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A R T I C L E S

The Dipole Moment, Polarizabilities, and First Hyperpolarizabilities of HArF. A Computational and Comparative Study

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Abstract: The electronic and vibrational contributions to the dipole moment, polarizabilities, and first hyperpolarizabilities of HArF are reported. These have been computed by using a series of systematically built basis sets and a hierarchy of computational methods. HArF has a very large first hyperpolarizability along the z axis. This has been rationalized by invoking the difference in the electronic structure between the ground and the first excited state. The argon fluorohydride has been recently derived and characterized. The present study provides complementary data for the understanding of the electronic structure of this interesting argon derivative.

I. Introduction

The investigation of the properties of noble gases has been the subject of many studies in recent years.[1,2] Pauling proposed that stable molecules could be formed by the heavier noble gases.[3] This prediction has been experimentally verified.[2] Recently, Khriachtchev et al.[4] reported the synthesis of HArF (argon fluorohydride) from the photolysis of hydrogen fluoride in a solid argon matrix. They noted that this is the first, experimentally observed, covalent neutral condensed phase argon derivative.[5] They also performed ab initio computations using the MP2 and CCSD(T) methods as well as the aug-cc-pVnZ family of basis sets. They found that the above stable argon derivative is linear. Natural bond orbital (NBO) analysis has shown that this molecule is strongly ionic. Khriachtchev et al.[4] discussed the bonding of HArF in terms of ionic and covalent contributions. Runeberg et al.[5] suggested that the hydrido argon fluoride should be stable in the gas phase as well. This remark relies on ab initio computations.

M. W. Wong has found the following charge distribution for HArF: H(0.179), Ar(0.562), and F(−0.741).[6] These are NBO charges, computed with the method QCISD/6-311++G**. Similar is the NBO charge distribution found by Khriachtchev et al.,[4] using the method MP2/aug-cc-pVTZ. The above results show the magnitude of the charge transfer. One also observes that most of the positive charge is on Ar. Wong employing

topological properties at the bond critical point found that the bonds ArF and HAr are dominated by electrostatic and covalent interactions, respectively. This author noted that the stabilization of HArF could be rationalized in terms of the strong Coulomb attraction between HAr⁺ and F⁻.

Lundell et al.[7a] reported a computational study, at the MP2 and CCSD(T) levels, for the structures and vibrational spectra of HRgF, where Rg = He, Ne, Ar, Kr, Xe, or Rn. These derivatives are metastable in comparison with the global minimum HF+Rg. Berski et al.[7b] proposed from a topological analysis of the electron localization function that HArF is a resonance hybrid between the structures H−Ar⁺F⁻(66%), H−Ar⁻F⁺(18%), and H⁺ Ar F⁻(16%). The contributions of the corresponding structures are given in parentheses.

Several rare-gas (Rg) hydrides (at least 13), which could be described by the formula HRgY, where Y is an electronegative element or group (e.g., halogen, OH, CN, SH) have been recently studied both experimentally and theoretically.[8−10] These derivatives are strongly polar and correspond to local minima in the potential energy surface. Decomposition is prevented by protecting high-energy barriers.[11] An important development in the rare-gas chemistry is the prediction of the insertion compounds of Xe into unsaturated hydrocarbons, which could be described by the type H−Xe−R, where R = C_2H, C_6H_5, OC_6H_5, and so forth.[11,12]

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The objective of the present study is to report the polarizabilities and hyperpolarizabilities of HArF, because it would be interesting and useful to find out what is the effect of the inserted Ar in HF on the considered properties. The observed large first hyperpolarizability is interpreted in terms of the difference between the ground and the first excited state. The reported data and analysis illuminate specific aspects of the electronic and vibrational structure and bonding of HArF. It is known that the polarizabilities and hyperpolarizabilities mainly depend on and illustrate the behavior of the valence electrons. Thus, the present work is complementary to the pioneering work of Räsänen et al.,[4,5] who discussed some important points of the electronic structure and bonding of HArF. In particular, we note that through comparisons of the properties of HArF with those of other related compounds (e.g., HF, HF···Ar, etc.) the properties and structure of HArF are better understood. We also compare the properties of HArF with those of well-known prototype nonlinear optical derivatives to document the impressive magnitude of the properties of argon fluorohydride. The first step of this study was to demonstrate that the reported properties are reliable and thus the resulting analysis trustworthy. This was achieved by using a systematically built sequence of basis sets and a hierarchy of methods. Recent works have investigated the bonding in HArF. The present study reports complementary material for the understanding of the electronic structure of this interesting molecule.

