

Ab Initio and Density Functional Study on the First Hyperpolarizabilities of Squaric Acid Homologues

FU, Wei-Wei^a(付伟伟) ZHOU, Li-Xin^{*,a,b}(周立新)

^a College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou, Fujian 350002, China

^b Department of Chemistry, Jinan University, Guangzhou, Guangdong 510632, China

The first hyperpolarizabilities of four squaric acid homologues: squaric acid, 1,2-dithiosquaric acid, 1,2-diselenosquaric acid and 1,2-ditellurosquaric acid have been calculated using *ab initio* and DFT methods. The effects of equilibrium geometries, basis set and electron correlation on the first hyperpolarizabilities of these molecules were investigated. The frequency dispersion effect and solvent effect, which are essential to get reliable outputs in comparison to the experimental results, have also been explored. On the basis of these investigations, it is worthy to point out that the heavy atom effect takes effect for these squaric acid homologues.

Keywords first hyperpolarizabilities, electron correlation effect, frequency dispersion effect, solvent effect, heavy atom effect

Introduction

In the past decades, the study on the nonlinear optical (NLO) properties of squaric acid and its derivatives have been carried out.¹⁻⁵ For most theoretical researches were performed at semi-empirical or simple Hartree-Fock level of theory, the results can only be accepted qualitatively or semi-quantitatively. Due to the well-developed computational procedures and expanded computer capabilities, it is now possible to calculate the hyperpolarizability accurately for some medium-sized molecules like squaric acid homologues.

In this article, the first hyperpolarizabilities of four squaric acid homologues: 3,4-dihydroxy-3-cyclobutene-1,2-dione (OOSQ), 3,4-dihydroxy-3-cyclobutene-1,2-dithione (SOSQ), 3,4-dihydroxy-3-cyclobutene-1,2-diselenone (SeOSQ) and 3,4-dihydroxy-3-cyclobutene-1,2-ditellurone (TeOSQ) in which two carbonyl O atoms remain or are substituted by S, Se and Te, respectively have been investigated. Some influential factors on the calculated values of molecules' first hyperpolarizabilities were considered in order to get more accurate results.

Basis set dependence is an important factor that should be considered to get accurate values of molecule's NLO properties.⁶⁻⁹ In order to check how many diffuse and polarization functions should be adopted, four basis sets 6-311G, 6-311 + G(d,p), 6-311 + + G(3d,2p) and 6-311 + + G(3df,2p) were introduced to conduct the NLO calculations. Electron correlation effect is another vital factor that should be taken into account in order to get accurate NLO results.^{6,10-15} The

first hyperpolarizabilities were calculated at the second Møller-Plesset Perturbation level of theory (MP2), which has been proved to be a good choice for its effectiveness in comparison to the fourth MP4 results.^{10,15} For density functional theory also includes some electron correlation factors, it has been used in this article to calculate the molecules' NLO properties.

Frequency dispersion effect^{8,16-19} and solvent effect^{15,16,19-21} are necessary to be taken into account in the calculation of molecules' NLO properties in order to get calculated values comparable to the experimental observations. Although there are no experimental observation for most of the molecules studied here, frequency dispersion effect and solvent effect have been investigated to get more detailed information about the NLO properties of squaric acid homologues.

After some influential factors on the molecules' first hyperpolarizabilities have been investigated, it is worthy to point out that the heavy atom effect which has been found in furan homologues still take effect for these four squaric acid homologues.

Computational approach

The geometries of these four molecules were optimized with 6-311 + G(d,p) basis set at various theoretical levels: HF, MP2 and DFT, respectively for there have been some researches regarding that variation of geometry parameters also plays a comparatively important role on molecules' NLO properties.²² All the geometries are characterized by the frequency analysis and they are proved to be the most stable point on the poten-

* E-mail: lxzhoumail@163.com

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tial energy surface.

