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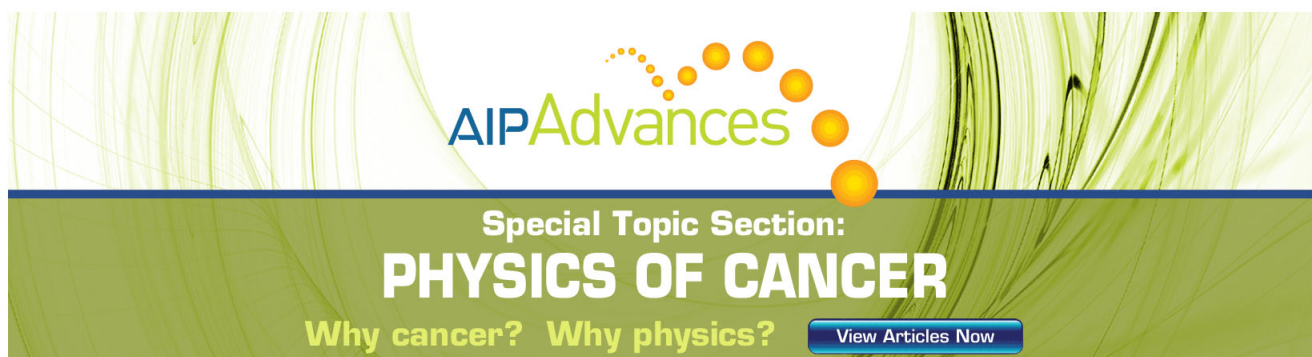
Second order optical nonlinearity in octupolar aromatic systems

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We investigate the second-order nonlinear optical properties of octupolar molecules, as opposed to traditional charge transfer dipolar molecules. We consider in particular the case of hexasubstituted aromatic rings, trianiline, trinitrobenzene, and tri-amino-,tri-nitro-benzene (TATB).

I. INTRODUCTION

Certain classes of organic molecules possess large second-order nonlinear optical coefficients, β. A particularly well studied class of such molecules are the disubstituted benzenes, in which an electron donor and electron acceptor are interacting from opposite sides of a benzene ring.[1] In these molecules, the nonlinear optical properties are believed to arise from an optically-intense electronic state in which electron density is transfered from the electron donor to the electron acceptor, traditionally referred to as a charge-transfer state. However, the electronic asymmetry which gives rise to the charge transfer state also gives rise to a property which may present problems from a materials standpoint; a large permanent dipole moment in the ground electronic state. On crystallization, the dipoles tend to oppose one another, leading to unit cells with a center of symmetry and thus a bulk material without nonlinear optical properties [$\chi^{(2)} = 0$]. One means of constructing bulk materials with finite $\chi^{(2)}$ is to embed the molecules in a host polymer and induce a net alignment by application of an external poling electric field.[2] The value of $\chi^{(2)}$ produced by poling is lower than that of an ideal crystal due to dilution of the optical chromophore and the limited alignment following a Langevin statistics. In addition, the resulting materials are often unstable due to a slow decay of the induced alignment.

Molecules which possess large nonlinear optical properties but which do not possess a permanent dipole moment could circumvent the crystallization problem discussed above. Construction of such molecules is indeed possible since the hyperpolarizability, β is a third-rank tensor property, while the dipole moment is a vector property. One example are molecules which possess a C_3 symmetry axis, such as the octupolar molecule shown in Fig. 1(b).[3] It has been shown that among molecules with a C_n symmetry axis, molecules with a C_3 symmetry axis are the only ones with no dipole moment but finite β.[4]

One way of viewing the octupolar molecule, Fig. 1(b), is as a superposition of three dipolar molecules, Fig. 1(a), rotated by 0°, 120°, and 240°, respectively. Such a summation cancels the dipole moment but leaves a finite β. The extent to which this view is justified comprises a central theme of this paper. We begin by discussing the symmetry properties of the dipolar and octupolar molecules and, in particular, how the increased symmetry of the octupolar molecules forces modifications to the two-level model for β. We then introduce a simple model Hamiltonian for the dipolar and octupolar molecules and study the effects of electron correlation on β. These studies are then repeated using a more sophisticated π-electron model.

II. SYMMETRY CONSIDERATIONS

We will focus primarily on the static, nonresonant, hyperpolarizability. Although experiments routinely measure second harmonic generation, these experiments are usually performed sufficiently far off resonance that resonance enhancement is not a dominant effect. The static second-order polarizability, $P^{(2)}$, is characterized by a third-rank symmetric tensor β, defined such that $P_i^{(2)} = 2\beta_{ijk}E_jE_k$, where E is the electric field. The factor of 2 is present since both second-harmonic generation and optical rectification contribute to $P^{(2)}$ at zero frequency.

It will be useful to transform β from the Cartesian representation used above to a spherical representation. The static hyperpolarizability contains both a $J=1$ (vector) spherical tensor component, $\beta^{(1)}$, and a $J=3$ spherical tensor component, $\beta^{(3)}$,

$$\beta = \beta^{(1)} \oplus \beta^{(3)}. \tag{1}$$

The Cartesian coordinate system is shown in Fig. 1. The molecule lies in the x,y plane with the x,z plane being a plane of symmetry. The nonzero components of the hyperpolarizability tensor are β_{xxx}, β_{xyy}, β_{yxy}, and β_{yyx}, the last three being equal due to Kleinmann symmetry in nonresonant β. Since $\beta^{(1)}$ transforms as a vector, we must have

$$\beta_{xyy}^{(1)} = \tfrac{1}{3}\beta_{xxx}^{(1)}. \tag{2}$$

$\beta^{(3)}$, on the other hand, must be invariant to rotation by 120°, which implies

$$\beta_{xyy}^{(3)} = -\beta_{xxx}^{(3)}. \tag{3}$$

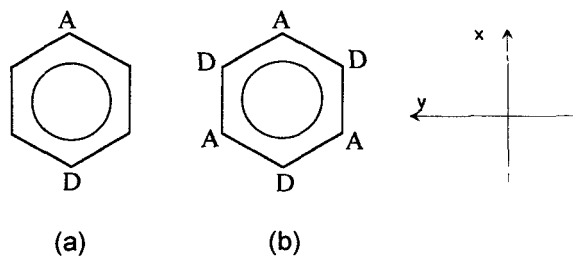β can then be decomposed as follows:

