



On the Electronic Structure of H–Ng–Ng–F (Ng = Ar, Kr, Xe) and the Nonlinear Optical Properties of HXe₂F

A. Avramopoulos,^{*,†,||} L. Serrano-Andrés,^{*,‡} J. Li,[§] and M. G. Papadopoulos^{*,†}

Institute of Organic and Pharmaceutical Chemistry, National Hellenic Research Foundation, 48 Vas. Constantinou Ave., Athens 116 35, Greece, Molecular Sciences Institute, Universitat de València, Apartado 22085, València ES-46071, Spain, Accelrys Inc., Telesis Court, San Diego, California 92121, United States, and Department of Informatics and Computer Technology, Lamia Institute of Technology, Third Km Old National Road, 35100, Lamia, Greece

Received August 23, 2010

Abstract: The electronic ground state of H–Ng–Ng–F (Ng = Ar, Kr, Xe) has been studied theoretically by employing the ab initio complete active space valence bond (CASVB) and multi-state complete active space perturbation theory (MS-CASPT2) methods. Both levels of theory confirm the diradicaloid character (DC) of the HNg₂F ground state, increasing in the order Ar > Kr > Xe. The very significant effect of the first and, even more, the second Xe atom on the (hyper)polarizabilities has been shown and interpreted. Thus, the present results demonstrate a mechanism for producing very large (hyper)polarizabilities.

I. Introduction

There is currently a great need for novel materials for photonic applications (e.g., optical communications, data storage, and signal processing). Such materials must have a series of properties, prominently among which is the large magnitude of their nonlinear optical (NLO) properties. Various mechanisms and phenomena have been investigated, which lead to such large NLO properties, for instance, conjugation or charge transfer.^{1–3} Some time ago, we reported that insertion of a noble gas atom into a chemical bond, for example, Ar into HF leading to HArF⁴ or Xe into HC₂H leading to HXeC₂H,⁵ dramatically enhances the NLO properties.

Pauling predicted that stable bonds could be formed by heavy noble gas atoms, due to the reduced stability of the outer electrons, caused by the strong screening of the inner electrons.⁷ The first Xe derivative, XePtF₆, was reported by Bartlett in 1962,⁸ and soon after that, Claassen et al. reported

that xenon and fluorine can react to form XeF₄ (solid), which is stable at room temperature.⁹ After Bartlett's work, a large number of Xe derivatives were synthesized, and as Christie noted, this discovery "triggered a world-wide frenzy in this area."¹⁰

Various groups have inserted noble gas atoms in the bonds A–B (e.g., H–C, H–O, H–S, and C–C), leading to A–Ng–B and thus producing a large variety of compounds.^{11–14} Among those, one notes HNgY, where Y is an electronegative element or group (e.g., OH, CN, SH), which has been studied both experimentally and theoretically.^{15–17} These derivatives are metastable, with a global minimum HY + Ng. The bonding in HNgY involves the structure HNg⁺Y[–], where HNg⁺ is covalently bound and linked to Y[–] by a Coulombic attraction.¹⁸ It has been found that the inserted noble gas atom has a considerable positive charge.^{5,19} In general, there is a large energy barrier which prevents these molecules from dissociation.²⁰ A notable derivative in this series is HArF, which was synthesized by Khriachtchev et al.²¹ from the photolysis of hydrogen fluoride in a solid argon matrix. This is the first experimentally observed covalent neutral condensed phase argon derivative.²²

Among the most remarkable properties of the derivatives resulting by insertion of a noble gas atom are the linear and nonlinear optical (L&NLO) properties. It has been found that,

* Corresponding authors. E-mail: aavram@eie.gr (A.A.), Luis.Serrano@uv.es (L.S.-A.), mpapad@eie.gr (M.G.P.).

[†] National Hellenic Research Foundation.

^{||} Lamia Institute of Technology.

[‡] Universitat de València.

[§] Accelrys Inc.

for example, the insertion of Ar into HF (HArF) leads to a very large increase of the NLO properties.⁴ This has been confirmed by inserting Xe into $\text{H}-\text{C}_n-\text{H}$ (e.g., $\text{H}-\text{Xe}-\text{C}_2-\text{H}$, $\text{H}-\text{Xe}-\text{C}_4-\text{H}$, and $\text{H}-\text{C}_2-\text{Xe}-\text{C}_2-\text{H}$)⁵ and AuF leading to $\text{Au}-\text{Xe}-\text{F}$.²³

Derivatives involving the group Xe–Xe have also been considered. For example, Stein et al.²⁴ reported the formation of Xe_2^+ from the reduction of $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$. On the other hand, Drews and Seppelt²⁵ observed the formation of $\text{Xe}_2^+\text{Sb}_4\text{F}_{21}^-$ at -30°C , displaying a surprising, long Xe–Xe bond (3.087 Å). It was noted that this bond is not surpassed in length by any other element–element bond in main group chemistry.²⁵ Very recently, Frenking et al.⁶ reported the first quantum-chemical calculations on the stability of derivatives involving the Ng–Ng bond, where Ng = Ar, Kr, and Xe. The specific derivatives they investigated have the formula $\text{H}-\text{Ng}-\text{Ng}-\text{F}$.

Recently, Frenking et al.⁶ studied the insertion of *two* noble gas atoms in HF, leading to $\text{H}-\text{Ng}-\text{Ng}-\text{F}$, where Ng = Ar, Kr, and Xe. The present study reports on two questions related with $\text{H}-\text{Ng}-\text{Ng}-\text{F}$:

- (a) Which is the electronic structure of the ground state of these derivatives?
- (b) What is the effect of the second Xe atom on the linear and NLO properties of the resulting derivative?

Of considerable importance for this work is the analysis of the diradical character of HNg_2F . The literature connected with this feature and the NLO properties has been recently reviewed.²⁶

For this study, we have used a series of state-of-the-art quantum-chemical techniques (e.g., CCSD(T), CASPT2, and CASVB), and we have proved the need for a multiconfigurational description of the electronic structure of the mentioned systems, which turned out to have a large diradicaloid character in their ground state.

II. Computational Methods

II.1. Electronic Structure Computations. The electronic structure of $\text{H}-\text{Ng}-\text{Ng}-\text{F}$ has been investigated by employing valence bond (VB), complete active space (CAS), and CASPT2 methods.

