electron-withdrawing nitro groups in the 10,10′-positions, and trifluoroacetoxylation is the favored reaction in this case. Reaction with acetonitrile was only observed for the cation radicals of anthracene and 9-methylanthracene.

Concluding Remarks

The state of knowledge in the area of the mechanisms of the reactions of cation radicals with nucleophiles can be summarized in a few sentences. The reactions are invariably complex because the initial intermediates are in unstable oxidation states and further reactions must take place to afford stable products. Electron transfer and acid–base equilibria are most often coupled to the reaction between the nucleophile and the cation radical. Because of the multistep nature of the processes and the large number of intermediates involved, reactions taking place by the same pathway may exhibit widely different kinetic behavior, depending upon the reaction conditions. This is especially true of the concentration range of the reactants. In discussing mechanisms of these reactions, it is imperative to consider that a mechanism well-established under a particular set of reaction conditions may not hold with even rather subtle changes in the conditions. A disappointing feature brought about by the general complexity of these reactions is that it is seldom possible to isolate single steps for the purpose of determining the effect of structure on reactivity. A good example of a failure of this nature was pointed out for the manifold of reactions that take place involving 9-substituted anthracene cation radicals in acetonitrile.

Much of the work discussed in this account was carried out in stimulating collaboration with Dr. Ole Hammerich and Dr. Ulla Svanholm. I thank the staff at the Department of Chemistry, University of Nevada, Reno, for their gracious hospitality during my sabbatical leave and the Norwegian Council for Scientific and Industrial Research for support.

Two-Photon Spectra of Aromatic Molecules

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Received June 29, 1983 (Revised Manuscript Received December 23, 1983)

In her doctoral thesis of 1931, Maria Goeppert-Mayer[1] discussed the possibility that a molecule might simultaneously absorb two photons. However, it was 30 years later that Kaiser and Garrett[2] first observed fluorescence from Eu^{2+} induced by absorption of two photons. Development of the tunable dye laser served as the impetus behind much of the activity in two-photon (TP) spectroscopy over the last decade. An important step in this regard was made in 1973 by Cagnac et al.[3] who showed that TP excitations can be induced by relatively low power but narrow line lasers. Ingenious technological developments for the detection of TP transitions have allowed this spectroscopy to become widespread. An Account by Johnson[4] discusses one such method, multiphoton ionization, while other common methods, such as direct absorption or fluorescence excitation, and thermal lensing are reviewed in Accounts by McClain[5] and Kliger,[6] respectively.

In the past few years much of the attention has been paid to the TP spectroscopy of aromatic molecules. Many remarkable similarities and regularities in the aromatic molecule TP spectra have become apparent. These spectra show that the chemical principles that have been successful in interpreting traditional one-photon (OP) spectra are equally successful in interpreting TP absorption, but that the two spectra are frequently opposite in their response to the same perturbation. Here we give an Account of the insight that has been gained concerning the mechanisms controlling TP absorption into the lowest excited states of aromatic molecules.

This complementary behavior begins with the gerade[7] ↔ gerade (g ↔ g) parity selection rule for a TP transition in a centrosymmetric molecule, contrasted to the well-known gerade ↔ ungerade (g ↔ u) OP rule.[5] This difference between TP and OP excitation is analogous to the difference between Raman and infrared spectroscopies. In the pioneering period, 1968–1977, when the basic photophysics of molecular TP absorption were being established, this rule led to the expectation that TP spectroscopy would be especially valuable in investigating the excited g states, largely unobservable by OP absorption. There have been important observations of g-parity states by this approach.[8] Some ex-

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(1) M. Goeppert-Mayer, *Ann. Phys.* **9**, 273 (1931).
(2) W. Kaiser and G. B. Garrett, *Phys. Rev. Lett.*, **7**, 229 (1961).
(3) B. Cagnac, G. Grynberg, and F. Biraben, *J. Phys. (Orsay, Fr.)*, **34**, 845 (1973).
(4) P. M. Johnson, *Acc. Chem. Res.*, **13**, 20 (1980).
(5) W. M. McClain, *Acc. Chem. Res.*, **7**, 129 (1974).
(6) D. S. Kliger, *Acc. Chem. Res.*, **13**, 129 (1980).
(7) Molecules with a center of symmetry possess electronic states classified as having parity: gerade if the wave function remains unchanged when the Cartesian coordinate system of the molecule is inverted through the center of symmetry and ungerade if it changes sign. For a lucid account of parity selection rules, see ref 5.

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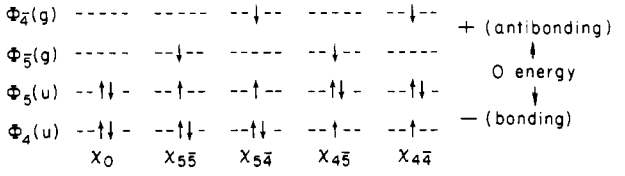
amples are as follows: detection of a g lowest excited singlet state in linear polyenes,[9] the observation of a $^1E_{1g}$ Rydberg state in benzene,[10] which had been previously hidden by the intense transition to the $^1B_{1u}$ valence state, and the location of the "phantom singlet" of stilbene,[11] which had been postulated purely on organic mechanistic grounds.[12]

A surprising development is that TP spectroscopy is fully as important in obtaining new information about g → u and nonparity transitions in low-symmetry molecules that have already been very well-studied by traditional OP procedures. This results from additional selection and perturbation rules that make the TP spectra of even many low-symmetry aromatics quite simple. These principles are discussed in this Account.

Excited States of Alternant Aromatic Hydrocarbons

Single-photon spectra of aromatic hydrocarbons exhibit weak, strong, and very strong bands progressing into the ultraviolet.[13] Attempting to understand this pattern, Platt[14] classified the bands in terms of the states of a parent $4n + 2$ C atom cyclic polyene (e.g., for benzene $n = 1$, for naphthalene $n = 2$). This description, when joined with an understanding of electron interactions in alternant hydrocarbons, explained the spectra.[15,16]

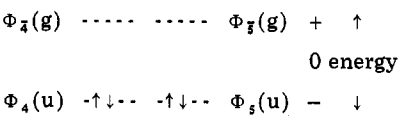
In the alternant hydrocarbon model[17] the $2p\pi$ molecular orbitals appear in bonding and antibonding pairs, Φ_r and $\Phi_{\bar{r}}$ with symmetric energies. For the 10-π-electron molecule, naphthalene, the five lowest electronic configurations are



In the diagram the ground-state configuration, $\Phi_1^2\Phi_2^2\Phi_3^2\Phi_4^2\Phi_5^2$, is represented by χ_0 and χ_{ij} represents the molecular orbital configuration arising from the promotion of an electron from Φ_i to $\Phi_{\bar{j}}$. The three lowest orbitals Φ_1, Φ_2, Φ_3, which remain filled in the diagram, are omitted for brevity. Note that a g-parity MO, e.g., $\Phi_{\bar{5}}$, does not change sign upon inversion, whereas a u-parity one does. Thus the product of two orbitals of identical parity is g, e.g., $\Phi_4(u)\Phi_5(u)$.

