

Two-photon spectroscopy of dipole-forbidden transitions. II. Calculation of two-photon cross sections by the CNDO-CI method

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In the first paper of this series we investigated the applicability of a CNDO/S scheme including double excited configurations for the calculation of excitation energies of larger unsaturated molecules. In this paper we show that the same scheme is very useful for the prediction of two-photon transition probabilities. If the proper expansion is used, the results converge quite well with increasing number of intermediate states. We also show that the inclusion of double excited configurations is not only necessary to obtain better energies for dipole-forbidden transitions to "covalent" excited states but also to obtain the correct order of magnitude for two-photon cross sections.

I. INTRODUCTION

Conventional UV spectroscopy, which is based on one-photon processes, is the main source of our knowledge of excited states. Transitions which can be observed in this type of spectroscopy have to be dipole allowed. This leads to a considerable reduction in the number of excited states which are accessible for such an investigation. Information on the other excited states which are of some importance for molecular properties, such as polarizabilities, radiationless transitions, and photochemical behavior, is often restricted to theoretical estimates.¹ To obtain direct information on these states, experimental methods have to be used which allow the observation of transitions which are dipole forbidden for one-photon processes (DFT). Among the methods which can be used for this purpose, two-photon spectroscopy became an extremely powerful technique due to the fact that DFT are often allowed with respect to two-photon selection rules.⁴

The measurement of two-photon spectra is, however, only part of the problem. The other part is the interpretation and assignment of the measured data. From conventional UV spectroscopy, we know that theoretical estimates of excitation energies and transition probabilities are important guidelines for the solution of this problem. The quantity which governs the intensity of a given transition in TPS is the two-photon cross section (TPC). Unfortunately, the TPC is a second order quantity, which in principle depends on the entire manifold of excited states. Therefore, the question is as follows: To what extent can we successfully calculate TPC? This question is even more serious for larger molecules where we are forced to use semiempirical methods. Earlier calculations of TPC using π -electron approximations^{5,6} concerned special applications, and did not deal with the general applicability of the calculational scheme.

In this paper, we show that a CNDO/CI method, which we recently proved to be successful in calculating excitation energies of both dipole-allowed and "covalent" dipole-forbidden transitions,⁷ is also very suitable for the calculation of two-photon transition probabilities. In Sec. II, we start with a short outline of the theory of the TPC for randomly oriented molecules with special

consideration of different approximations. In Sec. III, we briefly discuss the method used for our numerical calculations. In Sec. IV, we investigate the convergence of different types of summation. In Sec. V, we compare our results for a variety of molecules with available experimental data (which in some cases leads to questions concerning assignments made in the past). Finally, in Sec. VI, we summarize the very few examples in which a comparison of the absolute TPC can be made.

II. THEORY OF TWO-PHOTON CROSS SECTION

In the dipole approximation, the transition probability for a two photon transition $i \rightarrow f$ at energy

$$E_{if} = E_f - E_i = \hbar\omega_1 + \hbar\omega_2 \quad (1)$$

is given by^{5,6}

$$\delta_{12}^{if} = \left(\frac{e}{m}\right)^4 \cdot \frac{4\pi^2 g(\omega_1 + \omega_2)}{c^2 \omega_1 \omega_2} \cdot |M_{12}^{if}|^2, \quad (2a)$$

$$M_{12}^{if} = \sum_k \left[\frac{(P_{ik} \cdot e_1)(P_{kf} \cdot e_2)}{E_{ik} - \hbar\omega_1 + i\Gamma} + \frac{(P_{ik} \cdot e_2)(P_{kf} \cdot e_1)}{E_{ik} - \hbar\omega_2 + i\Gamma} \right]. \quad (2b)$$

e_1 and e_2 are the polarization vectors of the absorbed photons with energy $\hbar\omega_1$ and $\hbar\omega_2$, respectively; $|i\rangle$, $|f\rangle$, and $|k\rangle$ are initial, final, and intermediate states, respectively; P 's are matrix elements of the momentum operator between indicated states; $g(\omega_1 + \omega_2)$ is a line shape function and all other symbols have their usual meanings. The sum runs over all possible intermediate states. δ is given in $\text{cm}^4 \text{sec}/\text{photon molecule}$. The Γ 's are damping factors which prevent unjustified resonances in cases where $\hbar\omega$ comes very close to the excitation energy of one of the intermediate states. An average value of 400 cm^{-1} has been recommended for Γ .^{2(d)} As we deal with low resolution spectra measured in solution, we only consider photon energies which are smaller than the first excitation energy E_{i1} :

$$\Delta E = E_{i1} - \hbar\omega > 0.$$

The smallest ΔE value which appears in our examples (Sec. V) is 4600 cm^{-1} . For ΔE values of this magnitude, inclusion of damping factors changes the calculated δ values by less than 1%. We therefore neglect the damping factors in our further treatment.

Equation (2b) can be rearranged as

$$M_{12}^{if} = \mathbf{e}_1 \mathbf{M}^{if} \mathbf{e}_1. \quad (3)$$

In Cartesian coordinates ($\alpha, \beta \in \{x, y, z\}$), the second rank tensor \mathbf{M}^{if} has the following components:

$$M_{\alpha\beta}^{if} = \sum_k \left(\frac{P_{ik}^\alpha \cdot P_{kf}^\beta}{E_{ik} - \hbar\omega_1} + \frac{P_{ik}^\beta \cdot P_{kf}^\alpha}{E_{ik} - \hbar\omega_2} \right). \quad (4)$$

The tensor \mathbf{M}^{if} is usually regarded to be the molecular property which corresponds to the transition moment in conventional UV spectroscopy. However, in contrast to the latter which does not depend on experimental conditions, \mathbf{M}^{if} depends on the partitioning of the excitation energy E_{if} onto the two photons. For any two states a and b , the identity

$$\mathbf{P}_{ab} = \langle a | m \nabla | b \rangle = \frac{im}{\hbar} E_{ba} \cdot \langle a | \mathbf{r} | b \rangle = \frac{im}{\hbar} E_{ba} \cdot \mathbf{R}_{ab} \quad (5)$$

allows the velocity form \mathbf{P}_{ab} of the transition matrix elements to be replaced by the corresponding dipole form \mathbf{R}_{ab} ⁹:

$$\delta_{12}^{if} = \frac{(2\pi e)^4}{(\hbar \cdot c)^2} \frac{g(\omega_1 + \omega_2)}{\hbar\omega_1 \hbar\omega_2} |\mathbf{e}_1 \tilde{\mathbf{S}}^{if} \mathbf{e}_2|^2, \quad (6a)$$

$$\tilde{\mathbf{S}}_{\alpha\beta}^{if} = \sum_k E_{ik} \cdot E_{kf} \left(\frac{R_{ik}^\alpha R_{kf}^\beta}{E_{ik} - \hbar\omega_1} + \frac{R_{ik}^\beta R_{kf}^\alpha}{E_{ik} - \hbar\omega_2} \right). \quad (6b)$$

Making further use of the commutator relations

$$\begin{aligned} [(\mathbf{e}_1 \cdot \mathbf{R}), (\mathbf{e}_2 \cdot \mathbf{P})] &= i\hbar(\mathbf{e}_1 \cdot \mathbf{e}_2), \\ [(\mathbf{e}_1 \cdot \mathbf{R}), (\mathbf{e}_2 \cdot \mathbf{R})] &= 0, \end{aligned} \quad (7)$$

the product of excitation energies ($E_{ik} \cdot E_{kf}$) can be replaced by the product of photon energies ($\hbar\omega_1 \cdot \hbar\omega_2$),^{5,9} which is independent of the summation index k :

$$\tilde{\mathbf{S}}_{\alpha\beta}^{if} = \hbar\omega_1 \hbar\omega_2 S_{\alpha\beta}^{if} \quad (i \neq f), \quad (8)$$

$$\delta_{12}^{if} = \frac{(2\pi e)^4}{(\hbar c)^2} g(\omega_1 + \omega_2) \hbar\omega_1 \hbar\omega_2 |\mathbf{e}_1 \mathbf{S}^{if} \mathbf{e}_2|^2, \quad (9a)$$

$$S_{\alpha\beta}^{if} = \sum_k \frac{R_{ik}^\alpha R_{kf}^\beta}{E_{ik} - \hbar\omega_1} + \frac{R_{ik}^\beta R_{kf}^\alpha}{E_{ik} - \hbar\omega_2}. \quad (9b)$$

Equations (6) and (9) are equivalent as long as the summation is carried over all possible intermediate states including i and f which do not contribute in Eqs. (6) due to the energy factor. However, if the summation is truncated, as it always has to be in calculations, this is no longer true. Both forms have been used in earlier work: Eqs. (6) in Ref. 5 and Eqs. (9) in Ref. 6. In a "note added in proof," Honig, Jortner, and Szöke suggest that Eqs. (9) might be more useful for calculations in which only a limited number of intermediate states are taken into consideration. However, so far, no detailed investigation has been made on the convergence behavior of either form. We will come back to this point in Sec. IV.

