

NEW EXPERIMENTAL INFORMATION FROM TWO-PHOTON SPECTROSCOPY  
AND COMPARISON WITH THEORY

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**Abstract** - From a specially designed experiment, allowing the measurement of two-photon absorption spectra and two-photon polarization parameters over a wide spectral range new experimental information is obtained on the location of electronically excited states usually not seen in the UV-spectrum. By comparison with theory it is shown that in most of the examples investigated up to now the ordering of the low lying excited states is different from what is usually expected. Correlation strongly influences the ordering especially in those systems which consist of loosely coupled  $\pi$ -systems.

I. INTRODUCTION

In 1967 the great Czechoslovakian quantum chemist Jaroslav Koutecky published a paper with the unspecific title '*Some properties of semiempirical hamiltonians*' (1). Among other items, Koutecky pointed out in this paper, that the number of low lying electronically excited states of conjugated  $\pi$ -systems might be considerably larger and their ordering quite different from what was usually believed. As examples he showed calculations for butadiene and hexatriene which lead to the result that there might exist a low lying singulet state of symmetry  $A_g$  in the vicinity or even below the lowest excited singlet state of symmetry  $B_u$ . When the first experimental evidence for the existence of a low lying excited singlet state of symmetry  $A_g$  was found in diphenyl-octatetraene and in undecapentaene (2-4), the prediction of Koutecky had been overlooked. The reason for the appearance of these low lying excited  $A_g$ -states was rediscovered by Schulten and Karplus (5), and later on analysed in great detail by Schulten, Onnime and Karplus (6). The basic result of all theoretical studies, which will be explained in more detail in Section II, is:

A calculation scheme successful in the prediction of the UV-spectra of even a wide variety of unsaturated compounds is not sufficient to draw conclusions on the whole manifold of low lying excited states and on their relative ordering. Different calculation schemes can be developed which lead to nearly identical results for the UV spectra, but to totally different predictions for low lying excited states not seen in the UV spectrum, due to vanishing dipole transition moments.

The only possibility to decide between different theoretical approximations is a direct experimental observation of the dipole forbidden transitions. Such an experimental proof became possible after invention of tunable lasers, since in the intense photon field of a laser transitions can be caused by simultaneous absorption of two photons (7, 8). As selection rules are different for two-photon excitation compared to one-photon excitation (9), new and independent information may be obtained from the measurement of two-photon absorption spectra. It has yet been pointed out by Koutecky (1), that especially those A-states, which most drastically change their position in different calculation schemes, might be detectable with this type of spectroscopy.

Pioneering experimental work has been done by Bergman and Jortner (10) and especially by McClain and his coworkers (11). All spectra published up to 1980 were, however, not sufficient to give a genuine answer to the question whether the case of polyenes is an unusual exception or whether the order of low lying excited states is different from what is usually expected also in other molecules with a conjugated  $\pi$ -system (12). We therefore built up a specially designed experiment to measure two-photon absorption spectra with a resolution comparable to conventional UV-spectra and over an energy range as large as possible (13). In the present paper we give a survey of the results available up to now. It will be shown that in most molecules the number of

low lying states is larger than usually assumed.

## II. THEORY

In the usual MO picture where we start from delocalized molecular orbitals, the ground state  $\psi_0$  of a closed shell molecule is described by the orbital occupation A. Excited states are described in a configuration interaction scheme (CI) by superposition of singly (B, C, D), doubly (E) and higher excited configurations:

$$\psi = c_0 \psi_0 + \sum c_i^u \psi_i^u + \sum c_{ij}^{uv} \psi_{ij}^{uv} + \dots$$

The low lying excited states are usually assumed to result mainly from singly excited configurations (SEC). Correlation effects can lead, however, to a considerably mixing with doubly (DEC) and higher excited configurations.

