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(Hyper)polarizability of carbon diselenide

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Abstract

We have obtained the static dipole polarizability and hyperpolarizability of carbon diselenide from finite-field Møller-Plesset and coupled cluster calculations. We have designed a systematic sequence of Gaussian-type basis sets in order to observe clearly the convergence of the calculated values at all levels of theory. Our best results for the mean and anisotropy of the dipole polarizability are $\bar{\alpha} = 75.92$ and $\Delta\alpha = 83.53 \text{ e}^2\text{a}_0^2\text{E}_h^{-1}$, respectively, at the equilibrium bond length $R_e(\text{C-Se}) = 1.692169 \text{ \AA}$. For the mean hyperpolarizability we report $\bar{\gamma} = 25.56 \times 10^3 \text{ e}^4\text{a}_0^4\text{E}_h^{-3}$. For the symmetric stretching of the C-Se bond, the derivatives of the above properties at R_e are estimated as $\bar{\alpha}' = 29.0$ and $\Delta\alpha' = 51.8 \text{ e}^2\text{a}_0\text{E}_h^{-1}$, $\bar{\gamma}' = 7.1 \times 10^3 \text{ e}^4\text{a}_0^3\text{E}_h^{-3}$.

1. Introduction

Little is known about the electric properties of carbon diselenide (CSe_2). In a recent paper, Benkova and Sadlej reported theoretical calculations of the quadrupole moment (Θ) and the longitudinal dipole polarizability (α_{zz}) of CSe_2 [1]. We are not aware of other recent work on this molecule. A few experimental investigations, related to the electric properties of CSe_2 , have appeared over the years. We note the determination of the dipole moment derivative for the asymmetric stretching of the C-Se bond, extracted from gas phase measurements of the infrared intensity by Wentink and Bauer [2]. Garetz and Khosrofian measured the optical Kerr susceptibility of liquid CSe_2 [3]. The Raman and infrared spectra of solid CSe_2 were measured by Torrie et al. [4]. Last, Brereton et al. [5] extracted the quadrupole moment from measurements of the field-gradient birefringence constant of CSe_2 as a solute in CCl_4 .

The aim of this paper is to provide a high-level ab initio investigation of the electric polarizability ($\alpha_{\alpha\beta}$) and second hyperpolarizability ($\gamma_{\alpha\beta\gamma\delta}$) of carbon diselenide. These properties are of primary importance for the simulation of fluids [6] and the nonlinear optics of molecules [7]. Our approach to the calculation of the (hyper)polarizability is based on the finite-field method [8] and has been presented in detail in previous work [9-13]. We place particular emphasis on the construction of suitable basis sets of Gaussian-type functions (GTF). As there is very little computational experience on CSe_2 , we have designed a sequence of purpose-oriented basis sets. In this way, we are in a position to provide a systematic analysis of basis set effects on the calculated properties. Last, in addition to the dipole (hyper)polarizability we also present values for the quadrupole (Θ) and hexadecapole (Φ) moment.

2. Theory

We rely on Buckingham's work for terminology and notation [14]. Following Buckingham [15] and McLean and Yoshimine [16], we write the energy (E^P) and electric dipole (μ_α^P), quadrupole ($\Theta_{\alpha\beta}^P$) and octopole ($\Omega_{\alpha\beta\gamma}^P$) moment of a system perturbed by a weak, static electric field as:

$$\begin{aligned}
 E^P &\equiv E^P(F_\alpha, F_{\alpha\beta}, F_{\alpha\beta\gamma}, F_{\alpha\beta\gamma\delta}, \dots) \\
 &= E^0 - \mu_\alpha F_\alpha - (1/3)\mathbf{\Theta}_{\alpha\beta} F_{\alpha\beta} - (1/15)\mathbf{\Omega}_{\alpha\beta\gamma} F_{\alpha\beta\gamma} - (1/105)\mathbf{\Phi}_{\alpha\beta\gamma\delta} F_{\alpha\beta\gamma\delta} + \dots \\
 &\quad - (1/2)\alpha_{\alpha\beta} F_\alpha F_\beta - (1/3)\mathbf{A}_{\alpha,\beta\gamma} F_\alpha F_{\beta\gamma} - (1/6)\mathbf{C}_{\alpha\beta,\gamma\delta} F_{\alpha\beta} F_{\gamma\delta} \\
 &\quad - (1/15)\mathbf{E}_{\alpha,\beta\gamma\delta} F_\alpha F_{\beta\gamma\delta} + \dots \\
 &\quad - (1/6)\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - (1/6)\mathbf{B}_{\alpha\beta,\gamma\delta} F_\alpha F_\beta F_{\gamma\delta} + \dots \\
 &\quad - (1/24)\gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots
 \end{aligned} \tag{1}$$

$$\begin{aligned}
 \mu_\alpha^P &= \mu_\alpha + \alpha_{\alpha\beta} F_\beta + (1/3)\mathbf{A}_{\alpha,\beta\gamma} F_{\beta\gamma} + (1/2)\beta_{\alpha\beta\gamma} F_\beta F_\gamma \\
 &\quad + (1/3)\mathbf{B}_{\alpha\beta,\gamma\delta} F_\beta F_{\gamma\delta} + (1/6)\gamma_{\alpha\beta\gamma\delta} F_\beta F_\gamma F_\delta + \dots
 \end{aligned} \tag{2}$$

$$\Theta_{\alpha\beta}^P = \Theta_{\alpha\beta} + \mathbf{A}_{\gamma,\alpha\beta} F_\gamma + \mathbf{C}_{\alpha\beta,\gamma\delta} F_{\gamma\delta} + (1/2)\mathbf{B}_{\gamma\delta,\alpha\beta} F_\gamma F_\delta + \dots \tag{3}$$

$$\Omega_{\alpha\beta\gamma}^P = \Omega_{\alpha\beta\gamma} + \mathbf{E}_{\delta,\alpha\beta\gamma} F_\delta + \dots \tag{4}$$

