Problems in the comparison of theoretical and experimental hyperpolarizabilities

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Frequently it is useful to compare experimental values of the hyperpolarizabilities β and γ with calculated values. It is also often helpful to compare experimental values of β obtained from dc-electric field induced second harmonic generation (dc-SHG) experiments, e.g., with values obtained using the solvatochromism method. In order to do this the hyperpolarizabilities must be defined using consistent conventions. In this paper, four commonly used conventions are discussed and simple factors for converting between them presented. In addition, the sum-over-states expression for the calculation of β and γ is described and its correct use in comparing with hyperpolarizabilities obtained using other experimental and theoretical techniques discussed. As an illustration of the consistent use of conventions, *ab initio* and semiempirical calculations on para-nitroaniline are compared with experimental dc-SHG values. This comparison highlights the difference between theoretical values of the hyperpolarizability with the molecule in a gas phase environment and experimental values obtained in polar solvents—a difference that has in the past been obscured by inconsistent choice of conventions.

I. INTRODUCTION

Different conventions have been used to define hyperpolarizabilities making it difficult to compare calculated and experimental values and to compare experimental values obtained using different techniques. In many cases the problem of comparison is further complicated because the precise convention used is not clearly stated. This has led to a situation in the literature where, for example, experimental values are frequently directly compared to calculated values that use a completely different convention. Certainly it would be preferable to have a single universal convention. Short of this, it seems useful to have clearly defined procedures for switching among conventions.

In this work, four frequently used conventions are discussed and compared; one based on a Taylor series expansion of the induced dipole moment in terms of an external electric field,[1] one based on a perturbation series expansion,[2] one used by many experimentalists to describe solution results,[3-5] and one in which all numerical factors are included in the hyperpolarizabilities.[6] The first two of these conventions possess the useful property that hyperpolarizabilities of the same order extrapolate to the same value as the frequencies approach zero. This property not only makes it easy to compare frequency-dependent measurements with theoretical values calculated using static electric fields, but also allows direct comparison of experimental results obtained using different techniques. For example, third harmonic generation experiments that measure the second order hyperpolarizability $\gamma(-3\omega;\omega,\omega,\omega)$ have been used to estimate the value of $\gamma(-2\omega;\omega,\omega,0)$ in the analysis of dc-electric field induced second harmonic generation (dc-SHG or EFISH) data.[4] In this case, use of either a Taylor series or a perturbation series convention allows straightforward transferability of the $\gamma(-3\omega;\omega,\omega,\omega)$ value to the second harmonic analysis since far below resonance $\gamma(-3\omega;\omega,\omega,\omega) \sim\gamma(-2\omega;\omega,\omega,0)$. This is shown in Fig. 1 which compares third harmonic $\gamma(-3\omega;\omega,\omega,\omega)$, electric field induced second harmonic $\gamma(-2\omega;\omega,\omega,0)$ and Kerr effect $\gamma(-\omega;\omega,0,0)$ measurements of the hyperpolarizability using either the Taylor series or the perturbation series definition. Note that, as the frequency ω approaches zero, all three second order hyperpolarizabilities become equal.

We also point out the changes required to the sum-over-states expressions[7-9] in order to compare properly sum-over-states values of the hyperpolarizabilities with experimental values or values calculated using analytic derivatives of the energy with respect to an external electric field (or equivalent finite field methods) (see, e.g., Ref. 10). This discussion is also important for correct evaluation of β using the solvatochromic technique.[11,12]

It is certainly true that in many, if not most cases, it is the relative values of the hyperpolarizabilities that are important—and provided that quantities measured using the same technique are being compared, absolute values are not as important. Conclusions about trends in comparable hyperpolarizabilities [e.g., β_0^{theory} (para-nitroaniline) vs β_0^{theory} (4,4′ nitroaminostilbene) or $\beta^{\text{expt}}(-2\omega;\omega,\omega)$ (para-nitroaniline) vs $\beta^{\text{expt}}(-2\omega;\omega,\omega)$ (4,4′ nitroaminostilbene)] are unaffected by differences in conventions. However, for comparison of $\beta^{\text{theory}}(-2\omega;\omega,\omega)$ and $\beta^{\text{expt}}(-2\omega;\omega,\omega)$ knowledge of the differing conventions

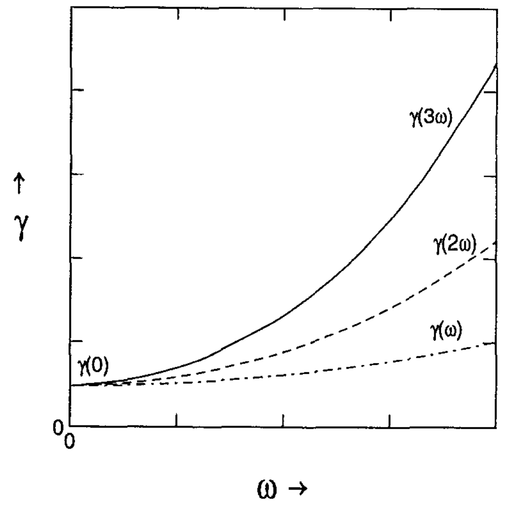

FIG. 1. Plot of the third harmonic $\gamma(3\omega) \equiv \gamma(-3\omega;\omega,\omega,\omega)$, dc-electric field induced second harmonic $\gamma(2\omega) \equiv \gamma(-2\omega;\omega,\omega,0)$ and Kerr effect $\gamma(\omega) \equiv \gamma(-\omega;\omega,0,0)$ hyperpolarizabilities vs frequency using either the Taylor series or the perturbation series definition. All values converge to the static value, $\gamma(0) \equiv \gamma(0;0,0,0)$ as the frequency ω approaches zero.

and the conversion factors between them is essential. Similarly, comparison of a value of $\beta(-2\omega;\omega,\omega)$ obtained using the solvatochromic technique that relies on a two-level model approximation to the sum-over-states expression for the hyperpolarizability with the same value from a dc-SHG measurement also requires understanding of the conventions in use. In many cases when comparisons of this type are made, they are done incorrectly (see, e.g., Refs. 3, 7, and 8).

In the next section, four of the most frequently used conventions for defining β and γ will be discussed and the factors for conversion among them will be presented. In Sec. III, the relationship between the sum-over-states expression for β and γ and these conventions is discussed. Section IV illustrates the consistent use of these conventions by comparing a variety of *ab initio* and semiempirical results with each other and with experimental results. In making this comparison the effect of the solvent environment on the experimental values must be explicitly considered.

