

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

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The two-photon excitation spectra of biphenyl and fluorene in dilute solution have been measured up to 50000  $\text{cm}^{-1}$ . Both spectra exhibit a medium intense band system in the range 32000–42000  $\text{cm}^{-1}$ , and a strong band above 45000  $\text{cm}^{-1}$ . The lowest frequency feature is assigned to a  $B_2$  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  $\text{cm}^{-1}$ . 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  $\text{cm}^{-1}$ .

### 1. Introduction

In a recent publication [1] we reported on the two-photon absorption (TPA) of stilbene in the energy range 29000–51000  $\text{cm}^{-1}$ . 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, several 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 ( $\phi = 10^\circ$ ) [46,47]. Biphenyl is twisted around the central C–C bond in solution ( $\phi = 20^\circ$ – $35^\circ$ )

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[22,45,48–50] and in gas phase ( $\phi = 40^\circ - 50^\circ$ ) [51,52]. The twist angle  $\phi$  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).

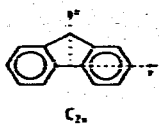
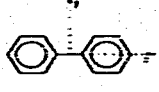
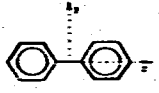
## 2. Choice of coordinate systems

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  $\pi \rightarrow \pi^*$  transitions in biphenyl and fluorene

 C <sub>2v</sub>	A <sub>1</sub>		B <sub>2</sub>		
	z		y		OP
	short		long		
	y <sup>2</sup> , z <sup>2</sup>		yz		TP
			$\Omega = 3/2$		
 D <sub>2h</sub>	A <sub>g</sub>	B <sub>2g</sub>	B <sub>1g</sub>	B <sub>3g</sub>	
	y		z		OP
	short		long		
	y <sup>2</sup> , z <sup>2</sup>		yz		TP
			$\Omega = 3/2$		
 D <sub>2</sub>	A	B <sub>2</sub>	B <sub>1</sub>	B <sub>3</sub>	
	y		z		x
	short		long		short
	x <sup>2</sup> , y <sup>2</sup> , z <sup>2</sup>		yz		TP
	$\Omega = 3/2$		$\Omega = 3/2$		$\Omega = 3/2$

allowing the determination of the cross sections  $\delta_{\pi\pi}$  and  $\delta_{\pi\pi\pi}$  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  $\Omega = \delta_{\pi\pi\pi}/\delta_{\pi\pi}$ , 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<sup>-1</sup> 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<sup>-2</sup> to 10<sup>-3</sup> 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  $\Delta E$  (in  $1000 \text{ cm}^{-1}$ ) and transition parameters.  $f$  is the oscillator strength,  $\xi_{11}$  is the two-photon cross section for two parallel linearly polarized photons of equal energy in units of  $10^{-50} \text{ cm}^4 \text{ s}$ ,  $\Omega$  is the two-photon polarization, %D is the percentage of doubly excited configurations,  $\phi$  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				
			$\Delta E$	$f$	$\xi_{11}$	$\Omega$	$\Delta E$	$f$	$\xi_{11}$	$\Omega$	%D
biphenyl $\phi = 0^\circ$											
$L_x(-)$	$B_{1u}$	l	38.8	0.8328			38.9	0.3391			0.3
$L_b(+)$	$B_{2g}$		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
$L_x(+)$	$A_g$		48.6		69.90	0.78	45.1		2.10	0.90	1.6
$B_b(+)$	$B_{2g}$		48.5		0.02	1.50	50.2		0.01	1.50	4.3
$B_x(-)$	$B_{1u}$	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 $\phi = 30^\circ$											
$L_b(-)$	$B_2$	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
$L_x(-)$	$B_1$	l	40.1	0.7779	0.08	1.50	40.4	0.3119	0.00	1.50	0.3
$L_x(+)$	A		48.5		60.75	0.78	45.1		0.89	0.94	0.9
$B_x(-)$	$B_1$	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
$L_x(-)$	$B_2$	l	38.9	0.5020	0.30	1.50	38.9	0.0319	0.13	1.50	1.4
$L_x(+)$	$A_1$	s	46.5	0.0164	33.18	0.71	44.0	0.0011	1.25	0.91	1.5
$B_x(-)$	$B_2$	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 prob-

