

Theoretical calculations of molecular dipole moment, polarizability, and first hyperpolarizability of glycine–sodium nitrate

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Abstract

In order to calculate the energy gap, molecular dipole moment, polarizability, and first hyperpolarizability of glycine–sodium nitrate ($\text{Na}(\text{NO}_3)\cdot\text{C}_2\text{H}_5\text{NO}_2$), a series of basis sets including polarized and diffuse functions have been employed at the framework of: Hartree–Fock, Density Functional Theory, and Möller–Plesset Perturbation Theory methods. Geometry optimization was carried out with DFT-B3LYP 6-311++G(d,p). The geometrical differences between the optimized molecule and the molecule in solid phase were attributed to intramolecular and intermolecular forces that are present in solid phase. In addition, the results have revealed that hydrogen bonds not only play an important role determining the crystal structure of glycine–sodium nitrate but also decreasing its energy gap. Further, it was confirmed that glycine–sodium nitrate has absolute value of dipole moment which is mainly caused by both the glycine dipolar character and the molecular geometry. Likewise, the calculations gave non-zero values of polarizability and first hyperpolarizability which are related to the linear and nonlinear responses, respectively.

Introduction

In order to allow the second harmonic generation (SHG) process, the materials must possess an absolute value of the susceptibility ($\chi^{(2)}$) which is a bulk property and generally is associated with non-centrosymmetric crystalline structures. From a



microscopic point of view, the description of the bulk property ($\chi^{(2)}$) is analogous to the molecular response named first hyperpolarizability (β).

It is common that some organic molecules own absolute β values. What is more, some of these molecules tend to crystallize in non-centrosymmetric crystalline structures; therefore efficient SHG process is achieved in these materials. As a result, photonic technologies have created an interest not only for the traditional inorganic materials but also organic materials for nonlinear optical (NLO) applications.

Materials based on aminoacids have already proved to achieve SHG when they were irradiated by a Nd:YAG laser source ($\lambda \sim 1064$ nm) [1–5]. For example, some molecular crystals based on glycine have showed this phenomenon [6–10]. In particular, glycine–sodium nitrate (GSN) showed efficient SHG [6]. Besides, from ab-initio calculations some of its physical and chemical properties were determined [11–13].

Ab-initio calculations are excellent alternative methods in the design of NLO molecules and help to predict some properties of the new materials, such as molecular dipole moments, polarizabilities, and hyperpolarizabilities [14–18]. However, in order to obtain reasonable NLO properties it is necessary to use a sequence of basis sets and, at a given level of theory the convergence can be achieved. Nevertheless, the basis sets which the convergence could be achieved are generally large. On the other hand, the Möller–Plesset (MP2) methods are desirable for this purpose [19–20] but they are more computationally expensive. Consequently, NLO calculations have great computational cost due to the large basis sets employed plus the MP2 methods.



On the basis depicted above, a sequence of diffuse and correlation consistent polarized valence basis sets were employed with the aim of calculate the energy gap, dipole moment, polarizability and first hyperpolarizability of GSN at Hartree–Fock (HF), Density Functional Theory (DFT) and MP2 methods.

Computational details

Calculations were carried out using Gaussian 03W [21] package of programs. Gaussian 03W has already proved to be an important tool predicting molecular structures, spectroscopic properties, and molecular origins of NLO properties [22–26].

The single GSN molecule consists of a glycine molecule, a nitrate group and a sodium atom (Fig. 1). Its atomic positions, selected bonds and angles were taken from literature [27]. The optimization was completed by the Becke–Lee–Yang–Parr hybrid exchange-correlation three-parameter functional (B3LYP) [28] and 6-311++G(d,p) basis set.