In Pariser-Parr-Pople-type theories occupied and unoccupied orbitals of alternant hydrocarbons are strictly "paired" (14). In this approximation we find excited states to which configurations like C and D contribute with equal weight but in such a fashion that their individual transition moments either add (+states) or subtract (-states). Since -states only mix with -states in the CI-expansion, transitions from  $\psi_0$  to -states are forbidden for a one-photon excitation. Correspondingly, two-photon transitions from  $\psi_0$  to +states are forbidden under pairing symmetry. Since the "pairing theorem" only holds up to a certain limit of approximation, selection rules based on pairing symmetries are only approximately valid. From the UV spectra of alternant hydrocarbons we know, however, that the underlying assumption is not too bad. Transitions to -states are usually weak. In most cases a transition to a -state is only detectable if the -state is the lowest excited one (as e.g. in naphthalene or phenanthrene). The energetic position of the low lying -states is therefore usually not known experimentally.

Semiempirical calculation schemes like well parametrized PPP- (14, 15) or CNDO- (16) methods very successfully describe the energetic position and the relative intensity of the transitions showing up in the UV-spectrum. Due to this success, it was often assumed that these calculation schemes may also yield reasonable predictions for the position of states not directly observable in the UV-spectrum. It was first Koutecky (1) who pointed out that this assumption might not be true. He showed that correlation effects in excited states described by a non-negligible contribution of doubly and higher excited configurations in the CI-expansion may be quite different for + and -states, depending on the steepness of the function  $\gamma(R)$ , by which the distance dependence of the electron interaction (two center electron repulsion integrals) is described in the theoretical model. This is most easily understood if we look at the limiting cases of very short range and long range electron interaction (1, 6). In the limit of very short range electron interaction, the low lying excited states all result from covalent structures in the VB-description (Fig. 1). Excited states resulting from ionic structures lie at considerable higher energies. In the limit of long range electron interaction the energy of the excited states is best described by orbital energy differences in the usual MO-picture. In this approximation + and -states are degenerate. It can now be shown (6) that with decreasing range of the electron interaction +states of the MO description correlate with ionic states of the VB description and -states with covalent states. From this

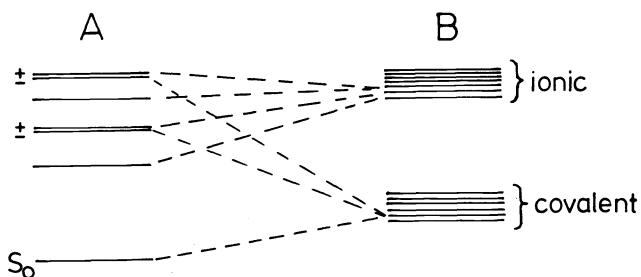
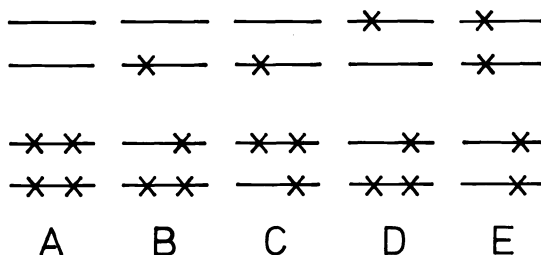


Fig. 1 - Correlation between excited states described in different limiting cases. A: MO-picture, long range electron interaction. B: VB-picture, short range electron interaction.



correlation (Fig. 1) it becomes obvious that with decreasing range of the electron interaction the number of low lying covalent or  $\pi$ -states increases. For an electron interaction of intermediate range it is therefore quite possible that a calculation scheme which gives the correct order of ionic or  $\pi$ -states does not lead to a correct prediction of the covalent states. To decide whether the range of the actual electron interaction is short or long, one has to know the location of the covalent states.

In order to compare our experimental results with calculations which either include correlation effects or not we use the following two calculation schemes (17):

- i The standard CNDO/S procedure invented by Del Bene and Jaffé where one takes into account 60 SEC and uses the Mataga-Nishimoto formula (18) to describe the electron interaction  $\gamma(R)$ . These calculations are labelled SCI in section IV.
- ii A CNDO/S procedure where we include the 200 lowest energy-selected singly and doubly  $\pi\pi^*$ -excited configurations and use the Pariser formula (19) to describe  $\gamma(R)$ . These calculations are labelled SDCI in section IV.

