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Large Second-Order Optical Nonlinearities in Open-Shell Chromophores. Planar Metal Complexes and Organic Radical Ion Aggregates

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Abstract: Attempts to discover molecular chromophores with large hyperpolarizabilities have largely focused on *closed-shell* organic species. This contribution explores the use of sum over states (SOS) perturbation theory and the computationally efficient intermediate neglect of differential overlap (INDO) model Hamiltonian, combined with single configuration interaction (SCI) techniques, to calculate frequency-dependent quadratic molecular hyperpolarizabilities of both coordination complexes and organic radical ion chromophore aggregates having *open-shell* doublet ground state electronic structures. The correct evaluation of the lowest-lying excited states has been tested by comparison with experimental optical spectra. In the cases considered here, the INDO/SCI-SOS method provides both a good description of linear optical transitions and an adequate prediction of second-order nonlinearity. It is seen that the larger second-order nonlinearities of systems having open-shell electronic states, as compared to those having analogous closed-shell structures, are a consequence of accessible lower-lying charge-transfer excited electronic states. The INDO/SCI-SOS model is attractive for designing new, highly efficient open-shell second-order nonlinear optical chromophores.

Introduction

Research on molecule-based materials having large second-order nonlinear optical (NLO) responses[1,2] has greatly benefited from the development of chemically-oriented, quantum chemical formalisms for the description of NLO properties and the design of new molecular architectures having optimized molecular response.[3] Various theoretical approaches for calculating microscopic quadratic hyperpolarizabilities, β_{ijk}, using ab initio or semiempirical Hamiltonians, based on coupled or perturbative models, have appeared in the literature.[3−5] Actually, both coupled (field-dependent) and perturbative (field-independent) schemes can be implemented for any model Hamiltonian while correlation effects are treated at various levels of sophistication. Hyperpolarizabilities can be computed for any molecular spin state with currently available ab initio software packages, such as Gaussian-94,[6] ACES II,[7] and HONDO-95.3.[8] Nevertheless, accurate ab initio calculations are still limited to small molecules.[4,5] In addition, dynamic (frequency-dependent) hyperpolarizabilities can only be computed for closed-shell electronic structures (i.e., for systems having no unpaired electrons), while for open-shell systems (i.e., those having unpaired electrons), they can only be obtained in the static limit.

Semiempirical model Hamiltonians, largely used in combination with the sum over excited states (SOS) perturbative formalism,[9] have been extensively and successfully employed to predict the second-order NLO response of “real-world” molecular chromophores[3,10] and to design optimized NLO architectures.[11] Nevertheless, to date such semiempirical approaches have been limited to calculating the static and dynamic hyperpolarizabilities of *closed-shell* systems. On the other hand, the investigation and development of NLO materials having *open-shell* electronic structures is in its infancy, and there is, in fact, recent evidence that species having open-shell electronic states, such as organic radicals[12,13] or transition metal com-

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plexes,[14] can exhibit very large second-order hyperpolarizabilities in comparison with analogous closed-shell systems.

We present here the first successful implementation of the INDO/SCI-SOS formalism for the calculation of frequency-dependent second-order hyperpolarizabilities of open-shell doublet electronic states in both coordination complexes and organic radical ion aggregates as well as theoretical evidence that *very large NLO responses can be achieved in the case of open-shell ground state systems.*

Theoretical Method

Within the framework of SOS perturbation theory,[9] the electronic states created by the perturbing laser field (ω) are treated as an infinite expansion over a complete set of unperturbed Ψ_n and $\Psi_{n'}$ particle−hole excited states. Thus, the individual tensor components of the molecular hyperpolarizability (within a perturbation series expansion employing the Ward definition),[9,15] for instance for second harmonic generation, $\beta_{ijk}(-2\omega;\omega,\omega)$, can be related exactly to *all* the excited states of the molecule in terms of the difference, $\hbar\omega_{ng}$, between excited and ground state energies, dipole moment matrix elements, r^i_{gn} and $r^i_{nn'}$, between unperturbed ground and excited states and between two excited states, respectively, and the dipole moment change, $\Delta r^i_n = r^i_{nn} - r^i_{gg}$, between excited ($n$) and ground states ($g$) (eq 1).[9] The solution of eq 1 allows the accurate calculation of the frequency-dependent (nonresonant) NLO response for any molecular spin state, when an appropriate description of the molecular ground and excited state wave functions is achieved.