F_α , $F_{\alpha\beta}$, etc. are the field, field gradient, etc. at the origin. E^0 is the energy of the unperturbed molecule. The coefficients of the above expansions (**in bold**) are the permanent electric properties of the system: electric moments (μ_α , $\Theta_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$, $\Phi_{\alpha\beta\gamma\delta}$) and (hyper)polarizabilities ($\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$, $\mathbf{A}_{\alpha,\beta\gamma}$, $\mathbf{C}_{\alpha\beta,\gamma\delta}$, $\mathbf{E}_{\alpha,\beta\gamma\delta}$, $\mathbf{B}_{\alpha\beta,\gamma\delta}$). The subscripts denote Cartesian components. A repeated subscript implies summation over x, y and z. For very weak fields, the expansions of equations (1-4) converge rapidly. The electric properties can be conveniently obtained from the perturbed energy or the induced multipole moments [11,17-19].

The number of independent components needed to specify the above defined tensors is regulated by symmetry [14]. For a linear centrosymmetric molecule, as CSe_2 , there is only one independent component for the non-vanishing moments, $\Theta \equiv \Theta_{zz}$, $\Phi \equiv \Phi_{zzzz}$ (with z as the molecular axis). The dipole polarizability and hyperpolarizability have two and three

independent components, respectively. In addition to the Cartesian components, we also compute the invariants of the (hyper)polarizability, defined as [14]:

$$\begin{aligned}\bar{\alpha} &= (\alpha_{zz} + 2\alpha_{xx})/3 \\ \Delta\alpha &= \alpha_{zz} - \alpha_{xx} \\ \bar{\gamma} &= (3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz})/15 \\ \Delta_1\gamma &= 3\gamma_{zzzz} - 4\gamma_{xxxx} + 3\gamma_{xxzz} \\ \Delta_2\gamma &= \gamma_{zzzz} + \gamma_{xxxx} - 6\gamma_{xxzz}\end{aligned}\quad (5)$$

Electron correlation effects were estimated via conventional **ab initio** methods, Møller-Plesset perturbation theory and coupled cluster techniques. Rigorous presentation of the self-consistent field (SCF) and the MP2, MP4, CCSD and CCSD(T) post-Hartree-Fock methods can be found in standard references [20-24]. The highest level of theory used in this work is CCSD(T), coupled clusters with singles and doubles with an estimate of connected triple excitations by a perturbational treatment. The electron correlation correction (ECC) to the SCF values is defined as

$$\text{ECC} = \text{CCSD(T)} - \text{SCF} \quad (6)$$

Last, correlated values of the electric moments were calculated at the MP2 level via the MP2 density [25].

3. Computational details

The basis sets used in this work were built upon a (9s5p/17s13p6d) C/Se substrate taken from the Karlsruhe database [26]. This substrate was contracted to [5s3p/6s5p2d] as [51111;311/842111;64111;51]. The substrate was systematically augmented, following a computational philosophy successfully tested in previous work [11-13, 27-30]. We will not give details of this computational methodology here. In summary, (a) diffuse s- and p-GTF are added on both centres, (b) a d-GTF is added on C with exponent chosen to minimize the energy of the free molecule E^0 , (c) d-GTF are added on both C and Se with exponents chosen to maximize the mean polarizability $\bar{\alpha}$. The composition of the basis sets has as follows (optimized exponents in bold):

$$\mathbf{B0} \equiv [5s3p/6s5p2d]$$

$$\mathbf{B1} \equiv [6s4p/7s6p2d] = \mathbf{B0} + \text{C: } s(0.0488618), p(0.0383649) \\ + \text{Se: } s(0.0514942), p(0.0328912).$$

$$\mathbf{B2} \equiv [6s4p2d/7s6p2d] = \mathbf{B1} + \text{C: } d(\mathbf{0.3934}, \mathbf{0.0840})$$

$$\mathbf{B3} \equiv [6s4p2d/7s6p3d] = \mathbf{B2} + \text{Se: } d(\mathbf{0.1096})$$

$$\mathbf{B4} \equiv [6s4p3d/7s6p4d] = \mathbf{B3} + \text{C: } d(0.1818) \\ + \text{Se: } d(0.3145)$$

$$\mathbf{B5} \equiv [6s4p3d1f/7s6p4d1f] = \mathbf{B4} + \text{C: } f(0.1818) \\ + \text{Se: } f(0.3145)$$

$$\mathbf{B6} \equiv [6s4p4d1f/7s6p5d1f] = \mathbf{B5} + \text{C: } d(0.0388) \\ + \text{Se: } d(0.0382)$$

$$\mathbf{B7} \equiv [6s4p4d2f/7s6p5d2f] = \mathbf{B6} + \text{C: } f(0.0840) \\ + \text{Se: } f(0.1096)$$

5D and 7F GTF were used on all basis sets.

All optimizations and subsequent calculations were performed at the experimental equilibrium geometry defined by $R_e(\text{C-Se}) = 1.692169 \text{ \AA}$ [31].

Weak, homogeneous fields of $0.0025 \text{ e}^{-1} a_0^{-1} E_h$ were found to be suitable for the calculation of the perturbed molecular energies. The GAUSSIAN 98 [32] program was used in all calculations.

Unless otherwise specified, atomic units are used throughout this paper. Conversion factors to SI units are, Energy, $1 E_h = 4.3597482 \times 10^{-18} \text{ J}$, Length, $1 a_0 = 0.529177249 \times 10^{-10} \text{ m}$, Θ , $1 \text{ ea}_0^2 = 4.486554 \times 10^{-40} \text{ Cm}^2$, Φ , $1 \text{ ea}_0^4 = 1.256363 \times 10^{-60} \text{ Cm}^4$, α , $1 \text{ e}^2 a_0^2 E_h^{-1} =$

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$1.648778 \times 10^{-41} \text{ C}^2\text{m}^2\text{J}^{-1}$ and $\gamma, 1 \text{ e}^4\text{a}_0^4\text{E}_\text{h}^{-3} = 6.235378 \times 10^{-65} \text{ C}^4\text{m}^4\text{J}^{-3}$. The calculated molecular properties are given as pure numbers, that is Θ/ea_0^2 , Φ/ea_0^4 , $\alpha/\text{e}^2\text{a}_0^2\text{E}_\text{h}^{-1}$ and $\gamma/\text{e}^4\text{a}_0^4\text{E}_\text{h}^{-3}$.