These two calculation schemes have been found to be sufficiently sensitive to discriminate situations where correlation effects become important (17).

In addition to excitation energies and oscillator strengths ( $f$ ) we have calculated cross sections for TPA (definitions are given in section III) using a method described in (12). It has to be mentioned that the nonvalidity of the pairing theorem has great influence on the calculated TPA cross sections. While  $f$ -values calculated in the CNDO/S approximation (where the pairing theorem does not hold) are not too different from those calculated in PPP-approximation (where the pairing theorem holds), one finds large differences in the case of TPA cross sections. For example, the fourth excited state in naphthalene (Fig. 2) is an  $A_g^+$ -state and a transition to this state from the ground state is therefore two-photon forbidden in PPP-approximation. In CNDO the TPA cross section calculated for this transition is even larger than the one for the third transition  $1A_g \rightarrow 1B_{3g}$  in accordance with the experimental finding.

### III. TWO-PHOTON SPECTROSCOPY

In two-photon absorption (TPA) we measure the simultaneous absorption of two quanta  $h\nu_1$  and  $h\nu_2$  of incident radiation. Since the cross section for TPA is in the order of  $1 \text{ gm} = 10^{-50} \text{ cm}^4 \text{ s}$ , TPA became only observable in the intense photon field produced by lasers. There often is only one laser used in order to stimulate TPA (single beam experiment). In this case we have  $h\nu = h\nu_1 = h\nu_2$ . The selection rules for one- and two-photon transitions to electronically excited states are similar to the selection rules for IR and Raman scattering (also a two-photon process) (9, 17). This means that for molecules with a center of symmetry, the principle of mutual exclusion holds: from a gerade ground state, transitions are only allowed to ungerade excited states in one-photon absorption (OPA) and to gerade excited states in TPA. This is the reason why two-photon spectroscopy is so attractive as a tool in the search and the investigation of  $g \leftrightarrow g$ -transitions.

If the sample is a solution two independent molecular quantities can be measured by a single beam experiment (20). Most usefully these two quantities are expressed as a two-photon absorption cross section  $\delta$ , e.g.

$\delta_{\uparrow\uparrow}$  the TPA cross section for two equally linearly polarized photons

and a polarization parameter

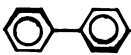
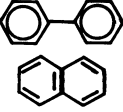
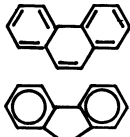
$$\Omega = \frac{\delta_{\text{cc}}}{\delta_{\uparrow\uparrow}} \quad \begin{array}{l} 0 < \Omega < 3/2 \text{ in general} \\ 1/4 < \Omega < 3/2 \text{ in planar systems} \end{array}$$

where  $\delta_{\text{cc}}$  is the TPA cross section for two equally circularly polarized photons.  $\Omega$  is a symmetry indicator, since its value is often determined by symmetry alone, as shown in tab. 1. Similar to the degree of polarization (PG) in OP-spectroscopy,  $\Omega$  seldom reaches its limiting values, due to overlapping bands and vibronic coupling. However, as well as in the OP case, the relative trends in the  $\Omega$ -curve (maxima or minima) give a very good indication for the symmetry of the corresponding transition.

In order to use two-photon spectroscopy in the way outlined above, one needs TPA-spectra ( $\delta(\nu)$  and  $\Omega(\nu)$ ), which cover nearly the same spectral range as conventional UV-spectra (onset of absorption to about  $50.000 \text{ cm}^{-1}$ ) and which are of comparable resolution. Since spectra which fulfil all these conditions

were not available in the literature, we built up our own experiment. Therefore, the aim of our work is clearly different from the widely and successfully done high resolution work in two-photon spectroscopy.