lem 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 ex-

change (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  $B_{3g}$

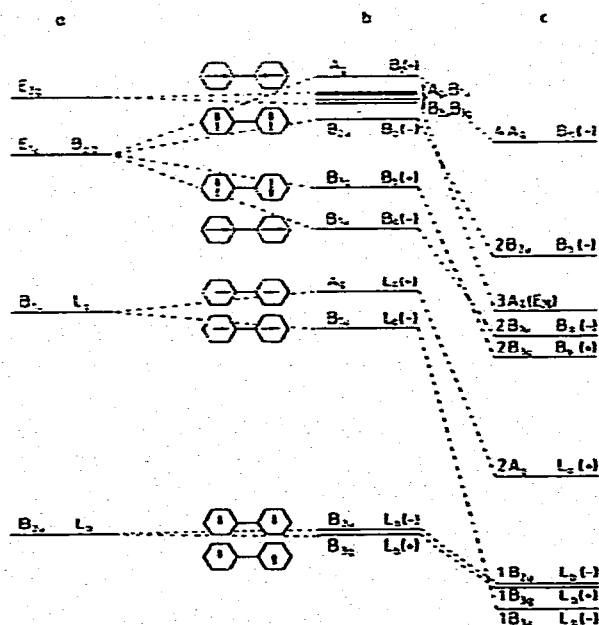


Fig. 1. Schematic development of the  $\pi\pi^*$  excited states for planar biphenyl from the parent benzene states: (a) parent states, (b) exciton approximation, (c) comparison to CNDO SCDI results.

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	$\Delta E$ ( $\text{cm}^{-1}$ )	phase or solute	ref.	sym.	pol.	$\Delta E$ ( $\text{cm}^{-1}$ )	phase or solute	ref.	sym.	pol.			
one-photon absorption														
H1	$L_b(+)$	$\leftarrow$ GS	0-0	33816	argon matrix 6.5 K	73	$B_{2g}?$	0-0	33773	vapor	63			
			0-0	33373	0-0 of fluorescence <i>n</i> -heptane matrix 77 K	66		0-0	33783	supersonic expansion	62			
			0-0	33348	0-0 of fluorescence <i>n</i> -heptane matrix 4.2 K	67	$B_2$	0-0	33174	<i>n</i> -heptane matrix 15 K	64			
			0-0	33128	crystal 4.2 K	67	$B_{2g}$	0-0	33200	heptane	90			
								0-0	33300	ethanol				
								0-0	33250	ethanol glass 77 K	24	$B_2$	1	
								0-0	32900	crystal reflection	33	$B_2$	1	
								0-0	33039	crystal 15 K	64	$B_2$	1	
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	$B_1$	1	max.	37600	ethanol glass 77 K	24	$B_2$	1
			max.	39700	polyethylene matrix	34	$B_1$	1	max.	35100	polyethylene	34	$B_2$	1
			max.	39000	crystal reflection	72	$B_{1u}$	1	max.	37100	crystal reflection	33	$B_2$	1
X	$B_b(+)$	$\leftarrow$ GS						sh	44200	heptane	90			
								sh	44200	ethanol				
								max.	44000	ethanol glass 77 K	24	$B_2$	1	
								sh	43600	polyvinylalcohol	35	$B_2$	1	
								sh	44400	polyethylene	34	$B_2$	1	
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	$B_2(-)$	$\leftarrow$ GS	max.	51700	vapor ( $f = 0.65$ )	72		max.	48900	heptane	90			
			max.	49800	light petroleum	90		max.	48100	polyethylene	34	$B_2$	1	
			max.	49500	polyethylene	34	$B_1$	1	max.	47400	crystal reflection	33	$B_2$	1
			max.	50000	crystal reflection	72	$B_{1u}$	1						
			max.	57300	vapor ( $f = 0.10$ )	72		max.	52600	crystal reflection	33	$B_2$	1	
			sh	56200	crystal reflection	72	$B_{1u}$	1						
			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	$B_{1u}$	1						