II. Methods

We have computed the harmonic frequencies, the dipole moment, polarizabilities, and hyperpolarizabilities of HArF employing the SCF, MP2, CCSD, and CCSD(T) methods.[13a] These techniques were selected to define a hierarchy of methods because (i) MP2 is perhaps the simplest and most frequently used approach to compute the correlation contribution to molecular properties and in addition it has been reported to give reliable hyperpolarizabilities for several gas-phase molecules,[13b] (ii) CCSD(T) is one of the most powerful correlation techniques, and (iii) CCSD in connection with CCSD(T) allows to have an estimate of the contribution of the connected triple excitations. The properties have been computed using the Pol basis set[14,15] and the aug-cc-pVnZ family, where $n = 2$–5.[16–18] Pol has been selected because it gives reasonable electric property values at low computational cost.[19–21] The sets aug-cc-pVnZ define a series of systematically derived orbitals, which allow to find the convergence limit of the studied property. Electronic and vibrational contributions to the properties of interest have been calculated.

The electric property p may be considered as a sum of an electronic and a vibrational contribution:

$$p = p^{e} + p^{vib} \tag{1}$$

$$p^{vib} = p^{zpva} + p^{pv} \tag{2}$$

where p^{e} is the electronic property, p^{zpva} is associated with the zero-

point vibrational averaging, and p^{pv} is the so-called pure vibrational contribution. The static electronic contributions have been computed by employing the finite field perturbation method. The adequacy of the finite field strength which was used (0.001 au) was checked with analytic calculations[22] at the Hartree–Fock level and properties calculated by fitting the field-dependent energies to a polynomial (field strengths: 0.0, ±0.001, ±0.002, ±0.005, ±0.007, ±0.01, ±0.02 au). The frequency dependent properties have been computed by using time-dependent Hartree–Fock theory (TDHF),[22] and at the MP2 level by employing a scaling relation, which will be discussed at the end of this section.

In the present work, the following formulas have been used for the calculation of the vibrational properties:[23–25]

$$\alpha^{pv} = [\mu^2]^{(0,0)} + [\mu^2]^{(2,0)} + [\mu^2]^{(1,1)} + [\mu^2]^{(0,2)} \tag{3}$$

$$\beta^{pv} = [\mu\alpha]^{(0,0)} + [\mu\alpha]^{(2,0)} + [\mu\alpha]^{(1,1)} + [\mu\alpha]^{(0,2)} + [\mu^3]^{(1,0)} + [\mu^3]^{(0,1)} \tag{4}$$

$$p^{zpva} = [p^{e}]^{(1,0)} + [p^{e}]^{(0,1)} \tag{5}$$

$$[p^{e}]^{(0,1)} = -\frac{\hbar}{4}\sum_a \frac{1}{\omega_a{}^2}\left(\sum_b \frac{F_{abb}}{\omega_b}\right)\left(\frac{\partial P^{e}}{\partial Q_a}\right) \tag{6}$$

and

$$[p^{e}]^{(1,0)} = \frac{\hbar}{4}\sum_a \frac{1}{\omega_a}\left(\frac{\partial^2 P^{e}}{\partial Q_a{}^2}\right) \tag{7}$$

where α^{pv} and β^{pv} denote the pure vibrational contributions to the polarizability, α, and first hyperpolarizability, β, respectively, ω_a is the harmonic frequency, F_{abb} is the cubic force constant, and Q_a is the normal coordinate. Bishop et al. have derived analytical expressions for the computation of $[A]^{(n,m)}$, where n and m define the orders of the electrical and mechanical anharmonicities, respectively.[25] In the present study, we use potential energy derivatives up to the fourth order, dipole moment derivatives up to the third order, and polarizabilities and first hyperpolarizabilities up to the second order. We will also employ the double-harmonic approximation for the analysis of our results. So we report the formulas we have used for this analysis:

$$\alpha_{zz}{}^{pv} = [\mu^2]^{(0,0)} = \sum_a \frac{\left(\frac{\partial\mu_z{}^{e}}{\partial Q_a}\right)_0{}^2}{\omega_a{}^2} \tag{8}$$

$$\beta_{zzz}{}^{pv} = [\mu\alpha]^{(0,0)} = 3\cdot\sum_a \frac{\left(\frac{\partial\mu_z{}^{e}}{\partial Q_a}\right)_0\left(\frac{\partial\alpha_{zz}{}^{e}}{\partial Q_a}\right)_0}{\omega_a{}^2} \tag{9}$$

where μ_z, α_{zz}, and β_{zzz} denote the dipole moment, polarizability, and first hyperpolarizability, respectively, along the z axis, which coincides with the molecular axis of HArF. At the SCF level, the derivatives

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have been computed analytically,[26] except of the second derivative of the first hyperpolarizability, which was computed numerically. This derivative is required for the calculation of the zpva contribution to the first hyperpolarizability. At the MP2 level, the required derivatives for the computation of the vibrational properties have been computed numerically.

We shall also present the frequency dependent properties, which will be determined by TDHF and a scaling procedure at the MP2 level. Various authors[27−29] have demonstrated that reasonable estimates of the frequency dependent properties can be estimated by using a scaling relation like eq 10:

$$P[MP2(\omega)] = \{P[SCF(\omega)]/P[SCF(0)]\} \times P[MP2(0)] \quad (10)$$

where $P[MP2(\omega)]$ and $P[MP2(0)]$ are the frequency dependent and static property values, respectively, computed at the MP2 level. The symbols $P[SCF(\omega)]$, $P[SCF(0)]$ are defined in a similar way. The frequency dependent zpva corrections have also been computed using the scaling relation (eq 10). The reliability of the employed scaling scheme (SCF-$(\omega) \rightarrow$ MP2(ω)) has been confirmed, since it has been successfully used to compute the polarizability and hyperpolarizability values for several systems (e.g., H_2O,[30a] NH_2CO,[30b] C_6H_6,[30c] etc). The calculated results were in satisfactory agreement with the available experimental data. The range of applicability of eq 10 has also been discussed by Dalskov et al.[30d]

For the computations presented in this work, we have used the following software: DALTON,[31] GAMESS,[22] CADPAC,[26] SPECTRO,[32] NUMDER,[33] and Gaussian 98.[34]

III. Results and Discussion

The bond lengths of HArF, which is a linear molecule,[4] have been computed using the methods HF/Pol, MP2/Pol, and CCSD-(T)/Pol (Table 1). These data are reported because they are essential for the computation of the vibrational properties. In addition, for the above properties, there are high-quality data

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Table 1. The Bond Lengths (in Å) and the Harmonic Frequencies (in cm^{-1}) of HArF

	R(Ar–H)	R(Ar–F)	ν(Ar–F)	ν(Ar–H)	δ(H–Ar–F)[a]
HF/Pol[b]	1.280	2.060	435.4	2835.8	703.1
MP2/Pol[b]	1.349	2.006	473.9	2173.3	720.2
CCSD(T)/Pol[b]	1.381	2.016	472.2	1787.8	691.0
CCSD(T)/aug-cc-pVQZ[c]	1.334	1.980	480	2097	729
CCSD(T)/aug-cc-pV5Z[c]	1.329	1.969			
CCSD(T)/aug-cc-pV∞Z[c,d]	1.329	1.963			
experimental[e]			435.7	1969.5	687.0

[a] δ indicates a bending vibration.[4] [b] The d orbitals of the Pol basis set involve six components. [c] Reference 5. [d] An estimate of the property at the complete basis set limit, using eq 1 of ref 5. [e] The experimental results are for H−^{40}Ar− F.[4] The experimental frequencies are fundamentals.

in the literature and thus comparison of our property values to those may provide evidence for the reliability of our computational procedures. Räsänen et al.[4,5] have used several sets of the family aug-cc-pVnZ, reported by Dunning et al.[16−18] These basis sets have been used in connection with the CCSD(T) method. It is observed that the HF/Pol underestimates R(H−Ar) and overestimates R(Ar−F), while CCSD(T)/Pol overestimates both the above distances. The best results are given by the MP2/Pol method.