If experiments are done in solution, one has to deal with randomly oriented molecules and an average has to be taken over all possible orientations. Monson and McClain have shown¹⁰ that, under these conditions, the TPC can be separated in three terms which only depend on the polarization of the incident beams and three

other terms which contain the molecular information:

$$\delta_{av} = \text{const} \cdot |\mathbf{e}_1 \mathbf{S} \mathbf{e}_2|^2 = F \cdot \delta_F + G \cdot \delta_G + H \cdot \delta_H, \quad (10)$$

with

$$\delta_F = \frac{\text{const}}{30} \left(\sum_\alpha S_{\alpha\alpha} \right) \cdot \left(\sum_\beta S_{\beta\beta}^* \right), \quad (11a)$$

$$\delta_G = \frac{\text{const}}{30} \left(\sum_{\alpha\beta} S_{\alpha\beta} \cdot S_{\alpha\beta}^* \right), \quad (11b)$$

$$\delta_H = \frac{\text{const}}{30} \left(\sum_{\alpha\beta} S_{\alpha\beta} \cdot S_{\beta\alpha}^* \right), \quad (11c)$$

and

$$F = -|\mathbf{e}_1 \cdot \mathbf{e}_2^*|^2 + 4|\mathbf{e}_1 \cdot \mathbf{e}_2|^2 - 1, \quad (12a)$$

$$G = -|\mathbf{e}_1 \cdot \mathbf{e}_2^*|^2 - |\mathbf{e}_1 \cdot \mathbf{e}_2|^2 + 4, \quad (12b)$$

$$H = 4|\mathbf{e}_1 \cdot \mathbf{e}_2^*|^2 - |\mathbf{e}_1 \cdot \mathbf{e}_2|^2 - 1. \quad (12c)$$

To obtain the maximum information on \mathbf{S} which can be gained from a solution experiment, the three molecular parameters δ_F , δ_G , and δ_H have to be determined independently. This can be done by carefully designed experiments with different combinations of the polarization of the two photons.¹¹ If both photons have the same energy ($\omega_1 = \omega_2 = \omega$), as it is the case in most of the experiments carried out up to now (where both photons are absorbed from the same laser beam), the tensor \mathbf{S} becomes symmetric. This leads to

$$\delta_{G'}(\omega) = \delta_G(\omega) = \delta_H(\omega). \quad (13)$$

Only two independent molecular parameters can be obtained from such an experiment, e. g.,

$$\delta_{11}(\omega) = 2\delta_F + 4\delta_{G'}, \quad (14a)$$

$$\Omega(\omega) = \frac{\delta_{CC}}{\delta_{11}} = \frac{-\delta_F + 3\delta_{G'}}{\delta_F + 2\delta_{G'}}. \quad (14b)$$

As in conventional UV spectroscopy, a great deal of information can be gained from symmetry considerations due to the fact that the components of \mathbf{S} transform as the products of the corresponding coordinates. For many important molecular symmetries (e. g., D_2 , D_4 , C_{2v} , C_{4v} , D_{2h} , D_{2d} , T , and O), \mathbf{S} consists either of diagonal elements only or off-diagonal elements only. If this happens, some interesting limiting cases follow directly from the definition of the three δ values (11):

(A) If all the diagonal elements of \mathbf{S} are zero (as for $A_g \rightarrow B_{ng}$ transitions in D_{2h}), $\Omega = 3/2$, irrespective of what the photon energies $\hbar\omega_1$ and $\hbar\omega_2$ are.^{10,11}

(B) If one diagonal element is considerably larger than all the other elements of \mathbf{S} , $\Omega = 2/3$, a value often approached in experimental spectra for transitions which lead to totally symmetric excited states.¹²

(C) If all off-diagonal elements are zero and the diagonal elements are of equal magnitude and possess the same sign, $\Omega = 0$. However, no Ω value lower than 0.4 has been reported showing that (C) is a very unfavorable case.

(D) If all off-diagonal elements are zero and two diagonal elements are nearly equal but much larger than

the third one, $\Omega = 1/4$. This case is much more probable than (C) for planar unsaturated molecules where the transitions moment perpendicular to the plane is always small (see also the Appendix).

(E) We have the same as (D) but with the two dominant diagonal elements having opposite signs. Although the final state is totally symmetric in this case, Ω approaches $3/2$ as in (A).

At this point, it should be mentioned that limiting values of Ω —as derived from symmetry considerations—will not be found very often in low resolution spectra.

A similar situation is very common in conventional polarization spectroscopy. Deviations from limiting values are frequently caused by overlapping bands and by vibronic coupling which introduces components of "wrong" polarization.

III. METHOD OF CALCULATION

Three different types of CNDO–CI calculations are used in this paper to evaluate two-photon transition probabilities. These are denoted as follows: SCI/M is the standard CNDO/S scheme proposed by Del Bene and Jaffe.¹³ The Mataga–Nishimoto approximation¹⁴ is used for two-center coulomb repulsion integrals (γ integrals) and 60 energy selected single excited configurations (SEC) are taken into account in the CI calculation. SDCI/M is an extended CNDO/S scheme including single and double excited configurations, but with parameters as in standard CNDO/S. SDCI/P is equivalent to SDCI/M but now Pariser's approximation¹⁵ is used for γ integrals instead of Mataga's.

For the SDCI calculations, 200 configurations were selected according to a criterion which is based on the lowest energy of the diagonal element.⁷ For planar unsaturated molecules, more than 50% of these configurations are usually of overall $\sigma\pi^*$ symmetry (e.g., 133 out of 200 for naphthalene) and do not contribute to low lying excited states of $\pi\pi^*$ symmetry. However, for most of the systems investigated in this paper, we do not find excited states of overall $\sigma\pi^*$ symmetry below $50\,000\text{ cm}^{-1}$. In these cases, a second calculation was performed in which only configurations of overall $\pi\pi^*$ symmetry ($\pi-\pi^*$, $\sigma-\sigma^*$, $\pi\pi-\pi^*\pi^*$, $\sigma\sigma-\sigma^*\sigma^*$, and $\sigma\pi-\sigma^*\pi^*$) were taken into account (200 $\pi\pi^*$ calculations). As shown in the Appendix, intermediate states of $\sigma\pi^*$ symmetry only yield negligible contributions to the TPC of $\pi\pi^*$ excitations. Thus, two-photon transition probabilities obtained from the 200 $\pi\pi^*$ calculations are influenced very little by the omission of $\sigma\pi^*$ configurations but the CI basis is virtually expanded to 400–500 configurations. As shown in Ref. 7, such a number is usually sufficient to reach a point in the CI expansion where the calculated energies of low lying transitions do not change very much with further increase of configuration space. In Tables II–VII, the number of configurations which has been used for a given calculation is specified at the top of the corresponding column.

