Nonlinear-optical processes in lower-dimensional conjugated structures


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Reduced dimensionality and quantum confinement in conjugated organic and polymer structures enhance the effects of electron correlation on virtual electronic excitation processes and nonlinear-optical responses. A microscopic many-electron description of the third-order susceptibilities \( \gamma_{ijkl}(\omega_1, \omega_2, \omega_3) \) of conjugated structures is reviewed for one-dimensional chains and extended to two-dimensional conjugated cyclic structures. Electron correlation effects in effectively reduced dimensions result in highly correlated \( \pi \)-electron virtual excitations that lead to large, ultrashort nonresonant nonlinear-optical responses. The increase of dimensionality from linear to cyclic chains is found to reduce the nonresonant isotropic third-order susceptibility \( \gamma_3 \). Resonant experimental studies of saturable absorption and optical bistability in ultrathin films of quasi-two-dimensional naphthalocyanine oligomers are also presented. In the saturable-absorption studies, the resonant nonlinear refractive index \( n_2 \) was measured to be \( 1 \times 10^{-4} \text{ cm}^2/\text{kW} \) in the wavelength range of operating laser diodes. Based on this result, electronic absorptive optical bistability is observed on a nanosecond time scale in a nonlinear Fabry–Perot interferometer employing the saturably absorbing naphthalocyanine film as the nonlinear-optical medium.

1. INTRODUCTION

Conjugated \( \pi \)-electron organic and polymer structures are now well known to exhibit unusually large nonresonant macroscopic second-order, \( \chi^{(2)}_{ijk}(-\omega_2, \omega_1, \omega_2) \), and third-order, \( \chi^{(3)}_{ijkl}(\omega_1, \omega_2, \omega_3) \), nonlinear-optical susceptibilities\(^1\) and their microscopic origin and mechanism can be successfully described by the quantum field theory of many-electron systems in one and two dimensions.\(^2\)–\(^11\) In this description, as the spatial dimensionality of the many-electron system is effectively lowered, the motion among the many electrons becomes highly correlated.\(^12\) Electron correlation plays a major role in determining \( \chi^{(2)}_{ijk} \) and \( \chi^{(3)}_{ijkl} \) in conjugated \( \pi \)-electron systems, and, as we shall review, its effects cannot be neglected in properly accounting for the nonlinear-optical properties of conjugated structures.

Reduced dimensionality and quantum confinement occur in material structures having effective confinement length scales \( L \) of less than one to several tens of nanometers. The opposite limit occurs in regular three-dimensional bulk structures, where \( L > 100 \text{ nm} \), and the electrons behave as a Fermi gas of weakly interacting particles. In this case, the electron motions are usually weakly correlated and well described by single-particle theory in the effective-mass approximation.

Conjugated \( \pi \)-electron organic and polymer structures are viewed as lower-dimensional systems in which quantum confinement effects are important. For instance, in conjugated linear chains the many-electron system is confined in two dimensions, with \( L < 0.5 \text{ nm} \) transverse to the linear chain axis, and thus the \( \pi \)-electrons are delocalized in their motion only in one dimension, along the longitudinal chain axis. As a result, the repulsive Coulomb interactions among electrons are strong, and electron motion becomes highly correlated, wherein the motion of any single electron depends on all the other remaining many electrons. The origin of the nonresonant \( \chi^{(3)}_{ijkl} \) for these and related polymer structures then appears to reside in strong correlation behavior in virtual two-photon \( \pi \)-electron states.\(^8\)–\(^11\) This microscopic many-electron correlation description of nonlinear-optical properties of conjugated structures is described in Section 2. First we review the nonlinear-optical properties of linear polyenes as a function of both conformation and length as prototype one-dimensional conjugated chains. The nonresonant microscopic nonlinear-optical susceptibility is a strong function of the length of the polyene chain and is not significantly dependent on structural conformation.

The role of dimensionality in nonlinear-optical properties is further examined by a theoretical study of a two-dimensional conjugated cyclic structure with \( L < 0.5 \text{ nm} \) perpendicular to the molecular plane. Through comparison with the linear chain results, the microscopic origin of the nonlinear-optical properties is shown to be similar for the two cases. A remarkable effect of increased dimensionality, however, is the decrease of the isotropically averaged third-order susceptibility owing to an actual reduction in the effective length available for the \( \pi \) electrons to respond to an applied optical electric field.
In Section 3 we present experimental measurements of the resonant nonlinear-optical properties of thin films formed of large, two-dimensional conjugated cyclic structures. Saturable absorption is observed in spin-coated thin films of a naphthalocyanine derivative having an exceptionally large Q-band \( \pi \)-electron absorption \( (\alpha \approx 1 \times 10^9 \text{ cm}^{-1}) \) centered at 810 nm. No unsaturable-absorption background is observed. For laser frequencies near 810 nm, we find an intensity-dependent refractive index \( n_2 \) of \( 1 \times 10^{-4} \text{ cm}^2/\text{W} \). Based on the results of the saturable-absorption studies, we demonstrate electronic absorptive optical bistability in a thin-film Fabry–Perot etalon at nanosecond time scales.

2. MICROSCOPIC DESCRIPTION OF NONRESONANT \( \gamma_{ijk}(-\omega; \omega_1, \omega_2, \omega_3) \) FOR ONE- AND TWO-DIMENSIONAL STRUCTURES

The macroscopic nonlinear-optical properties of organic molecular and polymer structures in condensed states are best described by starting from the individual responses of isolated molecular or polymer chain units.\(^1\) This approach, which clarifies the origin of \( \chi^{(2)}_{ijk} \) and \( \chi^{(3)}_{ijk} \), is, however, not applicable to other material classes, such as inorganic semiconductors, for which it is difficult to identify analogous microscopic sources of nonlinear polarization. For the moment neglecting intermolecular interactions, if the nonlinear susceptibility of an isolated molecule is known, then \( \chi^{(2)}_{ijk} \) or \( \chi^{(3)}_{ijk} \) of the macroscopic ensemble of molecules is determined by the orientational distribution function of the independent units. Local field factors must also be included to account for the effect of the dielectric environment on the electric field strength at the molecular site. The macroscopic frequency-dependent second- and third-order susceptibilities \( \chi_{ijk}^{(2)}(-\omega; \omega_1, \omega_2) \) and \( \chi_{ijk}^{(3)}(-\omega; \omega_1, \omega_2, \omega_3) \) can then be expressed in terms of the molecular susceptibilities \( \beta_{ijk}(-\omega; \omega_1, \omega_2) \) and \( \gamma_{ijk}(-\omega; \omega_1, \omega_2, \omega_3) \) as\(^13\)

\[
\chi_{ijk}^{(2)}(-\omega; \omega_1, \omega_2) = N_u \sum_{s=1}^{c} R^s_{im} R^s_{kn} R^s_{l\text{m}l'} \beta_{ijk}^{(s)}(-\omega; \omega_1, \omega_2) \]  
\[
\chi_{ijk}^{(3)}(-\omega; \omega_1, \omega_2, \omega_3) = N_u \sum_{s=1}^{c} R^s_{im} R^s_{kn} R^s_{l\text{m}l'} R^s_{p\text{m}p'} \gamma_{ijkl}^{(s)}(-\omega; \omega_1, \omega_2, \omega_3) \]