As seen from the diagram the third and fourth configurations $\chi_{5\bar{4}}$ and $\chi_{4\bar{5}}$ are degenerate but will be split by electron repulsion into $\psi^{\pm} = (\chi_{5\bar{4}} \pm \chi_{4\bar{5}})/\sqrt{2}$. Electron interaction is a positive quantiy lowering the energy of ψ^- below ψ^+ and, as it turns out, below $\chi_{5\bar{5}}$. The transition moments that describe the OP selection rules for optical excitations to the degenerate configurations $\chi_{5\bar{4}}$ and $\chi_{4\bar{5}}$ are approximately identical in magnitude and direction. Therefore the transition to the low-energy state, $\chi_0 \rightarrow \psi^-$, where the moments add out of phase, will be weak while that to the high-energy state, $\chi_0 \rightarrow \psi^+$, will be strong. This result can be formalized by the OP dipole selection rule $+ \nleftrightarrow -$.

The limitation of the alternant hydrocarbon model is that it does not systemize states except for the ± classification. The MO's Φ_4, Φ_5, $\Phi_{\bar{4}}$, $\Phi_{\bar{5}}$ of the cyclic polyene of naphthalene (i.e., the $C_{10}H_{10}$ ring) have the following energies:



Note from this diagram that the orbitals Φ_4 and Φ_5 as well as $\Phi_{\bar{4}}$ and $\Phi_{\bar{5}}$ are degenerate. Therefore the first four excited configurations $\chi_{4\bar{4}}$, $\chi_{5\bar{5}}$, $\chi_{4\bar{5}}$ and $\chi_{5\bar{4}}$ are also degenerate, but the symmetry of the polyene does not allow fourfold degeneracy. To break the degeneracy, ± combinations can be taken, resulting in the four states L_b^-, L_a^+ and the degenerate $B_{a,b}^+$ in this energy order. Wave functions comprised of χ_{ii} configurations are always designated as + states and the ground state as −, in conformity with alternant hydrocarbon rules.[15] This is the pattern of states in benzene. The a and b notation represents nodes through bonds and through atoms, respectively. In the cyclic polyene L_b^- (i.e., B_{2u}) and L_a^+ (i.e., B_{1u}) are forbidden states because of symmetry, a circumstance that cannot occur for catacondensed hydrocarbons. $B_{a,b}^+$ (E_{1u}) is allowed. Note that parity is a good quantum number for the centrosymmetric cyclic polyene.

Naphthalene is formed from the polyene by introducing a bond across the polyene ring in the cyclic polyene model. Moffitt[16] termed this kind of perturbation an odd perturbation since the sum of the numbers labeling the atoms involved in the bond formation (e.g., in naphthalene, 0 and 5) is odd. The consequence is that the forbidden L_a^+ and L_b^- states of the $C_{10}H_{10}$ cyclic polyene becomes mixed with the allowed cyclic polyene $B_{a,b}^+$ state. Since the $B_{a,b}^+$ state in the cyclic polyene is intensely allowed, L_a^+ and L_b^- in naphthalene may become allowed. For odd perturbations, such as bond formation (as in naphthalene) the B_b^+ character vanishes to the first order, and so this model explains why the strength of the lowest energy band (L_b^-), which depends on B_b^+ character, is weak in OP spectroscopy. However, the B_a^+ character does not vanish for an odd perturbation and the second band (L_a^+) is strong. Both are much weaker than the high energy allowed ($B_{a,b}^+$) band.[13]

Other perturbations can also be labeled odd or even in the Moffitt sense. Bond-stretching vibrations involving adjacent atoms are again odd (i.e., sum of the numbers labeling the atoms is odd). An inductive perturbation of a substituent, in contrast, is even since inductive substituents are considered to only perturb atoms, not bonds. The important link between even/odd perturbations and ± characters was made by Donath.[18] Odd perturbations preserve the ± character

(8) (a) K. B. Eisenthal, M. W. Dowley, and W. L. Peticolas, *Phys. Rev. Lett.*, **20**, 93 (1968); (b) D. M. Friedrich and W. M. McClain, *Annu. Rev. Phys. Chem.*, **31**, 559 (1980).
(9) L. S. Heimbrook, J. E. Kenny, B. E. Kohler, and G. W. Scott, *J. Chem. Phys.*, **75**, 4338 (1981) and references therein.
(10) P. M. Johnson, *J. Chem. Phys.*, **62**, 4562 (1975); **64**, 4143 (1976).
(11) T. M. Stachelek, T. A. Pazoha, and W. M. McClain, *J. Chem. Phys.*, **66**, 4540 (1977).
(12) J. A. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafirou, *Org. Photochem.*, **3**, 1 (1971).
(13) E. Clar, "Aromatische Kohlenwasseerstoffe", 2d ed.; Springer-Verlag: West Berlin, 1952.
(14) (a) H. B. Klevans and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1947); (b) J. R. Platt, *ibid.*, **17**, 484 (1949); **18**, 1168 (1950).
(15) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).
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Table I
Selection and Perturbation Rules for Aromatic Molecule L_b^- and L_a^+ Spectra

	one-photon		two-photon	
rule	L_b^-	L_a^+	L_b^-	L_a^+
selection				
parity[a]	allowed[c]	allowed[c]	forbidden[c]	forbidden[c]
pairing[b]	forbidden	allowed	allowed	forbidden
perturbation				
vibronic	weak	strong	strong	weak
inductive	strong	weak	weak	strong
resonance	weak	strong	strong	strong

[a] The OP and TP parity selection rules are g ↔ u and g ↔ g, respectively. [b] The OP and TP pairing selection rules are + ↔ − and ± ↔ ±, respectively. [c] For the cyclic polyene patent states.

of the paired alternant hydrocarbon wave function, but even ones destroy it by introducing opposite character. These conclusions are summarized in Table I.

