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Is the Hyperpolarizability of Cu_2 Negative? A Study of Basis Set and Electron Correlation Effects

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The dipole (hyper)polarizability of the copper dimer has been obtained from conventional ab initio and density functional theory calculations. A very large (23s16p12d6f) basis set consisting of 346 Gaussian-type functions is thought to provide reference results of near-Hartree−Fock quality for all properties. We obtain $\bar{\alpha} = 102.54$ and $\Delta\alpha = 41.89$ for the mean and the anisotropy of the dipole polarizability ($\alpha_{\alpha\beta}/e^2a_0{}^2E_h{}^{-1}$). For the Cartesian components and the mean of the hyperpolarizability ($10^{-3}\gamma_{\alpha\beta\gamma\delta}/e^4a_0{}^4E_h{}^{-3}$) we obtain $\gamma_{zzzz} = 309$, $\gamma_{xxxx} = 209$, $\gamma_{xxzz} = 87$, and $\bar{\gamma} = 244$. Electron correlation lowers $\bar{\alpha}$ but increases considerably $\Delta\alpha$. The effect on the hyperpolarizability is enormous, as the longitudinal component γ_{zzzz} is drastically reduced, while γ_{xxxx} and γ_{xxzz} are nearly halved. At the CCSD(T) level of theory with a [7s6p6d2f] basis set we obtain $\bar{\alpha} = 93.82$, $\Delta\alpha = 67.09$ and $\gamma_{zzzz} = 18$, $\gamma_{xxxx} = 101$, $\gamma_{xxzz} = 35$, and $\bar{\gamma} = 86$. The dipole polarizability varies as $[\bar{\alpha}(R) - \bar{\alpha}(R_e)]/e^2a_0{}^2E_h{}^{-1} = 28.09(R - R_e) + 4.69(R - R_e)^2 - 0.52(R - R_e)^3 - 0.36(R - R_e)^4$ and $[\Delta\alpha(R) - \Delta\alpha(R_e)]/e^2a_0{}^2E_h{}^{-1} = 49.58(R - R_e) + 11.92(R - R_e)^2 - 1.94(R - R_e)^3 - 1.32(R - R_e)^4$ around the experimental bond length $R_e = 2.2197$ Å. B3LYP density functional theory calculations with a [8s7p7d5f] basis set yield $\bar{\alpha} = 77.62$, $\Delta\alpha = 44.73e^2a_0{}^2E_h{}^{-1}$, and $\bar{\gamma} = (95.9 \times 10^3)e^4a_0{}^4E_h{}^{-3}$. These values differ from the conventional ab initio results. The present investigation shows that the longitudinal component and the mean of the hyperpolarizability are positive around R_e, in conflict with previous findings. The extension of (hyper)polarizability calculations to higher copper clusters is highly nontrivial and will require the development of new computational strategies.

The structure of copper clusters has been the object of numerous theoretical and experimental studies.[1−7] Of particular interest are efforts focusing on the general physicochemical behavior of these systems. Such work includes the bonding of acetylene to copper clusters,[8] the reaction of Cu_2 with ethylene,[9] the bonding of ammonia, carbon monoxide, and ethylene to copper atom, dimer, and trimer,[10] the optical spectra of copper dimer and trimer in superfluid helium,[11] the bonding of CO and NO to Cu_2,[12] the simulation of copper cluster deposition on copper,[13] the physisorption of copper microclusters on MgO(100),[14] the bonding of ammonia to small copper clusters,[15] the collision between Cu_2 and an Ar film,[16] the identification of the $Cu_2(N_2)_n$ complexes,[17] and the optical properties and redox behavior of copper clusters.[18] More, in-depth experimental[19−22] or theoretical[23−26] studies have been reported for the copper dimer. Remarkably few papers have been published on the dipole polarizability of copper clusters. Recent work by Calaminici et al.,[27] Jaqué and Toro-Labbé,[28] and Cao et al.[29] included density functional theory (DFT) calculations of the static dipole polarizability of copper clusters Cu_n, $n \leq 13$. Lastly, Shigemoto et al.[30] reported a study on the axial component of the dipole hyperpolarizability (γ_{zzzz}) of the copper dimer. Their findings brought forth the possibility of a negative dipole hyperpolarizability for this important diatomic molecule.

