An ab Initio Prediction of the Extraordinary Static First Hyperpolarizability for the Electron-Solvated Cluster $(FH)_2\{e\}(HF)$

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A theoretical prediction of the nonlinear optical (NLO) properties of the hydrogen fluoride trimer anion $(FH)_2\{e\}(HF)$ reveals that this electron-solvated cluster possesses exceptionally large static first hyperpolarizability. Using the d-aug-cc-pVDZ basis set supplemented with diffusive bond functions (BF), we obtained the mean static first hyperpolarizability (β_0) for $(FH)_2\{e\}(HF)$ and its neutral core $(HF)_2\{\}(HF)$ at the CISD level of theory. The β_0 is 8.1×10^6 au for $(FH)_2\{e\}(HF)$ and 5.1 au for $(HF)_2\{\}(HF)$. Obviously, the excess electron is the key factor in bringing to $(FH)_2\{e\}(HF)$ the significantly large NLO response. The other properties of $(FH)_2\{e\}(HF)$ are also much larger than those of its neutral core. The values of the static dipole moment, mean polarizability, and anisotropy of the polarizability are, respectively, $\mu = 1.5764$ au, $\alpha_0 = 654.67$ au, and $\Delta\alpha = 224.71$ au for the anion, and $\mu = 0.9351$ au, $\alpha_0 = 17.34$ au, $\Delta\alpha = 5.40$ au for the neutral core. In addition, the field dependences of the polarizability and first hyperpolarizability are obtained at the MP2/d-aug-cc-pVDZ+BF level of theory. And the influence of the secondary interaction, H-bond-excess electron attracting, on the static first hyperpolarizability of $(HF)_2\{e\}(HF)$ is also explored.

Introduction

Primarily because of their role in the nonlinear optical properties of molecules and their potential applications[1−3] in various fields, hyperpolarizabilities have recently received much attention, and many experimental[4−7] and theoretical efforts[8−13] were devoted to the investigation of the first hyperpolarizability of different types of materials.

Lately, several papers[14−22] have represented the great interest in studying and designing the materials possessing large nonlinear optical (NLO) response, especially the first hyperpolarizability. Their research interests have generally focused on organic molecules and organometallic complexes. Grüner and co-workers[17] reported the synthesis and large NLO response of a tropyl-substituted 1-carba-*closo*-dodecaborate anion that displayed an experimental β of 236 ($\pm$50) $\times 10^{-30}$ cm^5 esu $^{-1}$. Using *semiempirical* methods, Allis and Spencer[19] theoretically investigated a series of compounds of icosahedral carborane polyhedra bridge charged aromatic donor and acceptor moieties and obtained very large β values.

Because much of the current research involves the discovery of new materials efficient at technological applications, along with the determination of the important relationships between molecular architecture and nonlinear responses, the theoretical characterization of NLO species played a very important role in this area. The ab initio studies of NLO properties of some small molecules[9,23−24] and molecular clusters[11,12] had been reported at high levels, and most of their results answered well for the experimental data. However, as far as we know, the first hyperpolarizability of a cluster anion containing an excess electron has thus far not been theoretically and experimentally reported.

The existence of solvated electrons has been known since 1864 when they were observed in liquid ammonia.[25] Recently, several papers[26−31] have mentioned the situation that an excess electron was trapped in a molecular cluster. This is currently an active area of study. In recent research, Gutowski and co-workers have studied the theoretical and experimental existence of the cluster $(HF)_2\{e\}(HF)$.[32] It was called an asymmetric solvated electron, in which the dipole-bound anion of $(HF)_2$ is solvated by one HF monomer at the side of the excess electron. There are manifold interactions in $(FH)_2\{e\}(HF)$, and the excess electron is both dispersive and localized, which makes $(FH)_2\{e\}(HF)$ a typical and interesting cluster anion worthy of further study. The excess electron, which is a Rydberg-like state, occupies a dispersive orbital. A Rydberg atom or molecule in the gas phase possesses very high nonlinear optical susceptibilities, which are confirmed by the available experimental data and theoretical research.[33] Hence, we anticipated that the $(FH)_2\{e\}(HF)$ should possess special chemical and physical properties, e.g., the static first hyperpolarizability.