where \( N_u \) is the number of unit cells per unit volume, the summation is over all molecules in the unit cell, \( R \) is a rotation matrix describing the orientation of each molecule in the unit cell, and \( f \) is the frequency-dependent local field factor. The description of the macroscopic nonlinear-optical response is thus reduced to an understanding of the microscopic second- and third-order susceptibilities \( \beta_{ijk} \) and \( \gamma_{ijk} \) and knowledge of the orientational distribution of the molecular units in the condensed phase. As special cases, isotropic gases and liquids reduce Eqs. (1) and (2) to simpler forms. For example, for an isotropic ensemble,

\[
\chi_{iii}^{(3)}(-\omega; \omega_1, \omega_2, \omega_3) = N f^{(3)}\gamma_{ij}(-\omega; \omega_1, \omega_2, \omega_3),
\]

where \( N \) is the number density of molecules and \( \gamma_{ij} \) is the isotropically averaged susceptibility defined by

\[
\gamma_{ij} = \frac{1}{5} \sum_i \gamma_{iii} + \frac{1}{3} \sum_{ij} \left( \gamma_{iji} + \gamma_{iij} + \gamma_{jii} \right).
\]

where the indices \( i \) and \( j \) represent the Cartesian coordinates \( x, y, \) and \( z. \)

The above formalism is strictly appropriate only for gases such that the mean intermolecular distance is large enough for the interaction between molecules to be negligible. In condensed states, some modifications are required for the effects of intermolecular interactions to be included. In order to account for residual interactions with neighboring molecules, \( \beta_{ijk}(-\omega; \omega_1, \omega_2) \) and \( \gamma_{ijk}(-\omega; \omega_1, \omega_2, \omega_3) \) can be dressed to extend their applicability beyond isolated molecular units. For instance, in dc-induced second-harmonic generation (DCHSH) studies of dilute solutions,\(^3,4\) it was found that inclusion of dipole-mediated interactions between solvent and solute molecules provided excellent agreement of the theoretical values for an otherwise independent molecule with experimental measurements made in solution. In a more recent study\(^14,15\) of phase-matched second-harmonic generation in single crystals of 2-methyl-4-nitroaniline (MNA), the existence of closely oriented pairs of molecules in the unit cell crystal structure required treatment of an MNA–MNA pair as the fundamental source of second-order response. Because of the strong mutual effect of each molecule on the electronic structure of the other, calculation of \( \beta_{ijk}(-2\omega; \omega, \omega) \) for an appropriately oriented pair of MNA molecules was necessary in order to obtain agreement with experiment. In any case, the fact that the intramolecular interaction energy is much stronger than the intermolecular interaction energy in organic molecular crystals, liquids, solutions, and polymer thin films means that the starting point for understanding the macroscopic nonlinear optical properties of these various condensed phases lies in an accurate description of the microscopic response from an isolated molecular unit.

The general theoretical expression for the components of the microscopic third-order susceptibility tensor \( \gamma_{ijk}(-\omega; \omega_1, \omega_2, \omega_3) \) is derived from time-dependent, quantum electrodynamic perturbation theory. In order to avoid secular divergences that would occur when any subset of the input frequencies sums to zero, one employs the Bogoliubov–Miotopolsky method of averages.\(^16,17\) Owing to dispersive effects \( \gamma_{ijk}(-\omega; \omega_1, \omega_2, \omega_3) \) is dependent on the input and output frequencies involved for each of the various possible nonlinear-optical phenomena. For the particular case of third-harmonic generation, for example, one obtains...
\[ \gamma_{ijkl}(-3\omega; \omega, \omega, \omega) = \frac{1}{3!} \left( \frac{e^4}{4\hbar^3} \right) \sum_{n_1n_2n_3} \left\{ \frac{P_{ijkl}[r_{n_1r_{n_2r_{n_3n_4}}]}(\omega_{n_2} - 3\omega)(\omega_{n_3} - 2\omega)(\omega_{n_4} - \omega)}{\omega_{n_1}} + \frac{P_{ijkl}[r_{n_1r_{n_2r_{n_3n_4}}}]^*}{\omega_{n_2} + \omega}(\omega_{n_3} + 2\omega)(\omega_{n_4} - \omega)} + \frac{P_{ijkl}[r_{n_1r_{n_2r_{n_3n_4}}}]^*}{\omega_{n_1}} \right\}, \]

where \( r_{i,j,k,l} \) is the matrix element \((n_i)\langle \tilde{n}_j \rangle \langle \tilde{n}_k \rangle \langle \tilde{n}_l \rangle \) \((r^i = r^i - (r^i)_{\text{gg}}), \) \( \hbar \omega_{n,m} \) is the excitation energy of state \( n \), the prime on the summation indicates that the ground state is omitted, and \( P_{ijkl} \) denotes the sum over all permutations of those three indices. We will be concerned here with the case when all the optical frequencies are above the molecular vibrational and rotational modes but below the electronic excitation energies so that the nonlinear-optical response is strictly electronic in origin. In addition, for conjugated organic structures, \( \gamma \) is dominated by the delocalized \( \pi \)-electron contributions, which in general have both larger transition dipole moments and lower transition energies than the \( \sigma \)-electron excitations. Thus, with an accurate description of both the excitation energies and the transition moments of the \( \pi \)-electron manifold, one can calculate the frequency dependence of each of the different third-order nonlinear-optical processes by using expressions such as Eq. (5).

The theoretical method employed to achieve a proper description of the \( \pi \)-electron manifold of conjugated organic molecular structures for calculation of \( \gamma_{ijkl}(-\omega_3; \omega_1, \omega_2, \omega_2) \) described previously.\(^{10}\) It consists of a multiply excited configuration interaction calculation (SCF-MO-SDCI) performed on a molecular orbital basis obtained through self-consistent field theory in the rigid lattice CNDO/S approximation. This method, which was previously proved successful in calculations of \( \beta_{ijkl}(-\omega_2; \omega_1, \omega_2, \omega_2) \) for a variety of conjugated structures, will not be discussed here other than to reemphasize the many-electron nature of the general problem. Because of the reduced dimensionality, Coulomb interactions among \( \pi \) electrons result in marked electron correlation effects that render independent particle theories incomplete for the description of nonlinear-optical properties. This has already been demonstrated in the comparison of experimental and theoretical determinations of \( \beta_{ijkl}(-2\omega; \omega, \omega, \omega) \), for which calculations involving both single- and double-excited configuration interactions result in good agreement with experiment, whereas calculations with only single-excited configuration interactions differ by as much as 50%. In the case of \( \gamma_{ijkl} \) for the linear polyenes discussed below, independent particle models fare even worse, resulting not only in different magnitudes but also in opposite sign from single- and double-excited configuration interaction calculations and existing experimental data. Because independent particle results are not only quantitatively incorrect but also miss some important qualitative features of \( \beta_{ijkl} \) and \( \gamma_{ijkl} \), it is essential to take account of electron correlations through multiply excited configuration interactions in descriptions of nonlinear-optical processes.

