood. This is discussed in more detail in section 4.

In spite of the large number of theoretical investigations which are paralleled by a similar number of experimental studies [6–8,17,18,24,26,33–36,38–40,53,61–75], the assignment of the one-photon allowed transitions still is apparently under discussion. This discussion continues in part because much confusion exists in the literature due to assignments based on misquotations or lack of information about previous research. Therefore, we include a short review of the most recent experimental data (section 5) prior to the presentation of our own results (section 4) and the discussion of possible assignments (section 7).

2. Choice of coordinate systems

There is no unique choice of the coordinate system for biphenyl. Nearly all possible labelings of the axis have been used. Careful consideration must be given when comparing results from the literature. We follow the recommendations given in ref. [76] as does the majority of authors. This has the disadvantage that corresponding axes are labeled differently in biphenyl and fluorene. To avoid any confusion we use the notation "long" and "short" axis polarized for one-photon transition moment directions. The axis labeling and the relations between irreducible representations in different symmetries are summarized in table 1.

3. Experimental and calculational procedures

Two-photon excitation spectra (TPES) have been obtained with a microcomputer controlled spectrometer described in detail elsewhere [77]. The polarization of the laser light alternates between linear and circular from pulse to pulse, thus

Table 1
Symmetries and polarizations for one-photon (OP) and two-photon (TP) allowed $\pi\pi^*$ transitions in biphenyl and fluorene

C_{2v}	A_2		B_2		
	z short		y long		OP
	y^2, z^2		yz $\Omega = 3/2$		TP
D_{2h}	A_g	B_{2u}	B_{3u}	B_{1g}	
		y short	z long		OP
	y^2, z^2			yz $\Omega = 3/2$	TP
D_2	A	B_2	B_1	B_3	
		y short	z long	x short	OP
	x^2, y^2, z^2	xy $\Omega = 3/2$	xz $\Omega = 3/2$	yz $\Omega = 3/2$	TP

allowing the determination of the cross sections δ_{π} and $\delta_{\cap\cap}$ at virtually the same time. These cross sections are not corrected for variations in the fluorescence quantum yield as a function of excitation energy. Data obtained from the literature [78] indicate that the quantum yield varies only little with excitation energy for biphenyl. The two-photon polarization parameter $\Omega = \delta_{\cap\cap}/\delta_{\pi}$, which does not depend on the fluorescence quantum yield, shows very good reproducibility, and serves as symmetry indicator [4,5,79]. The spectral range from 30000 to 50000 cm^{-1} was covered using thirteen laser dyes. The sample was a 1 cm quartz cell containing biphenyl of fluorene in ethanol solution at room temperature with concentrations ranging from 10^{-2} to 10^{-3} m. The spectra obtained are shown in fig. 2 in section 6.

We use the results of CNDO/S CI calculations as a guideline for interpretation and assignment of the experimental spectra. Within this scheme, we calculate excitation energies, transition moments, and two-photon parameters. In recent applications, the latter have been found to be a reliable tool for the assignment of two-photon allowed transitions [1,14–16]. The calculations are based

Table 2
Calculated excitation energies ΔE (in 1000 cm^{-1}) and transition parameters. f is the oscillator strength, $\delta_{\uparrow\uparrow}$ is the two-photon cross section for two parallel linearly polorized photons of equal energy in units of 10^{-50} cm^4 s, Ω is the two-photon polarization, %D is the percentage of doubly excited configurations, ϕ is the angle of twist around the central single bond. For definition of symmetries (Sym.) and polarizations (Pol.) see table 1.

Assignment	Sym.	Pol.	SCI/M 60				SDCI/P 200				
			ΔE	f	$\delta_{\uparrow\uparrow}$	Ω	ΔE	f	$\delta_{\uparrow\uparrow}$	Ω	%D
biphenyl $\phi = 0°$											
$L_a(-)$	B_{1u}	l	38.8	0.8328			38.9	0.3391			0.3
$L_b(+)$	B_{3g}		37.0		2.21	1.50	39.2		0.36	1.50	2.2
$L_b(-)$	B_{2u}	s	37.3	0.0022			39.4	0.0019			1.7
$L_a(+)$	A_g		48.6		69.90	0.78	45.1		2.10	0.90	1.6
$B_b(+)$	B_{3g}		48.5		0.02	1.50	50.2		0.01	1.50	4.3
$B_a(-)$	B_{1u}	l	51.5	1.1434			51.2	1.3029			0.6
(E_{2g})	A_g		52.7		290.01	0.75	52.3		49.09	0.89	25.9
$B_b(-)$	B_{2u}	s	51.5	0.9772			54.9	0.8809			6.9
biphenyl $\phi = 30°$											
$L_b(-)$	B_2	s	37.5	0.0082	0.18	1.50	39.8	0.0025	0.08	1.50	1.3
$L_b(+)$	B_3	s	37.6	0.0002	1.47	1.50	39.9	0.0003	0.30	1.50	1.5
$L_a(-)$	B_1	l	40.1	0.7779	0.08	1.50	40.4	0.3119	0.00	1.50	0.3
$L_a(+)$	A		48.5		60.75	0.78	45.1		0.89	0.94	0.9
$B_a(-)$	B_1	l	51.7	1.0734	0.01	1.50	51.6	1.3501	0.02	1.50	0.5
$B_b(+)$	B_3	s	49.1	0.0408	0.01	1.50	51.7	0.0812			3.7
(E_{2g})	A		49.7		43.81	0.72	51.8		32.89	0.89	24.8
$B_b(-)$	B_2	s	51.1	0.6977	0.11	1.50	55.2	0.7918	0.02	1.50	6.1
fluorene											
$L_b(-)$	A_1	s	35.0	0.0001	0.29	1.11	37.5		0.21	0.57	2.2
$L_b(+)$	B_2	l	35.7	0.1246	2.01	1.50	37.9	0.1500	0.13	1.50	1.6
$L_a(-)$	B_2	l	38.9	0.5020	0.30	1.50	38.9	0.0319	0.13	1.50	1.4
$L_a(-)$	A_1	s	46.5	0.0164	33.18	0.71	44.0	0.0011	1.25	0.91	1.5
$B_a(-)$	B_2	l	47.4	1.0404	0.16	1.50	48.3	1.2339	0.05	1.50	1.5
$B_b(+)$	B_2	l	47.7	0.2115	0.00	1.50	49.5	0.1593	0.20	1.50	4.2
(E_{2g})	A_1	s	50.0	0.0130	113.52	0.84	51.5	0.1373	25.18	0.84	17.1
$B_b(-)$	A_1	s	48.5	0.7834	9.27	0.52	52.4	0.5511	4.31	1.02	11.1

