On the Vibrational Linear and Nonlinear Optical Properties of Compounds Involving Noble Gas Atoms: HXeOXeH, HXeOXeF, and FXeOXeF

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The vibrational (hyper)polarizabilities of some selected Xe derivatives are studied in the context of Bishop–Kirtman perturbation theory (BKPT) and numerical finite field methodology. It was found that for this set of rare gas compounds, the static vibrational properties are quite large, in comparison to the corresponding electronic ones, especially those of the second hyperpolarizability. This also holds for the dc-Pockels [$\beta(-\alpha\omega,\omega,0)$], Kerr [$\gamma(-\alpha\omega,\omega,0)$] and electric field second harmonic generation [$\gamma(-2\alpha\omega,\omega,0)$] effects, although the computed nuclear relaxation (nr) vibrational contributions are smaller in magnitude than the static ones. HXeOXeH was used to study the effects of electron correlation, basis set, and geometry. Geometry effects were found to lead to noticeable changes of the vibrational and electronic second hyperpolarizability. A limited study of the effect of Xe insertion to the nr vibrational properties is also reported. Assessment of the results revealed that Xe insertion has a remarkable effect on the nr (hyper)polarizabilities. In terms of the BKPT, this is associated with a remarkable increase of the electrical and mechanical anharmonicity terms. The latter is consistent with the anharmonic character of several vibrational modes reported for rare gas compounds. © 2013 Wiley Periodicals, Inc.

Introduction

The history of noble gas chemistry has its roots in 1962 when Bartle[1] and Hoppe[2] successfully synthesized and identified stable noble gas compounds. Since then a large number of experimental and theoretical groups have worked on the synthesis and elucidation of the nature of bonds involving Ng atoms (where Ng stands for noble gas).[3–5] Most of the synthesized compounds involved only Xe and Kr, as chemical inertness increases with decreasing atomic number of the Ng atom.[5,6] A new type of molecule of the form HNgY, where Y is an electronegative atom or group of atoms that has been synthesized. Examples of these derivatives are HArF, prepared by Khriachtchev et al.[7] HXeH synthesized by Feldman et al.[8], and HKF reported by Pettersson et al.[9] This class of molecules was prepared by photolysis of Hartree–Fock (HF) in a Ng matrix at low temperature and identified with the aid of vibrational spectroscopy. The above species have been shown to exhibit a large charge transfer character, the H–Ng bond is predominantly covalent and Ng–Y has a substantial ionic contribution.[4,10,11] An extensive literature survey on the chemistry of rare gas molecules can be found in Refs. [4] and [12].

Among the most remarkable developments in the chemistry of noble gas compounds, one may note: (i) the synthesis of fluorine-free organoxenon derivatives[13,14] and covalent CsF3XeF and CsF3XeCN compounds[15]; (ii) the X-ray crystal structures of the [Xe2OF3][PnF6] salts, where Pn = As, Sb, which contain the Z-shaped FXeOXeFXeF+ cation[16] and [H3O][PnF6]–2XeF2 in which the XeF2 molecules interact with the H3O+ cations; (iii) the formation of XeO2 at 0 °C by hydrolysis of XeF4 in water[17] HXeOH in low temperature Xe matrix,[18] and the neutral radical HXeO[19]; (iv) a metal–Xenon compound involving the Xe–Au bond[20,21]; and (v) the recent synthesis of halogenated xenon cyanides.[22]

Much less is known about derivatives involving the Ng–Ng bond. Seppelt reported the isolation of a salt with the cation Xe2–, that has a Xe–Xe bond of 3.087 Å.[23] However, Khriachtchev et al.[24] reported the synthesis of HXeOXeH, which contains two Xe atoms. Apart from the synthesis and identification of rare gas compounds, a number of theoretical groups have reported studies on the stability, formation mechanisms, structure, and bonding nature of several rare gas compounds.[5,6,25–35]

We have reported that insertion of an Ng atom remarkably enhances the nonlinear response of the resulting derivative.[36] This has been attributed to the noteworthy lowering of the excited states accompanied by more intense allowed electronic transitions.[36,37] Recently, we reported that the diradical matrix,[18] and the neutral radical HXeO[19]; (iv) a metal–Xenon compound involving the Xe–Au bond[20,21]; and (v) the recent synthesis of halogenated xenon cyanides.[22]

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character of HXeOXeH revealed the anharmonic character of some vibrational modes.\cite{24} The high anharmonic character of the Xe—H stretching mode has been also studied by the correlation-corrected vibrational self-consistent field method (CC-VSCF) combined with the second-order Møller–Plesset perturbation theory (MP2) level to compute the potential energy surface (MP2/CC-VSCF), in a series of HXeY molecules.\cite{43,44} The aim of this study is to present the vibrational (hyper)polarizabilities of HXeOXeH, HXeOXeF, and FxeOXeF derivatives and to perform a comparative study with the corresponding electronic contributions. Elaboration of the results will assist us to study the effect of the vibrational anharmonic character of several modes, found in rare gas derivatives, on their (hyper)polarizabilities. Furthermore, the analysis of the electronic and vibrational hyperpolarizability will allow to gain a broader and complete understanding on the origin of the high polarization character of derivatives formed by rare gas insertion. This knowledge can be used for improving the design of new molecules with very large nonlinear optical properties.

**Methods and Computational Details**

**Electronic L&NLO properties**

When a molecule is subject to a uniform static electric field \( F \), its energy, \( E \), may be expanded as follows:\cite{45}

\[
E = E^0 - \mu_i F_i - (1/2) x_{ij} F_i F_j - (1/6) \beta_{ijk} F_i F_j F_k - (1/24) \gamma_{ijkl} F_i F_j F_k F_l - \ldots, \quad (1)
\]

where \( E^0 \) is the field free energy of the molecular system, \( F_i, F_j, F_k \) are the field components, \( \mu_i, x_{ij}, \beta_{ijk} \) and \( \gamma_{ijkl} \) are the tensor components of the dipole moment, linear dipole polarizability, first and second hyperpolarizability, respectively. Summation over repeated indices is implied.

