Comparison of Property-Oriented Basis Sets for the Computation of Electronic and Nuclear Relaxation Hyperpolarizabilities

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S *Supporting Information*

ABSTRACT: In the present work, we perform an assessment of several property-oriented atomic basis sets in computing (hyper)-polarizabilities with a focus on the vibrational contributions. Our analysis encompasses the Pol and LPol-ds basis sets of Sadlej and co-workers, the def2-SVPD and def2-TZVPD basis sets of Rappoport and Furche, and the ORP basis set of Baranowska-Łączkowska and Łączkowski. Additionally, we use the d-*aug*-cc-pVQZ and *aug*-cc-pVTZ basis sets of Dunning and co-workers to determine the reference estimates of the investigated electric properties for small- and medium-sized molecules, respectively. We combine these basis sets with *ab initio* post-Hartree–Fock quantum-chemistry approaches (including the coupled cluster method) to calculate electronic and nuclear relaxation (hyper)polarizabilities of carbon dioxide, formaldehyde, *cis*-diazene, and a medium-sized Schiff base. The primary finding of our study is that, among all studied property-oriented basis sets, only the def2-TZVPD and ORP basis sets yield nuclear relaxation (hyper)polarizabilities of small molecules with average absolute errors less than 5.5%. A similar accuracy for the nuclear relaxation (hyper)polarizabilites of the studied systems can also be reached using the *aug*-cc-pVDZ basis set (5.3%), although for more accurate calculations of vibrational contributions, i.e., average absolute errors less than 1%, the *aug*-cc-pVTZ basis set is recommended. It was also demonstrated that anharmonic contributions to first and second hyperpolarizabilities of a medium-sized Schiff base are particularly difficult to accurately predict at the correlated level using property-oriented basis sets. For instance, the value of the nuclear relaxation first hyperpolarizability computed at the MP2/def2-TZVPD level of theory is roughly 3 times larger than that determined using the *aug*-cc-pVTZ basis set. We link the failure of the def2-TZVPD basis set with the difficulties in predicting the first-order field-induced coordinates. On the other hand, the *aug*-cc-pVDZ and ORP basis sets overestimate the property in question only by roughly 30%. In this study, we also propose a low-cost composite treatment of anharmonicity that relies on the combination of two basis sets, i.e., a large-sized basis set is employed to determine lowest-order derivatives with respect to the field-induced coordinates, and a medium-sized basis set is used to compute the higher-order derivatives. The results of calculations performed at the MP2 level of theory demonstrate that this approximate scheme is very successful at predicting nuclear relaxation hyperpolarizabilities.
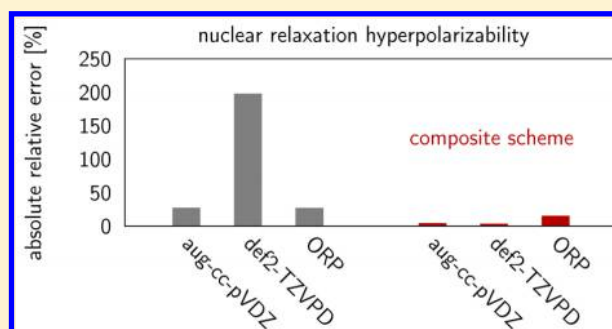
■ INTRODUCTION

First-principle predictions of molecular electric properties may be, in general, an alternative to the complicated and expensive experimental measurements. However, it is required that the quantum-chemical calculations of the properties in question are carried out using state-of-the-art *ab initio* methods. Provided that the basis set is selected adequately, for small- and medium-sized systems, reliable estimates can be delivered by coupled cluster-based methods, in particular, the single and double excitation coupled cluster method (CCSD), preferably with inclusion of triple excitations, e.g., through a noniterative perturbational

treatment (CCSD(T)). The augmented correlation consistent basis sets of Dunning and co-workers (n-*aug*-cc-pVXZ)[1−3] combined with post-Hartree–Fock methods is a common and successful route to determine electric properties. Whenever large organic systems are investigated, the need to employ accurate and computationally expensive methods and large basis sets is opposed by the necessity of reducing the total cost of the calculations. To decrease the computational costs in such cases,

we can use either smaller size property-oriented basis sets together with highly accurate methods or less accurate methods with large basis sets. Both of these approaches have advantages and disadvantages, which are widely reported in the literature (for an exhaustive survey, we refer to ref 4).

There are several families of basis sets tailored for the accurate determination of electric-dipole properties. The Pol family of polarized basis sets developed over the years by Sadlej and co-workers was originated from the model of a harmonic oscillator in a static electric field,[5] and it has been generalized in recent years to the case of a time-dependent electric field.[6] Similarity between the solutions of the Schrödinger equation and Gaussian-type functions led to the idea of adding optimized first-order polarization functions to a previously known and carefully selected set of core and valence orbitals, yielding the Pol basis set. Over the years, the traditional Pol basis set has been shown to be competitive with respect to larger all-purpose basis sets in the evaluation of electric properties despite its relatively small size. A decade ago, the traditional medium-size Pol basis set underwent a substantial reduction, yielding the small and compact ZPol set,[7] dedicated to the evaluation of dipole moments and polarizabilities of noninteracting molecules. The ZPol set has proven to be a very efficient tool for evaluating molecular electric dipole polarizabilities: see, for instance, the work of Kowalski et al. on the polarizability of fullerene C_{60}.[8] Obviously, the compactness of the ZPol set hampers its application to accurate descriptions of nonlinear electric properties.[9] Another group of polarized sets of the Pol family is the larger and more flexible LPol-n sets developed for evaluating nonlinear and interaction-induced electric properties.[10] Our recent investigations have shown that the LPol-n sets often outperform the larger augmented correlation consistent polarized basis sets of Dunning and co-workers in the evaluation of linear and nonlinear electric properties of isolated molecules[9,11,12] and hydrogen-bonded complexes.[13,14] In particular, the smallest in the LPol-n family, the LPol-ds basis set, yields values of electric properties of noninteracting systems of comparable quality to those delivered by the *aug*-cc-pVTZ basis set, where the former is approximately 20% smaller than the latter. There is also a promising family of electric property-oriented basis sets proposed by Rappoport and Furche.[15] These sets were developed from the Karlsruhe segmented contracted basis sets of split-valence to quadruple-ζ valence quality[16] primarily for the evaluation of linear electric properties. The very small size of the Rappoport and Furche SVPD and TZVPD basis sets makes them well suited for studies of electric-dipole properties of large systems. It has been only quite recently that the optical rotation prediction (ORP) basis set has been developed by some of the present authors for the investigation of the specific rotation of organic molecules.[17] The ORP basis set is derived from the VTZ basis set of Ahlrichs et al.,[18] augmented with one diffuse s-type and one diffuse p-type function. The size of the ORP basis set is very close to that of the LPol-ds basis set; however, it was found to be more resistant to the occurrence of linear dependencies in the molecular basis set. Contrary to the Pol family, the ORP set does not utilize the model of a harmonic oscillator in an external electric field. Instead, it contains three uncontracted first-order polarization functions whose orbital exponent values were chosen from a large set of tested exponents as those that minimize the differences between the finite field (FF) restricted open-shell Hartree−Fock (ROHF) atomic polarizability values and the accurate reference values reported by Stiehler and Hinze.[19] The ORP basis set has been recently employed in MP2, CCSD, and