FIG. 1. Structures of investigated molecules. (a) represents a traditional dipolar molecule, an aromatic ring with acceptor (A) and donor (D) groups. (b) represents an octupolar molecule, where acceptors and donors alternate around the benzene ring.
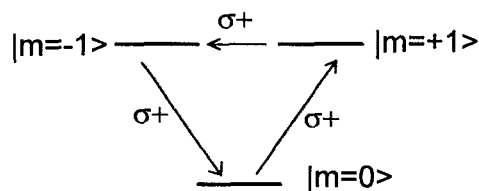

FIG. 2. Three-level model used to account for the second-order nonlinearities of an octupolar molecule. The arrows represent the three $\sigma+$ transitions contributing to $\beta_{\sigma\sigma\sigma}$.

$$\begin{cases} \beta_{xxx}=\frac{3}{4}(\beta_{xxx}+\beta_{xyy})+\frac{1}{4}(\beta_{xxx}-3\beta_{xyy}) \\ \beta_{xyy}=\frac{1}{4}(\beta_{xxx}+\beta_{xyy})-\frac{1}{4}(\beta_{xxx}-3\beta_{xyy}) \end{cases}, \qquad (4)$$

where the first term corresponds to $\beta^{(1)}$ and the second term corresponds to $\beta^{(3)}$. (Note that the first term cancels for a pure $J=3$ tensor and the second term cancels for a pure $J=1$ tensor.) Below, we will make comparisons between norms of the various tensors, defined as

$$|\beta|=\sqrt{\sum_{ijk}\beta_{ijk}^2}. \qquad (5)$$

The $J=1$ and 3 spherical components of the tensor being orthogonal, the squares of their norms add to the square of the total tensor norm, i.e. $|\beta|^2=|\beta^{(1)}|^2+|\beta^{(3)}|^2$.

Let us compare the hyperpolarizabilities of the dipolar molecule, β_{dip}, and the octupolar molecule, β_{oct}. Quite generally the D_{3h} symmetry obeyed by the octupolar molecule implies that β_{oct} has no $J=1$ component, $\beta_{\text{oct}}^{(1)}=0$. We first consider the situation in which the effects of the electron acceptor and donor are small and may be treated by low-order perturbation theory. In this case, the effects of the acceptors and donors are additive and β_{oct} will be the tensorial sum of the β's for three dipolar molecules, rotated by 0°, 120°, and 240°. The additivity results from the fact that β is first order in the perturbations arising from the electron donors and acceptors, Δ in the model presented below. Since $\beta^{(1)}$ transforms as a vector, it cancels and the octupolar molecule has no $\beta^{(1)}$ component, as deduced above from symmetry alone. Since $\beta^{(3)}$ is invariant to rotation by 120°, $|\beta_{\text{oct}}^{(3)}|$ will be three times that of the dipolar molecule, $|\beta_{\text{dip}}^{(3)}|$. In the two level model discussed below, the charge transfer transition along the x-axis of the dipolar molecule causes β_{xxx} to be the dominant Cartesian tensor component of β_{dip}. Note that this does not correspond to a pure $\beta^{(1)}$ tensor but rather a ratio $|\beta^{(1)}|/|\beta^{(3)}|=\sqrt{3}$ [see Eq. (4)], or $|\beta_{\text{dip}}^{(1)}|/|\beta_{\text{dip}}|=\sqrt{3}/2$ and $|\beta_{\text{dip}}^{(3)}|/|\beta_{\text{dip}}|=1/2$. Since within perturbation theory $|\beta_{\text{oct}}|$ is three times $|\beta_{\text{dip}}^{(3)}|$, we expect $|\beta_{\text{oct}}|/|\beta_{\text{dip}}|=3/2$.

Treating the interaction with the electric field as a perturbation, the following expression is obtained for β:

$$\beta_{ijk}=\frac{3}{2}\mathscr{P}\sum_{m,n\neq0}\frac{\langle0|\mu_i|n\rangle\langle n|\Delta\mu_j|m\rangle\langle m|\mu_k|0\rangle}{E_{0n}E_{0m}}, \qquad (6)$$

where $\mathscr{P}$ is the symmetrization operator over the three indices of the tensor and $\Delta\mu=\mu-\langle0|\mu|0\rangle$. If we assume that the nonlinear optical properties are dominated by a single charge-transfer state, then the above expression reduces to

$$\beta_{xxx}=\frac{3\mu_{01}^2\Delta\mu_{11}}{2E_{10}^2}, \qquad (7)$$

where μ_{01} is the dipole transition moment between the ground state, $|0\rangle$, and the charge transfer state, $|1\rangle$, and $\Delta\mu_{11}$ is the change in permanent dipole moment accompanying such a transition. The design paradigm which arises from this two-level model for β centers around the existence of an optimal strength for the electron donor and acceptor. The donor and acceptor should be strong enough to create a large change in dipole moment on excitation, but should not be so strong that the electronic transition becomes unallowed.

The above two level model is clearly not suitable for the octupolar molecule since, by symmetry, the permanent dipole moment must be zero. However, since within perturbation theory β of the octupolar molecule is a tensor sum of β for three dipolar molecules, we expect the dominant electronic states in the octupolar molecule to possess the character of the charge-transfer states of the dipolar molecule. In the D_{3h} symmetry group of the octupolar molecule, we may label the states according to the component of orbital angular momentum along the C_3 or z-axis, m. The $m=0$ states are singly degenerate states, while the $m=\pm1$ states correspond to the doubly degenerate states. It is convenient to consider interaction with circularly polarized light, since the selection rule is $\Delta m=+1$ (modulo 3) for a $\sigma+$ photon and $\Delta m=-1$ (modulo 3) for a $\sigma-$ photon. While the degenerate $m=1$ and -1 states do not possess a permanent dipole moment, there is a dipole moment matrix element between them. These doubly degenerate states in the octupolar molecule are thus the analogues of the charge transfer states in dipolar molecules.