on the hamiltonian of Del Bene and Jaffe [80] using the final parameterization of this method [81] without change. However, doubly excited configurations (DEC) have been included to account for possible correlation effects. Calculations employing only singly excited configurations (SCI/M) used 60 configurations and the Mataga/Nishimoto [82] approximation for Coulomb repulsion integrals, as is standard in CNDO/S. The calculations including DEC (SDCI/P) used the Pariser–Parr formula [83] and included 200 energy-selected configurations [84]. Two-photon parameters have been calculated as previously described [85] using all eigenvectors of the CI problem as intermediate states. Geometries were obtained from X-ray data [44,47,86] after averaging equivalent bond lengths and angles to yield D_{2h} (biphenyl) or C_{2v} (fluorene) symmetry. Twisted conformations for biphenyl were approximated using the same bond lengths and angles as in the planar form. The results are shown in table 2.

4. Excited states of biphenyl in the composite molecule model

The composite molecule or molecules-in-molecules (MIM) approach [17,54–60] is a valuable

tool to discuss the origin of electronically excited states in systems composed from subsystems with known electronic structure. Its main advantage is that it relates the electronically excited states of a composite system to the electronically excited states of the subsystems from which it is composed, thus yielding a nomenclature which is independent of the details of a specific calculation in cases where the model is applicable. Since it is this aspect in which we are interested, we do not deal with more sophisticated versions of the composite molecule model introduced to derive more quantitative results [30,54,55,58].

If a molecule consists of two identical subsystems, the composite molecule model is especially convenient and biphenyl has served as a paradigm in many applications [17,18,22,30,54,55,57,59]. In the following, we give a brief account of the concurring results which, nevertheless, often disagree in their quantitative details. If the two subsystems do not interact at all, the spectrum of the composite system is just the superposition of the subsystem spectra. In the case of two identical subsystems, this means that each state of the composite system is at least doubly degenerate. An interaction between the subsystems will first remove this degeneracy, leading to a symmetrical splitting of each zero-order state. In the exciton approximation [57] the interaction is due to the coupling of the transition dipole moments. Thus, transitions with vanishing electric transition dipole moment [dipole forbidden transitions (DFT)] do not split in this approximation. More detailed consideration of the Coulomb interaction between the subsystems and inclusion of resonance interactions further affect the splitting and, in the case of DFT, introduce it. The latter splitting can be viewed as a result of transition dipoles induced in one subsystem by the presence of the other. The splitting caused by Coulomb and resonance interactions can bring states of different origin but of same symmetry close together, resulting in further mixing and repulsion of these states.

So far, all states are represented by wavefunctions constructed from excitations which are localized on each subsystem. However, additional transitions are possible involving an exchange of electrons between the subsystems. These charge exchange (CE) configurations must be included in calculations in order to extract quantitative results. For a qualitative discussion, CE configurations are important only if their energy is comparable to that of the low-lying local excitations. Fortunately, in biphenyl all the CE configurations have energies higher than the first three singlet excitations in benzene [22]. Consequently they affect the visible and near UV spectrum primarily in pushing the lower excited states further towards lower energies.

The various stages of this development are schematically represented in fig. 1. Since only singlet states are considered, we do not apply a multiplicity index together with state symbols. In the exciton approximation, we obtain four pairs of excited states for biphenyl (fig. 1b) from the lowest three excited states of benzene (fig. 1a). In the planar conformation, one state of each pair is symmetry allowed and the other symmetry forbidden for one-photon transitions with the ground state. The benzene $L_b(B_{2u})$ state splits into a B_{3g}

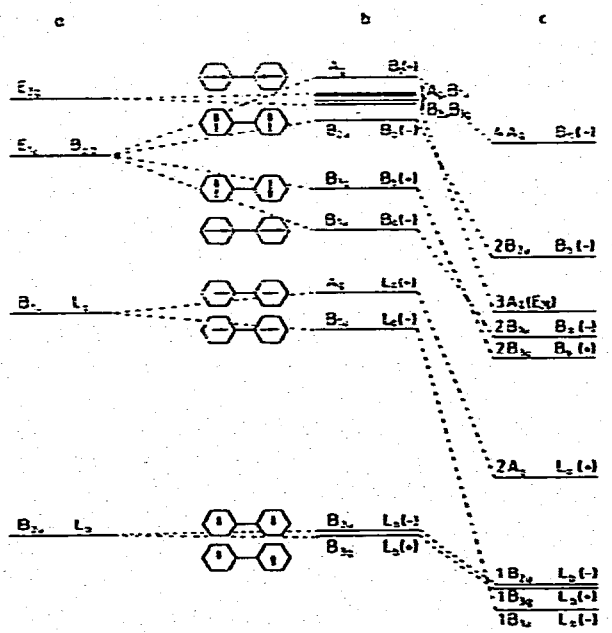

Fig. 1. Schematic development of the ππ* excited states for planar biphenyl from the parent benzene states: (a) parent states, (b) exciton approximation, (c) comparison to CNDO SCDI results.

and a B_{2u} state in first order. The splitting is very small due to the forbidden character of the B_{2u} transition in benzene. For planar biphenyl, theory predicts the ordering $B_{3g} < B_{2u}$ [31,36]. However, in the twisted conformations, this order may change [31].

The $L_a(B_{1u})$ state of benzene splits into a B_{1u} and an A_g state, the latter being higher in energy. The degeneracy of the benzene $B_{a,b}(E_{1u})$ state is removed through the mutual interaction, with B_a splitting into A_g and B_{1u}, and B_b splitting into B_{2u} and B_{3g}. Due to the strongly allowed character of the $1E_{1u} \leftarrow 1A_{1g}$ transition in benzene, this splitting is quite large and the predicted energetic order of the resulting states is $B_{1u} < B_{3g} < B_{2u} < A_g$. The exciton splitting brings the two B_{1u} states, $L_a(-)$ and $B_a(-)$ close together, causing further mixing and repulsion, as indicated in fig. 1c. In spite of this mixing, we specify only the leading contribution to characterize a given state. The order of states shown in fig. 1c corresponds to the order found from our SDCI/P calculation for planar biphenyl (table 2). Inspection of the wavefunctions allowed a unique correlation of the first eight excited states to the states derived in the framework of the composite molecule model.