The VB calculations were performed using the code VB2000,^{27–29} integrated in GAMESS. VB2000 is an *ab initio* electronic structure package based on an Algranbrant algorithm.³⁰ A unique feature in VB2000 is its general implementation of McWeeny's group function theory (GFT)³¹ and the combination of GFT and VB methods. The program allows a user to specify multiple groups of electrons, and each one of them can be treated with correlated methods, such as the complete active space valence bond (CASVB) method. In this way, more electrons can be included in VB calculations in an affordable way. The electrons in the molecules HNgNgF (assuming that all atoms are placed on the z axis) can be divided into four groups as follows:

- six π electrons in the three valence p_x orbitals of the three heavy atoms
- six π electrons in the three valence p_y orbitals of the three heavy atoms

- six σ electrons, which are shared among the four atoms
- the remaining valence and the core electrons

All 18 valence electrons of the first three groups have the potential to describe the weak bonding in the molecules. Therefore, for a rigorous treatment of the derivatives without discrimination, all 18 electrons were included in VB calculations, and the remaining electrons were treated as a Hartree–Fock core. The orbital symmetry of the valence electrons provides a natural way of grouping the electrons, and each group is strongly orthogonal to the others. In this study, all groups were treated by the CASVB method. Each of the two π -electron groups has six electrons in six orbitals (each heavy atom contributes two p orbitals). Such a treatment can be denoted as $\text{CASVB}(6,6) \cdot \text{CASVB}(6,6) \cdot \text{CASVB}(6,4)$, according to the “dot” notation, introduced in VB2000.^{28,29}

The above multigroup VB method is a natural extension of the conventional CASSCF and generalized VB (GVB) methods, both of which can be considered as special cases of a group function treatment. In the conventional complete active space self-consistent field (CASSCF) method, only one group is treated with correlation, and this group can have various numbers of electrons and orbitals. On the other hand, GVB can be considered as a multigroup VB treatment in which each VB group has two electrons in two orbitals. VB2000 has the most general implementation of the group function method: multiple groups can be included, and each group can have different numbers of electrons and orbitals and can be treated with different methods, such as VBSCF or CASVB. The wave functions are obtained by energy minimization under the strong orthogonality constraints between groups.

The electronic structure CASSCF/CASPT2^{32,33} computations were performed by using the ANO-RCC relativistic basis set³⁴ contracted to Xe [7s6p4d], Kr [6s5p3d], Ar [5s4p1d], F [5s3p1d], and H [3s1p]. The Douglas–Kroll procedure was included to consider relativistic effects.³⁴ The calculations were performed in the C_{2v} point group, where the C_2 axis coincides with the z molecular axis for all considered (linear) geometries. For these computations, one needs to take into account the existence of two electronic singlet states in A_1 symmetry ($^1\Sigma^+$ in $C_{\infty v}$ symmetry) mainly involving the σ and σ^* orbitals. The strong interaction between the states makes necessary the use of a two-state model. One may notice the different levels of calculation used in the present work. First, one can run a single- or multiple-root CASSCF calculation. In the former case, this is named state average (SA) CASSCF and provides orthogonal states and wave functions for the averaged states, unlike what happens for single-root CASSCF, in which the states are not orthogonal with the other states of the same spin and spatial symmetry. On top of the CASSCF wave function (single-root or SA), one can perform a state-specific (SS) CASPT2 calculation, providing also nonorthogonal states. Using the SS-CASPT2 states as a reference, it is possible to apply the multistate (MS) CASPT2 technique, a procedure which makes the SS-CASPT2 states interact, leading to orthogonal states and wave functions, the latter named perturbatively modified complete active space configuration

interaction (PMCAS-CI) wave functions.^{35–37} As a summary, we have two sets of results available: CASSCF wave functions and CASPT2 state energies and PMCAS-CI wave functions and MS-CASPT2 state energies. We have applied here different procedures to establish the most accurate results. In the final calculations, we run a state-average (SA) CASSCF calculation considering the two states (one of them being the ground state) and then the multistate (MS) CASPT2 technique. The lowest $^1\Pi$ state was also computed. Different active spaces were employed to ensure the convergence and accuracy of the results, as described later. Except otherwise mentioned, the calculations are reported using the 4440/12 active space ($a_1b_1b_2a_2$ /active electrons in the C_{2v} symmetry) corresponding to four σ - and four π -type orbitals. In the σ space, the HOMO–1 and HOMO orbitals have been included (four electrons in this space) as well as two correlating ones. The occupied orbitals involve the valence orbital p_z of F and the p_z of Rg. The π space involves two strongly occupied (eight electrons) and two correlating π orbitals. The former are the π valence orbitals of Rg. The CASPT2 calculations were performed using the MOLCAS suite of programs.³⁴

II.2. Calculation of the L&NLO Properties. When a molecule is set in a uniform static electric field F , its energy, E , may be expanded as follows:³⁸

$$E = E^0 - \mu_i F_i - (1/2)\alpha_{ij} F_i F_j - (1/6)\beta_{ijk} F_i F_j F_k - (1/24)\gamma_{ijkl} F_i F_j F_k F_l - \dots \quad (1)$$

where E^0 is the field free energy of the atom or the molecular system; F_i , F_j , F_k , and F_l are the field components; μ_i , α_{ij} , β_{ijk} , and γ_{ijkl} are the tensor components of the dipole moment, linear dipole polarizability, and first and second hyperpolarizability, respectively. Summation over repeated indices is implied. A finite field approach was used to compute the longitudinal components of the polarizability (α_{zz}) and the first (β_{zzz}) and second hyperpolarizability tensors (γ_{zzzz}), since these are dominant among the other tensor components and are sufficient to demonstrate the effect of the Xe atoms on the NLO properties.

The nonlinear optical properties of interest were computed by employing a series of methods including (i) the CCSD(T), which involves the iterative calculation of single and double excitation amplitudes as well as a perturbative treatment of triple excitations, and (ii) CASSCF/CASPT2. CCSD(T) is known to provide a satisfactory estimate of the electron correlation contribution.³⁹ CCSD(T), in connection with an appropriate basis set, is known to be one of the most accurate methods for the computation of the L&NLO properties. In addition, MS-CASPT2 is particularly suitable for systems with diradical character like HXe_2F . Thus, a comparative study of the L&NLO properties of HXe_2F , involving both CCSD(T) and MS-CASPT2, is expected to provide reliable L&NLO properties.