Thus, besides rationalizing the spectral pattern in aromatic hydrocarbons, Moffitt's ideas showed how the greatly different sensitivities of L_b^- and L_a^+ spectra to vibrational distortions and to inductive perturbations arise from the odd/even perturbation character. Inductive substituents that cause an even perturbation by introducing the + character B_b^+ cyclic polyene state into L_b^- greatly affect L_b^- absorption. In contrast vibrational coupling bands that are caused by odd perturbations are observed to be weak in L_b^- and strong in L_a^+. The spectra also show that memory of the cyclic polyene parent-state parity persists even in low symmetry aromatic hydrocarbons.

In subsequent sections, we will show how these ideas of ± character, cyclic polyene g, u parentage and classification of catacondensed hydrocarbon states, and the even or odd nature of perturbations explain and interpret a large body of TP spectra of aromatic molecules.

Two-Photon Spectroscopy of Alternant Aromatic Hydrocarbons

The basic principles of molecular TP spectroscopy have been discussed in several comprehensive articles[5,8,19-22] and will be reviewed only briefly here. In OP spectroscopy, the electric dipole transition moment

$$M_{of}^{\ i} = \int \Psi_o r_i \Psi_f d\tau \qquad (i = x, y, z) \qquad (1)$$

describes the amplitude and selection rules of an optical transition between states Ψ_o and Ψ_f. In order for M_{of} to be different from zero, the integrand, $\Psi_o r_i \Psi_f$, must be an even function (i.e., contain a totally symmetric component).

The u parity of the position vector, r, requires Ψ_o and Ψ_f to have different parities for an electric dipole allowed OP transition. Thus the overall electric dipole selection rule for centrosymmetric molecules is g ↔ u, + ↔ − (recalling the ± rule from the previous section). In OP spectroscopy a strong ultraviolet transition at 250 nm (40 000 cm^{-1}) with unit oscillator strength corresponds to $M_{of} \approx 1.5$ Å.

The quantity of interest in TP spectroscopy is a transition tensor, S_{of}, which is formed by the product of two electric dipole transition vectors

$$S_{of}^{\ ij} \propto M_{ok}^{\ i} M_{kf}^{\ j} \qquad (i, j = x, y, z) \qquad (2)$$

Therefore TP transitions can only take place between states of *identical* parity *and* ± character. The particularly simple form of eq 2 for cyclic polyenes results from the single strongly allowed (high lying) OP transition from the ground state, to the intermediate k state $B_{a,b}^+$ present in these molecules.[23] The $B_{a,b}^+$ state enters in because of the perturbation of the intense laser light, even though the radiation does not actually excite this state. The lack of resonances with the laser radiation causes the TP spectra to be simple and eq 2 can be used to analyze the essential mechanisms controlling aromatic molecule TP spectra.

The g ↔ g and − ↔ − TP selection rules complement the electric dipole rules of OP spectroscopy. Two 1.5-Å transition moments are sufficient to produce a TP absorptivity $\delta \sim 10^{-48}$–10^{-49} cm^4 s (reported in Goeppert-Mayers (GM) = 10^{-50} cm^4 s) under the resonance and line-shape conditions that exist in aromatic molecules. A 10^2 GM absorptivity corresponds to an intense and in general readily observable TP band.

Callis, Scott, and Albrecht[24b] recognized that the odd/even perturbation rules derived by Moffitt can be extended to TP spectra. Their approach provides a powerful intuitive insight for understanding the TP spectra of aromatic molecules. For example, the lowest excited singlet $B_{2u}(L_b^-)$ state of naphthalene is TP allowed by the ± rule but is parity forbidden from the A_g^- ground state. To make this transition allowed a parity changing, ± conserving odd perturbation is required. Such a perturbation is provided by a bond-stretching u type vibration. An inductive substituent, however, will not be effective for L_b^- since an even perturbation changes − to +. Inductive perturbations will be effective for L_a^+, where the perturbation changes + to −, making the transition TP allowed from the − ground state.

For OP transitions, the lowest four cyclic polyene u-parity configurations account for the spectra to the lowest excited states. These have incorrect parity to be perceived by TP absorption. To obtain TP intensity in naphthalene, for example, higher energy (TP allowed) g-parity configurations must mix into the u-parity L_b^- wave function. When these g-parity configurations enter the TP tensor (2), the tensor becomes large for certain vibrations.

In OP spectroscopy of the low-lying L_b^- state, extension of the π-electron system is generally masked by the inductive effect of the substituent group until the

(18) W. Donath, *J. Chem. Phys.*, **41**, 626 (1964).
(19) W. M. McClain and R. Harris, *Excited States*, **3**, 2–56 (1977).
(20) H. Mahr, "Quantum Electronics: A. Treatise", H. Rabin and C. L. Tang, Ed., Academic Press, New York, 1975, Vol. 1A, pp 285–361.
(21) F. Metz, W. E. Howard, L. Wunsch, H. J. Neusser, and E. W. Schlag, *Proc. R. Soc. London, Ser. A*, **363**, 381 (1978).
(22) D. M. Friedrich, *J. Chem. Educ.* **59**, 472 (1982).

(23) The transition amplitude for simultaneous absorption of two identical photons (in a single laser experiment, as is the case for all the spectra discussed in this article) of wavenumber $h\omega$ is given (to the second order) by $S_{of}^{\ ij} = \sum_k M_{ok}^{\ i} M_{kf}^{\ j} / (\Delta E_{ok} - h\omega)$, where $\Delta E_{ok} = (E_k - E_o)/h$. The summation over virtual intermediate states k includes all states of the system. For aromatic molecules there are two important simplifications regarding the virtual intermediate states. The first stems from the lack of important low-lying intermediate states so that resonances (or near resonances) with these states are not encountered in TP spectroscopy of aromatics. The second stems from the dominant contribution of the strongly allowed $B_{a,b}^+$ states present in cyclic polyenes[24,25] so that the single-term form of eq 2 is valid.

(24) (a) T. W. Scott, P. R. Callis, and A. C. Albrecht, *Chem. Phys. Lett.*, **93**, 111 (1982); (b) P. R. Callis, T. W. Scott, and A. C. Albrecht, *J. Chem. Phys.*, **78**, 16 (1983); (c) P. R. Callis, *Chem. Phys. Lett.*, **107**, 125 (1984).