A. One Dimension: Conjugated Linear Chains
We briefly review here the origin of the microscopic third-order susceptibility \( \gamma_{ijkl}(-\omega_3; \omega_1, \omega_2, \omega_2) \) in prototype conjugated linear chains as revealed by the theoretical method described above.\(^{8-11}\) In particular, we consider the linear polyenes, which are hydrocarbon chains in which each carbon site is covalently bonded to a hydrogen and its two nearest-neighbor carbons. The remaining valence electron of each carbon atom contributes to a delocalized, strongly correlated \( \pi \)-electron distribution along the carbon chain. The ground state of this system is a spin-singlet, broken-symmetry state in which the carbon lattice possesses a single-bond/double-bond alternation. We have performed calculations on polyenes ranging in length from four to sixteen carbon sites \((N = 4 \text{ to } 16)\) in both the all-trans and cis-transoid conformations.

Although the self-consistent field calculation of the ground state includes all the valence shell electrons for each atom in the molecule, configuration interaction theory needs only to consider \( \pi \)-electron orbitals since the low-lying excitations are \( \pi \rightarrow \pi^* \) transitions and for conjugated systems the \( \pi \)-electron contributions to \( \gamma_{ijkl}(-\omega_3; \omega_1, \omega_2, \omega_2) \) dominate those from \( \sigma \) electrons. Because the polyenes are members of the \( C_{2n} \) symmetry group, all the \( \pi \)-electron states must possess either \( A_g \) or \( B_u \) symmetry. Within the centrosymmetric \( C_{2n} \) group, these two symmetries are of opposite parity, leading to optical dipole selection rules. The ground state is always \( 1A_g \) and therefore the \( 1B_u \) states are one-photon-allowed transitions observable in the linear absorption spectrum. The excited \( 1A_g \) states, on the other hand, are one-photon forbidden but two-photon allowed. Experimental and theoretical studies\(^{18-24}\) of one-photon and two-photon resonant processes in finite polyenes have shown that below the first optically allowed, dominant \( 1B_u \) state is located a strongly electron correlated two-photon \( 2^1A_g \) state.

Because the \( \pi \)-electron distribution is easily deformable
It is instructive to consider the individual terms in the sum-over-states perturbation expansion. Based on Eq. (5) and the symmetry selection rules described above, it is evident that the \( \pi \)-electron states in a third-order process must be connected in the series \( g \to 1B_u \to 1A_g \to 1B_u \to g \). For centrosymmetric structures, third-order processes necessarily involve virtual transitions to both one-photon and two-photon states. For \textit{trans}-OT, there are \( (153)^3 \) terms involved in the summation of Eq. (5). However, two of these terms are an order of magnitude larger than all the others and constitute 70% of \( \gamma_{xxx} \). The remaining terms to a large extent cancel one another, resulting in a much smaller net contribution. In both of the dominant terms, the only \( 1B_u \) state involved is the dominant low-lying one-photon \( 1^1B_u \) \( \pi \)-electron excited state. In addition to its low excitation energy, this state is important because its 7.8 \( D \) transition dipole moment with the ground state is more than three times larger than any other ground-state transition moment. One of the two major terms comes from the double sum of Eq. (5), with both of the intermediate states being the \( 1^1B_u \). In the case of the double sum, the middle intermediate state is always the ground state. This term makes a negative contribution to \( \gamma_{xxx} \) below resonance, since both the numerator and the denominator are positive but the double sum has an overall negative contribution. The other major term is from the triple sum with the \( 6^1A_g \) state as the middle intermediate. This state, calculated at 7.2 eV, has a large transition moment with \( 1^1B_u \) of 13.2 \( D \). This term makes a positive contribution to \( \gamma_{xxx} \) and is larger than the first, leading to an overall positive value for \( \gamma_{xxx} \). Importantly, the \( 6^1A_g \) consists of 60% double-excited configurations, indicating that it is highly correlated. Single-excited configuration interaction calculations obtain a negative value for \( \gamma_{xxx} \) because they do not adequately describe this state and therefore omit its large contribution.

Figure 2 displays the calculated dispersion curve for \( \gamma_{xxx}(3\omega; \omega, \omega, \omega) \) of \textit{trans}-OT as a function of the input photon energy. The first resonance, located at 1.47 eV (\( \lambda = 0.844 \mu m \)) and indicated by the vertical dashed lines, is due to the \( 3\omega \) resonance of the \( 1^1B_u \) state. The second singularity, located at 2.08 eV (\( \lambda = 0.6 \mu m \)), is from the \( 2\omega \) resonance of

\[ \gamma_{xxx}(3\omega; \omega, \omega, \omega) \]

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the 2 $1^1A_g$ state. As can be seen from Eq. (5), the $1^1B_u$ states will have both $3\omega$ and $\omega$ resonances in third-harmonic generation, whereas the $1^1A_g$ states will have only $2\omega$ resonances. Other third-order processes have different resonance selection rules. For example, in dc-induced second-harmonic generation both the $1^1B_u$ and $1^1A_g$ states (or, more generally, both one-photon and two-photon states) have $2\omega$ and $\omega$ resonances, while there are no $3\omega$ resonances. It should also be noted that in real systems natural broadening of electronic states will prevent divergence at the resonances. This is accounted for theoretically by making the excitation energies in Eq. (5) complex with the inclusion of an imaginary damping term. Unfortunately, damping constants cannot be reliably calculated, and one must therefore use empirical values.

In order to determine the influence of structural geometry on nonlinear-optical properties, we have also calculated $Y_{ijkl}$ for the cis-transoid (cis) conformation of polyenes [Fig. 1(b)] over the same range of chain lengths. The results for the cis conformations are in direct analogy to those for trans, indicating that geometry is not a predominant factor. For the range of chain lengths that we have considered, we find that the transition energies of the $1^1B_u$ and $2^1A_g$ states of the cis conformation are just slightly red shifted from the values for trans by 0.02–0.10 eV. For example, for trans-OT the $1^1B_u$ state is calculated at 4.42 eV and the $2^1A_g$ at 4.16 eV, while for cis-OT the values are 4.37 and 4.11 eV, respectively. Furthermore, just as for trans, the dominant tensor component of $\gamma_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3)$ is $\gamma_{xxxx}$, and the most significant virtual transitions and the dispersion are essentially the same as discussed above. The mechanism for $\gamma_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3)$ is still a symmetry-dictated virtual excitation process involving strongly correlated $\pi$-electron states. The calculated dispersion of $\gamma_{xxxx}(-3\omega; \omega, \omega, \omega)$ for cis-OT is compared with that of trans-OT in Fig. 2. The two curves are similar, and the most significant difference is the smaller nonresonant value in the case of cis-OT. Because of the nearly equal excitation energies, the first two resonances occur near the same energies for the two different structural conformations.

