

Assessment of DFT Exchange–Correlation Functionals for Evaluating the Multipolar Contributions to the Quadratic Nonlinear Optical Responses of Small Reference Molecules

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S Supporting Information

ABSTRACT: The hyper-Rayleigh scattering responses as well as the multipolar contributions to the first hyperpolarizabilities are calculated by means of density functional theory for a series of reference molecules (acetonitrile, dichloromethane, trichloroacetonitrile, chloroform, carbon tetrachloride), covering the whole range of dipolar/octupolar character. The performance of various exchange–correlation functionals is addressed by comparison to CCSD(T) calculations. The best functionals turn out to be LC-BLYP, M05-2X, and M06-2X.

1. INTRODUCTION

Because of the strong basis set dependence as well as the importance of the electron correlation and of the surrounding, the prediction of the (electronic) first hyperpolarizabilities (β) of small molecules remains a challenging task for quantum chemistry. Highly correlated coupled-cluster (CC) calculations performed at the CCSD, CCSD(T), or even higher CCSDT and CCSDTQ levels in combination with extended basis sets have provided reference β values for isolated diatomic and small polyatomic molecules¹ as well as for clusters and more extended push–pull systems.² On the other hand, it has been shown that an accurate consideration of the environment effects is crucial when comparing the computed molecular nonlinear optical (NLO) properties to data issued from measurements carried out in solution.³ Among the available approaches to describe solvent effects, the most popular ones are likely the polarizable continuum models (PCM), in which the molecular surrounding is replaced by a structureless medium characterized by its dielectric permittivity.⁴ However, although these approaches have been extensively used to predict the second-order NLO responses of organic molecules in various solvents,^{5,6} they cannot catch the impact of specific local interactions between the molecule and its environment. This is particularly problematic for molecular liquids such as carbon tetrachloride, where the permanent multipolar interactions between neighboring molecules induce geometrical distortions and orientational correlations that provoke variations in the quadratic NLO responses comparable in magnitude to the unimolecular responses themselves.⁷ However, the explicit description of intermolecular interactions implies performing quantum chemical calculations on clusters that include (at least) both the molecule and its first solvation shell, which is out of reach of computationally expensive methods, such as CC or even perturbative Møller–Plesset schemes.

In this context and owing to continuous developments of algorithms and exchange–correlation (XC) functionals,⁸ density functional theory (DFT) appears as the natural alternative for computing the first hyperpolarizabilities of large-size aggregates at low computational costs, while including electron correlation effects. However, its use is not straightforward. Indeed, as already pointed out more than a decade ago for push–pull π -conjugated systems, DFT approaches using conventional XC functionals present serious drawbacks when applied to the calculation of the linear and nonlinear electric field responses.⁹ Therefore, as a part of a broader project aiming at quantifying the surrounding effects on the NLO responses of molecular liquids, we address here the performance of various XC functionals for predicting the quadratic NLO properties of a series of reference molecules, namely, acetonitrile ($\text{CH}_3\text{—CN}$), dichloromethane ($\text{CH}_2\text{—Cl}_2$), trichloroacetonitrile ($\text{CCl}_3\text{—CN}$), chloroform (CHCl_3), and carbon tetrachloride (CCl_4), that we have recently characterized in a joint theoretical and experimental study.¹⁰ This particular series of compounds was chosen to highlight the relationships between the symmetry of the scatterers and their first hyperpolarizability, by progressively going from a pure dipolar molecule ($\text{CH}_3\text{—CN}$) to a pure octupolar molecule (CCl_4). We focus our study on the NLO responses that can be measured in hyper-Rayleigh scattering (HRS) experiments, namely, the HRS first hyperpolarizabilities β_{HRS} and the depolarization ratios as well as the spherical invariants $\beta_{J=1}$ and $\beta_{J=3}$, which determine the dipolar and octupolar contributions to the quadratic NLO responses. All β values are given in atomic units (au) using the *T* convention as defined in ref 11.

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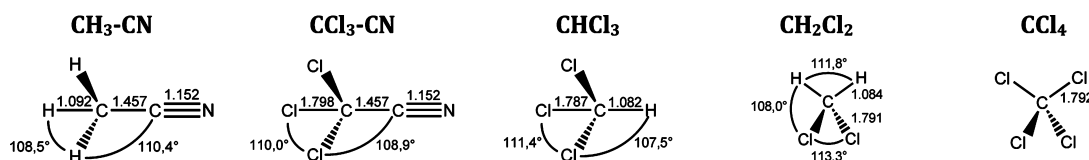


Figure 1. Bond lengths (Å) and angles (degrees) of the investigated compounds.

2. THEORETICAL AND COMPUTATIONAL DETAILS

The molecular structures were optimized at the B3LYP/6-311G(d) level in the gas phase. The geometrical features (bond lengths and angles) of the five compounds are shown in Figure 1.