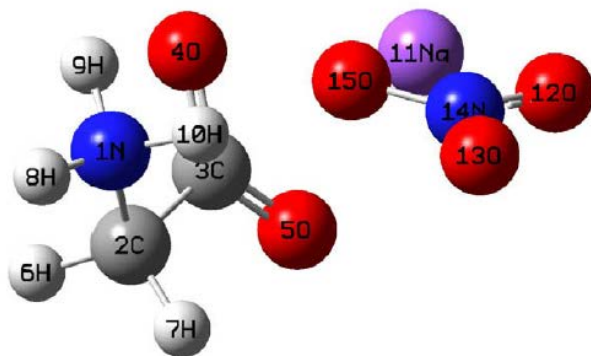


Fig. 1. The molecular structure of GSN determined from B3LYP/6-311++G(d,p) calculations.

Results and discussion

Geometry optimization



The optimized molecular geometry (Fig. 1) represents an isolated molecule under ideal conditions with a stationary point at the potential energy surface; the convergence was confirmed by observing no imaginary vibrational wavenumbers. Table 1 shows the selected bond lengths and angles for GSN molecular unit in solid phase along with the B3LYP/6-311++G(d,p) optimized molecule.

According to B3LYP/6-311++G(d,p) calculations, the glycine molecule exists in dipolar form. Besides, in the optimized molecule the glycine unit is close to the geometry in solid phase (Table 1)

Table 1
Selected bond lengths and angles of GSN from B3LYP/6-311++G(d,p) calculations and X-ray data.

<i>Non-optimized [27]</i>			
4O-3C	1.242	3C-2C	1.520
5O-3C	1.247	2C-6H	0.970
1N-8H	0.890	2C-7H	0.970
1N-9H	0.890	12O-14N	1.246
1N-10H	0.890	15O-14N	1.241
1N-2C	1.480	13O-14N	1.235
12O-14N-15O	119.07	4O-3C-5O	126.02
12O-14N-13O	120.46	4O-3C-2C	117.77
13O-14N-15O	120.46	3C-2C-1N	111.92
<i>Optimized B3LYP/6-311++G(d,p)</i>			
4O-3C	1.261	3C-2C	1.553
5O-3C	1.242	2C-6H	1.091
1N-8H	1.018	2C-7H	1.087
1N-9H	1.034	12O-14N	1.257
1N-10H	1.056	15O-14N	1.298
1N-2C	1.504	13O-14N	1.219
12O-14N-15O	115.92	4O-3C-5O	128.00
12O-14N-13O	123.48	4O-3C-2C	113.97
13O-14N-15O	120.60	3C-2C-1N	104.69

except for the C-H and N-H bonds which are overestimated by DFT calculations. The bond length differences are in the interval from 0.005 to 0.033 Å and the angle differences are from 1.98° to 7.23°. In the case of nitrate group the calculated geometry is also close to the geometry in solid phase with bond differences from 0.011 to 0.057 Å as well as its angles very close to 120°.



Furthermore, direct comparison between the molecular geometry obtained in this work from ab-initio calculations and the molecular geometry reported in solid phase [27], evidences that hydrogen bonds play an important role determining the molecular structure of GSN in solid phase. Since they distort the molecular geometry mainly due to interactions between molecules and for this reason GSN reaches an optimum three-dimensional arrangement.

Energy gap

In general the energy gap values obtained from HF and MP2 methods are close between each other (Table 2). The HF convergence was achieved at the minimum value of 0.41583 a.u. calculated with aug-cc-pVQZ basis set (Fig. 2). Likewise, it is clear from Fig. 2 that MP2 curve shows the same tendency. Consequently one should expect that the convergence could be achieved with the aug-cc-pVQZ basis set. In the case of DFT method, the computed values were approximately 45% lower than those calculated from HF and MP2 methods.

It is known that hydrogen-bonded molecular crystals commonly have lower energy gap than an isolated molecule in gas phase. The latest is because hydrogen bond interactions between the charged species tend to decrease the energy gap [32]. For this reason, in this work a greater HOMO–LUMO energy gap of GSN isolate molecule was calculated. This observation is supported by the energy gap measured experimentally [11].

Optical activity



At molecular level, the response of an isolate molecule to an electric field can be quantified by the dipole moment (μ_i):

$$\mu_i = \mu_i^{(0)} + \sum_j \alpha_{ij} E_j + \sum_{jk} \beta_{ijk} E_j E_k + \sum_{jkl} \gamma_{ijkl} E_j E_k E_l + \dots \quad (1)$$

where the term $\mu_i^{(0)}$ represents the static dipole moment, α is the polarizability and β is the first hyperpolarizability.