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4. Results and discussion

4.1. Electric moments. SCF and MP2 values for the quadrupole and hexadecapole moment are given in table 1. The 19 innermost MO were kept frozen in the MP2 calculations. Our best SCF values are those calculated with basis B7 and are $\Theta = 4.0857$ and $\Phi = 221.38$. At the MP2 level of theory we obtain $\Theta = 3.7788$ and $\Phi = 173.23$, or 7.5 and 21.7% lower than the respective SCF values. For Θ and B0-B2 we observe that SCF < MP2 but this is reversed for the remaining B3-B7 basis sets. For Φ , MP2 reduces systematically the SCF values. For both properties, the SCF and MP2 values converge smoothly to the B7 results as B0→B7.

4.2. Dipole (hyper)polarizability. Dipole polarizability and hyperpolarizability values for $\text{Re}(\text{C-Se})$ are given in tables 2 and 3, respectively. The 19 innermost MO were kept frozen in the post-Hartree-Fock calculations. We have tested this approximation by performing calculations at the MP2(FULL)/B6 level of theory. The inclusion of all electrons increases both Cartesian components of the dipole polarizability but the effect is well below 1%.

The SCF/B7 values of the dipole polarizability are $\alpha_{zz} = 126.50$, $\alpha_{xx} = 47.38$, $\bar{\alpha} = 73.75$ and $\Delta\alpha = 79.11$. The longitudinal component is significantly larger than the transversal one, thus the molecule is characterized by a large anisotropy $\Delta\alpha$. As expected, α_{xx} shows considerable basis set dependence as B0→B7 and this leads to a strong reduction of the anisotropy with increasing basis set size. Electron correlation increases both Cartesian components of the polarizability. Our CCSD(T)/B7 values for the invariants are $\bar{\alpha} = 75.92$ and $\Delta\alpha = 83.53$ or 2.9 and 5.6% above the respective SCF values. We note that for the mean and the anisotropy the MP2 are close to the CCSD values, and the MP4 close to the CCSD(T) ones.

The effects of basis set size are more pronounced in the case of the second hyperpolarizability, as expected. Our SCF/B7 values for the Cartesian components of $10^{-3} \times \gamma_{\alpha\beta\gamma\delta}$ are $\gamma_{zzzz} = 24.42$, $\gamma_{xxxx} = 16.41$ and $\gamma_{xxzz} = 16.16$. Electron correlation increases all components of the hyperpolarizability. The CCSD(T)/B7 is 26.56×10^3 , 23.1% above the SCF/B7 of 21.57×10^3 . A very strong increase is also observed for the magnitude of the anisotropies $\Delta_1\gamma$ and $\Delta_2\gamma$.

The bond-length dependence of $\bar{\alpha}$, $\Delta\alpha$ and $\bar{\gamma}$ for the symmetric stretching of C-Se is given in table 4. Calculations were performed with basis B6 at all levels of theory for displacements $[\text{R}(\text{C-Se}) - \text{R}_e(\text{C-Se})]/\text{\AA} = \pm 0.1, \pm 0.2, \pm 0.3$ and ± 0.4 . In figures 1, 2 and 3 we have traced this R-dependence for all three invariants. Figures 1 and 2 are quite similar. At

short distances all curves are well grouped together but diverge with increasing $R(\text{C-Se})$. In both cases, at the largest separation the MP4 curve is above all others as this method predicts a very rapid increase for $\bar{\alpha}$ and $\Delta\alpha$. The derivatives of these properties at R_e vary as:

$$\left(\frac{d\bar{\alpha}}{dR}\right)_e = 23.7 \text{ (SCF)}, 33.7 \text{ (MP2)}, 30.9 \text{ (MP4)}, 29.6 \text{ (CCSD)} \text{ and } 29.0 \text{ (CCSD(T))}$$

$$\left(\frac{d\Delta\alpha}{dR}\right)_e = 35.2 \text{ (SCF)}, 68.1 \text{ (MP2)}, 59.4 \text{ (MP4)}, 53.3 \text{ (CCSD)} \text{ and } 51.8 \text{ (CCSD(T))}.$$

We find that the R -dependence of the mean and the anisotropy of the polarizability at the CCSD(T) level is very well described by the expansions

$$[\bar{\alpha}(R) - \bar{\alpha}(R_e)] = 29.03\Delta R + 7.57\Delta R^2 + 0.44\Delta R^3 + 1.71\Delta R^4$$

$$[\Delta(R) - \Delta(R_e)] = 51.78\Delta R + 22.57\Delta R^2 + 6.04\Delta R^3 + 3.78\Delta R^4, \text{ where } \Delta R = (R - R_e).$$

Figure 3 shows that for distances $R > R_e$ MP2, MP4 and CCSD(T) predict a very rapid decrease of the mean $\bar{\gamma}$. This is in marked disagreement with the behaviour of the SCF and CCSD methods. At the SCF and CCSD levels we obtain for the derivative $\left(\frac{d\bar{\gamma}}{dR}\right)_e = 1.6 \times 10^3$ and 3.8×10^3 , respectively. Restricting our attention to just a part of the $\bar{\gamma}(R)$ curve, we estimate $\left(\frac{d\bar{\gamma}}{dR}\right)_e = 7.1 \times 10^3$ with $-0.2 < \Delta R/\text{\AA} < 0.1$.

