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Citation: *The Journal of Chemical Physics* **79**, 593 (1983); doi: 10.1063/1.445806

View online: <http://dx.doi.org/10.1063/1.445806>

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Two-photon $\tilde{A} \leftarrow \tilde{X}$ spectra of benzonitrile and styrene vapors: Tests of perturbation rules

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(Received 7 March 1983; accepted 4 April 1983)

The two-photon vapor $\tilde{A} \leftarrow \tilde{X}$ spectra of benzonitrile and styrene have been studied by fluorescence excitation at room temperature. Because of low frequency internal torsional vibrations, the styrene spectrum was also obtained using multiphoton ionization in a supersonic jet. Despite the totally symmetric symmetry of the excited state, the polarization properties of the styrene Franck-Condon spectrum show that the two-photon electronic intensity mechanism predominantly involves the symmetric tensor and not the scalar tensor. Comparison with the corresponding ${}^1B_{2u} \leftarrow {}^1A_g$ spectrum of phenylacetylene shows that the cross section for the two-photon spectra of the three molecules are roughly equal ($\sim 10^2$ gm) despite a large dissimilarity in the one-photon spectra. The near equality of the three cross sections in molecules without special symmetry properties confirms both the pseudoparity (\pm) basis of the Callis-Scott-Albrecht inductive perturbation selection rule, and the rule that orbitally allowed \leftrightarrow transitions should be very strong for alternant aromatic hydrocarbon two-photon spectra.

I. INTRODUCTION

Patterns emerging from studies on the two-photon (TP) transitions of aromatic molecules¹ have resulted in development of selection rules. Of particular interest is the complementary nature of the rules for one-photon (OP) and TP optical transitions, arising from the pseudoparity (\pm) classification of paired states in alternant hydrocarbons.² An example is provided by the $+\leftrightarrow$ OP selection rule,² in contrast to the pseudoparity conserving $\pm \leftrightarrow \pm$ TP rule.³

This complementary pattern extends into perturbation mechanisms, and two rules have recently been formulated for $-\leftrightarrow-$ transitions:

(1) Pseudoparity conserving (odd⁴) perturbations enhance TP spectra, while pseudoparity altering (even⁴) ones do not.⁷

(2) Weak mesomeric substituents (such as $-\text{CH}_3$) strongly intensify symmetry forbidden aromatic TP spectra.⁸ An alternate formulation of this rule is that orbitally allowed $-\leftrightarrow-$ TP transitions in aromatic alternant hydrocarbons should be very strong.

These rules have great potential for obtaining an understanding of mechanisms for TP intensities in aromatic molecules, but need to be thoroughly validated.

Confirmation of the first rule for an even perturbation is found in the TP spectra of inductively perturbed benzenes. Two studies involve the effect of fluorine⁹ and heterocyclic nitrogen¹⁰ substitution on the TP parity forbidden ${}^1B_{2u}(L_b) \leftarrow A_g^+$ band. A third is on the $L_a^+ \leftarrow {}^1A^-$ transition in fluorobenzene.¹¹ These results appear to agree with the inductive perturbation selection rule (i.e., rule 1), since in the L_b^+ studies the allowed (i.e., Franck-Condon) portion of the substituted benzene spectrum is weak. And, in contrast, the ${}^1B_{1u}(L_a)$ benzene transition appears to be significantly enhanced by the fluorine substitution.

Confirmation of the conjugation rule is also found in substituted benzene TP spectra: in the $L_b \leftarrow A$ transition in toluene¹² and in polymethylbenzenes.^{1(c)} A more general test of both rules, however, requires examination of spectra of derivatives of an alternant hydrocarbon lacking the unique symmetry properties of benzene.

(In fact, the special symmetry properties of the benzene molecule lead to the same predictions without resorting to the pairing properties of alternant hydrocarbon wave functions.¹³)

In this paper we report such proof by comparing the TP spectra for the $\tilde{A} \leftarrow \tilde{X}$ transitions in three π -isoelectronic molecules: phenylacetylene, benzonitrile and styrene. There is little memory of the benzene L_b spectrum in the alternant hydrocarbon, phenylacetylene, with the transition behaving as if it were delocalized throughout the molecule^{14,15} [e.g., note the strong activity of the C-C \equiv C bending mode in Fig. 1(b)]. The large inductive effect of the nitrile group (see Sec. III) thus provides a clear exposition of the inductive rule.

The $\tilde{A} \leftarrow \tilde{X}$ OP spectrum of styrene, redshifted from the corresponding spectrum of phenylacetylene by ~ 1000 cm^{-1} still exhibits the weak character of a $-\leftrightarrow-$ transition, but it is stronger,¹⁶ indicating that the OP $-\leftrightarrow-$ selection rule is partially broken. Rotational contour analysis of the 0-0 band¹⁷ brings out a fundamental difference between the OP spectra of these two molecules. The electronic transition moment is found to be along the long in-plane axis in styrene,¹⁸ unlike phenylacetylene where it is known to lie along the short in-plane axis.¹⁴ The interpretation of changes in rotational constants of styrene and substituted styrenes²⁰ is also consistent with delocalization of the $\tilde{A} \leftarrow \tilde{X}$ transition. This conclusion is supported by thorough vibrational analyses of the one-photon absorption²¹ and single vibronic level fluorescence spectra.²²

McClain's work demonstrates the sensitivity of polarization behavior of TP transitions to scalar contributions in the intensity mechanism.²³ The scalar component must vanish for the $B_2 \leftarrow A_1$ transition in phenylacet-