By using the finite difference method, the diagonal components of the polarizability \( (\chi_{ii}) \), first hyperpolarizability \( (\beta_{iij}) \), and second hyperpolarizability \( (\gamma_{iiij}) \) were obtained as the second-, third-, and fourth-order derivatives of the field-dependent energy, respectively. The Romberg approach\cite{46} was used to safeguard the numerical stability of the results and to remove higher-order contaminations. A number of field strengths of magnitude \( 2^m F \) were used, where \( m = 0, 1, 2, 3, 4 \) and the base field \( F = 0.0008 \) a.u. For all the reported computations in this study, the molecules lie in the XZ plane (Fig. 1), and only the in-plane diagonal components of the electronic (hyper)polarizabilities were considered. All the reported electronic (hyper)polarizabilities were computed by using a series of methods, HF, MP2, coupled cluster, which involves the iterative computation of single and double excitation amplitudes (CCSD), as well as the perturbative treatment of triples excitations (CCSD(T)), with the aug-cc-pVNZ (\( N = D,T,Q,5 \)) basis sets.\cite{48} For Xe, we use the small-core relativistic effective potential of Ref. \cite{48}, with 28 core electrons, together with corresponding basis sets aug-cc-pVNZ-PP (PP: Pseudo Potential). It has been reported that effective core potentials can give reliable (hyper)polarizability values.\cite{49}

**Vibrational L&NLO properties**

The vibrational contributions to (hyper)polarizabilities can be of significant importance.\cite{52} Several methods have been developed for their computation, using, for example, vibrational self-consistent field theory and correlated versions.\cite{50,51} Bishop and Kittrnan\cite{42a-d} introduced several techniques for the computation of the vibrational L&NLO properties among which we
note those which are based on perturbation theory, and the finite field nuclear relaxation (nr) approach developed by Bishop et al.\cite{52} and implemented by Luis et al.\cite{53} In the latter approach, the molecular geometry is optimized in the presence of static electric fields rigorously enforcing the Eckart conditions.\cite{54,55} The method requires the computation of the energy in the presence of a uniform static electric field $F$, allowing the nuclei to relax to field-dependent equilibrium positions. By denoting $R_0$ and $R_1$ the equilibrium geometries with $F = 0$ and $F \neq 0$, respectively, one may write the difference of the property $\Delta P_{(F)} = P^*(R_1F) - P^*(R_0,0)$, where the frequency argument ' $0$ ' denotes static (hyper)polarizability. The nr vibrational contribution to dipole moment is

$$
\Delta \mu_{ijlj}(F) = b_iF_j + \frac{1}{2}b_2F_iF_j + \frac{1}{6}b_3F_iF_jF_k + \frac{1}{24}b_4F_iF_jF_kF_l + \ldots , \tag{2}
$$

where $ijlj$ denote Cartesian axes. The coefficients $b_{nm} = 1, 2, 3, 4$ correspond to the total value of the nth-order property:

$$
b_1 = [\mu_i(0)]^{(el)} + [\mu_i(0)]^{(nr)} \tag{3}
$$

$$
b_2 = [\mu_{ij}(0,0,0)]^{(el)} + [\mu_{ij}(0,0,0)]^{(nr)} \tag{4}
$$

$$
b_3 = [\mu_{ijk}(0,0,0)]^{(el)} + [\mu_{ijk}(0,0,0)]^{(nr)} \tag{5}
$$

$$
b_4 = [\mu_{ijkl}(0,0,0,0)]^{(el)} + [\mu_{ijkl}(0,0,0,0)]^{(nr)} \tag{6}
$$

where the frequency argument ‘ $0$ ’ denotes static (hyper)polarizability. The nr vibrational contribution to dipole moment is zero. The static nr vibrational (hyper)polarizability [eqs. (4)--(6)] can also be derived by using the corresponding Taylor expansion of the change of the dipole moment ($\Delta \mu_{ijlj}(F_R)$) in the field of an external field. If one uses in expansion (2) instead of the energy change of the first hyperpolarizability ($\Delta \mu_{ijlj}(F_R)$) or the change of the first hyperpolarizability ($\Delta \beta_{ijlj}(F_R)$), the procedure allows the computation of dynamic vibrational nr contributions in the infinite optical frequency approximation (IOFA). In terms of perturbation theory, named as Bishop–Kirtman perturbation theory (BKPT), the average and diagonal components of nr vibrational contributions (static and dynamic) are given by the following analytical formulas:\cite{40,42,43}

$$
\chi^{nr}(0;0) = [\mu^2]^{(0,0)} \tag{7}
$$

$$
\beta^{nr}(0;0,0,0) = [\mu_2]^{(0,0)} + [\mu_3]^{(1,0)} + [\mu_4]^{(0,1)} \tag{8}
$$

$$
\gamma^{nr}(0;0,0,0) = [\mu_2]^{(0,0)} + [\mu_3]^{(1,0)} + [\mu^2_2]^{(1,0)} + [\mu_2^2]^{(0,1)} + [\mu_2^3]^{(0,2)} \tag{9}
$$

$$
\beta(-\omega;0,0,0)_{\omega \rightarrow \infty} = \frac{1}{3}[\mu_{2\omega}]^{(0,0)} \tag{10}
$$

$$
\gamma^{nr}(-\omega;0,0,0)_{\omega \rightarrow \infty} = \frac{1}{3} [\mu_2]^{(0,0)} + \frac{1}{2} [\mu_3]^{(0,0)} + \frac{1}{6} [\mu_2^2]^{(0,0)} + [\mu_2^3]^{(0,0)} \tag{11}
$$

$$
\gamma^{nr}(-2\omega;0,0,0)_{\omega \rightarrow \infty} = \frac{1}{4} [\mu_2]^{(0,0)} \tag{12}
$$

The superscripts $n$ and $m$ in the notation $[A]^{n,m}$, denote the level of the electrical and mechanical anharmonicities, respectively. The above equations for the computation of the vibrational dynamic hyperpolarizabilities imply the IOFA, which requires that for all vibrational transition frequencies ($\omega$) and optical frequencies ($\omega_0$), the ratio $\omega_0/\omega$ is negligible compared to unity.\cite{42,44} According to eqs. (7)--(12), all vibrational contributions through first-order in mechanical and/or electrical anharmonicity and some of the second-order terms are included in the finite field nr approach. Higher-order vibrational corrections, which are called curvature contributions, are usually smaller and their computation is very time-consuming.\cite{53,55} They will not be considered in this study.