4.3. Dipole (hyper)polarizability in CO_2 , CS_2 and CSe_2 . Relying on reference SCF values from previous work, we add here a few remarks on the evolution of the electric (hyper)polarizability in carbon dioxide, carbon disulfide and carbon diselenide. Thus,

CO_2 : $\bar{\alpha} = 15.87$, $\Delta\alpha = 11.75$ and $\bar{\gamma} = 862$ (Basis set Q2, table 1 in [33]).

CS_2 : $\bar{\alpha} = 55.44$, $\Delta\alpha = 56.56$ and $\bar{\gamma} = 10520$ (Basis set B7, table 3 in [34]).

CSe_2 : $\bar{\alpha} = 73.75$, $\Delta\alpha = 79.11$ and $\bar{\gamma} = 21.57 \times 10^3$ (Basis set B7, present investigation).

We show in figure 4 the evolution of $\bar{\alpha}$ and $\Delta\alpha$ in CX_2 , $X = \text{O}, \text{S}$ and Se with increasing Z_X . All three systems are characterized by relative large dipole anisotropies, as the longitudinal

component of $\alpha_{\alpha\beta}$ is dominant in all cases. The evolution of $\bar{\gamma}$ follows more or less the same pattern as that of $\bar{\alpha}$.

4.4. Comparison with previous theoretical results and experiment. In their recent work on the electric properties of carbon dichalcogenides Benkova and Sadlej [1] reported high-level calculations for the quadrupole moment and longitudinal dipole polarizability component of CSe₂. Their calculations rely on the HyPolX basis sets. For Θ they obtained SCF and MP2 values of 4.114 and 3.921, respectively. Our values agree well with both. For α_{zz} they report SCF and CCSD(T) values of 126.39 and 132.31, our respective B7 values are 126.50 and 131.60.

The only experimental data available for the electric properties of CSe₂ are those of Brereton et al. [5]. They deduced a value $\Theta = 3.4 \pm 0.6$. Our results agree well with this estimate. Gray and Gubbins [6] reference an experimental estimate of the mean $\bar{\alpha} \approx 72.88$, obtained from refractivity data (see ref. 128, a private communication between the authors and Prof. G.L.D.Ritchie). Our best CCSD(T)/B7 value is a few percent higher.

We note that we have not included relativistic effects here, as this is rather beyond the scope of this paper. The interested reader will find a detailed discussion of these effects on Θ and α_{zz} in the above cited paper by Benkova and Sadlej [1].

Conclusions

We have reported an ab initio investigation of the electric moments, dipole polarizability and hyperpolarizability of carbon diselenide. We have designed a sequence of purpose-oriented basis sets in order to obtain information on the basis set dependence of calculated values at all levels of theory. Our best values for the electric moments have been obtained at the MP2 level of theory and are $\Theta = 3.7788 \text{ ea}_0^2$ and $\Phi = 173.23 \text{ ea}_0^4$. Our best values for the (hyper)polarizability are calculated at the CCSD(T) level of theory and are $\bar{\alpha} = 75.92$ and $\Delta\alpha = 83.53 \text{ e}^2\text{a}_0^2\text{E}_h^{-1}$, $\bar{\gamma} = 25.56 \times 10^3 \text{ e}^4\text{a}_0^4\text{E}_h^{-3}$. Our final estimates for these properties are $\bar{\alpha} = 75.9 \pm 0.6$ and $\Delta\alpha = 83.5 \pm 0.8 \text{ e}^2\text{a}_0^2\text{E}_h^{-1}$, $\bar{\gamma} = (25.6 \pm 2.6) \times 10^3 \text{ e}^4\text{a}_0^4\text{E}_h^{-3}$. In addition, we have calculated the bond-length dependence of the (hyper)polarizability for the symmetric stretching of C-Se. Our estimates are based on CCSD(T) calculations and are $\left(\frac{d\bar{\alpha}}{dR}\right)_e = 29.0 \pm 0.9$ and $\left(\frac{d\Delta\alpha}{dR}\right)_e = 51.8 \pm 1.6 \text{ e}^2\text{a}_0^2\text{E}_h^{-1}$, $\left(\frac{d\bar{\gamma}}{dR}\right)_e = (7.1 \pm 1.4) \times 10^3 \text{ e}^4\text{a}_0^3\text{E}_h^{-3}$.

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Table 1. Electric quadrupole and hexadecapole moment of carbon diselenide at $R_e(\text{C-Se}) = 1.692169 \text{ \AA}$.

Basis set	Method ^a	Θ	Φ
B0 [5s3p/6s5p2d]	SCF	2.3056	191.75
	MP2	2.7020	151.01
B1 [6s4p/7s6p2d]	SCF	2.4085	209.23
	MP2	2.7969	169.05
B2 [6s4p2d/7s6p2d]	SCF	3.7075	210.40
	MP2	3.9779	170.68
B3 [6s4p2d/7s6p3d]	SCF	3.9785	222.82
	MP2	3.8304	177.98
B4 [6s4p3d/7s6p4d]	SCF	4.1277	221.23
	MP2	3.7307	169.92
B5 [6s4p3d1f/7s6p4d1f]	SCF	4.0656	220.78
	MP2	3.7576	172.17
B6 [6s4p4d1f/7s6p5d1f]	SCF	4.0849	221.56
	MP2	3.7768	173.24
B7 [6s4p4d2f/7s6p5d2f]	SCF	4.0857	221.38
	MP2	3.7788	173.23

^a The 19 innermost MO were kept frozen in the MP2 calculations.

Table 2. Electric dipole polarizability of carbon diselenide at $R_e(\text{C-Se}) = 1.692169 \text{ \AA}$.