In this paper we report conventional ab initio and DFT calculations of the static (hyper)polarizability of Cu_2. We rely on a finite-field approach,[31] presented in some detail in previous work.[32−34] Our study includes an investigation of electric correlation effects on the dipole properties and their bond-length- or R-dependence around the experimental equilibrium bond length R_e. Electron correlation correction effects were obtained via Møller−Plesset perturbation theory (MP) and coupled-cluster techniques (CC).[35−41] Thus, the conventional ab initio methods adopted in this work are self-consistent field (SCF), second- (MP2) and fourth-order (MP4) Møller−Plesset perturbation theory, single and double excitation coupled cluster theory (CCSD), and its extension CCSD(T) which includes an estimate of connected triple excitations by a perturbational treatment. In addition to the above methods, we have added calculations performed with a widely used DFT method, B3LYP.[42,43] We expect our B3LYP results to provide valuable information on the performance of DFT methods on copper clusters. Special attention has been paid to the design of suitable basis sets of Gaussian-type functions (GTF). This is a matter of basic importance to molecular property calculations.[44−46] We have designed basis sets for Cu_2 relying on a variety of substrates. Thus, we eschew as much as possible the appearance of systematic errors linked to their composition. We rely mostly on a rich, (17s10p6d) primitive basis set contracted to A0 ≡ [6s3p3d] as [842111;631;411].[47] We considered a sequence of basis sets built upon this substrate. Their compositions are as follows:

A1 ≡ [7s6p5d1f], 114 contracted GTF, from A0 + s(0.013896), p(0.099537, 0.036540), d(0.0847, 0.0252), and f(0.0252)

A2 ≡ [7s6p6d], 110 CGTF, from A0 + s(0.013896), p(0.099537, 0.036540), and d(0.5206, 0.0847, 0.0252)

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A3 $\equiv$ [7s6p6d1f], 124 CGTF, from A2 + f(0.0252)

A4 $\equiv$ [7s6p6d2f], 138 CGTF, from A1 + d(0.0462) and f(0.0462)

A5 $\equiv$ [7s6p6d4f], 166 CGTF, from A2 + f(0.5206, 0.284208625, 0.0847, 0.0252)

A6 $\equiv$ [8s7p7d1f], 142 CGTF, from A3 + s(0.004976), p(0.013414), d(0.0462)

A7 $\equiv$ [8s7p7d5f], 198 CGTF, from A6 + f(0.5206, 0.284208625, 0.0847, 0.0462)

Three relatively large basis sets (HA1, HA2, and HA3) were obtained from a Horn/Alrichs[48] (14s9p6d) primitive set contracted to [8s5p4d]. HA3 is of exactly the same size as HA1 but more diffuse. In summary,

HA1 $\equiv$ [9s8p7d3f], 178 CGTF, from [8s5p4d] + s(0.0154225), p(0.2755692, 0.0986857, 0.0353409), d(0.520367, 0.155050, 0.084636), f(0.28404778701, 0.155050, 0.084636)

HA2 $\equiv$ [9s8p7d3f1g], 196 CGTF, from HA1 + g(0.084636)

HA3 $\equiv$ [9s8p7d3f], 178 CGTF, from [8s5p4d] + s(0.0154225), p(0.2755692, 0.0986857, 0.0353409), d(0.084636, 0.046199, 0.025218), f(0.084636, 0.046199, 0.025218)

Last, we employed two very large uncontracted basis sets. KoTa $\equiv$ (21s14p11d5f) and PA $\equiv$ (23s16p12d6f) were used for the calculation of reference SCF values. They were built upon (20s11p9d)[49] and (20s12p9d)[50] substrates. Their compositions are

KoTa $\equiv$ (21s14p11d5f), 306 GTF, from (20s11p9d) + s(0.0136467), p(0.2191479, 0.0862877, 0.0339751), d(0.0533370, 0.0193175), f(1.0116754, 0.40661468, 0.14726709, 0.0533370, 0.0193175)

and

PA $\equiv$ (23s16p12d6f), 346 GTF, from (20s12p9d) + s(0.013650, 0.004804, 0.001691), p(0.079298, 0.032177, 0.013057), d(0.053362, 0.019328, 0.007000), f(1.012386, 0.406773, 0.147331, 0.053362, 0.019328, 0.007000)