II. CONVENTIONS FOR DEFINING HYPERPOLARIZABILITIES

A. The induced dipole moment

The total dipole moment induced by the field, μ_{Ind}, is often written as a Taylor series[1]

$$\mu_{\mathrm{Ind}} = \mu_0 + \alpha^T F + \frac{1}{2!}\beta^T F^2 + \frac{1}{3!}\gamma^T F^3 + \cdots \tag{1}$$

in the electric field F (where we use the superscript T to denote the Taylor series definition). Here μ_0 is the permanent dipole moment, α^T the linear polarizability, and β^T, γ^T the hyperpolarizabilities. In general, α^T, β^T, and γ^T are frequency dependent. For a static field,

$$\mu_{\mathrm{Ind}} = \mu_0 + \alpha_0^T F_0 + \frac{1}{2!}\beta_0^T F_0^2 + \frac{1}{3!}\gamma_0^T F_0^3 + \cdots, \tag{2}$$

where α_0^T, β_0^T, and γ_0^T are the static (at $\omega=0$) values of the linear polarizability and first and second order hyperpolarizabilities, respectively. A great advantage of the Taylor series definition is that a corresponding Taylor series expansion applies to each order, e.g.,

$$\alpha_{\mathrm{Ind}} = \alpha_0 + \beta^T F + \frac{1}{2!}\gamma^T F^2 + \frac{1}{3!}\epsilon^T F^3 + \cdots \tag{3}$$

and

$$E = E_0 - \mu^T F - \frac{1}{2!}\alpha^T F^2 - \frac{1}{3!}\beta^T F^3 - \frac{1}{4!}\gamma^T F^4 - \cdots. \tag{4}$$

The dependence of μ_{Ind} on the applied field frequencies is expressed through the functions α^T, β^T, γ^T,.... For example, $\gamma^T \equiv \gamma^T(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$ relates the induced dipole moment oscillating at frequency $\omega_\sigma = (\omega_1+\omega_2+\omega_3)$ to the term of F^3, which oscillates at frequency ω_σ and which contains the product of the amplitudes of the field components at frequencies ω_1, ω_2, and ω_3. Thus for the time-dependent field, $F = F_0 + F_\omega \cos \omega t$ [or equivalently, $F = F_0 + \frac{1}{2}F_\omega(e^{i\omega t} + e^{-i\omega t})$], the induced dipole moment is

$$\begin{aligned}\mu_{\mathrm{Ind}} = {} & \mu_0 + \alpha_0^T F_0 + \alpha^T(-\omega;\omega)F_\omega \cos \omega t + \tfrac{1}{2}\beta_0^T F_0^2 + \beta^T(-\omega;\omega,0)F_0 F_\omega \cos \omega t + \tfrac{1}{4}\beta^T(0;\omega,-\omega)F_\omega^2 \\ & + \tfrac{1}{4}\beta^T(-2\omega;\omega,\omega)F_\omega^2 \cos 2\omega t + \tfrac{1}{6}\gamma_0^T F_0^3 + \tfrac{1}{2}\gamma^T(-\omega;\omega,0,0)F_0^2 F_\omega \cos \omega t + \tfrac{1}{4}\gamma^T(0;\omega,-\omega,0)F_0 F_\omega^2 \\ & + \tfrac{1}{4}\gamma^T(-2\omega;\omega,\omega,0)F_0 F_\omega^2 \cos 2\omega t + \tfrac{1}{24}\gamma^T(-3\omega;\omega,\omega,\omega)F_\omega^3 \cos 3\omega t + \tfrac{1}{8}\gamma^T(-\omega;\omega,\omega,-\omega)F_\omega^3 \cos \omega t + \cdots,\end{aligned} \tag{5}$$

where, for example, the terms of third order in the field arise from

$$\begin{aligned}\frac{1}{3!}(F_0 + F_\omega \cos \omega t)^3 &= \frac{1}{3!}\left[F_0^3 + 3F_0^2 F_\omega \cos \omega t + \tfrac{3}{2}F_0 F_\omega^2 + \tfrac{3}{2}F_0 F_\omega^2 \cos 2\omega t + \tfrac{1}{4}F_\omega^3 \cos 3\omega t + \tfrac{3}{4}F_\omega^3 \cos \omega t\right] \\ &= \frac{F_0^3}{6} + \left(\frac{F_0^2 F_\omega}{2}\right)\cos \omega t + \left(\frac{F_0 F_\omega^2}{4}\right) + \left(\frac{F_0 F_\omega^2}{4}\right)\cos 2\omega t + \left(\frac{F_\omega^3}{24}\right) + \left(\frac{F_\omega^3}{8}\right)\cos \omega t.\end{aligned} \tag{6}$$

A second important feature of these expressions is that as the applied field frequencies approach zero, each frequency-dependent hyperpolarizability tends towards its static value, e.g., $\gamma^T(-\omega_\sigma;\omega_1,\omega_2,\omega_3)\rightarrow\gamma^T(0;0,0,0)\equiv\gamma_0^T$. This feature is demonstrated by Eq. (5) where the second order terms in the field on the right-hand side become $\frac{1}{2}\beta_0^T(2F_0)^2$ and the third order terms become $\frac{1}{6}\gamma_0^T(2F_0)^3$ as $F\rightarrow 2F_0$ in the static limit, consistent with Eq. (2).

Consider the dc-SHG experiment as an example of the consistent application of the convention embodied in Eq. (1). In a dc-SHG experiment one measures an effective second order hyperpolarizability $\langle\gamma\rangle$ which is a quantity thermally averaged over the orientations of a dipolar molecule in a static electric field,[13]

$$\langle\gamma\rangle^T=\bar{\gamma}^T+\frac{\mu_0\beta_\parallel^T}{3kT}, \tag{7}$$

where $\beta_\parallel$ denotes the vector component of the third order tensor β_{ijk} in the direction of the dipole moment, $\beta_\parallel=\frac{1}{5}\Sigma_\xi\{\beta_{z\xi\xi}+\beta_{\xi z\xi}+\beta_{\xi\xi z}\}$ $(\xi=x,y,z)$, and $\bar{\gamma}$ is the scalar component of the fourth order tensor γ_{ijkl}, $\bar{\gamma}=1/15\Sigma_{\xi\eta}\{\gamma_{\xi\xi\eta\eta}+\gamma_{\xi\eta\eta\xi}+\gamma_{\xi\eta\xi\eta}\}$ $(\xi,\eta=x,y,z)$. The dc-SHG measurement corresponds to the third order term in Eq. (5) with cos $2\omega t$ dependence. This term is

$$\begin{aligned}\mu_{\text{Ind}}(2\omega)&=\frac{1}{4}\,\langle\gamma^T(-2\omega;\omega,\omega,0)\rangle F_0F_\omega^2\cos 2\omega t\\&=\frac{1}{4}\left(\bar{\gamma}^T(-2\omega;\omega,\omega,0)+\frac{\mu_0\beta_\parallel^T(-2\omega;\omega,\omega)}{3kT}\right)\\&\quad\times F_0F_\omega^2\cos 2\omega t\\&=\frac{1}{4}\left(\bar{\gamma}^T(-2\omega;\omega,\omega,0)+\frac{\mu_0\beta_z^T(-2\omega;\omega,\omega)}{5kT}\right)\\&\quad\times F_0F_\omega^2\cos 2\omega t,\end{aligned} \tag{8}$$