(continued on next page)

Table 3 (continued)

Assignment		Biphenyl			Fluorene		
empirical	this work	$\Delta E$ ( $\text{cm}^{-1}$ )	phase or solute	ref. sym. pol.	$\Delta E$ ( $\text{cm}^{-1}$ )	phase or solute	ref. sym. pol.
two-photon excitation							
a = H1	$L_b(+)\leftarrow\text{GS}$	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	$\text{CCl}_4$	6 B			
b	vibronic	max. 35600	ethanol	?	max. 35700	benzene	7 $A_1$
		36000					
		-39000	$\text{CCl}_4$	6 ?	max. 34800	ethanol	
c		max. 38100	ethanol	A	max. 38100	cyclohexane	7 $A_1$
d	$L_a(+)\leftarrow\text{GS}$	sh 40000	ethanol	A	sh 40000	ethanol	$A_1$
e	$A(E_{2g})\leftarrow\text{GS}$	43000			42000		
		-47000	$\text{CCl}_4$	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 transi-

tion (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  $33754\text{ cm}^{-1}$ , 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  $626\text{ cm}^{-1}$   $b_{2u}$  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  $45000\text{ cm}^{-1}$ , 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  $35500\text{ cm}^{-1}$  [33,64]. This corresponds to a shallow minimum at  $36000\text{ cm}^{-1}$  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  $\approx 35700\text{ cm}^{-1}$ . Taken together, these findings indicate that the onset of the H2 band in fluorene is located somewhere between  $35000$  and  $36000\text{ cm}^{-1}$ . 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.  $40500\text{ cm}^{-1}$ ) than in fluorene (max.  $37500\text{ cm}^{-1}$ ). 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

$\approx 45000\text{ cm}^{-1}$  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  $\phi$  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  $50000\text{ cm}^{-1}$  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  $70000\text{ cm}^{-1}$ . 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  $57300\text{ cm}^{-1}$ , a strong long axis polarized band at  $61800\text{ cm}^{-1}$  ( $f=0.67$ ), and a further weak short axis polarized band at  $67000\text{ cm}^{-1}$  ( $f=0.07$ ). Tanaka [33] has studied the crystal reflection spectra of fluorene up to  $\approx 54000\text{ cm}^{-1}$ . He identified a further long axis polarized band with maximum at  $52600\text{ cm}^{-1}$  and a short axis polarized band at  $\approx 54000\text{ cm}^{-1}$ .

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  $\Omega$  indicating that most of the two-photon

intensity above  $39000\text{ cm}^{-1}$  is related to final states of symmetry A. No clear decision, however, is reached as to whether the two-photon absorption between  $36000$  and  $39000\text{ cm}^{-1}$  is due to an