The static hyperpolarizabilities were calculated using DFT in combination with either the coupled-perturbed Kohn–Sham (CP-KS) method¹² or a finite-field (FF) procedure in which the third-order derivatives of the energy with respect to the external fields are computed numerically. In that case, a Romberg procedure was employed in order to remove contaminations from higher orders in the FF differentiations. External fields varying from ± 0.0004 to ± 0.0064 au were used, which is small enough to obtain converged numerical β values, i.e., identical to those computed analytically to within 0.1 au or less. The performance of various XC functionals is addressed by comparison to reference results obtained at the CCSD(T) level. The Hartree–Fock (HF) and second-order Møller–Plesset (MP2) results are also reported for comparison. While HF constitutes the noncorrelated reference, which computationally scales like hybrid DFT, MP2, which scales like double hybrid DFT, is usually assumed to include the major part of the electron correlation effects when calculating the second-order NLO responses.^{2,13} All calculations were performed using the doubly augmented correlation-consistent valence triple- ζ Dunning’s basis set (d-aug-cc-pVTZ), which has been shown to perform well for predicting the NLO responses of small molecules such as water, acetonitrile, chloroform, and *para*-nitroaniline,¹⁴ and to provide converged hyperpolarizability values at the HF level for the series of compounds investigated here.¹⁰ Indeed, the hyperpolarization effects in small molecules are generally complex and require the use of extended basis sets containing diffuse and polarization functions for a proper description.¹⁵ The convergence behavior of the NLO responses with respect to the basis set has also been assessed at the DFT level using the LC-BLYP and M06-2X functionals (see Table S1 and Figure S1, Supporting Information). In addition, solvent effects were taken into account by using the integral equation formalism (IEF) version of PCM.¹⁶ Atomic radii were taken from the UA0 force field, in which hydrogen atoms are enclosed in the sphere of the heavy atom to which they are bonded. All calculations were carried out using Gaussian09.¹⁷ However, to ensure consistency with our previously published results, the PCM solvent parameters defined by defaults in Gaussian03 were used. Note that PCM parameters are not available for the CCl₃–CN molecule, so that those of acetonitrile were used instead.

The XC functionals considered in this study can be classified into four categories:

- (i) The functionals based on the generalized gradient approximation (GGA), where the XC potential depends on the density and on its first derivative: BLYP, which combines the Becke exchange functional¹⁸ and the Lee–Yang–Parr (LYP) correlation functional.¹⁹
- (ii) The hybrid GGA functionals, where exchange is described by a combination of GGA and HF expressions: B3LYP and BHandHLYP, where the GGA correlation is provided by the LYP expression and the exchange part is a mixture of the Becke exchange functional with 20% and 50% of HF exchange, respectively; B3P86 and B3PW91, which use the nonlocal Perdew or Perdew–Wang correlation in combination with the Becke 3-parameter exchange functional including 20% of HF exchange; PBE0 (also noted PBE1PBE), which mixes the Perdew–Burke–Ernzerhof²⁰ pure GGA with 25% of HF exchange;²¹ mPW1PW91, which combines Perdew–Wang exchange as modified by the inclusion of 25% of HF exchange²² with the PW91 correlation; MPW1K, which contains 42.8% of HF exchange;²³ and the Becke functional B97²⁴ in the version modified by Wilson, Bradley and Tozer, (B97-2)²⁵ as well as in its 1998 revision (B98),²⁶ which contain 21% and 21.98% of HF exchange, respectively. Long-range corrected hybrid GGA functionals were also considered: the LC-BLYP functional, which applies the long-range correction (LC) of Hirao and co-workers to BLYP, i.e., containing only long-range HF exchange with a range separation parameter (μ) of 0.47;²⁷ CAM-B3LYP, which adds a long-range correction using the Coulomb-attenuating method and includes 19% of HF exchange at short-range and 65% at long-range with $\mu = 0.33$ ²⁸ as well as the functionals from Head–Gordon and co-workers, ω B97X (15.77% and 84.23% of short-range and long-range HF exchange with $\mu = 0.30$)²⁹ and ω B97X-D (22.20% and 77.80% of short- and long-range HF exchange with $\mu = 0.20$),³⁰ the second one including also empirical dispersion forces.
- (iii) The hybrid meta-GGA functionals, which depend explicitly on the local kinetic energy density or encompass the second-order derivative of the electron density in the XC potential, together with a part of HF exchange: BMK, which uses 42% HF exchange,³¹ TPSSH with a low content of HF exchange (10%),³² and from the Minnesota collection, M05-2X³³ as well as M06, M06-2X, and M06-HF,³⁴ which include, respectively, 56%, 27%, 54%, and 100% of HF exchange.
- (iv) The double hybrid functionals, in which MP2 correlation is added to the local DFT correlation: B2-PLYP, characterized by percentages of HF exchange and MP2 correlation of 47% and 27%, respectively,³⁵ and mPW2-PLYP, which combines 45% of HF exchange and 25% of MP2 correlation.³⁶

The systematic calculations reported here are motivated by the fact that the reliability of DFT with conventional XC functionals to evaluate molecular electronic hyperpolarizabilities has been questioned in a large number of studies. Indeed, after the early works having reported the overall good performance of pure LDA and GGA functionals to predict β of small molecules,³⁷ several groups have pointed out the need

for a correct description of the asymptotic behavior of the XC potential.³⁸ On the other hand, for extended systems (one-dimensional as well as two- and three-dimensional), it was shown that the errors on β (as well as on the linear polarizability α and the second hyperpolarizability γ) can be very large and even attain several orders of magnitude.^{9,39} This error was further attributed to the incorrect electric field dependence of the “response part” of the X(C) potential, which lacks a linear term counteracting the applied electric field.⁴⁰ Since the HF exchange displays both the correct long-range behavior and also the correct counteracting term owing to its ultranonicity, hybrid functionals, such as B3LYP and BHandHLYP, were shown to improve the quality of the results for large systems, including push–pull π -conjugated systems, short single-walled carbon nanotubes, and transition-metal complexes or organic electrides.⁴¹ For instance, Suponitsky et al.^{41b} have optimized a computational protocol for rational design of NLO compounds that is based on the use of hybrid XC functionals with high percentage of HF exchange and on the relative β values among compounds, rather than their absolute values. Still, in the case of large π -conjugated systems, a fraction of HF exchange remains often insufficient, even qualitatively when investigating the effects of enlarging the π -conjugated bridge or modifying its chemical composition (double versus triple bonds).^{2a} Further strategies have then been used to further correct for the shortsightedness of the XC functionals. These include the use of an optimized effective potential (OEP)⁴² or of long-range corrected functionals, using either the scheme introduced by Iikura et al.²⁷ or the Coulomb-attenuating model (CAM) of Yanai et al.²⁸ Then, using the LC-BLYP or CAM-B3LYP XC functionals enables better predictions of β for extended push–pull conjugated systems.^{2a,5f,43} The LC-BLYP functional was also combined with an electrostatic interaction scheme to evaluate the macroscopic second-order susceptibilities of anil crystals⁴⁴ and provided results of comparable quality to MP2. However, other studies have evidenced that the improvement of long-range corrected functionals over HF is not systematic to determine the β responses of small molecules¹⁴ as well as to evaluate the β contrast in molecular NLO switches⁴⁵ or γ of polydiacetylene and polybutatriene chains.⁴⁶