We also report the harmonic frequencies of HArF (Table 1). At the Hartree−Fock level, the frequencies ν(Ar−F) and δ-(H−Ar−F) are in very good agreement with the experimental ones. The vibrational frequencies, which we report in this study, correspond to an isolated HArF molecule. In the experimental conditions, there is a low concentration of HArF in a solid argon matrix.[4,5] Thus, one needs to take into account the effect of the argon cage to facilitate comparison with experiment. Runeberg et al. have approximated this effect by six octahedrally placed argon atoms. At the LMP2/aug-cc-pVDZ level, the six nearest neighbors modify ν(Ar−F), ν(Ar−H), and δ(H−Ar−F) by −9, 38, and −7 cm^{-1}, respectively.[5] Because of these correction factors, our computed harmonic vibrational frequencies (CCSD-(T)/Pol) approach even more the experimental values. The stretching vibration H−Ar is highly anharmonic and the corresponding anharmonic correction has been estimated to be 210 cm^{-1}.[4] Taking into account this correction, we observe that the difference of the CCSD(T)/Pol frequency from the experimental one increases, while this correction improves the MP2/Pol prediction. Overall, the HF/Pol and CCSD(T)/Pol do not describe satisfactorily the frequency ν(H−Ar), but MP2/Pol and CCSD(T)/aug-cc-pVQZ[5] give much more satisfactory results for this frequency.

The results of Tables 2−3 present the electronic contributions to μ_z, α_{zz}, and β_{zzz} for HArF. In Table 2, we present the above properties of HArF, computed at the HF, MP2, CCSD, and CCSD(T) levels. The geometry which was used for these computations was determined by the HF/Pol. The main conclusion, which is emerging from these results, is that the dominant components of the polarizabilities and hyperpolarizabilities are those along the z axis. In particular, the value of β_{zxx} could be considered as negligible in comparison to that of β_{zzz}. Thus, we shall focus our analysis on α_{zz} and β_{zzz}.

The results of Table 3 present the electronic dipole moment, polarizability, and hyperpolarizabilities of HArF along the z axis. These have been computed by using the methods SCF, MP2, and CCSD(T). Five different basis sets have been employed: Pol and aug-cc-pVnZ, where $n = 2−5$. The best, currently

Table 2. The Electronic Dipole Moment, Polarizabilities, and First Hyperpolarizabilities of HArF Computed Using the Methods HF, MP2, CCSD, and CCSD(T)[a,b]

	HF	MP2	CCSD	CCSD(T)
μ_z	3.473	3.078	3.110	2.963
α_{xx}	14.13	16.13	15.68	16.07
α_{zz}	34.25	52.01	50.34	58.46
α	20.84	28.09	27.23	30.20
β_{zxx}	6.6	5.2	7.1	2.0
β_{zzz}	−561.5	−1329.9	−1286.4	−1801.5
β	−329.0	−791.7	−763.3	−1078.5

[a] The properties have been computed using the Pol basis set. The geometry which was employed was optimized using the HF/Pol method (Table 1). The d orbitals of the basis set (Pol) involve six components. [b] The property values are in au.

Table 3. The Electronic Dipole Moment, μ_z, Polarizability, α_{zz}, and First Hyperpolarizability, β_{zzz}, of HArF[a,b]

	μ_z	α_{zz}	β_{zzz}
Pol			
SCF	3.139	37.61	−597.8
MP2	2.691	55.37	−1220.9
CCSD(T)	2.578	59.80	−1418.1
aug-cc-pVDZ			
SCF	3.176	37.34	−635.9
MP2	2.729	55.08	−1285.6
CCSD(T)	2.615	59.42	−1476.3
aug-cc-pVTZ			
SCF	3.121	37.74	−608.2
MP2	2.662	54.82	−1197.5
CCSD(T)	2.573	57.93	−1324.2
aug-cc-pVQZ			
SCF	3.104	37.80	−590.7
MP2	2.650	54.41	−1145.8
aug-cc-pV5Z			
SCF	3.085	37.80	−578.7
MP2	2.653	54.01	−1102.5