where $\beta_\parallel=\frac{3}{5}\beta_z$ and β_z is the z component of the vector quantity frequently used by experimentalists, $\beta_z=\frac{1}{3}\Sigma_\xi\{\beta_{z\xi\xi}+\beta_{\xi z\xi}+\beta_{\xi\xi z}\}$ $(\xi=x,y,z)$ where z is the axis of the permanent dipole moment. If Kleinman symmetry[14] is assumed then $\beta_\parallel=\frac{3}{5}\Sigma_\xi\beta_{z\xi\xi}$ $(\xi=x,y,z)$ and $\bar{\gamma}=\frac{1}{5}\Sigma_{\xi\eta}\gamma_{\xi\xi\eta\eta}$ $(\xi,\eta=x,y,z)$. In principle, the "$\mu\beta$" term may be extracted separately from $\langle\gamma\rangle$ by taking measurements over a range of temperatures. This is often possible in the gas phase but not in solution since in solution only a small range of temperatures are experimentally accessible. In many molecules with large β values, the contribution from $\bar{\gamma}^T(-2\omega;\omega,\omega,0)$ may be assumed to be negligible and the value of $\langle\gamma\rangle^T$ assumed to be entirely due to the $\mu\beta$ term.

B. Relations among conventions

There are a number of conventions in common use that differ from the one employed in the previous section. The relations among the different conventions are illustrated by considering the dc-SHG terms given by Eq. (8), rewritten to display the parentage of the numerical factors,

$$\begin{aligned}\mu_{\text{Ind}}(2\omega)=&\left\{\frac{1}{2!}\right\}\left[\frac{1}{2}\right]\frac{3}{5}\beta_z^T(-2\omega;\omega,\omega)F_\omega^2\cos 2\omega t\left(\frac{\mu_0}{3kT}F_0\right)\\&+\left\{\frac{1}{3!}\right\}\left[\frac{3}{2}\right]\bar{\gamma}^T(-2\omega;\omega,\omega,0)F_0F_\omega^2\cos 2\omega t.\end{aligned} \tag{9}$$

The numerical factor in braces $\{A\}$ is the $1/n!$ in the nth order term of a Taylor series ("$1/n!$ factor") while the numerical factor in brackets $[B]$ is the coefficient of the term in F^n which contains the desired product of field amplitudes and oscillates at the desired frequency ("field product factor"). Note that the factor $\mu_0F_0/3kT=\langle\cos\theta\rangle$ containing F_0, where θ is the angle between the electric field and the dipole moment direction, arises from the orientational averaging of the second order terms in Eq. (5). Most of the conventions in common use correspond to choices of the factors $\{A\}$ and $[B]$ that are displayed explicitly and those that are implicit in the definition of the hyperpolarizability. These conventions may be systematically labeled according to which of the factors $\{A\}$ and $[B]$ are displayed explicitly: *AB* (both factors explicit), *A* ($1/n!$ factor explicit), *B* (field product factor explicit), and *X* (both factors absorbed). Thus the Taylor series definition *T* of the previous section is convention *AB* in this scheme.

Absorbing the $1/n!$ factor gives convention *B*, in which the induced dipole moment is written as a simple perturbation series expansion,[2]

$$\mu_{\text{Ind}}=\mu_0+\alpha^BF+\beta^BF^2+\gamma^BF^3+\cdots. \tag{10}$$

In this case the energy expression is not as simply related to Eq. (10) as Eq. (4) is to Eq. (1),

$$E=E_0-\mu F-\tfrac{1}{2}\alpha^BF^2-\tfrac{1}{3}\beta^BF^3-\tfrac{1}{4}\gamma^BF^4-\cdots. \tag{11}$$

The expression, in this convention, for the dipole moment induced by the time-dependent field $F=F_0+F_\omega\cos\omega t$ may be obtained from Eq. (5) by multiplying the second and third order terms by 2! and 3!, respectively. The induced dipole moment measured in a dc-SHG experiment is given by the analog of Eq. (8),

$$\begin{aligned}\mu_{\text{Ind}}(2\omega)&=\frac{3}{2}\left[\bar{\gamma}^B(-2\omega;\omega,\omega,0)\right.\\&\quad\left.+\frac{\mu_0\beta_\parallel^B(-2\omega;\omega,\omega)}{9kT}\right]F_0F_\omega^2\cos 2\omega t\\&=\frac{3}{2}\left[\bar{\gamma}^B(-2\omega;\omega,\omega,0)\right.\\&\quad\left.+\frac{\mu_0\beta_z^B(-2\omega;\omega,\omega)}{15kT}\right]F_0F_\omega^2\cos 2\omega t,\end{aligned} \tag{12}$$

and hyperpolarizabilities defined in the Taylor series ($T\equiv AB$) and perturbation series (B) conventions are simply related by factors of 2! and 3! for β and γ, respectively, for all of the different types of frequency-dependent pro-

TABLE I. Expressions for the total dipole moment measured in a dc-electric field induced second harmonic generation experiment

			Zero freq. convergence[a]	
Label	Convention	$[\mu_{\rm Ind}(2\omega)]/(F_0F_\omega^2\cos 2\omega t)$	$\to\beta_0$	$\to\gamma_0$
$AB\equiv T$	Taylor series	$\frac{1}{4}\left[\bar{\gamma}^T(-2\omega;\omega,\omega,0)+\frac{\mu\beta_z^T(-2\omega;\omega,\omega)}{5kT}\right]$	+	+
B	Perturbation series	$\frac{3}{2}\left[\bar{\gamma}^B(-2\omega;\omega,\omega,0)+\frac{\mu\beta_z^B(-2\omega;\omega,\omega)}{15kT}\right]$	+	+
B^*	EFISH only	$\frac{3}{2}\left[\bar{\gamma}^{B*}(-2\omega;\omega,\omega,0)+\frac{\mu\beta_z^{B*}(-2\omega;\omega,\omega)}{5kT}\right]$	−	+
A	Not used	$\frac{1}{6}\left[\bar{\gamma}^A(-2\omega;\omega,\omega,0)+\frac{3\mu\beta_z^A(-2\omega;\omega,\omega)}{5kT}\right]$	−	−
X	Phenomenological	$\left[\bar{\gamma}^X(-2\omega;\omega,\omega,0)+\frac{\mu\beta_z^X(-2\omega;\omega,\omega)}{5kT}\right]$	−	−

[a] Columns three and four indicate whether the convention does (+) or does not (−) converge to β_0 or γ_0 as $\omega\to 0$.

cesses. Thus $\beta^T=2\beta^B$ and $\gamma^T=6\gamma^B$, and also $\beta^B(-\omega_\sigma;\omega_1,\omega_2)\to\beta_0^B$ and $\gamma^B(-\omega_\sigma;\omega_1,\omega_2,\omega_3)\to\gamma_0^B$ in the static limit.