CCSD(T) calculations of induced electric dipole moments, polarizabilities, and hyperpolarizabilities in test hydrogen-bonded complexes, and it has been shown to yield results very close to those obtained using the LPol-ds and LPol-dl basis sets.[20] Finally, it should be mentioned that extensive basis set assessments for property calculations of small systems were performed by Maroulis and collaborators.[21−24]

The development of property-oriented basis sets, outlined in the preceding paragraph, was performed with a focus only on the purely electronic (hyper)polarizabilities. Likewise, most of the benchmark studies regarding the performance of the basis sets in calculations of electric properties were performed solely for the electronic counterpart. Although the choice of basis set is crucial for reliable predictions of geometry and vibrational structure in the case of post-Hartree−Fock methods,[25,26] the influence of the basis set on vibrational hyperpolarizabilities has been scarcely studied.[27,28] Despite new developments regarding the treatment of electric properties, including effects of molecular vibrations,[29−37] a systematic study of the performance of property-oriented basis sets in computations of vibrational (hyper)-polarizabilities including anharmonicity is still lacking. In an attempt to fill this gap, in the present work we investigate electric properties (electronic and vibrational) using the property-oriented Pol and LPol-ds basis sets of Sadlej and co-workers,[10,38] the def2-SVPD and def2-TZVPD sets of Rappoport and Furche,[15] and the ORP basis set reported recently by Baranowska-Łączkowska and Łączkowski.[17] Additionally, we use the *aug*-cc-pVXZ and d-*aug*-cc-pVXZ (X = D, T, Q) basis sets of Dunning and co-workers.[1−3] We combine these basis sets with the second-order Møller and Plesset perturbation theory (MP2) approach and CCSD(T) method to evaluate the diagonal components of the static electronic dipole polarizability and first and second hyperpolarizabilities. In order to determine the vibrational counterpart of the first and second hyperpolarizabilities, including anharmonic contributions, we employ the MP2 and CCSD methods. Carbon dioxide, formaldehyde, *cis*-diazene, and a photochromic Schiff base (2-((methylimino)-methyl)phenol, cf. Figure 1) have been chosen as model
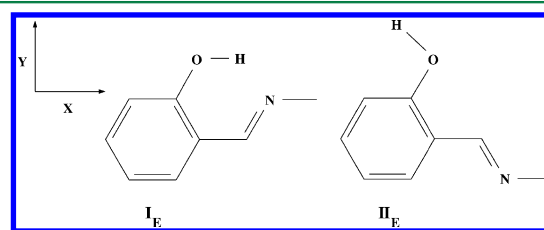
Figure 1. Photochromic Schiff base studied in this work and its orientation in the Cartesian coordinate system.

systems for the basis set assessment. Electric properties of carbon dioxide and formaldehyde have already been studied extensively by other authors.[39−51] In the case of the Schiff base, the two most stable structures correspond to Z and E conformers, and we refer to these structures as I_E and II_E, respectively. Due to the presence of a hydrogen bond between the hydroxyl group and the nitrogen atom, the former is much more rigid than the latter; thus, significantly different vibrational properties can be expected for these two systems. Consequently, we consider the I_E and II_E conformers to be suitable medium-sized test structures to assess the performance of the basis set in vibrational (hyper)-polarizability calculations.

■ COMPUTATIONAL DETAILS

In the presence of an external electric field (F), the Cartesian component of the total dipole moment μ_i may be expressed as a Taylor series[52]

$$\mu_i(\omega_\sigma) = \mu_i^0 \delta_{\omega_\sigma,0} + \sum_j \alpha_{ij}(-\omega_\sigma;\omega_1)F_j(\omega_1)$$

$$+ \frac{1}{2!}K^{(2)}\sum_{jk}\beta_{ijk}(-\omega_\sigma;\omega_1,\omega_2)F_j(\omega_1)F_k(\omega_2)$$

$$+ \frac{1}{3!}K^{(3)}\sum_{jkl}\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)F_j(\omega_1)F_k(\omega_2)F_l(\omega_3) + \ldots$$

$$(1)$$

where μ_i^0 is the ith component of the permanent dipole moment; α_{ij}, β_{ijk}, and γ_{ijkl} are the components of the polarizability and first and second hyperpolarizability tensors, respectively. ω_σ is the sum of the external field frequencies ω_i, and $K^{(2)}$ and $K^{(3)}$ are factors ensuring that all hyperpolarizabilities of the same order have the same static limit. Within the Born−Oppenheimer (BO) approximation, the molecular (non)linear optical properties defined by eq 1 may be separated into pure electronic (P^{el}) and pure vibrational (P^v) contributions as well as the zero-point vibrational averaging (ZPVA) correction[53]

$$P = P^{el} + P^{v} + P^{ZPVA} \qquad (2)$$

where $P = \alpha, \beta, \gamma$. Alternatively, one can divide the property P into electronic, nuclear relaxation (P^{nr}), and curvature (P^{curv}) contributions[53]

$$P = P^{el} + P^{nr} + P^{curv} \qquad (3)$$

In the present study, we rely on the latter separation and focus on the nuclear relaxation contribution to hyperpolarizabilities. The P^{nr} terms are usually larger than P^{curv} terms. In order to treat the effect of molecular vibration on electric properties, Bishop and Kirtman proposed a double (electrical and mechanical) perturbation theory (BKPT) treatment.[54] The P^{nr} contributions are given by leading terms of each type of "square bracket" terms of the BKPT pure vibrational contributions. Within this approach, the nuclear relaxation first and second hyperpolarizabilities may be expressed in square bracket notation as

$$\beta^{nr} = [\mu\alpha]^{(0,0)} + [\mu^3]^{(1,0)} + [\mu^3]^{(0,1)} \qquad (4)$$

$$\gamma^{nr} = [\alpha^2]^{(0,0)} + [\mu\beta]^{(0,0)} + [\mu^2\alpha]^{(1,0)} + [\mu^2\alpha]^{(0,1)}$$
$$+ [\mu^4]^{(2,0)} + [\mu^4]^{(0,2)} + [\mu^4]^{(1,1)} \qquad (5)$$

Each square bracket involves products of normal coordinate derivatives of the indicated electronic electrical properties, as well as harmonic vibrational frequencies and anharmonic force constants. Each term is identified by a pair of superscripts (n, m) denoting the order of electrical and mechanical anharmonicities, respectively.

In the present study, we use the finite-field nuclear relaxation method (FF-NR)[55,56] to determine the nuclear relaxation second hyperpolarizability, whereas the field-induced coordinates (FICs) approach is used[57,58] to determine the nuclear relaxation first hyperpolarizability as well as some terms contributing to the nuclear relaxation second hyperpolarizability. FICs are linear combinations of field-free normal coordinates associated with the change in equilibrium geometry induced by a static electric field. The displacement of the ith field-free normal coordinate at the field-relaxed geometry is given by[57]

$$Q_i^F(F_x,F_y,F_z) = -\sum_a^{x,y,z} q_1^{i,a}F_a - \sum_{a,b}^{x,y,z}\left[q_2^{i,ab} - \sum_{j=1}^{3N-6}\frac{a_{21}^{ij,a}}{a_{20}^{ii}}q_1^{i,b}\right.$$

$$\left. + \sum_{j,k=1}^{3N-6}\frac{3a_{30}^{ijk}}{2a_{20}^{ii}}q_1^{j,a}q_1^{k,b}\right]F_aF_b + \ldots$$

$$(6)$$

where

$$a_{nm}^{ij\ldots ab\ldots} = \frac{1}{n!m!}\left(\frac{\partial^{(n+m)}V(Q_1,\ldots,Q_{3N-6},F_x,F_y,F_z)}{\partial Q_i\partial Q_j\cdots\partial F_a\partial F_b\cdots}\right)_{Q=0,F=0}$$

$$(7)$$

and

$$q_1^{i,a} = \frac{a_{11}^{i,a}}{2a_{20}^{ii}}, \qquad q_2^{i,ab} = \frac{a_{12}^{i,ab}}{2a_{20}^{ii}} \qquad (8)$$