Clearly Table 2 shows that GSN molecule owns non-zero values of dipole moment which depict accurately its molecular characteristics, particularly the glycine dipolar character. The results displayed in Table 2 are also presented in Fig. 3. By observing the Fig. 3, it is noticed that the increase of the basis sets size tends to achieve the convergence and therefore to obtain reliable values of dipole moment. For example, at HF is clear that the convergence has been achieved since aug-cc-pVTZ and aug-cc-pVQZ basis sets gave the same value of dipole moment (6.5661 Debye). Besides, the values obtained from HF are only 8% and 7% larger than those obtained from DFT and MP2, respectively, with the advantage of less computational cost.

Polarizability is described by a second rank tensor, but its average value (α_{Total}) can be obtained by considering only the diagonal elements as follows:

$$\alpha_{\text{total}} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

The calculated α values are showed in Table 2 and Fig. 4. In general, the tendency is as follows; the more diffuse and polarization functions are considered, the larger is the value of α . In the HF scheme the values obtained are in the interval from 50.9769 to 66.3325 a.u. Further, the convergence was achieved with aug-ccpVQZ basis



set, because the value obtained with aug-cc-pVQZ is only 0.18 % larger than that obtained with aug-cc-pVTZ basis set. On the other hand, the values obtained from HF diverge from 1.2% to 7.2% in relation to those obtained from MP2, and they are 12.87% smaller than those obtained from DFT.

Table 2
Self consistent field energy (SCF), HOMO-LUMO GAP, total dipole moment ($\mu^{(0)}$), polarizability (α) and first hyperpolarizability (β) of GSN at HF, DFT (B3LYP) and MP2 levels of theory.

Method	Basis set	SCF (a.u.)	GAP (a.u.)	$\mu^{(0)}$ (Debye)	α_{total} (a.u.)	β_{total} (a.u.)	
HF	LanL2DZ	-581.5317	0.44884	7.0524	52.4457	13.919	
	6-31G	-723.3701	0.44676	6.9492	50.9769	12.4992	
	6-311G	-723.5365	0.43818	6.8743	53.4445	16.6014	
	6-31++G	-723.3953	0.42054	6.9384	59.2099	21.1643	
	6-311++G	-723.5521	0.41947	6.9043	60.1686	20.9487	
	6-31++G(d,p)	-723.6737	0.42337	6.7444	61.9854	18.5891	
	6-311++G(d,p)	-723.814	0.42273	6.7328	62.0295	19.2484	
	aug-cc-pVDZ	-723.7515	0.41977	6.5758	65.621	16.1219	
	aug-cc-pVTZ	-723.8846	0.41939	6.5661	66.2126	14.262	
	aug-cc-pVQZ	-723.9214	0.41583	6.5661	66.3325	13.8826	
	DFT/B3LYP	LanL2DZ	-564.9549	0.21374	6.3931	58.6148	24.8681
		6-31G	-726.9173	0.21628	6.3782	58.189	60.5017
6-311G		-727.0973	0.2154	6.2664	61.1283	38.7114	
6-31++G		-726.9514	0.21146	6.3728	68.7073	44.7777	
6-311++G		-727.1164	0.21119	6.3463	69.5134	44.3388	
6-31++G(d,p)		-727.1568	0.21394	6.2288	71.8767	45.3197	
6-311++G(d,p)		-727.3125	0.21514	6.207	71.764	44.2713	
aug-cc-pVDZ		-727.2284	0.21282	6.0722	75.4335	37.9341	
aug-cc-pVTZ		-727.3711	0.21426	6.0673	75.9254	36.7701	
aug-cc-pVQZ		-727.4112	0.21965	6.079	72.973	36.9085	
MP2		LanL2DZ	-562.8476	0.44885	6.3674	59.3347	4.61
		6-31G	-724.4328	0.44716	6.4681	51.9598	452.9449
	6-311G	-724.6808	0.43818	6.3819	52.8079	711.7344	
	6-31++G	-724.4838	0.42154	6.4887	62.3142	543.6517	
	6-311++G	-724.7164	0.41732	6.4933	61.2055	804.2209	
	6-31++G(d,p)	-725.2432	0.42343	6.3233	66.7954	230.8557	
	6-311++G(d,p)	-725.4912	0.42273	6.2847	65.9213	336.0218	
	aug-cc-pVDZ	-725.4047	0.41859	6.1935	69.2824	371.9711	