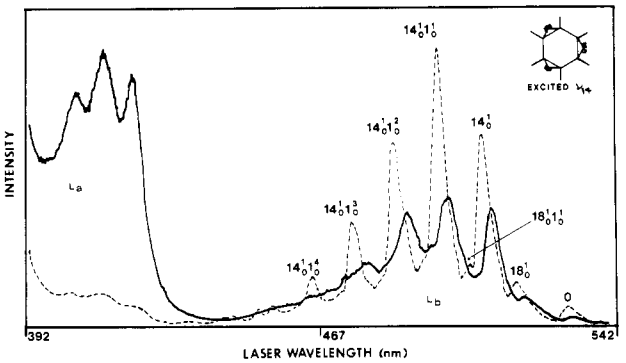


Figure 1. Comparison of two-photon L_b and L_a fluorescence excitation spectra for benzene (---) and fluorobenzene (—) solutions in *n*-hexane. The L_a band intensity should be multiplied by ~3 to compensate for fluorescence yield variations. *O* designates the origin band missing in the benzene vapor spectrum but made allowed by solution perturbation. Reproduced from Scott, Callis, and Albrecht[24a] by permission. Copyright American Institute of Physics, 1983.

delocalization is large, such as for NH_2. Delocalization introduces charge-transfer states into the perturbation scheme. These may be hydrocarbon → substituent states due to an energetically low-lying vacant π MO of the substituent (as in NO_2) or states arising by promoting an electron in a filled π-substituent MO to an empty MO of the hydrocarbon (as in OH).

As discussed earlier, the + terms brought into the TP tensor by the even-perturbation inductive effect do not cause any intensity. The major effect on the L_b^- TP intensity caused by a substituent group is then through the parity destroying charge-transfer effect. The substituent perturbation on the TP tensor for the L_b^- state is proportional to the amount of charge-transfer character introduced into the excited state. For the TP spectrum, even weak resonance effects, as produced by CH_3, for example, may become important, since the inductive effect vanishes to the first order.[25]

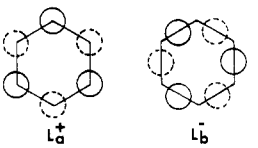
The selection and perturbation rules for the TP spectroscopy of the L_b^- state of alternant aromatic hydrocarbons are summarized in Table I and contrasted to those for OP spectra.

Two-Photon Spectrum of Benzene

Since the L_b^-, L_a^+ transitions in benzene are parity forbidden, the TP spectra are vibronically induced. These are the familiar $^1B_{2u}$, $^1B_{1u} \leftarrow {}^1A_{1g}$ transitions found in traditional benzene near-UV spectra. In 1975, Friedrich and McClain[26] and Wunsch, Neusser, and Schlag[27] independently demonstrated that the main strength in the B_{2u} band system is due to b_{2u} vibrations. Since these initial studies, many other papers have appeared on the TP $^1B_{2u} \leftarrow {}^1A_{1g}$ spectrum of benzene for the vapor,[28] liquid[24a,32] and low-temperature crystal phases.[29] The most comprehensive list of bands have been given by Wunsch et al. for the room-temperature vapor[28d] and Sur et al.[30] for the molecule cooled in a supersonic jet. As shown in Figure 1, the most important perturbing vibration is the primarily skeletal mode, ν_{14}.[31] The hydrogen wagging e_{1u} mode ν_{18} is also strongly active, although considerably less so than ν_{14}. In addition, the Franck–Condon ring breathing vibration, ν_1, appears built on all these modes. A review of the spectrum is given by Ziegler and Hudson.[32]

The region of the second excited singlet transition in benzene, $^1B_{1u} \leftarrow {}^1A_{1g}$, has received much less attention than $^1B_{2u}$. A weak absorption corresponding to the TP $^1B_{1u}$ transition has been detected in pure liquid benzene and in solution in *n*-hexane by both direct absorption and fluorescence excitation.[24a,33] Comparison of the fluorescence excitation spectra in *n*-hexane solution for both regions is shown in Figure 1. The spectra reveal only diffuse vibrational structure in the $^1B_{1u}$ region, parallel to that found for the OP spectrum. Most importantly, this TP transition is seen to be much weaker than the highly structured $^1B_{2u}$, opposite to that found for OP absorption.

The $^1B_{2u} \leftarrow {}^1A_{1g}$ and $^1B_{1u} \leftarrow {}^1A_{1g}$ transitions involve the $- \leftrightarrow -$ TP allowed L_b^- and $- \leftrightarrow +$ forbidden L_a^+ excitations, respectively. The weakness of the latter and strength of the former provide striking confirmation of the perturbation rules that predict that ± conserving vibrational perturbations can appear only in the B_{2u} transition.[24a-c] The benzene spectrum provided insight into Herzberg–Teller vibronic mixing in forbidden TP transitions. The mechanism for the activity of these vibrations is thought to involve coupling of the B_{2u} state to the A_{1g} ground state,[24c,25a,26,34] with high activity of the Kekulé mode, ν_{14}, rationalized from the congruence of ν_{14} with the sign alternation in the L_b^- ground-state transition density[24b,c] Lack of parallel vibronic activity



in L_a^+ is justified by vanishing density in bond positions.

Two-Photon Spectra of Catacondensed Hydrocarbons

There have been several studies of TP spectra for aromatic hydrocarbons larger than benzene. Much of the pioneering work in this area was carried out by Eisenthal and Peticolas,[8a,35a] McLain,[35b] and by Jort-

(25) (a) L. Goodman and R. P. Rava, *Adv. Chem. Phys.*, **54**, 177–250 (1983); (b) R. P. Rava and L. Goodman, *J. Am. Chem. Soc.*, **104**, 3815 (1982); (c) L. Goodman and R. P. Rava, *J. Chem. Phys.*, **74**, 4826 (1981).

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(28) (a) J. R. Lombardi, D. M. Friedrich, and W. M. McClain, *Chem. Phys. Lett.*, **38**, 213 (1975); (b) J. R. Lombardi, R. Wallenstein, T. W. Hansch, and D. M. Friedrich, *J. Chem. Phys.*, **65**, 2537 (1976); (c) L. Wunsch, H. J. Neusser, and E. W. Schlag, *Chem. Phys. Lett.*, **38**, 216 (1976); (d) L. Wunsch, F. Metz, H. J. Neusser, and E. W. Schlag, *J. Chem. Phys.*, **66**, 386 (1977).