All of the multiconfigurational NLO property computations, corrected with CASPT2,³⁴ were performed by using the PolX⁴⁰ basis set, developed by Sadlej, where X denotes the element symbol. For all computations, the C_{2v} point group was used, where the C_2 axis, as noted above, coincides with the z molecular axis. In order to check the effect and the

Table 1. The Structure Weights of HAr_2F from CASVB(6,6)·CASVB(6,6)·CASVB(6,4) Calculations with Different Basis Sets

structure	weight [3-21G*]	weight [cc-pVTZ]	weight [MCP-TZP]	type
I. F Ar Ar H	0.88	0.87	0.88	diradical, F and H
II. F [−] Ar ⁺ Ar H	0.01	0.01	0.01	diradical, Ar ⁺ and H
III. F Ar Ar ⁺ H [−]	0.10	0.11	0.10	diradical, F, Ar ⁺
IV. F [−] Ar Ar ⁺ H	0.0	0.0	0.0	
V. F [−] Ar ⁺ Ar ⁺ H [−]	0.0	0.0	0.0	
VI. F [−] Ar Ar H ⁺	0.0	0.0	0.0	
VII. F Ar ⁺ Ar H [−]	0.0	0.0	0.0	

adequacy of the active space on the computed (hyper)polarizabilities, a number of different spaces and correlating electrons were considered. All of the multiconfigurational computations were performed by using the finite-field approach employing a number of field strengths along the C_2 axis. For the finite-field CASPT2 computations, one needs to take into account the near degeneracy of the two low-lying states of $^1\Sigma^+$ symmetry. These two states will be coupled by the electric field of A_1 symmetry (z direction). In order to account properly for this effect, we use first the (SA) CASSCF, considering the ground and the first excited state and then the multistate (MS) CASPT2^{35,36} technique, which leads to orthogonal states and smooth convergence with the finite field procedure.

The aug-cc-pVDZ series was also employed. For Xe, a small core (28 electrons), energy consistent, relativistic pseudopotential has been used.⁴¹ The 4spd outer-core shell is treated explicitly together with 5sp valence-orbitals. The usefulness and reliability of the pseudopotentials for the computation of the (hyper)polarizabilities has been documented.⁴²

All of the property values were computed by employing the Romberg approach,⁴³ in order to safeguard the numerical stability of our results and to remove higher order contaminations. A number of field strengths of the magnitude $2^m F$, where $m = 1, 2, 3$, and 4 and base field (F) is 0.0008 au, were used. The Gaussian 03 software⁴⁴ has been employed for all of the CCSD(T) calculations, while for the CASSCF/CASPT2 ones, the MOLCAS suite of programs was used.³⁴

III. Results

We shall first investigate the electronic ground state of HNg_2F , where Ng = Ar, Kr, Xe by employing CASVB, CASSCF/CASPT2 and MS-CASPT2 methods and subsequently we shall discuss the L&NLO properties of HXe_2F . All the computations were performed with geometries taken from ref.⁶

III.1. The Ground State of HNg_2F by CASVB Calculations. HAr_2F and HKr_2F . Tables 1 and 2 show the structure weights for HAr_2F and HKr_2F , computed with the Chirgwin–Coulson method⁴⁵ and by employing three different basis sets in order to check the sensitivity of the results. It was found that all three basis sets give quite similar results. It is observed that the total weight of the resonance structures, with diradical characteristics, is, approximately, 99% for HAr_2F and 97–98% for HKr_2F (depending on the basis set). The structure weights computed with different basis sets are

Table 2. The Structure Weights of HKr₂F from CASVB(6,6)•CASVB(6,6)•CASVB(6,4) Calculations with Different Basis Sets

structure	weight [3-21G*]	weight [cc-pVTZ]	weight [MCP-TZP]	type
I. F Kr Kr H	0.81	0.81	0.81	diradical, F and H
II. F ⁻ Kr ⁺ Kr H	0.04	0.05	0.05	diradical, Kr ⁺ and H
III. F Kr Kr ⁺ H ⁻	0.13	0.12	0.11	diradical, F, Kr ⁺
IV. F ⁻ Kr Kr ⁺ H	0.01	0.01	0.01	
V. F ⁻ Kr ⁺ Kr ⁺ H ⁻	0.00	0.00	0.0	
VI. F ⁻ KrKr H ⁺	0.00	0.01	0.01	
VII. FKr ⁺ KrH ⁻	0.01	0.01	0.01	

Table 3. The Structure Weights of HXe₂F from CASVB(6,6)•CASVB(6,6)•CASVB(6,4) Calculations (Basis Set: MCP-TZP)

structure	weight	type
I. F Xe Xe H	0.53	diradical, F and H
II. F ⁻ Xe ⁺ Xe H	0.17	diradical, Xe ⁺ and H
III. F Xe Xe ⁺ H ⁻	0.14	diradical, F, Xe ⁺
IV. F ⁻ Xe Xe ⁺ H	0.06	
V. F ⁻ Xe ⁺ Xe ⁺ H ⁻	0.04	
VI. F ⁻ XeXe H ⁺	0.02	
VII. FXe ⁺ XeH ⁻	0.01	

Table 4. Atomic Partial Charge of HAR₂F from CASVB(6,6)•CASVB(6,6)•CASVB(6,4) Calculations (Basis Set: cc-pVTZ)

atomic charge	VB (a)	VB (b)	MP2/NBO ^a
H	0.34	-0.27	0.42
Ar (1)	0.58	0.27	0.51
Ar (2)	0.01	0.01	0.05
F	-0.93	-0.01	-0.98

^a Method of computation: MP2/def2-TZVPP//MP2/Def2-TZVPP.⁶**Table 5.** The Structure Weights of the Two CASVB Solutions of HAR₂F (Basis Set: cc-pVTZ)

structure	state a	state b
I. F Ar Ar H	0.00	0.87
II. F ⁻ Ar ⁺ Ar H	0.02	0.01
III. F ArAr ⁺ H ⁻	0.00	0.11
IV. F ⁻ Ar Ar ⁺ H	0.57	0.00
V. F ⁻ Ar ⁺ Ar ⁺ H ⁻	0.01	0.00
VI. F ⁻ ArAr H ⁺	0.38	0.00
VII. FAr ⁺ ArH ⁻	0.00	0.00

remarkably similar; thus any possible uncertainty due to basis set choice is eliminated.