The similarity between the two conformations is further emphasized in the transition density matrix contour diagrams that graphically illustrate the electron redistribution on virtual excitation. The transition density matrix $\rho_{nm'}$ is defined through the expression

$$
\langle \mu_{nm'} \rangle = -e \int r \rho_{nm'}(r) dr,
$$

with

$$
\rho_{nm'}(r) = \int \psi_n^*(r_1, r_2, \ldots, r_M) \psi_m'(r_1, r_2, \ldots, r_M) dr_2 \ldots dr_M.
$$

where $M$ is the number of valence electrons included in the molecular wave function $\psi$. Contour diagrams for $\rho_{nm'}$ of the ground and $6^1A_g$ states with the $1^1B_u$ state for both cis-OT and trans-OT are compared in Fig. 3, where solid and dashed lines correspond to increased and decreased charge density. The contour cut is taken 0.4 Å above the molecular plane since $\pi$ orbitals vanish on the atoms. The antisymmetry of $\rho_{nm'}$ is a requirement for a one-photon transition, and for a large transition dipole moment $\mu_{nm'}$ the contours should have well-separated increased and decreased densities with particularly large magnitudes toward the ends. Of course, the actual charge density of any state, given by $\rho_{nm'}$, must be symmetric because of the centrosymmetry of the molecule so that all states will have vanishing dipole moments. In Fig. 3 the cis [Fig. 3(a)] and the trans [Fig. 3(b)] virtual $g \rightarrow 1^1B_u$ transition results in a somewhat modulated redistribution of charge with transition moment $x$ components of 7.9 and 13.2 D, respectively. For the $1^1B_u \rightarrow 6^1A_g$ transition, however, there results a highly separated charge distribution in the cis [Fig. 3(c)] and trans [Fig. 3(d)] conformations. The corresponding transition moments are 12.0 and 13.2 D for the cis and trans cases, respectively.

There are few experimental data available for $\gamma_{ijkl}(-\omega_4; \omega_1, \omega_2, \omega_3)$ of finite polyenes. Our calculations compare quite well with the experimental values that have been reported for two of the shortest polyenes. Accounting for the proper fundamental photon energy, isotropic orienta-
tional averaging, and the small estimated $\sigma$-electron contribution, our results are in good agreement\textsuperscript{10} with the gas-phase dc-induced second-harmonic generation measurements of butadiene ($N = 4$) and hexatriene ($N = 6$) by Ward and Elliott.\textsuperscript{25} Comparison of calculated results with experimental measurement of both the sign and magnitude of $\gamma$ is obviously an important test of the validity of a theoretical method, but it has all too often been neglected in recent literature.

Analysis of the chain-length dependence of $\gamma_{xxxx}$ for the trans and cis conformations shows that the two are further unified by a common power-law dependence of $\gamma_{xxxx}$ on $L$, defined as the distance in the $x$ direction between the two end carbon sites. The power-law exponent was found to be $4.6 \pm 0.2$, with several common features leading to this rapid growth of $\gamma_{xxxx}$ with chain length. First, the excitation energies decrease with increased chain length. Second, the magnitudes of transition dipole moments along the chain axis increase steadily with chain length. Third, while for octatetraene and the shorter chains the nonlinear susceptibility is almost entirely composed of the contributions from only a few states, longer chains have significant contributions from an increasingly larger number of both $^1B_u$ and $^1A_g$ states.

B. Two Dimensions: Conjugated Cyclic Chains

In this subsection we extend the microscopic description of $\gamma_{ijkl}$ for one dimension to two dimensions and consider a specific example within the class of conjugated cyclic structures known as annulenes. As a major case, we consider the planar structure of cyclo-octatetraene (COT), the cyclic analog to octatetraene with $N = 8$, illustrated schematically in Fig. 4. Although the geometrically relaxed ground state of COT is known to be a nonplanar, bent structure, we will examine only the planar structure of COT here. The purpose is to explore the effect of dimensionality on the microscopic features of $\gamma_{ijkl}(-\omega_1, \omega_1, \omega_2, \omega_3)$. Because the inclusion of the geometrically relaxed distortions of the physically observed COT structure unnecessarily complicates comparison of cyclic structure results with those described above for linear chains, we consider only the planar structure. Analogies and contrasts between linear and cyclic structures are clearest when the only distinction is the in-plane $x$ and $y$ directions. The power-law exponent was found to be $4.6 \pm 0.2$, with several common features leading to this rapid growth of $\gamma_{xxxx}$ with chain length.

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**Fig. 4.** Schematic diagram of the molecular structure of planar COT.

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For linear chains, since the $x$ component of the transition dipole moments is much larger than the $y$ and $z$ components, the isotropically averaged susceptibility $\gamma_x$ is effectively determined by the $\gamma_{xxxx}$ component, while all components involving transverse fields make negligible contributions. This reduces Eq. (4) to

$$\gamma_x \approx \frac{1}{5} \gamma_{xxxx}. \quad (8)$$

But for cyclic structures, since the in-plane $x$ and $y$ directions are equivalent, $\gamma_{xxxx}$ and $\gamma_{yyyy}$ should be of equal magnitude. Furthermore, components such as $\gamma_{xyxy}$ will also be significant since they involve these two directions as well. The corresponding nonnegligible terms of Eq. (4) are

$$\gamma_x \approx \frac{1}{5} \left[ \gamma_{xxxx} + \gamma_{yyyy} + \frac{1}{2} \gamma_{xyxy} + \gamma_{yyyy} + \gamma_{yyyy} \right]. \quad (9)$$

It seems, therefore, that one might be able to enhance $\gamma_x$ by moving from linear to cyclic conjugated structures and opening pathways for new components of the $\gamma_{ijkl}$ tensor to contribute. We shall demonstrate below, however, a most striking, opposite finding. We show that, because of the relevant length scales involved in the two problems, the conjugated cyclic structure will necessarily have a smaller $\gamma_x$ than the corresponding conjugated linear chain with an equal number of carbon sites.

Our planar model of COT is a member of the dihedral $D_{th}$ symmetry group, which is non-Abelian and, hence, has two-dimensional irreducible representations denoted as $E$ classes. The allowed-state symmetries for $\pi$-electron excitations are $A_{1g}, A_{2g}, B_{1g}, B_{2g}$, and $E_u$. Of these, only states of $^1E_u$ symmetry are one-photon-allowed excitations from the $^1A_{1g}$ ground state. The $^1E_u$ states are doubly degenerate, with the two representations related by a $\pi/2$ rotation about the $z$ axis perpendicular to the molecular plane. All the remaining symmetries listed above describe nondegenerate, two-photon states. A typical feature of conjugated cyclic molecules, including phthalocyanines and porphyrins, is the existence of a relatively low-frequency absorption in the visible or near ultraviolet and a higher-frequency absorption deeper in the ultraviolet.\textsuperscript{25} This feature appears in our model COT with the weak low-frequency $^1E_u$ state at 4.4 eV and the much stronger, higher-frequency $^2E_u$ state at 6.5 eV. In the case of phthalocyanines, however, it is always the low-frequency band that is stronger.