Usually L_b, L_a and $B_{a,b}$ are the local singlet excitations considered in an exciton treatment of biphenyl. However, for the application of two-photon spectroscopy, we wish to include the lowest two-photon allowed state of benzene. This state is believed to be $1E_{2g}$ which has been located somewhat above the $1E_{1u}$ state [87]. The $1E_{2g} \leftarrow 1A_{1g}$ transition is dipole forbidden in benzene, so only induced dipole transition moments contribute to the splitting which consequently will be very small and comparable to the splitting between $L_b(+)$ and $L_b(-)$. Four closely spaced states of symmetry B_{1u}, B_{1g}, B_{2u} and A_g will result. Most likely these states will be located *below* the A_g state evolving from the benzene $1E_{1u}$ state. Configuration interaction among the A_g states will consequently yield predominant L_a, E_{2g} and B_a character for the states $2A_g$, $3A_g$, and $4A_g$ of biphenyl, as indicated in fig. 1c.

Twisting around the single bond changes the symmetry of biphenyl from D_{2h} to D_2, transforming the irreducible representations A_g, B_{3g}, B_{1u}, and B_{2u} of D_{2h} into A, B_3, B_1 and B_2 of D_2. As long as only $\pi\pi^*$ excitations are considered, no new coupling between the excited states of biphenyl is introduced on twisting. However, the splitting predicted by the exciton model is reduced for the L_b and B_b states. The B_3 states of D_2 are symmetry allowed for one-photon absorption with polarization perpendicular to the long axis of the molecule. The symmetry selection rules and polarization characteristics are summarized in table 1.

5. Summary of previous investigations

At this point it is necessary to provide a critical analysis of the present knowledge on excited states of biphenyl and fluorene because, even in very recent years, conflicting results have been published and contradicting assignments have been proposed. As far as possible, we will use Suzuki's empirical band labeling scheme [22] in this section (compare fig. 3, section 6), since we only want to summarize experimental facts without being biased by theoretical considerations. A comparison of experimental and theoretical findings is presented in section 7 after discussing the results of our two-photon measurements.

The existence of two L_b-type transitions in the absorption spectrum of biphenyl was already inferred by Platt [88]. Because they are "hidden" under the intense A-band, these bands were called H-bands by Suzuki [22]. Since the A-band (also termed "first conjugation band" [18,22]) exhibits a strong hypsochromic shift accompanied by considerable loss in intensity with increasing twist around the central C–C bond, the uncovering of a weak L_b-like band can be observed in the solution spectra of o, o'-substituted biphenyls [18,22,24,53]. Linear dichroism (LD) measurements on biphenyl embedded in stretched polymere sheets [34,35] have revealed a very weak short axis polarized contribution at the beginning of the A band, but no further details about the symmetry of the final state can be obtained from these spectra. An indication for the H band is also found in MCD spectra [61,69,70].

The existence of two hidden transitions (H1 and H2) leading to final states of different symme-

Table 3
Experimental data for biphenyl and fluorene. Data without reference are from the present study. Temperatures are given only if a temperature below room temperature is specified in the reference. The data from crystal reflection spectra are obtained by Kramers–Kronig transformation. For definition of symmetries (sym.) and polarizations (pol.) see table 1. For "?" see text

Assignment		Biphenyl						Fluorene					
empirical	this work		ΔE (cm^{-1})	phase or solute	ref.	sym.	pol.		ΔE (cm^{-1})	phase or solute	ref.	sym.	pol.
one-photon absorption													
H1	$L_b(+) \leftarrow GS$	0–0	33816	argon matrix 6.5 K	73	B_{3g}?		0–0	33773	vapor	63		
		0–0	33373	0–0 of fluorescence *n*-heptane matrix 77 K	66			0–0	33783	supersonic expansion	62		
								0–0	33174	*n*-heptane matrix 15 K	64		
		0–0	33348	0–0 of fluorescence *n*-heptane matrix 4.2 K	67	B_3		0–0	33200	heptane	90		
								0–0	33300	ethanol			
		0–0	33128	crystal 4.2 K	67	B_{3g}		0–0	33250	ethanol glass 77 K	24	B_2	l
								0–0	32960	crystal reflection	33	B_2	l
								0–0	33039	crystal 15 K	64	B_2	l
H2	$L_b(-) \leftarrow GS$	0–0	34387	argon matrix 6.5 K	73	B_{2u}?		0–0?	36000	ethanol glass 77 K	24	A_1	s
		0–0	33876	crystal 4.2 K	67	B_{2u}		0–0?	35700	cyclohexane	69		
								0–0?	35700	crystal reflection	33	A_1	s
								0–0?	35300	crystal	64	A_1	s
A	$L_a(-) \leftarrow GS$	max.	42000	vapor ($f = 0.36$)	72			max.	39300	vapor			
		max.	40500	light petroleum	90			max.	37800	heptane	90		
		max.	40500	ethanol				max.	38300	ethanol			
		max.	39500	ethanol glass 77 K	24	B_1	l	max.	37600	ethanol glass 77 K	24	B_2	l
		max.	39700	polyethylene matrix	34	B_1	l	max.	35100	polyethylene	34	B_2	l
		max.	39000	crystal reflection	72	B_{1u}	l	max.	37100	crystal reflection	33	B_2	l
X	$B_b(+) \leftarrow GS$							sh	44200	heptane	90		
								sh	44200	ethanol			
								max.	44000	ethanol glass 77 K	24	B_2	l
								sh	43600	polyvinylalcohol	35	B_2	l
								sh	44400	polyethylene	34	B_2	l
Y	?							max.	45300	heptane	90		
								sh	45700	ethanol			
								sh	44800	ethanol glass 77 K	24	A_1	s
								max.	45000	polyvinylalcohol	35	A_1	s
								max.	45100	polyethylene	34	A_1	s
B	$B_b(-) \leftarrow GS$	max.	51700	vapor ($f = 0.65$)	72			max.	47900	heptane	90		
		sh	48200	light petroleum	90			max.	47200	polyethylene	34	A_1	s
		max.	48200	polyethylene	34	?	s	max.	46000	crystal reflection	33	A_1	s
		max.	47200	crystal reflection	72		s						
C	$B_a(-) \leftarrow GS$	max.	51700	vapor ($f = 0.65$)	72			max.	48900	heptane	90		
		max.	49800	light petroleum	90			max.	48100	polyethylene	34	B_2	l
		max.	49500	polyethylene	34	B_1	l	max.	47400	crystal reflection	33	B_2	l
		max.	50000	crystal reflection	72	B_{1u}	l						
		max.	57300	vapor ($f = 0.10$)	72			max.	52600	crystal reflection	33	B_2	l
		sh	56200	crystal reflection	72	B_{1u}	l						
		max.	61800	vapor ($f = 0.67$)	72			onset	54000	crystal reflection	33	A_1	s
		max.	58000	crystal reflection	72		s						
		sh	67000	vapor ($f = 0.07$)	72								
		max.	65300	crystal reflection	72	B_{1u}	l						