The individual tensor components of the static first hyperpolarizability were obtained by the routine procedure implemented in Gaussian 98.²³ The Hartree-Fock level of theory both the numerical finite field method (FF)²⁴ and coupled perturbation method (CPHF)²⁵ were used to check the effectiveness of the numerical approach. Just like the results shown in some other research papers,^{10,15} there is rather little difference between FF results and CPHF results. Then the numerical approach was used with MP2 and DFT methods. In present DFT calculations the exchange-correlation energy functional hybrid method with Beck's exchange²⁶ and the correlation of Lee, Yang and Parr²⁷ denoted as B3LYP were adopted.

Frequency dependent first hyperpolarizabilities were calculated by a time-dependent Hartree-Fock theory (TDHF) method implemented in the GAMESS procedure.²⁸ When performing TDHF calculations, more strict options were selected in order to get reliable and accurate results: ICUT=20 (integrals less than 10^{-20} are ignored; default, 10^{-9}), ITOL=30 (products of primitives whose preexponential factor is less than 10^{-30} are skipped; default, 10^{-20}), INTPYP=HONDO (HONDO/Rys integrals used for all integral evaluations, slightly more accurate but slower than the default: Pople), and NCONV=10 (convergence is reached when the absolute value of the density change between two consecutive SCF cycles is less than 10^{-10} ; default, 10^{-5}).²² There are some different models in Gaussian 98 to simulate the interaction between solute and solvent: Onsager, PCM, IPCM and SCI-PCM. A simple Onsager model was accepted in this study.²⁹

There is no corresponding basis set 6-311G for atom Te unlike the other three atoms: O, S and Se. As we know, the accurate description of the outer region of atoms is more essential than the inner in NLO calculations. In this case an effective core potential (ECP) method was adopted to overcome this limitation after it had been checked by SeOSQ. When the impact of diffuse and polarization functions was considered, a set of exponents $\zeta(s)=0.02625$, $\zeta(p)=0.02625$, $\zeta(d)=0.237$ were assumed as suggested by Gaussian 98 procedure or

by the analogy between the exponents of this family atoms.

Some different treatments are often used to get the first hyperpolarizability from individual tensor components. In this article the following formulas were taken to get the first hyperpolarizabilities at the dipole moment direction (β_μ) where β_i is the first hyperpolarizability along i direction which can be derived from various tensor components β_{ijk} .

$$\beta_\mu = \sum_i \beta_i \mu_i / |\mu| \quad (i, j = x, y, z) \quad (1)$$

$$\beta_i = \beta_{iii} + (1/3) \sum_{i \neq j} (\beta_{ijj} + \beta_{jji} + \beta_{jji}) \quad (2)$$

Results and discussion

Geometry structures

Due to the (Z, Z) conformer is the most stable conformer as some earlier researches pointed out,^{1,30} in this study only the (Z, Z) conformers (shown in Figure 1) are optimized and adopted to conduct the NLO calculations for that in squaric acid. As all molecules have C_{2v} symmetry, only the independent bond lengths and bond angles are shown in Table 1. It was found that: (1) The C=X (O, S, Se, Te) bond lengths in different molecules show considerable difference, while other bond lengths show slight variation; (2) Bond lengths optimized with B3LYP/6-311+G(d,p) are at the middle of two other methods and they are more close to those optimized by MP2/6-311+G(d,p); (3) bond angles gotten by MP2/6-311+G(d,p) and B3LYP/6-311+G(d,p) methods are similar in most cases.

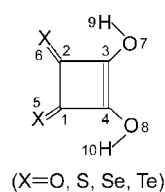


Figure 1 Molecular structure of squaric acid homologues in which X=O (OOSQ), X=S (SOSQ), X=Se (SeOSQ), X=Te (TeOSQ).