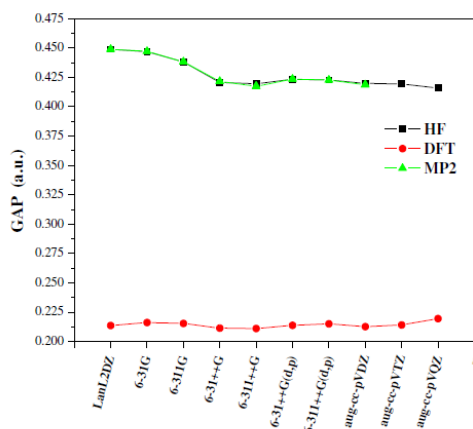


Fig. 2. GAP of GSN as a function of basis set.

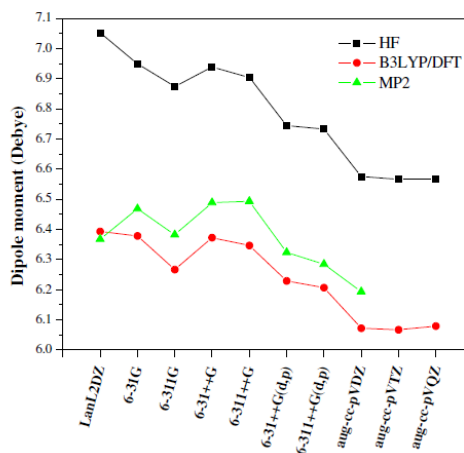


Fig. 3. Dipole moment (μ) of GSN as a function of basis set.

Therefore, the results suggested that at any level of theory, the aug-cc-pVQZ basis set most likely calculates the expected experimental value. The first hyperpolarizability is represented by a third rank tensor. The 27 components of the 3D



matrix can be reduced into 10 components according to Kleinman symmetry [33]. The Gaussian 03W output file provides the main ten components ($\beta_{xxx}, \beta_{xxy}, \beta_{xyy}, \beta_{yyy}, \beta_{xxz}, \beta_{xyz}, \beta_{yyz}, \beta_{xzz}, \beta_{yzz}, \beta_{zzz}$). can be defined in terms of the x, y, z components as [34]:

$$\beta_{\text{total}} = \frac{1}{5} (\beta_x + \beta_y + \beta_z)^{1/2} \quad (3)$$

where the components can be calculated as follows:

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad (4)$$

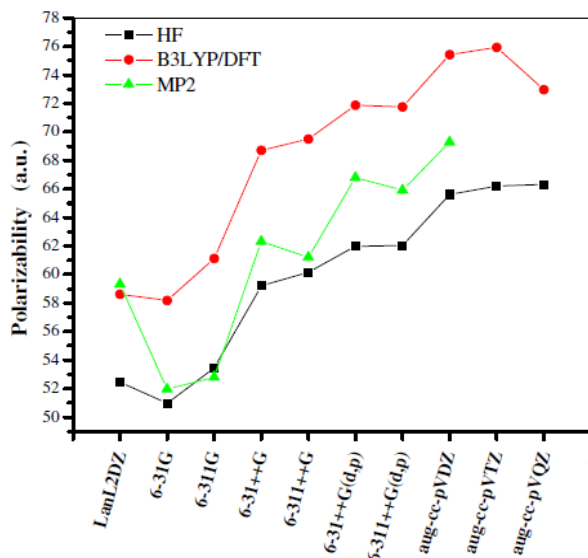


Fig. 4. Polarizability (α) of GSN as a function of basis set.