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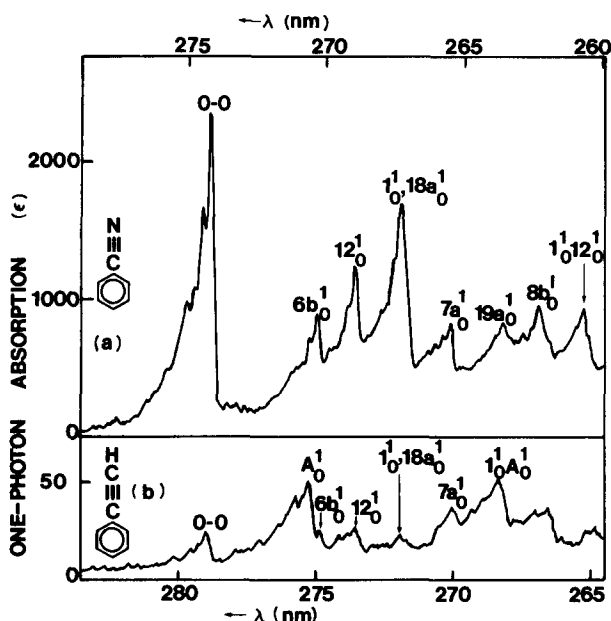


FIG. 1. One-photon room temperature gas phase $\tilde{A}^1B_2 - \tilde{X}^1A_1$ absorption spectra of (a) benzonitrile and (b) phenylacetylene. All modes [Wilson numbering (Ref. 30) are Franck-Condon except ν_{6b} and ν_A (the acetylenic group inplane bend)].

ylene, but may contribute to the $A' \sim A'$ transition, which involves states of identical symmetry in styrene. If there are important new intensity mechanisms generated by the lowered symmetry in styrene they should be most apparent through the intensity behavior in circularly polarized light.

The conjugation rule (rule 2) predicts that $\pi \leftrightarrow \pi$ TP spectra should be resistant to perturbations for strongly delocalized transitions and thus, despite the totally symmetric nature of the excited state, the styrene and phenylacetylene spectra should exhibit very similar polarization behavior.

II. EXPERIMENTAL DETAILS

Styrene (Aldrich) and benzonitrile (Eastman), used without further purification, were vacuum distilled into a 15 mm Suprasil cell. The room temperature TP fluorescence excitation spectra were obtained using light from 5150–5770 Å from a Molelectron MY32 Nd:YAG pumped DL 16 dye laser. The dye laser was operated in the third harmonic (5150–5640 Å) using Exciton dye 540A and in the second harmonic using dye 590 (5640–5770 Å), both in 5 mM ethanol solution. The incident laser beam was focused into the middle of the cell using a 150 mm focal length quartz lens. Linear and circular polarizations were effected using an intracavity and an Oriel 2760 polarizer, respectively. The EMI 6256 photomultiplier used to detect the total fluorescence was placed at 90° to the laser beam and shielded by 6 mm of Corning 7-54 filter. The laser pulse energy (300–600 μJ before focusing) was controlled to maintain non-saturation conditions by using a silicon photodiode to monitor the laser power.

The photomultiplier fluorescence and photodiode ref-

erence signals were processed using a PAR 162/164/165 boxcar integration system with an A/E² module. This yielded the intensity corrected spectrum using the 165 unit for fluorescence. The boxcar parameters adjusted to yield a maximum output signal were typically 1 μs delay, 10 ns gate aperture and 100 μs time constant.

To match and normalize each portion of the spectrum covered by the two dyes, two strong band systems (at ~5633 and ~5560–5600 Å) in the overlapping wavelength region were used.

Jet multiphoton ionization spectra²⁴ of styrene and phenylacetylene were recorded using a molecular beam formed by supersonic free expansion of the sample seeded into argon gas. (A similar experiment was not possible for benzonitrile because of the higher ionization potential.) The use of Ar as a carrier gas at low stagnation pressures makes it possible to avoid high-pumping rates²⁵ and allows efficient cooling of a polyatomic molecule, such as styrene. The diameter of the nozzle was 70 μ and the Ar pressure 160 Torr. The laser beam from a Molelectron DL 400 dye laser pumped by a UV-400 N₂ laser was focused by an 80 mm focal length lens, 2 mm in front of the nozzle and the ions produced were measured by a Channeltron 4039 multiplier. The output was fed to a Cary vibrating reed Model 31 electrometer, processed by a Brookdeal 425A/415 boxcar signal processing amplifier, and ultimately displayed on a recorder.

For the N₂-pumped dye laser, there is a gap between the power profiles of the two dyes (Exciton 540A and 590). Thus, it was not possible to match up the two portions of the spectrum using bands common to both as was carried out for the YAG pumped fluorescence spectra. Instead, the output was adjusted, by inserting a movable wedge in the N₂ laser beam, to the same power for the two dyes. To ensure that differences in the dye profiles and pulse structures did not contribute to discrepancies in the spectra, a check was performed by recording a strong band in the I₂ MPI spectrum (two photons to resonance plus two to ionization) at 5764 Å, common to both dyes.

The laser wavelength was calibrated using a Spex 1704 1 m spectrometer, with a frequency accuracy estimated as ± 3 cm⁻¹. Low resolution OP absorption spectra of styrene and benzonitrile vapors were recorded on a Cary 17 spectrometer using 0.1 nm slit widths and a 10 cm quartz cell.

III. $\tilde{A}^1B_2 \leftarrow \tilde{X}^1A_1$ SPECTRA OF BENZONITRILE

The OP $\tilde{B}_2^1 - \tilde{A}_1^1$ spectrum of phenylacetylene is weak ($f = 5 \times 10^{-4}$),¹⁴ with a feeble origin band (only ~1/3 the strength of the dominant vibronic coupling band [A_0^1 in Fig. 1(b)] involving the $\text{C} \equiv \text{CH}$ in-plane bend). The corresponding spectrum of benzonitrile [Fig. 1(a)] is strongly enhanced ($f = 10^{-2}$) with strong origin and Franck-Condon bands (Table I).²⁶ This result establishes that the nitrile inductive effect is the normal one for a $\pi \leftrightarrow \pi$ transition in OP absorption.

The moderate resolution gas-phase TP spectra are

TABLE I. Comparison of one-photon oscillator strengths and two-photon absorptivities for the $\tilde{A} \leftarrow \tilde{X}$ spectra of benzene, phenylacetylene, benzonitrile, and styrene.