Table 1 Selected geometric parameters of squaric acid homologues (bond lengths in 10^{-1} nm, bond angles in degree)

Parameters	OOSQ			SOSQ			SeOSQ			TeOSQ		
	HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP
C(1)—C(2)	1.535	1.555	1.555	1.504	1.519	1.516	1.495	1.506	1.505	1.488	1.507	1.499
C(2)—C(3)	1.476	1.490	1.487	1.448	1.464	1.458	1.441	1.460	1.451	1.435	1.456	1.446
C(3)—C(4)	1.351	1.383	1.375	1.365	1.395	1.389	1.373	1.395	1.395	1.383	1.398	1.401
C(1)—X(5)	1.176	1.210	1.202	1.608	1.618	1.627	1.775	1.763	1.774	1.976	1.949	1.983
C(3)—O(7)	1.309	1.324	1.322	1.300	1.318	1.313	1.295	1.320	1.311	1.291	1.323	1.311
O(7)—H(9)	0.945	0.968	0.969	0.948	0.971	0.973	0.949	0.971	0.975	0.950	0.972	0.976
X(5)—C(1)—C(4)	134.8	134.0	134.0	134.4	133.5	132.9	133.2	132.5	131.4	132.9	134.1	131.5
C(2)—C(1)—C(4)	86.4	86.7	86.5	87.3	87.6	87.5	87.6	87.8	87.8	87.9	87.8	88.1
C(1)—C(4)—O(8)	132.6	133.1	132.9	132.6	132.5	132.2	132.7	132.4	132.1	133.6	133.0	132.8
C(4)—O(8)—H(10)	110.8	107.7	109.4	110.4	106.8	108.3	110.3	106.5	107.9	110.6	106.5	108.0

In order to investigate the influence of different equilibrium geometries on the first hyperpolarizabilities, the first hyperpolarizabilities using three theoretical level methods: HF, MP2 and B3LYP within three different equilibrium geometries for molecules OOSQ, SOSQ and SeOSQ were calculated (results shown in Table 2). At the HF level, the results show maximal difference 0.10 esu for three molecules between the structures optimized by HF and MP2 methods. When efficiency is considered, an HF optimized structure is adequate to get reliable NLO results at HF level. While correlation effect is considered in the NLO calculations, at the MP2 level, a difference about 0.46 esu arises between the HF and MP2 optimized structures. For SOSQ and SeOSQ, it is about 0.6 esu and 0.9 esu respectively. An MP2 optimized structure is better to perform the NLO calculations when heavier atoms are engrafted in the molecules. As the results shown in Table 1, B3LYP is another good choice to get reliable geometries in favor of conducting the following electron correlated NLO calculations.

Basis set dependence

As is well known, it is essential to augment diffuse and polarization functions to get molecules' NLO properties accurately. However, we did not realize to what an extent this should be done for the molecules studied here, *i.e.* how many diffuse and polarization functions should be augmented. In this part, we adopted four basis sets 6-311G, 6-311+G(d,p), 6-311++G(3d,2p) and 6-311++G(3df,2p) to investigate the basis set dependence. It is also a certification whether one set of diffuse and polarization functions are enough for the NLO calculations.

For OOSQ, there is some difference between the 6-311++G(3d,2p) and 6-311+G(d,p) results just like that between 6-311+G(d,p) and 6-311G at various theoretical levels. For the NLO calculations of OOSQ, more diffuse and polarization functions are required. For SOSQ, there is also some difference between 6-311++G(3d,2p) and 6-311+G(d,p) just like that between 6-311+G(d,p) and 6-311G within HF and B3LYP calculations. While within the MP2 results a difference about 3 esu between 6-311+G(d,p) and 6-311G results and that of 1 esu between 6-311++G(3d,2p) and 6-311+G(d,p) appear. For SeOSQ, similar phenomenon like SOSQ appears and it should be noted that there is rather

little difference between the 6-311++G(3d,2p) and 6-311+G(d,p) results with the MP2 method. Base on MP2 results, it is shown that when substitute atoms become heavier, the importance of adding more diffuse and polarization functions decreases.

In order to examine the role *f* polarization function played on the NLO calculations, a basis set 6-311++G(3df,2p) was adopted at the MP2 correlation theoretical level to conduct the NLO calculation. Because of the computer limitations, only the first hyperpolarizabilities of OOSQ and SOSQ were calculated. There is only slight difference between the results gotten by two basis sets 6-311++G(3df,2p) and 6-311++G(3d,2p) in comparison with other basis set result differences. Including *f* polarization function is not absolutely necessary in the NLO calculations.