HXe₂F. Table 3 shows the structure weights for HXe₂F. A major difference of HXe₂F from the other two molecules is that the total weight for the nondiradical structures is, approximately, 13% for HXe₂F, while for HAR₂F and HKr₂F, it is 1% and 2–3% (depending on the basis set), respectively.

Diradical vs Charge Transfer State. Two VB wave functions with close total energies were obtained for HAR₂F. They differ by ~30 kcal/mol (lower is b, Table 4). The above solutions have very different charge distributions. The atomic charges obtained from the Mulliken population analysis of the two VB wave functions are shown in Table 4. The structure weights of states a and b show a dramatic difference (Table 5). Structures I–III have strong diradical characteristics [state b], while structures IV and VI have charge-

transfer features [state a]. We can label state a as a charge transfer state and b as a diradical. Similar results were obtained for HKr₂F. For HXe₂F, the VB calculations show only one diradical state. *Therefore, we believe that the derivatives HNg₂F have dominant diradical characteristics.*

III.2. The Ground State of HNg₂F by MS-CASSCF/CASPT2 Calculations. As the multiconfigurational calculations show, the HNg₂F systems display a number of close-lying excited states, in particular two of ¹Σ⁺ and one of ¹Π symmetry. Especially, the two ¹Σ⁺ states, related to the electronic configurations σ² and σσ* and belonging to the A₁ symmetry in the C_{2v} point group, strongly interact and require a large amount of electronic correlation to be properly described. This is mainly shown by the different descriptions obtained at different levels of theory. In particular, it will be shown that remarkable differences are observed between single vs multiple (two) root (state average, SA) CASSCF descriptions, and followed by MS-CASPT2 computations.

HAr₂F and HKr₂F. The electronic ground states of HAR₂F and HKr₂F have largely distinct descriptions at different levels of theory. Single reference methods like HF, MP2, or CCSD(T) give a closed-shell picture, characterizing the state as ¹Σ⁺(σ²), displaying a bound structure,⁶ a description at odds with that provided at the CASVB level in the previous section. When performing a single-root CASSCF/CASPT2 calculation, the resulting wave function has a predominantly closed-shell character. We have found, for instance for HAR₂F employing the 4440/12 active space, a weight of 70% of the (σ²) configuration, although the diradical-type (σσ*) configuration also contributes at 1%. However, the previous description remarkably changes a lot when performing a two-root state average SA (2) CASSCF calculation, followed by state-specific SS-CASPT2, which allows describing the state as ¹Σ⁺(σσ*), due to the predominance of the open-shell singlet diradical structure. For HAR₂F, the ground state wave function is composed of the following configurations: 24% (σ)² + 71% (σσ*), a description that does not change if we modify the number of averaged roots and that changes moderately when we apply the multi-state (MS) CASPT2 approach, which provides a PMCAS-CI description as 38% (σ)² + 56% (σσ*). The HOMO/LUMO orbitals are the same at the SA-CASSCF and PMCAS-CI levels. The HOMO σ orbital is mainly composed of the p_z of F, and the LUMO σ* orbital is mainly formed by the s of H with small contributions of the noble gas atoms. On the other hand, the low-lying excited state of the same symmetry (2¹Σ⁺), placed 0.036 au (0.98 eV) above the ground state, is given by 56% (σ)² + 38% (σσ*).

The picture of HKr₂F is similar to that of HAR₂F. Although the nonorthogonal single-state CASSCF/CASPT2 result provides a closed shell character for the ground state [75% (σ)²], the more accurate two-state MS-CASPT2 procedure yields a ground state description given by 40% (σ)² + 53% (σσ*). The 2¹Σ⁺ excited state lies 0.072 au (1.959 eV) above the ground state and is given by 53% (σ)² + 39% (σσ*) at the MS-CASPT2 level. These values were computed employing the 4440/12 space.

So far, it seems clear that the ground states of HAR₂F and HKr₂F can be characterized as ¹Σ⁺(σσ*), displaying a

predominantly diradicaloid and dissociative nature, as proved by CASVB and the most complete approach SA-CASSCF/CASPT2 and PMCAS-CI/MS(2)-CASPT2 multiconfigurational calculations. The most striking aspect is undoubtedly the dramatic change of the wave function composition displayed from the predominantly closed-shell single-root SR-CASSCF description to the two-root SA-CASSCF and PMCAS-CI characterizations, with prevalent open-shell singlet diradical structures. The latter is not entirely unexpected. Although both approaches display a multiconfigurational character, a single-root CASSCF wave function is nonorthogonal with respect to the other states of the same spin and spatial symmetry. If the single-root state strongly interacts with neighboring states like here, the obtained wave function can be incorrectly mixed or collapse, favoring one of the possible solutions, the closed-shell singlet here. This is common in cases of near degenerate states like conical intersections or avoided crossings.³⁶ Therefore, at least a two-state model needs to be used. SA-CASSCF wave functions are orthogonal for the computed states ($1^1\Sigma^+$ and $2^1\Sigma^+$ here), although the following second-order perturbation theory SS-CASPT2 solution actually displays nonorthogonal CASPT2 states.^{36,37} In cases like the present one, it is therefore compulsory to provide a PMCAS-CI/MS-CASPT2 multistate solution that finally yields fully orthogonal states and wave functions at the highest correlated level.

HXe₂F. A single-root CASSCF/CASPT2 calculation on HXe₂F gives a ground $1^1\Sigma^+$ state of predominantly closed-shell character [90% (σ^2)]. Different from the cases of the HAr₂F and HKr₂F molecules, the two-root state average CASSCF level (followed by state-specific (SS) CASPT2) provides a description where the closed-shell character slightly predominates, 49% (σ^2) + 44% ($\sigma\sigma^*$), a dominance that increases to 58% (σ^2) + 35% ($\sigma\sigma^*$) at the final PMCAS-CI/MS(2)-CASPT2 level. The orbital description is similar to that mentioned above for the other systems. The $2^1\Sigma^+$ excited state lies 0.114 au (3.099 eV) above the ground state and is described by 43% (σ^2) + 49% ($\sigma\sigma^*$) and 34% (σ^2) + 58% ($\sigma\sigma^*$) at the two-state SA-CASSCF/CASPT2 and PMCAS-CI/MS(2)-CASPT2 levels of theory, respectively.

