On the determination of the molecular static first hyperpolarisability: how reliable are literature data?

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The shortcomings of the two-level model in extrapolating the molecular static first hyperpolarisability, $\boldsymbol{\beta_0}$, are discussed in the context of literature data. However, except for some spurious $\boldsymbol{\beta_0}$ data, in many other cases, the reported $\boldsymbol{\beta_0}$ values can be considered reasonably reliable due to a *balancing of effects.*

The past two decades have witnessed intense research activity on second-order nonlinear optical (NLO) molecule-based materials.[1] In this regard, the microscopic first hyperpolarisability (β) is an important parameter for the characterisation of these molecular materials. Two main techniques, electric field-induced second harmonic generation (EFISH) and hyper-Rayleigh scattering (HRS), have been employed to obtain the molecular first hyperpolarisability. A very broad range of β values, ranging from 10×10^{-30} esu for prototypical dipolar *p*-nitroaniline-like chromophores to orders of magnitude larger ($>10^3 \times 10^{-30}$ esu) for large organic chromophores or metal complexes, have been achieved.[1,2] Both β_{EFISH} or β_{HRS}-derived data are frequency-dependent values, thus they need to be extrapolated to zero frequency ($\hbar\omega = 0.0$ eV; $\lambda = \infty$) to estimate the static, intrinsic first hyperpolarisability, β_0. The static hyperpolarisability represents the most important figure of merit when comparing the molecular second-order NLO response of different chromophores.

In this regard, the simple two-level model of Oudar and Chemla[3] has been adopted to extrapolate β_0 [eqn. (1)]. For instance, for second harmonic generation and assuming that one tensor component (β_{iii}) dominates the NLO response [in the case of a unidirectional charge-transfer (CT) transition], we have:

$$\beta_{iii}(-2\omega;\omega,\omega) = D(\omega)\beta_0 \qquad (1)$$

where β_0 is given by

$$\beta_0 = \frac{3e^2}{2}\frac{(r_{\mathrm{ge}})^2\Delta\mu_{\mathrm{ge}}}{(\hbar\omega_{\mathrm{ge}})^2} \qquad (2)$$

and

$$D(\omega) = \frac{(\hbar\omega_{\mathrm{ge}})^4}{[(\hbar\omega_{\mathrm{ge}})^2 - (2\hbar\omega)^2][(\hbar\omega_{\mathrm{ge}})^2 - (\hbar\omega)^2]} \qquad (3)$$

In eqn. (2), $\hbar\omega_{\mathrm{ge}}$ is the frequency of the lowest CT transition ($\omega_{\mathrm{ge}} = E_{\mathrm{ge}}/\hbar$, $2\pi c/\lambda_{\mathrm{ge}}$), r_{ge} and $\Delta\mu_{\mathrm{ge}}$ are, respectively, the transition dipole moment and the dipole moment variation between the ground (g) and the involved excited (e) state. This model assumes that only the lowest CT excited electronic state is coupled with the ground state by an applied electric field, $\hbar\omega$, to contribute to β_{iii} and that the simple unitless dispersion factor, $D(\omega)$, [eqn. (3)] accounts for the frequency dependence of $\beta(-2\omega;\omega,\omega)$. There are, however, several limitations[1] in applying this model to extrapolate β_0 and they have often been ignored.

In the hypothesis that a single excited state contributes to nonlinearity and a single diagonal β_{iii} tensor dominates the NLO response, eqn. (1) is valid only in the non-resonant regime, that is when $\hbar\omega_{\mathrm{ge}} \gg 2\eta\omega$. In the other cases, when the harmonic frequency approaches resonance with the lowest CT transition, the simple dispersion formula [eqn. (3)] is inadequate to describe β since it overestimates the resonance enhancement relative to β_0 and diverges for $2\hbar\omega = \hbar\omega_{\mathrm{ge}}$. Only the inclusion of some damping corrections to prevent the divergence in the dispersion formula can give reliable β_0 values. Most of the β_0 values reported in the literature, especially for large organic chromophores and metal complexes, have been obtained from β measurements in the resonant regime and extrapolated by using eqn. (1). Therefore, for the above reasons, they should be considered approximate.