When the results produced with the basis sets 6-311++G(3d,2p) and 6-311+G(d,p) are considered, it is obvious that there are some differences between them, especially for OOSQ and SOSQ. The basis set 6-311+G(d,p) is not a good choice to get very accurate results with respect to the more robust basis set 6-311++G(3d,2p), but it is a good choice between accuracy and efficiency and the result variations between these two basis sets are consistent. In this article, one of our main purposes is to investigate the variations of the results made by substitution of heavy atoms. So in most calculations, the basis set 6-311+G(d,p) was still used.

Electron correlation effect

Correlation effect is crucial in determination of molecules' NLO properties. In this article calculations at the MP2 level were performed as some researchers pointed out:^{6,10} the first hyperpolarizabilities calculated at the MP2 level are in well agreement with more accurate methods MP4(SDTQ) and CCSD(T). In comparison with the HF results, OOSQ and SOSQ have about twice results by the MP2 method with the basis sets 6-311+G(d,p) and 6-311++G(3d,2p). As for SeOSQ and TeOSQ, there are significant difference about three times larger. However, it should be noted that there is opposite sign for the NLO results of TeOSQ. The first hyperpolarizabilities increase greatly when correlation effect is considered. It is suggested that correlation effect is a crucial factor that should be considered in NLO calculations.

Table 2 The first hyperpolarizabilities (10^{-30} esu) of squaric acid homologues calculated with 6-311+G(d,p) basis set

A ^a	HF			MP2			B3LYP		
	HF	MP2	B3LYP	HF	MP2	B3LYP	HF	MP2	B3LYP
OOSQ	-2.231	-2.334	-2.325	-3.909	-4.368	-4.262	-2.353	-2.438	-2.384
SOSQ	-4.850	-4.874	-4.577	-11.219	-11.794	-11.592	-4.952	-4.994	-4.772
SeOSQ	-4.208	-4.250	-3.676	-14.651	-15.554	-15.465	-5.318	-5.523	-5.173

^a A denotes the method for NLO calculation. ^b B denotes the method for geometry optimization.

Density functional theory method has been widely used for its consistency between accuracy (better than Hartree-Fock results and often comparable to various post Hartree-Fock results) and short computational time. However, as the results shown in Table 3, it is a pity to point out that there are no significant differences between HF and DFT results and there is great difference between the results gotten by DFT method and MP2 method. In this regard, its accuracy should be doubted and the exchange-correlation functions are probably not sufficient for the NLO calculations. Two alternative solutions might work: (1) Field induced functions (FIT) should be implemented;³¹ (2) A time-dependent density function theory (TDDFT) method should be a better selection.³²

When correlation effect is considered, the NLO results of the molecules should be based on the same geometry structure. As we can see from the results shown in Table 2, there is no significant difference for the NLO results with the same NLO calculation method and different equilibrium geometries in comparison with the great difference when correlation effect is considered. So in this section, correlation effect is considered on different equilibrium geometries.

Frequency dispersion effect

The results we got above are all at static limit. As we know that molecules' NLO properties depend upon different incident light frequencies, in this section, four

different incident frequencies: 1907, 1604, 633 and 500 nm were introduced to investigate the influence of foreign field. As the default implementation in GAMESS procedure, the dynamic first hyperpolarizabilities of three different processes: second-harmonic generation (SHG) $\beta(2\omega; \omega, -\omega)$, optical-rectification (OR) $\beta(0; \omega, -\omega)$ and electro-optic Pockels effect (EOPE) $\beta(-\omega; \omega, 0)$ are shown in Table 4 and Figure 2.

For these molecules, the dynamic first hyperpolarizabilities increase as incident light becomes strong. Under any incident light frequency, $\beta(2\omega; \omega, -\omega)$ is larger than $\beta(0; \omega, -\omega)$ and $\beta(-\omega; \omega, 0)$ and the latter two are identical in most cases. When the incident light frequency is 500 nm, there is an abnormality with the SHG process for molecule SOSQ. As the results shown in Table 4, 600–1000 nm is acceptable to be adopted as the external light frequency. This should be useful for the application of SOSQ once this molecule has been synthesized.