The above results demonstrate that the multisate CASPT2 is the correct theory for the description of the ground state of HNg₂F and illustrate how the weight of the closed-shell σ^2 configuration increases with the atomic number of the noble gas atom, while the weight of $\sigma\sigma^*$ decreases.

The sequence of lowest-lying singlet excited states in the three molecules also illustrates the differences in their electronic structure. The MS-CASPT2 results are, for HAr₂F, $1^1\Sigma^+(\sigma\sigma^*) = 0.00$ eV, $1^1\Pi(\pi\sigma^*) = 0.60$ eV, and $2^1\Sigma^+(\sigma^2) = 0.98$ eV; for HKr₂F, $1^1\Sigma^+(\sigma\sigma^*) = 0.00$ eV, $1^1\Pi(\pi\sigma^*) = 1.55$ eV, and $2^1\Sigma^+(\sigma^2) = 1.96$ eV; and for HXe₂F, $1^1\Sigma^+(\sigma^2) = 0.00$ eV, $2^1\Sigma^+(\sigma\sigma^*) = 3.09$ eV, and $1^1\Pi(\pi\sigma^*) = 3.18$ eV. The location and properties of these low-lying excited states are basic features of HNg₂F, which lead to large NLO properties.²⁶ This will be discussed more extensively in section III.5.

It is known⁴⁷ that the lowest singlet–triplet gap provides an indication for the diradical character of a system. The lowest triplet state $3^3\Sigma^+$ has been computed for all of the

Table 6. The Static Dipole Moment and (Hyper)Polarizabilities of HXe₂F Computed Using Different Methods

property (au)	method			
	HF	MP2	CCSD	CCSD(T)
μ_z	6.454 ^a 6.458 ^b	4.855 ^a 4.972 ^b	4.929 ^a 4.990 ^b	3.788 ^a 3.856 ^b
α_{zz}	206.96 ^a 207.61 ^b	349.05 ^a 343.46 ^b	312.63 ^a 316.08 ^b	420.43 ^a 423.99 ^b
β_{zzz}	−9633 ^a −9630 ^b	−19900 ^a −19010 ^b	−11040 ^a −10900 ^b	−11040 ^a −10700 ^b
$(\gamma_{zzzz} \times 10^{-3})$	720 ^a 700 ^b	853 ^a 745 ^b	−510 ^a −625 ^b	−4000 ^a −4500 ^b

^a aug-cc-pVDZ basis set. For Xe, an effective core potential was used.⁴¹ ^b PolX basis set.

studied HNg₂F derivatives. It has been found that the triplet state has a strong diradical character (96% $\sigma\sigma^*$). The natural occupation numbers are 1.0 for both HOMO and LUMO. At the MS-CASPT2/ANO level, the triplet state lies 0.2 eV (4.7 kcal/mol), 0.64 eV (14.7 kcal/mol), and 1.25 eV (28.7 kcal/mol) higher in energy than the singlet ground state for the Ar, Kr, and Xe derivatives, respectively. Wirz⁴⁸ suggested that a diradical is “a molecular entity whose lowest singlet and triplet state energies do not differ by much more than kT, say 2 kcal mol^{−1}. The expression ‘biradicaloid’ would then extend this range to say 24 kcal mol^{−1}”. According to this definition, all three species are diradicaloids. The diradicaloid character depends on Ng and decreases as the atomic number of the noble gas atom increases.

As a conclusion, both final sets of results, computed with the CASVB and MS-CASPT2 methods, confirm a strong diradical element in the ground state of H–Ng–Ng–F, which follows the sequence Ar > Kr > Xe.

For comparison we note that the electronic ground state of HXeF is described by (σ^2), at the MS-CASPT2 level of theory (4550/16 active space). This contributes 88% to the ground state configuration, implying that the state is dominated by a strong closed shell character. In the lowest-lying excited state, which lies 7.07 eV above the ground state and thus very weakly interacting with it, the contribution of $\sigma\sigma^*$ is 88%. A similar picture emerges at the CASSCF level. *Thus, the diradical character is clearly induced by the second Xe atom.*

III.3. The L&NLO Properties. The computed property values for HXe₂F are presented in Tables 6 and 7. This is the system with the largest σ^2 character in its ground state. We will focus our attention on the longitudinal components, since the other ones are much smaller. For example, at the CCSD(T)/PolX level, we found that α_{xx} is 9.75 times smaller than α_{zz} . The PolX results are in satisfactory agreement with those computed with the aug-cc-pVDZ set (Table 6). It is observed that the dynamic electron correlation effect is quite strong for all of the considered properties and especially for the second hyperpolarizability, where at the CC level of theory a change of sign for γ_{zzzz} has been found, in comparison to that observed with the HF and MP2 methods. At the HF level of theory, the dipole moment of the system is overestimated, while a significant reduction of μ_z is observed by taking into account correlation. The very large effect of triples on γ_{zzzz} is noted.

Table 7. MS-CASPT2 Dipole Moment and (Hyper)Polarizability of HXe₂F. The PolX Basis Set was Used

property (au)	A ₁ B ₁ B ₂ A ₂ /act.elect.						
	2000/2	3000/4	2220/6	4220/8	2440/10	4440/12	4550/16
μ_z	3.347	3.841	4.938	4.454	5.007	4.290	4.719
α_{zz}	460.49	407.04	472.51	[3.564] ^a 372.74	[4.603] ^a 456.41	[3.926] ^a 398.94	383.20
β_{zzz}	−5460	−2450	−22640	[382.95] ^a −10200	[383.00] ^a −23990	[340.30] ^a −8300	−13800
$(\gamma_{zzzz} \times 10^{-3})$	−3670	−4130	−4120	[NC] ^b −3100	[−27000] ^a −4000	[−16100] ^a −3660	−3500
						[−15000] ^a	

^a Single root calculation. ^b Nonconvergence.**Table 8.** The Dipole Moment and the (Hyper)Polarizabilities of HF, HXeF, and HXe₂F^a

property (au)	method					
	HF			CCSD(T)		
	HF ^b	HXeF ^c	HXe ₂ F ^c	HF ^b	HXeF ^c	HXe ₂ F ^c
μ_z	0.759	2.283	6.454	0.703	1.975	3.788
α_{zz}	5.59	51.25	206.96	6.19	59.59	420.43
β_{zzz}	−9.8	−436.7	−9633	−11.5	−582.1	−11040
$(\gamma_{zzzz} \times 10^{-3})$	0.219	16.9	720	0.284	22.7	−4000

^a The computations were performed with the aug-cc-pVDZ basis set. For Xe, an effective core potential of 28 was used.⁴¹ ^b The experimental geometry was used.⁵⁴ ^c The geometries were taken from ref 6.