In Table 2 we list the symmetries, energies, and relevant transition dipole moments for the eight lowest calculated excited states of COT. Again, a total of 153 states are calculated. The third and fourth columns list the $x$ and $y$ components, respectively, of the transition moment between a given state and the ground state, while the column labeled $\mu^x_{n,2E}$ lists the $x$ component of the transition moments of that state with the two degenerate representations of the $^2E_u$ state; the $y$ components are given in the $\mu^y_{n,2E}$ column. Although the $x$ and $y$ directions are equivalent in COT, it is seen from Table 2 that these components of the transition moments are not always equal, and this is a direct result of the double degeneracy of the $E_u$ states. Transition moments involving any degenerate pair of $^1E_u$ states with a two-photon state are clearly related by a $\pi/2$ rotation or $x \rightarrow y$, $y \rightarrow -x$. Thus the appearance of negative signs in some of the transition moments merely reflects the choice of basis in Hilbert space and has no absolute physical meaning. By choosing an appropriate basis for the degenerate pair, the
Table 2. Symmetries, Energies, and Selected Transition Dipole Moments of the Calculated Low-Lying States of COT

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Energy (eV)</th>
<th>$\mu_{n,n}^x (D)$</th>
<th>$\mu_{n,n}^y (D)$</th>
<th>$\mu_{n,2g} (D)$</th>
<th>$\mu_{n,2e} (D)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^1A_{2g}$</td>
<td>2.24</td>
<td>0.00</td>
<td>0.00</td>
<td>-1.60</td>
<td>-2.40</td>
</tr>
<tr>
<td>$2^1A_{2g}$</td>
<td>3.19</td>
<td>0.00</td>
<td>0.00</td>
<td>0.14</td>
<td>0.09</td>
</tr>
<tr>
<td>$1^1E_u$</td>
<td>4.41</td>
<td>0.05</td>
<td>-0.03</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>$1^1E_u$</td>
<td>4.41</td>
<td>0.05</td>
<td>0.00</td>
<td>-0.33</td>
<td>0.50</td>
</tr>
<tr>
<td>$1^1B_{2g}$</td>
<td>5.21</td>
<td>0.00</td>
<td>0.00</td>
<td>1.03</td>
<td>0.68</td>
</tr>
<tr>
<td>$1^1B_{1g}$</td>
<td>5.94</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$2^1E_u$</td>
<td>6.48</td>
<td>4.58</td>
<td>-3.04</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$2^1E_u$</td>
<td>6.48</td>
<td>3.04</td>
<td>4.58</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

As for octatetraene, there is one dominant term in the double summation that is due to the state with the largest oscillator strength, in this case the $2^1E_u$ state. The dominant contributions from the triple sum also all involve the $2^1E_u$ state, but rather than just one term, there are several significant contributions for COT. Each one is smaller than the dominant negative term from the $2^1E_u$ state, but together they again lead to positive values for the nonresonant tensor components $\gamma_{ijk}$. The significant contribution from several terms involving different intermediate two-photon states is similar to what was found for the linear polyenes longer than octatetraene.

In Fig. 5 the transition density matrix $\rho_{\text{av}}$ is shown for the ground state with the two representations of the $2^1E_u$ state. The $\pi/2$ rotational relationship of the two representations is also clear here, as in Table 2. The charge redistribution for this transition is fairly modulated, as is for the linear chains. In the particular basis shown for the representation of the doubly degenerate $2^1E_u$ state, the transition moments along the $x$ and $y$ directions are comparable, as can be seen from the figure.

The calculated dispersion of the isotropic third-order susceptibility $\gamma_3(3\omega; \omega, \omega, \omega)$ is given in Fig. 6. The nonresonant value is quite small compared with those of the linear chains. Sharp resonances occur at 1.47 eV because of a $3\omega$ resonance to $1^1E_u$ and 1.60 eV owing to a $2\omega$ resonance with $2^1A_{2g}$. Since both of these states have small transition moments (Table 2), they make significant contributions only
directly on resonance. Calculations including imaginary damping terms to account for the finite width of the electronic excitations show that these resonances become completely washed out and the dispersion remains flat in this part of the spectrum. Experimental dispersion measurements, therefore, likely would not give evidence of significant resonant enhancement until the $3\omega$ resonance to the $2E_u$ state, which occurs at 2.16 eV.

The calculated values of $\gamma_{ijkl}(-3\omega, \omega, \omega, \omega)$ for COT at the nonresonant fundamental photon energy of 0.65 eV are $\gamma_{xxxx} = 0.75$ and $\gamma_{xxxy} = 0.21 \times 10^{-36}$ esu. Because of the $D_{4h}$ symmetry, $\gamma_{xxxx} = \gamma_{yyyy}$ and $\gamma_{xxyy}$ is equal to all other components that involve two $x$-component fields and two $y$-component fields. This equivalence between the $x$ and $y$ directions is in contrast to the linear polyene case, in which the $y_{xxxx}$ component dominates all others. Furthermore, the $y_{xxxx}$ component of octatetraene ($15.5 \times 10^{-36}$ esu) is far larger than any of the components of COT. However, since COT has significant components in both the $x$ and $y$ directions, it is more reasonable to compare values of the isotropically averaged susceptibility. For COT, $\gamma_y = 0.38 \times 10^{-36}$ esu, compared with $3.4 \times 10^{-36}$ esu for trans-OT. As in the case of comparing values for the trans and cis conformations of linear polyenes, here also we must consider the actual length scale involved in the problem.

The important length for nonlinear-optical responses is the largest length over which charge can be separated because of the presence of an optical electric field. For the linear polyenes, that length is the distance along the conjugation axis separating the end carbons. For COT, the equivalent length is between two points on either end of a diameter of the ring. Additionally, since $\pi$-electron motion is constrained along the carbon lattice, the relevant length is one half of the circumference of the molecular structure. This distance is 5.3 Å for COT. For comparison, for trans-hexatriene ($N = 6$), $\gamma_y = 0.75 \times 10^{-36}$ esu at $h\nu = 0.65$ eV, and the end-to-end length $L$ is 6 Å. Thus, for these two quite different structures in which the relevant lengths are nearly equal, we find that the calculated values of $\gamma_y$ are also comparable. In the case of cyclic structures, the length that determines the magnitude of $\gamma_y$ appears to be one half of the circumference; this is a general finding in calculations that we have performed for other sizes of rings and will be reported in a later publication.

3. RESONANT $\chi^{(3)}$ MEASUREMENTS IN QUASI-TWO-DIMENSIONAL RING STRUCTURES: SATURABLE ABSORPTION AND OPTICAL BISTABILITY

We showed in Section 2 that increased dimensionality from linear to cyclic chains leads to a decrease in the isotropic susceptibility $\gamma_y$ rather than to an enhancement, as one might first expect. This is due to an effective reduction in the length available for the $\pi$ electrons to respond to an applied optical electric field. There are, however, other compelling reasons to investigate conjugated cyclic structures for their nonlinear-optical properties. Primary among these is the presence of optically intense low- and high-frequency bands in the visible and ultraviolet generally observed in large diverse classes of related ring structures that, in addition, exhibit important secondary material properties such as thermal and chemical stability and ease of fabrication and processing. Among such classes are the well-known, large ring porphyrin and phthalocyanine structures, which exhibit well-defined intense $Q$ and Soret bands in the visible and near ultraviolet, respectively. Free-base porphyrin, for example, has long been identified as an analog of 18-annulene, which possesses nine double bonds. Although, in general, we expect the nonresonant $X_{ijkl}^{(3)}$ of ring structures not to be large, porphyrinlike structures provide many attractive features for studying resonant $X_{ijkl}^{(3)}$ processes.