In this work, we focus on the second-harmonic generation (SHG) response that can be deduced from hyper-Rayleigh scattering (HRS) measurements. This quantity, abbreviated as β_{HRS} in the following, is related to the HRS intensity for a nonpolarized incident light and observation of plane-polarized scattered light made perpendicularly to the propagation plane. Assuming an incident light propagating along the X direction and a harmonic light scattered at 90° along the Y direction and vertically polarized (along the Z axis), β_{HRS} reads

$$\langle \beta_{\text{HRS}}^2 \rangle = \langle \beta_{\text{ZZZ}}^2 \rangle + \langle \beta_{\text{ZXX}}^2 \rangle \quad (1)$$

where the $\langle \beta_{\text{ZZZ}}^2 \rangle$ and $\langle \beta_{\text{ZXX}}^2 \rangle$ terms are orientational averages whose complete expressions as a function of the 18 nonredundant Cartesian components of the SHG β tensor have been established by Bersohn and colleagues.⁴⁷ The associated depolarization ratio:

$$\text{DR} = \frac{\langle \beta_{\text{ZZZ}}^2 \rangle}{\langle \beta_{\text{ZXX}}^2 \rangle} \quad (2)$$

depends on the symmetry of the molecular scatterer and ranges between 1.5 for octupolar compounds and 9 for pure dipolar

molecules. Moreover, since HRS measurements are often analyzed using the irreducible spherical representation of the hyperpolarizability,⁴⁸ the multipolar components of the β tensor have also been calculated. Using the mixed spherical–Cartesian formalism, the two HRS invariants involved in eq 1 are expressed as

$$\langle \beta_{\text{ZZZ}}^2 \rangle = \frac{9}{45} \beta_{J=1}^2 + \frac{6}{105} \beta_{J=3}^2 \quad (3a)$$

$$\langle \beta_{\text{ZXX}}^2 \rangle = \frac{1}{45} \beta_{J=1}^2 + \frac{4}{105} \beta_{J=3}^2 \quad (3b)$$

where $\beta_{J=1}$ and $\beta_{J=3}$ (we considered their absolute values) are the dipolar and octupolar contributions of the β response, respectively. The relative contribution of the octupolar and dipolar components is given by the nonlinear anisotropy ratio $\rho = \beta_{J=3}/\beta_{J=1}$.

Because the accuracy of DFT calculations depends on the number of points used in the numerical integrations, especially when using meta-GGA functionals,⁴⁹ we preliminary performed a grid-convergence analysis on the static β_{HRS} and β_J responses. As representative examples, the results obtained for the LC-BLYP and M06 functionals are gathered in Table S2a,b, Supporting Information, respectively. Six different integration grids were considered: (i) the (75,302) grid, which is used by default in Gaussian09 and involves 75 radial shells around each atom and 302 angular points in each shell; (ii) the (99,590) grid, referred to as the ultrafine grid in Gaussian09; and (iii) the (99,974), (120,974), and (150,974) grids with increasing number of shells for similar numbers of angular points as well as (iv) the (96,32,64) spherical product grid having 96 radial shells, and $2 \times 32 \times 64 = 4096$ angular points in each shell. The results reported in Table S2a, Supporting Information, show that the NLO properties calculated using LC-BLYP depend little on the choice of the integration grid. Deviations of 21% and 8% on the $\beta_{J=1}$ values of CHCl_3 with respect to the finest (96,32,64) grid are nevertheless observed when using the pruned (75,302) and (99,590) grids, but the absolute difference is smaller than 0.2 au. Overall, the ultrafine grid is sufficient as shown by the β variations of only a few hundredths of au with respect to the largest grids. So, $\beta_{J=1}$ of CCl_4 amounts to less than 0.03 au, whereas by symmetry, it should exactly vanish.

In contrast, the β values obtained at the M06/d-aug-cc-pVTZ level (Table S2b, Supporting Information) depend more on the number of points used in the numerical integrations. Clearly, the pruned (75,302) grid does not provide converged β values. The deviations on β_{HRS} systematically attain 10–16% with respect to the values obtained using the reference (96,32,64) grid, which corresponds to absolute differences ranging from 0.9 to 2.8 au. For the $\beta_{J=3}$ values the absolute differences can attain 6.3 au, but on a relative scale, the impact of using the default grid is smaller. On the other hand, the effects are more dramatic on $\beta_{J=1}$ because the absolute differences also attain 5–8 au, but the amplitudes are quite smaller (with the exception of $\text{CH}_3\text{—CN}$). As a consequence, the ρ value of CHCl_3 is poorly estimated, whereas that of CCl_4 is far from its ∞ value. Although using the tighter (99,590) grid provides better results, non-negligible deviations persist for the $\beta_{J=1}$ values of CH_2Cl_2 (–11%) and $\text{CCl}_3\text{—CN}$ (+8%). These are further reduced to less than 5% when using the (99,974) grid. Contrary to the LC-BLYP data, when using M06, the behavior of the different β values with the number of radial shells and angular points is not