The indices i, j, k refer to normal coordinates, whereas a, b, c label the Cartesian directions along the molecular axes. $a_{nm}^{ij\ldots ab\ldots}$ involves the nth and mth derivatives of the potential energy $V(Q,F)$ with respect to normal coordinates and field components, respectively. The first-order FICs

$$\chi_1^a = -\sum_{i=1}^{3N-6}q_1^{i,a}Q_i \qquad (9)$$

are sufficient to compute the static nuclear relaxation's contribution to the first hyperpolarizability[57]

$$\beta_{abc}^{nr}(0;0,0) = \sum_{i=1}P_{abc}a_{12}^{i,ab}q_1^{i,c} - \sum_{i,j=1}P_{abc}a_{21}^{ij,a}q_1^{i,b}q_1^{j,c}$$

$$+ \sum_{i,j,k=1}P_{abc}a_{30}^{ijk}q_1^{i,a}q_1^{j,b}q_1^{k,c}$$

$$(10)$$

whereas the second-order FICs

$$\chi_2^{ab} = -\sum_{i=1}^{3N-6}\left(q_2^{i,ab} - \sum_{j=1}^{3N-6}\frac{a_{21}^{ij,a}}{a_{20}^{ii}}q_1^{j,b} + \sum_{j,k=1}^{3N-6}\frac{3a_{30}^{ijk}}{2a_{20}^{ii}}q_1^{j,a}q_1^{k,b}\right)Q_i$$

$$(11)$$

are necessary to determine the static nuclear relaxation second hyperpolarizability

$$\gamma_{abcd}^{nr}(0;0,0,0) = \sum_{i=1}P_{abcd}\left(a_{13}^{i,abc}q_1^{i,d} + \frac{a_{12}^{i,ab}}{2}q_2^{i,cd}\right)$$

$$- \sum_{i,j=1}P_{abcd}(a_{22}^{ij,ab}q_1^{i,c}q_1^{j,d} + 2a_{21}^{ij,a}q_1^{i,b}q_2^{j,cd})$$

$$+ \sum_{i,j,k=1}P_{abcd}\left(3a_{30}^{ijk}q_1^{i,a}q_1^{j,b}q_2^{k,cd} + a_{31}^{ijk,a}q_1^{i,b}q_1^{j,c}q_1^{k,d}\right.$$

$$\left. + \frac{a_{21}^{ij,a}a_{21}^{jk,b}}{a_{20}^{jj}}q_1^{i,c}q_1^{k,d}\right) - \sum_{i,j,k,l=1}P_{abcd}\left(a_{40}^{ijkl}q_1^{i,a}q_1^{j,b}q_1^{k,c}q_1^{l,d}\right.$$

$$+ \frac{3a_{30}^{ijk}a_{21}^{kl,a}}{a_{20}^{kk}}q_1^{i,b}q_1^{j,c}q_1^{l,d}\right)$$

$$+ \sum_{i,j,k,l,m=1}P_{abcd}\left(\frac{9}{4}\frac{a_{30}^{ijk}a_{30}^{klm}}{a_{20}^{kk}}q_1^{i,a}q_1^{j,b}q_1^{l,c}q_1^{m,d}\right)$$

$$(12)$$

$\sum P_{ab\ldots}$ indicates the sum over all permutations of the indices a, b, ...

The electronic contributions to (hyper)polarizabilities were evaluated fully numerically based on the differentiation of the energy or dipole moment with respect to an external electric field

using the Rutishauser−Romberg procedure in order to remove contamination from higher-order derivatives.[59] In that event, we employed the field values $\pm 2^n F_0$, where $F_0 = 0.0004$ au and $n = 0$, 1, ..., 6. All electronic and vibrational structure calculations were performed with the GAUSSIAN suite of programs,[60] and property calculations were carried out using custom computer programs.

RESULTS AND DISCUSSION

This section is organized as follows. We start the analysis with the basis set assessment for diagonal electronic (hyper)-polarizabilities of carbon dioxide, formaldehyde, and *cis*-diazene. For these molecules, we further analyze the performance of the basis sets in evaluating diagonal nuclear relaxation (hyper)-polarizabilities. Following the same order, we then discuss these electrical properties for a medium-sized photochromic Schiff base. For convenience, the number of contracted basis functions in spherical harmonic representation for each basis set is shown in Table 1. For the molecules studied, the number of contracted

Table 1. Number of Contracted Basis Functions in Spherical Harmonic Representation for the Molecules Studied[a]

|	carbon dioxide	formaldehyde	diazene	Schiff base
def2-SVPD	66	59	56	275
def2-TZVPD	117	95	92	454
Pol	72	66	66	321
LPol-ds	108	98	98	477
ORP	96	90	90	437
aug-cc-pVDZ	69	64	64	311
d-*aug*-cc-pVDZ	96	90	90	437
aug-cc-pVTZ	138	138	138	667
d-*aug*-cc-pVTZ	186	188	188	908
aug-cc-pVQZ	240	252	252	1214
d-*aug*-cc-pVQZ	315	334	334	1608

[a]Note that def2-SVPD and def2-TZVPD basis sets have a different number of p-type functions for oxygen and carbon/nitrogen atoms.

basis functions in the case of def2-SVPD, *aug*-cc-pVDZ, and Pol is only about one-fifth that of d-*aug*-cc-pVQZ, whereas the number of contracted basis functions for ORP, d-*aug*-cc-pVDZ, LPol-ds, and def2-TZVPD is roughly one-third.