(continued on next page)

Table 3 (continued)

Assignment		Biphenyl					Fluorene				
empirical	this work		ΔE (cm^{-1})	phase or solute	ref.	sym. pol.		ΔE (cm^{-1})	phase or solute	ref.	sym. pol.
two-photon excitation											
a = H1	$L_b(+) \leftarrow GS$	max.	33128	crystal	71	B_{3g}	0–0	33783	supersonic expansion	74	
		sh	33600	ethanol		B	0–0	34100	benzene		B
							0–0	33300	ethanol		B
			33000								
			~36000	CCl_4	6	B					
b	vibronic	max.	35600	ethanol		?	max.	35700	benzene	7	A_1
			36000								
			~39000	CCl_4	6	?	max.	34800	ethanol		
c		max.	38100	ethanol		A	max.	38100	cyclohexane	7	A_1
	$L_a(+) \leftarrow GS$						max.	38100	ethanol		A_1
d		sh	40000	ethanol		A	sh	40000	ethanol		A_1
e	$A(E_{2g}) \leftarrow GS$		43000					42000			
			~47000	CCl_4	6	A		~47000	cyclohexane		A_1
			45500	ethanol		A		45000			
								~47500	ethanol		A_1

try was first inferred by Coffman and McClure [17] from low-temperature spectra of a single crystal. The assignment of the lower of these two transitions (H1) to $1B_{3g} \leftarrow 1A_g$ was finally established by Hochstrasser and Sung [71] who studied the angular dependence of the two-photon absorption. In the crystal, the 0–0 transition (excitation energies and references are collected in table 3) was found to be electric dipole forbidden but magnetic dipole allowed for one-photon processes [67]. This result was questioned recently by Wakayama [75] who, as a result of the new findings on the crystal structure [46,47], assigned the appearance of the 0–0 transition to the presence of non-planar molecules. In *n*-heptane matrix the 0–0 transition is no longer electric dipole forbidden [67]. From the changes in dipole selection rules between planar and non-planar conformations (table 1), it was concluded that biphenyl is not planar in the matrix. Similar results have been found in an argon matrix as substrate [49,73]. Recently it has been argued, that the "sharp" spectra obtained from the matrix investigations are due to mainly planar molecules and therefore contain no information on the twisted species [73]. The polarization of the origin of the second transition (H2) is in accordance to a final B_{2u} state [67]. The 0–0 transition of the H2-band is not observed in the two-photon spectrum in agreement with the selection rules for two-photon transitions [71]. At 33754 cm^{-1}, a relatively strong long axis (B_{1u}) polarized band is observed in the crystal spectrum [67]. It was interpreted as a false origin resulting from a 626 cm^{-1} b_{2u} vibration coupling to the 0–0 transition of $1B_{3g} \leftarrow 1A_g$. Most likely it is this transition which more recently was attributed as the long axis polarized 0–0 transition of the crystal spectrum [72]. Strong coupling to vibrations which introduce overall B_{1u} symmetry is also found in an ethanol glass where most of the fluorescence is long axis polarized [24].

The OPA spectrum of fluorene differs from that of biphenyl insofar as two bands are observed between 33000 and 45000 cm^{-1}, with both showing vibrational fine structure. The 0–0 transition of the first band is well resolved in vapor, solution and crystal. The transition is one- and two-photon allowed [74]; the transition moment is oriented parallel to the long axis [34,35]. Both observations agree with a B_2 assignment of the final state, which in turn relates the first band of fluorene to the H1-band of biphenyl. The relatively high one-

photon intensity of this band has been attributed to strong mixing between transitions H1 and A, since both belong to the irreducible representation B_2 in C_{2v} [24]. From this it has been concluded [24] that the two-band structure found in fluorene and also in 9,10-dihydrophenanthrene should not be present in 4,5,9,10-tetrahydropyrene, since a mixing between H1 and A is not possible in D_2. Indeed this was observed by Yoshinaga et al. [35], who apparently were unaware of the earlier proposal. Some short axis polarized intensity has been found in the single crystal spectra around 35500 cm^{-1} [33,64]. This corresponds to a shallow minimum at 36000 cm^{-1} in the fluorescence polarization studied in ethanol glass at 77 K [24] and to the onset of a more diffuse absorption in gas phase [63]. In the MCD spectrum [69] strong indications are observed for an independent electronic transition at ≈ 35700 cm^{-1}. Taken together, these findings indicate that the onset of the H2 band in fluorene is located somewhere between 35000 and 36000 cm^{-1}. A weak short axis polarized absorption at the low-energy side of the 0–0 transition of H1 has been reported [35] for the stretched sheet LD spectra. However, no such absorption has been seen in any of the other measurements.