TABLE 1. Possible irreducible representations and nonvanishing matrix elements for  $f$  and  $\delta$  of  $\pi\pi^*$ -excitations in different symmetries

$D_2$ 				$D_{2h}$ 				$C_{2v}$ 			
	$f$	$\delta$	$\Omega$		$f$	$\delta$	$\Omega$		$f$	$\delta$	$\Omega$
A	$-x^2, y^2, z^2$			$A_g$	$-y^2, z^2$			$A_1$	$z, y^2, z^2$		
$B_1$	$z$	$xy$	$3/2$	$B_{1u}$	$z$	-	-	$B_2$	$y$	$yz$	$3/2$
$B_2$	$y$	$xz$	$3/2$	$B_{2u}$	$y$	-	-				
$B_3$	$x$	$yz$	$3/2$	$B_{3g}$	-	$yz$	$3/2$				

From the different possibilities to measure TPA cross-sections, we have used the "fluorescence method", where the  $S_1 \rightarrow S_0$  emission caused by a two-photon  $S_0 \rightarrow S_n$  excitation is observed (21, 10). With this method we do not directly obtain  $\delta(\nu)$ , but instead  $\delta(\nu)\eta(\nu)$ , where  $\eta(\nu)$  is the wave length dependent emission rate. Measured spectra should resemble all basic features of the true  $\delta$ -curve as long as  $\eta(\nu)$  is a slowly varying function, which is very likely in the examples studied here.  $\Omega$ , however, is not influenced by  $\eta$ . All the details of our experimental setup are described in ref. (13), especially the method we used in order to obtain "polarization control" necessary to measure  $\delta_{\uparrow\uparrow}$  and  $\delta_{\circ\circ}$  with comparable accuracy. In this connection we would like to mention that due to the limited tuning range of a single dye, the spectra we show in section IV had to be constructed of up to 13 partial spectra. For the sake of comparison with the OPA spectra the energy scale shows already the excitation energy of the molecule which is twice the energy of the exciting radiation. All spectra are taken at room temperature.

#### IV. RESULTS AND DISCUSSION

Our two-photon spectra of naphthalene, acenaphthene, and anthracene have been published together with detailed discussions (22). In the present context it is therefore sufficient to summarize the main results.

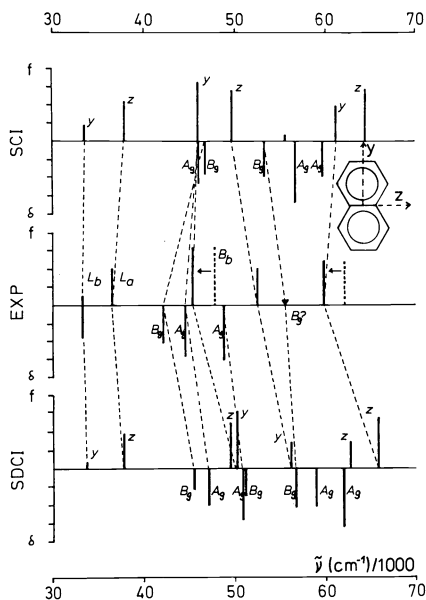


Fig. 2

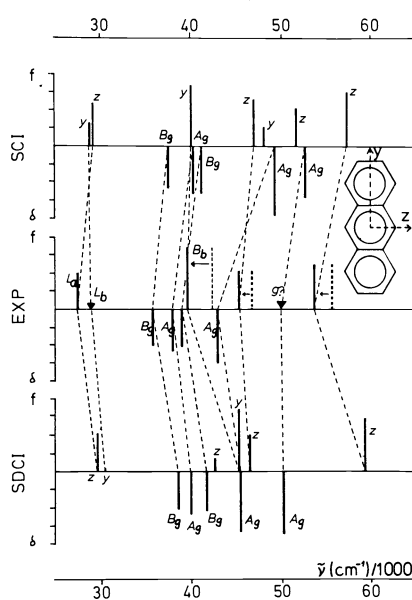


Fig. 3

Comparison of experimental data (EXP) with the results of SCI and SDCI calculations. The length of the upper bars corresponds to  $\log f$ , that of the lower bars to  $\log \delta_{\uparrow\uparrow}$ . Arrows indicate solvent shifts.