Basis	Method ^a	α_{zz}	α_{xx}	$\bar{\alpha}$	$\Delta\alpha$
B0	SCF	121.33	18.39	52.70	102.93
	MP2	129.34	19.04	55.81	110.29
	MP4	122.53	19.20	53.64	103.33
	CCSD	129.81	18.99	55.93	110.82
	CCSD(T)	124.74	19.15	54.35	105.59
	ECC	3.42	0.76	1.64	2.66
B1	SCF	126.20	27.35	60.30	98.84
	MP2	135.98	28.71	64.47	107.26
	MP4	129.01	29.05	62.37	99.96
	CCSD	136.48	28.89	64.76	107.59
	CCSD(T)	131.43	29.12	63.22	102.31
	ECC	5.23	1.77	2.92	3.47
B2	SCF	121.82	34.63	63.69	87.19
	MP2	132.41	35.77	67.98	96.64
	MP4	127.82	36.15	66.71	91.67
	CCSD	130.89	36.02	67.64	94.86
	CCSD(T)	128.85	36.33	67.17	92.52
	ECC	7.04	1.71	3.48	5.33
B3	SCF	123.87	46.22	72.10	77.65
	MP2	135.29	46.90	76.36	88.39
	MP4	131.63	47.26	75.38	84.37
	CCSD	134.47	47.22	76.3	87.24
	CCSD(T)	132.54	47.44	75.81	85.10
	ECC	8.67	1.23	3.71	7.45
B4	SCF	126.13	46.49	73.04	79.64
	MP2	133.14	46.03	75.07	87.11
	MP4	130.29	46.36	74.34	83.94
	CCSD	133.21	46.35	75.30	86.86
	CCSD(T)	131.14	46.46	74.69	84.68
	ECC	5.01	-0.03	1.65	5.04
B5	SCF	126.51	46.91	73.44	79.59
	MP2	133.68	47.23	76.05	86.45
	MP4	130.74	47.50	75.25	83.24
	CCSD	133.60	47.34	76.10	86.26
	CCSD(T)	131.62	47.59	75.60	84.03
	ECC	5.11	0.68	2.16	4.44
B6	SCF	126.5	47.37	73.74	79.13
	MP2	133.72	47.75	76.41	85.97
	MP4	130.77	47.99	75.58	82.77
	CCSD	133.60	47.82	76.42	85.78
	CCSD(T)	131.63	48.08	75.93	83.55
	ECC	5.14	0.71	2.19	4.42
B7	SCF	126.50	47.38	73.75	79.11
	MP2	133.70	47.75	76.40	85.95
	MP4	130.74	47.99	75.57	82.75
	CCSD	133.57	47.82	76.40	85.74
	CCSD(T)	131.60	48.07	75.92	83.53

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ECC	5.10	0.69	2.16	4.41
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^a The 19 innermost MO were kept frozen for the post-Hartree-Fock calculations.

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Table 3. Second hyperpolarizability (as $10^{-3} \times \gamma_{\alpha\beta\gamma\delta}$) of carbon diselenide at $R_c(\text{C-Se}) = 1.692169 \text{ \AA}$.

Basis	Method ^a	γ_{zzzz}	γ_{xxxx}	γ_{xxzz}	$\bar{\gamma}$	$\Delta_1\gamma$	$\Delta_2\gamma$
B0	SCF	-14.79	0.14	0.48	-2.50	-43.50	-17.52
	MP2	-27.01	0.18	0.16	-5.18	-81.27	-27.78
	MP4	-9.95	0.31	0.21	-1.66	-30.48	-10.89
	CCSD	-25.51	0.17	0.27	-4.79	-76.38	-26.97
	CCSD(T)	-7.73	-0.02	0.12	-1.46	-22.74	-8.49
	ECC	7.06	-0.16	-0.36	1.04	20.77	9.03
B1	SCF	3.07	5.97	6.26	8.81	4.14	-28.54
	MP2	-0.81	7.33	8.40	10.47	-6.55	-43.90
	MP4	16.25	7.43	8.05	13.65	43.21	-24.64
	CCSD	1.36	7.65	8.90	11.47	0.17	-44.39
	CCSD(T)	20.62	7.88	8.82	15.38	56.78	-24.41
	ECC	17.54	1.91	2.55	6.57	52.64	4.13
B2	SCF	9.77	7.16	5.42	10.11	16.95	-15.61
	MP2	6.50	8.37	7.47	11.74	8.45	-29.97
	MP4	12.03	8.69	7.73	13.22	24.51	-25.64
	CCSD	10.08	8.58	7.62	12.69	18.77	-27.06
	CCSD(T)	18.77	9.07	7.92	14.92	43.77	-19.66
	ECC	9.00	1.91	2.49	4.81	26.82	-4.05
B3	SCF	8.90	7.34	6.35	10.78	16.43	-21.87
	MP2	3.27	8.69	8.83	12.35	1.54	-40.99
	MP4	6.79	8.99	8.91	13.28	11.16	-37.68
	CCSD	5.22	8.62	8.85	12.72	7.70	-39.25
	CCSD(T)	12.95	8.91	9.03	14.57	30.31	-32.32
	ECC	4.05	1.57	2.68	3.79	13.89	-10.45
B4	SCF	10.39	7.58	6.95	11.68	21.72	-23.75
	MP2	6.02	8.60	9.08	13.05	10.89	-39.86
	MP4	9.16	8.77	8.93	13.65	19.19	-35.63
	CCSD	6.61	8.50	8.86	12.95	12.41	-38.07
	CCSD(T)	13.85	8.74	9.03	14.65	33.68	-31.60
	ECC	3.46	1.16	2.08	2.97	11.96	-7.86
B5	SCF	13.74	10.21	8.39	14.91	25.53	-26.38
	MP2	10.75	11.76	11.13	17.32	18.57	-44.24
	MP4	14.15	11.86	11.12	18.05	28.36	-40.70
	CCSD	10.92	11.49	10.73	16.89	19.00	-41.97
	CCSD(T)	18.58	11.81	11.09	18.89	41.77	-36.16
	ECC	4.84	1.60	2.70	3.98	16.24	-9.78
B6	SCF	17.20	13.63	11.57	19.96	31.77	-38.58
	MP2	15.18	16.01	15.41	23.90	27.72	-61.25
	MP4	18.06	15.89	14.95	24.04	35.48	-55.72
	CCSD	14.89	15.37	14.61	22.86	27.03	-57.43
	CCSD(T)	22.72	15.96	14.98	25.04	49.26	-51.22
	ECC	5.52	2.33	3.42	5.08	17.50	-12.64
B7	SCF	18.90	14.20	12.77	21.57	38.22	-43.53
	MP2	16.93	16.65	16.64	25.58	34.12	-66.25
	MP4	20.13	16.70	16.45	26.09	42.96	-61.89
	CCSD	16.72	15.88	15.81	24.46	34.05	-62.24