$$\begin{aligned}\beta_{ijk}(-2\omega;\omega,\omega) = -\frac{e^3}{4\hbar^2}\Bigg[\sum_{n\neq g}\sum_{\substack{n'\neq g\\ n'\neq n}}\Bigg\{&(r^i_{gn'}r^j_{n'n}r^k_{gn} + r^k_{gn'}r^i_{n'n}r^j_{gn}) \times \\ &\left(\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}+\omega)} + \frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}-\omega)}\right) + \\ &(r^i_{gn'}r^j_{n'n}r^k_{gn} + r^i_{gn'}r^k_{n'n}r^j_{gn})\left(\frac{1}{(\omega_{n'g}+2\omega)(\omega_{ng}+\omega)} + \right. \\ &\left.\frac{1}{(\omega_{n'g}-2\omega)(\omega_{ng}-\omega)}\right) + (r^j_{gn'}r^k_{n'n}r^i_{gn} + r^k_{gn'}r^j_{n'n}r^i_{gn}) \times \\ &\left(\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}-2\omega)} + \frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}+2\omega)}\right)\Bigg\} + \\ 4\sum_{n\neq g}\Bigg\{&[r^j_{gn}r^k_{gn}\Delta r^i_n({\omega_{ng}}^2 - 4\omega^2) + r^i_{gn}(r^k_{gn}\Delta r^j_n + r^j_{gn}\Delta r^k_n)({\omega_{ng}}^2 + \\ &2\omega^2)]\frac{1}{({\omega_{ng}}^2-\omega^2)({\omega_{ng}}^2-4\omega^2)}\Bigg\}\Bigg]\end{aligned} \tag{1}$$

A more realistic treatment of the complete dispersion of $\beta_{ijk}(-2\omega;\omega,\omega)$ requires, however, consideration of damping corrections which account for the various spectral broadening processes. The $\beta_{ijk}(-2\omega;\omega,\omega)$ tensor terms are then allowed to be complex (eq 2).[15] Here, $\Omega_{ng} = \omega_{ng} + i\Gamma/2$ and $\Omega_{ng}{}^* = \omega_{ng} - i\Gamma/2$ are, respectively, the complex continuation of ω_{ng} and its complex conjugate, and $\Gamma \cong \Gamma_{ng} \equiv \Gamma_n - \Gamma_g$ is a damping parameter. In the present approach, the damping term Γ is treated phenomenologically by using the peak half-width at half-maximum deduced from the optical absorption spectrum. A comparison with experiment is possible through $|\beta_{ijk}|$, eq 3,

$$\begin{aligned}\beta_{ijk}(-2\omega;\omega,\omega) = -\frac{e^3}{4\hbar^2}\Bigg[\sum_{n\neq g}\sum_{\substack{n'\neq g\\ n'\neq n}}\Bigg\{&(r^j_{gn'}r^i_{n'n}r^k_{gn} + r^k_{gn'}r^i_{n'n}r^j_{gn}) \times \\ &\left(\frac{1}{(\Omega_{n'g}-\omega)(\Omega_{ng}{}^*+\omega)} + \frac{1}{(\Omega_{n'g}{}^*+\omega)(\Omega_{ng}-\omega)}\right) + \\ &(r^i_{gn'}r^j_{n'n}r^k_{gn} + r^i_{gn'}r^k_{n'n}r^j_{gn})\left(\frac{1}{(\Omega_{n'g}{}^*+2\omega)(\Omega_{ng}{}^*+\omega)} + \right. \\ &\left.\frac{1}{(\Omega_{n'g}-2\omega)(\Omega_{ng}-\omega)}\right) + (r^j_{gn'}r^k_{n'n}r^i_{gn} + r^k_{gn'}r^j_{n'n}r^i_{gn}) \times \\ &\left(\frac{1}{(\Omega_{n'g}-\omega)(\Omega_{ng}-2\omega)} + \frac{1}{(\Omega_{n'g}{}^*+\omega)(\Omega_{ng}{}^*+2\omega)}\right)\Bigg\} + \\ 4\sum_{n\neq g}\Bigg\{&[r^j_{gn}r^k_{gn}\Delta r^i_n({\omega_{ng}}^2 - 4\omega^2) + r^i_{gn}(r^k_{gn}\Delta r^j_n + r^j_{gn}\Delta r^k_n) \times \\ &({\omega_{ng}}^2 + 2\omega^2)]\frac{1}{({\Omega_{ng}}^2-\omega^2)({\omega_{ng}}^2-4\omega^2)}\Bigg\}\Bigg]\end{aligned} \tag{2}$$

where $\mathrm{Re}(\beta_{ijk})$ and $\mathrm{Im}(\beta_{ijk})$ are the real and imaginary parts of the complex $\beta_{ijk}(-2\omega;\omega,\omega)$ tensor terms.