**Naphthalene (Fig. 2).** For a long time the  $2B_{2u}$  state was assumed to be the third excited singlet state in naphthalene. This state is responsible for the intense OPA at  $45.000\text{ cm}^{-1}$  called  ${}^1B_b$ -band in Platt's nomenclature (23) (As far as possible the Platt nomenclature is given in addition to the symmetry notation). It is now certain that two g-states lie below  $2B_{2u}$ . Their order with increasing energy, is  $1B_{3g}$  and  $2A_g$ , confirming the assignment of Mikami and Ito (24) and not the one given later by Tavan and Schulten (25). A further  $A_g$ -state (probably  $3A_g$ ) is found at about  $50.000\text{ cm}^{-1}$ , leading to an intense TPA-band. The appearance of a further  $A_g$ -state in the vicinity of  $2B_{2u}$  cannot be reproduced by PPP- or CNDO-type calculations which take into account only SEC, even if the parameters of these semiempirical methods are varied within reasonable limits. Only after inclusion of DEC the order of the excited states is in satisfying agreement with the now established experimental sequence. This agreement does not only hold for excitation energies and f-values, but also for the relative two-photon intensities. For the comparison of calculated and observed excitation energies one has to take into account that the intense one-photon allowed transitions exhibit much stronger solvent shifts (up to  $3.000\text{ cm}^{-1}$ ) than those with low or even zero dipole-transition moments. The available band positions observed in gas phase are indicated as hatched lines in the figures.

**Anthracene (Fig. 3).** In anthracene two g-states ( $1B_{3g}$  and  $2A_g$ ) lie certainly and a third one ( $2B_{3g}$ ) most likely below  $2B_{2u}$  the state responsible for the very intense OPA at about  $40.000\text{ cm}^{-1}$  ( ${}^1B_b$ ). Again a further g-state (probably  $3A_g$ ) is found at slightly higher energies than  $2B_{2u}$ . Similar to naphthalene, the appearance of three g-states in the gap between the first and the second band of the OPA spectrum and especially the close energetic neighbourhood of  $3A_g$  and  $2B_{2u}$  can only be reproduced if DEC are included in the CI-calculation. From the first ten states ( $E-E_0 < 48.000\text{ cm}^{-1}$ ) predicted by such a calculation, nine are now assigned experimentally.

**Biphenyl (Fig. 4).** We now turn to a molecule which with respect to its  $\pi$ -system can be considered to be built from two weakly coupled subunits. In solution biphenyl is not planar as it is in the crystal. The torsion angle between the planes of the two phenyl rings lies in the order of  $30^\circ$ . In fluorene the two phenyl rings are forced to coplanarity, but the symmetry is reduced to  $C_{2v}$ . The coordinate systems used are shown in table 1, together with the irreducible representations of the possible  $\pi\pi^*$ -excitations.

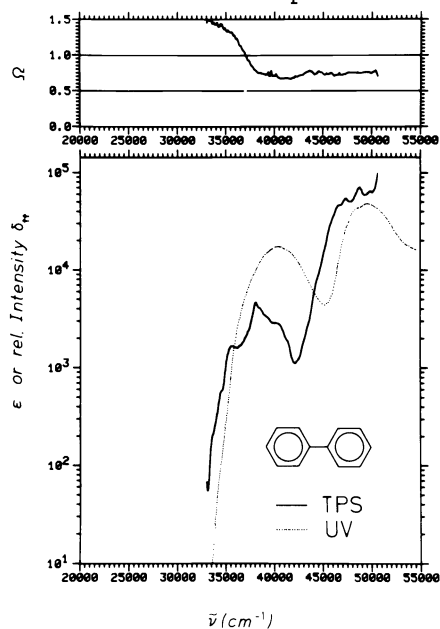


Fig. 4a. Experimental TPA-spectra  $\delta_{++}$  and  $\Omega$  (TPS) and conventional UV-spectrum (UV) of biphenyl