[a] The computation of the properties has been performed by employing the geometry optimized, using the method CCSD(T)/aug-cc-pV5Z.[4] The d and f orbitals involve five and seven components, respectively. The number of basis functions is denoted in parentheses: Pol (65), aug-cc-pVDZ (59), aug-cc-pVTZ (119), aug-cc-pVQZ (210), and aug-cc-pV5Z (338). [b] The property values are in au.

available, dipole moment for HArF is 2.56 au.[4] This has been computed using the CCSD(T)/ aug-cc-pV5Z method. It is observed that the CCSD(T)/aug-cc-pVTZ method gives 2.57 au (Table 3), in very good agreement with the literature value.

A point of major importance is the reliability of the presented property (μ_z, α_{zz}, and β_{zzz}) values. We present our opinion on this issue in the following paragraph. At the MP2 level, we have used the sequence aug-cc-pVnZ (denoted by nZ), $n = 2-5$. From the computed property values, in terms of these basis sets (Table 3), the following observations have been made. First, the dipole moment values computed with the sets 4Z and 5Z differ by 0.003 au. Second, the difference between the α_{zz} values computed with the sets 4Z and 5Z is 0.4 au. Third, the β_{zzz} values, computed with the 4Z and 5Z differ by 43.3 au (this difference is 3.9%). We believe that all three property values computed with the 5Z basis set are close to the basis set limit. Thus, the property values calculated with the method MP2/5Z are the most reliable results presented in this work. For completeness, we add that the property values reported in Table 2 (e.g., α_{xx}, α, etc.) have a varying degree of accuracy, which may be inferred (up to a certain extent) by comparing the α_{zz}

and β_{zzz} values, presented in Table 2, with the more accurate data of Table 3.

The conclusion concerning the reliability of our results is further supported by noting that Woon and Dunning[35] studied the performance of aug-cc-pV5Z (as well as other hierarchical basis sets) on the computation of the polarizability. They found for α of Ne the values 2.675 and 2.709 au at the MP2 level, using the sets aug-cc-pV5Z and q-aug-cc-pVQZ (q-aug stands for quadruply augmented), respectively. Similarly, Larsen et al.[36] found for BH, $\alpha = 23.165$ au and $\beta = 40.567$ au ($\beta_{\parallel}$ in their notation) employing the CC2/aug-cc-pV5Z method. The estimated basis set limits were 23.13 ± 0.06 au and 39.2 ± 2 au, respectively. The excellent performance of aug-cc-pV5Z for the computation of the polarizability and the first hyperpolarizability has been confirmed by using other correlated wave functions as well (e.g., CCS, CCSD[37]) and in other small molecules (e.g., HF[37]).

It is observed that the Sadlej basis set approximated reasonably well the convergence limit of the considered properties, taking into account that the HF/Pol results for μ_z, α_{zz}, and β_{zzz} differ by 1.8 (1.4), 0.5 (2.5), and 3.3 (10.7)%, from those computed by employing the HF/aug-cc-pV5Z method, respectively. The corresponding percentages at the MP2 level are shown in parentheses. The hierarchical basis sets of Dunning et al.[16−18] and the Pol sets of Sadlej et al. provide independent and complementary evidence for the reliability of our results. A literature survey shows that the Sadlej basis sets have given satisfactory polarizabilities for a very large number of molecules.[19−21]

The approaches HF/Pol and MP2/Pol will be used to compute the vibrational properties of HArF. The above methods were selected because it has been shown that they can give reasonable properties at a low computational cost. Pol has also been used to study the electronic and vibrational properties of various other systems (e.g., ref 19). This choice will facilitate comparison with our earlier work.