The purpose of this paper is predicting the theoretical values of the NLO properties, especially the static first hyperpolarizability of the electron-solvated cluster $(FH)_2\{e\}(HF)$, trying to find a new potential class of NLO species, and understanding the contribution of the excess electron to the NLO properties.

The β_0 calculated for $(FH)_2\{e\}(HF)$ is extraordinarily huge: 8.1×10^6 au, even much larger than that of some organic conjugated molecules.[17,19,34] For instance, the β_0 is 62.7 times larger than that of the organic compound anion $[(C_7H_6)$-$C_2B_{10}H_{10}-B_{12}H_{10}(C_5H_4)]^{-2}$.[17] Undoubtedly, the excess electron plays a crucial role here. The previous studies have yielded many approaches in designing new materials with enhanced second-order responses, e.g., using extended π-conjugated organic bridges with strong electron donor and acceptor groups,[15] incorporation of the ligated metal into the plane of the organic π-system,[14] and lengthening the chain between donor and acceptor through hydrogen bonding,[16] etc., but the factor of the excess electron has hitherto not been explored.

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Since the existence of solvated electrons in some organic and inorganic clusters and polymers has been recognized for many years, our work may provide a new idea and model to design the materials possessing large nonlinear optical responses. There is some future in the development of such electron-trapped materials that exhibit desirable nonlinear optical properties.

Computational Details

In those calculations for the molecular cluster anions, several recent papers[35−38] have shown that inclusion of electron correlation effects leads to a sizable stabilization of the dipole-bound anions, and it is necessary to employ flexible basis sets and to include high-order correlation effects to adequately describe the dynamical correlation contribution. Simons and coworkers[39] first noted that the diffusive bond functions should be used in the calculations of molecular cluster anions. In this work, calculation of geometric optimization was performed at the second-order Møller−Plesset perturbation (MP2) level, with the d-aug-cc-pVDZ basis set supplemented with diffuse s and p bond functions (BF). The lowest exponent of the four-term sp basis set is equal to 4.8×10^{-5} au, and the geometric progression ratio is equal to 5.0 for the BF. The location of the BF is determined by optimizing geometric structure for the $(FH)_2\{e\}(HF)$ with the MP2/d-aug-cc-pVDZ+BF method.

The calculations of the first hyperpolarizability (β_0) and related properties (μ, α_0, and $\Delta\alpha$) of $(FH)_2\{e\}(HF)$ relied on the finite-field approach.[40] In the presence of an applied electric field, the energy of a system is a function of the field strength. Hyperpolarizability is defined as the coefficients in the Taylor series expansion of the energy in the external electric field.[41] When the external electric field is weak and homogeneous, this expansion becomes:

$$\boldsymbol{E} = E^\circ - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma + \ldots \quad (1)$$

where E° is the energy of the unperturbed molecules, F_α is the field at the origin, μ_α, $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability, and the first hyperpolarizabilities, respectively. (The repeated Greek subscript implies summation over the Cartesian coordinates x, y, and z.)

We computed the total static dipole moment μ, the mean polarizability α_0, the anisotropy of the polarizability $\Delta\alpha$, and the mean first hyperpolarizability β_0. They are defined as:[11,14]

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha_0 = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

$$\Delta\alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2]^{1/2}$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (2)$$

and

$$\beta_x = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})$$

$$\beta_y = (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})$$

$$\beta_z = (\beta_{zzz} + \beta_{xxz} + \beta_{yyz}) \quad (3)$$

With the method introduced above, the NLO properties of $(FH)_2\{e\}(HF)$ were calculated at the MP2 level with five basis sets to study the basis set effects. With the d-aug-cc-pVDZ+BF basis set, the β_0, along with the related properties of $(FH)_2\{e\}$-(HF) and its neutral core (keeping all geometry parameters of $(FH)_2\{e\}(HF)$ constant but removing the electron from the anion), was calculated using HF MP2, MP3, MP4(SDQ), and CISD methods, respectively.