Carbon Dioxide, Formaldehyde, and *cis*-Diazene. We start the discussion with the assessment of property-oriented basis sets in the computation of diagonal electronic properties for carbon dioxide, formaldehyde, and *cis*-diazene. These molecules are oriented in the Cartesian coordinate system in such a way that the rotational principal axis with the highest moment of inertia is parallel to the Cartesian z axis. The electronic property calculations were performed using the CCSD(T) method for molecular geometries optimized at the MP2/*aug*-cc-pVQZ level of theory. The results of the calculations are shown in Figures 2−4 and in the Supporting Information (Tables S1−S3). CCSD(T)/d-*aug*-cc-pVQZ was chosen as the reference level of theory. The absolute relative error for the diagonal electronic polarizability is, for all of the employed basis sets and three molecules, smaller than 2.2%, except for the def2-SVPD value of *cis*-diazene, whose error is 4.7%. For carbon dioxide and formaldehyde, the largest errors are 2.2% for Pol and 1.6% for def2-SVPD basis sets, respectively. It should be highlighted that the errors associated with the application of Dunning's correlation-consistent basis sets of triple- and quadruple-ζ size are smaller than 0.6%, thus demonstrating very good convergence of the electronic polarizability. In the case of the
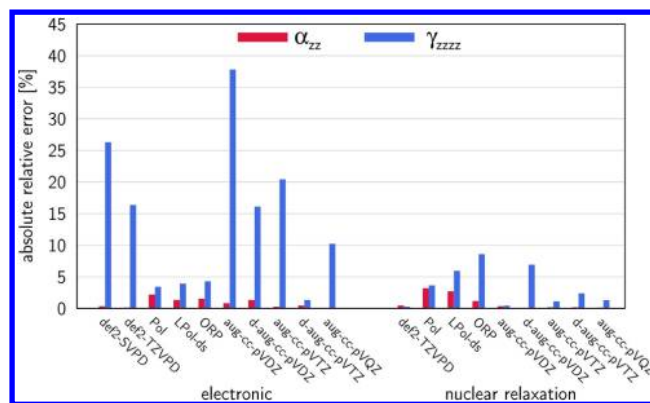
Figure 2. Absolute relative errors (%) of the diagonal property P computed at level L with respect to the reference R $(((P[L] - P[R])/P[R]) \times 100\%)$ for carbon dioxide. In the case of electronic properties, L = CCSD(T)/indicated basis set and R = CCSD(T)/d-*aug*-cc-pVQZ, whereas in the case of nuclear relaxation contributions, L = MP2/indicated basis set and R = MP2/d-*aug*-cc-pVQZ.
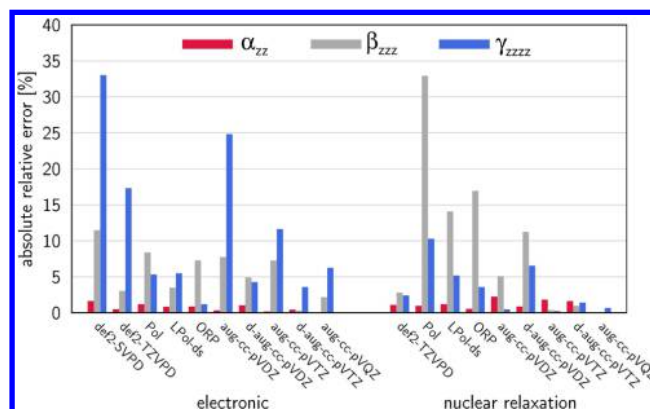
Figure 3. Absolute relative errors (%) of the diagonal property P computed at level L with respect to the reference R $(((P[L] - P[R])/P[R]) \times 100\%)$ for formaldehyde. In the case of electronic properties, L = CCSD(T)/indicated basis set and R = CCSD(T)/d-*aug*-cc-pVQZ, whereas in the case of nuclear relaxation contributions, L = MP2/indicated basis set and R = MP2/d-*aug*-cc-pVQZ.
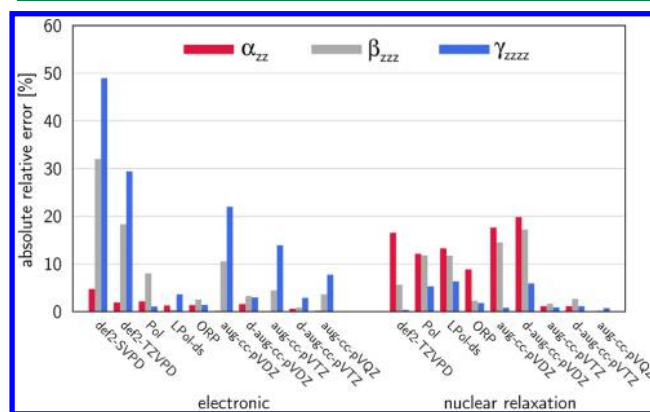
Figure 4. Absolute relative errors (%) of the diagonal property P computed at level L with respect to the reference R $(((P[L] - P[R])/P[R]) \times 100\%)$ for *cis*-diazene. In the case of electronic properties, L = CCSD(T)/indicated basis set and R = CCSD(T)/d-*aug*-cc-pVQZ, whereas in the case of nuclear relaxation contributions, L = MP2/indicated basis set and R = MP2/d-*aug*-cc-pVQZ.

electronic first hyperpolarizability, the relative errors are much larger, and they reach up to 32.0% in the case of the def2-SVPD

Table 2. Nuclear Relaxation (Hyper)polarizabilities of Formaldehyde, Carbon Dioxide, and Diazene (in au) Computed at the MP2 Level of Theory[a]

	$\bar{\alpha}^{nr}$	α_{zz}^{nr}	$\overline{[\mu\alpha]}^{(0,0)}$	$\overline{[\mu^3]}^{(1,0)}$	$\overline{[\mu^3]}^{(0,1)}$	$\bar{\beta}^{nr}$	β_{zzz}^{nr}	γ_{zzzz}^{nr}	α_{zz}^{nr}	γ_{zzzz}^{nr}
	H$_2$CO								CO$_2$	
def2-TZVPD	0.495	0.931	−1.68	−5.62	1.20	−6.10	−8.31	1567	2.697	1243
Pol	0.500	0.932	−4.38	−5.92	1.13	−9.17	−5.42	1770	2.623	1201
LPol-ds	0.505	0.952	−2.99	−5.96	1.20	−7.75	−6.94	1688	2.782	1320
ORP	0.503	0.947	−3.03	−5.88	1.21	−7.70	−6.71	1662	2.740	1353
aug-cc-pVDZ	0.500	0.921	−2.72	−5.79	1.13	−7.38	−8.49	1598	2.718	1251
d-*aug*-cc-pVDZ	0.504	0.933	−2.80	−5.89	1.13	−7.56	−7.17	1710	2.707	1332
aug-cc-pVTZ	0.491	(1.015) 0.924	−2.16	−5.59	1.18	−6.57	(−16.64) −8.11	(1296) 1602	(3.517) 2.714	(949) 1232
d-*aug*-cc-pVTZ	0.491	0.926	−1.91	−5.61	1.18	−6.34	−8.00	1627	2.704	1276
aug-cc-pVQZ	0.495	(1.033) 0.941	−2.03	−5.61	1.22	−6.42	(−16.68) −8.08	(1288) 1595	(3.507) 2.712	(950) 1230
d-*aug*-cc-pVQZ	0.494	0.940	−1.94	−5.60	1.21	−6.33	−8.08	1605	2.709	1246
	N$_2$H$_2$									
def2-TZVPD	0.271	0.106	−15.62	−1.80	−0.11	−17.53	−15.20	1242		
Pol	0.244	0.101	−16.30	−1.51	−0.11	−17.92	−16.09	1303		
LPol-ds	0.253	0.103	−16.60	−1.61	−0.11	−18.32	−16.09	1316		
ORP	0.237	0.083	−14.02	−1.37	−0.07	−15.46	−14.07	1216		
aug-cc-pVDZ	0.251	0.108	−16.50	−1.58	−0.12	−18.20	−16.48	1248		
d-*aug*-cc-pVDZ	0.254	0.109	−17.17	−1.62	−0.12	−18.91	−16.87	1311		
aug-cc-pVTZ	0.255	(0.092) 0.092	−15.10	−1.56	−0.09	−16.75	(−13.83) −14.63	(1061) 1227		
d-*aug*-cc-pVTZ	0.255	0.093	−15.39	−1.56	−0.09	−17.04	−14.78	1252		
aug-cc-pVQZ	0.258	(0.089) 0.091	−14.98	−1.57	−0.09	−16.64	(−13.40) −14.36	(1061) 1230		
d-*aug*-cc-pVQZ	0.258	0.091	−15.06	−1.57	−0.09	−16.72	−14.39	1238		

[a]Results in parentheses were obtained employing the CCSD wavefunction.