Molecule	One-photon			Two-photon ^d			
	f_{FC}	f_{VC}	f_{total}	δ_{00}	δ_{FC0}	$\delta_{(14^1)}$	δ_{total}
Benzene ^a	0	1.4×10^{-3}	1.4×10^{-3}	0	0	8.7	(26)
Phenylacetylene ^b	1.3×10^{-4}	3.7×10^{-4}	5×10^{-4}	23	59	(9)	(121)
Styrene ^c	(5×10^{-3})	...	5×10^{-3}	20	58	(9)	(122)
Benzonitrile	$(9.6 \times 10^{-3})^c$	$(4 \times 10^{-4})^c$	$1 \times 10^{-2}^e$	25	59	(9)	(119)

^aOP values Ref. 41, TP Ref. 29.^bOP values Ref. 14, TP measured from cold jet spectrum reported here.^cOP values this work, TP measured from cold jet spectrum.^d δ values in gm units (Ref. 29) are estimated by assuming that the cross section of the vibronic coupling band 14_0^1 is unchanged from benzene, i.e., = 8.7 gm. δ_{total} for benzene is estimated as $\sim 3 \times \delta(14_0^1)$. δ_{FC} represents the sum of all Franck-Condon fundamentals and the origin band. $\delta_{total} = \delta_{00} + 2(\delta_{FC} - \delta_{00}) + 2\delta$. The intensity due to FC modes ($\delta_{FC} - \delta_{00}$) is counted twice in the total intensity (δ_{total}) because FC modes built on other FC modes.^eReference 42.

shown in Fig. 2. In order to compare the cross sections, we make use of the TP vibronic coupling mode ν_{14} which is localized in the benzene ring in the excited state.²⁷ This localization persists even under external mass perturbations,²⁸ allowing use of the 14_0^1 band ab-

sorptivity [8.7 Goeppert-Mayers (gm)²⁹] as an internal intensity standard to compare the phenylacetylene and benzonitrile cross sections. Figure 2 shows that the TP spectra of both molecules appear similar, exhibiting the same Franck-Condon and vibronic coupling modes, and when normalized to equal 14_0^1 absorptivity, the same origin band strength. On the same basis, the total absorptivities ($\delta \sim 10^2$ gm) are almost identical (Table I).

IV. $\tilde{A}^1A' \leftarrow X^1\tilde{A}'$ SPECTRA OF STYRENE

A. Comparison of OP and TP spectra

Figures 3(a) and 3(b) illustrate the OP room temperature absorption and the TP room temperature fluorescence excitation spectra respectively, while Fig. 4 shows the fundamental region of the TP supersonic jet ionization spectrum. The ionization spectrum represents two photons to resonance and two additional photons to ionization. Among the similarities between the first two spectra are the prominence of the same bands including the origin at $34\,761 \pm 3$ cm⁻¹, and fundamentals such as ν_{25} (corresponding to benzene mode ν_{12} ³⁰), ν_{24} (benzene ν_1), ν_{18} (ν_{7a}), and the same overtone and sequence transitions.

The congested region around +960 cm⁻¹ from the origin is well resolved into several fundamentals in the jet spectrum of Fig. 4 and these match with those reported in the OP spectrum.²¹ Furthermore, the numerous cross-sequence bands between the low-frequency modes ν_{42} and ν_{41} (ethylene group torsional rotation and out-of-plane bend, respectively, assigned by Hollas and Ridley in their OP single vibronic level study²² appear in the room temperature TP spectrum. The "cleanness" of the jet spectrum results in part from cooling out these bands as is illustrated by comparison of Figs. 3(b) and 4.

Finally, the two room temperature spectra [Figs. 3(a) and 3(b)] show similar vibrational envelopes with the exception of bands arising from a fundamental at +1567 cm⁻¹ seen in the TP spectrum, but not reported in OP studies.

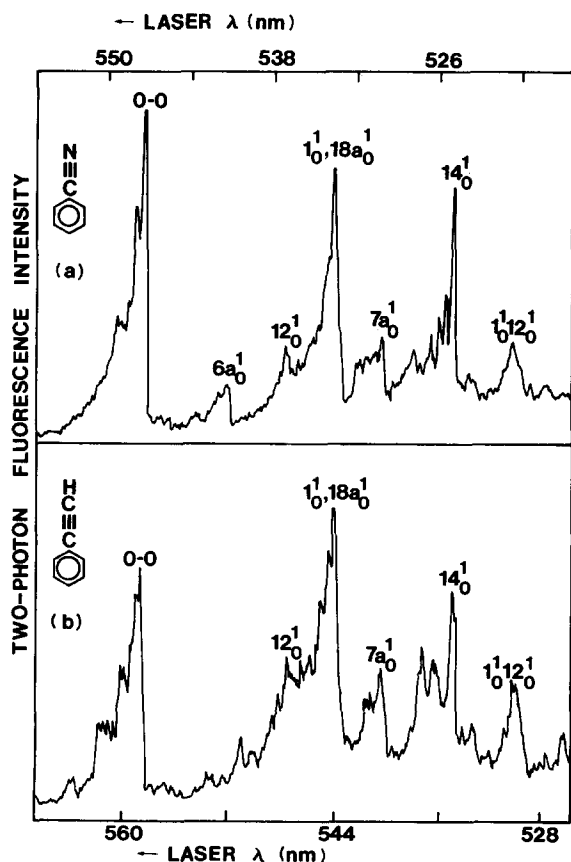


FIG. 2. Normalized two-photon room temperature vapor $\tilde{A}^1B_2 \leftarrow \tilde{X}^2A_1$ fluorescence excitation spectra (a) benzonitrile, (b) phenylacetylene. All modes (Wilson numbering) are Franck-Condon except ν_{14} .