The two level model described above for the dipolar molecule must be extended to a three level model in the octupolar case. As is evident from Eq. (6), the hyperpolarizability involves three transitions, originating and terminating at the ground electronic state, with total $\Delta m=0$ (modulo 3). There are only two ways to achieve this condition, with three $\sigma+$ transitions or with three $\sigma-$ transitions. The contribution β_{111} to the hyperpolarizability corresponding to three $\sigma+$ transitions is shown in Fig. 2,

$$\beta_{111} = \frac{3|\mu_{01}|^2 \mu_{1\bar{1}}}{2E_{01}^2},\qquad (8)$$

where μ now represents the $\sigma+$ component of the dipole moment. The other contribution $\beta_{\bar{1}\bar{1}\bar{1}}$, associated to three $\sigma-$ transitions, is of equal magnitude due to the reflection invariance. Note that singly degenerate, $m=0$, states other than the ground state can be ignored. Transforming into Cartesian coordinates yields

$$\beta = \beta_{111}\left[\left(\frac{e_x + ie_y}{\sqrt{2}}\right)^3 + \left(\frac{e_x - ie_y}{\sqrt{2}}\right)^3\right]$$

$$= \frac{\beta_{111}}{\sqrt{2}}\,(e_x \otimes e_x \otimes e_x - e_y \otimes e_y \otimes e_x - e_y \otimes e_x \otimes e_y$$

$$- e_x \otimes e_y \otimes e_y). \qquad (9)$$

Comparison with Eq. (4) shows this to be a pure $J=3$ tensor with norm $|\beta_{111}|\sqrt{2}$.

III. MODEL HAMILTONIAN

In creating a model which is applicable to a large class of substituted benzenes, the effects of the electron donors and acceptors must be included in a generic manner. In this section, we concentrate on the aromatic ring, and view the electron donors and acceptors as perturbing the electronic structure of this ring. We use the Pariser–Parr–Pople (PPP) π-electron Hamiltonian for benzene modified such that the on-site energy of a carbon atom which is attached to an electron donor (or acceptor) is raised (or lowered) by an amount Δ. Since we consider only six sites and six electrons, it is possible to obtain exact numerical solutions of the Hamiltonian including electron–electron interactions. Modeling substituted benzenes as perturbed benzene should be quite good for weak electron donors and acceptors, i.e., small Δ. For large Δ, the relation between the model and actual substituted benzenes is problematic, since in the latter case the amount of charge transfered outside of the benzene ring is known to be significant. However, some interesting qualitative conclusions may be drawn even in this limit.

The PPP Hamiltonian is[5]

$$H = \sum_{\mu} \epsilon_{\mu} n_{\mu} + \sum_{\mu \neq \nu, \sigma} t_{\mu\nu} a_{\mu\sigma}^{+} a_{\nu\sigma} + \sum_{\mu} \frac{\gamma_{\mu\mu}}{2} n_{\mu}(n_{\mu} - 1)$$

$$+ \sum_{\mu \neq \nu} \frac{\gamma_{\mu\nu}}{2} (n_{\mu} - z_{\mu})(n_{\nu} - z_{\nu}), \qquad (10)$$

where $n_{\mu} = \Sigma_{\sigma} a_{\mu\sigma}^{+} a_{\mu\sigma}$ is the total population (spin up and spin down) on site μ, ϵ_{μ} is the on-site energy, $t_{\mu\nu}$ is the transfer matrix, and z_{μ} is the atomic charge. We use the Ohno formula for the Coulomb two-center integrals

$$\gamma_{\mu\nu}(\text{eV}) = \frac{14.397}{\sqrt{\left(\frac{14.397}{11.26}\right)^2 + [r_{\mu\nu}(\text{Å})]^2}}. \qquad (11)$$

In our model, the on-site energy, ϵ_{μ}, is either zero for an unsubstituted carbon atom, $+\Delta$ for a donor-substituted site, or $-\Delta$ for an acceptor-substituted site. The one-
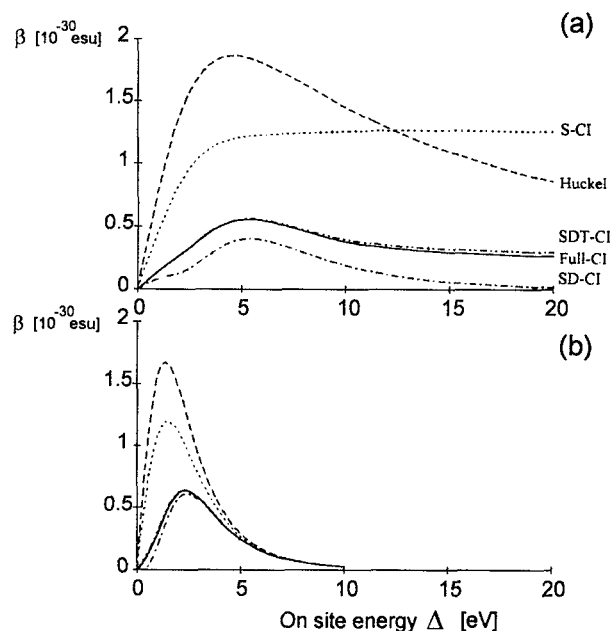

FIG. 3. Hyperpolarizability obtained using the sum-over-states method for (a) the di-substituted benzene ring, and (b) the hexa-substituted ring. The approximations used are Hückel (dashed line), single-CI (dotted), double-CI (dot–dashed line), triple-CI (double-dot–dashed line) and full-CI (solid line).

electron transfer matrix $t_{\mu\nu}$ includes only nearest-neighbor interactions, with a transfer integral of -2.4 eV. All atomic charges, z_{μ}, are equal to 1.