5d, 7f, and 9g GTF were used in all cases. The experimental bond length for Cu_2 is 2.2197 Å.[51] Weak, homogeneous fields of $0.0025e^{-1}a_0^{-1}E_h$ were used in the calculations. The GAUSSIAN 94 and 98 programs[52,53] were used in this work.

SCF and post-Hartree−Fock results are given in Table 1. Reference, near-Hartree−Fock values have been obtained with our KoTa and PA basis sets. Our SCF/PA[54] values are $\bar{\alpha} = 102.54$ and $\Delta\alpha = 41.89e^2a_0^2E_h^{-1}$ for the polarizability and $\bar{\gamma} = 244 \times 10^3$, $\Delta_1\gamma = 353 \times 10^3$, and $\Delta_2\gamma = (-6 \times 10^3)e^4a_0^4E_h^{-3}$ for the hyperpolarizability. The KoTa basis gives $\bar{\alpha} = 102.48$ and $\Delta\alpha = 41.94e^2a_0^2E_h^{-1}$ for the polarizability and $\bar{\gamma} = (236 \times 10^3)e^4a_0^4E_h^{-3}$, in very good agreement with the PA values. All other basis sets yield SCF dipole polarizabilities convincingly close to the above. As rather expected, agreement is slightly worse for the hyperpolarizability. The A1 result $\bar{\gamma} = (225 \times 10^3)e^4a_0^4E_h^{-3}$ is ≈8% lower than the presumably most accurate PA value. Agreement is much better for the larger basis sets in Table 1. Consider the A4, A5, and A6 sequence: $\bar{\alpha}/e^2a_0^2E_h^{-1} = 102.90$ (A4), 103.21 (A6), 102.55 (A7) and $10^{-3}\bar{\gamma}/e^4a_0^4E_h^{-3} = 227$ (A4), 240 (A6), 244 (A7). It should be noted that convergence to the Hartree−Fock limit for the hyperpolarizability is far from obvious. To make this clear, we have calculated the (hyper)polarizability with the HA1, HA2, and HA3 basis sets. HA1 gives $\bar{\alpha} = 102.86$ and $\Delta\alpha = 43.21e^2a_0^2E_h^{-1}$, $\bar{\gamma} = 182 \times 10^3e^4a_0^4E_h^{-3}$. In comparison HA3, which is of the same size but more diffuse than HA1, gives $\bar{\alpha} = 102.87$ and $\Delta\alpha = 43.64e^2a_0^2E_h^{-1}$, $\bar{\gamma} = 232 \times 10^3e^4a_0^4E_h^{-3}$. Agreement with the SCF/PA and KoTa hyperpolarizability values is significantly better for HA3. We add here a few remarks about the effect of g-GTF on the SCF values of the dipole (hyper)polarizability. Adding one g-GTF on HA1, we obtain the basis HA2 $\equiv$ [9s8p7d3f1g], which yields SCF values of $\bar{\alpha} = 102.94$ and $\Delta\alpha = 43.26e^2a_0^2E_h^{-1}$, $\bar{\gamma} = (188 \times 10^3)e^4a_0^4E_h^{-3}$. Thus, the addition of the g-GTF results in an increase of the HA1 values by 0.08, 0.12, and 3% for $\bar{\alpha}$, $\Delta\alpha$, and $\bar{\gamma}$, respectively.