We have employed the T_1 diagnostic in order to find an indication for the importance of nondynamical correlation effects. A T_1 value of 0.03 was found, another indication that the results from single reference methods are potentially unreliable.^{49–51}

The multiconfigurational computations are presented in Table 7, for which the MS-CASPT2/PolX method was employed. In order to check the reliability of the results, the effect of the enlargement of the active space is considered. Several spaces and a number of correlating electrons were used in order to fully support the adequacy of the multiconfigurational results. It is observed that inclusion of correlating π orbitals is quite important in order to get reliable hyperpolarizability values (e.g., one may compare the results of the computations 2000/2 and 2220/6). This indicates the importance of the dynamic electron correlation effect on the considered properties. By further enlarging the 2220 space with two σ orbitals (one occupied, one correlated), a remarkable diminishment of the first and second order hyperpolarizability values is observed. By proper addition of π orbitals leading to either 4440/12 or 4550/16 spaces, a smaller dependence of the computed property values on the active space is observed. It is seen that SS-CASPT2 hyperpolarizability (β and γ) values differ remarkably in comparison with the MS-CASPT2 ones. This difference is particularly pronounced for γ_{zzzz} . The MS-CASPT2 property values, computed with the 4550/16 space, are in reasonable agreement with the CCSD(T) ones (Table 6).

III.4. The Effect of Xe Insertion. In this section, we shall consider the effect of inserting one and two Xe atoms in the HF system (leading to HXeF and HXe₂F) on the L&NLO properties (Tables 8 and 9).

Electron Correlation Effects. The electron correlation correction (ECC) for a property p , where $p = \mu_z, \alpha_{zz}, \beta_{zzz}$, or

Table 9. The Transition Dipole Moment (μ_{ge}), the Excitation Energy (ΔE), and the Dipole Moments of the Ground $1^1\Sigma^+$ (μ_g) and the Lowest-Lying $2^1\Sigma^+$ Excited State (μ_e)^a

property (au)	method					
	CCSD			MS-CASPT2 ^b		
	HF ^c	HXeF ^d	HXe ₂ F ^d	HF ^c	HXeF ^d	HXe ₂ F ^d
ΔE	0.681	0.259	0.117	0.521	0.256	0.107
$ \mu_{ge} $	0.463	1.647	3.948	0.502	1.761	4.199
μ_e				−0.513	−1.376	2.325
μ_g	0.709	2.051	4.990	0.650	1.956	4.719
$\Delta\mu_{eg}$				−1.163	−3.332	−2.394
β_{zzz}^e				−3.2	−473	−11070

^a All the properties were computed with the PolX basis set.

^b The 4550 space in C_{2v} point group was employed in these MS-CASPT2 computations. ^c The experimental geometry was used.⁵⁴ ^d The geometries were taken from ref 6. ^e Value computed by employing a two state model approximation.

γ_{zzzz} , is defined as $p^{ECC} = p[\text{CCSD(T)}] - p[\text{HF}]$ (HF: Hartree–Fock). It is observed that ECC decreases the value of μ_z and increases the values of α_{zz} , $|\beta_{zzz}|$, and $|\gamma_{zzzz}|$ (Table 6). The effect of ECC increases remarkably with the number of Xe atoms (Table 8). For example, insertion of one and two Xe atoms increases the value of γ_{zzzz} by 89.9 and 813.8 times, respectively.

Effect of Xe Insertion on the (Hyper)Polarizabilities. Comparing the results of HXe₂F with those of the HXeF and HF (hydrogen fluoride) systems, it is evident that Xe insertion significantly modifies all the presented properties, whereas its effect is quite enhanced, especially on β_{zzz} and γ_{zzzz} (Table 8). For example, the ratio $\gamma_{zzzz}[\text{HXeF}]/\gamma_{zzzz}[\text{HF}]$ is 80, while $\gamma_{zzzz}[\text{HXe}_2\text{F}]/\gamma_{zzzz}[\text{HXeF}]$ is −176. It is noted that the enhancement of the property, due to Xe, is multiplicative, that is,

$$p(\text{HXe}_2\text{F})/p(\text{HF}) = [p(\text{HXeF})/p(\text{HF})][p(\text{HXe}_2\text{F})/p(\text{HXeF})] \quad (\text{HF: hydrogen fluoride})$$

In order to further quantify the effect of the insertion of one and two Xe atoms in the HF system, we have computed the differential (hyper)polarizability, a property useful in the analysis of electron delocalization and bonding.⁵² These properties are defined as

$$\text{DP} = \alpha_{\text{diff}} = \alpha_{zz}(\text{HXe}_2\text{F}) - \alpha_{zz}(\text{HF}) - 2\alpha(\text{Xe}) \quad (1a)$$

$$\text{DHP} = \gamma_{\text{diff}} = \gamma_{zzzz}(\text{HXe}_2\text{F}) - \gamma_{zzzz}(\text{HF}) - 2\gamma(\text{Xe}) \quad (2)$$

We found, at the CCSD(T)/aug-cc-pVDZ level, $\text{DP} = 363.2$ au and $\text{DHP} = -3994.9 \times 10^3$ au. The corresponding

properties for the Xe atom are $\alpha = 27.87$ au and $\gamma = 20.03 \times 10^3$ au. *The dramatic effect on the (hyper)polarizabilities, induced by two Xe atoms, is quite clear.*

III.5. Interpretation of the Results. In this section, we will interpret the computed linear and nonlinear optical properties.

In particular, we would like to explain the very big change of β_{zzz} by inserting one and two Xe atoms in HF. We shall employ a two state-model (TSM), based on the sum over states (SOS) approach:⁵³

$$\beta_{zzz}(0) \approx \frac{3(\mu_e - \mu_g)\mu_{ge}^2}{(\Delta E)^2} \quad (3)$$

where μ_e and μ_g are the excited- and ground-state dipole moments, respectively, μ_{ge} is the transition dipole moment, and ΔE is the transition energy. The MS-CASPT2(4550/16) method with two roots and the PolX basis set were employed in order to compute the lowest-lying $2^1\Sigma^+$ excited state. Thus, for the implementation of eq 3, we have used μ_e , μ_g , and μ_{ge} values computed at the PMCAS-CI level, while the excitation energies were calculated by employing MS-CASPT2 theory.