The computed values (Table 2 and Fig. 5) show that GSN have an absolute β value. This feature is responsible for the second order nonlinear optical properties as SHG; therefore the values suggested the possibility of technological applications of GSN.

By observing the Fig. 5 it is clear that the computed values were quite affected by the level of theory. The values obtained from DFT are 50% larger than those obtained



from HF and the values obtained from MP2 are extremely larger than those obtained from HF and DFT.

On the other hand, the Fig. 5 shows clearly that at HF and DFT methods the convergence could be achieved with aug-cc-pVQZ basis sets. Unfortunately, experimental values for the first hyperpolarizability have not been reported in literature, therefore it is difficult to conclude which level of theory computes reliable values of β .

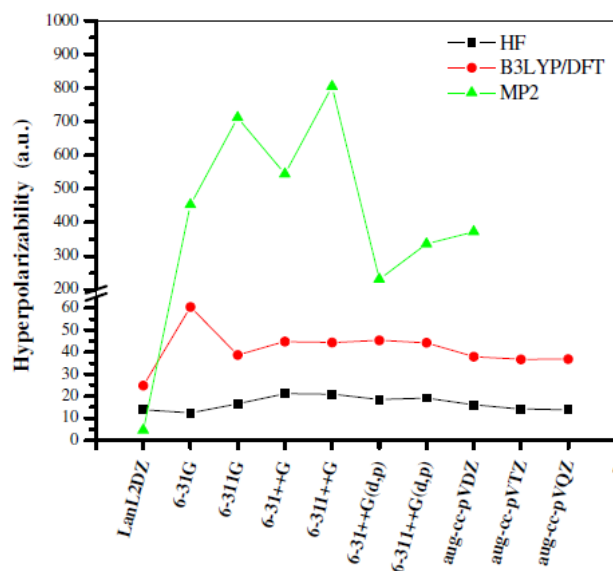


Fig. 5. First hyperpolarizability (β) of GSN as a function of basis set.

Conclusions

The implementation of HF, B3LYP and MP2 methods were used to analyze optical properties of GSN. The geometry obtained from ab-initio calculations suggested that hydrogen bonds play an important role determining the molecular structure of GSN in solid phase as well as tend to decrease its energy gap. Besides, it was observed that the energy gap can be calculated with HF level of theory with the same accuracy and lesser computational cost than MP2 method. Further, dipole moment, polarizability, and



first hyperpolarizability values showed that GSN can respond to an external electric field and allow efficient SHG. Finally, ab-initio calculations proved to be a useful tool to analyze the molecular structure and the optical properties of the new materials.

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References

- [1] Xiaojing Liu, Zeyan Wang, Guanghui Zhang, Xinqiang Wang, Aidong Duan, Zhihua Sun, Luyi Zhu, Dong Xu, *J. Cryst. Growth* 308 (2007) 130–132.
- [2] J. Madhavan, S. Aruna, A. Anuradha, D. Premanand, I. Vetha Potheher, *Opt. Mater.* 29 (2007) 1211–1216.
- [3] V. Rajendran, D. Shyamala, M. Loganayaki, P. Ramasamy, *Mater. Lett.* 61 (2007) 3477–3479.
- [4] Yun Zhang, Hua Li, Bin Xi, Yunxia Che, Jimin Zheng, *Mater. Chem. Phys.* 108 (2008) 192–195.
- [5] S.A. Martin Britto Dhas, M. Suresh, G. Bhagavannarayana, S. Natarajan, *J. Cryst. Growth* 309 (2007) 48–52.
- [6] M. Narayan Bhat, S.M. Dharmaprakash, *J. Cryst. Growth* 235 (2002) 511–516.
- [7] K. Ambujam, K. Rajarajan, S. Selvakumar, J. Madhavan, Gulam Mohamed, P. Sagayaraj, *Opt. Mater.* 29 (2007) 657–662.
- [8] T. Balakrishnan, K. Ramamurthi, *Mater. Lett.* 62 (2008) 65–68.