Figure 3 shows the norm of the hyperpolarizability, $|\beta|$, as a function of Δ for para-substituted (a) and hexa-substituted (b) benzene molecules. Calculations were performed at the Hückel level and at various levels of configuration interaction, including all single excitations (S-CI), all single and double excitations (SD-CI), all single, double and triple excitations (SDT-CI), and all possible excitations (full-CI) from the Hartree–Fock ground state. Full-CI corresponds to an exact solution of the model Hamiltonian. β was calculated using the sum-over-states method [Eq. (6)].

According to the design paradigm for para-disubstituted benzenes, there is an optimal strength for the electron donors and acceptors. They should be strong enough to ensure large charge transfer but not so strong that the charge-transfer transition becomes weak.[6,7] Our model calculations do in fact find an optimal value for Δ, ~ 4 eV. It is somewhat surprising that the optimal value of Δ obtained using the Hückel theory is nearly the same as that seen in the full-CI calculations. A difference does exist for values of Δ larger than the optimal value, where the decrease in β is more rapid in the Hückel calculations than in the full-CI calculations. This may result from the effect of electron correlation on the large Δ limit of β. For very large Δ, the substituted sites decouple from the molecule leaving two independent ethylene molecules. In the absence of electron–electron interactions, β is zero since the ethylene molecules are centrosymmetric. Inclusion of electron repulsion leads to a nonzero β since the ethylene mol-

TABLE I. Ratios of the β tensor components in Cartesian and spherical coordinates for the dipolar molecule, and ratio of the norms of the octupolar to dipolar β's, for vanishing values of Δ. Sum-over-states or finite-field (FF) methods are used, only at the Hartree–Fock (HF) or SD-CI level in the latter case.

Approximation	Hückel	S-CI	SD-CI	SDT-CI	full-CI	HF(FF)	SD-CI (FF)
$\beta_{xyy}^{\text{dip}}/\beta_{xxx}^{\text{dip}}$	−0.33	−0.72	0.44	−0.02	0.05	−0.68	−0.05
$|\beta_{\text{dip}}^{(3)}|/|\beta_{\text{dip}}|$	0.87	0.99	0.13	0.53	0.43	0.98	0.57
$|\beta_{\text{oct}}|/|\beta_{\text{dip}}|$	2.59	2.97	0.38	1.60	1.29	2.95	1.72

ecules are influenced by the net negative charge on the $-\Delta$ site and the net positive charge on the $+\Delta$ site. It is important to use caution in interpreting the large Δ limit of the model since strong electron donors and acceptors do not simply perturb the electronic structure of the benzene ring. Nevertheless, the following qualitative conclusion may be drawn: In the strong electron donor–acceptor limit, it is important to include electron correlation since net charges on the donors and acceptors have effects on the remainder of the molecule.

The large Δ limit of the octupolar molecule is more problematic. In this limit, all six sites decouple from one another. This leads to a band gap that increases as 2Δ and causes β to go to zero in the large Δ limit, due to the energy denominator in the sum-over-states expression of β. This is most likely an artifact of our inclusion of only six sites. In an actual hexa-substituted benzene, the attached groups would decouple from the carbon atoms, leaving a (possibly charged) benzene ring perturbed by net charges on the substituents. For the remainder of this section we will consider the small Δ limit, where a perturbed-benzene model should be accurate.

For small Δ, where first order perturbation theory in Δ is valid, $|\beta|$ of the octupolar molecule is three times the norm of the $J=3$ tensor component of the dipolar molecule, $|\beta_{\text{dip}}^{(3)}|$ (see Sec. II). This relation holds as long as first order perturbation theory in Δ is applicable, i.e., in the region of Fig. 3 over which $|\beta|$ rises linearly with Δ. Within this region, the ratio $|\beta_{\text{oct}}|/|\beta_{\text{dip}}|$ can be obtained once the tensor character of β for the dipolar molecule is known, $|\beta_{\text{dip}}^{(3)}|/|\beta_{\text{dip}}|$. A summary of the results obtained in the limit $\Delta \to 0$, are shown in Table I. Inclusion of electron correlation has a large effect on the tensor character of β in the dipolar molecule, and thus $|\beta_{\text{oct}}|/|\beta_{\text{dip}}|$. This is not surprising since the tensor character of β is determined by the redistribution of charge in the excited electronic states. Electron correlation must be included to accurately describe the effects of the transfered charge on the charge distribution in the remainder of the molecule. At the full-CI level, β of the dipolar molecule lies almost entirely along the x-axis, i.e., β_{xxx} is the only nonzero component. As discussed in the symmetry section, this implies that $|\beta_{\text{oct}}|/|\beta_{\text{dip}}|$ is near 3/2, the exact value being 1.29 at the full-CI level.

Examination of Fig. 3, shows that for all but the largest values of Δ, inclusion of electron correlation lowers the predicted norm of β. First, note that the S-CI predictions for $|\beta|$ are somewhat lower than the results obtained at the Hückel level. This decrease results from an attraction

between the positive charge on the donor and the negative charge on the acceptor which tends to inhibit a large charge transfer. A more substantial decrease in $|\beta|$ occurs between the S-CI and full-CI calculations. The origin of this effect is subtle and we will begin by examining, in detail, the origin of β at the S-CI level.

Figure 4(a) represents the energy levels of benzene, the dipolar molecule, and the octupolar molecule, as obtained at the S-CI level with $\Delta = 1$ eV. This value of Δ lies within the region where first order perturbation theory is applicable. The states are labeled with both the D_{6h} point group notation and the component of the orbital angular momentum along the C_6 axis, m. The label m is included for convenience, since the optical selection rules are $\Delta m = \pm 1$. The only state which is accessible from the ground state is the $1E_{1u}(m = \pm 1)$ state. From this state, the angular momentum selection rule allows access to either the $1E_{2g}(m = \pm 2)$ or $2E_{2g}(m = \pm 2)$ states; however, due to an additional selection rule arising from particle-hole symmetry, only the $2E_{2g}(m = \pm 2)$ is actually allowed. As expected for benzene (D_{6h}), β is zero since the absorption of an additional photon cannot return the molecule to the ground electronic state [see Eq. (6)].