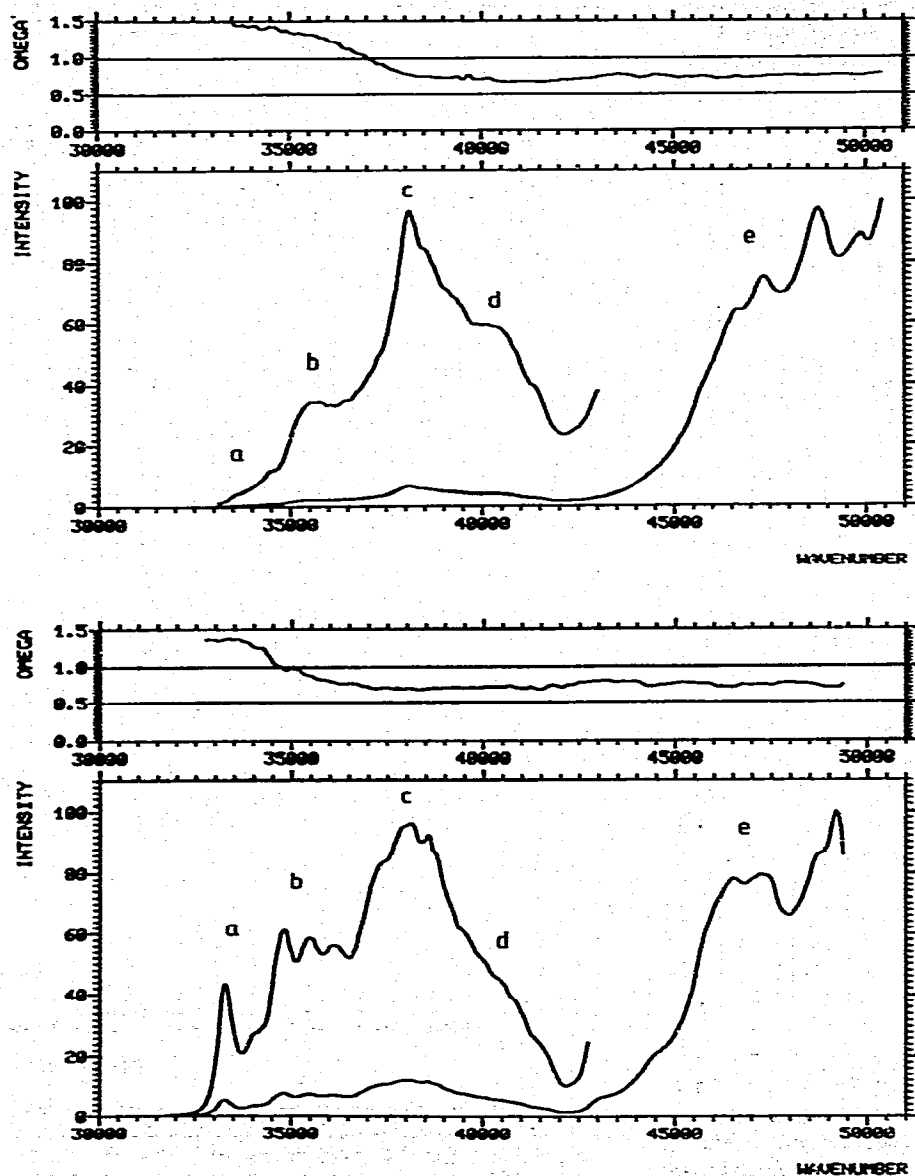


Fig. 2. Two-photon excitation spectra for biphenyl and fluorene for two parallel linearly polarized photons of equal energy ( $\delta_{\parallel}$ ) in arbitrary units. The two-photon polarization parameter is given on top of each spectrum.

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  $43000\text{ cm}^{-1}$ . For fluorene, definite assignments for an  $A_1$  state at  $\approx 38000\text{ cm}^{-1}$  and again at least one  $A_1$  state above  $42000\text{ cm}^{-1}$  are made. From a pronounced minimum in  $\Omega$  at  $35700\text{ cm}^{-1}$  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  $\Omega$  which generally can lie between 0 and 1.5 is therefore 1.5 for all these transitions. For transitions which have A symmetries,  $\Omega$  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  $\Omega$  found by these authors in the first part ( $33000\text{--}37000\text{ cm}^{-1}$ ) 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 ( $32000\text{--}42000\text{ cm}^{-1}$ ) shows a distinct substructure: a very weak shoulder starting at  $\approx 33000\text{ cm}^{-1}$ , a shallow maximum at  $35600\text{ cm}^{-1}$ , a sharp maximum at  $38000\text{ cm}^{-1}$ , and another shoulder at  $\approx 40000\text{ cm}^{-1}$ . These four structures are labelled a, b, c and d in fig. 2. The two-photon polarization parameter  $\Omega$  starts with a value close to the theoretical upper limit 1.5 in the region of structure a