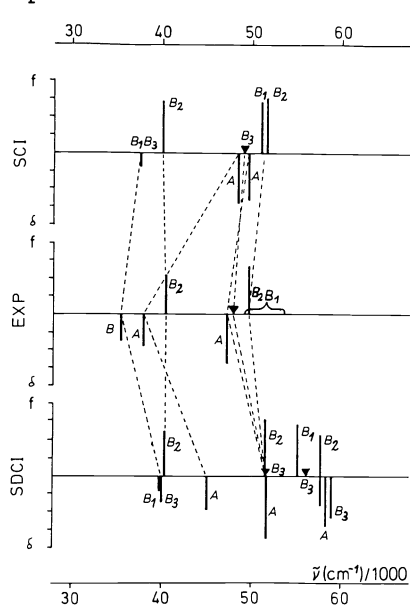


Fig. 4b. Comparison of experimental data (EXP) with the results of SCI and SDCI calculations. Presentation as in Fig. 2.

The OPA spectrum (Fig. 4a) consists of only two broad bands with maxima at  $40.500$  and  $49.500\text{ cm}^{-1}$ , which can be assigned to  $B_2$ -transitions (26). From comparison with fluorene and also o-methylated biphenyls (27) it is, however, known that a further band (called H-band) is hidden under the long wavelength tail of the first  $B_2$ -band. A further  $B_3$  transition has been assumed to lie

at about  $47.000\text{ cm}^{-1}$  and a  $B_1$  transition somewhere between  $49.000$  and  $54.000\text{ cm}^{-1}$  (27). Theory predicts not only one but two close lying transitions at the beginning of the spectrum with symmetry  $B_1$  and  $B_3$ . Experimentally the lowest excited state was found to be  $1B_3$ , when biphenyl is embedded in a durene matrix (28). Since in this matrix biphenyl is most likely planar as it is in the crystal, the order of the first two excited states need not be necessarily the same in solution. In fluorene the  $1B_3$  transition of biphenyl becomes  $1B_2$ , which means that it can couple to the allowed  $B_2$  transitions. Correspondingly,  $1B_2$  shows up as a well resolved band in the OPA of fluorene.

TPA (Fig. 4a) starts  $1500\text{ cm}^{-1}$  earlier than OPA. In the energy range  $33000$  to  $36.000\text{ cm}^{-1}$   $\Omega$  clearly indicates B symmetry for the corresponding transition (Biphenyl is an example where we really observe the upper limiting value of  $\Omega$ ). It is not possible to decide whether this absorption is due to  $1B_1$  or  $1B_3$  or even to a superposition of both. Theory predicts the higher TPA cross section for  $1B_3$  (compare Fig. 4b). The most interesting feature in the TPA spectrum of biphenyl is the band starting at  $38.000\text{ cm}^{-1}$ . Without knowledge of the polarization parameter one probably would have assigned this TPA to the  $1B_2$  transition which becomes two-photon allowed in  $D_2$  symmetry. For  $\Omega$  there is, however, no doubt that this absorption results from a transition to an A-state, as well as the strong TPA starting at  $42.500\text{ cm}^{-1}$ . Corresponding transitions with A-symmetry are also found in the TPA spectrum of fluorene.

The finding of such a low lying A-state in biphenyl-type systems is completely unexpected. In earlier investigations (26, 27, 28) it is assumed that  $2A$  lies somewhere around the beginning of the second strong OPA which means at least  $7.000\text{ cm}^{-1}$  higher in energy than it is now located. Our SCI calculation (Fig. 4b) yields the same result as these earlier studies. Though inclusion of DEC stabilizes  $2A$  with respect to all other low lying excited states, the calculated stabilization is by far too small to bring  $2A$  below  $1B_2$ . The ratios of the calculated TPA cross sections are nevertheless in good agreement with the observed intensities. Especially we do not find any significant two-photon intensities for the transitions  $1B_2$  and  $2B_2$  which dominate the one-photon spectrum. This is not astonishing, since we have only a slight distortion from  $D_{2h}$ -symmetry where transitions to  $B_{2u}$ -states are two-photon forbidden.