$$|\beta_{ijk}| = (\mathrm{Re}(\beta_{ijk})^2 + \mathrm{Im}(\beta_{ijk})^2)^{1/2} \tag{3}$$

In the present approach, the all-valence INDO model Hamiltonian[16] is employed to compute SCF ground state wave functions of the open-shell molecules. The monoexcited configuration interaction (MECI) approximation is employed to describe the excited states. The CI procedure is a critical point for the description of the excited states, especially for open-shell ground state configurations, since a correct description requires an extensive CI treatment which would generate a large number of configuration state functions (CSFs). In the present approach, the MECI method is implemented so that an appropriate number of *lowest energy* transitions between SCF electronic configurations can be chosen to undergo CI mixing and to be included in the SOS summation (eqs 1 and 2). In analogy to previously investigated closed-shell molecules,[3] this procedure allows a good description of lower energy excited states, even with the inclusion of a relatively low number of CSFs and, in turn, a rapid convergence of computed $\beta_{ijk}(-2\omega;\omega,\omega)$ values. The transition moment matrix elements are computed in dipole length form using LCAO-MO coefficients and the Pariser approximation[17] for matrix elements over atomic orbitals.

Results and Discussion

Within the SOS formalism, the microscopic second-order NLO response is related to all the excited states of the molecule (eq 1). Nevertheless, in the majority of the closed-shell systems investigated thus far, it has been found that the lowest-lying charge-transfer states are generally responsible for the second-order optical nonlinearity.[3] It is therefore expected that the correct evaluation of the lowest-lying excited states, which can be straightforwardly tested by the comparison with experimental

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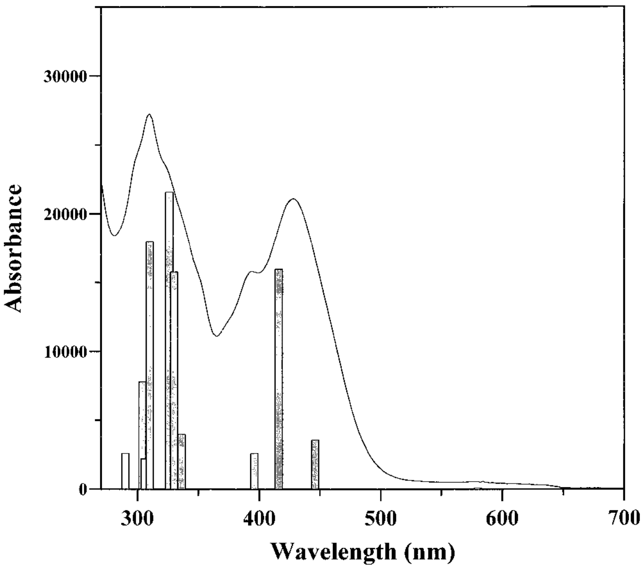
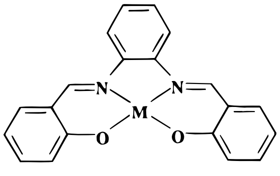


Figure 1. INDO/SCI-derived electronic transitions of the complex Cu(salophen). The bars represent the oscillator strength of the various transitions in arbitrary units, adjusted to the strongest transition in the experimental optical spectrum in chloroform solution (solid line).

optical spectra, should find their counterpart in the quantitative prediction of β_{ijk}, even in the case of open-shell ground state systems.

In the following discussion are presented several diverse examples of doublet open-shell ground state systems in which the present INDO/SCI-derived optical spectra and $\beta_{ijk}(-2\omega;\omega,\omega)$ values are compared with experimental data.