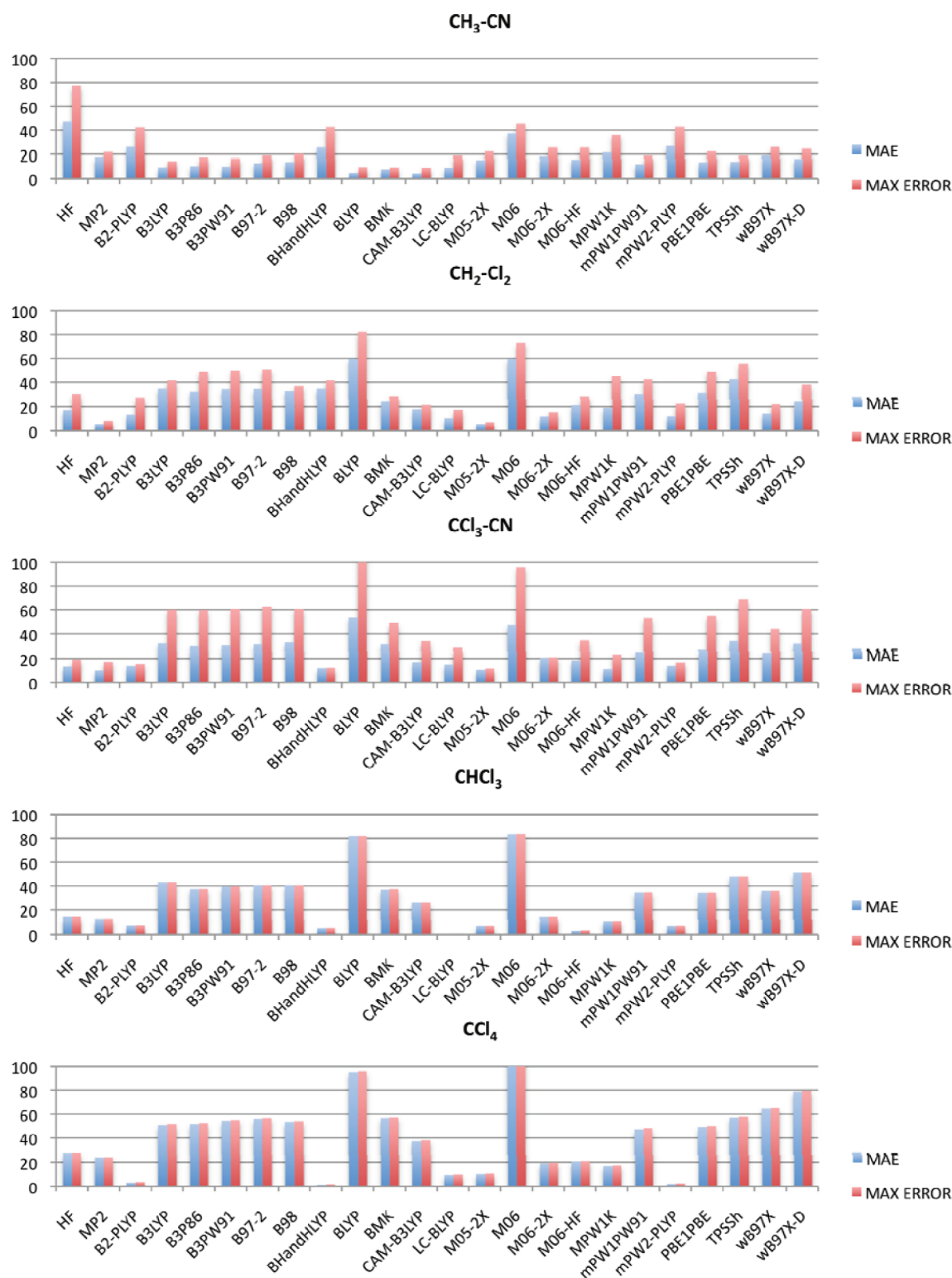


Figure 2a. MAE and maximal absolute errors on the β_{HRS} , $\beta_{j=1}$, and $\beta_{j=3}$ values relative to the reference CCSD(T) results for molecules in gas phase. Errors on $\beta_{j=1}$ are excluded from the statistics for CHCl_3 and CCl_4 .

systematically smooth, demonstrating the need for tuned grids when computing high-order properties like the first hyperpolarizabilities. Moreover, it is noteworthy that except when using the tightest (96,32,64) grid, M06 predicts an unphysical non-negligible $\beta_{j=1}$ value for CCl_4 . This is not the case with the other types of XC functionals, which all predict near-zero $\beta_{j=1}$ values, consistent with the pure octupolar symmetry of the

molecule, even when using coarser integration grids. In view of these results, unless otherwise mentioned, the (99,974) grid was used in all the calculations.