The Pol basis set shows the following:

$$\mu_z(\text{SCF}) > \mu_z(\text{MP2}) > \mu_z(\text{CCSD(T)}) \tag{11}$$

that is, correlation decreases the value of the dipole moment. A similar trend has been found for several other molecules.[19] The aug-cc-pVnZ family confirms this trend. The reverse trend is observed for the values of α_{zz} and $|\beta_{zzz}|$. The effect of correlation, at the MP2 level, on both α_{zz} and β_{zzz} is very significant. The effect of the correlation contribution determined at the CCSD(T) level is noticeable but smaller in comparison with that observed at the MP2 level. Comparing the results at the MP2 and CCSD(T) levels using the basis sets aug-cc-pVnZ, where $n = 2-3$, we find that the MP2 technique approximates reasonably well the properties of interest at relatively low computational cost (Table 3).

The inserted Ar atom greatly modifies the properties of HF (hydrogen fluoride), taking into account that μ_z, α_{zz}, and β_{zzz} are 0.701 (0.744), 6.449 (5.59), and −10.11 (−7.39) au. This observation is remarkable indeed, considering that Ar has a

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Table 4. Static and Frequency Dependent[a] Properties of HArF[e]

method	HF[b]			MP2[c]		
	p^{el}	p^{pv}	p^{zpva}	p^{el}	p^{pv}	p^{zpva}
μ_z	3.473		0.034	2.778		−0.05
$\alpha_{zz}(0;0)$	34.25	34.31	1.43	59.24	41.87	4.96
$\alpha_{zz}(-\omega;\omega)$	35.69	−0.03	1.68	65.57^d	-0.18^b	5.49^d
$\beta_{zzz}(0;0,0)$	−561.5	285.9	−68.4	−1443.4	−710.5	−146.0
$\beta_{zzz}(-\omega;\omega,0)$	−637.3	−68.5	−88.0	-1859.8^d	−333.6	-188.2^d
$\beta_{zzz}(-2\omega;\omega,\omega)$	−835.4	1.50		−3723.9	21.3	

a The frequency dependent properties have been computed for $\omega = 0.072$ au. This circular optical frequency is frequently used in measurements (He−Ne laser) and in computations.[24] *b* The properties have been computed using the geometry optimized with the method HF/Pol. This choice has been made because the vibrational properties are computed at the equilibrium geometry, which corresponds to the employed method. *c* The properties have been computed using the geometry optimized with the method MP2/Pol. *d* The property has been evaluated using the scaling relationship given by eq 10. *e* The electronic and vibrational contributions are given. The property values are presented in au.

closed shell electronic structure. The above quoted properties of the hydrogen fluoride have been computed at the MP4-[SDTQ] level;[38] the property values computed by using the HF/Pol method are given in parentheses, while at this level, α_{zz} for Ar is 10.61 au. The corresponding properties of HArF are given in Tables 2−4.

The NBO (natural bond order) partial charges for argon and fluorine are +0.54 and −0.76, respectively.[4] These have been computed by employing the MP2/aug-cc-pVTZ theory. Slightly different charge values have been found by Wong.[6] These data and the large dipole moment of HArF indicate a large charge transfer in the considered derivative. The charge transfer in the ground state, in connection with that observed in the first excited state, will be discussed in more detail below.

The static first hyperpolarizability $\beta(0;0,0)$ may be rationalized by invoking the two-state model, derived by perturbation theory:[39−41]

$$\beta(0) \propto \frac{3(\mu_{ee} - \mu_{gg})(\mu_{ge})^2}{E_{ge}^2} \qquad (12)$$

where μ_{ee}, μ_{gg} are excited- and ground-state dipole moments, respectively, while μ_{ge} is the transition dipole moment and E_{ge} is the transition energy. The two-state model predicts $\beta_{zzz} = -340.7$ au, while the corresponding, computed Hartree−Fock value is −561.5 au (Table 3). We shall use this model in a comparative way to discuss $\beta_{zzz}(0)$ of HArF and HF, for which the values −561.01 and −7.39 au, respectively, have been found at HF/Pol level. The required data, in au, are μ_{gg} (3.473; 0.745), μ_{ee} (−0.814; −0.907), μ_{ge} (+1.419; −0.611), and E_{ge}(0.276; 0.570). These have been computed by employing the methods HF/Pol and CIS/Pol (for the excited-state properties and the transition dipole moment; CIS stands for configuration interaction with single excitations). The first value in parentheses is for HArF and the second for HF. All the above properties contribute so that β_{zzz} of HArF is much larger than that of HF. It is observed that the difference $\mu_{ee} - \mu_{gg}$ and the property μ_{ge} are considerably larger for HArF than HF, and E_{ge} for HArF is much smaller than that of HF. The considered properties, being connected with the first hyperpolarizability, provide a qualitative explanation for the large magnitude of $\beta(0)$ for HArF.