(*N*,*N*′-Bis(salicylidene)-1,2-phenylenediamino)M(II) Complexes [M(salophen); M = Cu, Co]. Cu(salophen) **(1)** possesses a planar structure[18,19] and is paramagnetic (d^9), having a single unpaired electron.[20,21] The experimental optical spectrum in relatively nonpolar chloroform solution[14] and calculated INDO/SCI-derived electronic transitions for the $^2A_2$ $[(d_{xy})^1]$ ground state[21] of **1** are compared in Figure 1. The agreement between calculated and experimental data is very good, in terms of both energy and relative intensities (oscillator strengths). In particular, the intense feature centered at $\lambda_{max} = 428$ nm ($r_{gn} = 7.27$ D) can be related to three electronic transitions, the strongest of which ($\lambda_{max}^{calc} = 413$ nm; $r_{gn} = 8.56$ D) possesses metal-to-ligand [Cu (d_{xz}), O ($2p_z$), Ph (π) → C=N (π^*), Ph (π^*)] charge-transfer (MLCT) character ($\Delta\mu^{calc} = -3.1$ D). The experimentally observed, modest negative solvatochromism associated with this band ($\Delta\mu = -4.1$ D)[14] further supports this assignment. The shorter wavelength feature ($\lambda_{max} = 310$ nm) can be related to a set of seven electronic transitions, some of which have CT character. The very good theoretical prediction of the electronic spectrum of **1** finds a counterpart in an accurate prediction of the second-order nonlinearity. In particular, the calculated hyperpolarizability value ($\beta_{vec}^{calc} = -53.7 \times 10^{-30}$ cm^5 esu^{-1}; $\hbar\omega = 0.92$ eV) is in excellent agreement with the EFISH-derived value in chloroform solution ($\beta_{vec}^{expt} = -50.0 \times 10^{-30}$ cm^5 esu^{-1}; $\hbar\omega = 0.92$ eV;[14] β_{vec} is the vector hyperpolarizability component along the chromophore dipole moment direction).[1]



M = Cu (1), Co (2), Ni (3)

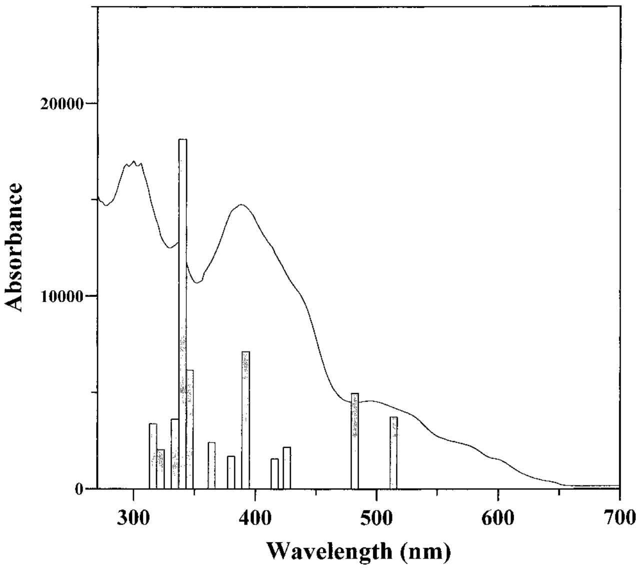


Figure 2. INDO/SCI-derived electronic transitions of the complex Co(salophen). The bars represent the oscillator strength of the various transitions in arbitrary units, adjusted to the strongest transition in the experimental optical spectrum in chloroform solution (solid line).

Similarly to complex **1**, Co(salophen) **(2)** is planar[22] and paramagnetic (low-spin d^7),[21,23] thus having a single unpaired electron. Calculated electronic transitions for the $^2A_1$ $[(d_{z^2})^1]$ ground state[21,23] of **2** are compared with the experimental chloroform solution optical spectrum[14] in Figure 2. The intense feature centered at $\lambda_{max} = 388$ nm and the shoulder at 435 nm, both exhibiting a negative solvatochromism,[14] are accurately predicted and can be related to a set of five transitions, all having MLCT character. In contrast, the lowest calculated optical transitions ($\lambda_{max}^{calc} = 483$, 514 nm), also having some MLCT character, appear to be somewhat overestimated in energy relative to the lower energy spectral features ($\lambda^{expt} = 500-600$ nm). Due to the presence of these additional lower energy CT transitions, the calculated second-order nonlinearity ($\beta_{vec}^{calc} = -105.1 \times 10^{-30}$ cm^5 esu^{-1}; $\hbar\omega = 0.92$ eV) is about 2 times larger than that of the Cu(II) complex **1** (Table 1). The comparison between the calculated β_{vec} value for **2** with the partially resonant experimental EFISH data in chloroform ($\beta_{vec}^{expt} = (-170 \pm 40) \times 10^{-30}$ cm^5 esu^{-1}; $\hbar\omega = 0.92$ eV)[14] is favorable, but somewhat less satisfactory. This is due to the aforementioned blue shift of calculated lowest electronic transition energies, which results in larger denominators and, in turn, smaller second-order response (eq 1). In fact, even within the simple two-state model for the dispersion of β (eq 4),[24] it can be inferred that, in this frequency range, a 100 nm displacement in the calculated energy of the lowest CT transition roughly doubles the β value.