(29) (a) R. M. Hochstrasser, J. E. Wessel, and H. N. Sung, *J. Chem. Phys.*, **60**, 317 (1974); (b) R. M. Hochstrasser, C. M. Klimak, and G. R. Meredith, *ibd.*, **70**, 870 (1979); **72**, 3440 (1980); (c) R. M. Hochstrasser, G. R. Meredith, and H. P. Trommsdorf, *ibid.*, **73**, 1009 (1980).

(30) A. Sur, J. Knee, and P. Johnson, *J. Chem. Phys.*, **77**, 654 (1982).

(31) Vibrations are numbered by the convention of E. B. Wilson, Jr. [*Phys. Rev.*, *45*, 706 (1934)]. Vibronic bands will be designated by sub- and superscripts indicating the number of quanta excited in the lower and upper states, respectively, e.g., 6_0^1.

(32) L. D. Ziegler and B. S. Hudson, *Excited States*, *5*, 41–140 (1982).

(33) (a) A. S. Twarowski and D. S. Kliger, *Chem. Phys.*, **20**, 259 (1977); (b) L. D. Ziegler and B. S. Hudson, *Chem. Phys. Lett.*, 71, 113 (1981).

(34) R. P. Rava, L. Goodman, and K. Krogh-Jespersen, *J. Chem. Phys.*, **74**, 273 (1981).

(35) For example, see (a) M. W. Dowley, K. B. Eisenthal, and W. L. Peticolas, *J. Chem. Phys.* **47**, 1609 (1967); (b) P. R. Monson and W. M. McClain, *ibid.* **53**, 29 (1970); **56**, 4817 (1972); (c) A. Bergman and J. Jortner, *Chem. Phys. Lett.*, **15**, 309 (1972); **26**, 323 (1974).

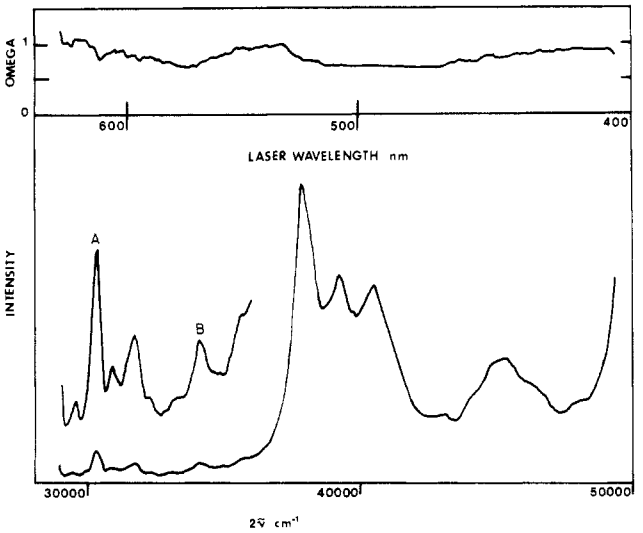

Figure 2. Two-photon fluorescence excitation spectra of phenanthrene in 10^{-3} M ethanol solution. The lower spectrum is for linearly polarized laser light; the upper spectrum represents the ratio of the intensities in linearly and circularly polarized light, omega. Reproduced from Dick and Hohlneicher[39a] by permission. Copyright North-Holland, 1983.

ner[35c] in the late 1960s and early 1970s. In this early work, the polarization dependence of TP absorption and the first TP absorption of a molecule were among the notable contributions. Vibrational analyses of the TP L_b spectrum of naphthalene and phenanthrene exist for the gas[35] and/or crystal[36] phases, as well as lower resolution TP spectra of higher energy states in solution.[37,38] Much of the recent work on the TP spectra of larger condensed aromatics has been carried out in solution by Dick and Hohlneicher.[38,39a-c]

The naphthalene $L_b^-(B_{2u})$ TP spectrum is parity forbidden as in benzene. The polarization characteristics of the spectrum reveals that the major active vibrations are b_{2u} modes which conserve the – character while coupling to A_{1g} states. The motion in these vibrations, alternate compression and expansion of C–C bonds around the rings, is similar to the major vibration in benzene, ν_{14}. Thus there is a strong parallel to the efficient vibronic coupling mechanism present in benzene which is thought to also involve the ground state.[40] Despite the forbiddeness the TP absorptivity is large. The TP transition to the L_a^+ state on the other hand is very weak, in accord with the vibronic rule that + states may only be perturbed by + states.

The TP spectra of larger centrosymmetric aromatic hydrocarbons such as anthracene and those lacking a center of symmetry show strong TP transitions to the lowest singlet L_b^- states and weak transitions to L_a^+. Parity is no longer a factor in these latter molecules, and the TP spectra still complement the weak and strong OP transitions exhibited by L_b^- and L_a^+, respectively. This kind of behavior, shown by biphenyl, phenanthrene, stilbene, acenaphthalene, pyrene, and fluorene,[38,39,41] is in accord with the alternant hydrocarbon – ↔ – TP selection rule. The TP spectra of phenanthrene[39a] (the solution spectrum is given in Figure 2) is a case in point. The long wavelength region of the spectrum near 30 000 cm^{-1} represents the L_b^- transition. High-resolution studies of this TP transition at low temperature clearly proves its allowed character, and most of the strong vibrational lines can be assigned as totally symmetric fundamentals.[37c] However, even though there is no center of symmetry, there is a very intense band (A in Figure 2) induced by vibrational motion (now totally symmetric) analogous to that found in benzene and naphthalene. At 34 000 cm^{-1} a weak feature (B in Figure 2) appears in the TP spectrum which coincides with the OP L_a^+ 0–0 transition.

A major feature in the TP spectra of the larger aromatics is the discovery of higher energy g-parity valence states.[38,39] These states are allowed by a TP transition from the g ground state and were previously obscured in OP spectroscopy by the strong transitions to the $B_{a,b}^+$ OP-allowed states. In fact, the most intense portion of the phenanthrene TP spectrum in Figure 2 appears between 37 000 and 42 000 cm^{-1}. The polarization spectrum given in the upper part of Figure 2 shows that this band is strongly attenuated in circularly polarized light. Polarization experiments are very useful in TP spectroscopy since use of circularly polarized light usually leads to attenuation of only totally symmetric bands.[19] A_1 symmetry is then indicated and this band probably can be attributed to a state with g parity in the $C_{14}H_{14}$ cyclic polyene parent to phenanthrene.