The A band is found to be long axis polarized in biphenyl as well as in fluorene [33–35,64]. A short axis polarized band was proposed to underlie the A band from two stretched sheet LD studies [34,35]. The existence of such a further band had been assumed earlier because of the great bandwidth [65]. This band was reported to be stronger in biphenyl (max. 40500 cm^{-1}) than in fluorene (max. 37500 cm^{-1}). It was interpreted as the short axis polarized, electric dipole allowed H2 band, disregarding the information discussed above on the origin of this band. No indications for the existence of a short axis polarized band underlying the A band have been found in the crystal spectra [33,64] or in fluorescence anisotropy studies [24,26]. We therefore believe that the short axis polarized band found in refs. [34,35] results from the assumption of equal orientation factors K_x and K_y for biphenyl and fluorene. At least for polyethylene sheets these two factors differ considerably in the case of fluorene ($K_x = 0.14$, $K_y = 0.26$) [89].

The second band system of biphenyl, starting at ≈ 45000 cm^{-1} consists of at least two bands (B and C). These two bands seem to nearly coincide in the free molecule [72] but they are well separated in spectra taken from crystals [72] or with a polymer as substrate [34,35]. Fluorescence anisotropy studies showed [24] that at least the onset of the B band is polarized perpendicular to the A band. This finding was confirmed by all later work [26,34,35,72] which also provided evidence for a long axis polarization of band C [26,34,72]. Bands B and C seem to become more equally polarized when the twist angle ϕ is increased through o,o'-substitution [26] in accordance with our earlier proposal [24].

For fluorene, the situation with respect to the second band system is more complex. Some structure is observed at the low-energy onset of a broad structureless band which compares quite well with the B, C band of biphenyl. We label these two structures as X and Y (fig. 3, section 6). From fluorescence anisotropy studies we know that while X is still long axis polarized, the polarization changes in the vicinity of Y [24]. This has been confirmed by LD measurements on stretched sheets [34, 35] and single crystals [33]. From one of the stretched sheet investigations [34] and independently from the crystal spectra [33], it was concluded that the first part (band B) of the broad structureless absorption between 46000 and 50000 cm^{-1} is short axis polarized and the second part (band C) is long axis polarized. Thus, for B and C the findings are the same as for biphenyl.

McLaughlin and Clark [72] have measured the vapor spectrum of biphenyl up to 70000 cm^{-1}. To obtain information on the polarization of the VUV-bands they also investigated crystal reflection spectra. Their findings are as follows: a short axis polarized band ($f = 0.10$) with maximum (vapor) at 57300 cm^{-1}, a strong long axis polarized band at 61800 cm^{-1} ($f = 0.67$), and a further weak short axis polarized band at 67000 cm^{-1} ($f = 0.07$). Tanaka [33] has studied the crystal reflection spectra of fluorene up to ≈ 54000 cm^{-1}. He identified a further long axis polarized band with maximum at 52600 cm^{-1} and a short axis polarized band at ≈ 54000 cm^{-1}.

Information on additional low-lying excited states, especially those related to A_g states of

planar biphenyl is up to now only available from the previously cited work of Drucker and McClain [6–8]. For biphenyl, these authors observe a rapid drop of Ω indicating that most of the two-photon intensity above 39000 cm^{-1} is related to final states of symmetry A. No clear decision, however, is reached as to whether the two-photon absorption between 36000 and 39000 cm^{-1} is due to an

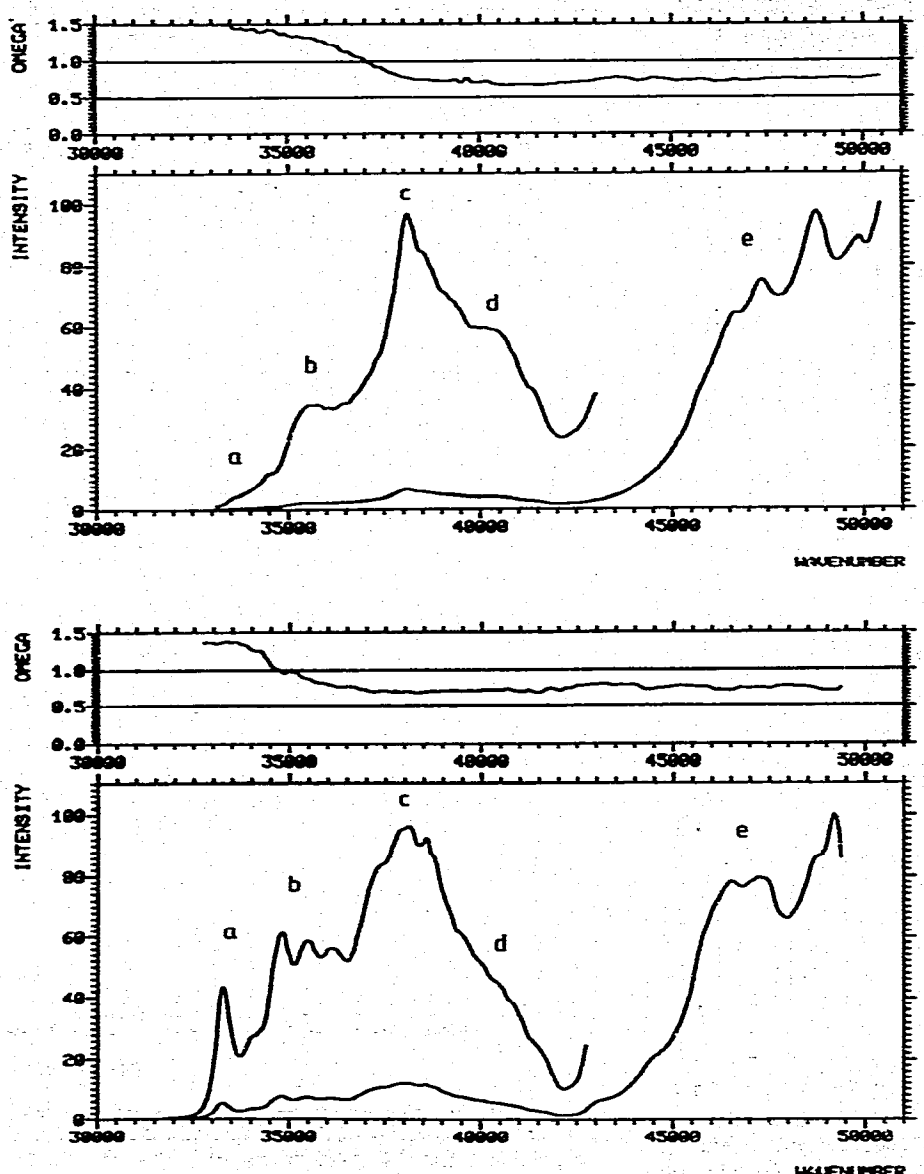

Fig. 2. Two-photon excitation spectra for biphenyl and fluorene for two parallel linearly polarized photons of equal energy (δ_{π}) in arbitrary units. The two-photon polarization parameter is given on top of each spectrum.

electronic state of symmetry A or to vibronic perturbation of one of the lower lying B states. At least one A state is observed above 43000 cm^{-1}. For fluorene, definite assignments for an A_1 state at ≈ 38000 cm^{-1} and again at least one A_1 state above 42000 cm^{-1} are made. From a pronounced minimum in Ω at 35700 cm^{-1} it is concluded that the origin of the H2-band is directly observed in the TPES.