Similar results as for biphenyl and fluorene have been found for *stilbene* (13b). Four  $A_g$  transitions have been detected in the TPA spectrum with the same relative intensity as predicted by the SDCl calculation. In relation to the  $B_u$  transitions seen in OPA, the  $A_g$  states lie in the mean  $4000\text{ cm}^{-1}$  lower than calculated. Compared to the SCI result, the mean shift of the observed  $A_g$  states is, in relation to the  $B_u$  states, again in the order of  $7.000\text{ cm}^{-1}$ .

Phenanthrene (Fig. 5). As a last example we now consider an alternant hydrocarbon which does not have a center of symmetry. The same transitions are therefore expected to be seen in the one- and in the two-photon absorption spectrum.

In OP-spectroscopy seven  $S \rightarrow S_n$  transitions have been observed below  $53.000\text{ cm}^{-1}$  (13b). A further state lying at about  $48.700\text{ cm}^{-1}$  was observed in  $S_1 \rightarrow S_n$  spectroscopy (30). This state is most likely not identical with the state around  $47.300\text{ cm}^{-1}$  seen in the UV spectrum. Situations should lead to gerade final states.

In TPA (Fig. 5a) the transitions to  $2A_1$  ( $1L_b$ ) and  $1B_2$  ( $1L_a$ ) are of similar intensity, while in OPA  $1L_b$  is about a hundred times weaker than  $1L_a$ . The  $3A_1$  state ( $1B_b$ ) which only had been detected by polarization measurements in OP-spectroscopy (31) now leads to the most intense transition, whereas  $3B_2$ , responsible for the dominant band ( $1B_a$ ) in OPA, does not show up in TPA. Even in the  $\Omega$  spectrum we do not find an upward trend in the range of the  $1B_a$ -band as one would expect for an excited state of  $B_2$ -symmetry. This experimental observation is in full accordance with our theoretical results where the intensity ratios  $L_b/L_a$  and  $1B_b/1B_a$  are reversed, when we compare one- and two-photon absorption. In spite of the lack of a center of symmetry we thus still find relatively strong transitions in TPA, where we find weak transitions in OPA and vice versa. This seems to prove right for transitions  $5A_1$  and  $4B_2$  lying around  $46.000\text{ cm}^{-1}$ , too. While in biphenyl a similar observation could be explained by an only slight distortion from a system with a center of symmetry, such an explanation is no longer possible in phenanthrene. Another interesting feature in the TPA spectrum of phenanthrene is the occurrence of an apparently  $B_2$  polarized transition around  $35.000\text{ cm}^{-1}$  clearly seen in the  $\Omega$  spectrum. This transition has not been observed up to now, but its appearance again is in accordance with our theoretical results (see Fig. 5b).

A more detailed analysis of the one- and two-photon spectra of phenanthrene (13b) leads to the assignment given in Fig. 5b. All calculated transitions

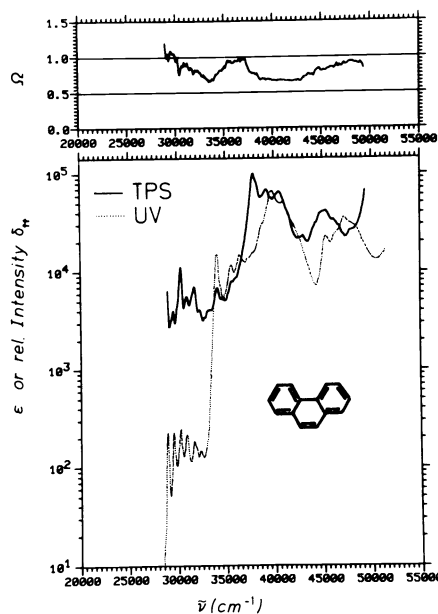


Fig. 5a. Experimental TPA-spectra  $\delta_{\uparrow\uparrow}$  and  $\Omega$  (TPS) and conventional UV-spectrum (UV) of phenanthrene