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CCSD(T)	24.42	16.41	16.16	26.56	56.08	-56.13
ECC	5.51	2.21	3.39	4.99	17.86	-12.61

^a The 19 innermost MO were kept frozen for the post-Hartree-Fock calculations.

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Table 4. Bond-length dependence of the electric (hyper)polarizability for the symmetric stretching of C-Se. Basis set B6 = [6s4p4d1f/7s6p5d1f].

(R-Re)/Å	SCF	MP2	MP4	CCSD	CCSD(T)	ECC
$\bar{\alpha}$						
-0.4	58.71	58.02	58.61	58.73	58.67	-0.04
-0.3	61.71	61.44	61.83	62.16	62.01	0.30
-0.2	65.31	65.61	65.72	66.30	66.05	0.74
-0.1	69.37	70.57	70.26	71.08	70.70	1.33
0	73.74	76.41	75.58	76.42	75.93	2.19
0.1	78.27	83.23	82.09	82.21	81.71	3.44
0.2	82.80	91.16	90.61	88.31	88.05	5.26
0.3	87.17	100.16	102.28	94.54	95.07	7.90
0.4	91.22	109.94	117.98	100.64	102.96	11.73
$\Delta\alpha$						
-0.4	58.12	53.95	55.33	56.93	55.92	-2.20
-0.3	62.04	59.15	59.93	62.04	60.79	-1.25
-0.2	66.95	65.94	65.76	68.50	66.95	0.00
-0.1	72.71	74.71	73.15	76.42	74.51	1.79
0	79.13	85.97	82.77	85.78	83.55	4.42
0.1	85.93	100.27	96.18	96.46	94.24	8.31
0.2	92.78	118.05	116.15	108.19	106.78	14.00
0.3	99.35	139.25	146.44	120.52	121.61	22.26
0.4	105.27	162.91	189.82	132.82	139.46	34.19
$10^{-3} \times \bar{\gamma}$						
-0.4	21.25	23.87	24.08	22.44	23.53	2.28
-0.3	20.28	23.37	23.66	21.95	23.12	2.84
-0.2	19.80	23.30	23.88	21.87	22.99	3.19
-0.1	19.74	23.58	24.19	22.26	23.89	4.15
0	19.96	23.90	24.04	22.86	25.04	5.08
0.1	20.40	23.94	23.16	23.78	26.58	6.18
0.2	21.10	22.72	16.68	24.64	27.63	6.53
0.3	22.20	19.38	0.71	25.64	26.96	4.76
0.4	24.10	16.04	-24.25	26.94	20.41	-3.69