6. Two-photon spectra

For point groups D_{2h}, D_2 (biphenyl) and C_{2v} (fluorene) all two-photon transitions with B symmetry have vanishing diagonal elements of the two-photon transition tensor. The two-photon polarization Ω which generally can lie between 0 and 1.5 is therefore 1.5 for all these transitions. For transitions which have A symmetries, Ω has often values around 2/3, a value expected if a single diagonal element of the tensor dominates. For planar biphenyl (D_{2h}), selection rules for one- and two-photon transitions are mutually exclusive due to the presence of a center of symmetry. Since the deviation from planarity is not too large for biphenyl in solution, we expect the one-photon allowed transition still to be weak in TPA and vice versa.

Our two-photon spectra are shown in fig. 2. For comparison with the OPA spectra the TPES are also included in fig. 3. The overall features of our spectra are in good agreement with the earlier measurements of Drucker and McClain [6,7]. We cannot, however, reproduce the strong variations in Ω found by these authors in the first part (33000–37000 cm^{-1}) of the fluorene spectrum in spite of the fact that the vibrational structure seen in $\delta_{\pi\pi}$ is better resolved in our spectrum

The first band system in the TPES of biphenyl (32000–42000 cm^{-1}) shows a distinct substructure: a very weak shoulder starting at ≈ 33000 cm^{-1}, a shallow maximum at 35600 cm^{-1}, a sharp maximum at 38000 cm^{-1}, and another shoulder at ≈ 40000 cm^{-1}. These four structures are labelled a, b, c and d in fig. 2. The two-photon polarization parameter Ω starts with a value close to the theoretical upper limit 1.5 in the region of structure a

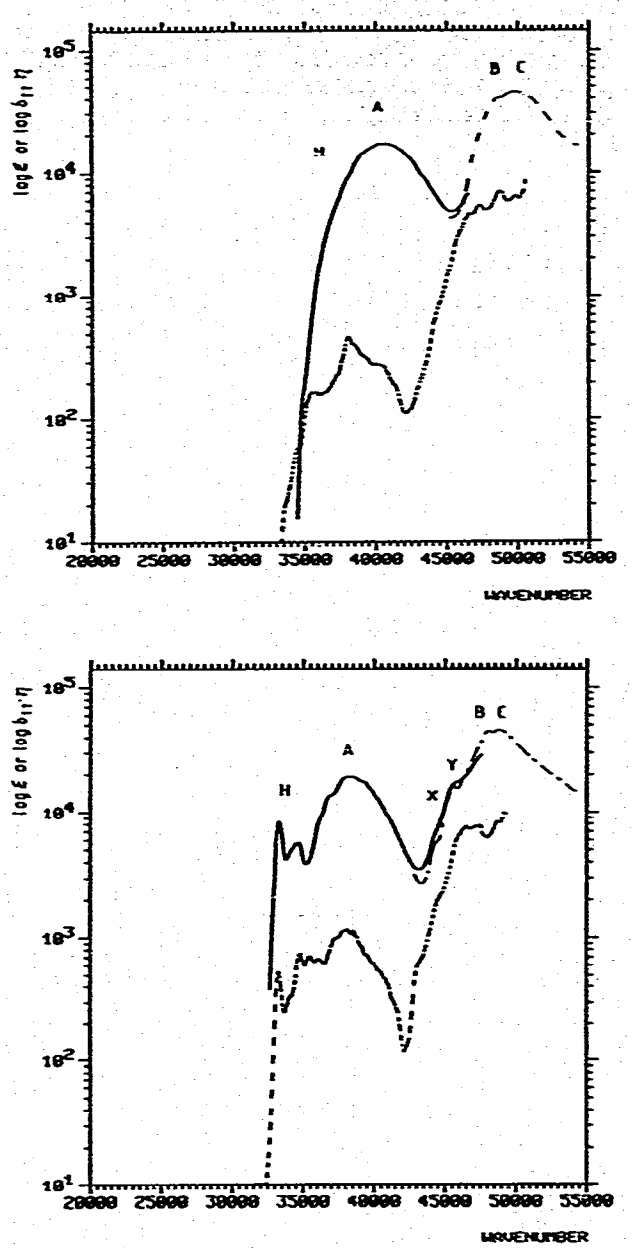

Fig. 3. One-photon absorption (———) and two-photon excitation (- - - - - -) spectra for biphenyl (top) and fluorene (bottom) in ethanol at room temperature. $\eta\delta_{\pi\pi}$ in arbitrary units. ----- OPA for biphenyl in light petroleum at room temperature [90]. — - — OPA for fluorene in heptane at room temperature [90].

and reaches a value of ≈ 0.7 in the vicinity of maximum c. For the remainder of the spectrum, Ω stays between 0.65 and 0.8 indicating that c and d and all that is seen of the second band system must be related to final states of symmetry A. Correspondingly, structure a must result from a final state of symmetry B. In the region of b, Ω drops from ≈ 1.4 to 0.7, indicating either an overlap of a transition of symmetry B with a transition of symmetry A or vibronic coupling between the transitions responsible for a and c. The maximum of the first strong band in the one-photon spectrum (band A) lies at 40000 cm^{-1}, ≈ 1500 cm^{-1} at higher energies than c. This and the fact that only transitions to final B states are one-photon allowed in D_2 strongly indicate that structures c and d in the TPES do not result from the state responsible for the A band in the one-photon spectrum. Similarly, the second band of the UV-spectrum which has its maximum at 48000 cm^{-1}, cannot be responsible for the strong two-photon absorption (e) observed in the same energy range, since the latter is related to a final state of symmetry A and not to a final state of symmetry B.