Optical bistability in saturable absorbers has long been under intense study, first, to enhance understanding of bistable phenomena and their relationships to the mediating intensity-dependent refractive index $n_2$ and, second, to aid in developing thin-film nonlinear-optical devices. Based on the microscopic descriptions discussed in Section 2, we have selected phthalocyanine structures in order to conduct saturable-absorption and optical-bistability studies in quasi-two-dimensional conjugated ring structures. We have succeeded in designing ultrathin naphthalocyanine films possessing large resonant $n_2$ values and in implementing wide-aperture Fabry–Perot thin-film étalons for optical-bistability studies. In addition to primary nonlinear-optical properties, the design of the thin film étalons incorporated important secondary material properties: (i) large saturable absorption with zero unsaturable background, (ii) saturable absorption centered in the spectral range of operating laser diodes, (iii) thin-film formation, (iv) spin-coatable films and high-throughput fabrication, and (v) photolithographic properties for micrometer-sized pattern features.

A first major example of this type of film is the silicon naphthalocyanine oligomer (SINC) with the molecular structure shown in Fig. 7. Both pure-SINC and SINC solid-solution ultrathin films were directly fabricated by spin-coating techniques. The films were homogeneous and of high optical quality with typical thicknesses of 80 and 420 nm for pure dye and solid solution, respectively. Figure 8 shows the linear absorption spectra of the pure-SINC film (solid curve) and a solid-solution film of SINC in polymethyl methacrylate (dashed curve). The optical spectrum exhibits an intense $Q$ band centered in the near infrared at 810 nm (1.53 eV) for the pure dye and 774 nm (1.60 eV) for the solid solution, with a linewidth (FWHM) of 0.1 eV and a linear absorption coefficient $\alpha$ of $1 \times 10^6$ cm$^{-1}$. The molecular symmetry of SINC is $D_{4h}$, and the doubly degenerate $Q$ band is analogous to the $1^{1}A_{1g} \rightarrow 1^{1}E_u$ $\pi$-electron transition of COT described in Section 2.

We first present a physical model for the optical excitations of the thin film and then present saturable-absorption studies. A Maxwell–Bloch two-level model is used for the dependence of the saturation threshold power on pulse duration, and the experimental results support this simple picture. For laser frequencies near the absorption maximum, we find an effective $n_2$ of $1 \times 10^{-4}$ cm$^2$/kW. Based on the saturable-absorption behavior, electronic absorptive optical bistability at nanosecond time scales is then observed in thin-film Fabry–Perot étalons. Bistability behavior is studied as a function of longer pulse duration purposely to distinguish thermally induced bistable effects.

A. Glassy Polymer Dye Model and Saturable Absorption

In this subsection we present a physical model for optical excitations in the SINC ultrathin films. The films obtained
Fig. 7. Schematic diagram of the molecular structure of SINC.

Fig. 8. Linear absorption spectra of pure-SINC (solid curve) and SINC solid-solution (dashed curve) thin films. The large oscillator strength Q-band absorption peaks at 1.53 eV (810 nm) in pure-SINC film and 1.60 eV (774 nm) in SINC solid-solution film.

by spin coating do not possess either positional or orientational long-range order. Because of this random distribution of SINC molecules in the films, the excitations are strictly on-site π-electron transitions, which have a typical absorption coefficient $\alpha$ of $10^5$ cm$^{-1}$. The on-site π-electron optical excitations in an isolated molecule have an intrinsic, temperature-independent natural linewidth of the order of 0.1 to 1 GHz with a corresponding radiative decay lifetime of 1 to 10 nsec.

The large linewidth of the Q band observed in Fig. 8 is primarily due to inhomogeneous broadening. This site broadening in the thin film has a Gaussian shape, which is a consequence of the statistical distribution of resonance frequencies of the optical centers owing to a variation in local environment in the polymer matrix. Within the inhomogeneously broadened Gaussian envelope of the Q band is a series of narrow homogeneously broadened resonances for which the characteristic temperature dependence of the linewidth depends on the microscopic broadening mechanism. The linewidth of the homogeneous broadening in amorphous media can be accounted for by using the two-level-system (TLS) glass models introduced by Anderson et al. that have been fairly successful in accounting for many of the physical properties (e.g., specific heat, thermal conductivity, ultrasonic absorption) of disordered systems such as glasses and polymerlike matrices. The Hamiltonian of the glassy polymer dye thin film on a substrate can be written as

$$H = H_0 + H_{12} + H_{23},$$

where $H_0$ is the noninteracting Hamiltonian of the molecule (the difference $\epsilon_1 - \epsilon_0$ corresponding to the Q-band absorption), the TLS, and the phonons; $H_{12}$ is the electrostatic dipole interaction between the molecule and the TLS; and $H_{23}$ is the interaction between the TLS and the phonons, i.e., the strain field $\varepsilon$ is coupled to the TLS.

Each homogeneous line under the Gaussian envelope is approximated by a Lorentzian function, and the width is related to the temperature-dependent population and phase relaxation rate of the excited state by Fourier transformation. The amorphous material surrounding an optical site can be considered an ensemble of noninteracting TLS flip-flopping between two eigenstates as they emit or absorb acoustic phonons. The homogeneous line broadening in amorphous media comes from the dipole coupling of the optical sites with the TLS's, and the line width can be expressed in terms of TLS lifetime (or flip-flopping rate), the temperature dependence of which is determined from the coupling between the TLS and the strain field manifested as acoustic phonons. In this way, the line width of optical sites in the amorphous media is predicted to have $T^{1+\delta}$ ($0 < \delta \leq 1$) dependence, and the absolute magnitude can be obtained once all the physical parameters for the TLS are known.
For various organic molecules in different polymeric matrices, the theoretically predicted temperature dependence of the homogeneous linewidth is in good agreement with spectral hole-burning data. According to photochemical hole-burning data on porphyrins and phthalocyanines in various glasses and polymeric matrices, the homogeneous linewidth of the naphthalocyanine oligomer at room temperature is estimated to be between 10 and 100 GHz. For SINC films, comparison of the homogeneous linewidth (100 GHz) with the inhomogeneous width (0.1 eV) shows that the Gaussian envelope contains of the order of ten thousand Lorentzian-broadened resonances.

Saturable-absorption behavior within the Q band of the pure-SINC and SINC solid-solution thin film was investigated as a function of pulse duration and wavelength of the pure-SINC and SINC solid-solution thin film. The pulse-duration dependence of the saturation-absorption behavior is identical for both pure-SINC and SINC solid-solution films. In the case of the pure-SINC films, the threshold powers for saturation were 100 MW/cm² and 440 kW/cm² for 30-ps and 10-ns pulses, respectively. The threshold power for the 10-ns pulse is lower than that for the 30-ps pulse, but this trend saturates at or near the 10-μsec scale. Importantly, for the SINC solid-solution thin film, the threshold power for the 30-ps pulse was also 100 MW/cm², the same value as that of the pure-SINC film. The fact that the saturable-absorption behavior is identical for both pure-SINC and SINC solid-solution film is quite striking and can be accounted for by the absence of any positional and orientational order between molecular sites in the thin-film phase; thus there is no phase coherence between optical sites. From this we can conclude that the on-site π-electron excitations of the Q band in individual molecular sites are responsible for the large resonant nonlinear-optical response.