Most importantly, the experimental and calculated nonlinearities of both the Cu(II) and Co(II) complexes **1** and **2** are

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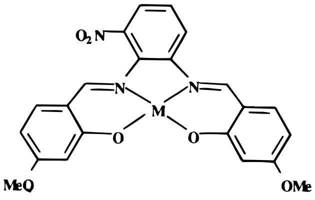
Table 1. INDO/SCI-SOS and Experimental EFISH-Derived[14,25] Second-Order NLO Response Data (10^{-30} cm^5 esu^{-1}) for Coordination Complexes Having Open-Shell Doublet Ground State Electronic Structures[a]

compd	$\hbar\omega$ (eV)	$\beta_{\mathrm{vec}}^{\mathrm{calc}}$	$\beta_{\mathrm{vec}}^{\mathrm{expt}}$
1 (Cu(salophen))	0.0	−37.2	
	0.92	−53.7	−50.0 ± 5[b]
2 (Co(salophen))	0.0	−40.1	
	0.92	−105.1	−170 ± 40[b]
3 (Ni(salophen))	0.0	−11.5	
	0.92	−17.3	−20.5 ± 2[b]
4 (Co(4-OMe-sal-3-NO$_2$-ophen))	0.0	−90.4	
	0.92	−250	
5 (Ni(4-OMe-sal-3-NO$_2$-ophen))	0.0	−25.6	
	0.92	−55.2	−55 ± 5[c]

[a] Data for the homologous closed-shell Ni(II) complexes are reported for comparison. [b] From ref 14. [c] From ref 25.

$$\beta_{ijk} \propto \frac{\omega^4}{(\omega_{ng}{}^2 - \omega^2)(\omega_{ng}{}^2 - 4\omega^2)} \tag{4}$$

substantially larger than those of the closed-shell Ni(salophen) **(3)** homologue[14] (Table 1). This difference can be directly related to the existence of the aforementioned additional low-lying CT states, absent in the case of the Ni(II) complex (lowest CT state, $\lambda_{\max}^{\mathrm{calc}} = 387$ nm), which contribute to larger nonlinearities. Analogously, the calculated hyperpolarizability for the $^2A_1$ [$(d_{z^2})^1$] ground state of the donor−acceptor-substituted Co(4-OMe-sal-3-NO$_2$-ophen) derivative **(4)**($\beta_{\mathrm{vec}}^{\mathrm{calc}} = -250 \times 10^{-30}$ cm^5 esu^{-1}; $\hbar\omega = 0.92$ eV) is predicted to be substantially larger than that calculated and observed experimentally for the homologous closed-shell Ni(II) complex **5** ($\beta_{\mathrm{vec}}^{\mathrm{calcd}} = -55.2 \times 10^{-30}$ cm^5 esu^{-1}; $\beta_{\mathrm{vec}}^{\mathrm{expt}} = -55 \times 10^{-30}$ cm^5 esu^{-1} in chloroform solution; $\hbar\omega = 0.92$ eV).[25] In this case, the existence of low-lying CT excited states ($\lambda_{\max}^{\mathrm{calc}} = 540$, 500, 477 nm vs 491 nm in the Ni(II) derivative **5**) again contributes to the larger nonlinearity.