The energy levels for the para-substituted molecule are shown in Fig. 4. The state labels, e.g., $1E_{1u}'(m = \pm 1)$, refer to the symmetry of the unperturbed benzene state. The perturbation due to the para-substitution has a Δm odd selection rule and mixes the $1E_{1u}(m = \pm 1)$ and $2E_{2g}(m = \pm 2)$ states discussed above. To lowest order in Δ, this mixing leads to two separate contributions to β. First, the transition moment between the $1E_{1u}(m = \pm 1)$ and $2E_{2g}(m = \pm 2)$ states gives rise to a permanent dipole moment in the $1E_{1u}'(m = \pm 1)$ state. The sum over states expression for β then contains the path $1A_{1g}'(m = 0) \to 1E_{1u}'(m = \pm 1) \to 1E_{1u}'(m = \pm 1) \to 1A_{1g}'(m = 0)$. Second, the transition between the $2E_{2g}'(m = \pm 2)$ and the ground state becomes allowed, introducing the path $1A_{1g}'(m = 0) \to 1E_{1u}'(m = \pm 1) \to 2E_{2g}'(m = \pm 2) \to 1A_{1g}'(m = 0)$. For small Δ, the first path contributes 160% of β_{xxx} and the second path contributes -60%.

The energy levels of the hexa-substituted molecule are shown in Fig. 4. The octupolar substitution mixes states which differ by $\Delta m = 3$. Just as for the para-substitution, the $1E_{1u}(m = \pm 1)$ states mix with the $2E_{2g}(m = \pm 2)$ states, however, due to the higher symmetry of the octupolar molecule, the resulting states remain doubly degenerate. The paths that are introduced into β_{111} [see Eq. (9)],
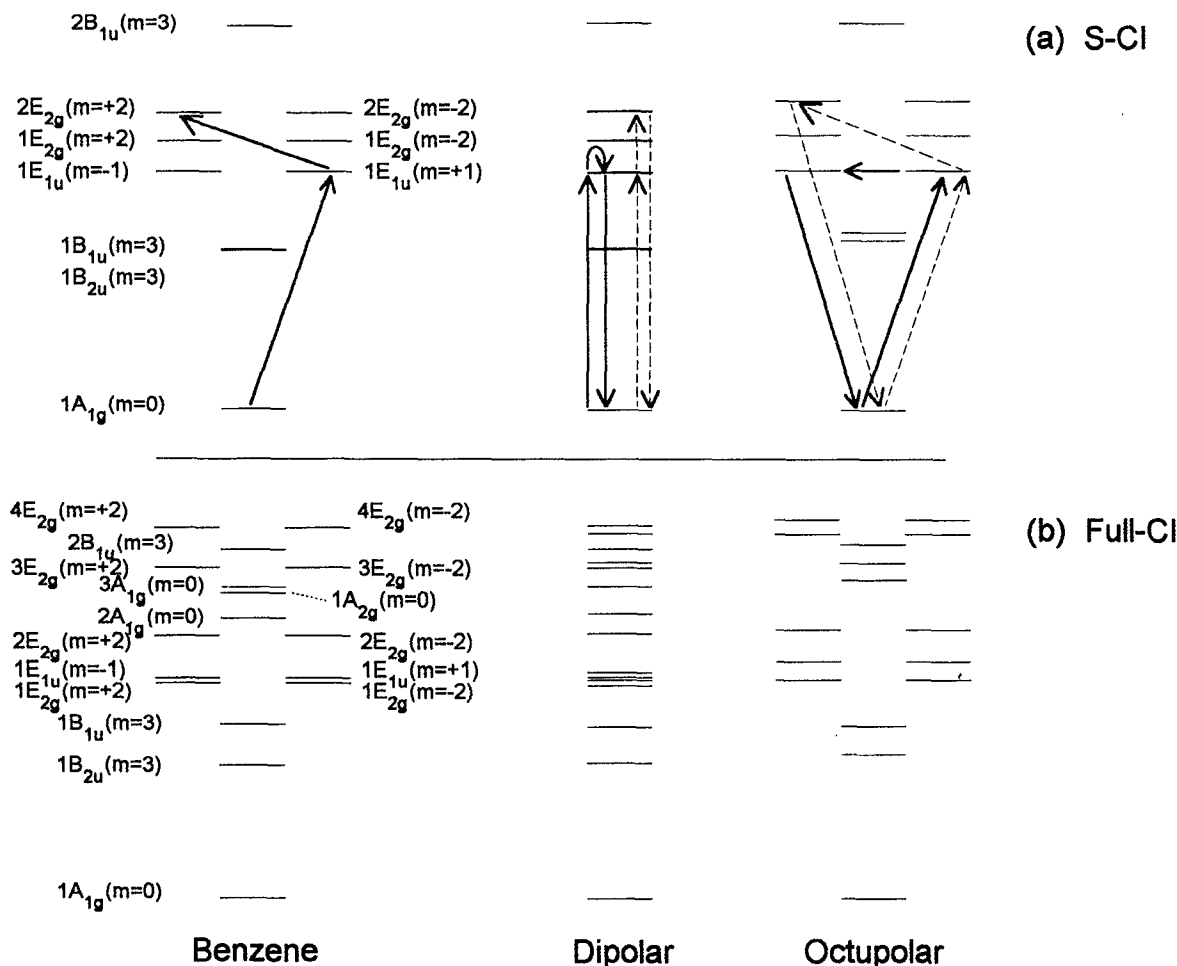
FIG. 4. Lower energy states of benzene and of the model molecules, dipolar and octupolar, for $\Delta = 1$ eV. The approximation level is either S-CI (a) or full-CI (b). In the text, the states of the dipolar and octupolar molecules are labeled according to the benzene states from which they originate. The most important transitions contributing to β_{xxx} or to $\beta_{\sigma\sigma\sigma}$ are indicated by arrows.

are directly analogous to those discussed above for the dipolar molecule $1A'_{1g}(m = 0) \rightarrow 1E'_{1u}(m = 1)$ $\rightarrow 1E'_{1u}(m = -1) \rightarrow 1A'_{1g}(m = 0)$ (72% of $|\beta|$) and $1A'_{1g}(m = 0) \rightarrow 1E'_{1u}(m = 1) \rightarrow 2E'_{2g}(m = 2)$ $\rightarrow 1A'_{1g}(m = 0)$ (28% of $|\beta|$).