The pulse-duration dependence of the saturation-absorption threshold power is well explained in terms of a two-level optical system interacting with the resonant incident light. The dynamic transmission can be described by two coupled rate equations:

\[
\frac{dn(x, t)}{dt} = -I(x, t)\sigma[n(x, t) - [N_0 - n(x, t)]] - \frac{n(x, t)}{\tau_s},
\]

(12)

\[
\frac{dI(x, t)}{dx} = -I(x, t)\sigma[[N_0 - n(x, t)]] - n(x, t),
\]

(13)

where \(N_0\) is the total number of molecules per unit volume, \(n(x, t)\) is the number of molecules in the excited state at depth \(x\) and time \(t\), \(\sigma\) is the absorption cross section per molecule, and \(\tau_s\) is the radiative decay time of the excited state. Now let the incident pulse shape \(f(t)\) be normalized by the incident light intensity,

\[
I(0, t) = \int I_0 f(t). \int
\]

As the light pulse passes through the absorbing molecule, the pulse is distorted as well as attenuated. The change in the pulse shape can be expressed in terms of a transmission function \(T(x, t)\) at depth \(x\) and time \(t\), defined as

\[
I(x, t) = I_0 f(t)T(x, t).
\]

(15)

The two equations (12) and (13) can be reduced to one equation for the transmission \(T(x, t)\):
To characterize fully the nonlinear absorption properties of the pure-SINC film, we measured the dispersion of the Q-band nonlinear absorption. A Spectra-Physics 380B cw ring dye laser using LDS 821 dye and tunable between 790 and 860 nm was used as the light source with typical peak powers of 150 mW. The cw dye output of 5-MHz bandwidth was chopped by an acousto-optic modulator, so that 10-μsec pulses were produced at a low duty cycle ($10^{-4}$) to eliminate any heating effects. A light intensity of approximately 80 kW/cm² was obtained by focusing the laser output directly onto the sample with a microscope objective lens.

The dispersion of the nonlinear absorption of the thin film is compared in Fig. 10 with the linear absorption spectrum. It is clear that the change in absorption is maximum on resonance and decreases moving away from the peak. The dashed curves are a least-squares fit to a Gaussian envelope model for the linear absorption, and the dispersion was derived from the Kramers–Kronig relations. The dotted curves are the fitted curves for the nonlinear absorption and dispersion. We can see that the maximum change of refractive index as obtained from Eq. (18) occurs at 776 nm, and the maximum $n_2$ at 776 nm results from a linear superposition of the refractive-index changes of each homogeneously broadened envelope.

### B. Optical Bistability

SINC thin films can be employed as the nonlinear medium in Fabry–Perot étalons for optical-bistability studies. The étalon was formed by spin coating a wide-area (2–5 cm in diameter) thin film of approximately 80-nm thickness onto the front mirror of two highly reflecting dielectric mirrors of a Burleigh RC-110 Fabry–Perot interferometer. The free spectral range of the cavity was adjustable and set at 12.5 GHz. Initial cavity detuning was adjusted by varying the high voltage applied to a piezoelectric transducer (PZT) annular ring that held the output mirror (the PZT had total motion of 2.21 μm/1000 V), and when this output mirror was scanned, a Fabry–Perot interference pattern with a finesse of 2 was obtained with the sample in the cavity.

The optical-bistability experimental layout (Fig. 11) was basically the same as the arrangement used for measuring the dispersion of saturable absorption. The laser output was partially reflected by a pellicle beam splitter to a reference silicon detector, and the transmitted beam was tightly focused upon the thin film, which had been spin coated directly onto the front mirror. The output fringes were collimated and passed through a 500-μm pinhole, and a sample silicon detector monitored the intensity at the central part of the bull’s-eye interference fringe. Silicon P-I-N photodiodes were used for reference and sample arms, and the output intensity versus input intensity was directly displayed on a 1-GHz oscilloscope operating in the x-y mode and externally triggered. At nanosecond time scales, initial measurements were attempted at 813 nm, using the output from the Nd:YAG-pumped methane Raman cell as the laser source; but later, more stable and smooth pulses at 799 nm from a single-mode pulsed Ti:Al₂O₃ laser pumped by a frequency-doubled Nd:YAG laser were used. Figure 12 shows the bistable hysteresis behavior observed when 40-μsec pulses with intensity 160 kW/cm² at 799 nm were incident upon the nonlinear Fabry–Perot interferometer. We found

$$\frac{\partial \ln T(x, t)}{\partial (t/\tau_s)} + \ln T(x, t) = 2\sigma_{se}I_0 f(t)[1 - T(x, t)] + \ln T_0,$$

(16)

where $I_0$ is the incident light intensity, $T_0$ is the low-intensity transmission, and $f(t)$ is the incident light pulse profile. From numerical simulation of Eq. (16), the saturation threshold intensity $I_s$ can be obtained for a given pulse width and excited-state lifetime $\tau_s$. Furthermore, the ratio of saturation threshold for two given pulse widths can be used to determine $\tau_s$ uniquely. Using 230 as the ratio of threshold powers at 30 psec and 10 nsec as determined from our experiment, we find the excited-state lifetime to be 5 nsec, in good agreement with previous independent relaxation measurements on related structures.³⁰,4²

From the saturable-absorption measurement²⁸ we can also estimate the nonlinear refractive index $n_2$. The nonlinear-optical susceptibility $\chi(\omega)$ for a Bloch-type system is given by

$$\chi(\omega) = \left(\frac{\alpha_0\omega}{4\pi}\right)\left(1 + \frac{\Delta}{1 + \Delta^2 + I/I_s}\right),$$

(17)

where $\alpha_0$ is the linear absorption coefficient, $\Delta$ is the detuning $(\omega - \omega_0)/\Gamma$, and $I_s$ is the saturation power. The nonlinear refractive index $n_2$ is the derivative of the intensity-dependent refractive index $n$ with respect to the intensity $I$, so for this model

$$n_2 = \frac{1}{3} \left(\frac{4\pi}{n_0}\right)^2 \chi^{(3)} = \left(\frac{\alpha_0\lambda}{4\pi I_s}\right)\left(\frac{\Delta}{1 + \Delta^2}\right).$$

(18)

From this expression, we obtain a value of $n_2$ for the pure-SINC thin film of $1 \times 10^{-4}$ cm²/kW.

---

**Fig. 10.** Dispersion of saturable absorption between 1.45 and 1.55 eV measured with a 10-μsec pulse. The solid curve is the linear absorption curve. The dashed curve is the Gaussian function least-squares-fit curve of the linear absorption, and the dotted curve is a similar least-squares fit of the nonlinear absorption. The curves with maxima occurring at $\lambda = 776$ nm correspond to the real parts of the refractive indices obtained from the Kramers–Kronig relations.
that for zero cavity detuning (φ = 0.0) the bistable behavior was the largest, while when the cavity was detuned (φ = π) the shape of the hysteresis curve changed and the effect became much smaller. In each case, the data were reproducible through many cycles of increased and decreased incident light intensity. Further, the data were also reproducible by focusing at different areas of each film sample. This kind of initial cavity detuning dependence is typical of absorptive optical bistability, which results from saturable absorption and a subsequent change in the loss of the interferometer cavity, permitting higher transmission than is possible at low light levels. However, the greatly reduced effects observed for nonzero cavity detuning indicate only a small dispersive contribution.