We have obtained CCSD(T) results with the A1, A3, and A4 basis sets. The 18 innermost MOs were kept frozen in the post-Hartree−Fock treatments. The electron correlation effect on the dipole polarizability is quite strong. One immediately remarks that the MP methods predict a negative effect for the longitudinal component α_{zz}. The correction is positive for the CC methods. Overall, the total correction ECC is negative for the mean and largely positive for the anisotropy. This is caused by the strong reduction of the transversal component α_{xx}. Our A4/CCSD(T) results predict ECC corrections of −9.09 and $23.17e^2a_0^2E_h^{-1}$ for $\bar{\alpha}$ and $\Delta\alpha$, respectively. Very similar results are obtained with A1 and A3: −9.20 and 23.91 (A1), −9.48 and 23.75 (A3). The effect of electron correlation correction on the components of $\gamma_{\alpha\beta\gamma\delta}$ is quite impressive. The performance of MP and CC methods is markedly different for the hyperpolarizability. The MP2 values reveal a very strongly negative second-order correction for all Cartesian components. What is more, MP4 predicts negative values for all γ_{zzzz}, γ_{xxxx}, and γ_{xxzz}. In contradistinction to the MP predictions, both CCSD and CCSD(T) predict positive values for all Cartesian components of the hyperpolarizability. Our best results for the ECC ($10^{-3}\gamma_{\alpha\beta\gamma\delta}/e^4a_0^4E_h^{-3}$) are −261, −97, and −47 for γ_{zzzz}, γ_{xxxx}, and γ_{xxzz}, respectively. The effect on the longitudinal component is obviously enormous. This drastic change of the relative magnitude components is reflected in the ECC of the invariants: −141 ($\bar{\gamma}$), −537 ($\Delta_1\gamma$), and −74 ($\Delta_2\gamma$). Overall, it is interesting to notice the stability of the CCSD(T) values of the mean hyperpolarizability, $10^{-3}\gamma_{\alpha\beta\gamma\delta}/e^4a_0^4E_h^{-3} = 88$ (A1), 87 (A3), and 86 (A4). We have also performed post-Hartree−Fock calculations with an increased number of correlated electrons, keeping only the 10 innermost MP frozen. These improved A1 results, obtained at a considerable increase of the computational cost, are also listed in Table 1. The CCSD(T)/A1 values (calculated with only the 10 innermost MOs frozen) for the dipole polarizability are $\bar{\alpha} = 93.94$ and $\Delta\alpha = 67.76e^2a_0^2E_h^{-1}$, a change appreciably less than 1%. The mean hyperpolarizability is $\bar{\gamma} = (96 \times 10^3)e^4a_0^4E_h^{-3}$. The improvement is $(8 \times 10^3)e^4a_0^4E_h^{-3}$, rather small compared to the SCF/A1 value of $(225 \times 10^3)e^4a_0^4E_h^{-3}$. Thus, the improved values do not modify significantly the previous picture.[55] Last, we have performed MP2 calculations (18 innermost MO frozen) with HA1 $\equiv$ [9s8p7d3f] and HA2 $\equiv$ [9s8p7d3f1g] in order to test

TABLE 1: Electric (Hyper)polarizability[a] for Cu_2 at the Experimental Bond Length 2.2197 Å[b]