The results found for biphenyl are confirmed by the two-photon spectra of fluorene. The TPES of fluorene is very similar to that of biphenyl. The first band system, however, exhibits a somewhat better resolved fine structure. The two-photon polarization again confirms that c and d, as well as the second band system starting at ≈ 43000 cm^{-1}, result from final states of symmetry A. In spite of the fact that in the one-photon spectrum the maximum of the A band is shifted ≈ 2000 cm^{-1} to lower energies compared to biphenyl, the maxima c have nearly identical energies in both compounds. In addition to the two-photon polarization this confirms that band c results from an independent electronic transition. For fluorene the 0–0 transition of the first band is clearly resolved and coincides with the 0–0 transition of the one-photon spectrum. Again Ω indicates B symmetry. There is also a clearly resolved maximum at the beginning of structure b, which coincides with a maximum in the one-photon spectrum. The Ω curve drops from ≈ 1.3 to ≈ 1.0 at the beginning of structure b and shows a distinct inclination at 34700 cm^{-1}, again indicating either a superposition of two transitions or vibronic coupling.

The experimental information obtained from our two-photon spectra is included in table 3.

7. Discussion

We now compare the experimental findings discussed in sections 5 and 6 with theoretical predictions in order to establish a consistent assignment of the low-lying electronically excited states of the biphenyl chromophore. The results of the large number of calculations performed on biphenyl are similar, in spite of the variety of methods used. In particular, the relative oscillator strengths of different transitions as well as the dependence of the oscillator strengths and excitation energies on the twist angle ϕ are qualitatively the same in most calculations. Thus, the results shown in table 2 can be taken as an average example. The major areas in which the results of different calculations deviate are in the predicted orders of the states $B_a(-)$, $B_b(+)$, 3A and $B_b(-)$. Some calculations predict $B_a(-)$ at lower energies than $B_b(-)$ [21–25,28,30,36] and others give the reversed order [27,29,31,35]. All calculations including DEC yield the first result (compare table 2). The most extensive theoretical investigation performed up to the present time is probably the one by Baraldi et al. [36] who took into account up to triply excited configurations (TEC) in a PPP-calculation. The influence of TEC on order and energy separation of the low-lying excited states was found to be only minor in this study. The main effect of the TEC is a considerable stabilization of all low-lying excited states with respect to the ground state (GS), thus shifting the overestimated excitation energies of the SDCI calculation back to the proper range.

The first two excited states of planar or nearly planar biphenyl have to be assigned $L_b(+)$ and $L_b(-)$ since their experimentally established symmetries are B_{3g} [71] and B_{2u} [67] respectively. Thus, the majority of calculations (see refs. [21,26] for exceptions) and even the simple exciton model yield the correct energetic order $L_b(+) < L_b(-)$. The calculated energy difference, however, is usually less than half of the observed splitting (748

cm^{-1} in the crystal [67]; 571 cm^{-1} in an argon matrix [73]) A change in the order of the first two excited states with increasing twist angle ϕ, as predicted e.g. in ref. [31] and by our own calculations (table 2) therefore should not be overestimated in its significance.

Several authors [37,40,73] argue about a relatively steep potential of the lowest excited state with respect to ϕ. This argument is difficult to understand when we consider the nature of the first two excited states [75] and the nearly ϕ independent excitation energies for $L_b(+) \leftarrow GS$ and $L_b(-) \leftarrow GS$ found in almost all calculations. In addition, the assumption of a strongly ϕ dependent potential for these states is not in agreement with the nearly unchanged position of the H-band in o- and o,o'-substituted biphenyls.

The results obtained from biphenyl embedded in *n*-heptane or argon matrices confirm an unchanged order of $L_b(+)$ and $L_b(-)$ as well as little change in the energy of the first two excitations. However, since it is not absolutely certain that the matrix results are indeed related to twisted conformations [73] such findings do not yield an unambiguous proof.

When considered alone, our TPES of biphenyl do not provide new information on the order of the two lowest excited states in the twisted conformation, since we are unable to distinguish among B_1, B_2 and B_3 transitions. Our calculations (table 2) predict $L_b(-) \leftarrow GS$ to be slightly two-photon allowed for $\phi = 30°$. This would allow an assignment of band a to $L_b(-) \leftarrow GS$ and of band b to $L_b(+) \leftarrow GS$ in accordance with a reversed order of the first two excited states. Such an assignment, however, becomes unlikely when we consider the results obtained for fluorene. As discussed previously, the first excited state of fluorene is undoubtedly B_2. Therefore, it must be assigned $L_b(+)$ and not, as our calculations predict, $L_b(-)$. The similarity of the positions and the intensity ratio of bands a and b in fluorene and biphenyl strongly suggest that in biphenyl, too, band a must be assigned $L_b(-)$ and that, in accordance with the matrix results, the order of the two lowest excited states in biphenyl does not change from planar to twisted conformation.

Accepting this assignment, structure b in the TPES of biphenyl must be the result of vibronic coupling with the nearby A state responsible for band c (see below). We cannot determine from our low-resolution spectra whether the coupling is stronger for $L_b(+)$ of $L_b(-)$, nor could this question be resolved from the high-resolution spectra [71]. In fluorene, structure b could result from $L_b(-) \leftarrow GS$ since $L_b(-)$ belongs to symmetry A_1. The maximum at 34800 cm^{-1}, however, lies at lower energies than the estimated 0–0 transition of $L_b(-) \leftarrow GS$ (table 3). Since we were not able to confirm the pronounced minimum in Ω at 35700 cm^{-1} observed by Drucker and McClain [7], we assign the main body of structure b as vibrational structure belonging to $L_b(+) \leftarrow GS$. The drop in Ω between 34000 and 35000 cm^{-1} indicates that some of the intensity in this energy range is due to vibronic coupling between $L_b(+)$ and $3A_1(L_a(+))$. Above 35000 cm^{-1}, $L_b(-)$ also may contribute to structure b but definite assignments cannot be made from our low-resolution spectra.