There is a third convention in wide use by experimentalists[3-5] which does not fit into our scheme, but which is closely related to convention B and will be labeled B^*. This convention is only defined for the dc-SHG experiment, where the induced dipole moment is given by

$$\mu_{\rm Ind}(2\omega)=\frac{3}{2}\left[\bar{\gamma}^{B*}(-2\omega;\omega,\omega,0)+\frac{\mu_0\beta_z^{B*}(-2\omega;\omega,\omega)}{5kT}\right]F_0F_\omega^2\cos 2\omega t. \qquad (13)$$

The difference between B and B^* conventions is that the field product factor (3/2) appears instead of (1/2) in the $\mu\beta$ term [see Eq. (9)]. Recall that the $\mu\beta$ term describes, not a third order nonlinear optical process, but instead arises from cascading of a second order nonlinear optical process (second harmonic generation mediated by β) and a first order process (field-induced molecular orientation). The replacement of (1/2) by (3/2) arises through neglect of this distinction and leads to the awkward result that $\beta^{B*}(-2\omega;\omega,\omega)\to\frac{1}{3}\beta_0^B$ in the static limit. Thus $\beta^{B*}(-2\omega;\omega,\omega)$ must be multiplied by 3 in order to compare with theoretical values determined using the perturbation series convention B, and multiplied by 6 to compare with values defined using the Taylor series convention AB. The distinction between conventions B and B^* is not widely recognized. Frequently in the literature β_z^{B*} obtained from a dc-SHG measurement is directly compared to a calculated value of β_z^B. This is clearly wrong.

The convention A in this scheme would give

$$\mu_{\rm Ind}(2\omega)=\frac{1}{6}\left[\bar{\gamma}^A(-2\omega;\omega,\omega,0)+\frac{3\mu_0\beta_z^A(-2\omega;\omega,\omega)}{5kT}\right]F_0F_\omega^2\cos 2\omega t, \qquad (14)$$

but to our knowledge this convention has never been used. The final convention, X, is the most purely phenomenological. All the numerical factors appearing explicitly in Eq. (5) are, in this case, absorbed into the definitions of the hyperpolarizabilities. For dc-SHG this gives

$$\mu_{\rm Ind}(2\omega)=\left[\bar{\gamma}^X(-2\omega;\omega,\omega,0)+\frac{\mu_0\beta_z^X(-2\omega;\omega,\omega)}{5kT}\right]F_0F_\omega^2\cos 2\omega t. \qquad (15)$$

In this convention, β^X or γ^X has a different definition for every different nonlinear optical process, and these definitions are not equal in the static limit.

The relations between the hyperpolarizabilities in the various conventions, for dc-SHG, may be determined by comparing Eqs. (8), (12), (13), (14), and (15). For $\bar{\gamma}(-2\omega;\omega,\omega,0)$ and $\beta_z(-2\omega;\omega,\omega)$ one has

$$\tfrac{1}{6}\gamma^T=\gamma^B=\gamma^{B*}=\tfrac{1}{9}\gamma^A=\tfrac{2}{3}\gamma^X \qquad (16)$$

and

$$\tfrac{1}{2}\beta^T=\beta^B=3\beta^{B*}=\beta^A=2\beta^X. \qquad (17)$$

It should be noted that the numerical relations in Eqs. (16) and (17) are particular to dc-SHG. In the case of the electro-optic effect, e.g., $2\beta^B(-\omega;\omega,0)=\beta^X(-\omega;\omega,0)$ and $3\gamma^B(-\omega;\omega,0,0)=\gamma^X(-\omega;\omega,0,0)$, as may be ascertained by inspection of the coefficients of the $F_0F_\omega\cos\omega t$ and $F_0^2F_\omega\cos\omega t$ terms in Eq. (5) (multiplied by 2! and 3!, respectively). These five conventions and their zero frequency limiting behavior are summarized for the dc-SHG experiment in Table I.

III. SUM-OVER-STATES EXPRESSIONS

The sum-over-states method is often used to calculate hyperpolarizabilities.[15,16] It also forms the basis of the solvatochromic method for determining β (Refs. 11 and

12) when reduced to a two-level model. The sum-over-states expression is derived from a perturbation theory expansion of the energy, where we write

$$E=E_0+\lambda E_1+\lambda^2E_2+\lambda^3E_3+\cdots \tag{18}$$

and E_1, E_2, E_3 denote the first, second, and third order corrections to the energy, respectively, for a perturbation $V=-\mu F$ where $H=H_0+\lambda V$. The sum-over-states expression for β comes from the third order term (λ^3) in this expansion.

If we choose the definition of the (hyper)polarizabilities based on the Taylor series expansion of the energy [Eq. (4)], then the corresponding sum-over-states expression for the linear polarizability $\alpha^{(\mathrm{ss})T}$ corresponds to the second order energy multiplied by (2!), and that for the first hyperpolarizability $\beta^{(\mathrm{ss})T}$ to the third order energy multiplied by (3!), [where the superscript (ss) refers to the sum-over-states expression]. The third order term thus gives[17]

$$\beta_{ijk}^{(\mathrm{ss})T}(-\omega_\sigma;\omega_1,\omega_2)$$

$$=\frac{1}{\hbar^2}P(i,j,k;-\omega_\sigma,\omega_1,\omega_2)\times\sum_{l\neq0}\sum_{m\neq0}\frac{\langle0|\mu_i|l\rangle\langle l|\bar{\mu}_j|m\rangle\langle m|\mu_k|0\rangle}{(\omega_{0l}-\omega_\sigma)(\omega_{0m}-\omega_2)}, \tag{19}$$

where $\langle l|\bar{\mu}_j|m\rangle=\langle l|\mu_j|m\rangle-\langle0|\mu_j|0\rangle\,\delta_{lm}$; ω_{0l} is the energy difference between the ground state and excited state, l; and i, j, k correspond to the molecular axes, x, y, and z. $P(i,j,k;-\omega_\sigma,\omega_1,\omega_2)$ is a permutation operator defined such that for any permutation of (i,j,k) an equivalent permutation of $(-\omega_\sigma,\omega_1,\omega_2)$ is made simultaneously, where $\omega_\sigma=(\omega_1+\omega_2)$. Thus for each pair of molecular energy levels l and m, the contribution to $\beta_{ijk}(-\omega_\sigma;\omega_1,\omega_2)$ is the sum of six terms.