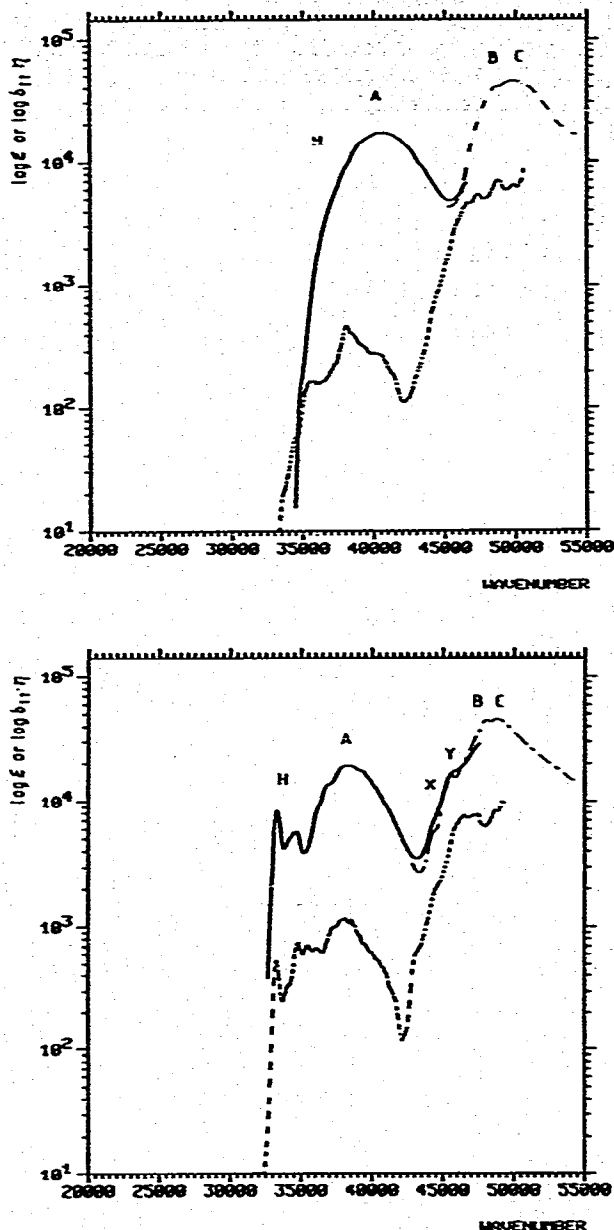


Fig. 3. One-photon absorption (—) and two-photon excitation (-----) spectra for biphenyl (top) and fluorene (bottom) in ethanol at room temperature.  $\eta\delta_{\pi\pi}$  in arbitrary units. ----- OPA for biphenyl in light petroleum at room temperature [90]. ---- OPA for fluorene in heptane at room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

and reaches a value of  $\approx 0.7$  in the vicinity of maximum c. For the remainder of the spectrum,  $\Omega$  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,  $\Omega$  drops from  $\approx 1.4$  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  $40000 \text{ cm}^{-1}$ ,  $\approx 1500 \text{ cm}^{-1}$  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  $48000 \text{ cm}^{-1}$ , 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  $\approx 43000 \text{ cm}^{-1}$ , 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  $\approx 2000 \text{ cm}^{-1}$  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  $\Omega$  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  $\Omega$  curve drops from  $\approx 1.3$  to  $\approx 1.0$  at the beginning of structure b and shows a distinct inclination at  $34700 \text{ cm}^{-1}$ , again indicating either a superposi-

tion 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  $\phi$  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