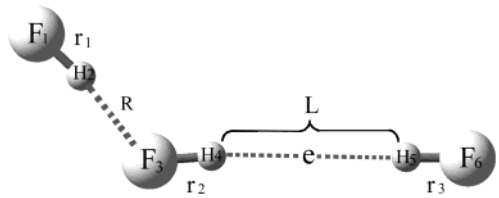

Figure 1. Geometrical parameters for the electron-solvated cluster $(FH)_2\{e\}(HF)$.

TABLE 1: Geometrical Parameters of $(FH)_2\{e\}(HF)$ at the MP2/d-aug-cc-pVDZ+BF Level of Theory[a]

bond length	r_1	r_2	r_3	R	L
	0.94247	0.959	0.94386	1.6781	3.00388
angle	θ(H2F3F1)	θ(H2F3H4)	θ(F3H4H5)	θ(H4H5F6)	
	2.785	124.508	175.191	179.657	

[a] Distances are in angstroms and angles are in degrees.

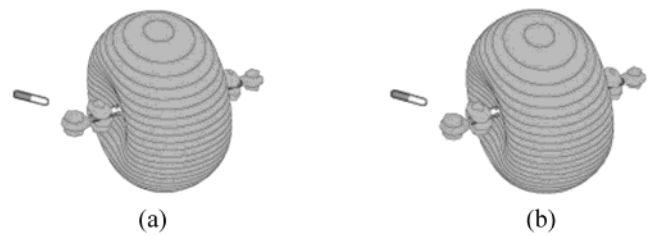

Figure 2. Singly occupied molecular orbitals for $(FH)_2\{e\}(HF)$ are similar in different EDF: (a) at zero EDF and (b) with an 0.0001 au. EDF. The orbitals are plotted with the 0.02 contour surfaces.

To choose the proper external electric field in the computations of NLO properties, the vertical electron detachment energy (VDE) of $(FH)_2\{e\}(HF)$ was calculated at the MP2/d-aug-cc-pVDZ+BF level with a series of fields from 0.0001 to 0.0009 au. According to the effect of the electric dipole field (EDF) on the VDE, we finally chose a very weak EDF as 0.0001 au in the calculations with a large basis set at high level of theory to obtain credible results.

All the calculations were performed with the Gaussian 98 program package,[42] and two- or three-dimensional plots of molecular orbitals were generated with the Molden program.[43]

Results and Discussion

A. Geometrical Characteristics of $(FH)_2\{e\}(HF)$. The optimized geometry of the $(FH)_2\{e\}(HF)$ is presented in Figure 1 and Table 1. The six atoms of $(FH)_2\{e\}(HF)$ are all in a plane. The bond length, L, of the monoelectron dihydrogen bond H···e···H[29] in $(FH)_2\{e\}(HF)$ is defined as the distance between the two positively charged H atoms (H4 and H5) in Figure 1 and Table 1. The highest occupied molecular orbital (HOMO) from the MP2/d-aug-cc-pVDZ+BF calculation of $(FH)_2\{e\}(HF)$ is presented in Figure 2a. The HOMO plot for $(FH)_2\{e\}(HF)$ is typical of an electron-solvated cluster: the single-occupied orbital is concentrated between the two positively charged H atoms (H4 and H5). That is, the two hydrogens (H4 and H5) are linked by a large electron density of the excess electron.