basis set for diazene. Likewise, the very same basis set delivers the largest error (11.5%) for the diagonal first hyperpolarizability of a formaldehyde molecule. The performance of other property-oriented basis sets for this property is system-dependent. However, on average, for the three smallest basis sets, Pol and *aug*-cc-pVDZ are clearly better choices than def2-SVPD. To obtain more accurate electronic first hyperpolarizabilities (errors smaller than 3.5%), LPol-ds is computationally the cheapest selection for formaldehyde and diazene. It also should be emphasized that the performance of the newly developed ORP basis set in the computation of first hyperpolarizability is similar to that of the *aug*-cc-pVTZ basis, although the former is far smaller than the latter. In the case of diagonal electronic second hyperpolarizability, there are large variations of relative errors among the employed basis sets. The performance of the def2-SVPD, *aug*-cc-pVDZ, and def2-TZVPD basis sets are far from being satisfactory, since they yield maximum errors equal to 48.9% (N$_2$H$_2$), 37.8% (CO$_2$), and 29.4% (N$_2$H$_2$), respectively. Considering the size of *aug*-cc-pVTZ, its reliability is also quite low, with a maximum error of 20.4% (CO$_2$). We note the excellent performance of the small-size Pol and medium-size ORP basis sets, which predict electronic second hyper-polarizabilities with relative errors not exceeding 5.3 and 4.3%, respectively. It should be highlighted that such accuracy is not offered even by the *aug*-cc-pVQZ basis set, for which the errors are in the range of 6.2% (formaldehyde) to 10.2% (carbon dioxide).

Due to the unsatisfactory performance of the def2-SVPD basis set in predicting electronic properties, we have not attempted to determine nuclear relaxation (hyper)polarizabilities employing the basis set in question. Computational results of these properties for carbon monoxide, formaldehyde, and *cis*-diazene are shown in Tables 2 and 3 and Figures 2−4. Determining the anharmonic contributions to vibrational properties is computa-tionally much more expensive than evaluating electronic

Table 3. Breakdown of Nuclear Relaxation Second Hyperpolarizability[a]

	$[\alpha^2]_{zzzz}^{(0,0)}$	$[\mu\beta]_{zzzz}^{(0,0)}$	γ_{zzzz}^{nr}
CO$_2$	(1070) 1247	(−523) −421	1246
H$_2$CO	772	629	1605
N$_2$H$_2$	894	190	1238

[a]All values are given in au and were obtained at the MP2/d-*aug*-cc-pVQZ level of theory. The values obtained at the CCSD/d-*aug*-cc-pVTZ level of theory by Naves et al.[51] are given in parentheses.

(hyper)polarizabilities. Thus, the MP2/d-*aug*-cc-pVQZ level of theory was chosen as the reference level. Judging by the convergence of the vibrational property with respect to the size of the basis set at the CCSD level (cf. Table 2), this choice is well-supported. Before we analyze the performance of property-oriented basis sets in predicting nuclear relaxation contributions, we first analyze the importance of anharmonicity for these molecules (cf. Tables 2 and 3). First, anharmonic contributions to the average first hyperpolarizability of diazene are found to be quite small (i.e., about 10%). On the contrary, the sum of first-order electrical and mechanical anharmonicity contributions to $\bar{\beta}$ prevails over harmonic term in the case of formaldehyde (i.e., about 70%). Note that for this molecule there are large variations in values of $\overline{[\mu\alpha]}^{(0,0)}$ determined using property-oriented basis sets. On the other hand, differences in anharmonic contributions are much less pronounced. In the case of diagonal second hyperpolarizability, judging by the differences between nuclear relaxation hyperpolarizability and the sum of harmonic terms, we conclude that the net anharmonic contribution is substantial only for carbon dioxide, i.e., 33.7% (CO$_2$), 12.7% (H$_2$CO), and 12.4% (N$_2$H$_2$). Note that there is also fair agreement with values for CO$_2$ reported by Naves et al.[51]

We will now discuss the contributions of the diagonal nuclear relaxation to the properties. In the case of polarizability, the

triple- and quadruple-ζ basis sets yield relative errors smaller than 2.2% for all three molecules. The errors associated with determining this property are quite small for carbon dioxide and formaldehyde, and they do not exceed 3.2% (Pol) and 2.0% (*aug*-cc-pVDZ), respectively. As far as the determination of α_{zz}^{nr} is concerned, the diazene molecule is particularly difficult. The errors found for the property-oriented basis sets span from 8.8% (ORP) to 16.5% (def2-TZVPD). However, *aug*-cc-pVDZ and d-*aug*-cc-pVDZ, which are Dunning's basis sets that are similar in size to the property-oriented basis sets, also performed poorly in the calculation of α_{zz}^{nr} of N_2H_2, leading to relative errors larger than 18%. *aug*-cc-pVTZ is the smallest basis set that is able to accurately reproduce the d-*aug*-cc-pVQZ α_{zz}^{nr} value for N_2H_2 (i.e., error smaller than 1.1%). Very large relative errors (32.9% for H_2CO) are also found in the case of the small Pol basis set for predicting the diagonal nuclear relaxation first hyperpolarizability (the error in the average property for the Pol basis set reaches up to 44.9%). Although the performance of the LPol-ds and ORP basis sets is not as poor, their relative errors for formaldehyde β_{zzz}^{nr} are still larger than 14.1%. Slightly smaller relative error values are found for the diagonal nuclear relaxation first hyperpolarizability of diazene computed using property-oriented basis sets, i.e., from 2.2% (ORP) to 11.8% (Pol). On the other hand, def2-TZVPD delivers quite satisfactory estimates for this property, and the associated error is 5.6 and 2.8% for diazene and formaldehyde, respectively. Predictions of the nuclear relaxation first hyperpolarizability using Dunning's triple- and quadruple-ζ basis sets are similar to what has been found for the nuclear relaxation polarizability, i.e., the errors are less than 2.7%. Contrary to β^{nr}, the diagonal nuclear relaxation second hyperpolarizability is much easier to predict, and the errors do not exceed 10.3%. The worst estimates of this property are delivered by Pol (10.3% for H_2CO), ORP (8.6% for CO_2), d-*aug*-cc-pVDZ (6.9% for CO_2), and LPol-ds (6.3% for N_2H_2). The satisfactory performance of the def2-TZVPD basis set, i.e., errors less than 2.4%, should not be overlooked. For very accurate predictions of nuclear relaxation contributions to α, β, and γ, we recommend Dunning's basis set of at least triple-ζ quality, as the *average* absolute relative error for three small molecules is less than 1%.

Medium-Sized Molecules: Photochromic Schiff Bases. We now turn to the assessment of property-oriented basis sets in calculating the electronic contributions to electrical properties for a medium-sized photochromic Schiff base molecule. The Supporting Information contains results from the calculations of the diagonal components of the static dipole polarizability and the first and second hyperpolarizabilities of conformers I_E and II_E computed at various levels of theory (RHF, MP2, CCSD, CCSD(T)). Note that due to high computational demands *aug*-cc-pVTZ is chosen as the reference at the CCSD(T) level and the CCSD(T)/*aug*-cc-pVTZ results are available only for the axial components of electric properties for structure I_E. A summary of this data is presented in Figure 5. The use of the def2-SVPD basis set leads to an error in the α_{xx} value equal to 3.1%. However, it should not be overlooked that the size of this basis set is exceptionally small. For all other basis sets, the CCSD(T) polarizability results indicate that the associated errors are well below 1.0%. It should be highlighted that the compact Pol basis set delivers very satisfactory results for this property (i.e., relative error equal to 0.1%). Accurate evaluation of electric dipole hyperpolarizabilities is more difficult. The use of the def2-SVPD basis set leads to an error equal to 5.1% for the first hyperpolarizability. Other basis sets are more successful in predicting this property, and the errors do not exceed 2.3%.
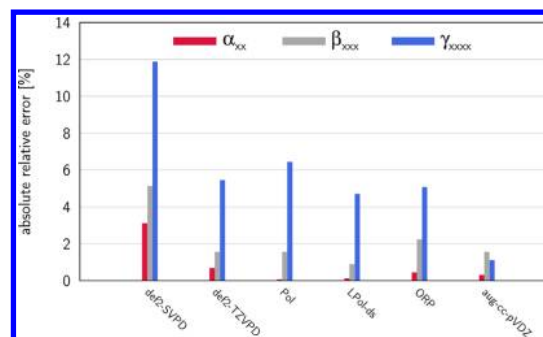
Figure 5. Absolute relative errors (%) for the diagonal electronic property P computed at level L with respect to the reference R ((($P[L]$ − $P[R])/P[R]) \times 100$%) for a Schiff base molecule (conformer I_E). All values correspond to geometry optimized at the CCSD/*aug*-cc-pVDZ level of theory in the orientation shown in Figure 1, with L = CCSD(T)/ indicated basis set and R = CCSD(T)/*aug*-cc-pVTZ.