Inserting one and, even more, two Xe atoms in HF leads to an increase of μ_{ge} and decrease of ΔE . Similarly $|\Delta\mu_{eg}| = |\mu_e - \mu_g|$ is larger for HXeF and HXeXeF, in comparison to that of HF. The above features explain the very big effect of one and, even more, two Xe atoms on the first hyperpolarizability. It is noted that β_{zzz} of HF, HXeF, and HXeXeF, computed by TSM (Table 9), is $-11\,070$ ($-11\,040$), -473 (-582.1), and -3.2 (-11.5) au, respectively. In parentheses are the corresponding CCSD(T) values (Table 8). Thus, the TSM model gives β_{zzz} values in qualitative agreement with those computed with the CCSD(T) method. A very good agreement between the TSM and the CCSD(T) values for the first hyperpolarizability of HXeXeF is observed, indicating the significant contribution of the $\sigma\sigma^*$ transition to the NLO response of this derivative.

Frenking et al.⁶ noted the following: “The substantial activation barrier, which is predicted at different levels of theory, suggests that HXeXeF could be observed in a low-temperature xenon matrix”. However, currently, HXeXeF is unlikely to be useful as an NLO material. The present NLO results are useful, because they demonstrate a mechanism (that is, insertion of noble gas atoms in a bond) for producing very large hyperpolarizabilities. Thus, although HXeXeF, currently, could not be considered as a material, it may show a way to produce one.

IV. Concluding Remarks

CASVB and CASPT2 computations have shown the diradicaloid character of the ground state of the HNg₂F systems, which decreases in the noble gas atom (Ng) order Ar > Kr > Xe. The diradicaloid character relies on the predominance of the $\sigma\sigma^*$ open-shell configuration in the ground state, the smallest in HXe₂F. The proper description of the state electronic structure requires the use of multiconfigurational approaches, but not only that. As the two low-lying states of the $^1\Sigma^+$ symmetry strongly interact, a two-level treatment

like that provided by SA(2)–CASSCF/CASPT2 or, better, PMCAS–CI/MS(2)–CASPT2 is required, whereas single-root SR–CASSCF procedures may lead to nonorthogonal improper solutions. The decreasing diradicaloid character upon increasing the noble gas atomic number is confirmed by both the increasing singlet–triplet energy gap, which diminishes the diradical character of the ground state, and the singlet excited state structure, which evidences the stabilization of the closed-shell σ^2 configuration in the heaviest HXe₂F system. Both CCSD(T) and MS–CASPT2 computations have shown the great effect of the two Xe atoms on the NLO properties. Specifically, it has been found that insertion of one and two Xe atoms leads to an increase of β_{zzz} by 51 [= ($\beta_{zzz}\{\text{HXeF}\}/\beta_{zzz}\{\text{HF}\}$)] and 960 [= ($\beta_{zzz}\{\text{HXe}_2\text{F}\}/\beta_{zzz}\{\text{HF}\}$)] times, respectively, at the CCSD(T) level (Table 8). The corresponding increases of $|\gamma_{zzzz}|$ are 80 and 14 085 times, respectively.

Acknowledgment. The authors thank Professor G. Frenking for his useful comments. The research reported has been supported by the Spanish MICINN/FEDER projects CTQ2007-61260, CTQ2010-14892, and CSD2007-0010 Consolider-Ingenio in Molecular Nanoscience and by the Generalitat Valenciana. Grants in computing time from TerraGrid (USA) and DEISA (7th Framework Programme) are gratefully acknowledged.

References

- (1) Papadopoulos, M. G.; Waite, J. *J. Chem. Soc., Faraday Trans.* **1990**, 86, 3525.
- (2) Waite, J.; Papadopoulos, M. G. *J. Phys. Chem.* **1990**, 94, 6244.
- (3) Waite, J.; Papadopoulos, M. G. *J. Chem. Phys.* **1985**, 82, 1427.
- (4) Avramopoulos, A.; Reis, H.; Li, J.; Papadopoulos, M. G. *J. Am. Chem. Soc.* **2004**, 126, 6179.
- (5) Avramopoulos, A.; Serrano-Andrés, L.; Li, J.; Reis, H.; Papadopoulos, M. G. *J. Chem. Phys.* **2007**, 127, 214102.
- (6) Jiménez-Halla, C. O. C.; Fernández, I.; Frenking, G. *Angew. Chem., Int. Ed.* **2009**, 48, 366.
- (7) Pauling, L. *J. Am. Chem. Soc.* **1933**, 55, 895.
- (8) Bartlett, N. *Proc. Chem. Soc. London* **1962**, 218.
- (9) Claassen, H. H.; Selig, H.; Malm, J. G. *J. Am. Chem. Soc.* **1962**, 84, 3593.
- (10) Christie, K. O. *Angew. Chem., Int. Ed.* **2001**, 40, 1419.
- (11) Berski, S.; Sivi, B.; Lundell, J.; Noury, S.; Latajka, Z. *New Trends in Quantum Systems in Chemistry and Physics*, Maruani, J., Minot, C., McWeeny, R., Smeyers, Y. G., Wilson, S., Eds.; Kluwer Academic Publishers: Norwell, MA, 1999; Vol. 1, p 259.
- (12) Brown, E.; Cohen, A.; Gerber, R. B. *J. Chem. Phys.* **2005**, 122, 171101.
- (13) Khriachtchev, L.; Taskanen, H.; Lundell, J.; Pettersson, M.; Kiljunen, H.; Räsänen, M. *J. Am. Chem. Soc.* **2003**, 125, 4696.
- (14) Papadopoulos, M. G.; Avramopoulos, A. *CP963, Computational Methods in Science and Engineering. Theory and Computation: Old Problems and New Challenges*. Maroulis, G., Simos, G., Eds.; American Institute of Physics: College Park, MD, 2007; p 316.