The geometries used for the computation of the nr vibrational properties of the reported Xe derivatives were optimized using MP2 and CCSD with the aug-cc-pVXZ ($X = T, Q$) basis sets, without imposing symmetry constraints. All the Xe derivatives considered in this study are planar, and are placed in the XZ plane (Fig. 1). In the context of the finite field nr method, field strengths from 0.0008 to 0.0064 a.u were used in the Eckart constrained optimizations, applied along the x and z axis only. Only the energies of the optimized structures were analyzed by using a numerical Romberg differentiation\cite{46} in order to ensure the numerical stability of the results.

The zero point vibrational averaging (ZPVA) contributions to $x$ and $\beta$ presented in this work were computed using the BKPT\cite{40,42}. This correction provides a part of the curvature contribution which arises from the change of the zero point vibrational energy caused by the applied field. According to BK perturbation theory, the ZPVA correction is evaluated as a double perturbation series in mechanical and electrical anharmonicity and is given by a sum of the nonvanishing odd order terms:\cite{42}

$$
\rho^{ZPVA} = \rho[1,0] + \rho[3,0] + \ldots, \tag{13}
$$

where $P$ denotes the electronic property ($\mu, x, \beta$), $[P] = [P]^{(1,0)} + [P]^{(1,1)}$, while $[P]^{(n,m)} = [P]^{(n,0)} + [P]^{(2,1)} + [P]^{(3,1)} + [P]^{(0,3)}$ where $(n,m)$ superscripts stand for the order of the electrical and mechanical anharmonicity contribution, respectively. The first-order term is given by

$$
|\rho^{ZPVA}| = -\frac{h}{4} \sum_{\alpha} \frac{1}{\alpha^2} \left( \sum_{b \neq 0} \frac{F_{\alpha b}}{\alpha b} \left( \frac{\partial \rho}{\partial \alpha b} \right) + \frac{h}{4} \sum_{\alpha} \frac{1}{\alpha^2} \left( \frac{\partial^2 \rho}{\partial \alpha^2} \right) \right) \tag{14}
$$

where $P = x\beta$, $F_{\alpha b}$ denotes the cubic force constant, and $\alpha_0$ the harmonic vibrational frequency of the normal mode $Q_0$. The purpose of our first-order ZPVA calculations is to check if the sequence $P^0$, $P^1$, $P^{(3,0)}$ is initially convergent (i.e., $P^1 < P^0$).\cite{42} The evaluation of the higher-order ZPVA [eq. (13)] and other higher-order curvature terms requires the computation of higher-order force constants and electronic property derivatives. For convergent $P^1$, $P^3$, and $P^{(3,0)}$ series, the higher-order vibrational terms are usually very small. Furthermore, their computation is very time consuming and then they were not considered in this study. The cubic force constants used in eq. (14) were computed numerically as first derivatives of the analytical force constants, while the derivatives $\partial^2 \rho/\partial \alpha^2$ were computed numerically from the corresponding properties.

Software. The GAUSSIAN 09 software\cite{56} has been used for the optimization and (hyper)polarizability computations with the
aug-cc-pVNZ basis sets, where \( N = D, T, \) and \( Q.\) NWChem\cite{57} was used for the computation of the (hyper)polarizabilities employing the aug-cc-pV5Z basis set.

### Results and Discussion

#### Electronic (hyper)polarizabilities

As the computation of the vibrational (hyper)polarizabilities depends on the electronic properties, we have performed a limited study of the dependence of the electronic contribution on the basis set, electron correlation and geometry.

**Basis set effect.** The effect of the basis set on the static electronic (hyper)polarizabilities of HXeOHeX is presented in Table 1. The study has been performed at the MP2 level using the MP2/aug-cc-pVQZ geometry. For all computations the (d)-aug-cc-pVNZ basis set series has been used, where \( N = D, T, Q, 5.\) It is seen that the basis set has a large effect on the electronic first and second hyperpolarizabilities. For example, \( \gamma_{xxxx} \) increases by 70.7\% by switching from aug-cc-pVDZ to aug-cc-pV5Z. The effect on the polarizability components is significantly smaller where the \( \alpha_{xx} \) is increased by 2.7\%. Even between the largest basis sets, aug-cc-pVQZ and aug-cc-pV5Z, the hyperpolarizabilities differ substantially, where an increase of 31\% is observed for \( \gamma_{xxxx}.\) The substantial change of \( \gamma_{xxxx} \) upon basis set change implies that the use of aug-cc-pVNZ basis sets may not be adequate for a proper basis set limit estimation of the property. We also computed the diagonal in-plane (hyper)polarizability values by using the d-aug-cc-pVNZ basis set series for H, C, O atoms, where \( N = T, Q.\) For Xe, we use the small-core relativistic effective potential of Ref. [48], with 28 core electrons, together with corresponding basis sets aug-cc-pVNZ-PP augmented with extra diffuse functions. A very large basis set effect is observed for the first and second hyperpolarizability values (Table 1) when the second set of diffuse functions are added to the basis set. It is seen that \( \gamma_{xxxx} \) (d-aug-cc-pVPTZ) = 2.67 \times \gamma_{xxxx}(aug-cc-pVQZ), while \( \gamma_{xxxx} \) (d-aug-cc-pVQZ) = 1.47 \times \gamma_{xxxx}(aug-cc-pVQZ). Noticeable is also the effect on the first hyperpolarizability (e.g., \( \beta_{xx}(d-aug-cc-pVQZ) = 1.37 \times \beta_{zzz}(aug-cc-pVQZ)\)). Contrary to the single augmented series, the hyperpolarizabilities can be considered converged at the d-aug-cc-pV5Z basis set. It is seen that \( \gamma_{xxxx} \) (d-aug-cc-pVQZ) changes only by 2.2\% with respect to \( \gamma_{xxxx} \) (d-aug-cc-pVPTZ).

**Electron correlation.** For all studied geometries, the electron correlation effect is larger for the \( x \) diagonal tensor component of the second hyperpolarizability than for the \( z \) diagonal component (Table 2). It is observed that electron correlation at the CCSD(T) level decreases the \( \gamma_{xxxx} \) (HF) value by 38.5\%, 51.1\%, and 57.1\%, for the geometries, CCSD/aug-cc-pVQZ and MP2/aug-cc-pVQZ, MP2/aug-cc-pVPTZ, respectively. Similarly, the effect of electron correlation (CCSD(T)) on the \( \gamma_{zzzz} \) diagonal component increases the HF value by 41\%, computed at the MP2/aug-cc-pVQZ geometry. The effect of the perturbatively computed triples correction is significant on the diagonal \( x \) tensor component of the second hyperpolarizability, for example, \( \gamma_{xxxx} \ (CCSD(T)) = -15.7 \times 10^3 \) a.u., (CCSD/aug-cc-pVQZ geometry).