3. RESULTS

The absolute values of the static β_{HRS} and β_j values of the five molecules as well as the ρ and DR ratios are gathered in Tables

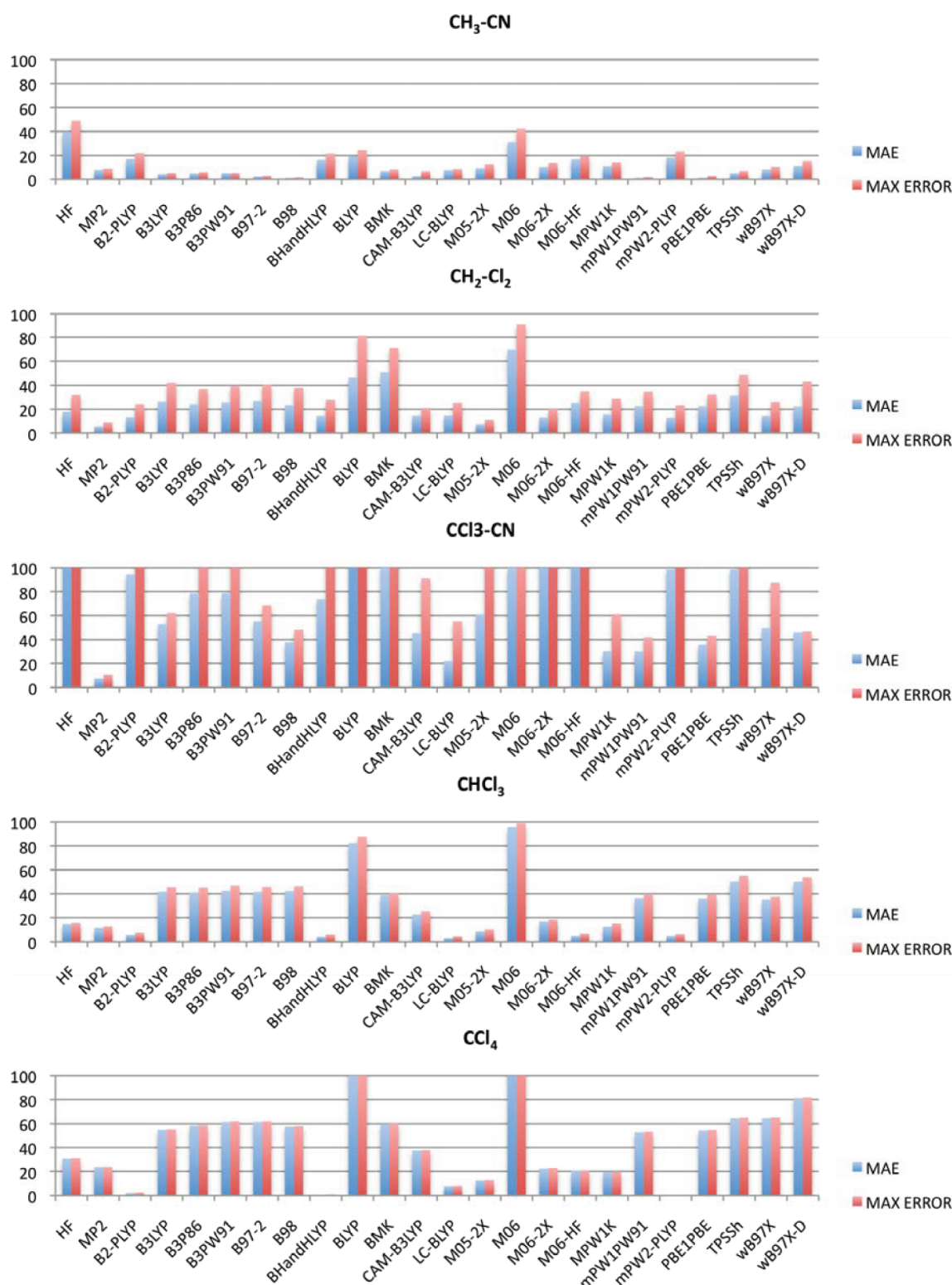


Figure 2b. MAE and maximal absolute errors on the β_{HRS} , $\beta_{j=1}$, and $\beta_{j=3}$ values relative to the reference CCSD(T) results for molecules in solution. Errors on $\beta_{j=1}$ are excluded from the statistics for CHCl_3 and CCl_4 .

S3–S7, Supporting Information. The mean absolute errors (MAE) and maximal absolute errors relative to the reference CCSD(T) results are reported in Figure 2a and 2b for molecules in gas phase and in solution, respectively. Note that for the CHCl_3 and CCl_4 molecules, relative errors on $\beta_{j=1}$ are not significant since they are related to very small absolute values; hence, they were not accounted for in the graphical

representations. Numerical values used to construct Figures 2a and 2b are reported in Table S8a,b, Supporting Information, respectively.

3.1. Acetonitrile. The static β_{HRS} and β_j values as well as the ρ and DR calculated for the acetonitrile molecule in gas phase and in solution are reported in Tables S3a,b, Supporting Information, respectively. Considering gas phase values, only

half of the XC functionals predict a value smaller than 1 for the nonlinear anisotropy parameter ρ , which demonstrates the dominant dipolar character of the acetonitrile molecule. Among these, BLYP, B3LYP, BMK, CAM-B3LYP, LC-BLYP, and TPSSH display errors smaller than 20% with respect to the CCSD(T) results for each of the β_{HRS} , $\beta_{j=1}$, and $\beta_{j=3}$ quantities. With BLYP, BMK, and CAM-B3LYP, the deviations with respect to CCSD(T) are even smaller than 10%. The DR value is also well reproduced by these six functionals; BLYP slightly overestimates the depolarization ratio by 11%, while the others underestimate it from 3% (BMK) to 12% (LC-BLYP). It is further interesting to point out that pure and hybrid DFT performs better than the HF method, which strongly underestimates $\beta_{j=1}$. These results are consistent with the study of ref 14 on β_{eff} , the β quantity that can be extracted from electric field induced second harmonic generation (EFISHG) experiments, where CAM-B3LYP is shown to perform better than B3LYP, PBE0, and PBE. On the other hand, double hybrid functionals do not necessarily provide an improvement with respect to MP2, since the accurate $\beta_{j=3}$ value is accompanied by a too small $\beta_{j=1}$.