Namely,

$$\begin{aligned}\beta_{ijk}^{(\mathrm{ss})T}(-\omega_\sigma;\omega_1,\omega_2)=\frac{1}{\hbar^2}\sum_{l\neq0}\sum_{m\neq0}\Bigg\{&\frac{\langle0|\mu_i|l\rangle\langle l|\bar{\mu}_j|m\rangle\langle m|\mu_k|0\rangle}{(\omega_{0l}-\omega_\sigma)(\omega_{0m}-\omega_2)}+\frac{\langle0|\mu_i|l\rangle\langle l|\bar{\mu}_k|m\rangle\langle m|\mu_j|0\rangle}{(\omega_{0l}-\omega_\sigma)(\omega_{0m}-\omega_1)}\\&+\frac{\langle0|\mu_j|l\rangle\langle l|\bar{\mu}_i|m\rangle\langle m|\mu_k|0\rangle}{(\omega_{0l}+\omega_1)(\omega_{0m}-\omega_2)}+\frac{\langle0|\mu_k|l\rangle\langle l|\bar{\mu}_i|m\rangle\langle m|\mu_j|0\rangle}{(\omega_{0l}+\omega_2)(\omega_{0m}-\omega_1)}+\frac{\langle0|\mu_k|l\rangle\langle l|\bar{\mu}_j|m\rangle\langle m|\mu_i|0\rangle}{(\omega_{0l}+\omega_2)(\omega_{0m}+\omega_\sigma)}\\&+\frac{\langle0|\mu_j|l\rangle\langle l|\bar{\mu}_k|m\rangle\langle m|\mu_i|0\rangle}{(\omega_{0l}+\omega_1)(\omega_{0m}+\omega_\sigma)}\Bigg\}.\end{aligned} \tag{20}$$

If we consider $\beta(-2\omega;\omega,\omega)$ for a two-level system and we assume that β_z is dominated by the component along the dipole axis, β_{zzz}, as is frequently the case, then Eq. (20) simplifies to

$$\beta_{zzz}^{(\mathrm{ss})T}(-2\omega;\omega,\omega)$$

$$=\frac{6\omega_{01}^2\langle0|\mu_z|1\rangle(\langle1|\mu_z|1\rangle-\langle0|\mu_z|0\rangle)\langle1|\mu_z|0\rangle}{\hbar^2(\omega_{01}^2-\omega^2)(\omega_{01}^2-4\omega^2)} \tag{21}$$

or, equivalently,

$$\beta_{zzz}^{(\mathrm{ss})T}(-2\omega;\omega,\omega)=\frac{6\mu_{01}^2(\mu_{11}-\mu_{00})\omega_{01}^2}{\hbar^2(\omega_{01}^2-\omega^2)(\omega_{01}^2-4\omega^2)}$$

$$=\frac{6\mu_{01}^2(\mu_{11}-\mu_{00})}{\hbar^2\omega_{01}^2(1-\omega^2/\omega_{01}^2)(1-4\omega^2/\omega_{01}^2)}, \tag{22}$$

where $\mu_{ll}=\langle l|\mu_z|l\rangle$ and $\mu_{0l}=\langle0|\mu_z|l\rangle$. $\beta^{(\mathrm{ss})T}(-2\omega;\omega,\omega)$ corresponds to $\beta_z^T(-2\omega;\omega,\omega)$ in Eq. (8) and thus the value of $\beta^{(\mathrm{ss})T}$ at zero frequency is

$$\beta_0^T\sim\beta_{zzz}^{(\mathrm{ss})T}(0;0,0)=\frac{6\mu_{01}^2(\mu_{11}-\mu_{00})}{\hbar^2\omega_{01}^2}. \tag{23}$$

Alternatively, if we use Eq. (11) to define the perturbation theory energy [consistent with the perturbation series definition of the induced dipole moment (10)] then the analogy to Eq. (22) is

$$\beta_{zzz}^{(\mathrm{ss})B}(-2\omega;\omega,\omega)=\frac{3\mu_{01}^2(\mu_{11}-\mu_{00})\omega_{01}^2}{\hbar^2(\omega_{01}^2-\omega^2)(\omega_{01}^2-4\omega^2)}$$

$$=\frac{3\mu_{01}^2(\mu_{11}-\mu_{00})}{\hbar^2\omega_{01}^2(1-\omega^2/\omega_{01}^2)(1-4\omega^2/\omega_{01}^2)}. \tag{24}$$

This expression is directly comparable to $\beta^B(-2\omega;\omega,\omega)$ in Eq. (12). Note again that $\beta^{(\mathrm{ss})T}(-2\omega;\omega,\omega)$ differs from $\beta^{(\mathrm{ss})B}(-2\omega;\omega,\omega)$ by a factor of 2.

An alternative definition of the two-level sum-over-states expression for the hyperpolarizability is also used[7–9,11,12] and is related to the fourth convention defined in Table I. This choice of convention has been discussed recently.[18] Namely,

$$\beta_{zzz}^{(\mathrm{ss})X}(-2\omega;\omega,\omega)=\frac{3}{2\hbar^2}\frac{\mu_{01}^2(\mu_{11}-\mu_{00})\omega_{10}^2}{(\omega_{01}^2-\omega^2)(\omega_{01}^2-4\omega^2)}. \tag{25}$$

Comparing Eqs. (22), (24), and (25), and in direct analogy with Eq. (17), we have

$$\tfrac{1}{3}\beta^{(\mathrm{ss})T}(-2\omega;\omega,\omega)=\beta^{(\mathrm{ss})B}(-2\omega;\omega,\omega)=2\beta^{(\mathrm{ss})X}(-2\omega;\omega,\omega), \tag{26}$$

where $\beta^{(\mathrm{ss})B}$ may be compared directly to β^B and $\beta^{(\mathrm{ss})T}$ to β^T. Note that β^{B*} may not be directly compared to $\beta^{(\mathrm{ss})X}$ as is very often done when sum-over-states calculated values or values obtained by solvatochromic methods are compared to dc-SHG values. Comparing Eqs. (17) and (24) we see that

$$\beta^B(-2\omega;\omega,\omega)=3\beta^{B*}(-2\omega;\omega,\omega)=2\beta^{(\mathrm{ss})X}(-2\omega;\omega,\omega). \tag{27}$$

A similar analysis may be performed to obtain sum-over-states expressions for γ. In a Taylor series definition, $\gamma^{(\mathrm{ss})T}$ is determined from $4!E_4$ [c.f. Eq. (4)] and $\gamma^{(\mathrm{ss})B}$ is determined from $4E_4$ [c.f. Eq. (11)], again with the factor of 6 difference between γ^T and γ^B.