**Geometry effect.** The effect of the change of the geometry on the second hyperpolarizability is quite large (Table 2). For example, it was found that \( \gamma_{xxxx} \) at the CCSD(T)/aug-cc-pVPTZ level of theory of the structure optimized at MP2/aug-cc-pVQZ differs by 37.7\% from the structure optimized at the CCSD/aug-cc-pVPTZ level, while for the \( z \)-component the above difference is 37.4\%. Even more pronounced is the geometry effect on the second hyperpolarizability at the MP2/aug-cc-pVQZ level theory. For example, we find that the MP2 \( \gamma_{xxxx} \) (MP2/aug-cc-pVQZ) value differs by 77\% from the \( \gamma_{xxxx} \) (CCSD/aug-cc-pVQZ).

### Table 1. Basis set study of the static electronic (hyper)polarizabilities of HXeOHeX. The properties have been computed by employing the MP2 method at the MP2/aug-cc-pVQZ optimized geometry.

| Basis set | \( N \) | \( D \) | \( T \) | \( Q \) | \( S \) |
|-----------|--------|-------|-------|-------|-------|
| aug-cc-pVNZ\((a)\) | | | | | |
| aug-cc-pVQZ\((b)\) | | | | | |
| aug-cc-pVTZ\((c)\) | | | | | |
| \( \alpha_{xx} \) | 177.86 | 180.43 | 181.96 | 182.63 |
| \( \alpha_{yy} \) | 72.27 | 74.29 | 75.52 | 74.73 |
| \( \beta_{zzz} \) | 4.1 | 11.7 | 36.6 | 39.2 |
| \( \gamma_{xxxx} \) | 26.94 \times 10^3 | 19.73 \times 10^3 | 35.11 \times 10^3 | 46.0 \times 10^3 |
| \( \gamma_{zzzz} \) | 16.74 \times 10^3 | 21.69 \times 10^3 | 27.81 \times 10^3 | 30.0 \times 10^3 |

All property values are given in a.u. \( [a] \) For Xe, the small-core relativistic effective potential of Ref. [48] with 28 core electrons was used. \( [b] \) Polarizability derivatives were used for the computation of the reported tensor components. \( [c] \) Energy derivatives were used for the computation of the reported tensor components.

### Table 2. A study of the geometry and the electron correlation effect on the static electronic polarizability and second hyperpolarizability \((\times 10^3)\) of HXeOHeX. All the reported values were computed by employing the aug-cc-pVQZ\((a)\) basis set, while the geometries have been optimized by using the specified method.

| Optimized geometry property (a.u.)\((a)\) | MP2/aug-cc-pVPTZ | CCSD/aug-cc-pVQZ | MP2/aug-cc-pVQZ |
|----------------------------------------|------------------|------------------|------------------|
| \( \alpha_{xx} \) | 176.89 | 154.4 | 13.5 |
| \( \alpha_{yy} \) | 154.24 | 78.6 | 19.6 |
| \( \gamma_{xxxx} \) | 190.69 | 130.0 | 12.35 |
| \( \gamma_{zzzz} \) | 190.99 | 113.0 | 13.90 |

\( [a] \) For Xe an effective core potential of 28 electrons was used. \( [b] \) Energy derivatives were used for the computation of the reported tensor components.
geometric parameters (bond length and bond angle) of HXeOXeH, optimized at the MP2 and CCSD levels with the aug-cc-pVQZ basis set. The basis set effect on the NLO properties: ΔR<sub>O</sub>-Xe (MP2/BS1-CCSD/BS1) = 0.047 Å, ΔR<sub>H</sub>-Xe (MP2/BS1-CCSD/BS1) = 0.013 Å, and ΔR<sub>C</sub>-XeOXe = (MP2/BS1-CCSD/BS1) = −15.1°.

In Figure 2, the variation of the γ<sub>xxxx</sub> with the angle <XeOXe is shown. It is seen that the effect of the change of the angle on the γ<sub>xxxx</sub> is significant and thus the angle alone can be used to qualitatively explain the differences observed due to the change of geometry (Table 2).

From the above limited study, we may conclude that both basis set (Table 1) and electron correlation effects (Table 2) are quite important for the reliable estimation of the electronic (hyper)polarizabilities of the molecules studied here. These results are in agreement with Ref. [38]. The change of the geometry due to the effect of either electron correlation or basis set (Fig. 1) leads to a substantial variation of the second hyperpolarizability (Table 2, Fig. 2). Although the MP2 geometries differ substantially from the more accurate CCSD geometries, due to computational restrictions the former will be used in the subsequent computations, which should be sufficient for a qualitative estimation and analysis of the magnitude of the vibrational (hyper)polarizabilities. The previous findings will assist us to study thoroughly the vibrational (hyper)polarizabilities.

Vibrational (hyper)polarizabilities

**Basis set effect.** In order to examine the effect of basis set on the nr vibrational (hyper)polarizabilities, the HXeOXeH molecule was selected as a test molecule. For both methods, BKPT (Table 3) and the numerical finite field nr (Supporting Informa-

**Table 3. Basis set study of the static electronic (El) (hyper)polarizabilities, static and IOFA dynamic nuclear relaxation (NR) vibrational contributions to the polarizability, first and second hyperpolarizability of HXeOXeH.**