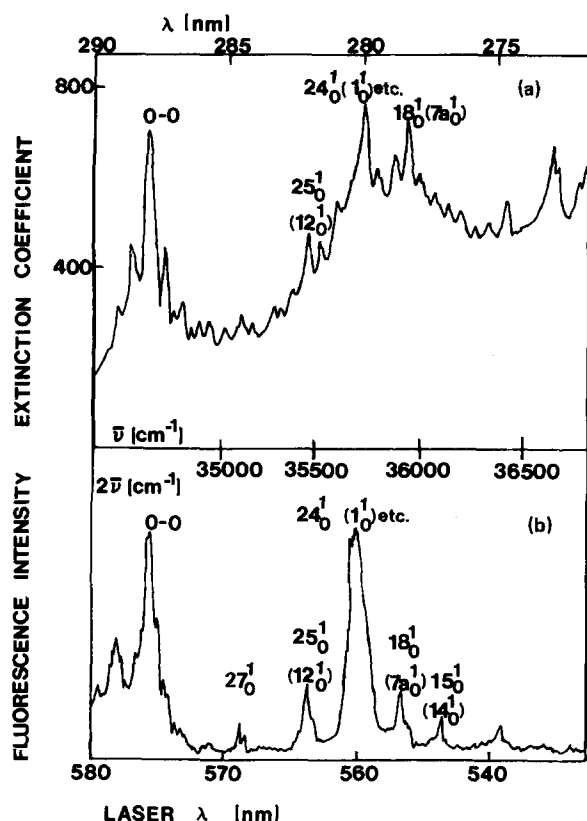


FIG. 3. (a) $\tilde{A} \leftarrow \tilde{X}$ one-photon absorption spectrum of styrene vapor at room temperature. (b) Normalized two-photon fluorescence excitation spectrum. Band designations are those of Ref. 21; in parentheses, Wilson notation (Ref. 30).

B. Vibrational analysis

The major bands and their assignments are given in Table II. The decrease in quantum yield with increasing photon energy (ϕ_{fl} at $+1000 \text{ cm}^{-1} \approx 0.75 \phi_{fl}$ at the origin³¹) is taken into account in the discussion below.

With the exception of the a'' modes ν_{41} and ν_{42} (which

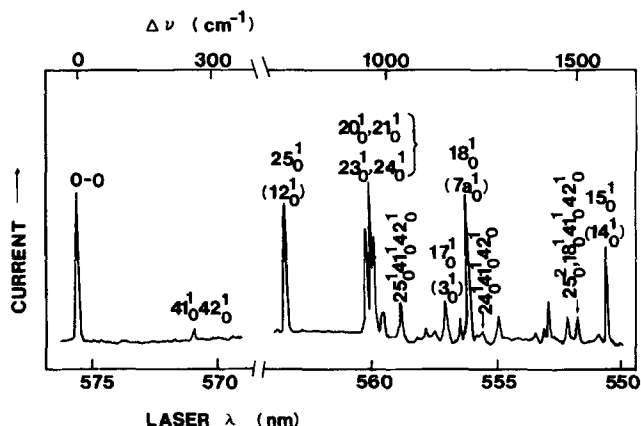


FIG. 4. Supersonic jet two-photon normalized resonance ionization spectrum of styrene vapor using argon as a carrier gas showing the simplicity of the $\tilde{A} \leftarrow \tilde{X}$ spectrum when the congestion due to ethylene torsional modes is cooled out.

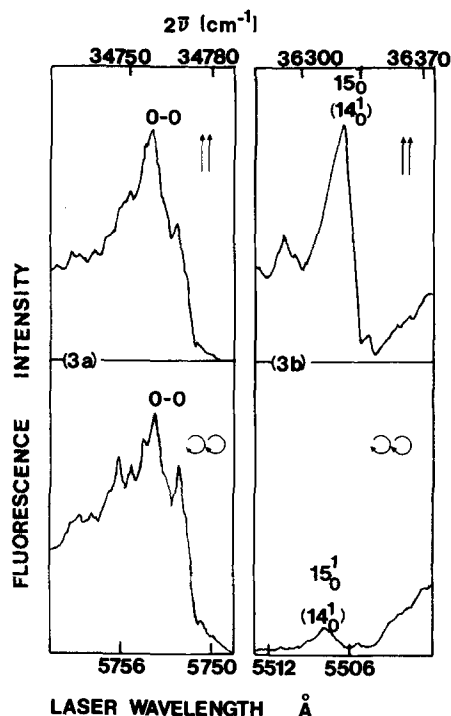


FIG. 5. Polarization [(tt) linear], [(θθ) circular] spectra of (a) the origin band, (b) the $15_0^1(14_0^1)$ band at $0+1567 \text{ cm}^{-1}$.

appear only in cross sequences yielding an overall A' symmetry), all the fundamentals, in the TP spectrum are of a' symmetry. For the most part, the prominent fundamentals are ring modes or ring-substituent stretch modes: 25_0^1 (benzene Kékulé mode 12_0^1), 24_0^1 (ring-breathing mode 1_0^1), 18_0^1 [$7a_0^1$, the X -sensitive (ν -C-CHCH₂) mode], 17_0^1 (3_0^1), and 15_0^1 (14_0^1). The ubiquitous ring-breathing mode ν_{24} (ν_1) in the L_b spectra of substituted benzenes is part of a cluster of four bands near 950 cm^{-1} in styrene and thus its intensity is difficult to ascertain. The jet MPI spectrum (Fig. 4), however, allows resolution of three of these bands at $+948$, 960 , and 967 cm^{-1} .

Assignment of the numerous cross combinations and sequences of ν_{41} and ν_{42} below $+400 \text{ cm}^{-1}$ was based on the OP single vibronic level study of Ref. 22. A satellite sequence 29_1^1 , appears with many of these bands as well as with a number of the higher-frequency modes.

With the exception of the $+1569 \text{ cm}^{-1}$ band, all the major bands in the TP spectrum undergo a slight intensity increase going from linearly to circularly polarized light. This is illustrated for the origin band in Fig. 5(a). The intensity of the $+1567 \text{ cm}^{-1}$ band strongly decreases, however, as shown in Fig. 5(b). The latter polarization behavior is indicative of a predominantly scalar contribution to the TP tensor. The different band contour (steeper blue side than for the other fundamentals) and a frequency close to those in benzene and other substituted benzenes^{1(b),8,9,12,15} all argue for assigning this band as ν_{15} (the analog of benzene ν_{14}), the most prominent vibronic coupling mode in the TP spectra of substituted benzenes. Despite ν_{15} having the same formally allowed a' symmetry as Franck-Condon (FC) modes

TABLE II. Analysis of the styrene two-photon $\tilde{A} - \tilde{X}$ spectrum.