B. Choice of the Basis Set and the EDF. The choice of a suitable basis set to calculate the NLO properties of $(FH)_2\{e\}$-(HF) is important. The effects of basis sets on calculations of NLO properties are studied at the MP2 level of theory with

TABLE 2: Total Dipole Moment, the Mean and Anisotropy Dipole Polarizability, and the Mean Hyperpolarizablity of $(FH)_2\{e\}(HF)$ Calculated at MP2 Level with Five Basis Sets

basis set	μ	α_0	$\Delta\alpha$	β_0
aug-cc-pVDZ(96)	1.4547	120.98	203.87	6.8×10^3
d-aug-cc-pVDZ(135)	1.5390	468.32	103.10	4.2×10^4
aug-cc-pVDZ+BF(116)	1.5296	493.18	86.47	1.6×10^7
d-aug-cc-pVDZ+BF(151)	1.5312	516.84	90.28	9.2×10^6
t-aug-cc-pVDZ+BF(190)	1.5353	524.97	101.62	8.1×10^6

TABLE 3: Total Static Dipole Moment, the Mean Polarizability, the Anisotropy of the Polarizability, and the Mean First Hyperpolarizability of $(FH)_2\{e\}(HF)$ Calculated at the MP2/d-aug-cc-pVDZ+BF Level in Different EDF[a]

field	VDE	μ	α_0	$\Delta\alpha$	β_0
0.0001	450.18	1.5312	516.84	90.28	9.2×10^6
0.0002	498.28	1.5312	537.17	83.85	4.5×10^7
0.0003	750.06	1.5312	2.94×10^5	12.37	8.9×10^7
0.0004	1001.96	1.5312	2.20×10^5	11.02	5.0×10^7
0.0005	1253.92	1.5312	1.76×10^5	10.14	3.2×10^7
0.0006	1505.91	1.5312	1.47×10^5	9.50	2.2×10^7
0.0007	1757.94	1.5312	1.26×10^5	9.01	1.6×10^7
0.0008	2009.99	1.5312	1.10×10^5	8.63	1.2×10^7
0.0009	2262.05	1.5312	9.80×10^4	8.32	9.9×10^6

[a] The VDE is in meV, and the properties are all in atomic units.

aug-cc-pVDZ, aug-cc-pVDZ+BF, d-aug-cc-pVDZ, d-aug-cc-pVDZ+BF, and t-aug-cc-pVDZ+BF basis sets (an electric field of 0.0001 au is applied). The results are listed in Table 2. The data (the first two lines of Table 2) show that the β_0 calculated without diffusive BF are clearly smaller than the others (even if the basis set used is larger), and the β_0 values calculated with BF are all around 10^7 au. As can be seen, the diffusive bond functions are very important and must be used in the NLO calculations of cluster anions.

The results calculated with the d-aug-cc-pVDZ+BF basis set are basically close to that with the t-aug-cc-pVDZ+BF basis set. The change in β_0 is 73.91% from aug-cc-pVDZ+BF to d-aug-cc-pVDZ+BF, while the value of β_0 differs 11.96% from d-aug-cc-pVDZ+BF to t-aug-cc-pVDZ+BF. The value of μ varies only 0.26%, and α_0 and $\Delta\alpha$ change 1.55% and 11.16%, respectively, from d-aug-cc-pVDZ+BF to t-aug-cc-pVDZ+BF. Thus, the d-aug-cc-pVDZ+BF basis set is considered to be able to describe the electronic properties of $(FH)_2\{e\}(HF)$ adequately. In addition, the location and coefficients of diffusive bond functions were optimized with the d-aug-cc-pVDZ+BF basis set. Hence, the d-aug-cc-pVDZ+BF basis set was chosen in the calculations of β_0 and related properties by higher methods.

To find a proper EDF used in the calculations of NLO properties, the VDE of $(FH)_2\{e\}(HF)$ was calculated at the MP2/d-aug-cc-pVDZ+BF level in a series of fields from 0 to 0.0009 au. The EDF dependence of the VDE is displayed in Table 3. The data of Table 3 show that the VDE of $(FH)_2\{e\}(HF)$ becomes larger with the increase in EDF, but changes little when the EDF varies from 0.0000 au to a field as small as 0.0001 au. The VDE obtained in a zero field is 432.332 meV, while the VDE is 450.175 meV in an EDF of 0.0001 au; just an increase of 4.13% is discerned. The HOMOs of $(FH)_2\{e\}(HF)$ in an EDF of 0.0001 au (Figure 2b) and 0.0000 au (Figure 2a) are almost the same. We consider that the effect of the EDF of 0.0001 au on the system is little, i.e., the computational results obtained in this EDF can represent the system's original properties. Hence, the EDF of 0.0001 au is applied in the calculations of properties.