Excitation energies obtained with the extended CNDO scheme have been discussed in detail in Ref. 7. The Mataga approximation which was found to be very use-

ful in standard CNDO/S, where only a limited number of SEC is taken into account, tends to overestimate correlation effects if double excited configurations (DEC) are included.^{7,3} SDCI/P usually leads to a better overall agreement in experimental and theoretical excitation energies in the low energy region ($E < 50\,000\text{ cm}^{-1}$). In this paper, we show the results of both types of calculations to gain some information to what extent different γ approximations influence the calculated two-photon transition probabilities.

From the results of the CNDO–CI calculations, the transition matrix elements $\langle a|\gamma|b\rangle$ are obtained in a straightforward manner. Following Ref. 16, we include the one-center contribution

$$\langle s|x_i|p_{x_j}\rangle = \frac{5a_0}{2\sqrt{3}\xi_A} \delta_{ij} \quad (15)$$

Then the components of the two-photon transition tensor can be calculated for any pair of photon energies using either Eqs. (6) or (9). In going from \mathbf{S} to δ , a special choice has to be made for the line shape function $g(\omega)$, which in principle depends on ω and the system under consideration. A standardized value of $g = 5 \times 10^{-15}\text{ sec}$ has been used in all our calculations. The justification for this choice is discussed in Sec. VI.

IV. CONVERGENCE BEHAVIOR

It has been pointed out in Sec. II that the summation over intermediate states $|k\rangle$ can be performed in two different ways, namely, either by retaining the individual excitation energies within the summation (6) or by substituting the summation independent product of photon energies (9). To investigate the convergence behavior of both types of summation, we have performed a series of calculations with increasing number of intermediate states (IS) up to all 200 states resulting from the calculation with a total number of 200 configurations. All results are quite similar. As an example, we show in Fig. 1 the convergence behavior of the TPC for the six lowest $1A_g \rightarrow nA_g$ transitions of stilbene. The value of δ_i , obtained for a given number of IS is depicted relative to the value obtained with all 200 IS (= 100%). The absolute values calculated with 200 IS are collected in Table I.

Figure 1 clearly reveals the superiority of Eqs. (9), as was suggested in Ref. 5. Beyond about 100 IS, the TPC obtained from Eqs. (9) deviate less than 10% from the final value without any major oscillation. In contrast, results obtained from Eqs. (6) show strong oscillations and, for most of the states, there is no convergence at all. Therefore, we conclude that the absolute values obtained from Eqs. (6) with all 200 IS are just arbitrary. This is confirmed by the random deviation of the different numbers given in Table I.

The reason for the inapplicability of Eqs. (6) is mainly due to the energy factor $E_{ik} \cdot E_{kj}$. Also, if we neglect the fact that the calculated energies of the IS become increasingly poor with higher energy, this factor steadily increases the weight of higher excited states in the expansion of \mathbf{M}^{ij} . A truncation at an arbitrary point must lead to more or less arbitrary results. Contrary

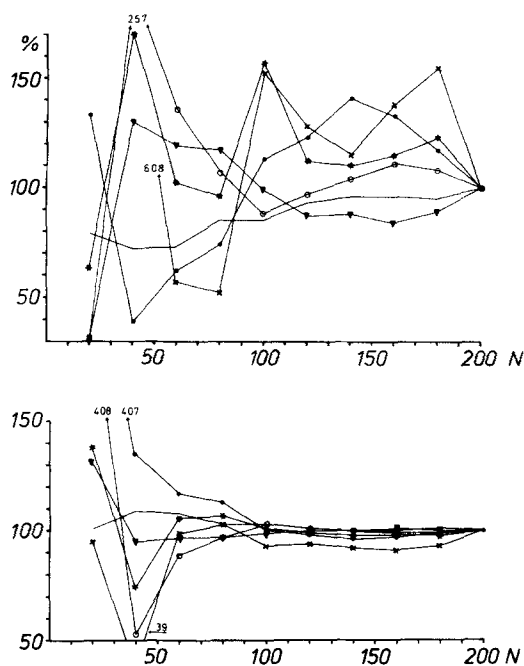


FIG. 1. Relative two-photon cross sections for the first six $1A_g \rightarrow nA_g$ transitions of stilbene as a function of the number (N) of intermediate states of increasing energies. The values obtained for 200 intermediate states are taken as 100%. Upper part: Eq. (6); lower part: Eq. (9).

to this, in Eq. (9), the importance of higher excited states steadily decreases due to the energy denominator. This leads to a physically much more reasonable picture, the major contributions to the TPA tensor now coming from low-lying excited states.

However, the following problem remains: In a minimal basis type calculation, as it is applied here, we only deal with valence excited states and not with Rydberg states (RS). Fortunately, the matrix elements R_{ik} decrease rapidly with increasing Rydberg character of the IS $|k\rangle$. If the final state $|f\rangle$ is a valence excited state, both terms in the product $R_{ik}^\alpha R_{kf}^\beta$ become small and the contribution of the RS should not be important. However, if $|f\rangle$ itself is a RS, the importance of the RS as an IS may be greatly increased.

V. COMPARISON WITH EXPERIMENT

Although the amount of available experimental data is now steadily increasing, there are some experimental and theoretical limitations for such a comparison:

(i) Up to now, there exists very little information on absolute TPC (we come back to this in Sec. VI). Therefore, we are usually not able to compare the TPC of different molecules.

(ii) If we restrict our discussion to relative cross sections, we have to look for examples for which the two-photon spectrum (TPS) has been measured over a wide spectral range and where at least two different transitions have been observed in the spectrum.

(iii) From the theoretical point of view, it is desirable to restrict a first comparison to hydrocarbons to avoid

any discussion of the suitability or unsuitability of heteroatom parameters.

In view of these limitations, we have selected the following systems (molecular symmetry in parenthesis): benzene (D_{6h}), naphthalene (D_{2h}), anthracene (D_{2h}), hexatriene (C_{2h}), stilbene (C_{2h}), and phenanthrene (C_{2v}). With the exception of phenanthrene, all of these molecules have a center of symmetry which gives rise to the following alternative selection rule: $u \rightarrow u$ and $g \rightarrow g$ transitions are always one-photon forbidden whereas $u \rightarrow g$ and $g \rightarrow u$ transitions are always two-photon forbidden. Accordingly, the conventional UV and two-photon spectra of these molecules should exhibit completely different transitions. However, "wrong" transitions can show up in either of these spectra due to the influence of vibronic coupling.

Most of the experimental data on two-photon transitions shown in Tables II–VIII are obtained with two-photon excitation (TPE), where fluorescence is used to monitor two-photon absorption (TPA) stimulated with a single laser beam. All these data have been measured in solution or with neat liquid. Relative TPC obtained from such a measurement are correct only if the fluorescence yield is constant over the investigated energy range. This assumption has been proved to be valid only for certain cases and only up to a certain energy.^{17–19}

As far as possible, the experimental data for the dipole-allowed transitions (DAT) are taken from gas phase measurements. This is more appropriate for comparison with theoretical calculations since DAT undergo increasing solvent shifts with increasing transition moment which reach up to 2500 cm^{-1} and more in nonpolar solvents. On the contrary, the shifts of low-lying DFT are usually small ($< 500 \text{ cm}^{-1}$).

In the tables, transitions are labeled by symmetry. Transitions of the same symmetry are numbered in order of increasing energy. Since all the states discussed here are singlet states, we have dropped the multiplicity index. For aromatic molecules, we also use the well established nomenclature of Platt²⁰ to denote the bands observed in the conventional UV spectrum. Excitation energies are given in 1000 cm^{-1} and δ values in $10^{-50} \text{ cm}^4 \text{ sec/photon molecule}$. For this quantity, McClain⁴

TABLE I. Comparison of different summations over intermediate states in the calculation of δ_{ii} . The results are for a SDCI/M calculation on the molecule stilbene including 200 configurations and taking into account all the resulting intermediate states.

Transition	Calculated TPC δ_{ii}	
	Eqs. (9)	Eqs. (6)
1 $A_g \rightarrow$		
2 A_g	1.44	7.91
3 A_g	131.4	84.9
4 A_g	2.34	3.02
5 A_g	2.10	0.936
6 A_g	4.60	3.05
7 A_g	272.5	281.9

TABLE II. Experimental and theoretical results for benzene: Excitation energies (EE) are in 1000 cm⁻¹ and δ in gm. Experimental f values are from Ref. 26. Experimental δ values are from Refs. 10 and 25 (see text).