To further clarify the difference between the ground and the first dipole-allowed excited state of HArF, in terms of resonance structures, complete active space valence bond (CASVB) calculations were performed with the efficient algorithm devised by Li and McWeeny,[42a] which combines group function theory with valence bond methods and has been implemented in VB2000.[42b] Eight electrons were included in the CAS space and distributed over six orbitals, four predominantly occupied and two unoccupied orbitals, all with σ symmetry. Sadlej's Pol basis set was employed, but the most diffused s and p basis functions on H and the most diffuse s, p, and d functions on Ar were deleted to be able to identify the localized VB orbitals uniquely as atomic orbitals. From this calculation, the following important resonance structures were found for the ground state (the weight is given in parentheses): H−Ar+F− (57%) ↔ H−Ar2+F− (21%) ↔ H+ArF− (15%). The first and third resonance structures are the same and have comparable weights as found by Berski et al.,[7b] but their second resonance structure, H−Ar−F+, is rejected by the CASVB/Pol(modified) calculation as energetically too unfavorable. For the excited-state we found H−Ar+F− (5%) ↔ H+ArF− (5%) ↔ H−Ar−F (42%) ↔ H−Ar+−F (21%), that is, the structure with a doubly positive Ar disappears and instead a nonpolar structure appears with a large weight. Additionally, the weight of the structure H−Ar+F−, which dominates in the ground state, is strongly reduced. These structures can therefore qualitatively explain the large difference of the dipole moment in ground and first dipole-allowed excited states.

We have also considered the system H−F...Ar (this is a van der Waals compex), where R(HF) = 0.917Å[42c] and R(F...Ar) = 1.963 Å.[4] For R(HF), we have used the experimentally found bond length and for R(F...Ar) we have employed the length computed with the method CCSD(T)/aug-cc-pV5Z for the hydride HArF.[4] The computations have been performed with the HF/Pol method. We have found $\mu_z = 0.983$ au, $\alpha_{zz} = 19.11$ au, and $\beta_{zzz} = -35.09$ au. NBO analysis of HF...Ar, at the Hartree−Fock level, shows that the charge of Ar is 0.02. The corresponding charge of Ar in HArF, at the same level of theory, is 0.56. One observes that there is a great difference between the properties of HArF and HF...Ar, which may be attributed, at least partially, to the significant difference in the charge, which is transferred in the two systems.

α_{zz} and β_{zzz} of HArF are very large indeed. This is shown by recalling that the polarizabilities of benzene are $\alpha_{xx} = \alpha_{yy}$

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= 80.03 au α_{zz} = 44.74 au, computed with the MP4[SDQ] theory,[43] while β_{zzz} of *p*-nitro-aniline (pNA) is 797.5 au calculated with the HF/Pol theory. The magnitude of the properties of HArF is further appreciated by considering that C_6H_6, pNA, and HArF have 42, 72, and 28 electrons, respectively.

The vibrational motion provides important information for the structure of HArF. Thus, it would be useful to report the vibrational component of the properties of interest and to discuss them in connection with the electronic contribution.