In the case of the second hyperpolarizability, the errors increase up to 12% for the def2-SVPD basis set. Other property-oriented basis sets lead to relative errors for γ_{xxxx} in the range of 4.7−6.4%. It should be underscored that the small *aug*-cc-pVDZ basis set successfully competes with the property-oriented basis sets in calculating the first and second hyperpolarizabilities. For γ^e, *aug*-cc-pVDZ leads to the smallest relative error (1.1%); for β^e, however, very reasonable results can be obtained with *aug*-cc-pVDZ (1.6%), and the larger LPol-ds basis set can be recommended to improve the results (0.9%). It is interesting that, as is known, the dependence of the electronic contributions to electrical properties on the basis set decreases when the size of the molecule increases.[61]

Table 4 contains MP2 values of the vibrational contributions to the average static polarizability and first hyperpolarizability for

Table 4. Nuclear Relaxation Polarizability and the Breakdown of the Average Static First Hyperpolarizability into Anharmonicity Contributions[a]

	$\overline{\alpha}^{nr}$	$\overline{[\mu\alpha]}^{(0,0)}$	$\overline{[\mu^3]}^{(1,0)}$	$\overline{[\mu^3]}^{(0,1)}$	$\overline{\beta}^{nr}$
			Schiff Base I_E		
MP2/def2-TZVPD	11.2	−172	64	−42	−150
MP2/ORP	10.9	−171	44	−33	−160
MP2/*aug*-cc-pVDZ	11.0	−170	52	−36	−154
B3LYP/*aug*-cc-pVDZ	11.0	−221	41	−30	−210
B3LYP/*aug*-cc-pVTZ	11.0	−226	37	−34	−223
			Schiff Base II_E		
MP2/def2-TZVPD	40.7	451	766	−4166	−2949
MP2/ORP	32.4	383	289	−1931	−1259
MP2/*aug*-cc-pVDZ	28.1	335	217	−1273	−721
MP2/*aug*-cc-pVTZ	29.8	347	421	−1759	−991
B3LYP/*aug*-cc-pVDZ	23.3	406	272	−909	−231
B3LYP/*aug*-cc-pVTZ	25.2	428	402	−1309	−479

[a]All values are given in au. $\overline{\beta} = \sum_{i\in\{x,y,z\}}\mu_i\beta_i/\|\mu\|$; $\beta_i = (3/5)\sum_{j\in\{x,y,z\}}\beta_{ijj}$.

molecules I_E and II_E obtained using two property-oriented basis sets, namely, def2-TZVPD and ORP, together with the *aug*-cc-pVDZ and *aug*-cc-pVTZ results. Due to its size, the *aug*-cc-pVTZ basis set has been employed to determine anharmonic contributions only for molecule II_E. The results of calculations for small molecules further support the choice of this reference basis set, as the average absolute error in estimating nuclear relaxation contributions to α, β, and γ was found to be less than

1.0%. We have also validated the choice of the MP2 method to study nuclear relaxation hyperpolarizabilities by computing the dominant yzz component of β^{nr} for molecule $\mathbf{II_E}$ using the CCSD method. The corresponding values, determined using the aug-cc-pVDZ basis set, are -1.5×10^3 au (MP2) and -1.4×10^3 au (CCSD) and thus their agreement can be considered to be fully satisfactory. First, it can be seen that nuclear relaxation polarizability is much larger for $\mathbf{II_E}$ than it is for $\mathbf{I_E}$. Moreover, all three basis sets yield similar values of α^{nr} for $\mathbf{I_E}$, and the relative errors with respect to values from MP2/aug-cc-pVDZ do not exceed 1.9%. On the contrary, one finds large variations of this property in the case of $\mathbf{II_E}$, i.e., the relative absolute error with respect to the MP2/aug-cc-pVTZ reference spans from 5.7% (aug-cc-pVDZ) to 36.6% (def2-TZVPD). Likewise, a much larger nuclear relaxation first hyperpolarizability is found for $\mathbf{II_E}$ than for $\mathbf{I_E}$ (Table 4). The significant difference in the values of the vibrational polarizability and first hyperpolarizability can be understood in terms of the different flexibility of the two structures. As discussed below, the nuclear relaxation (hyper)polarizability is predominantly controlled by low-frequency modes. The absence of a hydrogen bond in structure $\mathbf{II_E}$ enables a large amplitude (low-frequency) out-of-plane vibration of the hydroxyl group, which brings about the dramatic increase in the contribution of the nuclear relaxation to the property component perpendicular to the molecular plane. It should not be overlooked that the double harmonic approximation works satisfactorily only for molecule $\mathbf{I_E}$, i.e., neglecting the mechanical anharmonicity for $\mathbf{II_E}$ yields the wrong sign of the average nuclear relaxation first hyperpolarizability. Figure 6 presents the relative
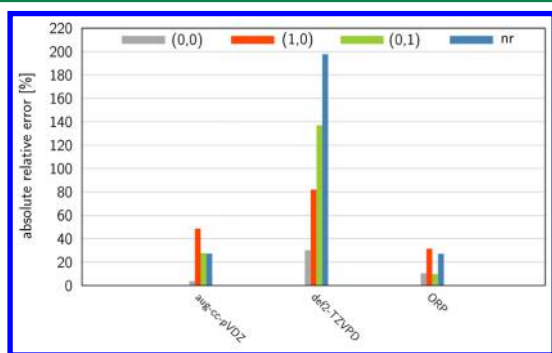
Figure 6. Absolute relative errors $((\overline{(\beta}\,[\text{MP2}] - \overline{\beta}\,[\text{MP2}/aug\text{-cc-pVTZ}])/\overline{\beta}\,[\text{MP2}/aug\text{-cc-pVTZ}]) \times 100\%)$ corresponding to harmonic $(\overline{[\mu\alpha]}^{(0,0)})$ and anharmonic $(\overline{[\mu^3]}^{(1,0)}, \overline{[\mu^3]}^{(0,1)})$ contributions to $\overline{\beta}^{nr}$ for $\mathbf{II_E}$.

errors of the contributions to the average first hyperpolarizability with respect to the MP2/aug-cc-pVTZ reference values for $\mathbf{II_E}$. It can be seen from Figure 6 that the best estimates of the nuclear relaxation first hyperpolarizability are predicted at the MP2/aug-cc-pVDZ and MP2/ORP levels of theory, with relative errors of 27.2 and 27.0%, respectively. We also studied the basis set convergence of the vibrational properties for $\mathbf{I_E}$ and $\mathbf{II_E}$ at the DFT level employing the B3LYP functional, and the results are presented in Table 4. We note that the absolute relative errors associated with the aug-cc-pVDZ basis set for $\mathbf{I_E}$ ($\mathbf{II_E}$) with respect to the B3LYP/aug-cc-pVTZ reference are less than 0.1% (7.5%) and 5.8% (51.8%) for α^{nr} and $\overline{\beta}^{nr}$, respectively. Similar to that at the MP2 level, the convergence of the $\overline{\beta}^{nr}$ values with respect to basis set extension is quite good for $\mathbf{I_E}$, whereas it is very poor for $\mathbf{II_E}$. Again, the key difference between $\mathbf{I_E}$ and $\mathbf{II_E}$ is

the role of the anharmonic contributions to $\overline{\beta}^{nr}$, which are negligible for the former and are the dominant term for the latter.