	IS	Exp.	SCI/M 60	SDCI/M 200	SDCI/P 200
B_{2u} (L_b)	EE	39.5 ^a	39.1	36.9	35.0
	f	0.0014	0.0	0.0	0.0
	$\delta_{\uparrow\uparrow}$	$3 \times \delta_{\uparrow\uparrow}^{B_{1u}}$	0.0	0.0	0.0
	Ω
B_{1u} (L_a)	EE	50.0 ^b	49.1	52.4	43.9
	f	0.094	0.0	0.0	0.0
	$\delta_{\uparrow\uparrow}$	< 0.1	0.0	0.0	0.0
	Ω
E_{1u} ($B_{a,b}$)	EE	56.3 ^b	55.0	55.9	54.5
	f	0.88	2.10	1.45	1.43
	$\delta_{\uparrow\uparrow}$...	0.0	0.0	0.0
	Ω
E_{2g}	EE	58.5 ^c	64.4	53.4	56.8
	f	...	0.0	0.0	0.0
	$\delta_{\uparrow\uparrow}$	$100 \times \delta_{\uparrow\uparrow}^{B_{1u}}$	45.3	1.08	1.04
	Ω	...	1.50	1.50	1.50

^aReference 22.

^bReference 23.

^cReference 24.

has proposed the abbreviation 1 gm in honor of the pioneering work of Maria Göppert-Mayer.²¹

Only theoretical results obtained from Eqs. (9) are used for further discussion and—corresponding to the experimental conditions—only values for the independent molecular properties $\delta_{\uparrow\uparrow}$ and Ω are shown.

A. Benzene (Table II)

The three well-known absorption bands in the UV spectrum of benzene at 39 000 (L_b), 50 000 (L_a), and 56 000 cm⁻¹ ($B_{a,b}$) are now unambiguously assigned to transitions which lead to states of symmetry B_{2u} , B_{1u} , and E_{1u} , respectively. Earlier suggestions that the second band (L_a) is due to an excitation to an E_{2g} state have not been confirmed by TPA.¹⁰ δ^{L_a} was found to be less than 0.1 gm, which is too small for a strongly allowed two-photon transition. Other suggestions which place the E_{2g} transition at 65 000 cm⁻¹ have also been found to be wrong. Birks²⁴ located this transition at about 58 000 cm⁻¹, an assignment which has been recently confirmed by TPS. Due to the fact that benzene does not show any emission if excited to higher states than $1B_{2u}$, a different technique, the so called "two-photon thermal blooming" method, had to be used to measure TPA in the high energy range.²⁵ The TPC for E_{2g} was found to be about 100 times greater than that for B_{1u} . Together with the result given in Ref. 10, this leads to $\delta(E_{2g}) < 10$ gm.

Standard CNDO/S calculations nearly reproduce the experimental excitation energies for the three u transitions, the oscillator strength for E_{1u} being too high by a factor of about 2. The energy of the E_{2g} state is overestimated by 6000 cm⁻¹ and the calculated TPC is fairly high. With Mataga integrals, the inclusion of DEC lowers the energy of the E_{2g} state to such an extent that the

ordering of E_{1u} and E_{2g} is reversed. This is an example of the overestimation of correlation effects by Mataga integrals mentioned earlier (see also the discussion in Ref. 7). If Pariser's approximation is used instead of Mataga's, the correct order is re-established. However, the energies of the lower excited states B_{2u} and B_{1u} are still too low.

In spite of pronounced differences in energies, the calculated values for f and δ are similar for both SDCI calculations. Compared to the SCI result, the f value for E_{1u} is reduced by 30% but $\delta^{E_{2g}}$ is reduced by a factor of about 50. To some extent, this reduction is due to the overall decrease of transition moments, but the main effect results from the strong contribution of DEC (33%) to the E_{2g} state.

B. Naphthalene (Table III)

The UV spectrum of naphthalene consists of three bands (L_b , L_a , and B_b) which are assigned to transitions into states of symmetry B_{2u} , B_{1u} , and B_{2u} , respectively. The TPS of naphthalene in solution has been investigated by Bergman and Jortner,²⁸ by Drucker and McClain,²⁹ and recently with a much better resolution by Mikami and Ito.³⁰ Drucker and McClain observe strong TPA around 44 000 cm⁻¹ which they attribute to a transition to the lowest excited A_g state ($2A_g$). Some additional structure found at about 42 000 cm⁻¹ was at-

TABLE III. Experimental and theoretical results for naphthalene. Excitation energies (EE) are in 1000 cm⁻¹ and calculated δ values in gm. Experimental f values are from Ref. 26. The experimental δ values, which are taken from Ref. 30 are only relative.

	IS	Exp.	SCI/M 60	SDCI/M 200 $\pi\pi^*$	SDCI/P 200 $\pi\pi^*$
$1B_{2u}$ (L_b)	EE	31.9 ^a	32.5	31.6	32.6
	f	0.002	0.0072	6×10^{-6}	0.0008
	$\delta_{\uparrow\uparrow}$	0.2 (γ)
	Ω
$1B_{1u}$ (L_a)	EE	35.9 ^a	35.4	38.2	35.7
	f	0.102	0.235	0.1	0.114
	$\delta_{\uparrow\uparrow}$
	Ω
$1B_{3g}$	EE	42.0	44.9	42.8	43.3
	f
	$\delta_{\uparrow\uparrow}$	1.0 (γ)	10.54	0.319	0.220
	Ω	~ 1.0	1.50	1.50	1.50
$2A_g$	EE	44.4	46.4	44.0	46.0
	f
	$\delta_{\uparrow\uparrow}$	6.0 (γ)	16.6	1.64	1.59
	Ω	~ 0.7	0.352	0.933	1.39
$2B_{2u}$ (B_b)	EE	48.5	45.4($2B_{3g}$)	47.7($3A_g$)	49.4($3A_g$)
	f
	$\delta_{\uparrow\uparrow}$	10 (γ)	0.0052	6.25	4.45
	Ω	...	1.50	0.835	0.672
$2B_{2u}$ (B_b)	EE	47.8 ^a	45.7	48.4	49.7
	f	1.70	1.92	1.23	1.35
	$\delta_{\uparrow\uparrow}$
	Ω

^aReference 27.

TABLE IV. Experimental and theoretical results for anthracene. Excitation energies (EE) are in 1000 cm⁻¹ and δ in gm. Experimental f values are from Ref. 26. Experimental δ values are from Ref. 34.

	IS	Exp.	SCI/M 60	SDCI/M 200 $\pi\pi^*$	SDCI/P 200 $\pi\pi^*$		
$1B_{2u}$ (L_a)	EE	27.0	26.8	30.3	27.7		
	f	0.1	0.287	0.124	0.124		
	δ_{11}	<0.01		
	Ω		
$1B_{1u}$ (L_b)	EE	29.0 ^a	28.5	30.7	30.4		
	f	...	0.019	0.010	0.004		
	δ_{11}	<0.1		
	Ω		
$1B_{3g}$	EE	32.0-36.0	35.7	36.9	36.5		
	f		
	δ_{11}	0.45-0.65	36.3	1.01	1.25		
	Ω	...	1.50	1.50	1.50		
$2B_{3g}$	EE	37.5	39.4	43.4	40.3		
	f		
	δ_{11}	3.00	54.9	0.138	1.27		
	Ω	...	1.50	1.50	1.50		
$2A_g$	EE	40.0	39.7	34.6	41.8	36.3	46.2
	f
	δ_{11}	8.0	46.3	10.1	11.2	5.58	33.8
	Ω	...	0.764	0.386	1.09	0.400	0.305
$2B_{2u}$ (B_b)	EE	42.3 ^b	40.0	44.5	45.4		
	f	2.3	2.87	1.60	2.17		
	δ_{11}		
	Ω		

^aReference 31.