Furthermore, BMK, LC-BLYP, and CAM-B3LYP also quantitatively reproduce the solvent-induced enhancement of the β_{HRS} and β_j values, while larger but still acceptable deviations (15–22%) on the $\beta_{\text{LIQ}}/\beta_{\text{GAS}}$ ratios are found with the other three functionals. As a general feature, most of the DFT functionals predict NLO responses closer to the CCSD(T) results in the case of the solvated molecules than for the isolated molecules. This is attributed to the better performance of the DFT functionals to describe molecules with stronger dipolar character.

3.2. Dichloromethane. Tables S4a,b, Supporting Information, gather the NLO quantities calculated for the dichloromethane molecule isolated and in solution, respectively. All XC functionals predict—and generally overestimate—the dominant octupolar character of the first hyperpolarizability, consistent with CCSD(T) results. Although underestimated, the gas-phase DR value, close to 2, is reproduced with reasonable accuracy by most of the functionals. Note that for CH_2Cl_2 , ρ is a better criterion than DR to assess the reliability of a method because the narrow 1.5–2.0 range for DR is associated with ρ values going from 9.3 to 2.9. The smallest deviations with respect to the CCSD(T) reference are obtained for CAM-B3LYP, LC-BLYP, M05-2X, and M06-2X. M05-2X provides results in quantitative agreement with CCSD(T), with deviations on β_{HRS} , β_j and DR smaller than 7%, while the MAEs obtained with the other three functionals are a bit larger, from 10% (LC-BLYP) to 17%, (CAM-B3LYP). Most DFT approaches, including M05-2X, overestimate $\beta_{j=3}$ and underestimate $\beta_{j=1}$. On the other hand, like M06, those functionals overestimating $\beta_{j=1}$ give also much larger values for $\beta_{j=3}$ and β_{HRS} . With the exception of the best functionals, like M05-2X, pure and hybrid DFT does not perform better than the HF method, whereas double hybrid DFT does not improve over MP2, except for β_{HRS} as a result of error cancellation.

The same conclusions hold when considering solvent effects, the $\beta_{\text{LIQ}}/\beta_{\text{GAS}}$ and $\text{DR}_{\text{LIQ}}/\text{DR}_{\text{GAS}}$ ratios being best reproduced (within 10–15%) by the M05-2X functional. So, with the exception of BHandHLYP, the $\beta_{\text{LIQ}}/\beta_{\text{GAS}}$ ratio amounts to 2.2 ± 0.2 , which is about 50% smaller than for acetonitrile, a more dipolar molecule. Still, the solvent effects are larger for $\beta_{j=1}$ than for $\beta_{j=3}$, which reinforces the dipolar character.

3.3. Trichloroacetonitrile. The results obtained for the trichloroacetonitrile in gas phase and in solution are reported in Table S5a,b, Supporting Information, respectively. Owing to its ρ value close to unity, as determined at the CCSD(T) level of approximation, this molecule presents similar amounts of dipolar and octupolar character, though the balance is slightly in favor of the latter. As a result, in addition to the total β_{HRS} value, a key parameter to assess the reliability of the method is ρ . All XC functionals except M06-HF represent an improvement over HF by predicting the slightly dominant octupolar character of the molecule, as characterized by the ρ value of 1.19 at the CCSD(T) level. However, most of the functionals give rise to large deviations (generally, overestimations larger than 20%) on at least one of the β_j quantities or on their sum. Only four XC functionals, namely BHandHLYP, M05-2X, and the double hybrids B2PLYP and mPW2-PLYP, provide gas-phase β responses in good agreement with CCSD(T), the largest relative error being equal to 17%. $\text{CCl}_3\text{-CN}$ is therefore a nice example where double hybrid DFT performs better than MP2, which underestimates $\beta_{j=3}$ and β_{HRS} . MPW1K and M06-2X also perform qualitatively well (with deviations not exceeding 24%), while the errors obtained on $\beta_{j=1}$ and DR with LC-BLYP are slightly larger, these quantities being underestimated by 28% and 24%, respectively.

The substantial enhancement of the anisotropy factor observed at the CCSD(T) level, corresponding to a large enhancement of the octupolar character, when accounting for solvent ($\rho = 24$) is not completely reproduced at the DFT level, since most of the functionals overestimate the $\beta_{j=1}$ contribution. This is however not the case for B98 as well as for all the long-range corrected functionals CAM-B3LYP, LC-BLYP, ωB97X , and $\omega\text{B97X-D}$, which on the contrary underestimate the dipolar component from 16–87%. Note that the β_{HRS} solvent enhancements are similar to those found in CH_2Cl_2 , but contrary to CH_2Cl_2 , they are larger for $\beta_{j=3}$ than for $\beta_{j=1}$, highlighting the complexity of deciphering these surroundings effects.

3.4. Chloroform. The results obtained for chloroform are reported in Tables S6a,b, Supporting Information. BHandHLYP, LC-BLYP, M05-2X, M06-2X, M06-HF, MPW1K as well as the double hybrids XC functionals B2-PLYP and mPW2-PLYP provide gas-phase β_{HRS} values in agreement with CCSD(T) to within 20%, while all XC functionals predict a value of 1.50 for the depolarization ratio, consistent with the effective octupolar symmetry of the molecule.