basis set	method[c]	α_{zz}	α_{xx}	$\bar{\alpha}$	$\Delta\alpha$	γ_{zzzz}	γ_{xxxx}	γ_{xxzz}	$\bar{\gamma}$	$\Delta_1\gamma$	$\Delta_2\gamma$
A1 ≡ [7s6p5d1f][c]	SCF	131.87	87.87	102.53	44.00	281	196	81	225	303	−10
	MP2	115.95	63.18	80.77	52.76	19	60	20	52	−123	−42
	MP4	119.21	53.86	75.64	65.35	−153	−8	−13	−45	−468	−81
	CCSD	135.18	72.17	93.17	63.01	58	111	41	104	−146	−78
	CCSD(T)	138.61	70.70	93.34	67.91	20	103	36	88	−242	−95
	ECC	**6.74**	**−17.17**	**−9.20**	**23.91**	**−261**	**−93**	**−45**	**−138**	**−545**	**−85**
A1 ≡ [7s6p5d1f][d]	SCF	131.87	87.87	102.53	44.00	281	196	81	225	303	−10
	MP2	115.41	62.15	79.90	53.26	9	56	18	46	−141	−43
	MP4	112.43	47.66	69.25	64.77	−215	−44	−28	−89	−552	−93
	CCSD	135.44	73.01	93.82	62.43	68	114	43	109	−121	−78
	CCSD(T)	139.12	71.35	93.94	67.76	32	108	40	96	−215	−98
	ECC	**7.25**	**−16.52**	**−8.59**	**23.77**	**−249**	**−88**	**−41**	**−130**	**−519**	**−88**
A3 ≡ [7s6p6d1f][c]	SCF	132.53	88.32	103.06	44.21	284	197	82	228	310	−11
	MP2	116.27	63.25	80.92	53.02	17	59	20	50	−126	−43
	MP4	119.15	53.67	75.49	65.48	−159	−14	−16	−52	−469	−78
	CCSD	135.54	72.45	93.48	63.09	59	109	42	104	−135	−83
	CCSD(T)	138.88	70.92	93.57	67.96	20	101	37	87	−234	−100
	ECC	**6.35**	**−17.40**	**−9.48**	**23.75**	**−264**	**−96**	**−45**	**−140**	**−544**	**−89**
A4 ≡ [7s6p6d2f][c]	SCF	132.19	88.26	102.90	43.92	279	197	83	227	297	−20
	MP2	116.02	63.86	81.25	52.16	14	51	18	45	−109	−44
	MP4	119.22	54.42	76.02	64.81	−169	−24	−20	−62	−471	−74
	CCSD	135.10	72.83	93.59	62.27	56	109	40	101	−147	−77
	CCSD(T)	138.54	71.45	93.82	67.09	18	101	35	86	−241	−94
	ECC	**6.36**	**−16.81**	**−9.09**	**23.17**	**−261**	**−97**	**−47**	**−141**	**−537**	**−74**
A6 ≡ [8s7p7d1f]	SCF	132.55	88.54	103.21	44.01	283	215	86	240	247	−18
A7 ≡ [8s7p7d5f]	SCF	130.72	88.47	102.55	42.26	307	210	88	244	344	−13
KoTa ≡ (21s14p11d5f)	SCF	130.44	88.49	102.48	41.94	311	197	86	236	405	−10
PA ≡ (23s16p12d6f)	SCF	130.47	88.58	102.54	41.89	309	209	87	244	353	−6

[a] The invariants are defined as follows. Dipole polarizability: mean, $\bar{\alpha} = (\alpha_{zz} + 2\alpha_{xx})/3$; anisotropy, $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$. Hyperpolarizability: mean, $\bar{\gamma} = (3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz})/15$; anisotropies, $\Delta_1\gamma = 3\gamma_{zzzz} - 4\gamma_{xxxx} + 3\gamma_{xxzz}$ and $\Delta_2\gamma = \gamma_{zzzz} + \gamma_{xxxx} - 6\gamma_{xxzz}$. The total electron correlation correction is defined as ECC ≡ CCSD(T)-SCF. [b] Hyperpolarizability values are given as $10^{-3}\gamma_{\alpha\beta\gamma\delta}$. All values are in atomic units. Conversion factors to SI units are as follows: length, $1a_0 = 0.529177249 \times 10^{-10}$ m; dipole polarizability, $1e^2a_0^2E_h^{-1} = 1.648778 \times 10^{-41}$ C^2 m^2 J^{-1}; hyperpolarizability, $1e^4a_0^4E_h^{-3} = 6.235378 \times 10^{-65}$ C^4 m^4 J^{-3}. [c] The 18 innermost MOs were kept frozen in the post-Hartree−Fock calculations. [d] The 10 innermost MOs were kept frozen in the post-Hartree−Fock calculations.

TABLE 2: Bond-Length-Dependence ($\Delta R \equiv (R - R_e)/a_0$) of the Electric (Hyper)polarizability of Cu_2 Calculated with the Basis Set A1 ≡ [7s6p5d1f] at the CCSD(T) Level of Theory[a]