C. The First Hyperpolarizability of $(FH)_2\{e\}(HF)$ and Its Neutral Core. With a 0.0001 au EDF applied, we calculated the first hyperpolarizability and related properties of the electron-solvated cluster $(FH)_2\{e\}(HF)$ at the HF, MP2, MP3, MP4(SDQ), and CISD levels with the d-aug-cc-pVDZ+BF basis set. The results of μ, α_0, $\Delta\alpha$, and β_0 are presented in Table 4.

TABLE 4: Total Static Dipole Moment, the Mean Polarizability, the Anisotropy of the Polarizability and the Mean First Hyperpolarizability Calculated with the d-aug-cc-pVDZ+BF Basis Set for $(FH)_2\{e\}(HF)$[a]

	μ	α_0	$\Delta\alpha$	β_0
HF	1.6739	1033.95	530.41	9.7×10^5
MP2	1.5312	516.84	90.28	9.2×10^6
MP3	1.5473	566.96	129.67	9.5×10^6
MP4(SDQ)	1.5402	556.02	109.82	7.0×10^6
CISD	1.5764	654.67	224.71	8.1×10^6
CISD-HF	−0.0975	−379.28	−305.70	7.1×10^6
(CISD-HF)/CISD	−6.2%	−57.9%	−136.0%	88.0%

[a] Properties are all in atomic units.

Previously, the static electronic properties of HF and $(HF)_2$ have been reported in detail by Bishop and Pipin,[44] Eckart and Sadlej,[45] and Maroulis.[12] The calculated absolute values of β_0 ranged from 3 to 10 au. However, the mean first hyperpolarizability of $(FH)_2\{e\}(HF)$ was very huge to be 8.1×10^6 au at the CISD level. Obviously, the excess electron plays a very important role in bringing to $(FH)_2\{e\}(HF)$ the significantly large NLO response. To exhibit the effect of the solvated electron, a comparison of NLO properties was also performed between $(FH)_2\{e\}(HF)$ and its neutral core $(FH)_2\{\}(HF)$ at the CISD level. For the anion, μ is 1.58 au (Table 4), nearly twice the μ of the neutral core (0.935 au), α_0 is 654.67 au, about 38 times that of its neutral core (17.34 au), and $\Delta\alpha$ is 224.71 au, about 42 times that of its neutral core (5.40 au).

The difference of β_0 between the anion and its neutral core is considerably large. The β_0 values are 8.1×10^6 au for $(FH)_2\{e\}(HF)$ and just 5.1 au for $(FH)_2\{\}(HF)$, and the difference between them is also huge: 8.1×10^6 au. It is especially noteworthy that the β_0 of 5.1 au is very near the $|\beta_0|$ of HF and $(HF)_2$ mentioned above. Thus, it can be concluded that the excess electron is the key factor in enhancing the NLO properties of the electron-solvated cluster $(FH)_2\{e\}(HF)$.

D. Effects of Electron Correlation. The CISD-HF part (in Table 4) mainly represents the contribution of electron correlation. The factor of electron correlation is very influential in the computations of NLO properties here. Its effects are quite important for $\Delta\alpha$, α_0, and β_0, but less so for μ. The CISD value of $\Delta\alpha$ is 136.0% lower than the corresponding HF value of 530.41 au, while μ and α_0 are 6.2% and 57.9% lower than the HF values of 1.6739 and 1033.95 au, respectively. The value of β_0 increases by 88%, from 9.7×10^5 to 8.1×10^6 au. The contribution of electron correlation to β_0 is very great at 7.13×10^6 au.