The general expression for $\gamma_{ijkl}^{(\mathrm{ss})T}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)$ is given by

$$\gamma_{ijkl}^{(\mathrm{ss})T}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)=\frac{1}{\hbar^3}P(i,j,k,l;-\omega_\sigma,\omega_1,\omega_2,\omega_3)\left\{\sum_{m\neq0}\sum_{n\neq0}\sum_{q\neq0}\frac{\langle0|\mu_i|m\rangle\langle m|\bar{\mu}_j|n\rangle\langle n|\bar{\mu}_k|q\rangle\langle q|\mu_l|0\rangle}{(\omega_{m0}-\omega_\sigma)(\omega_{n0}-\omega_2-\omega_3)(\omega_{q0}-\omega_3)}\right.$$
$$\left.-\sum_{m\neq0}\sum_{n\neq0}\frac{\langle0|\mu_i|m\rangle\langle m|\mu_j|0\rangle\langle0|\mu_k|n\rangle\langle n|\mu_l|0\rangle}{(\omega_{m0}-\omega_\sigma)(\omega_{n0}-\omega_3)(\omega_{n0}+\omega_2)}\right\}. \tag{28}$$

The permutation operator leads to 24 terms which in the case of the longitudinal component for the third harmonic process, $\gamma_{zzzz}^T(-3\omega;\omega,\omega,\omega)$ (the component which dominates the tensor for charge–transfer systems) reduces to

$$\gamma_{zzzz}^T(-3\omega;\omega,\omega,\omega)=\frac{1}{\hbar^3}\sum_{m\neq0}\sum_{n\neq0}\sum_{q\neq0}\langle0|\mu_z|m\rangle\langle m|\bar{\mu}_z|n\rangle\langle n|\bar{\mu}_z|q\rangle\langle q|\mu_z|0\rangle\left\{\frac{6}{(\omega_{m0}-3\omega)(\omega_{n0}-2\omega)(\omega_{q0}-\omega)}\right.$$
$$+\frac{6}{(\omega_{m0}+\omega)(\omega_{n0}-2\omega)(\omega_{q0}-\omega)}+\frac{6}{(\omega_{m0}+\omega)(\omega_{n0}+2\omega)(\omega_{q0}-\omega)}$$
$$\left.+\frac{6}{(\omega_{m0}+\omega)(\omega_{n0}+2\omega)(\omega_{q0}+3\omega)}\right\}$$
$$-\frac{1}{\hbar^3}\sum_{m\neq0}\sum_{n\neq0}\langle0|\mu_z|m\rangle\langle m|\mu_z|0\rangle\langle0|\mu_z|n\rangle\langle n|\mu_z|0\rangle\left\{\frac{6}{(\omega_{m0}-3\omega)(\omega_{n0}-\omega)(\omega_{n0}+\omega)}\right.$$
$$+\frac{6}{(\omega_{m0}+\omega)(\omega_{n0}+\omega)(\omega_{n0}-\omega)}+\frac{6}{(\omega_{m0}+\omega)(\omega_{n0}+3\omega)(\omega_{n0}+\omega)}$$
$$\left.+\frac{6}{(\omega_{m0}+\omega)(\omega_{n0}-\omega)(\omega_{n0}-3\omega)}\right\} \tag{29}$$

[where $\gamma^B(-3\omega;\omega,\omega,\omega)=\frac{1}{6}\gamma^T(-3\omega;\omega,\omega,\omega)=4\gamma^X(-3\omega;\omega,\omega,\omega)$]. The corresponding longitudinal component for the second harmonic process is given by

$$\gamma_{zzzz}^T(-2\omega;\omega,\omega,0)=\frac{1}{\hbar^3}\sum_{m\neq0}\sum_{n\neq0}\sum_{q\neq0}\langle0|\mu_z|m\rangle\langle m|\bar{\mu}_z|n\rangle\langle n|\bar{\mu}_z|q\rangle\langle q|\mu_z|0\rangle$$
$$\times\left\{\frac{2}{(\omega_{m0}-2\omega)(\omega_{n0}-\omega)(\omega_{q0})}+\frac{2}{(\omega_{m0}-2\omega)(\omega_{n0}-\omega)(\omega_{q0}-\omega)}\right.$$
$$+\frac{2}{(\omega_{m0}-2\omega)(\omega_{n0}-2\omega)(\omega_{q0}-\omega)}+\frac{2}{(\omega_{m0}+\omega)(\omega_{n0}-\omega)(\omega_{q0})}+\frac{2}{(\omega_{m0}+\omega)(\omega_{n0}+2\omega)(\omega_{q0})}$$
$$+\frac{2}{(\omega_{m0}+\omega)(\omega_{n0}+\omega)(\omega_{q0}+2\omega)}+\frac{2}{(\omega_{m0}+\omega)(\omega_{n0}-\omega)(\omega_{q0}-\omega)}$$
$$+\frac{2}{(\omega_{m0}+\omega)(\omega_{n0}+2\omega)(\omega_{q0}+2\omega)}+\frac{2}{(\omega_{m0}+\omega)(\omega_{n0}+\omega)(\omega_{q0}-\omega)}$$
$$\left.+\frac{2}{(\omega_{m0})(\omega_{n0}-2\omega)(\omega_{q0}-\omega)}+\frac{2}{(\omega_{m0})(\omega_{n0}+\omega)(\omega_{q0}-\omega)}+\frac{2}{(\omega_{m0})(\omega_{n0}+\omega)(\omega_{q0}+2\omega)}\right\}$$

$$-\frac{1}{\hbar^3}\sum_{m\neq0}\sum_{n\neq0}\langle0|\mu_z|m\rangle\langle m|\mu_z|0\rangle\langle0|\mu_z|n\rangle\langle n|\mu_z|0\rangle\left\{\frac{2}{(\omega_{m0}-2\omega)(\omega_{n0})(\omega_{n0}+\omega)}\right.$$
$$+\frac{2}{(\omega_{m0}-2\omega)(\omega_{n0}-\omega)(\omega_{n0})}+\frac{2}{(\omega_{m0}-2\omega)(\omega_{n0}-\omega)(\omega_{n0}+\omega)}+\frac{2}{(\omega_{m0}+\omega)(\omega_{n0})(\omega_{n0}+\omega)}$$
$$+\frac{2}{(\omega_{m0}+\omega)(\omega_{n0}-\omega)(\omega_{n0})}+\frac{2}{(\omega_{m0}+\omega)(\omega_{n0})(\omega_{n0}-2\omega)}+\frac{2}{(\omega_{m0}+\omega)(\omega_{n0}+2\omega)(\omega_{n0})}$$
$$+\frac{2}{(\omega_{m0}+\omega)(\omega_{n0}-\omega)(\omega_{n0}-2\omega)}+\frac{2}{(\omega_{m0}+\omega)(\omega_{n0}+2\omega)(\omega_{n0}+\omega)}$$
$$\left.+\frac{2}{(\omega_{m0})(\omega_{n0}-\omega)(\omega_{n0}+\omega)}+\frac{2}{(\omega_{m0})(\omega_{n0}-\omega)(\omega_{n0}-2\omega)}+\frac{2}{(\omega_{m0})(\omega_{n0}+2\omega)(\omega_{n0}+\omega)}\right\} \tag{30}$$

[where $\gamma^B(-2\omega;\omega,\omega,0)=\frac{1}{6}\gamma^T(-2\omega;\omega,\omega,0)=\frac{2}{3}\gamma^X(-2\omega;\omega,\omega,0)$].