For molecule SeOSQ, some discrepancies are discerned in comparison with OOSQ and SOSQ. First, the EOPE results $\beta(-\omega; \omega, 0)$ are greater than the OR results $\beta(0; \omega, -\omega)$ under any incident light frequency if the sign is omitted, and the difference become larger as the incident light frequency becomes stronger. Second, some negative values arise being difficult to explain. Third, even at a rather weak light frequency 1064 nm, SeOSQ shows a rather larger SHG results. As the maximal absorption wavelengths of SeOSQ are not

Table 3 The first hyperpolarizabilities (10^{-30} esu) calculated with different basis sets at various theoretical levels

Method	OOSQ	SOSQ	SeOSQ	TeOSQ ^a
HF/6-311G//HF/6-311+G(d,p)	-2.716	-5.512	-3.343	3.341
HF/6-311+G(d,p)//HF/6-311+G(d,p)	-2.231	-4.850	-4.208	8.675
HF/6-311++G(3d,2p)//HF/6-311+G(d,p)	-1.653	-5.156	-4.428	—
MP2/6-311G//MP2/6-311+G(d,p)	-5.147	-14.622	-18.584	-28.360
MP2/6-311+G(d,p)//MP2/6-311+G(d,p)	-4.368	-11.794	-15.554	-26.831
MP2/6-311++G(3d,2p)//MP2/6-311+G(d,p)	-3.560	-10.509	-15.334	—
MP2/6-311++G(3df,2p)//MP2/6-311+G(d,p)	-3.493	-10.354	—	—
B3LYP/6-311G//B3LYP/6-311+G(d,p)	-2.204	-4.060	-2.770	1.076
B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p)	-2.384	-4.772	-5.173	3.198
B3LYP/6-311++G(3d,2p)//B3LYP/6-311+G(d,p)	-1.951	-5.115	-6.022	—

^a Effective core potential basis set LANL2DZ was used for Te.

Table 4 Frequency-dependent first hyperpolarizabilities (10^{-30} esu) of squaric acid homologues

Compd.	Static	SHG				OR				EOPE			
		1907 ^a	1064	633	500	1907	1064	633	500	1907	1064	633	500
OOSQ	1.922	2.027	2.295	3.391	5.308	1.957	2.035	2.270	2.532	1.957	2.035	2.270	2.531
SOSQ	3.384	3.730	4.719	12.792	—	3.504	3.754	4.609	5.777	3.497	3.748	4.601	5.767
SeOSQ	-10.288	20.610	97.762	42379	—	11.046	8.205	64.959	627	16.256	20.338	-158	-4946
TeOSQ	-23.305	1307	15072	—	—	338	501	17702	225927	105	79.511	-7717	—

^a The unit of incident light frequency is nm.