λ (Å)	$\Delta\nu$ (cm ⁻¹) ^a	Intensity ^b	Assignment ^c	λ (Å)	$\Delta\nu$ (cm ⁻¹) ^a	Intensity ^b	Assignment ^c
5753.6		S	0-0	5600.7	948	M	23_0^1 ($18a_0^1$)
5752.0	10		29_1^1	5598.0	960	S	21_0^1 (15_0^1), 24_0^1 (1_0^1)
5744.2	57		$41_0^1 42_1^0$	5597.8	967	M	20_0^1 ($9a_0^1$)
5742.4	68		$41_0^1 42_1^0 29_1^1$	5595.2	983	W	
5736.0	107		$41_0^2 42_2^0$	5590.2	1015		24_0^1 etc. $41_0^1 42_1^0$
5734.6	115			5588.1	1028	W	$25_0^1 41_0^1 42_1^0$
5729.2	148		42_1^1	5574.1	1118	VW	
5728.0	155		$42_1^1 29_1^1$	5569.7	1146	W	17_0^1 (3_0^1)
5721.8	193		41_0^2	5563.7	1185	W	
5719.8	205		$41_0^2 29_1^1$	5560.1	1208	S	18_0^1 ($7a_0^1$)
5707.2	283	VW	$41_0^1 42_0^1$	5557.4	1226	VW	
5706.0	291		$41_0^1 42_0^1 29_1^1$	5554.1	1247	VW	$24_0^1 41_0^1 42_1^0$
5698.0	339		$41_0^2 42_1^1$	5548.1	1286	W	
5696.6	348		$40_0^1 41_0^1$	5534.1	1377	VW	
5695.2	357		$40_0^1 41_0^1 29_1^1$	5528.3	1415	W	
5689.8	390		$41_0^3 42_2^1$	5525.7	1432	VW	13_0^1 ($19b_0^1$)
5689.1	394		28_0^1 ($6a_0^1$)	5521.2	1462	W	12_0^1 ($19a_0^1$)
5682.6	434		27_0^1 (β -C=C)	5516.3	1494	W	25_0^2 and $18_0^1 41_0^1 42_1^1$
5632.6	746	S	25_0^1 (12_0^1)	5509.6	1538	VW	
5631.0	756		$25_0^1 29_1^1$	5505.2	1567	M	15_0^1 (14_0^1)
			...	5496.9	1622	VW	

^aSeparation from the origin band (34 761 cm⁻¹).^bIntensities refer to the MPI jet spectrum bands; the other bands are detected in the fluorescence excitation room-temperature spectrum.^cNumbering of the vibrations as in Ref. 21. The Wilson numbering (Ref. 30) for benzene analog modes is given in parentheses.

like ν_{24} , and despite the totally symmetric A' symmetry of the excited state, and the long axis polarization of the $\tilde{A}'A' - \tilde{X}'A'$ OP transition, ν_{15} derives most of its intensity through vibronic coupling with apparently the same ground-state mechanism as in benzene.^{13,28,32} The dominant portion of the TP spectrum, however, is FC and from the polarization behavior obtains its intensity from the symmetric term of the TP tensor, as in substituted benzenes of C_{2v} symmetry.

The increased origin band region structure in circularly polarized light [Fig. 5(a)] should be noted. Bands to the red of the origin peak, only partially resolved under linear polarization, are more clearly so under circular polarization. There is a clear implication from these spectra that although the symmetric term is predominant in the electronic intensity mechanism for $\tilde{A} - \tilde{X}$, the scalar term is nonvanishing.

By assuming that the mechanism for the intensity of 15_0^1 (14_0^1) is the same as in benzene the total TP absorptivity of styrene is estimated as $\sim 10^2$ gm. This assumption is discussed further in Sec. V.

C. Comparison of styrene and phenylacetylene $A \leftarrow X$ two-photon spectra

The polarization behavior described above suggests that the mechanism for inducing intensity into the styrene $\tilde{A}'A' - \tilde{X}'A'$ TP spectrum is similar to that for the $\tilde{A}'B_2 - \tilde{X}'A_1$ spectrum of phenylacetylene. Comparison of the jet ionization spectra of the two molecules (where sequence bands are not an interfering factor) shows that each origin band is approximately three times more intense than the principal vibronic coupling band [i.e., 14_0^1 (Wilson notation)]. The inference is that the TP absorptivities are similar despite the large difference in OP oscillator strengths for the $\tilde{A} - \tilde{X}$ band systems (Table I).

A subtle but important point arises from comparison of the room temperature fluorescence excitation spectra. Under these conditions the apparent styrene origin band strength relative to 15_0^1 (14_0^1) has increased from 3:1 to ~ 6 :1 whereas for phenylacetylene there is no discernable increase. A possible explanation involves a temperature effect arising from coupling of the torsional rotation of the vinyl group to the origin band in

styrene. Sequence transitions activated at room temperature are known to pile up within the origin band rotational contour,²² which may give a false appearance of high intensity. Added weight is given to this explanation by the similarity of the low-temperature jet ionization and room-temperature fluorescence excitation spectra of phenylacetylene, which lacks torsional vibrations. It is also possible that the difference between the two spectra arises from excitation into 14_0^1 opening up new ionization paths with consequent fluorescence depopulation compared to excitation into the origin band.³³

V. DISCUSSION

A. Phenylacetylene

For the general case of C_s electronic symmetry, all components of the TP tensor are formally allowed. The out-of-plane components are eliminated by invoking the π -electron approximation for the virtual intermediate states.¹³ The terms to be evaluated are then³⁴

$$S_{\sigma\sigma} = \sum_i \frac{1}{\Delta E_{i\sigma} - \hbar\omega} \langle g | \mu_\sigma | i \rangle \langle i | \mu_\sigma | f \rangle \quad (\sigma = y \text{ or } z), \quad (1)$$

$$S_{yy} = \sum_i \frac{1}{\Delta E_{i\sigma} - \hbar\omega} \langle g | \mu_y | i \rangle \langle i | \mu_z | f \rangle + \sum_j \frac{1}{\Delta E_{j\sigma} - \hbar\omega} \langle g | \mu_z | j \rangle \langle j | \mu_y | f \rangle, \quad (2)$$

where g is the ground state, i and j the intermediate states, f the final state, $\Delta E_{i\sigma}$ and $\Delta E_{j\sigma}$ energy differences between the ground and intermediate states, $\hbar\omega$ the laser energy, and μ the dipole moment operator. The coordinate orientation is shown in Fig. 6.