IV. COMPARISON BETWEEN CALCULATED AND EXPERIMENTAL HYPERPOLARIZABILITIES

Most measurements of gas-phase hyperpolarizabilities have been reported using the Taylor series convention or the perturbation series convention. dc-SHG measurements of chromophores in solution have been much less consistent in the use of conventions. The convention most widely used, although frequently not explicitly indicated, is the one summarized by Eq. (13). When this convention is used consistently, there is reasonable agreement among dc-SHG measurements made in different laboratories, provided the measurements are made at the same wavelength and in the same solvents. Table II illustrates this by comparing measurements of β_z^{B*} made by three different research groups on para-nitroaniline (PNA) and 2-methyl,4-nitroaniline (MNA).

In Table III the experimental values for PNA (from Table I and other sources, but now multiplied by the appropriate factor of 3) are compared with both *ab initio* and semiempirical values using the perturbation series convention. The *ab initio* self-consistent field (SCF) and second order perturbation theory (MP2) results reported in references 19 and 20 were determined using analytic derivative methods. The semiempirical AM1, MNDO, and PM3 values calculated in this work were determined using finite field techniques.[21] The semiempirical INDO/S hyperpolarizabilities were evaluated via the sum-over-states expressions and used the parametrization of Ridley and Zerner.[22]

TABLE II. Values of β_z^{B*} measured using the EFISH technique.[a]

	PNA		MNA	
	1064 nm	1907 nm	1064 nm	1907 nm
Refs. 34, 3	16.3	···	18.8	···
Ref. 4	···	···	···	8.7
Ref. 7	16.9	9.6	16.7	9.5

[a] All values of β_z^{B*} in units of 10^{-30} esu. All measurements made in 1,4-dioxane.

It should be noted that the theoretical results span a considerable range of values. Furthermore, comparison of the *ab initio* values and the experimental measurements *using the same convention* clearly highlights an apparent disagreement between *ab initio* calculations and experimental values.

All the theoretical calculations assumed the same model planar structure determined using second order perturbation theory (MP2).[20] Geometry optimizations relaxing the planarity constraint at the self-consistent field

TABLE III. Comparison of theoretical and experimental hyperpolarizabilities of paranitroaniline. Values in esu $\times 10^{-30}$ using the perturbation series convention (B).

	Wavelength	Theory		
	nm	Method	Value	Expt.
β_0^B	∞	MP2[a]	8.55	
β_0^B	∞	SCF[a]	4.4	
β_0^B	∞	MNDO[b]	8.03	
β_0^B	∞	AM1[b]	7.34	
β_0^B	∞	PM3[b]	8.20	
β_0^B	∞	INDO/S[c]	17.5	
$\beta_z^B(-2\omega;\omega,\omega)$	1910			27.6[f]
$\beta_z^B(-2\omega;\omega,\omega)$	1907	MP2[d]	9.6	28.8±1.5[g]
		INDO/S[e]	21.1(30.6)	
$\beta_z^B(-2\omega;\omega,\omega)$	1370	MP2[d]	10.5	35.4±0.9[g]
		INDO/S[e]	25.5(36.2)	
$\beta_z^B(-2\omega;\omega,\omega)$	1060	MP2[d]	12.0	50.7±1.2[g]
		INDO/S[e]	34.7(47.4)	48.9[h]
				50.4[i]
				77.7[j]

[a] *Ab initio* values from Ref. 19 (SCF) and Ref. 20 (MP2) using analytic derivative methods.

[b] Semiempirical values calculated using finite field methods.

[c] Semiempirical sum-over-states calculation.

[d] *Ab initio* frequency dependent values determined from static MP2 hyperpolarizability adjusted with an SCF frequency dependent correction (Ref. 20).

[e] INDO/S semiempirical values calculated using the sum-over-states formulation. Values in parentheses are those obtained from the two-level model [Eq. (22)].

[f] In acetone (Ref. 4).

[g] In 1,4-dioxane (Ref. 7).

[h] In 1,4-dioxane (Ref. 34).

[i] In chloroform (Ref. 34).

[j] In acetone (Ref. 34).

(SCF) and MP2 levels of theory indicate that the true gas-phase minimum corresponds to a nonplanar structure,[20] in line with x-ray crystallographic data.[23] However, the energy difference between the planar and nonplanar structures is only 1.33(0.53) kcal/mol at the MP2(SCF) level of theory and so for the purpose of this work we have used the planar geometry. Calculations of the hyperpolarizability at the nonplanar geometry using the SCF and semiempirical methods (AM1, MNDO, PM3, INDO/S) indicate that the hyperpolarizability decreases by about 18% from the value corresponding to the planar geometry—a factor that is reasonably consistent across these different methods. This decrease in β can be explained by the fact that the conjugation of the π system is adversely affected by the nonplanarity of the phenyl–NH_2 moiety. Molecular geometry alone thus cannot account for the large differences among the theoretical values and between theoretical and experimental values. Furthermore, although vibrational effects have not been taken into account, work to date[24] indicates that these have little effect on second harmonic generation values.

Comparison of the *ab initio* SCF and MP2 static hyperpolarizabilities (β_0) indicates that electron correlation increases the hyperpolarizability by about a factor of 2.[20] This large increase in β with electron correlation has also been observed for smaller molecules such as ammonia,[25] HCl,[26] and water,[27,28] where experimental gas-phase dc-SHG measurements[29,30] are available. In these cases there is reasonable agreement between the MP2 values and experiment (to within 10%–20%)—a fact which lends credence to the importance of electron correlation in the determination of β and to the reliability of the MP2 method for estimating this electron correlation effect.

The static hyperpolarizabilities determined with the MNDO, PM3, and AM1 semiempirical methods reported in Table III are obtained from finite field calculations of the energy.[25] These methods have been parametrized for such gas-phase properties as ground state geometries, dipole moments, and heats of formation,[31] and in the case of the MNDO method for α,[32] but not for the hyperpolarizabilities β and γ. The hyperpolarizability values obtained by these methods are intermediate in magnitude between the SCF and MP2 results.

The INDO/S semiempirical method is routinely used to aid in the interpretation of ultraviolet spectral data since this technique is suited to the calculation of excited state properties such as oscillator strengths and excitation energies.[22] In this case it is possible to determine the hyperpolarizability via the sum-over-states formulation [Eq. (19)] and these values are also reported in Table III. The INDO/S results for the two-level model are considerably larger than the MP2 results. This large difference is to some extent expected since the INDO/S method is known to overestimate the experimental gas-phase transition dipole moments $\langle 0|\mu|l\rangle$.[33] Furthermore, the importance of the properties of the first excited state on the hyperpolarizability is overemphasized when the summation is truncated at only two levels. The INDO/S result for the hyperpolarizability determined from the summation over all n valence electronic excited states is significantly smaller than the value from the two-level model. In this case, the accuracy of the calculated excited state properties, such as $\langle l|\mu|m\rangle$, is unknown since in most cases transition moments and dipole moments for excited states other than the lowest one are unavailable experimentally and *ab initio* calculations of the required accuracy are intractable for a system of this size.