Although the application of the simple two-level model [eqn. (1)] in the resonant regime should always involve underestimated β_0 values, since it overcorrects for the dispersion effect, there are, however, various pieces of evidence that allow us to consider that this is true only very close to resonance, *i.e.* when $2\hbar\omega \cong \hbar\omega_{\mathrm{ge}}$. In many other cases, due to *balancing effects*, estimated β_0 values can still be considered reasonable or, even, overestimated, especially those extrapolated from measurements at shorter incident laser wavelengths or when $2\hbar\omega > \hbar\omega_{\mathrm{ge}}$. This can be deduced from available β_0 data obtained from β_{EFISH} or β_{HRS} measurements at various incident laser wavelengths. For example, extrapolated β_0 values by means of eqn. (1) from accurate HRS measurements[4a] (corrected for two-photon fluorescence) on various chromophores at two incident laser wavelengths (1064 and 1319 nm), indicate that those obtained from strongly enhanced, $\beta_{\mathrm{HRS}}^{1064}$ data are generally larger than those from $\beta_{\mathrm{HRS}}^{1319}$ data, especially for large chromophores. For example, for crystal violet: $\beta_0 = 41.5 \times 10^{-30}$ esu (from $\beta_{\mathrm{HRS}}^{1319}$ data); $\beta_0 = 89.8 \times 10^{-30}$ esu (from $\beta_{\mathrm{HRS}}^{1064}$ data).[4a] Analogous results have been obtained for other series of donor–acceptor chromophores using two different excitation wavelengths (1064 and 1907 or 1507 and 1907 nm).[4b,c] On the other hand, in some cases, extrapolated β_0 values for homologous series of compounds, such as Ru$^{\mathrm{II}}$ 4,4′-bipyridinium complexes, even from resonantly enhanced $\beta_{\mathrm{HRS}}^{1064}$ data, apparently provided reasonable values, as demonstrated by the linear correlation between β_0 and $1/\hbar\omega_{\mathrm{ge}}^2$.[5a]

Within the approximation of the two-level model, the static hyperpolarisability can be simply estimated *via* eqn. (2) when linear spectroscopic parameters, $\hbar\omega_{\mathrm{ge}}$, r_{ge}, and $\Delta\mu_{\mathrm{ge}}$, are known. Stark spectroscopy affords dipole moment changes upon optical excitation, while the transition dipole moment can be easily evaluated from the optical absorption spectrum. Thus, β_0 values have recently been obtained for a series of

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pentaammine(pyridyl)Ru^{II} complexes and related 4-(dimethylaminophenyl)pyridinium organics.[5b] Note that, while for the series of Ru^{II} complexes β_0 values estimated using eqn. (2) are smaller than those extrapolated from resonantly enhanced β_{HRS}^{1064} data [*e.g.*, for the Ru^{II} *N*-phenyl-4,4′-bipyridinium derivative: $\beta_0 = 93 \times 10^{-30}$ esu, estimated from eqn. (2); $\beta_0 = 220 \times 10^{-30}$ esu, estrapolated from β_{HRS}^{1064} data],[5b] for the related pyridinium species the opposite is found: estimated β_0 values from eqn. (2) are larger than those extrapolated from β_{HRS}^{1300} data, obtained from measurements in a non-resonant regime [*e.g.*, for the *N*-phenyl-4,4′-bipyridinium salt: $\beta_0 = 75 \times 10^{-30}$ esu, estimated from eqn. (2); $\beta_0 = 23 \times 10^{-30}$ esu, estrapolated from β_{HRS}^{1064} data].[5b] Again, this indicates that extrapolated β_0 values from β measurements in the resonant regime for large molecular systems are substantially overestimated.

Altogether, these observations are consistent with an additional contribution of the higher energy excited states to β, especially for large molecular systems. This accounts for the observed strong enhancement of measured β values in the resonant regime, in which a substantial contribution to the enhancement comes from higher energy CT states. Therefore, in these cases, extrapolated β_0 values from β_{EFISH} or β_{HRS} measurements tend to be overestimated, especially those extrapolated from measurements in the resonant regime, because the correction for the dispersion effects involves only the lowest CT state. In contrast, when many excited states are involved, calculated β_0 values by means of the two-level model and linear spectroscopic parameters [eqn. (2)] are expected to be underestimated, because only the lowest CT state is considered. Actually, the contribution of various electronic states to β was recently demonstrated for various systems, especially for metal complexes,[6] both theoretically and experimentally.

Eqn. (1) is valid only for one-dimensional systems, that is, when a single tensor component dominates the NLO response, while it is well known that many dipolar or non-dipolar structures have multidimensional NLO character, being characterised by various tensor components.[7] Polarised HRS measurements allow the determination of the "overall" tensor, as well as of the individual components of the tensors. In these cases, β_0 cannot be extrapolated by means of the simple eqn. (1), because various electronic CT states will contribute to the NLO response. In addition, the contribution of various states to each β_{ijk} tensor will be different, especially for molecules possessing lower order ($n < 3$) axes.[8] In the case of octupolar, non-dipolar chromophores, a three-level model, in conjunction with the simple dispersion formula [eqn. (3)], was employed to extrapolate β_0.[7] However, the above limitations remain, even for this simplified model.

Recently, several models, which take into account various broadening mechanisms, have been proposed to correct the dispersion formula [eqn. (3)] with damping terms in the resonant regime. Either the inhomogeneously broadened Gaussian line shape, developed by Berkovic *et al.*,[9] or the overlapping of vibronic levels, developed by Wang,[10] have been considered to treat the broadening of the lowest optical absorption band, within an extended two-level model. The two treatments lead, however, to different results. While the Berkovic *et al.*[9] method correctly involves the same extrapolated β_0 value from data obtained in the resonant and off-resonant regimes, the Wang *et al.*[4b,c] treatment should involve different β_0 values from resonant and non-resonant β_{HRS} data, in apparent agreement with the experimental results.