P	method	−0.6	−0.4	−0.2	0	0.2	0.4	0.6
$\bar{\alpha}$	SCF	91.03	94.37	98.20	102.53	107.34	112.65	118.44
	MP2	67.94	71.91	76.18	80.77	85.68	90.89	96.42
	MP4	60.80	65.51	70.46	75.64	81.07	86.70	92.59
	CCSD	79.04	83.34	88.05	93.17	98.69	104.57	110.8
	CCSD(T)	78.24	82.88	87.91	93.34	99.14	105.28	111.72
	ECC	**−12.78**	**−11.49**	**−10.30**	**−9.20**	**−8.20**	**−7.37**	**−6.72**
$\Delta\alpha$	SCF	27.57	32.35	37.83	44.00	50.94	58.70	67.30
	MP2	34.00	39.41	45.68	52.76	60.67	69.42	78.93
	MP4	42.41	48.99	56.66	65.35	74.97	85.53	96.84
	CCSD	40.03	46.75	54.43	63.01	72.47	82.78	93.75
	CCSD(T)	42.70	50.06	58.49	67.91	78.26	89.50	101.35
	ECC	**15.14**	**17.71**	**20.66**	**23.91**	**27.32**	**30.80**	**34.05**
$\bar{\gamma}$	SCF	178	193	212	225	243	262	282
	MP2	34	40	50	52	53	62	67
	MP4	−43	−37	−40	−45	−57	−57	−70
	CCSD	89	92	102	104	91	103	93
	CCSD(T)	80	81	89	88	70	78	61
	ECC	**−99**	**−112**	**−123**	**−138**	**−173**	**−184**	**−222**

[a] The 18 innermost MOs were kept frozen. Hyperpolarizability values are given as $10^{-3} \times \gamma_{\alpha\beta\gamma\delta}$.

the effect of the g-GTF on the correlated values. The MP2/HA2 values (HA1 results in parentheses) are $\bar{\alpha} = 74.66$ (74.61) and $\Delta\alpha = 53.60$ (53.50)$e^2a_0^2E_h^{-1}$, $10^{-3}\gamma = 4$ (8)$e^4a_0^4E_h^{-3}$. The effect, considered in conjunction with the SCF values presented above, is small.

We show in Table 2 SCF, MP, and CC values calculated with the A1 basis set for displacements $(R - R_e)/a_0 \equiv \Delta R/a_0 = 0, \pm 0.2, \pm 0.4$, and ± 0.6. The results show clearly the bond-length-dependence of the ECC. The dipole polarizability displays a regular R-dependence, easily represented as

$$[\bar{\alpha}(R) - \bar{\alpha}(R_e)]/e^2a_0^2E_h^{-1} = 28.09(R - R_e) + 4.69(R - R_e)^2 - 0.52(R - R_e)^3 - 0.36(R - R_e)^4$$

$$[\Delta\alpha(R) - \Delta\alpha(R_e)]/e^2a_0^2E_h^{-1} = 49.58(R - R_e) + 11.92(R - R_e)^2 - 1.94(R - R_e)^3 - 1.32(R - R_e)^4 \quad (1)$$

The R-dependence of the components of $\gamma_{\alpha\beta\gamma\delta}$ is quite dissimilar. In Figure 1 we have plotted the R-dependence of the SCF, MP2, MP4, CCSD, and CCSD(T) values of the longitudinal component γ_{zzzz}. The SCF depends almost linearly on R. The MP4 values are consistently negative, their magnitude

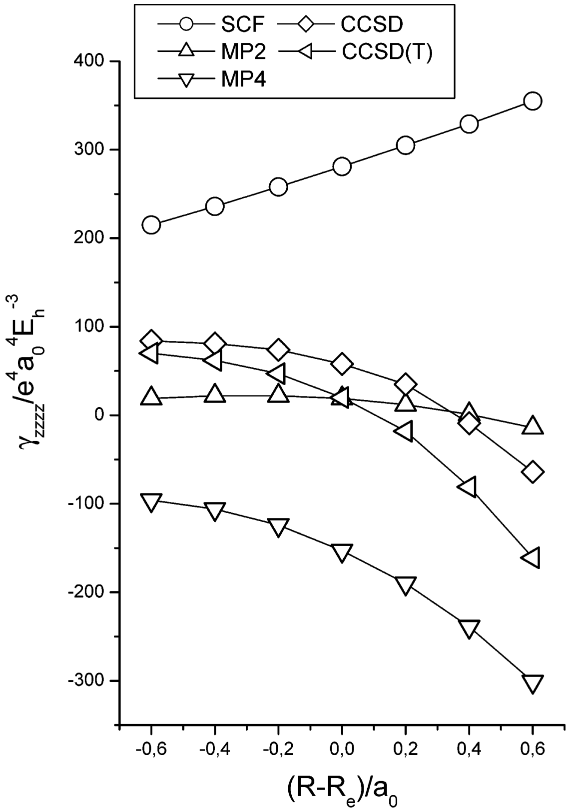

Figure 1. *R*-dependence of the axial component of the hyperpolarizability of Cu_2.