^bReference 32.

tributed to the $1B_{3g}$ state by Bergman and Jortner. The recent measurements of Mikami and Ito clearly resolve a shoulder at the low energy side of the $2A_g$ peak, but with lower intensity as in the low resolution spectrum of Bergman and Jortner. Both authors^{29,30} also report moderate TPA in the region of the L_b band. This absorption is discussed in detail in Ref. 30 in connection with vibronic coupling. The relative TPC given in Table III are from the work of Mikami and Ito.

For the dipole-allowed transitions, standard CNDO/S yields excitation energies and oscillator strengths which are in very good agreement with experiment. This calculation also predicts three dipole-forbidden transitions in this energy region, namely, $1B_{3g}$, $2B_{3g}$, and $2A_g$. After inclusion of DEC, $2A_g$ is shifted below $2B_{2u}$ (B_b) and another A_g state ($3A_g$) is predicted to lie close to $2B_{2u}$. In the case of naphthalene, there is not much difference between the results of SDCI/M and SDCI/P. Again, TPC are strongly reduced compared to SCI, the ratio of $\delta_{11}^{2A_g}/\delta_{11}^{1B_{3g}}$ now being of the order of 5 to 7, which is in excellent agreement with experiment. There is no doubt that the assignment given in Refs. 28 and 30 is correct. This is further confirmed by a drop of Ω from ~ 1.0 at about 42 000 cm⁻¹ to ~ 0.7 at 44 000 cm⁻¹, which was observed by Drucker and McClain,²⁹ but not discussed in their paper. (As has been pointed out in Sec. II, Ω should approach 1.5 for all B_g states in D_{2h}).

A strong TPA observed by Mikami and Ito at 48 500 cm⁻¹ has been attributed to a different excitation mechanism³⁰ (via an intermediate triplet state). From our

calculations, it is also likely that this absorption corresponds to the $1A_g - 3A_g$ transition. A careful reinvestigation of the naphthalene spectrum including polarization studies is necessary to clarify the assignment in this energy region.

C. Anthracene (Table IV)

The UV spectrum of anthracene shows only two bands in the low-energy region: L_a ($1A_g - 1B_{2u}$) and B_b ($1A_g - 2B_{2u}$). The L_b transition ($1A_g - 1B_{1u}$) is now hidden under the intense L_a band, but from polarization measurements³³ and from comparison with the UV spectra of aza-anthracenes this transition is known to lie between 29,000 and 30,000 cm⁻¹.

The TPS of anthracene in solution was investigated by Bergman and Jortner.³⁴ These authors give absolute TPC, but the resolution of the spectrum is low and the incident light was not strictly polarized. Three transitions leading to states of g symmetry have been assigned to the intense TPA observed in the region 32 000 to 40 000 cm⁻¹. This assignment, shown in Table IV, was based on a comparison with the early π calculations of Pariser.¹⁵

For the dipole-allowed transitions, the results of standard CNDO/S calculations are again in good agreement with experiment. For the dipole-forbidden transitions, the same sequence is obtained as in Pariser's work, the states $2B_{3g}$, $2A_g$, and $2B_{2u}$ lying close together. The situation is changed if DEC are included, the results being basically the same for SDCI/M and SDCI/P. The first excited A_g state ($2A_g$) is strongly lowered in energy, now lying somewhat below $1B_{3g}$, and a new A_g state ($3A_g$) with high TPC appears in the close vicinity of $2B_{2u}$ (B_b). Again the f values for the DAT are improved and the TPC are reduced to a factor of about 10. However, the differences in calculated δ values between SDCI/M and SDCI/P are larger than in the first two examples.

Our results cast some doubt on the assignments made by Bergman and Jortner. It is more likely that the two-photon transition found at 40 000 cm⁻¹ leads to the second excited A_g state ($3A_g$), the $1A_g - 2A_g$ transition overlapping with either $1B_{3g}$ (which is favored from the energy calculations) or $2B_{3g}$ (which is favored from the point of view of relative TPC). In any case, new experimental work has to be done to clarify the assignment of the g states in anthracene, including polarization measurements which should clearly distinguish between A_g and B_g states.

D. Hexatriene (Table V)

The shorter polyenes do not exhibit any detectable emission. Therefore, TPE cannot be used as an experimental technique to study two-photon absorption in these molecules. Recently, Twarowski and Klinger (TK) were able to measure the TPA of hexatriene with the "two-photon thermal blooming" method.⁶ These authors also calculated TPC for hexatriene in the π approximation including DEC and using Eqs. (9) for summation over IS. The results of these calculations are shown in Table V, together with some of the experimental data.

TABLE V. Experimental and theoretical results for hexatriene. Excitation energies (EE) are in 1000 cm^{-1} and δ in gm. [The δ values from Ref. 6 are calculated using $g(\omega) = 10^{-14}$ sec.]

IS	Exp.	PPP ^c		CNDO/S	
		SDCI 20	SCI/M 60	SDCI/M 200	SDCI/P 200
$2A_g$	EE	40.5	47.6	40.0	41.7
	f
	δ_{TT}	1.3	284.7	0.716	3.23
	Ω	...	0.68	1.29	1.04
$1B_u$	EE	39.8 ^a	42.9	38.7	45.2
	f	$\epsilon = 21\,000$...	1.37	0.58
	δ_{TT}
	Ω
$2B_u$	EE	47-52 ^b	48.6	53.5	46.1
	f	Very weak	...	0.0056	0.309
	δ_{TT}
	Ω
$1B_g$	EE	...	47.2	...	54.5
	f
	$(\sigma\pi)$ δ_{TT}	...	0.0025	0.00035	0.00058
	Ω	...	1.50	1.50	1.50
$3A_g$	EE	>51 ^c	60.1	56.6	59.9
	f
	δ_{TT}	>30.0 ^c	0	140.	161.2
	Ω	0.68	0.65
$2B_g$	EE	53.4	60.4
	f
	δ_{TT}	0.095	0.0089
	Ω	1.50	1.50

^aReference 35.

^bReference 36.

^cReference 6.

Excitation energies calculated with different types of approximation have been discussed extensively in Ref. 7 in connection with the possible assignment of structures observed in the one-photon absorption spectrum. Two important features have to be stressed in the context of the present paper:

(i) All calculations which include DEC predict a TPC of about 1 gm for the $1A_g \rightarrow 2A_g$ transition.

(ii) The CNDO-SDCI calculations predict a high TPC for $1A_g \rightarrow 3A_g$. This is in contrast to the result of TK, where $3A_g$ was found to be a plus state for which the TPC vanishes in the π approximation.

In their experimental investigation, TK find a strong increase of the TPC between 51 000 and 52 000 cm^{-1} leading to a band maximum which could not be reached with the used experimental setup. From other data given in the paper of TK, it has to be concluded that δ exceeds 30 gm around 52 000 cm^{-1} . The SDCI/P calculation predicts an excitation energy of 55 800 cm^{-1} and a TPC of 24 gm for $1A_g \rightarrow 3A_g$. We therefore conclude that the strong TPA observed by TK has to be assigned to the $1A_g \rightarrow 3A_g$ transition, a fact which could not be derived from the PPP-SDCI calculations. The only transition with large TPC was found at 69 000 cm^{-1} in these calculations.

In the low energy region, TK observed a TPC of about 2 gm at 42 000 cm^{-1} and of less than 0.5 gm below 38 500 cm^{-1} . From these findings, TK conclude the following: "We cannot confirm nor refute the prediction of single plus double CI-PPP theory that an excited 1A state lies below the 1B state in hexatriene. We have shown that the claims saying two-photon spectroscopy can reveal this state^{37,38} may not be true. This is because the TPC to the 1A state will be small while a state lying nearby at higher energy has a very large cross section.^{6,11} We cannot agree with this conclusion.