Even when extending these approaches to large organic chromophores or metal complexes, only in some cases would it be possible to correctly estimate β_0. Often, the overlapping nature of optical spectra precludes the correct evaluation of λ_{max} and the related bandwidth. Moreover, in the case of the contribution of many excited states to β or of multidimensional chromophores, the two-level model breaks down, thus precluding the use of the eqn. (1), even when including corrections in the dispersion formula. Finally, the inclusion of vibrational contributions to the molecular first hyperpolarisability, even in the static limit, may be of relevance in evaluating β_0, especially for push–pull conjugated polyenes.[11]

Clearly, in all these cases a correct evaluation of β_0 can uniquely come from accurate theoretical calculations, when they are able to reproduce experimental β values, or when the contribution of the individual excited states to β is known. In this last regard, in a recent study by Vance and Hupp,[12a] the static and dynamic hyperpolarisabilities of an octupolar Ru^{II} 2,2′-bipyridine-substituted complex were calculated by means of eqn. (1) and optical derived parameters (as the sum of the individual contribution of the two lowest CT states, as deduced from electroabsorption results), and compared with β_{HRS}-derived data from polarised HRS measurements. Again, both static ($\beta_0 = 300 \times 10^{-30}$ esu) and dynamic ($\beta^{820} = 5600 \times 10^{-30}$ esu) calculated β values[12a] are underestimated with respect to β_{HRS}-derived data ($\beta_{HRS}^{820} = 6500 \times 10^{-30}$ esu; $\beta_0 = 424 \times 10^{-30}$ esu),[12] likely due to the omission of higher lying excited states in the calculation of β and/or the omission of damping terms in the dispersion formula.

In summary, it is quite difficult to get reliable static first hyperpolarisabilities of "real-world" molecular chromophores. However, except for some spurious β_0 data extrapolated from β_{HRS} or β_{EFISH} measurements very close to resonance or from β_{HRS} measurements uncorrected for the two-photon induced fluorescence contribution,[13] many other β_0 data reported in the literature can be considered reasonably reliable due to a *balancing of effects*. Although the application of the simple two-level model leads to underestimated β_0 values, due to the omission of phenomenological damping terms in the dispersion formula, it is also true that the omission of the contribution of higher energy excited states to the NLO response tends to overestimate β_0 values, especially for large chromophores.

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Notes and references

1 N. P. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, 1991; *Nonlinear Optics of Organic Molecules and Polymers*, ed. H. S. Nalwa and S. Miyata, CRC Press, Boca Raton, FL, 1997.

2 The first hyperpolarisability, β, is expressed either in the cgs (cm^4 statvolt^{-1} = esu) or the SI (C m^3 V^{-2}) unit systems. The conversion from the SI to the cgs system is given by the relation: 10^{-50} C m^3 V^{-2} = 2.694×10^{-30} esu.

3 J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664.

4 (*a*) P. Kaatz and D. P. Shelton, *J. Chem. Phys.*, 1996, **105**, 3918; (*b*) C. H. Wang, J. N. Woodford and A. K.-Y. Jen, *Chem. Phys.*, 2000, **262**, 475; (*c*) C. H. Wang, J. N. Woodford and A. K.-Y. Jen, *Chem. Phys.*, 2001, **271**, 137.

5 (*a*) B. J. Coe, J. A. Harris, I. Asselberghs, A. Persoons, J. C. Jeffery, L. H. Rees, T. Gelbrich and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1999, 3617; (*b*) B. J. Coe, J. A. Harris, K. Clays, A. Persoons, K. Wostyn and B. S. Brunschwig, *Chem. Commun.*, 2001, 1548.

6 (*a*) S. Di Bella, *Chem. Soc. Rev.*, 2001, **30**, 355; (*b*) S. Barlow and S. R. Marder, *Chem. Commun.*, 2000, 1555.

7 J. Zyss and I. Ledoux, *Chem. Rev.*, 1994, **94**, 77.

8 S. Di Bella, I. Fragalà, I. Ledoux and J. Zyss, *Chem. Eur. J.*, 2001, **7**, 3738.

9 G. Berkovic, G. Meshulam and Z. Kotler, *J. Chem. Phys.*, 2000, **112**, 3997.

10 C. H. Wang, *J. Chem. Phys.*, 2000, **112**, 1917.

11 D. M. Bishop, B. Champagne and B. Kirtman, *Chem. Phys. Lett.*, 2000, **329**, 329, and references therein.

12 (*a*) F. W. Vance and J. T. Hupp, *J. Am. Chem. Soc.*, 1999, **121**, 4047; (*b*) This β_0 value has been roughly estimated by means of eqn. (1) on the basis of the experimental $\beta_{\mathrm{HRS}}^{820}$ value[12a] and assuming a two-level contribution of the electronic transition at 428 nm.[12a]

13 Although the two-photon induced fluorescence is the main source of the origin of spurious and irreproducible signals in HRS measurements, many other corrections, such as absorption, particulate scattering, *etc.*, should be taken into account in order to obtain reliable β_{HRS} data. See, for example: I. D. Morrison, R. G. Denning, W. M. Laidlaw and M. A. Stammers, *Rev. Sci. Instrum.*, 1996, **67**, 1445.