Substituent Effects

In general, a substituent destroys symmetry restrictions, and transitions to the L_b and L_a states become formally allowed. In many cases spectra of substituted aromatic hydrocarbons retain a strong resemblance to that of the parent molecule. However, as shown in Table I, the OP and TP spectra are expected to react oppositely to different substituent perturbations. Inductive substituents are predicted to enhance the OP L_b^- and TP L_a^+ spectra strongly but not the TP L_b^- spectrum. Contamination of the L_b^- wavefunction by CT states through weak resonance interaction is not effective in inducing OP intensity, because short-axis CT transitions (CT_b) are weak. The transition tensor (2) for TP transitions contains M_{ok} and M_{kf}, however. For k state $B_{a,b}$ in cyclic polyenes, the latter transition moment is very sensitive to destruction of the u character in L_b^-.[25b] Weak resonance interactions, which play only a second-order role in OP L_b spectra, are then predicted to be the major substituent effect on the intensity of the benzene TP L_b^- spectrum.

The most intensive studies of substituent effects on TP spectra have been on substituted benzenes[25,42] and

(36) U. Boesl, H. J. Neusser, and E. W. Schlag, *Chem. Phys.*, **15**, 167 (1976).

(37) (a) R. M. Hochstrasser and H. N. Sung, *J. Chem. Phys.*, **66**, 3266 (1977), and references therein; (b) N. Mikami and M. Ito, *Chem. Phys.*, **23**, 141 (1977); (c) V. Sethuraman, M. C. Edelson, C. K. Johnson, C. Sethuraman, and G. J. Small, *Mol. Cryst. Liq. Cryst.*, **57**, 89 (1980); (d) H. Otokazawa, S. Inomata, N. Mikami, and M. Ito, *Bull. Chem. Soc. Jpn.*, **50**, 2899 (1977).

(38) (a) B. Dick and G. Hohlneicher, *Chem. Phys. Lett.*, **84**, 471 (1981), and references therein.

(39) (a) B. Dick and G. Hohlneicher, *Chem. Phys. Lett.*, **97**, 324 (1983); (b) G. Hohlneicher and B. Dick, *Pure Appl. Chem.*, **55**, 261 (1983); (c) B. Dick, H. Gonska, and G. Hohlneicher, *Ber. Bunsenges. Phys. Chem.*, **85**, 746 (1981); (d) P. R. Salvi, P. Foggi, and E. Castellucci, *Chem. Phys. Lett.*, **98**, 206 (1983).

(40) (a) N. Makami and M. Ito, *Chem. Phys. Lett.*, **31**, 472 (1975); (b) G. Marconi and G. Orlandi, *J. Chem. Soc., Faraday Trans. 2*, **78**, 273 (1982).

(41) (a) A. Amlrav, U. Even, and J. Jortner, *J. Chem. Phys.*, **75**, 3151 (1981). (b) The $L_b^-(^1A_1) \leftarrow {}^1A_1$ TP spectrum of carbazole shows similar Herzberg–Teller activity for totally symmetric vibrations.[41c] (c) A. Bree, and C. Taliaic, *Chem. Phys. Lett.*, **98**, 62 (1983); (d) P. R. Salvi, E. Castellucci, P. Foggi, and R. Quacquarini, *Chem. Phys.*, **83**, 345 (1984).

Table II
Two-Photon Absorptivities[a] (Goeppert-Mayers) and One-Photon Oscillator Strengths[b] for Monosubstituted Benzene L_b 0-0 Bands

molecule	$\delta(0\text{-}0)$	$f(0\text{-}0)$
benzene	0	0
fluorobenzene	0.3	0.0072
chlorobenzene	2	0.0012
toluene	3	0.001
bromobenzene	4	0.0010
phenol	7	0.015
aniline	50	0.022

[a] The TP vapor-phase absorptivities have been estimated by comparing the origin band intensity to the strength of the vibronic coupling band 14_0^1 as a standard. Its strength is assumed to remain unchanged from that in benzene (δ = 8.7 GM).[25c] Both fluorescence excitation and multiphoton ionization measurements have been employed, and the relative intensity ordering is similar by either method when the factors mentioned in ref 57 are taken into account. While considerable error may ensue from this procedure for a strong substituent, such as amino, the values are believed to be qualitatively valid. [b] From ref 53c.

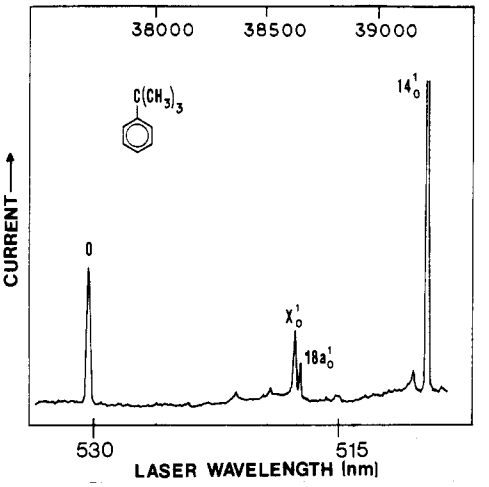

Figure 3. Fundamental region of the resonant two-photon L_b multiphoton ionization spectrum of *tert*-butylbenzene obtained in a seeded argon supersonic jet. The 14_0^1 band that is believed to have the same intensity as in benzene has been cut at half height. Note that the Franck–Condon band X_0^1 is largely 1_0^1.

naphthalenes.[35,38,43] Sources of intensity are now understood. Isotopic effects on vibronic intensities have been extensively studied,[30,44] and orientation rules for polysubstitution have been derived.[45] In the case of benzene derivatives the regularities for two-photon spectra corresponding to the $^1B_{2u} \leftarrow {}^1A_{1g}$ transition are now nearly as well-known as for the normal optical spectra.

Determination of absolute absorptivities of a TP transition is a difficult experiment involving complicated equipment (usually requiring an ability to measure very small intensity changes or interference between TP and CARS resonances),[22] and we will not comment on these techniques here. However, the localization of the vibronic coupling mode ν_{14} in the benzene ring (see Figure 1) allows use of the 14_0^1 cross section (for which an absolute absorptivity of 8.7 GM has been measured)[29c] as an internal standard. This localization persists even under external mass perturbation[44] and allows the TP cross sections for substituted benzenes to be compared.