Polarizability. The static pv contribution to α_{zz} is large and approximately of the same magnitude as the electronic contribution (Table 4). The pv contribution to α_{zz} according to the double harmonic approximation is given by the term $[\mu^2]^{(0,0)}$. At the MP2 level (static), $[\mu^2]^{(0,0)}$ = 38.79 au. The three harmonic frequencies 2173.3, 720.2, and 473.9 cm^{-1} (Table 1) contribute to $[\mu^2]^{(0,0)}$ 6.68, 0.0, and 32.11 au, respectively. The three anharmonic terms ($[\mu^2]^{(0,0)}$, $[\mu^2]^{(1,1)}$, and $[\mu^2]^{(0,2)}$) contribute to α_{zz}^{pv} 3.08 au. The above results show that, as it has been found in several other occasions,[19] the double harmonic approximation satisfactorily describes α_{zz}^{pv}. Most of α_{zz}^{pv} is associated with the small frequency (473.92 cm^{-1}). Correlation affects the pv contribution. The frequency dependent pv contribution could be considered as negligible. The zpva correction is small but not negligible and it is greatly affected by correlation at the MP2 level. The same trend has also been found for the electronic contribution.

Hyperpolarizability. The static pv contribution to β_{zzz} is of comparable magnitude as the electronic contribution (Table 4). However, the β_{zzz}^{pv} ($-\omega;\omega,0$) is small in comparison to $\beta^{el}(-\omega;\omega,0)$, but not negligible. Comparing the pure vibrational contributions we note

$$|\beta_{zzz}^{pv}(0;0,0)| > |\beta_{zzz}^{pv}(-\omega;\omega,0)| > \beta_{zzz}^{pv}(-2\omega;\omega,\omega)$$

in particular, $\beta_{zzz}^{pv}(-2\omega;\omega,\omega)$ is very small and it could be considered negligible at the HF level. Correlation has a great effect on both static and frequency dependent pv contributions. The zpva contribution has a significant magnitude at the considered levels of theory both in the static and frequency dependent case.

The double harmonic approximation of β_{zzz}^{pv} is given by $[\mu\alpha]^{(0,0)}$, which at the MP2 level(static) is -611.02 au. Our computations show that β_{zzz}^{pv} = -710.50 (Table 4). The frequencies 2173.3, 720.2, and 473.9 cm^{-1} are associated with the following contributions: -1295.16, 0.0, and 684.12 au,

respectively. Although the term $[\mu\alpha]^{(0,0)}$ approximates well to β_{zzz}^{pv}, this is due to cancellation of terms. For example, $[\mu^3]^{(0,1)}$ = 1002.18, $[\mu^3]^{(1,0)}$ = -646.06, and $[\mu\alpha]^{(0,2)}$ = -358.60 au. Analysis of the results has shown that, at the level of the double harmonic approximation, most of the pv contribution to α_{zz} is due to the Ar$-$F normal vibration, while most of the pv contribution to β_{zzz} is due to to the Ar$-$H normal vibration. The bending vibration does not contribute to the above components, because the corresponding derivative of the dipole moment with respect to the normal coordinate is zero (eqs 8 and 9). Anharmonicity of the pv contribution to β_{zzz} is expressed by terms of significant magnitude. However, the overall effect of anharmonicity is relatively small because of cancellation of terms.

The present results concerning the vibrational polarizabilities and hyperpolarizabilities of HArF are supported by our previous work and that reported in the literature by other teams.[44] For example, the electronic and vibrational contributions to $\beta(-\omega;\omega,0)$ of cyclopropenethione are of equal importance.[45] Computations of the polarizabilities and hyperpolarizabilities of acetonitrile have shown that $\alpha_{zz}^{pv}(-\omega;\omega)$ and $\beta_{zzz}^{pv}(-2\omega;\omega,\omega)$ are negligible.

IV. Concluding Remarks

We have computed the electronic and vibrational (pv and zpva) contributions to the dipole moment, polarizabilities, and first hyperpolarizabilities of HArF. The presence of Ar makes it a very unusual molecule. The considered derivative has very large α_{zz} and β_{zzz}. We have confirmed this finding by using a series of systematically built basis sets and a hierarchy of computational methods. Equation 12 provides the framework to interpret the computed hyperpolarizability of HArF in terms of the small-energy difference between the ground and the first excited state, as well as the large difference between their dipole moments. The reported comparative study provides evidence, which suggests that noble gases inserted in chemical bonds (e.g., C$-$H) may lead to nonlinear optical materials having the required large nonlinear optical properties. The conditions, under which such materials (the structure of which has already been reported[11]) could be processed, define a challenging problem, but it is beyond the scope of this work.

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