- (15) Ahokas, J.; Kunttu, H.; Khriachtchev, L.; Pettersson, M.; Räsänen, M. *J. Phys. Chem. A* **2002**, *106*, 7743.
- (16) Lundell, J.; Chaban, G. M.; Gerber, R. B. *J. Phys. Chem. A* **2000**, *104*, 7944.
- (17) Lundell, J.; Pettersson, M.; Khriachtchev, L.; Räsänen, M.; Chaban, G. M.; Gerber, R. B. *Chem. Phys. Lett.* **2000**, *322*, 389.
- (18) (a) Pettersson, M.; Lundell, J.; Räsänen, M. *Eur. J. Inorg. Chem.* **1999**, 729. (b) Lein, M.; Frunzke, J.; Frenking, G. *Struct. Bonding (Berlin)* **2004**, *106*, 181.
- (19) Lundell, J.; Chaban, G. M.; Gerber, R. B. *Chem. Phys. Lett.* **2000**, *331*, 308.
- (20) Ansbacher, T.; Gerber, R. B. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4175.
- (21) Khriachtchev, L.; Pettersson, M.; Runeberg, N.; Lundell, J.; Räsänen, M. *Nature* **2000**, *406*, 874.
- (22) Runeberg, N.; Pettersson, M.; Khriachtchev, L.; Lundell, J.; Räsänen, M. *J. Chem. Phys.* **2001**, *114*, 836.
- (23) Holka, F.; Avramopoulos, A.; Loboda, O.; Kellö, V.; Papadopoulos, M. G. *Chem. Phys. Lett.* **2009**, *472*, 185.
- (24) Stein, L.; Norris, J. R.; Downs, A. J.; Minihan, A. R. *J. Chem. Soc. Chem. Commun.* **1978**, 502.
- (25) Drews, T.; Seppelt, K. *Angew. Chem., Int. Ed.* **1997**, *36*, 273.
- (26) Serrano-Andrés, L.; Avramopoulos, A.; Li, J.; Labéquerie, P.; Bégué, D.; Kellö, V.; Papadopoulos, M. G. *J. Chem. Phys.* **2009**, *131*, 134312.
- (27) Li, J.; McWeeny, R. *Int. J. Quantum Chem.* **2002**, *89*, 208.
- (28) Li, J.; Duke, B. J.; Klapötke, T. M.; McWeeny, R. *J. Theor. Comput. Chem.* **2008**, *7*, 853.
- (29) Li, J.; Duke, B. J.; McWeeny, R. *VB2000*, version 2.1; SciNet Technologies: San Diego, CA, 2010. URL: <http://www.vb2000.net> (accessed Mar 2010).
- (30) Li, J.; Pauncz, R. *Int. J. Quantum Chem.* **1997**, *62*, 245.
- (31) McWeeny, R. *Proc. R. Soc. London, Ser. A* **1959**, *253*, 242.
- (32) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.
- (33) Roos, B. O.; Andersson, K.; Fülcher, M. P.; Malmqvist, P.-Å.; Serrano-Andrés, L.; Pierloot, K.; Merchán, M. *Adv. Chem. Phys.* **1996**, *93*, 219.
- (34) Aquilante, F.; De Vico, L.; Ferré, N.; Ghigo, G.; Malmqvist, P.-Å.; Pedersen, T.; Pitonak, M.; Reiher, M.; Roos, B. O.; Serrano-Andrés, L.; Urban, M.; Veryazov, V.; Lindh, R. *J. Comput. Chem.* **2010**, *31*, 224.
- (35) Finley, J.; Malmqvist, P.-Å.; Roos, B. O.; Serrano-Andrés, L. *Chem. Phys. Lett.* **1998**, *288*, 299.
- (36) Serrano-Andrés, L.; Merchán, M.; Lindh, R. *J. Chem. Phys.* **2005**, *122*, 104107.
- (37) Merchán, M.; Serrano-Andrés, L. *Ab Initio Methods for Excited States. Computational Photochemistry*; Olivucci, M., Ed.; Elsevier: Amsterdam, 2005.
- (38) Buckingham, A. D. *Adv. Chem. Phys.* **1967**, *12*, 107.
- (39) Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic Structure Theory*; Wiley: New York, 2000.
- (40) Sadlej, A. J. *Collect. Czech. Chem. Commun.* **1998**, *53*, 1995. (b) <http://www.qch.fns.Uniba.sk/Baslib/POL> (accessed date March, 2010).
- (41) Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2003**, *119*, 11113.
- (42) Jansik, B.; Schimmelpfennig, B.; Norman, P.; Mochizuki, Y.; Luo, Y.; Ågren, H. *J. Phys. Chem. A* **2002**, *106*, 395.
- (43) Davis, P. J.; Rabinowitz, P. *Numerical Intergration*; Blaisdell: London, 1967; p 166.
- (44) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T., Jr.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, V.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, S.; Clifford, A. G.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Gaussian, Inc.: Wallingford, CT, 2004.
- (45) Chirgwin, B. H.; Coulson, C. A. *Proc. R. Soc. London, Ser. A* **1950**, *201*, 196.
- (46) (a) Sakai, V.; Miyoshi, E.; Klobukowski, M.; Huzinaga, S. *J. Chem. Phys.* **1997**, *106*, 8084. (b) Miyoshi, E.; Sakai, Y.; Tanaka, K.; Masamura, M. *THEOCHEM* **1998**, *451*, 41. (c) Noro, T.; Sekiya, M.; Koga, T. *Theor. Chem. Acc.* **1997**, *98*, 25. (d) Sekiya, M.; Noro, T.; Osanai, Y.; Koga, T. *Theor. Chem. Acc.* **2001**, *106*, 297.
- (47) Bachler, V.; Olbrich, G.; Neese, F.; Wieghardt, K. *Inorg. Chem.* **2002**, *41*, 4179.
- (48) Wirz, J. *Pure Appl. Chem.* **1984**, *56*, 1289.
- (49) Lee, T. J.; Rice, J. E.; Scuseria, G. E.; Schaefer, H. F., III. *Theor. Chim. Acta* **1989**, *75*, 81.
- (50) Lee, T. J.; Taylor, P. R. *Int. J. Quant. Chem. Symp.* **1989**, *23*, 199.
- (51) Lee, T. J.; Head-Gordon, M.; Rendell, A. P. *Chem. Phys. Lett.* **1995**, *243*, 402.
- (52) Maroulis, G. *J. Chem. Phys.* **2008**, *129*, 044314.
- (53) Oudar, L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.
- (54) Cadet, P. E.; Huo, W. M. *J. Chem. Phys.* **1967**, *47*, 614.

CT100471K