The sums in Eqs. (1) and (2) may run over both virtual intermediate states and the ground and final states.³⁵ These latter terms are important only for strongly allowed transitions exhibiting large dipole moment changes.

The lowest singly excited configurations, χ_{ij} for phenylacetylene viewed as an even alternant hydrocarbon

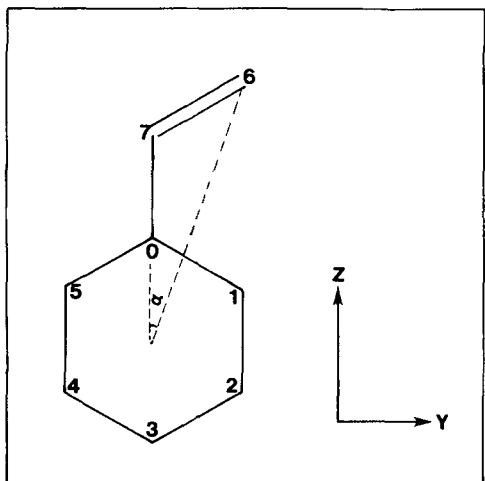


FIG. 6. Styrene coordinate and numbering system. The molecule is planar in the ground state and probably so in the \tilde{A} excited state (Refs. 21 and 22). The angle α defines the charge transfer dipole moment [$\mu(R \rightarrow S^*)$] direction.

MO	SYM.					
$\bar{1}$	B_1	—	—	—	—	—
$\bar{2}$	B_1	—	—	—	—	—
$\bar{3}$	A_2	—	—	—	+	+
$\bar{4}$	B_1	—	+	+	—	—
4	B_1	++	+	++	+	++
3	A_2	++	++	+	++	+
2	B_1	++	++	++	++	++
1	B_1	++	++	++	++	++
		χ_0	χ_{44}	χ_{34}	χ_{43}	χ_{33}

FIG. 7. Some of the lowest phenylacetylene and styrene excited configurations. χ_{34}^+ and χ_{43}^+ are degenerate and lead to paired states $\psi_{34}^\pm = 2^{-1/2}(\chi_{34}^+ \pm \chi_{43}^+)$.

are illustrated in Fig. 7. After configuration interaction the lowest excited state is the B_2 $L_b(-)$ paired state $\psi_{34}^- = 2^{-1/2}(\chi_{34}^+ - \chi_{43}^+)$. The $\tilde{A} - \tilde{X}$ transition is $\psi_{34}^- - \chi_0$. Since we are interested in a paradigm calculation in terms of the alternant hydrocarbon model we include only first-order configuration effects on the TP tensor by assuming the perfect pairing approximation (Table III).

We now consider the contributions of the various intermediate states to Eq. (2). For the C_{2v} symmetry phenylacetylene where the transition is $B_2 - A_1$, Eq. (1) vanishes. Using the simple l.c.a.o. orbitals of Fig. 8 the dominant contribution to Eq. (2) is made by the B_2^+ paired state ψ_{34}^+ . The electric dipole matrix element $\langle \chi_0 | \mu_y | \psi_{34}^+ \rangle$ is large since it represents a fully allowed ($V-N$) OP transition. Even larger is $\langle \psi_{34}^+ | \mu_z | \psi_{34}^+ \rangle$, resulting in the very large permanent dipole moment of molecular orbital Φ_4 , which is delocalized throughout the ring and acetylenic groups (Fig. 8). Other important contributions to S_{yy} also come from the A states χ_{44}^+ , χ_{33}^+ , and the B_2 state ψ_{23}^+ (note, however that the perfect pairing approximation may be poor for the upper states³⁶).

The calculated total absorptivity from the total S_{yy} in Table III is 90 gm. The large value suggests that this TP transition can be viewed as a $(V-N)^2$ process, i.e., as two sequential $V-N$ excitations. The experimental cross section $\sim 10^2$ gm¹⁵ is in basic agreement with this picture.

B. Benzonitrile

Perturbation selection rule (1) is expected to be only approximately valid since vanishing of inductive effect matrix elements is based on non-nearest-neighbor interactions.⁷ The lack of enhancement reported for the $\tilde{A}^- - \tilde{X}^-$ spectra compared to phenylacetylene (Sec. III) validates this assumption and shows that the perfect pairing approximation holds to a high degree for the \tilde{A}^- state.

TABLE III. Major two-photon tensor terms in the $\tilde{A} \rightarrow \tilde{X}$ transition for phenylacetylene and styrene.^a

Phenylacetylene				
Intermediate state	$\langle g \mu_\rho i \rangle^b$	$\langle i \mu_\sigma f \rangle^b$	$\Delta E_{if} - \hbar\omega$ (cm ⁻¹) ^c	$(S_{yy})_i \times 10^{-31}$ (cm ² s)
ψ_{34}^+	-0.537 j	2.185 k	33 673	-2.27
ψ_{23}^+	-0.433 j	-1.150 k	38 512	0.84
χ_{44}	0.907 k	-0.217 j	23 996	-0.53
χ_{33}	-0.500 k	0.217 j	25 608	-0.28
Total S_{yy} ^d				-2.13
Styrene				
Intermediate state	$\langle g \mu_\rho i \rangle$	$\langle i \mu_\sigma f \rangle$	$\Delta E_{if} - \hbar\omega$	$(S_{yy})_i$
ψ_{34}^+	-0.537 j	2.039 k	31 818	-2.24
ψ_{23}^+	-0.433 j	-1.045 k	38 104	0.77
χ_{44}	0.730 k	-0.217 j	24 636	-0.42
χ_{33}	-0.500 k	0.217 j	33 587	-0.21
Total S_{yy} ^d				-2.00
Intermediate state	$\langle g \mu_y i \rangle$	$\langle i \mu_y f \rangle$	$\Delta E_{if} - \hbar\omega$	$(S_{yy})_i$
ψ_{34}^+	-0.534 j	-0.252 j	31 818	0.28
χ_{44}	0.307 j	-0.217 j	24 636	-0.18
ψ_{24}^+	-0.258 j	0.306 j	35 523	-0.14
ψ_{23}^+	-0.433 j	-0.182 j	38 104	0.13
total S_{yy} ^d				0.20

^aOnly first-order (i.e., perfect pairing approximation) configurational interactions are included in the tensor terms.