| Method | Property<sup>[a]</sup> | MP2/aug-cc-pVTZ | MP2/aug-cc-pVQZ |
|--------|--------------------------|-----------------|-----------------|
|        | NR<sup>[b]</sup> | EL<sup>[c]</sup> | NR<sup>[d]</sup> | EL<sup>[d]</sup> |
| γ<sub>x<sub>x</sub>x<sub>x</sub></sub> (0;0) | 79.09 | 185.24 | 80.89 | 181.96 |
| γ<sub>x<sub>x</sub>y<sub>y</sub></sub> (0;0) | 80.57<sup>[e]</sup> | 187.70<sup>[e]</sup> | 54.90 | 55.30 |
| γ<sub>x<sub>x</sub>z<sub>z</sub></sub> (0;0) | 10.66 | 74.26 | 11.23 | 74.72 |
| Β<sub>x<sub>x</sub>x<sub>x</sub></sub> (0;0,0) | −1390 | 7.3 | −1425 | 36.6 |
| Β<sub>x<sub>x</sub>y<sub>y</sub></sub> (0;0,0) | −487 | 506 |
| γ<sub>x<sub>x</sub>x<sub>x</sub></sub> (0;0,0,0) | 1640 × 10<sup>3</sup> | 1.97 × 10<sup>3</sup> | 1630 × 10<sup>3</sup> | 35.11 × 10<sup>3</sup> |
| γ<sub>x<sub>x</sub>y<sub>y</sub></sub> (0;0,0,0) | 1970 × 10<sup>3</sup> | 43.46 × 10<sup>3</sup> | 107 | 103 |
| γ<sub>x<sub>x</sub>z<sub>z</sub></sub> (0;0,0,0) | 0.53 × 10<sup>3</sup> | 0.42 × 10<sup>3</sup> | |
| γ<sub>x<sub>x</sub>x<sub<x</sub>y<sub>y</sub></sub> (0;0,0,0,0) | 95.4 × 10<sup>3</sup> | 21.50 × 10<sup>3</sup> | |
| γ<sub>x<sub>x</sub>y<sub>y</sub></sub> (0;0,0,0,0) | 186.0 × 10<sup>3</sup> | 1990 | 0.053 | 10<sup>3</sup> |
| γ<sub>x<sub>x</sub>z<sub>z</sub></sub> (0;0,0,0,0) | 0.14 × 10<sup>3</sup> | −0.049 | 10<sup>3</sup> |
| γ<sub>x<sub>x</sub>y<sub>y</sub></sub> (0;0,0,0,0) | 33.4 × 10<sup>3</sup> | 30.3 | 0.32 | 10<sup>3</sup> |
| γ<sub>x<sub>x</sub>z<sub>z</sub></sub> (0;0,0,0,0) | −0.91 × 10<sup>3</sup> | −0.17 | 10<sup>3</sup> |
| γ<sub>x<sub>x</sub>x<sub<x</sub>y<sub>y</sub></sub> (0;0,0,0,0,0) | 32.0 × 10<sup>3</sup> | 0.053 | 10<sup>3</sup> |

All values are given in a.u. (a) The molecule is placed in the XZ plane. (b) β<sub>x<sub>x</sub>x<sub>x</sub></sub> and β<sub>x<sub>x</sub>y<sub>y</sub></sub> are zero by symmetry. (c) The Bishop–Kirtman perturbation theory approach has been used for the computation of the nr contribution. (d) The nr values were computed by employing the finite field approach with the MP2/aug-cc-pVTZ method. (e) Method: MP2/aug-cc-pVTZ.
have also computed the static nr $\gamma_{xxxx}$ component by using the d-aug-cc-pVTZ basis set. It is seen that the reported $\gamma_{xxxx}(\text{MP2/aug-cc-pVTZ})$ nr value differs by 16.7% from the $\gamma_{xxxx}(\text{MP2/d-aug-cc-pVTZ})$ one. On the contrary, the basis set effect on the electronic hyperpolarizabilities is considerable larger (see Basis set effect section).

**Electron correlation effect.** In order to examine the effect of electron correlation on the nr (hyper)polarizabilities, the HXeOXeH molecule was selected as a test case. The reported results (Table 4) were computed by using BKPT approach on the MP2 results and the finite field nr approach for the CCSD/aug-cc-pVTZ data. We have restricted our CCSD computations to the diagonal $x$-component of the vibrational polarizability and second hyperpolarizability, as this component is dominant for all the studied Xe derivatives (Table 4). It is observed that electron correlation has a significant effect on the nr contribution of $\chi_{xx}$ and $\gamma_{xxxx}$. It was found that the $\chi_{xx}$ (MP2) differs by 43.5% from $\chi_{xx}$ (CCSD), while $\gamma_{xxxx}$ (MP2) differs by 41.2% from $\gamma_{xxxx}$ (CCSD). Again, this large effect may be explained by the corresponding differences in the optimized geometries due to the effect of electron correlation, as computed by the MP2/aug-cc-pVTZ and CCSD/aug-cc-pVTZ, methods (Fig. 1). It is interesting to note that comparison between the CCSD and MP2 values shows that MP2 is able to estimate the correct order of magnitude for the nr second hyperpolarizability. However, this is not valid for the electronic second hyperpolarizability as shown in the results of Tables 2 and 4. The nuclear relaxation contributions to the second hyperpolarizabilities depend on the derivatives respect to the normal modes of electronic low order properties [see eqs. (9), (11), and (12)].

| Method | HXeOXeH | HXeOXeF | FXeOXeF |
|--------|---------|---------|---------|
|        | NR[c]   | EI      | NR[c]   | EI      | NR[c]   | EI      |
| $x_{x}(0,0)$ | 79.09 (140.02)[d] | 185.24 (190.69)[e] | 112.02 | 150.33 | 56.05 | 138.02 |
| $y_{y}(0,0)$ | 5.85 | 54.90 | 14.66 | 51.11 | 12.47 | 49.09 |
| $z_{z}(0,0)$ | 10.66 | 74.26 | 13.56 | 66.14 | 28.02 | 64.37 |
| $\beta_{xx}(0,0,0)$ | $-1390$ | 7.3 | 283 | $-22$ | 886 | $-77$ |
| $\beta_{yy}(0,0,0,0)$ | $-1$ | 0.01 | $-1248$ | 0 | 0 | 0 |
| $\beta_{zz}(0,0,0,0)$ | $-0.02$ | 44 | 390 |
| $\gamma_{xxxx}(0,0,0,0)$ | 1640 $\times 10^{3}$ (2790 $\times 10^{3}$)[d] | 1.97 $\times 10^{5}$ (128.70 $\times 10^{3}$)[e] | 2159 $\times 10^{3}$ | 64.45 $\times 10^{3}$ | 633 $\times 10^{3}$ | $-12.69 \times 10^{3}$ |
| $\gamma_{yyyy}(0,0,0,0)$ | 0.53 $\times 10^{3}$ | 13.8 $\times 10^{3}$ | 4.7 $\times 10^{3}$ |
| $\gamma_{zzzz}(0,0,0,0)$ | 95.4 $\times 10^{3}$ | 21.50 $\times 10^{3}$ | 102.6 $\times 10^{3}$ |
| $\gamma_{zzzz}(0,0,0,0)$ | 186.0 $\times 10^{3}$ | 81.2 $\times 10^{3}$ | 37.1 $\times 10^{3}$ |
| $\gamma_{zzzz}(0,0,0,0)$ | 0.01 $\times 10^{3}$ | 79.2 $\times 10^{3}$ | 6.92 $\times 10^{3}$ |
| $\gamma_{zzzz}(0,0,0,0)$ | 33.4 $\times 10^{3}$ | 1.1 $\times 10^{3}$ | 0.14 $\times 10^{3}$ |
| $\gamma_{zzzz}(0,0,0,0)$ | $-107 $ $\times 10^{3}$ | $-93.7$ $\times 10^{3}$ | 1.21 $\times 10^{3}$ |
| $\gamma_{zzzz}(0,0,0,0)$ | $-0.13 $ $\times 10^{3}$ | $-62.0$ $\times 10^{3}$ | $-6.9$ $\times 10^{3}$ |
| $\gamma_{zzzz}(0,0,0,0)$ | 0.32 $\times 10^{3}$ | $-80.0$ $\times 10^{3}$ | $-3.05$ $\times 10^{3}$ |