The dominant octupolar character is also evidenced by the large values of the anisotropy parameter ($\rho = 24$ at the CCSD(T) level). However, a large dispersion is found in the ρ values, which range between 10 and 244 for our selection of XC functionals, due to large relative deviations on the $\beta_{j=1}$ values. [Still, on an absolute scale the $\beta_{j=1}$ amplitudes deviate by less than 2.5 au with respect to the CCSD(T) results.] The best agreement with the reference values for the $\beta_{j=1}$ contribution is obtained using MPW1K and M05-2X, yet they provide values underestimated by 28% and 21%, respectively. Overall, apart from the six functionals mentioned above, DFT does not perform better than HF. One also notes that the double hybrids provide results closer to CCSD(T) than MP2 for the total HRS response and the dominant octupolar component, but neither for $\beta_{j=1}$ nor for ρ .

When accounting for the solvent effects, β_{HRS} is exalted by a factor of 2. The octupolar character becomes less dominant, as indicated by the larger values of DR (about 20% larger than in

Table 1. Best DFT XC Functionals for Evaluating the HRS Responses of Each Compound, Identified Following the Criteria Defined in the Text^a

best XC functionals	LC-BLYP	M05-2X	M06-2X
CH₃–CN			
BLYP ^b	β_{HRS} : 6%, –7%	β_{HRS} : –13%, –1%	β_{HRS} : –21%, –13%
B3LYP ^c	$\beta_{j=1}$: 2%, –8%	$\beta_{j=1}$: –22%, –13%	$\beta_{j=1}$: –25%, –14%
CAM-B3LYP	$\beta_{j=3}$: 19%, +7%	$\beta_{j=3}$: 11%, +4%	$\beta_{j=3}$: –8%, –4%
BMK, TPSSH ^d	DR: –12%, –8%	DR: –25%, –9%	DR: –16%, –6%
CH₂–Cl₂			
CAM-B3LYP ^e	β_{HRS} : –8%, –15%	β_{HRS} : 5%, 1%	β_{HRS} : 11%, 4%
ω B97X ^f	$\beta_{j=1}$: –17%, –25%	$\beta_{j=1}$: –5%, –11%	$\beta_{j=1}$: –10%, –15%
mPW2-PLYP ^g	$\beta_{j=3}$: –6%, –5%	$\beta_{j=3}$: 7%, 11%	$\beta_{j=3}$: 16%, 20%
	DR: –6%, –16%	DR: –5%, –15%	DR: –9%, –22%
CCl₃–CN^h			
BHandHLYP ⁱ	β_{HRS} : –16%, –6%	β_{HRS} : 10%, 13%	β_{HRS} : 21%, 20%
MPW1K ^{h,i}	$\beta_{j=1}$: –28%, –55%	$\beta_{j=1}$: 10%, 157%	$\beta_{j=1}$: 21%, 330%
B2PLYP, ⁱ	$\beta_{j=3}$: 0%, –6%	$\beta_{j=3}$: 12%, 12%	$\beta_{j=3}$: 20%, 17%
mPW2-PLYP ⁱ	DR: –24%, –1%	DR: –1%, 2%	DR: 1%, 6%
CHCl₃			
BHandHLYP ^{j,l}	β_{HRS} : –1%, –4%	β_{HRS} : 7%, 7%	β_{HRS} : 14%, 16%
M06-HF, ^{k,m}	$\beta_{j=1}$: –53%, –25%	$\beta_{j=1}$: –21%, –11%	$\beta_{j=1}$: 55%, 1%
MPW1K ^j	$\beta_{j=3}$: 0%, –1%	$\beta_{j=3}$: 7%, 10%	$\beta_{j=3}$: 14%, 18%
B2-PLYP, ^{j,l} mPW2-PLYP ^{j,l}	DR: 18%, –7%	DR: 12%, –5%	DR: 28%, –4%
CCl₄			
BHandHLYP	β_{HRS} : 9%, 8%	β_{HRS} : 10%, 13%	β_{HRS} : 19%, 23%
MPW1K	$\beta_{j=3}$: 10%, 8%	$\beta_{j=3}$: 11%, 13%	$\beta_{j=3}$: 20%, 23%
B2-PLYP, mPW2-PLYP			

^aErrors relative to CCSD(T) results (in the gas phase, in solution) are reported explicitly in the case of LC-BLYP, M05-2X, and M06-2X. In the first column, unless otherwise specified, the deviations are less than 20%. ^b22% on the LIQ/GAS ratio for β_{HRS} and $\beta_{j=1}$. ^c21% on the LIQ/GAS ratio for $\beta_{j=1}$. ^d26% and 31% on the LIQ/GAS ratio for β_{HRS} and $\beta_{j=1}$. ^e21% on $\beta_{j=3}$, ^f22% on $\beta_{j=1}$, ^g22% on $\beta_{j=3}$, ^h23% on $\beta_{j=3}$. ⁱLarge overestimations (from 60% to 234%) of the LIQ/GAS ratio for $\beta_{j=1}$. ^jLarge underestimations (from –28% to –89%) of $\beta_{j=1}$. ^k137% on $\beta_{j=1}$. ^lLarge overestimations (>450%) of the LIQ/GAS ratio for $\beta_{j=1}$. ^m–69% on the LIQ/GAS ratio for $\beta_{j=1}$.

gas phase) and the smaller values of the anisotropy factor [around 4 at the CCSD(T) level, which corresponds to a reduction by a factor of 6 with respect to the gas-phase value]. These features are well reproduced at the DFT level, whatever the choice of the functional. The LIQ/GAS ratios for the β_{HRS} , $\beta_{j=3}$ and DR quantities are overall well reproduced, while the solvent effects on $\beta_{j=1}$ are better described when using MPW1K or M05-2X.