^bIn units of $R(\text{\AA})$, the C-C bond length (assumed equal throughout). j and k represent unit vectors along the y and z axes, respectively, of Fig. 6.

^c $\hbar\omega = \Delta E_{if}/2 = 1.79 \times 10^4 \text{ cm}^{-1}$ for phenylacetylene and $1.74 \times 10^4 \text{ cm}^{-1}$ for styrene.

^dIncludes small contributions not listed in table.

^e S_{xx} is calculated to be negligible.

C. Styrene

We first approach styrene as a symmetry perturbed phenylacetylene, i.e., $C_{2v} \rightarrow C_s$. The asymmetric ethylene perturbation in styrene generates two effects. One is rotation of the electric dipole transition moments in the matrix elements of Eqs. (1) and (2) from their y or z directions. This topological effect causes the $S_{\sigma\sigma}$ terms of Eq. (1), that vanish for phenylacetylene, to appear even when the MO's of Fig. 8 are retained unchanged from the phenylacetylene ones. The second is a weak inductive effect, causing changes in the Coulomb integrals of the ring carbon atoms. The result of such an inductive perturbation is the mixing of the zeroth-order phenylacetylene states. This is equivalent to perturbing the MO's of Fig. 8.

The topological effect only slightly affects the S_{yy} term from that in phenylacetylene (Table III), in accord with the conjugation rule. Small S_{yy} and negligible S_{xx} components are also generated. The wave function perturbation caused by the inductive effect is evaluated using first-order perturbation theory and the state energies

of Table III, by changing the Coulomb integral of atom #1 (Fig. 6) for weak and strong field limits ($\delta_1 \approx -0.1$ eV and $\delta_1 = -1$ eV, respectively). All other carbon atoms are assumed unchanged. The perturbation calculations show that even in the strong field limit (which is somewhat larger than that caused by fluorosubstitution³⁷), the symmetric tensor S_{yy} is virtually unchanged from its phenylacetylene value. The scalar term S_{yy} vanishes because under an inductive perturbation only + states perturb ψ_{34} in accordance with the inductive rule. On the other hand, S_{xx} is allowed since it contains terms which are not eliminated by the perturbation selection rules. However, these terms contribute negligibly.

In summary, the alternant hydrocarbon model predicts that neither topological nor inductive perturbations should change the TP mechanisms significantly from phenylacetylene. We now approach styrene as a perturbed benzene. The strong delocalization of the $\tilde{A} \rightarrow \tilde{X}$ transition in phenylacetylene over the entire molecule indicates that strong coupling theory is required.¹³ By restricting

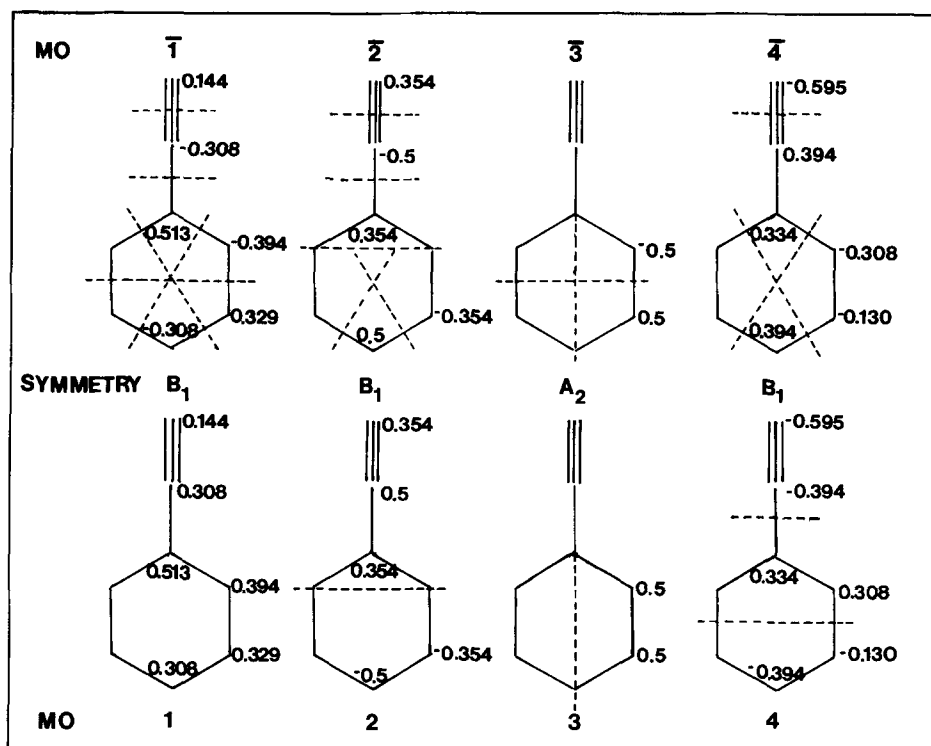


FIG. 8. Phenylacetylene Hückel molecular orbitals Φ_i showing nodal and delocalization properties.