Finally, we note that, at the MP2 level of theory, significant errors in contributions to vibrational hyperpolarizability are found for the def2-TZVPD basis set. These are 30.0, 81.9, 136.8, and 197.6% for $\overline{[\mu\alpha]}^{(0,0)}$, $\overline{[\mu^3]}^{(1,0)}$, $\overline{[\mu^3]}^{(0,1)}$, and $\overline{\beta}^{nr}$, respectively. The large variations between nuclear relaxation first hyperpolarizabilites computed using different basis sets at the MP2 level of theory for $\mathbf{II_E}$ are quite striking. The ratio of the averaged square bracket terms computed using def2-TZVPD and aug-cc-pVTZ basis sets follows the pattern

$$\left[\frac{[\mu\alpha]^{(0,0)}(\text{def2-TZVPD})}{[\mu\alpha]^{(0,0)}(aug\text{-cc-pVTZ})} = 1.30\right]$$
$$< \left[\frac{[\mu^3]^{(1,0)}(\text{def2-TZVPD})}{[\mu^3]^{(1,0)}(aug\text{-cc-pVTZ})} = 1.82\right]$$
$$< \left[\frac{[\mu^3]^{(0,1)}(\text{def2-TZVPD})}{[\mu^3]^{(0,1)}(aug\text{-cc-pVTZ})} = 2.37\right]$$

Since $[\mu\alpha]^{(0,0)}$, $[\mu^3]^{(1,0)}$, and $[\mu^3]^{(0,1)}$ depend on q_1, q_1q_1, and $q_1q_1q_1$, respectively (cf. eq 10), it is thus possible that the observed discrepancy is linked to the accuracy of matrix elements $q_1^{i,a}$. In order to increase the range of our analysis, we computed some of the terms that contribute to the static nuclear relaxation second hyperpolarizability given by eq 12 (Table 5). These terms

Table 5. Average Contributions to $\gamma^{nr}(0;0,0,0)$ for $\mathbf{II_E}$[a]

	q_1 $\overline{[\mu\beta]}^{(0,0)}$	q_1q_1 $\overline{[\mu^2\alpha]}^{(1,0)}$	$q_1q_1q_1$ $\overline{[\mu^4]}^{(1,1)}$
MP2/def2-TZVPD	−9719	738571	−997462
MP2/ORP	−5475	299211	−234642
MP2/aug-cc-pVTZ	−5372	281707	−231509

[a]All values are given in au. Note that in the case of the $[\mu^4]^{(1,1)}$ term the coupling between anharmonic constants is taken into account approximately. $\overline{\gamma} = \frac{1}{15}\sum_{i,j\in\{x,y,z\}}(\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji})$.

are grouped according to the dependence pattern on q_1. As was found in the case of the static first hyperpolarizability, there are also large variations in anharmonic contributions to the second hyperpolarizability computed using the def2-TZVPD and aug-cc-pVTZ basis sets. The corresponding ratio follows the sequence

$$\left[\frac{[\mu\beta]^{(0,0)}(\text{def2-TZVPD})}{[\mu\beta]^{(0,0)}(aug\text{-cc-pVTZ})} = 1.81\right]$$
$$< \left[\frac{[\mu^2\alpha]^{(1,0)}(\text{def2-TZVPD})}{[\mu^2\alpha]^{(1,0)}(aug\text{-cc-pVTZ})} = 2.62\right]$$
$$< \left[\frac{[\mu^4]^{(1,1)}(\text{def2-TZVPD})}{[\mu^4]^{(1,1)}(aug\text{-cc-pVTZ})} = 4.31\right]$$

Similar to what has been observed for the nuclear relaxation first hyperpolarizability, again the error can be associated with the power dependence on q_1. The matrix element $q_1^{i,a}$ is defined as the ratio of dipole moment derivative with respect to the normal coordinate ($a_{11}^{i,a} = (\partial\mu_a/\partial Q_i)_{Q=0}$) and the vibrational force constant ($a_{20}^{ii} = \omega_i^2$; cf. eq 8). Table 6 contains the two quantities for the two lowest-frequency normal modes of vibration with a focus on the perpendicular component of the dipole moment.

Table 6. Dipole Moment Derivatives with Respect to Normal Modes ($[au/(bohr\sqrt{amu})]$) and Corresponding Harmonic Vibrational Frequencies ($[cm^{-1}]$)[a]

ω_i	$\partial\mu_\perp/\partial Q_i$
MP2/def2-TZVPD	
57	0.0710
109	0.1102
MP2/ORP	
71	0.0585
112	0.1098
MP2/*aug*-cc-pVTZ	
67	0.0519
113	0.1069

[a]Shown are values for the component of the dipole moment perpendicular to the plane of II_E.

These two modes, shown in the Supporting Information, constitute 55% of the total vibrational nuclear relaxation polarizability $\alpha_{\perp\perp}^{nr}$ at the MP2/*aug*-cc-pVTZ level of theory, whereas the other two diagonal components of α^{nr} are roughly an order of magnitude smaller. It follows from Table 6 that the values of a_{11} are overestimated and the values of a_{20} are underestimated at the MP2/def2-TZVPD level of theory for the lowest-frequency mode. The errors add up to yield overestimated value of q_1 (in comparison to the MP2/*aug*-cc-pVTZ values). In fact, Figure 7
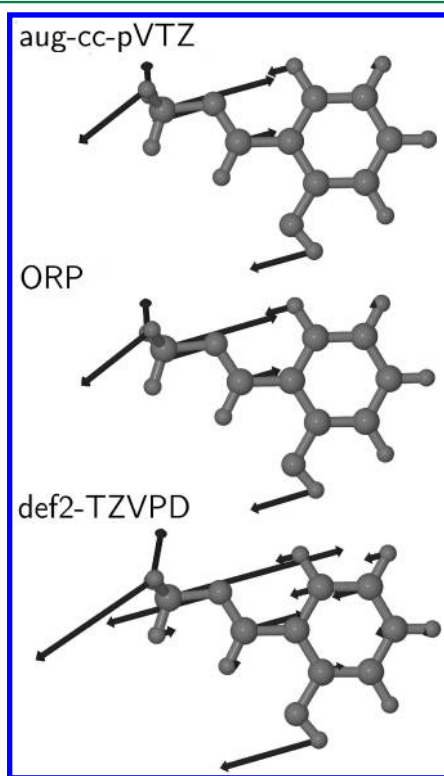
Figure 7. Atomic displacements for the mass-weighted first-order FIC in the direction perpendicular to the plane of II_E ($\chi_1^\perp$).

shows that there is a substantial difference in first-order FIC (involving q_1) in the direction perpendicular to the plane of molecule II_E, computed with the *aug*-cc-pVTZ and def2-TZVPD basis sets. One should not overlook the satisfactory performance of the ORP basis set in predicting the harmonic and anharmonic contributions to the static first and second nuclear relaxation hyperpolarizabilities.