All values are in a.u. 
[a] The molecule is placed in the XZ plane. [b] $\beta_{xx}$ and $\beta_{yy}$ of HXeOXeH and FXeOXeF, and $\beta_{zz}$ of HXeOXeF are zero by symmetry. [c] The Bishop–Kirtman perturbation theory approach has been used for the computation of the nr contribution. [d] The nr values were computed by employing the finite field approach with the CCSD/aug-cc-pVTZ method. [e] Method: CCSD/aug-cc-pVTZ.
than the corresponding electronic ones for all the derivatives, especially for the second hyperpolarizability. In order to quantify this, we will analyze the ratio \(P^{\text{nr}}/P^{\text{el}}\) at the MP2/aug-cc-pVTZ level. For \(\beta_{zzz}(\text{HxeOXeF})\), this ratio takes the value \(-6.24\) (Supporting Information Table S2), for \(\gamma_{xxxx}\) the ratio is 832.4, 33.5, and \(-49.9\), for HXeOXeH, HxeOXeF, and FxeOXeF, respectively. For \(\beta_{zzz}\), the \(P^{\text{nr}}/P^{\text{el}}\) is \(-190\) (HxeOXeH), \(-12.9\) (HxeOXeF), \(-11.5\)(FxeOXeF), and for \(\gamma_{zzzz}\, 4.4\) (HxeOXeH), 6.9 (HxeOXeF), and 5.4 (FxeOXeF). The opposite was found for the polarizability, where for all the studied compounds it was found that \(x_{ii}^{\text{el}} > x_{ii}^{\text{nr}} = x_{zz}\).

Let us now highlight some features observed for the computed nr contributions of the selected Xe derivatives. (a) A noticeable difference between the in-plane nr first hyperpolarizability components of HxeOXeF is found, \(\beta_{xx}(\text{nr}) - \beta_{zz}(\text{nr}) = -10.53 \times 10^3\) a.u. (MP2/FF). (b) The differences, \(x_{xx}(\text{nr}) - x_{zz}\text{(nr)}\) and \(\gamma_{xxxx}(\text{nr}) - \gamma_{xxxx}\text{(nr)}\) are largest for HxeOXeF (Table 4). (c) For the diagonal x-component, we found the sequence (Table 4) \(P^{\text{nr}}(\text{HxeOXeF}) > P^{\text{nr}}(\text{HxeOXeH}) > P^{\text{nr}}(\text{FxeOXeF})\), where \(P = x_{ii}^{\text{nr}}\).

A somehow different pattern is observed for the diagonal z-component of the (hyper)polarizability tensor components: \(x_{zz}^{\text{nr}}(\text{FxeOXeF}) > x_{zz}^{\text{nr}}(\text{HxeOXeF}) > x_{zz}^{\text{nr}}(\text{HxeOXeH})\), \(\beta_{zz}^{\text{nr}}(\text{HxeOXeF}) > \beta_{zz}^{\text{nr}}(\text{HxeOXeH})\), \(\gamma_{zzzz}^{\text{nr}}(\text{FxeOXeF}) > \gamma_{zzzz}^{\text{nr}}(\text{HxeOXeF}) > \gamma_{zzzz}^{\text{nr}}(\text{HxeOXeH})\). (d) For all the studied compounds, at both static and dynamic level of theory, the out of plane vibrational (hyper)polarizability component is smaller than the in-plane (Table 4), except for \(x_{yy}^{\text{nr}}\) of HxeOXeF, which is slightly larger than the \(x_{zz}^{\text{nr}}\).

Summarizing, we found that the vibrational first and second hyperpolarizabilities of the three studied Xe derivatives are larger than the electronic ones, with an especially large ratio \(P^{\text{nr}}/P^{\text{el}}\) for the second hyperpolarizability. Interestingly, the \(\gamma_{xxxx}^{\text{nr}}\) component dominates and reaches a maximum value for HxeOXeF.

**ZPVA (hyper)polarizabilities.** We shall now comment on the ZPVA correction, at the MP2/aug-cc-pVTZ level of theory, for the polarizability and first hyperpolarizability. For the polarizability, the ratio \([\chi^{\text{ZPVA}}]/\chi^{\text{el}}\) for the diagonal in-plane components of the reported Xe derivatives, is always smaller than unity, implying that the series \(P = P^{\text{el}} + [P^{\text{ZPVA}}]\) is convergent.\(^{[55,60]}\)

For the \(x\) (2) diagonal component of the polarizability, the ratio \([\chi^{\text{ZPVA}}]/\chi^{\text{el}}\) is: 0.02 (0.02), 0.03 (0.01), and 0.008 (0.006), for HxeOXeH, HxeOXeF, and FxeOXeF, respectively. Similarly for the \(x\) (2) diagonal component of the first hyperpolarizability, the ratio \([\beta^{\text{ZPVA}}]/\beta^{\text{el}}\) is 0.05 (0.12) and 0.04, for HxeOXeF and FxeOXeF, respectively.