the intermediate states to the strongly OP allowed $B_{a,b}$ states, Eq. (2) becomes¹⁵

$$S_{yz} = \frac{1}{\Delta E_{B_g} - \hbar\omega} \{ [\Lambda_{74}\lambda_{74}\mu_z(S \rightarrow R^*) + \Lambda_{28}\lambda_{28}\mu_z(R \rightarrow S^*)] \times \langle A^\circ | \mu_y | B_b^\circ \rangle + [l_{75}\lambda_{75}\mu_y(S \rightarrow R^*) + l_{38}\lambda_{38}\mu_y(R \rightarrow S^*)] \langle A^\circ | \mu_x | B_a^\circ \rangle \}, \quad (3)$$

where

$$\lambda_{ij} = \langle \psi_{L_b} | \psi_j^\circ \rangle, \quad \Lambda_{ij} = \langle \psi_{B_b} | \psi_j^\circ \rangle, \quad l_{ij} = \langle \psi_{B_a} | \psi_j^\circ \rangle,$$

in the expansion

$$\psi_n = \sum_k a_{kn} \psi_k^\circ.$$

The CT states (ψ_{74}° , ψ_{28}° , ψ_{75}° , ψ_{38}°) are given in terms of benzene orbitals ($\Phi_1 - \Phi_6$) and Φ_7 and Φ_8 , the bonding and antibonding bicentric orbitals localized on the ethylenic or acetylenic group.¹⁵ Thus, ψ_{74}° and ψ_{75}° states represent charge-transfer promotion from the substituent group to the ring ($S \rightarrow R^*$), while ψ_{38}° and ψ_{28}° represent charge transfer from the ring to the substituent group ($R \rightarrow S^*$). In this development we have made use of the idea that two-photon allowedness in the L_b^+ spectrum of substituted benzenes arises primarily from charge-transfer (CT) character in the intermediate and final state wave functions.^{1(b),8} Consistent with the context of the previous sections, non-nearest-neighbor interactions are neglected.

Only square terms remain from the alternant hydrocarbon condition $\lambda_{74} = -\lambda_{28}$ and $\Lambda_{28} = \Lambda_{74}$ ($\lambda, \Lambda > 0$).

The dipole moment terms μ are CT dipole moments, which to a point-charge approximation, are $\mu_z \pm 5/2 eR$ [for both $\mu(R \rightarrow S^*)$ and $\mu(S \rightarrow R^*)$]. The ground-state

permanent dipole moment μ_z is small (in the vicinity of 0.7 D) for both phenylacetylene³⁸ and styrene.³⁹ The electron-transfer moment, $\sim 5/2 eR$ is ~ 10 – 15 D, insuring that the CT dipole moment terms dominate the S_{yz} tensor.

For phenylacetylene, terms involving the B_a intermediate state vanish because the dipole moment terms have no short-axis (y) component. For styrene these terms contribute because the CT dipole moments are skewed off the long (z) axis, i.e., the topological effect. For small skew angles (α in Fig. 6) these terms, which vary with $\sin \alpha$ are much smaller than the terms with B_b as the intermediate state, which decrease by a factor of $\cos \alpha$.

The off-axis CT dipole moment also generates a scalar term, S_{yy} through $\mu_y = \mu \cos \alpha$ (assuming that the phenylacetylene and styrene dipole moments are identical):

$$S_{yy} = \frac{1}{\Delta E_{B_g} - \hbar\omega} \langle A^\circ | \mu_y | B_b^\circ \rangle [\Lambda_{74}\lambda_{74}\mu_y(S \rightarrow R^*) + \Lambda_{28}\lambda_{28}\mu_y(R \rightarrow S^*)] = (\sin \alpha) S_{yz}^{PA}. \quad (4)$$

In Eq. (4) S_{yz}^{PA} is the phenylacetylene symmetric tensor term and α is estimated as $\sim 19^\circ$ by the point-charge approximation. Comparing the dependence of the two tensor components on α we conclude that the scalar contribution to the $\tilde{A} - \tilde{X}$ styrene transition should be much less important than the symmetric tensor contribution, i.e., $\delta^{\text{scalar}}/\delta^{\text{symm}} \approx \tan^2 \alpha$. This conclusion and the predicted minor effect on intensity are the same as the ones arrived at by treating styrene as perturbed phenylacetylene.

The strong coupling model suggests that the strength

of the vibronic coupling band, 14_0^1 may be decreased from that in benzene contrary to the assumption made in Secs. III and IV. ν_{14} couples the ground state to the final state and consequently it is the matrix element $\langle \bar{X} | (\partial H / \partial Q_{14})_0 | \bar{A} \rangle$ that is relevant. Large scrambling of \bar{X} and \bar{A} with CT states will then weaken the strength of 14_0^1 because of the localization of the excited-state normal coordinate, Q_{14}' in the ring. Thus, use of 14_0^1 as an intensity standard tends to underestimate the total TP cross sections. Still, the predominance of ring modes in the spectrum and calculations made from approximate wave functions¹⁵ suggest that the error is probably not a gross one.

VI. CONCLUSIONS

The lack of enhancement of the TP $B_2^- - A_1^-$ transition in benzonitrile relative to the $B_2^- - A_1^-$ transition in phenylacetylene agrees with the inductive perturbation selection rule. Since there are not special symmetry factors in these molecules this result provides strong support for the generality of the rule and consequently for the pseudoparity basis.

The similar polarization behavior of the TP spectra of styrene and phenylacetylene in circularly polarized light implies that the scalar contribution to the TP cross section in styrene, formally allowed by symmetry, is unimportant. This result along with the large similar TP cross sections observed for the two molecules (despite their significantly different OP intensities) supports the generality of rule (2).

There is additional evidence for this rule. The TP spectra of the C_{2v} hydrocarbons fluorene and phenanthrene are very strong.^{40,43} And the $\bar{A} - \bar{X}$ TP spectrum of aniline (which can be viewed as a weakened benzyl anion transition) is also very intense.⁸

ACKNOWLEDGMENTS

We are grateful to the National Science Foundation for support, to Professor S. N. Thakur for valuable discussions, and to Dr. Richard P. Rava for critically reading the manuscript. The authors thank Mr. Nicodem Renaldi, our head machinist, for his timely and expert help with construction of the jet.

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