The actual distance between $2A_g$ and $1B_u$ predicted by different calculations depends to some extent on the approximation used for the γ integrals and on the number and type of configurations included. No experimental evidence has been found up to now that $2A_g$ lies really in front of $1B_u$. However, also if this is true in the gas phase, the order of these two states may well be reversed in solution. The Franck-Condon maximum of $1A_g \rightarrow 1B_u$ lies at 39 800 cm^{-1} in the gas phase,³⁵ somewhat lower than predicted by our SDCI/P calculation but still within the average range of accuracy. In neat liquid, as used in the experiments of TK, the corresponding band undergoes a solvent shift of about 2 400 cm^{-1} . Such a shift has to be expected for a transition with $f \approx 1$. The $1A_g \rightarrow 2A_g$ transition, however, is dipole forbidden and the corresponding band will exhibit a much smaller solvent shift (probably < 400 cm^{-1}). Therefore, we conclude that the increase of TPA observed around 40 000 cm^{-1} by TK has to be assigned to the famous low lying $2A_g$ state of polyenes and that, at least in solution, $2A_g$ is not the lowest excited state of hexatriene.

E. Stilbene (Table VI)

The UV spectrum exhibits three bands with Franck-Condon maxima at 33 800, 43 800, and 49 400 cm^{-1} (in ethanol).³⁹ These bands are usually labeled A, B, and C, respectively, in the order of increasing excitation energy.²⁶ The two-photon absorption spectrum has been recently measured by McClain and co-workers.¹² A broad band with a maximum at about 41 000 cm^{-1} was found. This energy corresponds to a minimum between bands A and B in the one-photon absorption spectrum. Towards lower excitation energy, a slow decrease of the TPC is observed which has been measured down to 34 400 cm^{-1} . From a determination of the absolute value of δ_{TT} at 38 870 cm^{-1} ,⁴⁰ values of about 14 gm at the maximum of the band and of about 2 gm at 36 000 cm^{-1} are derived.

If we compare experimental and theoretical excitation energies, we must take into account that the one-photon absorption spectrum has been measured in ethanol. A solvent shift of about 2000 cm^{-1} has to be estimated for each of the three observed bands. In addition to the states $1B_u$, $3B_u$, and $4B_u$ which are responsible for these bands, all calculations predict another B_u state ($2B_u$) and three A_g states in the low energy region. Two of these states ($2B_u$ and $2A_g$) have strong intramolecular charge-transfer character. Compared to the result of standard CNDO/S, the excitation energies are not al-

TABLE VI. Experimental and theoretical results for stilbene. Excitation energies (EE) are in 1000 cm⁻¹ and δ in gm. δ values from Refs. 12 and 40 (see text).

	IS	Exp.	SCI/M 60	SDCI/M 200 $\pi\pi^*$	SDCI/P 200 $\pi\pi^*$
B_u (A)	EE	33.8 ^a	33.8	37.9	36.0
	f	0.739 ^b ($\epsilon = 29\,000$) ^a	1.147	0.8998	0.8419
	δ
	Ω
$2B_u$	EE		35.8	37.5	38.7
	f		0.0176	0.1204	0.0105
	δ	
	Ω	
$2A_g$	EE	<37.0	35.8	37.5	38.7
	f	
	δ	<3	4.455	1.1534	1.063
	Ω	0.75-0.95	1.407	1.434	1.493
$3A_g$	EE	41.0 ^c	43.5	42.9	43.5
	f
	δ	14.0	289.27	73.62	13.207
	Ω	0.65-0.70	0.697	0.793	0.805
$4A_g$	EE		46.9	48.8	47.0
	f	
	δ		91.96	0.2554	74.677
	Ω		0.731	1.255	0.816
$3B_u$ (B)	EE	43.8 ^a	47.3	49.3	47.4
	f	$\epsilon = 16\,400$ ^a	0.620	0.4044	0.2866
	δ
	Ω
$4B_u$ (C)	EE	49.4 ^a	49.7	55.7	51.2
	f	$\epsilon = 24\,000$ ^a	0.404	0.506	0.739
	δ
	Ω

^aReference 39.

^bReference 26.

^cReference 40.

tered very much by inclusion of double excited configurations. The calculated TPC, however, are again reduced by a factor of 5 to 10. A comparison between SDCI/M and SDCI/P shows that the states $3A_g$ and $4A_g$ are interchanged if a steeper γ function is used. As discussed in more detail in Sec. VI, the absolute value for $\delta_{11}(3A_g)$ obtained from the SDCI/P calculation is in excellent agreement with the experimental findings. For $1A_g - 2A_g$, a δ value of about 1 gm and an Ω value which is close to the limiting value of 1.5 is obtained from both SDCI calculations. The Ω parameter as measured by McClain and co-workers¹² increases from about 0.7 at 38 000 cm⁻¹ up to about 0.95 at 34 400 cm⁻¹. In view of these findings, it is probable that the slow increase of the TPC observed in the experimental two-photon spectrum between 34 000 and 38 000 cm⁻¹ has to be attributed to the $2A_g$ state. An additional proof of the theoretical predictions should come from a measurement of the two-photon spectrum between 44 000 and 55 000 cm⁻¹. A strong two-photon absorption should be found in this region.

F. Phenanthrene (Table VII)

We finally come to an example where the molecule has no center of symmetry. The alternative selection

rules do not apply in such a case. With respect to symmetry (C_{2v}), all possible transitions are two-photon allowed and only transitions leading to A_2 states (which are of $\sigma\pi^*$ or $\pi\sigma^*$ type) are one-photon forbidden. As a consequence, the transitions which appear in the conventional UV spectrum also show up in the TPS⁴² with the exception of the intense B_a band at 40 000 cm⁻¹. The TPC is nearly constant between 38 000 and 43 000 cm⁻¹ and, what is more important, no upward trend is observed in Ω , as had to be expected for a strong contribution from a state of B_2 symmetry.

Two-photon spectroscopy definitely confirmed a state of symmetry $A_1(B_b)$ to lie somewhat below $3B_2(B_a)$, a conclusion derived earlier by one of us⁴³ using conventional polarization spectroscopy. Drucker and McClain⁴² also observe a relatively strong A_1 contribution around 35 000 cm⁻¹ which corresponds to a z -polarized structure reported in our earlier work. Drucker and McClain attribute this structure to a separate excited state of A_1 symmetry which is hidden under the intense L_a band in the conventional UV spectrum.

For the low energy region below 42 000 cm⁻¹, the results of standard CNDO/S are in good agreement with experiment and differ only in minor details from those obtained earlier from PPP calculations.⁴³ Inclusion of

TABLE VII. Experimental and theoretical results for phenanthrene. Excitation energies (EE) are in 1000 cm⁻¹. Relative δ values are from Ref. 42.

	IS	Exp.	SCI/M 60	SDCI/M 200 $\pi\pi^*$	SDCI/P 200 $\pi\pi^*$	
$2A_1$	EE	30.5 ^a	29.5	30.1	31.9	
	f	0.1	0.016	0.00083	...	
	δ	1.0(γ)	1.53	0.48	0.532	
	Ω	~1.0	0.305	1.082	1.022	
$1B_2$	EE	35.2	33.5	36.7	34.7	
	f	0.5	0.326	0.302	0.116	
	δ	6.0(γ)	0.017	0.011	...	
	Ω	0.8-1.2	1.50	1.50	...	
$2B_2$	EE		38.1	40.3	41.2	
	f		0.008	0.004	0.058	
	δ		0.0797	0.0007	0.065	
	Ω		1.50	1.50	1.50	
$3A_1$	EE	38.3 ^b	39.9	40.3	41.8	
	f	...	0.457	0.044	0.086	
	δ	10(γ)	4.13	4.02	1.810	
	Ω	0.70	0.639	0.574	0.451	
$3B_2$	EE	40.0 ^b	39.9	42.9	43.2	
	f	1.3	1.493	0.958	0.821	
	δ	...	0.0017	0.002	0.004	
	Ω	...	1.50	1.50	1.50	
$4A_1$	EE		42.0	41.7	44.1	
	f		0.201	0.272	0.173	
	δ		89.6	2.696	4.770	
	Ω		0.664	0.641	0.627	
Further A_1	EE	46.0	46.6	47.5	48.9	46.6
	f	<0.5	0.109	0.0069	0.001	0.100
	δ	>50(γ)	72.6	5.962	18.51	1.760
	Ω	...	0.542	0.967	0.71	0.701

^aReference 41.