The incident laser wavelength was moved to 780 nm, corresponding to near optimum conditions for possible dispersive contributions to the bistability. The same measurements were repeated, and under all conditions no bistable behavior was observed (Fig. 13). The absence of any bistable behavior at 780 nm, where a large dispersive effect is expected from the Kramers-Kronig relation analysis, means simply that the relatively broad Q band is not one single homogeneously broadened line but an inhomogeneously broadened envelope for many homogeneous lines and supports the microscopic picture of the glassy polymer SINC film. Thus, near maximum saturable absorption at 810 nm, naphthalocyanine thin films exhibit primarily absorptive optical bistability at nanosecond time scales. The above analysis is based on steady-state conditions for optical bistability because of the relevant time scales (pulse width, 40 nsec; relaxation time, 5 nsec; cavity round-trip time, 1 nsec), but transient effects may also play some role in the observed

Fig. 12. Absorptive optical bistability observed for a polymer dye étalon with pulse width \( r_p = 40 \) nsec and wavelength \( \lambda = 799 \) nm. In (a) the initial cavity detuning \( \phi_0 \) is set at 0, and in (b) the initial cavity detuning \( \phi_0 \) is set at \( \pi \).
hysteresis behavior, which continues to be examined in ongoing studies.

Since purely absorptive optical bistability is rarely observed, a systematic series of studies of possible thermally induced refractive-index changes in the thin films was performed as a function of increased pulse duration from 10^{-6} to 2 sec. The laser source used in these studies was the acousto-optic-modulator chopped, Spectra-Physics cw ring dye laser described above. Figure 14 shows an example of the optical bistability observed; the pulse width was 2.0 sec and the duty cycle 20%. When the cavity was tuned on resonance with the incident light wavelength (\(\phi = 0.0\); lower right in Fig. 14), no hysteresis loop was observed, indicating the lack of an absorptive bistability effect, and this was true even when the dye-laser output frequency was resonant with the linear absorption peak of the sample. However, for a negative \(\phi (-1.0\); at left in Fig. 14), bistable hysteresis with a counterclockwise circulation was observed, and for a positive \(\phi (0.75\); upper right in Fig. 14), the bistable hysteresis had clockwise circulation. With the pulse width and the resonant wavelength near the linear absorption peak of 810 nm, the bistable behavior is due to a thermally induced dispersive intensity-dependent refractive-index change. Most

importantly, this behavior is distinctly different from the fast-pulse bistability observed at nanosecond time scales.

For both electronic absorptive and thermal dispersive optical bistability, the hysteresis loops do not show a complete switching on and switching off. The reason for this is that, even though the resonant \(n_2\) value of the SINC thin film is fairly large, the film thickness (80 nm) is so small that the nonlinear phase shift experienced by the light inside the étalon is not large enough for complete switching to occur. Thicker SINC-containing films have been prepared in our continuing studies.

4. CONCLUSION

Electron correlation effects markedly determine the virtual electronic excitation processes and nonlinear-optical properties of the low-dimensional structures of conjugated linear and cyclic chains. Microscopic understanding of the origin of the large, ultrafast nonresonant \(\chi^{(3)}(\omega_1; \omega_2, \omega_3)\) and \(\chi^{(3)}(\omega_4; \omega_1, \omega_2, \omega_3)\) of these materials is obtained through many-electron calculations of the molecular susceptibilities \(\beta_{ij}(\omega_1; \omega_2, \omega_3)\) and \(\gamma_{ijkl}(\omega_1; \omega_2, \omega_3)\) and direct comparison with available experimental results. Details of the mechanism for \(\gamma_{ijkl}(\omega_1; \omega_2, \omega_3)\) of one-dimensional conjugated linear chains have been explained in terms of virtual transitions among highly correlated \(\pi\)-electron states, and contour diagrams of transition density matrices \(\rho_{ij}\) provided direct illustration of the most significant virtual transitions. The dependences of \(\gamma_{ijkl}(\omega_1; \omega_2, \omega_3)\) on chain length and structural conformation have been examined, and conformation was found to be significant only inasmuch as it affects the actual physical length of the chain. Results for the all-trans and cis-transoid conformations of polyenes are unified by a power-law dependence of the dominant tensor component \(\gamma_{xxxx}(\omega_1; \omega_2, \omega_3)\) on chain length and structural conformation have been examined, and conformation was found to be significant only inasmuch as it affects the actual physical length of the chain. Results for the all-trans and cis-transoid conformations of polyenes are unified by a power-law dependence of the dominant tensor component \(\gamma_{xxxx}(\omega_1; \omega_2, \omega_3)\) on chain length \(L\) with an exponent of 4.6 ± 0.2.

A theoretical study of \(\gamma_{ijkl}(\omega_1; \omega_2, \omega_3)\) in a two-dimensional conjugated cyclic structure permitted examination of the role of dimensionality in the nonlinear-optical properties of conjugated systems. The origin of \(\gamma_{ijkl}(\omega_1; \omega_2, \omega_3)\) in this case was found to be similar to that for the one-dimensional case, but the magnitudes of the various components of \(\gamma_{ijkl}\) are all smaller than the \(\gamma_{xxxx}\) component of the one-dimensional chain with an equal number of carbons. More important, the isotropically averaged third-order susceptibility \(\gamma_{ij}\) is also much less for the two-dimensional structure compared with the one-dimensional chain. Our analysis shows that this is a result of a reduction in the effective length over which \(\pi\) electrons can respond to an applied optical electric field. For two-dimensional cyclic structures, this length is one half of the circumference of the ring compared with the full end-to-end chain length in one-dimensional structures. As a general rule, two-dimensional conjugated cyclic structures are therefore expected to have smaller nonresonant \(\chi^{(3)}(\omega_1; \omega_2, \omega_3)\) values than their one-dimensional analogs.

The presence of large oscillator strength \(\pi\)-electron bands in the visible and near ultraviolet characteristic of conjugated quasi-two-dimensional structures provides attractive conditions for studying resonant \(\chi^{(3)}\) processes, especially in phthalocyanine-related structures that also possess outstanding secondary material properties. We have demon-
strated that such two-dimensional structures can be designed as wide-area, spin-coatable nonlinear-optical films and that these can be represented as a microscopic composite system of molecular optical sites in a TLS glass random medium. The resonant nonlinear-optical properties of homogeneously broadened lines contained in the inhomogeneously broadened Gaussian envelope were directly investigated by standard saturable-absorption measurements. These results showed for the SINC films that saturable absorption occurs at the peak maximum of the low-frequency Q band in individual molecular sites are responsible for the large resonant nonlinear-optical response \( n_2 \) of \( 1 \times 10^{-4} \text{cm}^2/\text{W} \) at 810 nm.

A careful study of optical bistability in thin-film étalons demonstrated that, near the peak maximum of the saturable Q band centered at 810 nm, SINC thin films exhibit primarily electronic absorptive optical bistability at fast time scales (nanoseconds). At long time scales (seconds), thermally induced dispersive bistability occurs, which is entirely different and distinct from the observed fast time behavior.

The present results represent a first report on studies centering on conjugated quasi-two-dimensional structures. Further theoretical and experimental studies of larger ring structures and micrometer-thick films of naphthalocyanines for their resonant and nonresonant X\(_{(3)}\) behavior have been completed and will be reported in a later publication.

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12. See, for example, J. Solyom, Adv. Phys. 28, 201 (1979), and references therein.