Alkylbenzenes. The weak hyperconjugative interaction of a methyl group increases the intensity of the benzene OP L_b^- band to about 0.1–0.2% of an allowed (f = 1) OP transition, (Table II). The same group enhances the TP L_b^- absorption strength to nearly 5% of an allowed σ = 100 GM TP transition.[25c] The ~ 50-fold disparity in the effect of hyperconjugative interaction is dramatic evidence for the differing importance of small charge migrations into or out of the ring in the two spectroscopies. The TP L_b^- spectrum of *tert*-butylbenzene in a seeded argon supersonic jet is given in Figure 3. The simplicity of the spectrum results from cooling out numerous bands involving torsional modes of the *tert*-butyl group seen at higher temperatures. This spectrum shows that substantial intensity is induced into the benzene TP spectrum even by the very weakly interacting *tert*-butyl group.

Halobenzenes. The fluorobenzene L_b TP spectrum is only one-tenth as strong as that of toluene (Table II) (Although the OP strength is 10 times stronger), illustrating the feebleness of an inductive perturbation on the TP L_b^- bands. On the other hand the L_a^+ spectrum (Figure 1) strongly increases in intensity over benzene in agreement with the rules given in Table I. This is the only known example of a substituent effect on the L_a^+ TP benzene spectrum.[58]

Comparison of the OP and TP L_b spectra of fluoro-, chloro-, and bromobenzenes (the TP spectrum of C_6H_5I has not been reported) provides a clear illustration of the different effects of resonance and inductive perturbations on the two spectra. The OP absorption grows in intensity from Br to F (Table II), reflecting the increasing inductive effect. The TP spectrum grows from F to Br, reflecting the increasing resonance migration into the ring.

Azabenzenes. The only nitrogen heterocyclic for which a $\pi\pi^*$ TP spectrum has been reported is the pyrimidine study of Callis, Scott, and Albrecht.[46] Even in this strongly perturbed benzene, where ring carbons are exchanged for nitrogens, the L_b^- spectrum remains weak in accord with the perturbation rules.

TP spectra corresponding to the $n\pi^*$ transitions in pyrazine,[47] pyrimidine,[46] and *s*-triazene[48] have all been reported, but the rules for these transitions are not as clear as for the $\pi\pi^*$ ones.

Phenol and Aniline. The TP L_b absorption strength of phenol and anisole are substantially larger than that for toluene in accord with increased resonance migration. The strongest band in the spectra is still the vibronic coupling transition 14_0^1, but many Franck–Condon bands are observed consistent with the increased allowed character.

(42) (a) R. Vasudev and J. C. D. Brand, *J. Mol. Spectrosc.*, **75**, 288 (1979); *Chem. Phys.*, **37**, 211 (1979); (b) K. Krogh-Jespersen, R. P. Rava, and L. Goodman, *Chem. Phys.*, **47**, 321 (1980); **44**, 295 (1979).
(43) R. P. Rava and L. Goodman, *Chem. Phys. Lett.*, submitted for publication.
(44) (a) L. Goodman and R. P. Rava, *Adv. Laser Spectrosc.*, 1, 21–53 (1982); (b) R. P. Rava, J. G. Philis, K. Krogh-Jespersen, and L. Goodman, *J. Chem. Phys.*, **79**, 4664 (1983).
(45) R. P. Rava, L. Goodman, and J. G. Philis, *J. Chem. Phys.*, **77**, 4912 (1982).
(46) P. R. Callis, T. W. Scott, and A. C. Albrecht, *J. Chem. Phys.*, **75**, 5640 (1981).
(47) P. Esherick, P. Zinsli, and M. A. El-Sayed, *Chem. Phys.*, **10**, 415 (1975).
(48) (a) J. D. Webb, K. M. Swift, and E. R. Bernstein, *J. Chem. Phys.*, **73**, 4891 (1980); (b) G. Fischer and B. Katz, *Chem. Phys. Lett.*, **96**, 47 (1983).

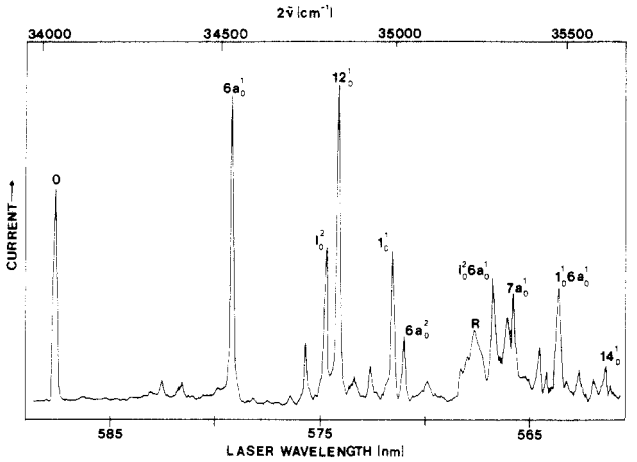

Figure 4. Normalized resonant two-photon $S_1 \leftarrow S_0$ multiphoton ionization spectrum of aniline in a seeded argon supersonic jet. All bands involve Franck–Condon modes (ν_I is the NH_2 inversion mode) except 14_0^1, which is derived from the vibronic coupling mode found in the benzene spectrum (and believed to have approximately the same intensity as in benzene), and R, which is probably a Rydberg transition.

The spectrum of aniline (taken in a seeded supersonic jet in order to freeze out strong low-frequency NH_2 inversion sequence bands (Figure 4)) shows that the residual benzene vibronic coupling band 14_0^1 is completely dominated by intense Franck–Condon bands. In this case the OP and TP spectra are both strongly allowed and almost identical. The prominence of bands due to the NH_2 inversion mode in both spectra is an indication of strong electron delocalization between NH_2 and the ring. On the basis of the relative strengths of the FC and 14_0^1 bands, the absorptivity exceeds 100 GM. Thus the aniline TP spectrum is very intense, much stronger than that for any other substituted benzene (Table II).

These facts suggest that the aniline spectrum may be more profitably approached as a benzyl anion band, somewhat modified by the inductive effect of the amino nitrogen, than as a perturbed benzene L_b^- transition.[49] The promotion of interest, consequently, does not represent a paired state and thus the ± selection rule does not apply. Both the OP and TP $S_1 \leftarrow S_0$ spectra are then expected to be intense, since the transition is delocalized throughout the molecule and possesses no special symmetry.[51]

Polysubstituted Benzenes. The complementary behavior of L_b^- OP and TP spectra persists when polysubstitution is considered. For example, the TP spectrum of a 1,4-homosubstituted benzene reverts to a forbidden transition because the g ↔ g rule is not satisfied, whereas the OP transition intensity is 4 times that for the monosubstituted benzene. The OP result is an example of the Sklar rules[53] given in Table III. The equivalent TP rules are also given there.