^bReference 43.

TABLE VIII. Comparison of experimental and calculated absolute δ values.

	Experiment			Calculation			
	Basic data	Absolute values derived from basic data		SCI/M		SDCI/P	
		E_a (1000 cm^{-1})	δ (gm)	E_a (1000 cm^{-1})	δ (gm)	E_a (1000 cm^{-1})	δ (gm)
Stilbene ^{12,40}	$\delta_{11} = 12.1 \pm 0.9$ gm at 38 870 cm^{-1}	< 37 41	$\delta_{11} < 7$ $\delta_{11} \approx 14$	35.8 43.5	4.46 290.	38.7 43.5 47.0	1.06 13.2 74.7
Naphthalene ^{28,30}	$\delta = 0.07$ gm at 37 700 cm^{-1}	42.0(B_{3g}) 44.4(A_g) 48.5	$\delta \approx 0.4$ $\delta \approx 2.3$ $\delta \approx 3.5$	44.9(B_{3g}) 46.4(A_g)	10.5 16.6	43.3(B_{3g}) 46.0(A_g) 49.4(A_g)	0.22 1.59 4.45
Anthracene ³⁴	$\delta = 3.0$ gm at 37 700 cm^{-1}	33.2(B_{3g}) 34.6–36 (B_{3g} + vib) 37.5(B_{3g}) 40.0(A_g)	$\delta \approx 0.45$ $\delta \approx 0.7$ $\delta \approx 3.0$ $\delta \approx 8.0$	35.7(B_{3g}) 39.4(B_{3g}) 39.7(A_g)	36.3 54.9 46.3	36.3(A_g) 36.5(B_{3g}) 40.3(B_{3g}) 46.0(A_g)	5.58 1.25 1.27 33.8

DEC has little influence on excitation energies in this case. The f value for $1A_1 \rightarrow 3A_1$ is reduced by a factor of about 10 in accordance with the low intensity of the B_g band in the one-photon absorption spectrum. The strong reduction of the δ value of $1A_1 \rightarrow 4A_1$ is mainly due to the fact that $4A_1$ contains about 20% of DEC in SDCI.

The transitions $1A_1 \rightarrow 2B_2$ and $1A_1 \rightarrow 3B_2$ which are predicted to lie in the region of the B_g band have small TPC, in accordance with the experimental finding that this band does not show up in the TPS. The $1A_1 \rightarrow 4A_1$ transition which is also predicted to fall into this energy range has δ and Ω values comparable to those of $1A_1 \rightarrow 3A_1$, which again is in accordance with the fact that the experimental data are nearly constant in this energy range.

The most important result obtained from our calculations is that we do not find any indication for a low-lying A_1 state which could be attributed to the structures around 35 000 cm^{-1} found in the conventional UV spectrum as well as in TPA. We therefore cannot agree with Drucker and McClain's assignment of these structures to a separate excited state of A_1 symmetry. Instead, we retain our original explanation that this A_1 polarized absorption is due to strong vibronic coupling.

VI. ABSOLUTE δ VALUES

In the preceding section, we have seen that there are usually great differences between δ values obtained from SCI or from SDCI calculations. These differences make an experimental proof of absolute values even more desirable. However, the number of experimental known, absolute TPC is very limited up to now. After a careful survey of the literature, we were left with only three sets of data which could be used in this context, namely, two from the low-resolution measurements of Bergman and Jortner^{28,34} and one from a very recent work of Anderson, Holtom, and McClain.⁴⁰ Earlier results obtained with ruby lasers scatter by a factor of about 50 and are usually much higher than the more recent ones.^{11,44–47} The collected data are shown in Table VIII

together with the corresponding theoretical results of SCI/M and SDCI/P.

Probably, the most reliable value is that measured for stilbene at 38 870 cm^{-1} with a three-wave mixing method.⁴⁰ Assuming a constant fluorescence yield the above value together with the data shown in Ref. 12 leads to $\delta_{11} \approx 14$ in the region of the maximum of the two-photon absorption band at about 41 000 cm^{-1} . This value is in excellent agreement with the result of our SDCI/P calculation.

For naphthalene, Bergman and Jortner²⁸ give a TPC of 0.07 gm at 37 700 cm^{-1} , a value which was obtained indirectly by comparison with anthracene but without strict polarization control. The energy at which this measurement was made corresponds to a minimum in TPA. Due to the low-resolution conditions, we therefore suggest this value to be an upper limit, provided that all the other quantities which enter into its evaluation (fluorescence yield, etc.) are correct. Combining the value of Bergman and Jortner with the relative cross sections from the high-resolution measurements of Mikami and Ito,³⁰ we obtain the data shown in Table VIII. Again the SDCI results are in good agreement with experiment, whereas the SCI results are much too high.

For anthracene, no detailed comparison can be made due to the uncertain assignment and the limitations in experimental information (see discussion in Sec. V). The available data only show that the SCI results are again by far too large, whereas SDCI yields at least the correct order of magnitude. The few data available for the discussion of absolute TPC show that δ values obtained from SCI calculations are mostly too high if a value of 5×10^{-15} sec is used for the line shape function. Other values proposed in the literature^{6,9} are even higher and experimental estimates for $g(\omega)$ ⁴⁵ confirm 5×10^{-15} sec to be probably a lower limit. In spite of these facts, one might argue that, in the framework of a semiempirical theory, the line shape function should be treated as an empirical parameter which can be used to rescale the calculated δ values. A closer inspection of the data presented in this paper shows, however,

that the reduction of δ values which is found after inclusion of DEC scatters over a range of 2–50. For the SCI results, the overall agreement between calculated and observed δ values cannot be improved very much by the use of a different value for $g(\omega)$. We therefore conclude that inclusion of the double excited configuration is necessary to obtain relative and absolute two-photon cross sections which can be used as guidelines for the interpretation of two-photon spectra.

VII. CONCLUSION

From the studies presented in this paper, we deduce the following results:

(i) For numerical calculations, where only a limited number of intermediate states are taken into account explicitly, an appropriate summation [Eqs. (9)] must be used to reach a reasonable convergence of calculated two-photon cross sections with increasing number of IS.

(ii) CNDO–CI calculations which include a limited number of double excited configurations yield relative two-photon cross sections which are in agreement with experiment for all examples where the assignment is unambiguous.

(iii) Different approximations for the Coulomb repulsion integrals have less influence on calculated TPC than on excitation energies. However, as Pariser's approximation usually leads to better overall results for the excitation energies of both one- and two-photon allowed transitions in SDCI calculations, it is appropriate to use this approximation for the calculation of TPC too.

(iv) As far as experimental data are available, a line shape function $g(\omega) = 5 \times 10^{-15}$ sec leads to a good agreement of absolute values.

Therefore, we conclude that CNDO–CI calculations which include double excited configurations together with an appropriate summation over intermediate states provides a very helpful tool for the assignment and analysis of two-photon spectra.

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APPENDIX

To discuss the influence of states of overall $\sigma\pi$ symmetry, we take a planar unsaturated molecule where the molecular plane (xy plane) is the only element of symmetry (point group C_{2v}). The ground state and all excited states of $\pi\pi^*$ symmetry belong to the representation A' , whereas excited state of $\sigma\pi^*$ symmetry belong to A'' . For an excitation of overall $\pi\pi^*$ symmetry, intermediate states $|k\rangle$ of $\sigma\pi^*$ symmetry only yield nonzero contributions to the two-photon transition probability if

$$\mathbf{R}_{ik} = \langle i | \mathbf{r} | k \rangle \neq 0$$

and also

$$\mathbf{R}_{kf} = \langle k | \mathbf{r} | f \rangle \neq 0,$$

which is only true for

$$\Gamma_{\mathbf{r}} = \Gamma_{|k\rangle} = A''.$$

This means that only the z components of \mathbf{R}_{ik} and \mathbf{R}_{kf} do not vanish. Therefore, $\sigma\pi$ states contribute only to the tensor element S_{zz} . From a similar consideration, it is evident that, for $\pi-\pi^*$ transitions, intermediate states of $\pi\pi^*$ symmetry do not contribute to S_{zz} and that $S_{xz}S_{yz}$, S_{xx} , and S_{yy} vanish for any kind of intermediate state in a planar system.