- [9] S.A. Martin Britto Dhas, S. Natarajan, *Opt. Commun.* 278 (2007) 434–438.
- [10] J. Thomas Joseph Prakash, N. Vijayan, S. Kumararaman, *Spectrochim. Acta A* 71 (2008) 1250–1252.
- [11] J. Hernández-Paredes, D. Glossman-Mitnik, H.E. Esparza-Ponce, M.E. Alvarez Ramos, A. Duarte-Moller, *J. Mol. Struct.* 875 (2008) 295–301.
- [12] J. Hernández-Paredes, Daniel Glossman-Mitnik, O. Hernández -Negrete, H. Esparza-Ponce, M.E. Álvarez R, R. Rodríguez Mijangos, A. Duarte-Moller, *J. Phys. Chem. Solids* 69 (2008) 1974–1979.
- [13] T. Vijayakumar, I. Hubert Joe, C.P. Reghunadhan Nair, V.S. Jayakumar, *J. Mol. Struct.* 877 (2008) 20–35.
- [14] Kechen Wu, Caiping Liu, Chaoyong Mang, *Opt. Mater.* 29 (2007) 1129–1137.
- [15] Tsonko M. Kolev, Denitsa Y. Yancheva, Bistra A. Stamboliyska, Momtchil D. Dimitrov, Rüdiger Wortmann, *Chem. Phys.* 348 (2008) 45–52.
- [16] Ihsan M. Kenawi, Aladin H. Kamel, Rifaat H. Hilal, *J. Mol. Struct. (THEOCHEM)* 851 (2008) 46–53.
- [17] P.A. Fantin, P.L. Barbieri, A. Canal Neto, F.E. Jorge, *J. Mol. Struct. (THEOCHEM)* 810 (2007) 103–111.
- [18] M. Drozd, M.K. Marchewka, *Spectrochim. Acta A* 64 (2006) 6–23.
- [19] T.L. Fonseca, H.C.B. de Oliveira, O.A.V. Amaral, M.A. Castro, *Chem. Phys. Lett.* 413 (2005) 356–361.
- [20] Miroslav Medved, Jozef Noga, Denis Jacquemin, Xavier Assfeld, Eric. A. Perpète, *J. Mol. Struct. (THEOCHEM)* 821 (2007) 160–165.



- [21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W.G. ill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J.A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- [22] A. Ben Ahmed, H. Feki, Y. Abid, H. Boughzala, A. Mlayah, *J. Mol. Struct.* 888 (2008) 180–186.
- [23] H. Unver, A. Karakas, A. Elmali, *J. Mol. Struct.* 702 (2004) 49–54.
- [24] Daniel Glossman-Mitnik, *J. Mol. Struct. (THEOCHEM)* 808 (2007) 81–84.
- [25] P. Srinivasan, T. Kanagasekaran, R. Gopalakrishnan, *Spectrochim. Acta A* 71 (2008) 592–596.
- [26] Asli Karakas, Ayhan Elmali, Huseyin Unver, *Spectrochim. Acta A* 68 (2007) 567–572.



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- [27] R.V. Krishnakumar, M. Subha Nandhini, S. Natarajan, K. Sivakumar, Babu Varghese, *Acta Cryst. C* 57 (2001) 1149–1150.
- [28] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [29] J.B. Foresman, J. Frisch, *Exploring Chemistry with Electronic Structure Methods*, second ed., Gaussian Inc., Pittsburgh, PA, 1996.
- [30] T.H. Dunning Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [31] D.E. Woon, T.H. Dunning Jr., *J. Chem. Phys.* 98 (1993) 1358.
- [32] Ch. Bosshard, R. Spreiter, L. Degiorgi, P. Gunter, *Phys. Rev. B* 66 (2002) 205107.
- [33] D.A. Kleinman, *Phys. Rev.* 126 (1962) 1977.
- [34] H. Kurtz, D. Dudis, Quantum mechanical methods for predicting nonlinear optical properties, in: K. Lipkowitz, D. Boyd (Eds.), *Reviews in Computational Chemistry*, Wiley-VCH, New York, 1998, pp. 241–279.