We now return to a discussion of the large decrease in the calculated value of β on going from the S-CI solution to the exact, full-CI solution. The energy levels of benzene, obtained at both the S-CI and full-CI level, are shown in Figs. 4(a) and 4(b). An analysis of the full-CI wave functions indicates that the $2E_{2g}(m = \pm 2)$ states interact strongly with doubly excited configurations, producing a state with an energy nearly equal to that of the $1E_{1u}(m = \pm 1)$ states. Since β results from the mixing of the $1E_{1u}(m = \pm 1)$ and $2E_{2g}(m = \pm 2)$, it is not surprising that electron correlation will have a profound effect on the nature of this mixing and on the resulting predictions for β. The lowering of the $2E_{2g}$ state due to correlation has been seen in a number of calculations, both at the semiempirical[8,9] and *ab initio*[10,11] levels, and has led to the experimental assignment[12] of a state 0.5 eV above the $1E_{1u}$ state as an E_{2g} state. This value of 0.5 eV is larger than that

predicted by us, -0.2 eV, and others.[8–11] However, even when the parameters in our model are adjusted to reproduce the experimentally observed energies of the $1E_{1u}$ and E_{2g} states, we still observe a large reduction in the calculated value for $|\beta|$ on going from a S-CI to a full-CI calculation. While the lowering of the E_{2g} state is probably the principal reason for the decrease in $|\beta|$, we note that at the full-CI level a number of excited states contribute to β, making the interpretation of the origin of β much less straightforward than at the S-CI level.

Finally, we would like to discuss the accuracy obtained at various levels of calculation. In the configuration interaction calculations, up to triple excitations are required to obtain good agreement with the exact, full-CI results. This can be rationalized by considering that the lowest order effect of correlation on the ground state is mixing with doubly excited configurations. If we consider the S-CI calculation as providing a zero-order picture of the excited states, correlation causes these states to mix with triply-excited configurations. Since the excited states are important in a sum-over-states calculation of β, [Eq. (6)], a correlated calculation of β should include up to at least triple

FIG. 6. Geometry and bond parameters used for the PPP calculation of TATB. The same geometry, with only the relevant substituents, has been used for the other molecules.
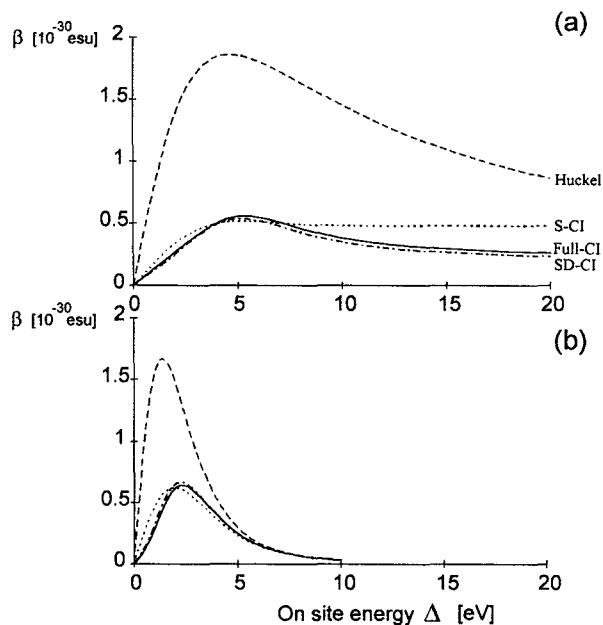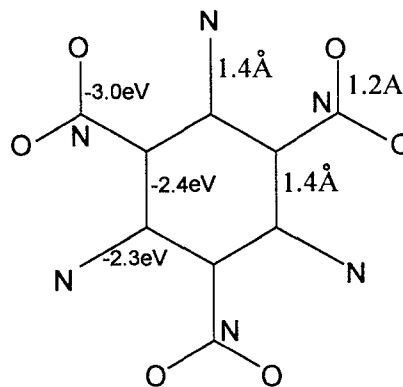
FIG. 5. Hyperpolarizability obtained using the finite-field method on the model Hamiltonian for (a) the disubstituted benzene ring, and (b) the hexa-substituted ring. The approximations used are Hückel (long dashed line), Hartree–Fock (dotted line), double-CI (dot–dashed line), and full-CI (solid line).

excitations. β can also be calculated using a finite-field approach. In this method, the electric field E is explicitly included in the Hamiltonian through the dipolar term $-\mu E$. The dipole moment of the ground state is then calculated for various finite values of the electric field. The derivative of the polarization with respect to electric field is then extracted,

$$\beta_{ijk}=\tfrac{1}{4}\mathscr{P}\,\frac{\partial^2 P_i}{\partial E_j \partial E_k}. \tag{12}$$

Since in this approach, the excited states are not used in the calculation of β, we expect that only doubly-excited configurations need to be included to obtain correlated results for β. Figure 5 confirms that the results obtained at the finite-field SD-CI level have converged to the exact full-CI result. While the finite-field SD-CI calculations give accuracy equivalent to the sum-over-states SDT-CI calculations with less computational effort, the lack of any information on the excited states makes a qualitative understanding of the results difficult.

Figure 4 also indicates that the octupolar molecule should present a better efficiency-transparency trade-off than the dipolar molecule. In the latter case, the B states, although weak, will be responsible for the onset of linear

absorption. However their contribution to β is minimal, resulting in an optical gap smaller than what would be expected from the value of β. For the octupolar molecule however, transition to the B states is forbidden because of the D_{3h} symmetry. The absorption onset now arises from a transition to the same electronic state which dominates β. Our model then predicts that octupolar molecules not only have a larger efficiency, but also a better transparency. We note that the selection rule might be relaxed in the solid phase. Furthermore the energy levels might be reordered in the solid or liquid phase.