3.5. Carbon Tetrachloride. The NLO properties calculated for the CCl₄ molecule are gathered in Tables S7a,b, Supporting Information. All XC functionals provide DR values of 1.5 and negligibly small ρ values, consistent with the pure octupolar character of the molecule. Among the functionals considered, B2-PLYP, BHandHLYP, LC-BLYP, M05-2X, M06-2X, MPW1K, and mPW2-PLYP reproduce the CCSD(T) results for β_{HRS} and $\beta_{j=3}$ to within less than 20% of error (the error on $\beta_{j=1}$ is not considered here since it is not significant). These functionals perform better than the HF and MP2 methods. Note that the nonzero $\beta_{j=1}$ values are evidence of the limitations of the numerical integration (grid) or finite difference derivatives (FF).

These seven best functionals also provide results in good agreement with CCSD(T) regarding the β_{HRS} and $\beta_{j=3}$ responses of solvated molecules, while the $\beta_{\text{LIQ}}/\beta_{\text{GAS}}$ ratios are well reproduced by the whole series of functionals. In this

case, the $\beta_{\text{LIQ}}/\beta_{\text{GAS}}$ ratio is close to 1.5, no matter which method is employed.

4. Further Discussions and Conclusions. The reliability of various DFT XC functionals to predict the HRS responses of a series of small molecules has been assessed with respect to reference CCSD(T) calculations. The total HRS first hyperpolarizability, β_{HRS} , the dipolar and octupolar contributions, $\beta_{j=1}$ and $\beta_{j=3}$, as well as the associated depolarization and anisotropy ratios have been considered. For each compound, Table 1 lists the XC functionals providing the best agreement with the CCSD(T) results, following two performance criteria: (i) the deviation on each of the β_{HRS} , $\beta_{j=1}$, $\beta_{j=3}$, DR, and ρ quantities, calculated for the isolated (gas phase) molecule, must be smaller than 20%, and (ii) the deviation on the solvent-induced enhancement of each of these properties, as measured by the LIQ/GAS ratios, must also be smaller than 20%.

Table 1 shows that none of the XC functionals meets the performance criteria for the five compounds. As a representative example, the popular B3LYP functional satisfactorily describes the NLO responses of the acetonitrile molecule, which presents a quasi-pure dipolar character, while it fails reproducing the CCSD(T) β values of the other compounds. The long-range correction in CAM-B3LYP significantly improves the β values of CCl₃–CN and CH₂Cl₂ but still fails to describe the NLO properties of CHCl₃ and CCl₄ for which

the octupolar contribution dominates. In contrast, the double hybrids XC functionals B2-PLYP and mPW2-PLYP describe well the NLO responses of the three scatterers having the most pronounced octupolar symmetry but do not perform well for the most dipolar ones. Within the series of XC functionals considered in this study, the best balance for describing the quadratic NLO responses of both dipolar and octupolar scatterers appears to be LC-BLYP, despite it leads to a quite large underestimation for the dipolar contribution of the $\text{CCl}_3\text{—CN}$ compound. The Minnesota functionals M05-2X and M06-2X also provide results in good agreement with CCSD(T) for $\text{CCl}_3\text{—CN}$, CH_2Cl_2 , CHCl_3 , and CCl_4 . However, they provide slightly larger deviations regarding the gas phase β values of acetonitrile.

Though drawing general conclusions on the XC requirements to predict accurate first hyperpolarizabilities for small molecules scanning the dipolar/octupolar range is difficult, several comments can be written: (i) The best functionals include substantial amounts of HF exchange; (ii) They are either hybrid functionals presenting good performance to describe transition states of chemical reactions or long-range corrected hybrids suitable to describe qualitatively the evolution of β in extended systems; (iii) The pure and hybrid functionals do not always perform better than the HF method (cf., CH_2Cl_2 and CHCl_3), whereas for dichloromethane, chloroform, and acetonitrile, the MP2 method is as good if not better than the double hybrid approaches.

These general conclusions can be compared to those of recent related studies, either on push–pull π -conjugated or on clusters. So, ref 39b recommended the M05-2X XC functional as a practical approach to predict relative β values. This approach, which enables the design of new NLO push–pull π -conjugated compounds, was later extended by Lu et al.,^{6e} who accounted for solvent effects by resorting to the PCM scheme and who highlighted the good performance of both hybrids GGA with a content of HF exchange larger than 40% or of the long-range corrected hybrids. On the other hand, for doped Si clusters, ref 2b showed the improved performance of hybrid GGA with 20–25% HF exchange over hybrids GGA with larger percentage of HF exchange or long-range corrected hybrids, demonstrating the strong system dependence of the XC functional performance when focusing on hyperpolarizabilities.

To conclude, these calculations allow identifying the most suitable DFT functionals to be used in the computation of the quadratic NLO responses of selected compounds. Future work will address the NLO properties of molecular aggregates by coupling CP-KS calculations with molecular dynamics, in order to probe more precisely the impact of local interactions with the surrounding molecules as well as the coherent contributions in the measured HRS intensities.

■ ASSOCIATED CONTENT

■ Supporting Information

Convergence behavior of the NLO responses with respect to the basis set using the LC-BLYP and M06-2X XC functionals (Table S1, Figure S1); NLO properties calculated at the LC-BLYP/d-aug-cc-pVTZ and M06-2X/d-aug-cc-pVTZ levels using different integration point grids (Tables S2a and S2b); NLO properties calculated in gas phase and in solution using the various XC functionals (Tables S3a to S7b); and MAEs and maximal errors relative to CCSD(T) results (Tables S8a and S8b). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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