**Rationalization of the nr results.** In this section, we will assess the origin of the computed large nr (hyper)polarizabilities on the basis of the BKPT theory, by comparing the contribution of various terms associated with given orders of mechanical and electrical anharmonicities. As, for all the studied Xe derivatives, the largest nr vibrational component is the \(x\) diagonal tensor component of the second hyperpolarizability (Table 4), our analysis will be restricted to this component by assessing the contribution of the following terms: eq. (9): \([x_{zz}^{\text{nr}}] = [\mu_{zz}^{\text{nr}}], [x_{zz}^{\text{nr}}], [\mu_{zz}^{\text{nr}}]\). The results are depicted in Figure 4 as a percentage of each contribution to the total value of \(\chi_{xxxx}^{\text{nr}}\). In order to facilitate our analysis, the various contributions have been grouped into harmonic \([x_{zz}^{\text{nr}}] = [\mu_{zz}^{\text{nr}}] + [x_{zz}^{\text{nr}}] + [\mu_{zz}^{\text{nr}}]\) and second-order \([\mu_{zz}^{\text{nr}}] = [\mu_{zz}^{\text{nr}}] + [\mu_{zz}^{\text{nr}}] + [\mu_{zz}^{\text{nr}}] + [\mu_{zz}^{\text{nr}}] + [\mu_{zz}^{\text{nr}}] + [\mu_{zz}^{\text{nr}}]\) terms. It is seen that for the Xe derivatives, the harmonic approximation fails to provide the correct order of magnitude of the nr vibrational second hyperpolarizability (Fig. 4). Apart from the large magnitude of the anharmonic contribution, the failure of the harmonic approximation is also attributed to the partial cancellation of the relevant harmonic terms, which for HxeOXeF is quite large \([x_{zz}^{\text{nr}}] = 3.19 \times 10^5, [\mu_{zz}^{\text{nr}}] = -3.75 \times 10^5\). The best performance of the harmonic approximation was found for FxeOXeF (25%). The anharmonicity has a similar weight for \(\gamma_{zzzz}^{\text{nr}}\) of FxeOXeF and HxeOXeH. For HxeOXeF (FxeOXeF), the harmonic terms contribute 20% (25%), the first-order 55% (51%), and the second-order 25% (24%) to the total value (Table 4). The term which dominates the first-order contribution is \([x_{zz}^{\text{nr}}] = 5.17 \times 10^5, [\mu_{zz}^{\text{nr}}] = 8.11 \times 10^5, [\mu_{zz}^{\text{nr}}] = 4.01 \times 10^5\) for HxeOXeH, HxeOXeF, and FxeOXeF, respectively. This term is connected with dipole moment and polarization second-order derivatives with respect to normal coordinates. For HxeOXeF, the major contribution (55%) to the total value originates from the second-order terms, where the \([\mu_{zz}^{\text{nr}}] = 9.96 \times 10^5\) is associated with higher-order dipole moment derivatives.\(^{[42c]}\) Therefore, we conclude that the large contribution of the anharmonic terms and especially those connected with electrical anharmonicities\(^{[42c]}\) are the reason for the high nr second hyperpolarizability values.

**The effect of Xe insertion on the vibrational nonlinear optical properties**

As shown previously, the insertion of an Ng atom leads to a substantial change of the electronic (hyper)polarizabilities.\(^{[37]}\) Thus, it will be of interest to study the effect of Xe insertion on the nr vibrational (hyper)polarizabilities. The HxeOXeH, HxeOXeF, and HxeOH, and H2O will be used in order to address several features associated with the change of the vibrational properties
upon Xe insertion. The results are reported in Table 5. In general, it is observed that the number of Xe atoms noticeably increases the magnitude of the nr contribution to the (hyper)polarizabilities, at both static and dynamic levels. It has been shown that the MP2/aug-cc-pVTZ method gives the correct order of magnitude of the vibrational (hyper)polarizabilities, compared with the more accurate CCSD values. Thus, this method can be used to describe the effect of Xe insertion to the nr vibrational (hyper)polarizabilities at least qualitatively.

The effect is largest for the diagonal component of the polarizability and second hyperpolarizability. It was found that:

\[
\frac{\gamma_{xx}^{nr}(H\text{XeOXeH})}{\gamma_{xx}^{nr}(\text{HOH})} = 608.4 (14.4) \text{ a.u}, \quad \frac{\gamma_{xxxx}^{nr}(H\text{XeOXeH})}{\gamma_{xxxx}^{nr}(\text{HOH})} = 4823(477) \text{ a.u.}
\]

In parenthesis, the ratio of the z-component is given.

The effect of Xe insertion is larger for the vibrational (hyper)polarizabilities than for the electronic ones. For example, for the x-component of the second hyperpolarizability,

\[
\frac{\gamma_{xxxx}^{nr}(H\text{XeOXeH})}{\gamma_{xxxx}^{nr}(\text{HOH})} = 4823 \text{ a.u, while } \frac{\gamma_{xxxx}^{el}(H\text{XeOXeH})}{\gamma_{xxxx}^{el}(\text{HOH})} = 3.2 \text{ a.u., while } \frac{\gamma_{xxxx}^{el}(H\text{XeOH})}{\gamma_{xxxx}^{el}(\text{HOH})} = 43.9 \text{ a.u.}
\]

Similar relationships were

Figure 4. Analysis of the contribution of the harmonic and anharmonic terms to the $\gamma_{xxxx}^{nr}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 5. Static electronic (El.) (hyper)polarizabilities, static and IOFA dynamic nuclear relaxation (NR) vibrational contributions of the polarizability, first and second hyperpolarizability of HOH, HXeOH, and HXeOXeH.

| Method          | HXeOXeH | HXeOH | HOH  |
|-----------------|---------|-------|------|
|                 | NR[1]   | EL    |      |
| $\alpha_{xx}(0,0)$ | 79.09   | 185.24|      |
| $\alpha_{yy}(0,0)$ | 10.66   | 74.26 |      |
| $\beta_{x\alpha}(0,0,0)$ | -1390   | 7.3   |      |
| $\beta_{x\beta}(0,0,0)$ | -487    | 7.3   |      |
| $\gamma_{xxxx}(0,0,0,0)$ | $1640 \times 10^3$ | 1.97 $\times 10^3$ |      |
| $\gamma_{yyyy}(0,0,0,0)$ | $95.4 \times 10^3$ | 21.54 $\times 10^3$ |      |
| $\gamma_{x\alpha\alpha}(0,0)$ | $186.0 \times 10^3$ | 0.38 $\times 10^3$ |      |
| $\gamma_{x\alpha\beta}(0,0,0)$ | $33.4 \times 10^3$ | 2.12 $\times 10^3$ |      |
| $\gamma_{x\beta\beta}(0,0,0)$ | -107 $\times 10^3$ | -10.3 $\times 10^3$ |      |
| $\gamma_{x\beta\beta}(0,0,0)$ | $0.32 \times 10^3$ | -0.91 $\times 10^3$ |      |