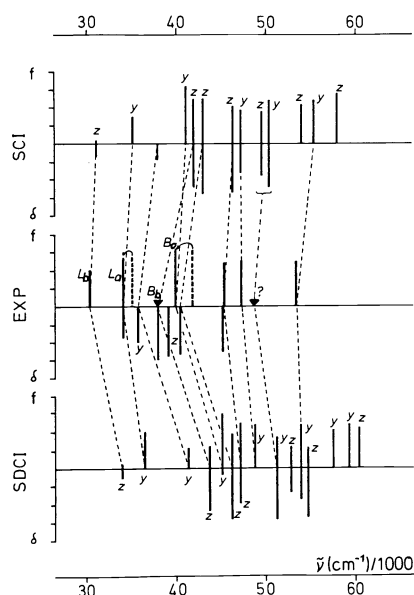


Fig. 5b. Comparison of experimental data (EXP) with the results of SCI and SDCI calculations. Presentation as in Fig. 2

with  $\Delta E < 50.000 \text{ cm}^{-1}$  can now be assigned to bands appearing either in the one- or in the two-photon spectrum. It is also seen from Fig. 5b that inclusion of DEC does not lead to any dramatic effects in the case of phenanthrene which is up to now the only investigated example for a molecule that does not have a center of symmetry and/or consists of weakly coupled partial systems.

## CONCLUSIONS

The examples discussed above clearly show how useful two-photon spectroscopy is for the investigation of electronically excited states. They also show how important the knowledge of  $\Omega$  is, if one tries to make assignments by comparison with theoretical results. The examples studied up to now are, however, only few. Generalizations have therefore to be handled with care. Within this limit the following results seem to show up behind the individual data:

- i In cases where the selection rules for one- and two-photon excitation are no longer mutual exclusive, due to the lack of a center of symmetry, the information obtained from TPA is still highly complementary to the one obtained from OPA. At least among the low lying  $S_0 \rightarrow S_n$  excitations in alternant hydrocarbons we find strong transitions in TPA, where we observe weak transitions in OPA and vice versa.
- ii In benzoid aromatic hydrocarbons without a center of symmetry like phenanthrene we do not find unexpectedly low lying A-states. The spectra are described equally well with and without inclusion of DEC.
- iii In benzoid aromatic hydrocarbons with a center of symmetry g-states are found at lower energies than predicted by calculation schemes which only take into account SEC. In naphthalene 2 and in anthracene 3 g-states lie below the  $1B_{2u}$  state, the state responsible for the very strong  $1B_b$ -band in the OPA spectrum of these molecules. These g-states can no longer be neglected in the discussion of photophysical processes as for example the deactivation of higher excited states or energy transfer process. They may even be important for photochemical reactions. Inclusion of a limited number of DEC seems to be sufficient to describe both, the covalent and the ionic states at a similar level of accuracy, when a proper parametrization is used for the distant dependence of the electron interaction.
- iv In addition to the known examples (polyenes and  $\omega\omega'$ -diphenylpolyenes) we have found two new examples where strong correlation effects lead to the appearance of unexpectedly low lying excited states: biphenyl and stilbene. All these molecules have a  $\pi$ -system, consisting of weakly coupled

subunits (double bonds and benzene rings). In all these molecules one finds A-states which lie in relation to the B-states up to  $10.000\text{ cm}^{-1}$  lower than estimated by calculations including only SEC. SDCI calculations of a type which gives a satisfactory description in cases like naphthalene or anthracene lead to a considerable stabilization of these states, but the stabilization is not sufficient to describe the energetic position of these states properly. Inclusion of a greater amount of DEC and probably of higher excited configurations, too, seems to be necessary in these cases.

- v The relative intensity of the bands observed in TPA is described reasonably well in a CNDO/S type calculation which includes about 200 energy selected singly and doubly  $\pi\pi^*$ -excited configurations. As far as the presently available experimental information is concerned this statement seems to hold also in cases where this calculation scheme does not give the correct order of the low lying excited states, due to an insufficient description of correlation effects.

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