The assignment of the A band to $L_a(-) \leftarrow GS$ is well established and does not need further elaboration. All calculations yield the experimentally observed high-energy shift with increasing ϕ. The origin of the A band is still not known for either compound. From the calculations, we estimate that the origin of the A band in planar biphenyl does not lie much more than 1000 cm^{-1} above the origin of the H2-transition.

The bands labeled c and d in the TPES of biphenyl and fluorene must result from excitations into final states of symmetry A and A1, respectively. We assign both bands to $L_a(+) \leftarrow GS$. The calculated two-photon cross section is about ten times as large for this transition as for $L_b(-) \leftarrow GS$. In twisted biphenyl and in fluorence the strong one-photon allowed transition $L_a(-) \leftarrow GS$ becomes slightly two-photon allowed but the calculated two-photon cross sections are still very small. Due to a possible vibronic coupling of this transition with higher two-photon allowed excitations we cannot exclude some contribution of $L_a(-)$ to the observed two-photon intensity. The fact, however, that bands c and d do not show the same shift as the A band when we compare biphenyl and fluorene strongly confirms that the main part of the two-photon intensity in this region does not

result from $L_a(-)$. On the other hand, $L_a(+) \leftarrow$ GS will not be observable in the OPA spectrum because of the presence of the strong one-photon allowed A band. $L_a(+) \leftarrow$ GS is one-photon forbidden in biphenyl even when twisted. In fluorene it is basically one-photon allowed, but the calculated oscillator strength is still very low.

The calculated excitation energy for $L_a(+) \leftarrow$ GS is ≈ 5000 cm^{-1} too high, compared to the one-photon allowed transitions $B_b(-)$, $B_a(-)$, and $L_a(+) \leftarrow$ GS. Inclusion of DEC yields a pronounced stabilization of $L_a(+)$ with respect to the other states (table 2), but this stabilization is not large enough to produce the experimentally observed energy separations.

Above 45000 cm^{-1} the assignment becomes somewhat more complicated since in this region the calculations predict different orders for the excited states. With regard to the experimentally observed polarizations, the only possible assignment is $B_b(-) \leftarrow$ GS (short axis polarized) for band B and $B_a(-) \leftarrow$ GS (long axis polarized) for band C. Our calculations (table 2) predict nearly the same energy for $B_a(-)$ and $B_b(-)$ as long as only SEC are considered. With inclusion of DEC, $B_a(-)$ has a significantly lower energy than $B_b(-)$, a result that is not acceptable in the light of the experimental findings.

In an earlier paper [24], we had attributed the short axis polarization at the beginning of band B to $B_b(+) \leftarrow$ GS. This transition is one-photon forbidden in planar biphenyl, however, it becomes weakly one-photon allowed for twisted conformations. The same assignment has been derived independently by Edwards and Simpson [26]. In the light of the more recent experimental observations, this assignment becomes uncertain. We know now that band B as a whole is short axis polarized and that it is also intense in the crystal spectrum. This rules out a $B_b(+) \leftarrow$ GS assignment for band B. Even if $B_b(+)$ is really somewhat lower in energy than $B_b(-)$, as a number of calculations predict (compare e.g. the SCI results in table 2), it cannot be detected by polarization measurements. It is impossible to observe a weak short axis polarized transition hidden in the low-energy tail of an intense transition which is also short axis polarized. Two-photon spectroscopy also assists little in this case. The calculated two-photon cross section for $B_b(+) \leftarrow$ GS is so low that there is very little chance to observe this transition. The situation, however, is completely different in fluorene. Here $B_b(+) \leftarrow$ GS becomes B_2 and therefore it is long axis polarized. The calculated oscillator strength is also considerably high due to the now possible mixing between $B_b(+)$ and $B_a(-)$. All this conforms well to an assignment of $B_b(+) \leftarrow$ GS to the structure labelled X in the one-photon spectrum of fluorene. From the close analogy between fluorene and biphenyl, we conclude that in biphenyl $B_b(+) \leftarrow$ GS is hidden in the low-energy onset of the B-band. The structure labelled Y in fluorene is then either the onset of the B-band or results from $A_1(E_{2g}) \leftarrow$ GS. The calculated f value for the latter transition is very low but vibronic coupling with the nearby $B_b(-) \leftarrow$ GS could make it observable in OPA.

The intense two-photon absorption starting at ≈ 45500 cm^{-1} (band e) is undoubtedly due to $A(E_{2g}) \leftarrow$ GS. The calculated two-photon cross section is about one order of magnitude larger than for $L_a(+) \leftarrow$ GS and about two orders of magnitude larger than for $L_b(+) \leftarrow$ GS. This increase in two-photon cross sections is congruent with the suggestion that the two-photon intensity of the lower electronic transitions in biphenyl is mainly derived from the two-photon allowed E_{2g} transition in benzene. As discussed in section 4, the $3A_g$ state of planar biphenyl is expected to have the highest parentage of benzene E_{2g} and indeed we find the highest experimental two-photon intensity for this state. Small deviations from the ideal D_{2h} symmetry, as in twisted biphenyl or in fluorene, which do not alter the nature of the different states greatly, do not seem to change this general pattern. It would be interesting, however, to investigate how the situation changes in highly twisted biphenyls where the exciton splitting between $B_a(-)$ and $B_a(+)$ is strongly reduced [24].

Due to the increasing density of excited states in the calculated spectra, and due to the increasing uncertainty of the calculations with increasing excitation energy, we do not attempt to assign the bands observed in the OPA spectra above 50000 cm^{-1}.

8. Conclusion

Combining the experimental information from one- and two-photon spectroscopy in a comparative study of biphenyl and fluorene we assigned eight electronically excited states in the energy range below $\approx 51000\ cm^{-1}$ in both molecules. These are all the excited states predicted by a variety of semi-empirical calculations for the low-energy range. As in the case of stilbene, we found the second excited A respectively A_1 state to appear at unexpectedly low energies. Even with inclusion of doubly excited configurations the calculated energy is much too high compared to the other states. These findings illustrate how important it is to search for these states experimentally when attempting to establish the order of the low-lying electronically excited states. Such information is necessary for the understanding of the photo-chemical and photo-physical properties of molecules.

Acknowledgement

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support, the Regionales Rechenzentrum Köln for providing the necessary computer time and Ms. B. Börsch-Pulm and Ms. M. Demmer for technical assistance.

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