As described in the preceding paragraph, the overestimated anharmonicity contributions to β^{nr} and γ^{nr} at the MP2/def2-TZVPD level can be presumably linked with the first-order field-induced coordinates. In order to further analyze this subject, we have computed nuclear relaxation hyperpolarizabilities by combining two basis sets at the MP2 level of theory, i.e., the *aug*-cc-pVTZ basis set was employed to determine q_1 and a_{12}, and the remaining property derivatives were computed using the *aug*-cc-pVDZ, def2-TZVPD, and ORP basis sets. The results are presented in Table 7. It follows from this table that in the case of all square bracket terms the errors are greatly reduced for the def2-TZVPD basis set, e.g., in the case of the $[\mu^4]^{(1,1)}$ term, the relative error for the def2-TZVPD basis set is reduced from 331 to 6%. This low-cost approximate treatment of anharmonicity by employing two different basis sets is very promising and worth further exploration. However, an attempt to combine the MP2/*aug*-cc-pVTZ level with density functional theory was not successful, at least for the B3LYP and BHandHLYP functionals (the results are shown in the Supporting Information).

■ SUMMARY AND CONCLUSIONS

In this work, we studied electronic and nuclear relaxation (hyper)polarizabilities of carbon dioxide, formaldehyde, *cis*-diazene, and two conformers of a medium-sized photochromic Schiff base, employing several property-oriented basis sets. These include Pol and LPol-ds of Sadlej and co-workers, def2-SVPD and def2-TZVPD of Rappoport and Furche, and the ORP basis set of Baranowska-Łączkowska and Łączkowski. For small molecules, we used the CCSD(T)/d-*aug*-cc-pVQZ and MP2/d-*aug*-cc-pVQZ methods to determine reference values of electronic and nuclear relaxation (hyper)polarizabilities, respectively. In the case of the Schiff base, the *aug*-cc-pVTZ basis set was used to determine the reference estimates of the investigated electric properties. Likewise, the CCSD(T) method was employed for electronic properties, and the MP2 method was used to determine the vibrational contributions. The following conclusions can be drawn based on the results of calculations performed for small systems. The small def2-SVPD basis set is the least reliable among all property-oriented basis sets as far as electronic (hyper)polarizabilities are concerned (vibrational contributions were not studied with this basis set). As expected, the relative errors are the largest for γ and the smallest for α. The def2-TZVPD basis set yields errors much larger for β^e and γ^e than for β^{nr} and γ^{nr}. On the contrary, ORP, Pol, and LPol-ds are more successful in predicting electronic relaxation (hyper)polarizabilities than they are nuclear relaxation (hyper)polarizabilities. By and large, the small Pol basis set is not recommended for computing nuclear relaxation contributions to average β and diagonal γ, as the associated errors reach up to 44.9 and 10.3%, respectively. The LPol-ds basis set yields similar errors in electronic as well as nuclear relaxation hyperpolarizabilities to those found for the ORP basis set. However, the latter is slightly smaller in size and does not suffer from linear dependencies. Dunning's correlation-consistent augmented basis sets of triple-ζ size offer very good accuracy (errors less than 3%) for nuclear relaxation contributions. In some instances, slightly larger errors are found for electronic properties. We have found that the *aug*-cc-pVDZ basis set yields substantial errors for electronic properties; in many instances, these exceed 10%. Overall, as far as small molecules are concerned, we recommend *aug*-cc-pVDZ, def2-TZVPD, or ORP to achieve average absolute errors not exceeding 5.5% for nuclear relaxation (hyper)polarizabilities. For more accurate calculations of vibrational contributions, i.e.,

Table 7. Breakdown of the Average Static First Hyperpolarizability into Anharmonicity Contributions for II_E Using the MP2 Method[a]

a_{12}, q_1	$a_{30}, a_{21}, a_{22}, a_{13}$	$\overline{[\mu\alpha]}^{(0,0)}$	$\overline{[\mu^3]}^{(1,0)}$	$\overline{[\mu^3]}^{(0,1)}$	$\overline{\beta}^{nr}$	$\overline{[\mu\beta]}^{(0,0)}$	$\overline{[\mu^2\alpha]}^{(1,0)}$	$\overline{[\mu^4]}^{(1,1)}$
aug-cc-pVTZ	aug-cc-pVTZ	347	421	−1759	−991	−5372	281707	−231509
aug-cc-pVTZ	aug-cc-pVDZ	347	341	−1721	−1033	−4799	272708	−210790
aug-cc-pVTZ	def2-TZVPD	347	325	−1628	−956	−5648	285320	−216634
aug-cc-pVTZ	ORP	347	332	−1822	−1143	−5323	284962	−235747

[a]All values are given in au. Note that in the case of the $[\mu^4]^{(1,1)}$ term the coupling between anharmonic constants is taken into account approximately. $\overline{\beta} = \sum_{i\in\{x,y,z\}}\mu_i\beta_i/\|\mu\|$; $\beta_i = (3/5)\sum_{j\in\{x,y,z\}}\beta_{ijj}$. $\overline{\gamma} = \frac{1}{15}\sum_{i,j\in\{x,y,z\}}(\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji})$.

average absolute errors less than 1%, the aug-cc-pVTZ basis set is recommended.

In the case of a medium-sized Schiff base, we have found that, similar to the results for small molecules, the def-SVPD basis set yields the largest errors for electronic properties among all employed property-oriented basis sets. Moreover, the def2-TZVPD, ORP, and LPol-ds basis sets deliver similar estimates for electronic properties. Contrary to what has been found for small molecules, the aug-cc-pVDZ basis set predicts electronic (hyper)polarizabilities accurately, and the errors do not exceed 2%.

It has been demonstrated that the anharmonic contributions to first and second hyperpolarizabilities are particularly difficult to accurately predict at the correlated level using property-oriented basis sets. For example, the value of the nuclear relaxation first hyperpolarizability of a Schiff base, computed at the MP2/def2-TZVPD level of theory, is roughly 3 times larger than that determined using the aug-cc-pVTZ basis set. We have linked the failure of def2-TZVPD basis set to the difficulties in predicting the first-order field-induced coordinate, which involves the dipole moment derivatives with respect to the normal coordinate and the vibrational force constant. On the other hand, the aug-cc-pVDZ and ORP basis sets, much smaller in terms of size than the aug-cc-pVTZ basis set, overestimate the nuclear relaxation first hyperpolarizability only by 27%. Overall, we have demonstrated that not all property-oriented basis sets are well-suited for determining vibrational contributions to hyperpolarizabilities at the correlated level and that the corresponding errors can be very large. In this study, we also propose a low-cost composite treatment of anharmonicity that relies on the combination of two basis sets, i.e., a large-sized basis set is employed to determine lowest-order derivatives with respect to the field-induced coordinates, and a medium-size basis set is used to compute the higher-order derivatives. The results of calculations performed at the MP2 level of theory demonstrate that this approximate and computationally cheap scheme is very successful at predicting nuclear relaxation hyperpolarizabilities of a Schiff base.

■ ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00434.

Calculations of electronic and vibrational contributions to (hyper)polarizabilities (PDF).

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Notes

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