IV. EXTENDED PPP HAMILTONIAN

We now use a more elaborate theory, taking into account all π electrons of the molecule. We still use the PPP Hamiltonian, extended to account for molecules with heteroatoms.[13] The Ohno formula [Eq. (11)] is replaced by

$$\gamma_{\mu\nu}(\text{eV})=\frac{14.397}{\sqrt{\left(\dfrac{2\times 14.397}{\gamma_\mu+\gamma_\nu}\right)^2+[r_{\mu\nu}(\text{Å})]^2}}, \tag{13}$$

where γ_μ depends on the atom present on site μ. The parameters, taken from Ref. 13, are shown in Table II. The exact geometry and the bond parameters $t_{\mu\nu}$ are shown in Fig. 6.

Table III shows the number of configurations to be considered for the different molecules we have studied. It appears that full-CI calculations, even using sophisticated

TABLE II. Parameters used for the PPP Hamiltonian.

Atom	z_μ	ϵ_μ	γ_μ
C	1	0.0	11.26
N	2	−18.4	15.00
O	1	−7.5	18.00

TABLE III. Number of states involved for different levels of configuration interaction.

Molecule	S-CI	SD-CI	SDT-CI	full-CI
aniline	13	91	255	490
tri-aniline	19	190	770	2520
nitro-benzene	21	231	1 071	5292
tri-nitro-benzene	37	1540	18 480	$\sim 5\times10^6$
pNA	25	325	1 805	$\sim 10^4$
TATB	73	2701	47 141	$\sim 7\times10^7$

TABLE IV. Norm of β obtained using the PPP Hamiltonian (10^{-30} esu).

Molecule	S-CI	SD-CI	SDT-CI	HF (FF)	SD-CI (FF)
aniline	0.58	0.35	0.42	0.38	0.41
tri-aniline	1.30	0.46	0.65	0.73	0.64
nitro-benzene	2.62	1.35	1.09	1.60	1.21
tri-nitro benzene	5.67	0.07		2.61	1.17
pNA	4.25	2.13	2.17	2.78	2.28
TATB	8.98			4.39	3.31

valence bond methods,[13] are not feasible for trinitrobenzene or TATB, due to the large number of states involved in the Hamiltonian. Since triple-CI calculations are not feasible by direct diagonalization of the Hamiltonian as employed here, we rely on the finite-field method at the SD-CI level to obtain accurate values of β for these molecules.

Table IV shows the norm of β for a variety of different molecules and level of approximations. A number of similarities with the model calculations presented in the previous section can be seen. For instance, β is significantly decreased by electron correlation. Also, the SDT-CI sum-over-states results, when available, are in good agreement with the SD-CI finite-field results. For aniline, for which full-CI calculations are feasible, both of these methods give results which are in good agreement with the exact results. This confirms our previous conclusion that convergence to the full-CI results occurs at the SDT-CI level in the sum-over-states method and at the SD-CI level in the finite-field method.

Table V shows the results for a number of components of β obtained at the SD-CI, finite-field level. While β_{xyy} can be neglected for aniline, this is not true for molecules with a nitro substituent, presumably because of the large polarizability of the oxygen π electrons along the *y*-axis. The table also compares $3|\beta_{dip}^{(3)}|$ with $|\beta_{oct}|$. If the substituents have a perturbative effect on benzene, these two quantities are equal since the octupolar molecule can be viewed as a linear superposition of three rotated dipolar molecules. Aniline and tri-aniline seem to be in the perturbative regime, $|\beta_{oct}|$ is equal to $3|\beta_{dip}^{(3)}|$ and examination of the energy levels shows that they are comparable to those obtained using the model Hamiltonian of the previous section, with $\Delta = 1$ eV. The value of $|\beta|$ obtained here is somewhat larger than that seen in the model calculations since transfer of charge outside of the benzene ring leads to a larger change in the permanent dipole moment on electronic excitation. Nitro-benzene and tri-nitro-benzene appear to lie outside of the regime where low-order perturbation theory is valid. Also, examination of the energy
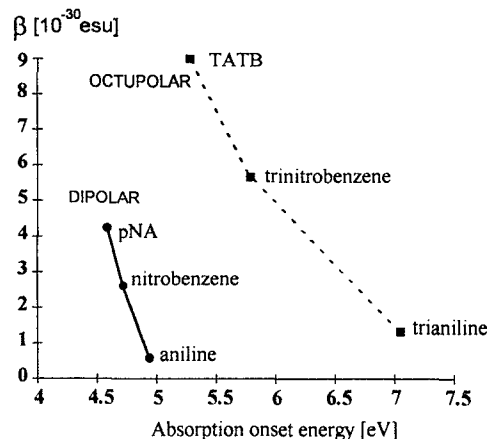

FIG. 7. Efficiency-transparency trade-off for the C_{2v} and D_{3h} molecules, as calculated at the single-CI level. This figure applies only for the gas phase, as solid-state effects may lower the symmetry of the octupolar molecule, and alter the selection rule responsible for the good transparency of the D_{3h} species.

levels shows that they are not simply perturbed benzene levels. The nonperturbative effect of the NO_2 group can also be deduced from the fact that *pNA* has a β larger than the sum of β for aniline and nitrobenzene. For all the molecules studied here, $|\beta_{oct}|$ is at least as large as $|\beta_{dip}|$ and is often significantly larger. The octupolar molecules are then good candidates for nonlinear optical materials.

Figure 7 represents the efficiency transparency trade-off, at the single-CI level, for the molecules studied above. It appears that the octupolar class has a much better trade-off than the dipolar class. As expected from the model of the previous section, this behavior results both from an increase in efficiency and from an increase in the optical gap, the latter being a direct consequence of the increased symmetry of the octupolar species.