| Method          | HXeOH   |      |
|-----------------|---------|------|
|                 | NR[1]   | EL    |
| $\alpha_{xx}(0,0)$ | 22.01   | 70.63 |
| $\alpha_{yy}(0,0)$ | 6.92    | 44.49 |
| $\beta_{x\alpha}(0,0,0)$ | -136.8  | 79.0  |
| $\beta_{x\beta}(0,0,0)$ | -121.3  | 79.0  |
| $\gamma_{xxxx}(0,0,0,0)$ | $53.7 \times 10^3$ | $27.21 \times 10^3$ |      |
| $\gamma_{yyyy}(0,0,0,0)$ | $13.1 \times 10^3$ | $9.68 \times 10^3$ |      |
| $\gamma_{x\alpha\alpha}(0,0)$ | 0.38 $\times 10^3$ | 0.20 $\times 10^3$ |      |
| $\gamma_{x\alpha\beta}(0,0,0)$ | 0.10 $\times 10^3$ | 0.10 $\times 10^3$ |      |
| $\gamma_{x\beta\beta}(0,0,0)$ | $21.22 \times 10^3$ | $9.04 \times 10^3$ |      |
| $\gamma_{x\beta\beta}(0,0,0)$ | -10.3 $\times 10^3$ | -0.006 $\times 10^3$ |      |

| Method          | HOH     |      |
|-----------------|---------|------|
|                 | NR[1]   | EL    |
| $\alpha_{xx}(0,0)$ | 0.13    | 10.01 |
| $\alpha_{yy}(0,0)$ | 0.74    | 9.55  |
| $\beta_{x\alpha}(0,0,0)$ | -5.0    | 12.2  |
| $\beta_{x\beta}(0,0,0)$ | -3.1    | 12.2  |
| $\gamma_{xxxx}(0,0,0,0)$ | $0.34 \times 10^3$ | $0.62 \times 10^3$ |      |
| $\gamma_{yyyy}(0,0,0,0)$ | $0.20 \times 10^3$ | $1.09 \times 10^3$ |      |
| $\gamma_{x\alpha\alpha}(0,0)$ | 0.10 $\times 10^3$ | 0.10 $\times 10^3$ |      |
| $\gamma_{x\alpha\beta}(0,0,0)$ | 0.034 $\times 10^3$ | 0.034 $\times 10^3$ |      |
| $\gamma_{x\beta\beta}(0,0,0)$ | 0.014 $\times 10^3$ | 0.014 $\times 10^3$ |      |

All values are in a.u.

(a) The molecule is placed in the XZ plane. The geometry of the derivatives has been optimized by using the MP2/aug-cc-pVTZ method. (b) $\beta_{x\alpha}$ and $\beta_{x\beta}$ of HXeOXeH and HOH, and $\beta_{x\alpha}$ of HXeOH are zero by symmetry. (c) The Bishop–Kirtman perturbation theory approach (BKPT) has been used for the computation of the nr contribution.
observed for the polarizability and first hyperpolarizability (Table 5).

In order to analyze the effect of Xe insertion on the nr vibrational (hyper)polarizabilities in more detail, we have studied the changes of various terms in the context of BKPT theory. Our analysis is restricted to the x diagonal component of nr second hyperpolarizability, as its contribution is the largest (Table 5). The results are depicted in Figure 4. As expected for H2O, the major contribution to \( \gamma^{(2)} \) originates from the harmonic term, associated with \( [\mu^2 x^2]_0 \). The addition of one Xe atom (HXeOH) results in a remarkable increase of the first-order contribution, accounting for 77% of the total value, where the major effect originates from the \( [\mu x^2]_0 \) term (6.29 \( \times 10^4 \)). The small effect of the harmonic contribution (less than 5%) for this molecule is due to the mutual cancellation of the relevant terms. The addition of the second Xe atom (HXeOXeH) has a large effect on all terms (Fig. 3), but especially on the anharmonic terms \( [\mu^2 x^2]_1 \) and \( [\mu x^4]_0 \), which dominate the total value of the second vibrational hyperpolarizability. In conclusion, we may say that Xe insertion significantly affects the nr vibrational (hyper)polarizabilities at both static and dynamic levels, especially \( \gamma^{(2)} \), due to the significant increase of the anharmonic terms (Fig. 4).

Conclusions

The goal of this study was to discuss the vibrational (hyper)polarizabilities of several noble gas derivatives. Three Xe derivatives, HXeOXeH, HXeOXeF, and FXeOXeF, known for their stability were used in order to investigate several features associated with the nr vibrational NLO properties. For their assessment, both BKPT and finite field nr methodologies were employed. For the three studied derivatives, remarkably high nr vibrational (hyper)polarizabilities, especially second hyperpolarizabilities, were computed. The effect of electron correlation was found to be significant. A limited study on the HXeOXeH showed that the computed electronic and nr (hyper)polarizabilities are strongly affected by changes of the equilibrium geometry. An analysis based on the BKPT method revealed that the large values are due to the large contributions of the anharmonic terms, especially the electrical anharmonic ones (Fig. 4). The same trend was also observed for the dynamic nr properties, although these are considerably smaller than the static ones. However, they are still large in magnitude.

The effect of Xe insertion on the nr properties was also studied. The HOH, HXeOH, and HXeOXeH molecules were used. As expected, the harmonic terms dominate for the nr properties of H2O. Addition of one Xe atom (HXeOH) remarkably changes the contribution of the first-order electrical and/or mechanical anharmonicity terms \( ([\mu^2 x^2])_0 \). Insertion of a second Xe atom (HXeOXeH) results in a significant increase of both first- and second-order terms of \( \gamma^{(2)} \) (Fig. 4).

From the reported results, we may conclude that the anharmonic character of several vibrational modes in the Xe compounds \(^{[33,44]} \) results in remarkable high vibrational (hyper)polarizabilities. Let us note that these compounds are unlikely to be useful as NLO materials. However, the present NLO results are useful, because they demonstrate a mechanism for designing molecules with very large hyperpolarizabilities. The efficient modeling of new NLO materials should take into account not only their electronic structure, but also their vibrational movements. Finally, a more rigorous study of the higher-order vibrational properties would require the use of methods as employed for the NH3 molecule in Ref. [61] and will be the subject of a forthcoming study.

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