$\text{cm}^{-1}$  in the crystal [67];  $571 \text{ cm}^{-1}$  in an argon matrix [73]) A change in the order of the first two excited states with increasing twist angle  $\phi$ , 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  $\phi$ . This argument is difficult to understand when we consider the nature of the first two excited states [75] and the nearly  $\phi$  independent excitation energies for  $L_b(+)\leftarrow\text{GS}$  and  $L_b(-)\leftarrow\text{GS}$  found in almost all calculations. In addition, the assumption of a strongly  $\phi$  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  $L_b(-)\leftarrow\text{GS}$  to be slightly two-photon allowed for  $\phi = 30^\circ$ . This would allow an assignment of band a to  $L_b(-)\leftarrow\text{GS}$  and of band b to  $L_b(+)\leftarrow\text{GS}$  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  $L_b(+)$  or  $L_b(-)$ , nor could this question be resolved from the high-resolution spectra [71]. In fluorene, structure b could result from  $L_b(-)\leftarrow\text{GS}$  since  $L_b(-)$  belongs to symmetry  $A_1$ . The maximum at  $34800 \text{ cm}^{-1}$ , however, lies at lower energies than the estimated 0-0 transition of  $L_b(-)\leftarrow\text{GS}$  (table 3). Since we were not able to confirm the pronounced minimum in  $\Omega$  at  $35700 \text{ cm}^{-1}$  observed by Drucker and McClain [7], we assign the main body of structure b as vibrational structure belonging to  $L_b(+)\leftarrow\text{GS}$ . The drop in  $\Omega$  between  $34000$  and  $35000 \text{ cm}^{-1}$  indicates that some of the intensity in this energy range is due to vibronic coupling between  $L_b(+)$  and  $3A_1(L_b(+))$ . Above  $35000 \text{ cm}^{-1}$ ,  $L_b(-)$  also may contribute to structure b but definite assignments cannot be made from our low-resolution spectra.

The assignment of the A band to  $L_a(-)\leftarrow\text{GS}$  is well established and does not need further elaboration. All calculations yield the experimentally observed high-energy shift with increasing  $\phi$ . 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  $1000 \text{ cm}^{-1}$  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  $A_1$ , respectively. We assign both bands to  $L_a(+)\leftarrow\text{GS}$ . The calculated two-photon cross section is about ten times as large for this transition as for  $L_b(-)\leftarrow\text{GS}$ . In twisted biphenyl and in fluorene the strong one-photon allowed transition  $L_a(-)\leftarrow\text{GS}$  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  $L_2(-)$ . On the other hand,  $L_2(+)\leftarrow$ GS will not be observable in the OPA spectrum because of the presence of the strong one-photon allowed A band.  $L_2(+)\leftarrow$ 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  $L_2(+)\leftarrow$ GS is  $\approx 5000\text{ cm}^{-1}$  too high, compared to the one-photon allowed transitions  $B_b(-)$ ,  $B_2(-)$ , and  $L_2(+)\leftarrow$ GS. Inclusion of DEC yields a pronounced stabilization of  $L_2(+)$  with respect to the other states (table 2), but this stabilization is not large enough to produce the experimentally observed energy separations.

Above  $45000\text{ cm}^{-1}$  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  $B_2(-)\leftarrow$ GS (long axis polarized) for band C. Our calculations (table 2) predict nearly the same energy for  $B_2(-)$  and  $B_b(-)$  as long as only SEC are considered. With inclusion of DEC,  $B_2(-)$  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  $B_2(-)$ . 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  $\approx 45500\text{ cm}^{-1}$  (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  $L_2(+)\leftarrow$ 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  $B_2(-)$  and  $B_2(+)$  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  $50000\text{ cm}^{-1}$ .

## 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  $\approx 51000 \text{ cm}^{-1}$  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.

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