The absolute value of S_{zz} is always small. All the one-center contributions $C_{\sigma\mu} \cdot C_{\pi\mu} \cdot \langle \mu | z | \mu \rangle$ vanish because $C_{\sigma\mu}C_{\pi\mu} = 0$ due to the $\sigma\pi$ separation. S_{zz} only depends on the one-center contributions $\langle s | z | p_x \rangle$ defined in Eq. (15). These contributions never lead to an S_{zz} which would yield a TPC larger than 0.1 gm. Only for very weak two-photon transitions, where S_{xx} , S_{yy} , and S_{xy} are very small itself or nearly cancel each other S_{zz} , and therefore intermediate states of $\sigma\pi^*$ symmetry may be of any importance to the final result. The complete neglect of intermediate states of $\sigma\pi$ symmetry is therefore a useful approximation in the calculation of the transition probabilities of intense two-photon transitions ($\delta > 1$ gm).

If a molecule possesses additional elements of symmetry, in addition to the molecular plane, S_{zz} contributes usually only to transitions from the totally symmetric ground state to totally symmetric excited states. For all other transitions, the neglect of intermediate states of $\sigma\pi^*$ symmetry is therefore not an approximation but gives the exact result.

¹A well known example for the problems involved in theoretical estimations are the polyenes, where the experimental detection of a low lying A_g state² lead to a revised theoretical description of excited electronic states.³

²(a) B. S. Hudson and B. E. Kohler, Chem. Phys. Lett. 14, 299 (1972); (b) B. S. Hudson and B. E. Kohler, J. Chem. Phys. 59, 4984 (1973); (c) G. R. Holtom and W. M. McClain, Chem. Phys. Lett. 44, 436 (1976); (d) R. R. Birge, J. A. Bennet, B. M. Pierce, and T. M. Thomas, J. Am. Chem. Soc. 100, 1533 (1978).

³K. Schulten, I. Ohmine, and M. Karplus, J. Chem. Phys. 64, 4422 (1976).

⁴W. M. McClain, Acc. Chem. Res. 7, 129 (1974).

⁵B. Honig, J. Jortner, and A. Szöke, J. Chem. Phys. 46, 2714 (1967).

⁶A. J. Twarowski and D. S. Kliger, Chem. Phys. Lett. 50, 36 (1977).

⁷B. Dick and G. Hohlneicher, Theor. Chim. Acta (submitted for publication).

⁸V. I. Bredikhin, M. D. Galanin, and V. N. Genkin, Sov. Phys. Usp. 16, 299 (1973).

⁹B. Honig and J. Jortner, J. Chem. Phys. 47, 3698 (1967).

¹⁰P. R. Monson and W. M. McClain, J. Chem. Phys. 53, 29 (1970).

¹¹P. R. Monson and W. M. McClain, J. Chem. Phys. 56, 4817 (1972).

- ¹²T. M. Stachelek, T. A. Pazoha, W. M. McClain, and R. P. Drucker, *J. Chem. Phys.* **66**, 4540 (1977).
- ¹³J. Del Bene and H. H. Jaffe, *J. Chem. Phys.* **48**, 1807, 4050 (1968); **49**, 1221 (1969); **50**, 1126 (1969).
- ¹⁴N. Nishimoto and N. Mataga, *Z. Physik*, **12**, 335 (1957); **13**, 140 (1957).
- ¹⁵R. Pariser, *J. Chem. Phys.* **21**, 568 (1953).
- ¹⁶R. L. Ellis, G. Kuehnlenz, and H. H. Jaffe, *Theor. Chim. Acta* **26**, 131 (1972).
- ¹⁷I. B. Berlman and A. Weinrib, *Mol. Phys.* **5**, 313 (1962).
- ¹⁸W. H. Melhuish, *J. Phys. Chem.* **65**, 229 (1961).
- ¹⁹R. E. Kellogg, *J. Chem. Phys.* **44**, 411 (1966).
- ²⁰J. R. Platt, *J. Chem. Phys.* **17**, 484 (1949).
- ²¹M. Göpper-Mayer, *Ann. Phys. (Leipzig)* **9**, 273 (1931).
- ²²J. H. Callomon, T. M. Dunn, and I. M. Mills, *Philos. Trans. R. Soc. (London) Ser. A* **259**, 499 (1966).
- ²³E. E. Koch and A. Otto, *Chem. Phys. Lett.* **12**, 476 (1972).
- ²⁴J. B. Birks, *Chem. Phys. Lett.* **3**, 567 (1969); R. Bonneau, J. Jousot-Dubien, and R. Bensasson, *Chem. Phys. Lett.* **3**, 353 (1969).
- ²⁵A. J. Twarowski and D. S. Kliger, *Chem. Phys.* **20**, 259 (1977).
- ²⁶H. Suzuki, *Electronic Absorption Spectra and Geometry of Organic Molecules* (Academic, New York, 1967).
- ²⁷Jean Pierre Loux, Dissertation, Köln (1978).
- ²⁸A. Bergmann and J. Jortner, *Chem. Phys. Lett.* **26**, 323 (1974).
- ²⁹R. P. Drucker and W. M. McClain, *Chem. Phys. Lett.* **28**, 255 (1974).
- ³⁰N. Mikami and I. Ito, *Chem. Phys. Lett.* **31**, 472 (1977).
- ³¹C. Kortüm and B. Einckh, *Z. Phys. Chem.* **52**, 263 (1942).
- ³²L. E. Lyons and G. C. Morris, *J. Mol. Spectrosc.* **4**, 480 (1960).
- ³³H. Zimmermann and N. Joop, *Ber. Bunsenges. Phys. Chem.* **64**, 1215 (1960).
- ³⁴A. Bergman and J. Jortner, *Chem. Phys. Lett.* **15**, 309 (1972).
- ³⁵R. M. Gavin and S. A. Rice, *J. Chem. Phys.* **60**, 3231 (1974).
- ³⁶R. M. Gavin, S. Risenberger, and S. A. Rice, *J. Chem. Phys.* **58**, 3160 (1973).
- ³⁷M. Karplus, R. M. Gavin, and S. A. Rice, *J. Chem. Phys.* **63**, 5507 (1975).
- ³⁸T. H. Dunning, R. P. Hosteny, and I. Shavitt, *J. Am. Chem. Soc.* **95**, 5067 (1973).
- ³⁹DMS-UV *Atlas* (Butterworths, London, 1971).
- ⁴⁰R. J. Anderson, G. R. Holtom, and W. M. McClain, *J. Chem. Phys.* **66**, 3832 (1977).
- ⁴¹Y. Kanda and R. Shimada, *Spectrochim. Acta* **15**, 211 (1959).
- ⁴²R. P. Drucker and W. M. McClain, *J. Chem. Phys.* **61**, 2616 (1974).
- ⁴³F. Dörr, G. Hohlneicher, and S. Schneider, *Ber. Bunsenges. Phys. Chem.* **70**, 803 (1966).
- ⁴⁴L. Peticolas, R. Norris, and K. E. Riekhoff, *J. Chem. Phys.* **42**, 4164 (1965).
- ⁴⁵R. Pantell, F. Pradere, J. Hanus, M. Schott, and H. Puthoff, *J. Chem. Phys.* **46**, 3507 (1967).
- ⁴⁶K. B. Eisenthal, M. W. Dowley, and W. L. Peticolas, *Phys. Rev. Lett.* **20**, 93 (1968).
- ⁴⁷I. Webman and J. Jortner, *J. Chem. Phys.* **50**, 2706 (1969).