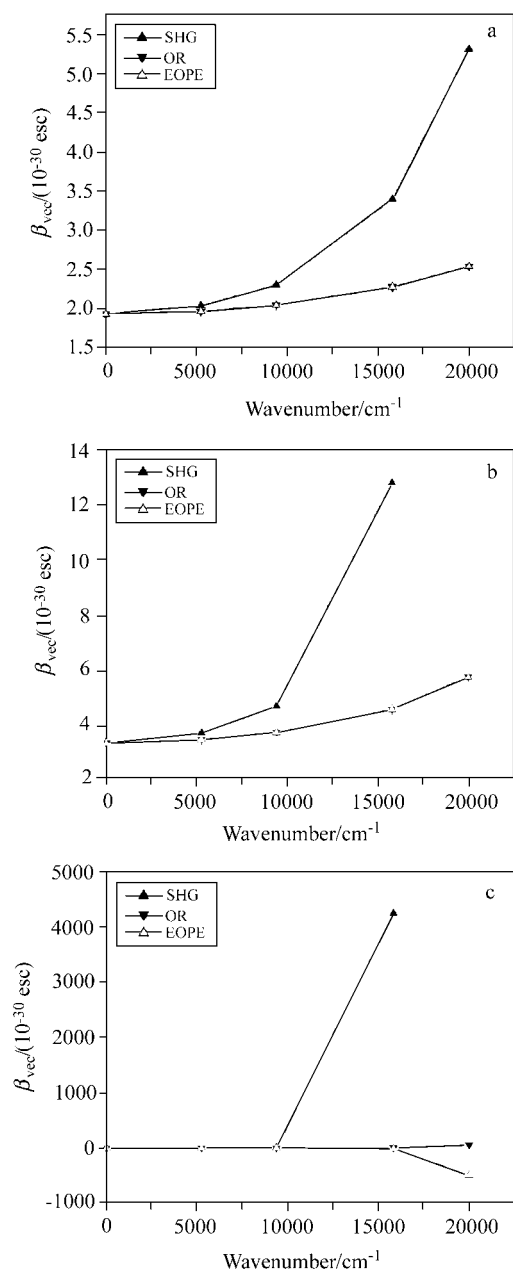


Figure 2 Frequency dependence of the first hyperpolarizabilities β_{μ} of OOSQ (a), SOSQ (b) and SeOSQ (c) for different NLO processes.

significantly different in comparison to SOSQ, it can only be explained that some other factors also play important roles in determination of the frequency dependent results or the results are not reliable at such frequency. For TeOSQ, when the external light frequency is 1907 nm, there is already significant increase in comparison with the static results. This is rather strange for that, to our knowledge, there is no molecule that has so large first hyperpolarizabilities. This provokes us to doubt the credibility of GAMESS when molecules including the fourth and fifth period atoms are accepted in the NLO calculations.

Solvent effect

Just as the results shown in Table 5, there is significant increase in the calculated values of the first hyperpolarizability at a solvent environment in comparison with gas phase results. The first hyperpolarizabilities displayed as functions of the dielectric constant ϵ are shown in Figure 3. The first hyperpolarizability β_{μ} increases monotonously as the dielectric constant ϵ increases except for HF results of TeOSQ. In most cases, β_{μ} increases rapidly as ϵ increases from 2.228 to 10.36 and then the increment becomes flat and there is no considerable difference when ϵ is greater than 20.7. When the substitute atom varies from O to S, Se and Te, a greater increase appears while ϵ increases. When heavier atoms are engrafted into the molecules, more attention should be paid to the solvent effect.

There is considerable difference between the first hyperpolarizabilities based on HF and B3LYP results for TeOSQ, just like the gas phase results. This phenomenon appears for opposite sign of some tensor components calculated by different theoretical methods.

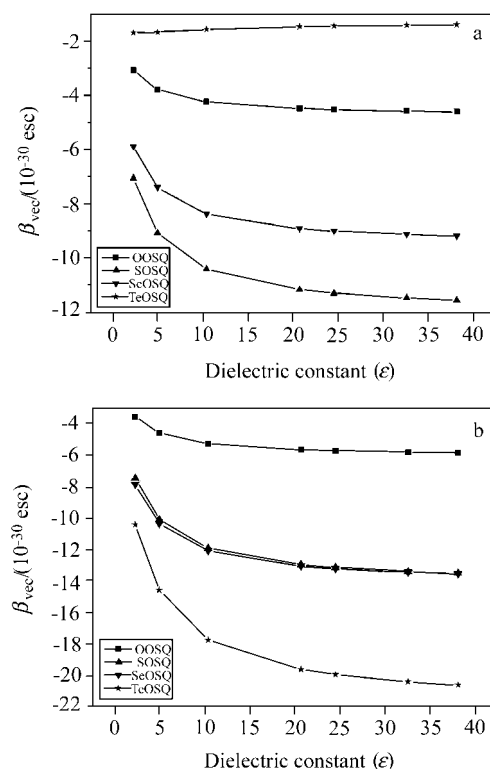


Figure 3 Relationship between the first hyperpolarizabilities β_{vec} [(a) HF/6-311+G(d,p) results; (b) B3LYP/6-311+G(d,p) results] and the solvent dielectric constant ϵ .