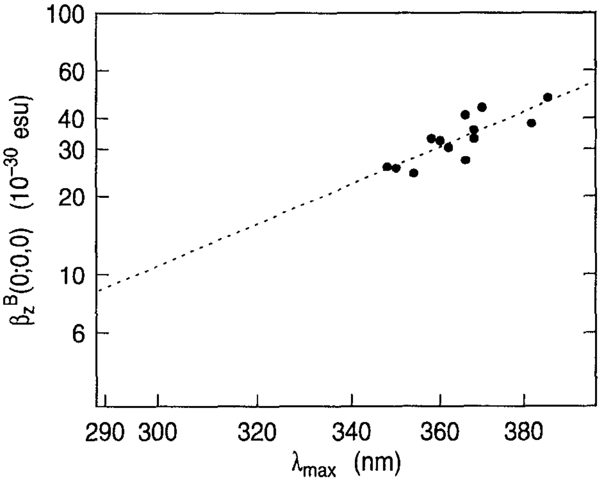

FIG. 2. A log–log plot of the hyperpolarizability extrapolated to zero frequency, $\beta_z^B(0;0,0)$, vs the wavelength of the first absorption maximum for paranitroaniline in solvents of varying polarity. The intercept represents extrapolation to a value corresponding to the gas-phase $\lambda_{max}=290$ nm. All data points are from Ref. 34.

It is important to compare experiment and theory on an equal footing. Experimental values of β_z^B for PNA have been obtained from dc-SHG measurements in a variety of solvents of different polarity.[34] On the other hand, all the calculations carried out in this work implicitly assume a gas-phase environment. One way to make such a comparison between theory and experiment is to extrapolate the experimental solution phase measurements to a static gas-phase value. This may be accomplished, for example, by extrapolating the experimental hyperpolarizability values to zero frequency using the two-level model [Eq. (22)], plotting these $\beta^B(0;0,0)$ values against the corresponding wavelength of maximum absorption, $\lambda_{max} \propto 1/\omega_{01}$ and finally extrapolating $\beta^B(0;0,0)$ to a value corresponding to the λ_{max} observed for PNA in the gas phase. This last procedure is illustrated in Fig. 2. Unfortunately, the λ_{max} values measured in solution are far from the value of 290 nm determined for λ_{max} of PNA in the gas phase[7] even for the least polar solvents, chloroform ($\epsilon=4.81$, $\lambda_{max}=348$ nm), dichloromethane ($\epsilon=7.77$, $\lambda_{max}=350$ nm), and 1,4 dioxane ($\epsilon=2.21$, $\lambda_{max}=354$ nm). (Dioxane is known to behave anomalously as a solvent of higher polarity than its dielectric constant would indicate.[35]) Thus the extrapolated values should only be considered as approximations to the true gas-phase hyperpolarizability. From this procedure we obtain an "experimental gas-phase static value" of $\beta_z^B(0;0,0)$ for PNA ranging from 6×10^{-30} to 15×10^{-30} esu, depending on the precise quantity extrapolated [e.g., $\mu\beta^B(-2\omega;\omega,\omega)$, $\beta^B(-2\omega;\omega,\omega)$, or $\beta^B(0;0,0)$]. These extrapolated experimental gas-phase static values are consistent with the theoretical static values but much smaller than the experimental values measured in solution and reported in Table III. Furthermore, the theoretical frequency-dependent hyperpolarizabilities are also significantly smaller than the corresponding experimental frequency-dependent solution-phase measurements in Table III, so there appears to be a significant difference between theory and experiment which cannot be accounted for by dispersion. We are lead to the conclusion that this difference is primarily due to the sensitivity of the hyperpolarizability β to the dielectric environment.

Another uncertainty that arises in the comparison of theoretical and experimental values involves the reference material used in the dc-SHG experiments. Almost all dc-SHG experiments are referred directly or indirectly to the second harmonic generation coefficient, d_{11}, for quartz. Two values for quartz have been obtained using different techniques.[36,37] They differ by a factor of 0.6. Choice of the more recent, but not necessarily more accurate, measurement for quartz would result in a 40% decrease in the experimental values reported in Table III.

Since there are no direct gas-phase experimental measurements for hyperpolarizabilities of charge–transfer systems such as PNA, it is difficult to establish the usefulness of the semiempirical methods for predicting quantitative values. We must stress, however, that none of the semiempirical methods employed in this work were parametrized for hyperpolarizabilities and thus expectations of quantitative accuracy are optimistic. Based on the usefulness of second order perturbation theory for the determination of β for small gas-phase molecules (see, e.g., Refs. 26, 27, and 38) and in the determination of β for a model charge–transfer system (relative to results from higher level calculations),[39] we concentrate on the difference between the *ab initio* MP2 gas-phase values and the experimental solution-phase measurements. As discussed above, extrapolation of the solution-phase measurements to a $\lambda_{\max}$ value corresponding to the gas-phase molecule results in a significant decrease in the experimental hyperpolarizability. Recent investigations[40] explicitly including the effect of an Onsager reaction field[41] in the determination of β for acetonitrile at the SCF and MP2 levels of theory indicate that the effect of the solvent environment on β may be significantly larger than the effect accounted for by the local field factors[41] routinely used in the analysis of the experimental data.[5] These reaction-field calculations demonstrate that the "molecular" hyperpolarizability deduced from solution-phase measurements may significantly overestimate the true molecular gas-phase value. To summarize there are a number of avenues to be explored in order to understand and explicitly account for the differences between the theoretical and experimental values. The main emphasis in this section has been on the importance of the consistent use of conventions in the definition of the hyperpolarizabilities and on the need to compare calculated and experimental values in similar dielectric environments.

V. CONCLUSIONS

In this work we have outlined and compared the most widely used conventions in the determination of hyperpolarizabilities. Both the Taylor series and perturbation series conventions have the useful feature that all the different frequency-dependent hyperpolarizabilities of the same order extrapolate to the same limiting value (i.e., the static value) as the frequency goes to zero. This not only leads to straightforward comparison between theoretical static values and experiment, but also leads to easy transferability of experimental values from one technique to another. We have also derived the corresponding sum-over-states formulas for these conventions, so that it is straightforward to compare experimental results from solvatochromism with dc-SHG measurements of $\beta(-2\omega;\omega,\omega)$ and calculations of frequency-dependent hyperpolarizabilities using the sum-over-states formulation with experimental measurements. Comparison of theoretical and experimental values for the hyperpolarizability of para-nitroaniline using the same convention highlights the large difference between theoretical gas-phase values and solution-phase measurements—a difference that we believe has in the past been obscured by inconsistent use of conventions.

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