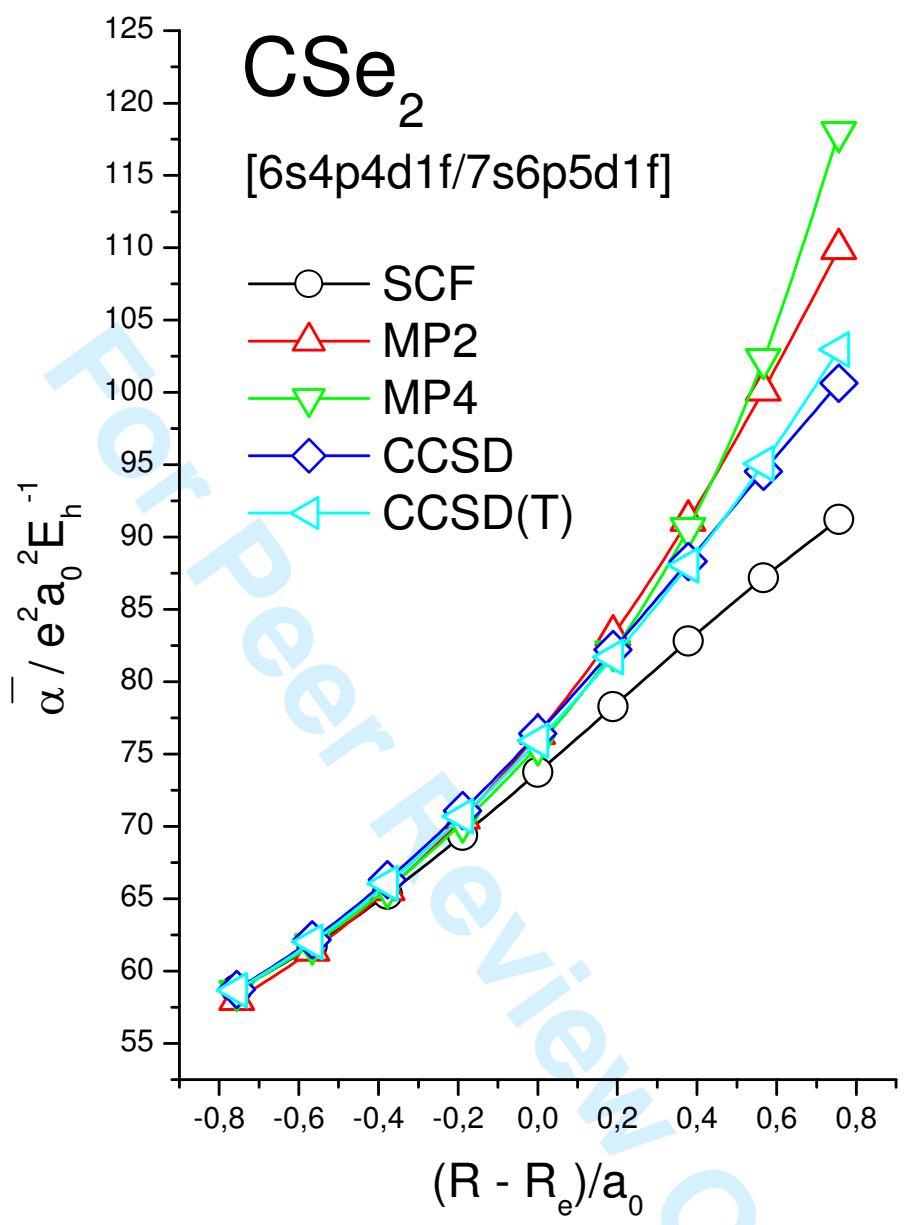


Figure 1. Bond-length dependence of the mean dipole polarizability for the symmetric stretching of C-Se.

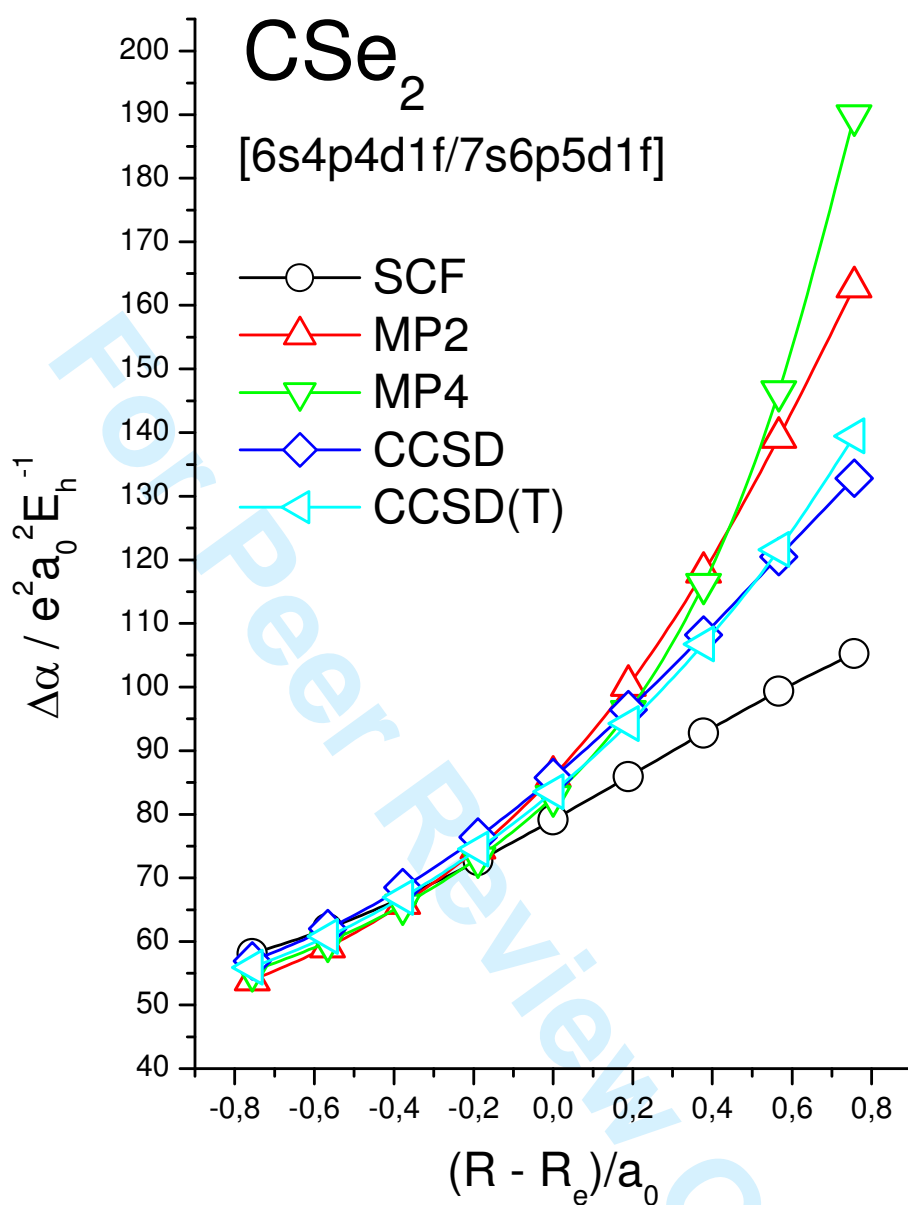


Figure 2. Bond-length dependence of the dipole polarizability anisotropy for the symmetric stretching of C-Se.