(49) An accurate account of the aniline transitions must lie between the descriptions of these two models as shown by the work of Godfrey and Murrell.[50]

(50) M. Godfrey and J. N. Murrell, *Proc. R. Soc. London*, **57**, 64, 71 (1964).

(51) The initial and final state terms, k = o and f in eq 2, may make a substantial contribution to the TP tensor if the dipole moment strongly alters with excitation,[52] as appears to be the case in benzyl anion.

(52) B. Dick and G. Hohlneicher, *J. Chem. Phys.*, **76**, 5755 (1982).

(53) (a) A. L. Sklar, *J. Chem. Phys.*, **10**, 135 (1942); (b) T. Forster, *Z. Naturforsch, A* **2**, 149 (1947); (c) J. Petruska, *J. Chem. Phys.*, **34**, 1111, 1120 (1961).

Table III
Effect of Substitution on Intensity of the L_b^- Benzene Bands[a,b]

	enhancement[b]			enhancement	
disubstitution	one-photon	two-photon	trisubstitution	one-photon	two-photon
ortho	1	3	1,2,3	0	4
meta	1	1	1,3,5	0	0
para	4	0	1,2,4	3	1

[a] Symmetry and the perturbation theory approach require holes to show the same intensity as substituents (e.g., penta- is equivalent to monosubstitution). [b] The enhancement factor is taken relative to the effect of monosubstitution.

One interesting conclusion is that despite being symmetry and parity allowed, the $A'_2 \leftarrow A'_1$ L_b TP transition in *s*-1,3,5-trisubstituted benzenes is perturbation forbidden. A parallel instance is found in OP spectra for 1,2,3-$C_6H_3X_3$, where the symmetry-allowed L_b band is predicted to revert to a forbidden transition. But the TP transition for this molecule is predicted to be the most intense of any orientation, illustrating once more the complementary behavior between OP and TP spectra.

These results are in agreement with the known TP spectra of polyfluoro- and polymethylbenzenes.[45,54] The circularly polarized light spectra of the 1,2 and 1,2,4 compounds provide a test of the perturbation ideas behind these rules. In these molecules both the origin and 14_0^1 vibronic coupling bands represent transitions between totally symmetric states. Despite the identical symmetry, the perturbation theory predicts that these transitions should show different polarizations and is confirmed by their respective enhancement and attenuation.[45,54] The polysubstitution intensities also suggest that CT intermediate states are relatively unimportant interpreting substituent effects.[45]

Unsaturated Aromatics

We have saved the unsaturated aromatic molecules, phenylacetylene, benzonitrile, and styrene, until last because the most convincing exemplification of the TP selection and perturbation rules is found in these aromatics, which lack the symmetry features paramount in benzene.

There is little memory of the benzene L_b^- transition in the low-lying $S_1^-(B_2) \leftarrow S_0^-(A_1)$ OP spectrum of phenylacetylene, with the transition behaving as if it were delocalized throughout the molecule (e.g., the C—C≡C bending mode is strongly active). The OP transition is weak ($f < 0.001$, even weaker than toluene), but the two-photon spectrum is strong ($\delta \sim 100$ gm),[55] in agreement with the – ↔ – selection rule of Table I.

The corresponding OP spectrum of benzonitrile is strongly enhanced ($f = 0.02$), establishing that the inductive effect is the normal one for a – ↔ – OP transition. But the TP spectra of phenylacetylene and benzonitrile are similar, exhibiting nearly the same origin band strengths when normalized to equal 14_0^1 absorptivity.[55]

(54) J. M. Hollas, B. J. Langham, H. Musa, and T. Ridley, *J. Mol. Spectrosc.*, **97**, 405 (1983); J. M. Hollas, H. Musa, and T. Ridley, *ibid.*, **98**, 125 (1983).

(55) (a) L. Chia and L. Goodman, *J. Chem. Phys.* **76**, 4745 (1982); (b) L. Chia, L. Goodman, and J. G. Philis, *ibid.* **79**, 593 (1983); (c) N. Periasamy and S. Doraisamy, *Pramana*, **21**, 79 (1983).

The corresponding $S_1(A') \leftarrow S_0(A')$ OP spectrum of styrene also exhibits the weak character of a $- \leftrightarrow -$ transition, but it is stronger than in phenylacetylene. This would seem to indicate that the perfect pairing approximation inherent in the $- \leftrightarrow -$ selection rule may not be as well fulfilled in styrene as in phenylacetylene. A more striking difference is that the electronic transition moment is found to be along the long axis in styrene, unlike phenylacetylene, where it is known to be along the short in-plane axis.[56] Despite these differences in the OP spectra of the two molecules, the TP spectra (except for a 1000-cm^{-1} frequency shift) are virtually identical,[55] suggesting that $S_1^- \leftarrow S_0^-$ TP transitions in unsaturated aromatics are fully allowed.

(56) J. M. Hollas and S. N. Thakur, *Mol. Phys.*, **25**, 1315 (1973); **27**, 1001 (1974).

(57) D. W. Squire, M. P. Barbalas, and R. B. Bernstein, *J. Phys. Chem.*, **87**, 1701 (1983).

(58) *Added in proof*: J. K. Rice (Ph.D. Thesis, University of California, Santa Cruz, 1983) has shown by thermal lensing experiments that the TP L_a intensities for toluene, phenol, and aniline are also strongly enhanced.

Concluding Remarks

The theme of this Account is that two-photon spectra of aromatic molecules are simple and understandable on the basis of several different kinds of selection rules (parity, symmetry, and pairing ($\pm$)). The rules and information gained are complementary to those obtained from one-photon spectra. Future developments should see two-photon spectroscopy assume its ultimate role—that of an electronic spectroscopy fully as important to electrons as Raman spectroscopy is to vibrations.

Financial support by National Science Foundation is gratefully acknowledged. We take this opportunity to especially acknowledge the influence that W. Martin McClain's work has had on our thinking about two-photon problems. We are the recipients of stimulating conversations with Professors McClain, A. C. Albrecht, G. Hohlneicher, and Patrik Callis and with our colleagues and members of the Rutgers two-photon spectroscopy group: Professors Karsten Krogh-Jespersen, Irwin Tobias, Surya N. Thakur and Drs. John G. Philis and Lucille Chia.