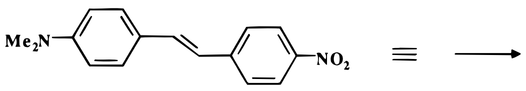


M = Co(**4**), Ni(**5**)

Table 2. Largest INDO/SCI-SOS-Derived Second-Order Tensor Component of the Complex Hyperpolarizability ($|\beta_{xxx}|$ (See Eq 3), 10^{-30} cm^5 esu^{-1}) for the DANS Monomer and DANS Dimer Aggregates at Various Incident Laser Frequencies

structure	$z\uparrow \xrightarrow{x}$	$\hbar\omega$ (eV)	$\lvert\beta_{xxx}\rvert$
6	→	0.0	43.1
		0.65	55.6
		1.17	123.0
7	⇄ +	0.0	90.2
		0.65	1330
		1.17	4375
8	⇉	0.0	68.1
		0.65	85.2
		1.17	161
9	⇉	0.0	70.1
		0.65	90.6
		1.17	179

Charged Radical Cation Chromophore Aggregates. It was recently found that chromophore-doped polymer films poled[1,2] using an in-plane electrode configuration contain charged radical cation chromophore aggregates (such as 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DANS, **6**) aggregates) and exhibit very large second-order optical nonlinearities and new (non-DANS) linear optical features in the 500−800 nm region, as well as distinctive second-order susceptibility ($\chi^{(2)}$) dispersion features compared to the response of films poled using a conventional electrode configuration (which contain isolated DANS chromophores).[12,13] The present calculations on the localized $^2A'$ ground state of the centrosymmetric, positively charged, open-shell (DANS)$_2{}^+$ dimer (**7**) reveal a very large second-order nonlinearity ($|\beta_{xxx}| > 1300 \times 10^{-30}$ cm^5 esu^{-1} at 0.65 eV, where β_{xxx} is the largest tensor component). In agreement with experiment,[12,13] the calculated NLO response is about 1 order of magnitude larger than that of either the isolated DANS chromophore **6** or of neutral noncentrosymmetric DANS dimers having H- (**8**) or J- (**9**) aggregate structures, over the range of frequencies investigated (Table 2). In addition, the calculated static (zero-frequency) hyperpolarizability of (DANS)$_2{}^+$ is larger than that of the neutral H-type **(8)** and J-type **(9)** DANS aggregates (Table 2). In Figure 3 are compared calculated electronic spectra of the neutral DANS monomer, the centrosymmetric neutral (DANS)$_2$ dimer, and the charged (DANS)$_2{}^+$ dimer. In the centrosymmetric (DANS)$_2$ dimer, in addition to the monomer-related excitonic CT transition ($\lambda_{\max}^{\mathrm{calc}} = 372$ nm), only two weaker cross-excitation transitions are found. In contrast, the calculated electronic spectrum of (DANS)$_2{}^+$ is richer as far as the number of transitions is concerned since, in addition to the monomer-related blue-shifted transitions, a new set of low-lying excited states is predicted in the region between 400 and 820 nm, as observed experimentally[12,13] (Figure 3). These excited states, either excitonic or cross-excitation in character, largely involve the HOMO, which represents the partially filled orbital. The electronic transitions associated with these states have appreciable oscillator strengths and dipole moment changes which contribute to the extremely large, resonantly enhanced nonlinearity of (DANS)$_2{}^+$. Due to existence of these low-energy CT (DANS)$_2{}^+$ states (lowest CT state $\lambda_{\max}^{\mathrm{calc}} = 826$ nm) and the consequent resonant enhancement of the nonlinearity, damping corrections[15] (see the Computational Details) were necessarily taken into account, and the $\beta_{ijk}(-2\omega;\omega,\omega)$ tensor terms were treated as complex.



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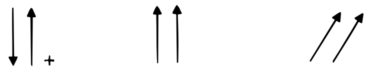

7 **8** **9**

Conclusions

This paper presents an efficient computational scheme to describe the frequency-dependent quadratic hyperpolarizabilities of large, open-shell molecular and multimolecular systems. The INDO/SCI semiempirical model Hamiltonian in connection with the SOS formalism has proven suitable for computation of the lowest-lying excited states and, in turn, evaluation of the second-order nonlinearity. In the cases considered here, the correct evaluation of the lowest-lying excited states, which has been

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(25) Di Bella, S.; Fragalá, I.; Ledoux, I.; Diaz-Garcia, M. A.; Lacroix, P. G.; Marks, T. J. *Chem. Mater.* **1994**, *6*, 881.