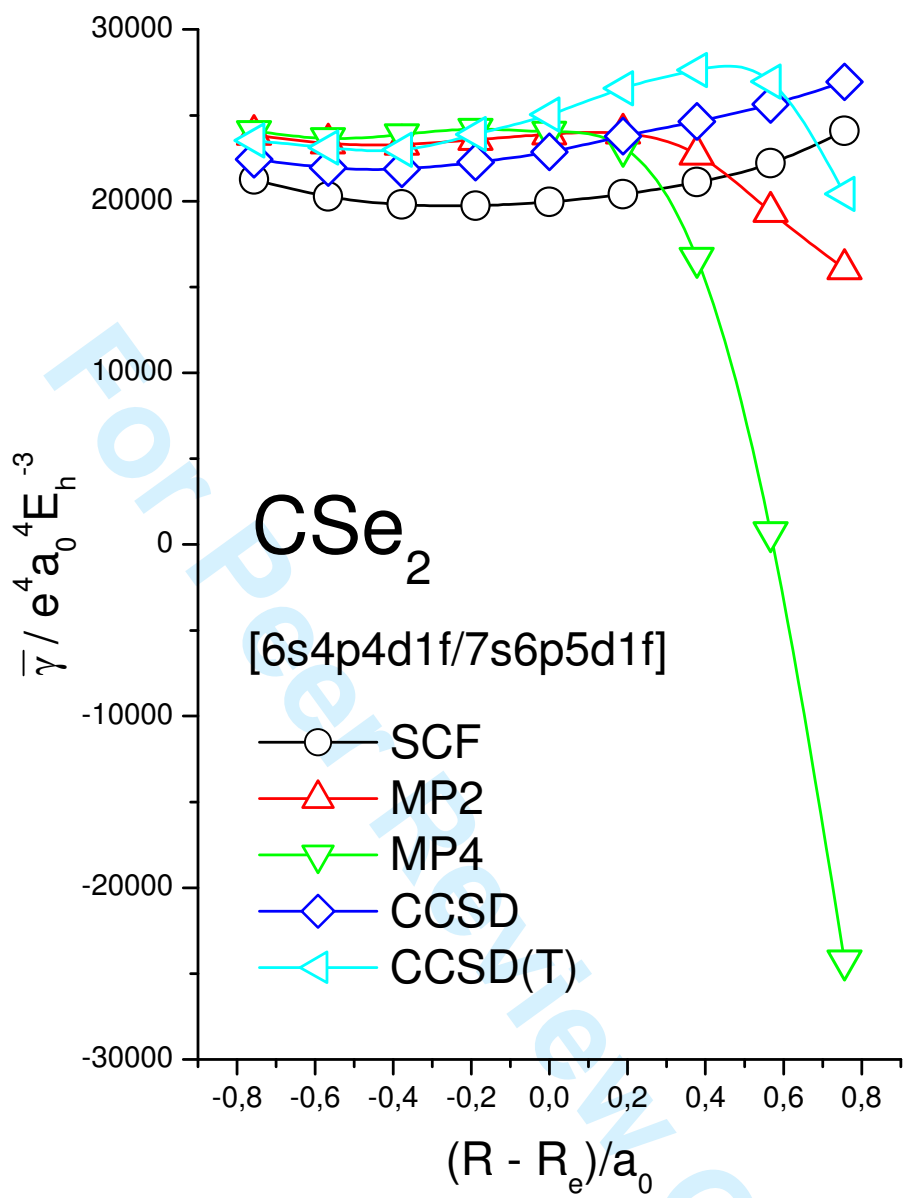


Figure 3. Bond-length dependence of the mean second hyperpolarizability for the symmetric stretching of C-Se.

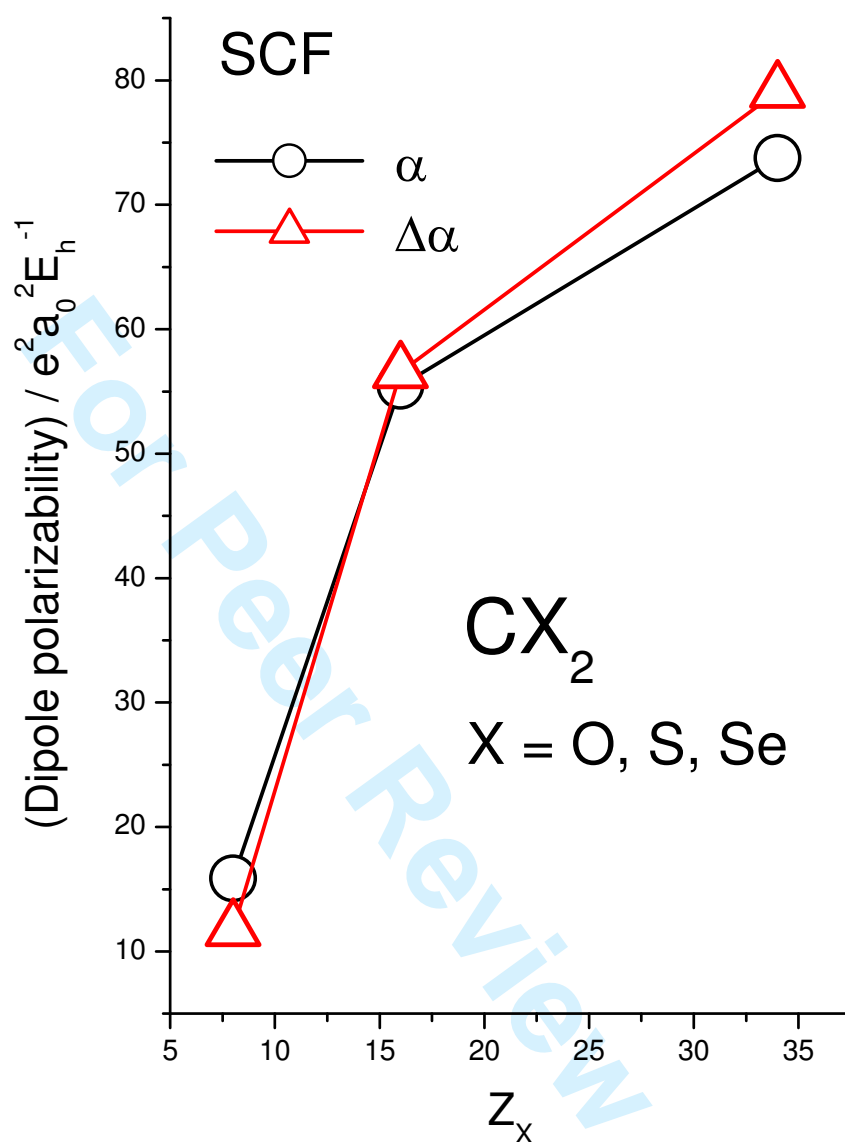


Figure 4. Evolution of the mean and the anisotropy of the dipole polarizability in CO_2 , CS_2 and CSe_2 .