Experimental values of β are most commonly obtained through EFISHG experiments, in which molecules are aligned by a static electric field and second harmonic generation of a laser beam is measured.[1] These experiments measure the quantity

$$\beta_{vec} = \beta_{xxx} + \tfrac{1}{3}(\beta_{xyy} + \beta_{yxy} + \beta_{yyx}) = \frac{2}{\sqrt{3}} |\beta^{(1)}|. \quad (14)$$

Since $|\beta^{(1)}| = 0$ for octupolar molecules, EFISHG is not applicable. The only experimental results available are from early experiments performed in the solid state.[3] While these experiments prove the existence of hyperpolarizability for octupolar molecules, no exact β values can be deduced due to uncertainty in the crystal structure. In contrast, disubstituted benzenes have been the subject of constant investigation. Recently, systematic measurements have been performed[14] on benzene derivatives. The results obtained for the molecules studied here are reported in Table VI. While the agreement is good for aniline, our theory strongly underestimates the hyperpolarizability of *pNA*. The parameters we used, while well accepted for carbon and nitrogen, have not been optimized for oxygen.[13] It is therefore expected that the theory could be

TABLE V. Components of β obtained at the SD-CI, finite-field level.

Substituents	$\|\beta^{dip}\|$	$\beta_{xyy}^{dip}/\beta_{xxx}^{dip}$	$\|\beta_{dip}^{(3)}\|/\|\beta_{dip}\|$	$3\|\beta_{dip}^{(3)}\|$	$\|\beta_{oct}\|$
NH_2	0.41	0.01	0.48	0.60	0.64
NO_2	1.21	0.21	0.17	0.62	1.17
$NH_2 + NO_2$	2.28	0.08	0.37	2.53	3.31

TABLE VI. Comparison of β_{vec} (10^{-30} esu) between the extended PPP results (FF-SDCI) and the experiments.

Molecule	Th.	Exp.
aniline	0.42	0.55
nitro-benzene	1.37	1.9
pNA	2.45	9.2

improved to properly account for the nitro group. A more serious limitation of the theory is the absence of σ electrons. While the direct contribution of σ electrons to β is known to be small, σ electrons must be included if the hybridization of the hetero-atoms changes during the charge transfer process.

Brédas et al.[15] have recently calculated the second-order hyperpolarizability of pNA and TATB using both ab initio and semiempirical theories, the latter including all valence electrons, at the AM1 or intermediate neglect of differential overlap (INDO-SD-CI) level. All three methods give similar values for $|\beta|$; in the range 8–12 for pNA, in good agreement with experiment, and 15–22 for TATB. While our results differ from these in absolute magnitude, we obtain similar results for the ratio between $|\beta|$ of TATB and that of pNA.

V. CONCLUSION

The calculations presented in this work suggest that the octupolar substituted benzenes may be a particularly worthwhile class of molecules for second-order nonlinear optics. While these molecules share many similarities with the more traditional dipolar molecules, such as large nonlinear optical coefficients, the presence of a threefold symmetry axis presents some distinct advantages. First, there is no permanent dipole moment in the ground state. This may make it easier to form crystals in which the unit cell is not centrosymmetric. Second, optical selection rules arising from the higher symmetry of the octupolar molecule lead to better transparency characteristics, at least in the gas phase. In both the dipolar and octupolar molecules, the nonlinear optical properties are enhanced by a low lying intense electronic transition. In the dipolar molecule, there are states below the lowest intense charge-transfer state which, while weak, are optically allowed. In the octupolar molecules, the analogous states are electronically forbidden, being accessible only through vibronic interactions.

The presence of the threefold symmetry axis in the octupolar molecule forces modifications to the standard two-level model used for dipolar molecules. In the two-level model, β results from a transition to an excited charge-transfer state which has a permanent dipole moment very different from that of the ground state. When using the angular momentum basis for the octupolar molecule, no electronic state may possess a permanent dipole moment; however, there are pairs of degenerate electron states with dipole moment connections between them. These doubly degenerate states are the analog of the charge-transfer state in the dipolar molecule, and together with the ground state comprise a three-level model for β.

We have developed a model treating the effects of the electron–donor and electron–acceptor substituents as a perturbation on the electronic states of benzene. To lowest order, the octupolar molecule can be viewed as a linear superposition of three dipolar molecules. On taking this linear superposition, the $J=1$ tensor components of β in the dipolar molecules cancel while the $J=3$ tensor components add. In our model calculations at the full-CI level, we find that the dominant component of β lies along the charge-transfer axis. Within perturbation theory, this implies that the norm of β for the octupolar molecule will be $\frac{3}{2}$ that of the dipolar molecule. Going beyond the simple perturbative model, we have also performed calculations using the PPP model and including all π electrons. The findings for aniline and tri-aniline are in good agreement with the perturbative regime of the model calculations. It appears, however, that tri-nitro-benzene and TATB are not in the perturbative regime.

In order to obtain quantitative agreement with experiment, it is necessary to include σ-electrons. This probably results from a change in the hybridization of the heteroatoms on transition to the excited charge-transfer states. By failing to describe this change in hybridization, π-electron theories fail to obtain the proper electron–donor, electron–acceptor strengths, however, a generic understanding of the effects of electron donors and acceptors on benzene can still be obtained. One advantage of the simple model presented here is the ability to study the effects of electron correlation. We find that it is important to include electron correlation in the calculation of properties that are sensitive to the spatial organization of charge in the molecule, for example the ratio of the $J=1$ to the $J=3$ tensor components of β. Also, electron correlation has a large effect on the energy spectrum of unsubstituted benzene. Calculations on substituted benzenes at the S-CI level indicate that β arises primarily from the mixing of the $1E_{1u}$ and $2E_{2g}$ electronic states. Electron correlation lowers the energy of the E_{2g} state, causing it to be nearly degenerate with the $1E_{1u}$ state. Clearly, such an effect must be incorporated if reliable results for β are to be obtained. Within the finite-field formalism for β, inclusion of doubly excited configurations (SD-CI) appears sufficient for accurate calculations of β. Since the sum-over-states formalism for β requires accurate descriptions of the excited states, triple excitations must be included (SDT-CI).

In conclusion, this work indicates that octupolar molecules will, in general, have hyperpolarizabilities as large or larger than dipolar molecules. If a noncentrosymmetric crystal can be formed from such a molecule, the crystal would likely exhibit large nonlinear optical activity along with optimal transparency.

ACKNOWLEDGMENTS

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