E. EDF Dependence. Different from the cluster anion in the common sense, the $(FH)_2\{e\}(HF)$ system contains an excess electron, and therefore the electron cloud is easy to be affected by the general external electric dipole field. However, the electron density is little affected in a very small EDF. From the comparison of HOMOs of $(FH)_2\{e\}(HF)$ at zero field and 0.0001 au field (see Figure 2a,b), it can be seen that the electron cloud distribution of the excess electron is very similar between them. The HOMO plots also show that 0.0001 au EDF is suitable in the calculation of NLO properties.

The EDF dependences of the dipole moment, the mean and the anisotropy of the polarizability, and the mean first hyperpolarizability of $(FH)_2\{e\}(HF)$ at MP2/d-aug-cc-pVDZ+BF level are shown in Table 3. The value of μ does not change

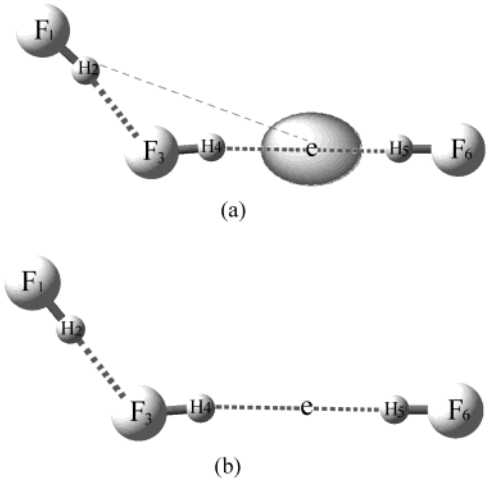

Figure 3. (a) The H-bond-excess electron interaction in $(FH)_2\{e\}$-(HF). (b) The angle of θ (F1H2F3) was changed to 180° to remove the secondary interaction.

with increasing EDF values. The values of α_0 and $\Delta\alpha$ are slightly changed when the EDF varies from 0.0001 to 0.0002 au, but a sharp increase occurs when the EDF varies from 0.0002 to 0.0003 au. When the EDF is larger than 0.0003 au, α_0, $\Delta\alpha$, and β_0 all display good descending convergence. Concerning the β_0, when $F = 0.0003$ au, it reaches a maximum of 8.9×10^7 au. As the EDF values increase, the value of β_0 begins to decrease, and when $F = 0.0009$ au, the β_0 (9.9×10^6 au) is near the result (9.2×10^6 au) obtained with an EDF of 0.0001 au. This shows that the EDF dependences of the β_0 are obvious and around the amount of about 10^7 au.

F. Secondary Interaction and the First Hyperpolarizability. There is a novel secondary interaction, H-bond-excess electron attracting,[29] in $(FH)_2\{e\}(HF)$ (see Figure 3a). The attraction bends the conventional hydrogen bond F−H···F in an opposite direction to $(HF)_2$.[46] The effect of the secondary interaction on the first hyperpolarizability is an interesting question. To study that, a structural model to approximately remove the secondary interaction was constructed (moving the H(2) atom onto the line defined by F(1) and F(3) and keeping all the other atoms of $(FH)_2\{e\}(HF)$ fixed; see Figure 3b), and then its NLO properties were computed at the MP2/d-aug-cc-pVDZ+BF level. The results were $\mu = 1.56$ au, $\alpha_0 = 525.31$ au, $\Delta\alpha = 94.60$ au, and $\beta_0 = 5.64 \times 10^7$ au. A comparison of β_0 between the model and $(FH)_2\{e\}(HF)$ shows that the secondary interaction accounts for the large decrease of β_0 (from 5.6×10^7 to 9.2×10^6 au). The reason may be that the H-bond-excess electron attracting interaction makes the excess electron be bound more tightly. That is, the diffusive degree of the excess electron is the key factor in deciding the magnitude of the first hyperpolarizability for electron-solvated cluster $(FH)_2\{e\}(HF)$.

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