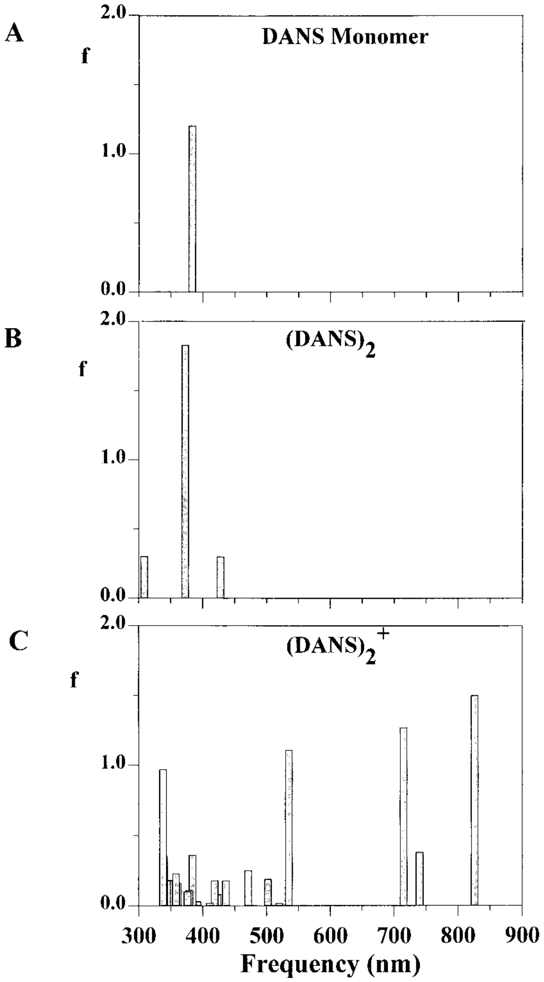

Figure 3. INDO/SCI-derived electronic transitions of the neutral DANS monomer (A), the centrosymmetric neutral $(DANS)_2$ dimer (B), and the centrosymmetric charged cation radical $(DANS)_2^+$ dimer (C).

straightforwardly tested by comparison with experimental optical spectra, is reflected in an adequate prediction of $\beta_{ijk}(-2\omega;\omega,\omega)$. From this investigation it is clear that the larger second-order response of systems having open-shell electronic states, compared to that of analogous closed-shell structures, is a consequence of the increased accessibility of lower-lying CT excited electronic states. The existence of these lower-lying CT states necessarily involves an SOS treatment for the evaluation of $\beta_{ijk}(-2\omega;\omega,\omega)$. In other words, the simple two-state model would be *inadequate* for describing the nonlinearity, since many excited states contribute to the NLO response of these open-shell systems.

The present results also raise a cautionary note in regard to experimental β_{vec} and $\chi^{(2)}$ determinations. Situations are conceivable in which oxidation, photooxidation, and/or poling-induced charge injection may create unexpected chromophore radical species with new linear optical features (especially at longer wavelengths) and very large second-order NLO responses.

Computational Details

The INDO/S model,[16] within the restricted open Hartree−Fock (ROHF) method, was employed to compute the ground state of the molecules under investigation. Standard parameters and basis functions were used.[16] In the present approach, the 150 lowest energy transitions between SCF and electronic configurations were chosen to undergo CI mixing. The resulting ~300 doublet configuration state functions were then included in the SOS procedure. This SOS truncation was found to be sufficient for complete convergence of the second-order response in all cases considered. In the case of calculations on the $(DANS)_2^+$ dimer, an average constant damping term ($\Gamma = 0.3$ eV, for all the computed *ng* transitions) was used to compute the complex $\beta_{ijk}(-2\omega;\omega,\omega)$ tensor. All calculations were performed using the ZINDO program[10,26] implemented on an IBM ES/9000 system.

Metrical parameters used for the calculations of M(salophen) complexes **1** and **2** were taken from crystal structure data,[18,19,22] assuming a C_{2v} planar geometry. Analogously, for substituted Co(II) complex **4**, a planar structure was assumed. The bond-alternating idealized (BAI) geometry was chosen for calculations on the monomeric DANS chromophore.[26] In all the dimeric structures studied, the molecular geometries were constructed assuming each DANS monomer to be planar and holding the interplanar distance (*R*) at 3.6 Å (corresponding to mean van der Waals interactions in typical organic molecular crystals and aggregates). In the case of the J-type $(DANS)_2$ aggregate **(9)**, a slip distance (*R′*) of 3.0 Å, corresponding to a tilt angle of 57°, was used.

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JA960561J

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[26] Kanis, D. R.; Marks, T. J.; Ratner, M. A. *Int. J. Quantum Chem.* **1992**, *43*, 61.