Heavy atom effect

After the investigations of some influential factors on the NLO properties of four squaric homologues, now it is appropriate to discuss heavy atom effect. As no more than 15 percent variation of the first hyperpo-

Table 5 Relationship between the first hyperpolarizabilities (10^{-30} esu) of squaric acid homologues and the solvent dielectric constant ϵ

ϵ	OOSQ		SOSQ		SeOSQ		TeOSQ	
	HF	B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP
2.228	-3.068	-3.540	-7.063	-7.466	-5.895	-7.854	-1.694	-10.429
4.9	-3.784	-4.573	-9.080	-10.103	-7.394	-10.369	-1.683	-14.605
10.36	-4.236	-5.264	-10.428	-11.944	-8.375	-12.092	-1.562	-17.792
20.7	-4.478	-5.644	-11.176	-12.988	-8.913	-13.064	-1.455	-19.669
24.55	-4.519	-5.711	-11.304	-13.167	-9.005	-13.226	-1.433	-19.997
32.63	-4.565	-5.792	-11.479	-13.430	-9.128	-13.465	-1.403	-20.448
38.2	-4.595	-5.827	-11.558	-13.527	-9.184	-13.567	-1.386	-20.654

larizabilities based on the same NLO calculation method and different equilibrium geometries, it should be pointed out that the equilibrium geometry difference is not an essential factor that should be taken into account when heavy atom effect is considered. When it turns to basis set dependence, there is some consistency between different basis set results while there is no incremental trend for the hyperpolarizabilities of OOSQ, SOSQ and SeOSQ. When correlation effect is considered in the NLO calculations, the incremental trend appears. Correlation effect is essential for the NLO calculation to take the heavy atom effect more obvious.

When the incident light frequency is the same for OOSQ, SOSQ and SeOSQ, the dynamic first hyperpolarizabilities of the last one is greater than those of the former two especially for the SHG processes. When heavier atom is substituted in the molecule, greater dynamic results are obtained.

When solvent effect is considered in the discussion of heavy atom effect, it is desirable to point out that within DFT results, TeOSQ has the greatest values of the first hyperpolarizability for these four squaric acid homologues and OOSQ have the smallest. Although we find no discrepancy for SOSQ and SeOSQ, the heavy atom effect is expected.

Conclusion

The first hyperpolarizabilities of four squaric acid homologues: OOSQ, SOSQ, SeOSQ and TeOSQ have been calculated. Some influential factors such as equilibrium geometries, basis set dependence, correlation effect were investigated. It is found that: (1) Accurate equilibrium geometry is necessary to get accurate NLO results, however it is not absolutely necessary when heavy atom effect is taken into account; (2) More robust basis set such as 6-311++G(3d,2p) is required for the NLO calculations of OOSQ and SOSQ while for SeOSQ it is appropriate to adopt a comparatively simple 6-311+G(d,p) basis set. For TeOSQ, an effective core potential LANL2DZ adopted for atom Te is enough. (3) Correlation effect is essential in NLO calculations there is 2 to 3 times larger increase of the first hyperpolarizabilities in comparison to HF results.

The first hyperpolarizabilities under external light frequencies are always greater than those at static limit. Among the three important dynamic processes, SHG is

more dependent upon the incident light frequency than OR and EOPE and the latter two are identical in most cases. For the dynamic first hyperpolarizabilities of SeOSQ and TeOSQ, some strange phenomena appear and this takes the credibility of GAMESS for NLO calculations into doubt. Solvent effect induces 2—3 times increase of the first hyperpolarizabilities of these squaric acid homologues. The dielectric constant of the solvent increases with the monotonous increasing of the first hyperpolarizabilities except for HF results of TeOSQ. There is great difference between HF and DFT results of TeOSQ and the credibility of the results is not guaranteed although the authors prefer to the DFT results.

Heavy atom effect, which has already been discovered for furan homologues, still takes effect for these four squaric acid homologues.

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