TABLE 3: B3LYP Density Functional Theory Calculations of the (Hyper)polarizability[a] of Cu_2 at $R_e = 2.2197$ Å

property	[7s6p6d]	[7s6p6d1f]	[7s6p6d4f]	[8s7p7d1f]	[8s7p7d5f]
α_{zz}	107.50	107.50	107.35	107.60	107.44
α_{xx}	60.97	61.40	62.43	61.74	62.71
$\bar{\alpha}$	76.48	76.77	77.40	77.03	77.62
$\Delta\alpha$	46.53	46.10	44.92	45.85	44.73
γ_{zzzz}	107.6	111.4	118.4	113.8	120.5
γ_{xxxx}	68.1	85.3	80.4	80.8	78.9
γ_{xxzz}	36.6	35.7	36.0	35.2	37.1
$\bar{\gamma}$	87.1	96.4	95.4	94.0	95.9
$\Delta_1\gamma$	160.0	100.2	141.7	123.9	157.1
$\Delta_2\gamma$	−44.0	−17.5	−17.3	−16.7	−23.2

[a] Hyperpolarizability values are given as $10^{-3}\gamma_{\alpha\beta\gamma\delta}$.

increasing monotonically with *R*. The CCSD and CCSD(T) are fairly similar, predicting $\gamma_{zzzz} > 0$ up to R_e but turning negative for large positive ΔR displacements. Overall, the mean $\bar{\gamma}$ is positive for $-0.6 < \Delta R/a_0 < 0.6$ for both CCSD and CCSD(T) but negative for MP4. At this stage, we have used experimental spectroscopic constants[51] and a well-tested scheme[56−58] to calculate the zero-point vibrational correction (ZPVC). Using property derivatives estimated from the contents of Table 2, we obtained 0.27 and $0.51e^2a_0^2E_h^{-1}$ for $\bar{\alpha}$ and $\Delta\alpha$, respectively. The ZPVC for $\bar{\gamma}$ is $<(-1 \times 10^3)e^4a_0^4E_h^{-3}$.

In Table 3 we give B3LYP (hyper)polarizabilities for a sequence of basis sets. This DFT method predicts a mean dipole polarizability significantly lower than those of both SCF and CCSD(T). It is rather remarkable that the B3LYP anisotropy is fairly close to the SCF prediction. The gap is wider for the hyperpolarizability where the B3LYP values of γ_{zzzz} are considerably larger than the CCSD(T) results obtained with the basis sets A1, A3, and A4.

We present in Table 4 recent results on the dipole polarizability of Cu_2 and our findings. Interestingly enough, all DFT predictions of $\bar{\alpha}$, including present values, are in fair agreement. Our $\Delta\alpha$ values are systematically higher than that reported by Calaminici et al.[27] Our SCF values agree quite well with the analogous results of Saue and Jensen[59] obtained with a large basis set.

TABLE 4: Theoretical Prediction of the (Hyper)polarizability[a] of Cu_2

method	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\gamma}$	ref
DFT	78.50	39.62		27
DFT	77.574			28
DFT	76.58			29
SCF	101.9	42.3		59
DFT	77.62	44.73	95.9	*b*
SCF	102.54	41.89	244	*c*
CCSD(T)	93.82	67.09	86	*d*

[a] Hyperpolarizability values are given as $10^{-3}\gamma_{\alpha\beta\gamma\delta}$. [b] Present investigation, basis set [8s7p7d5f]. [c] Present investigation, basis set (23s16p12d6f). [d] Present investigation, basis set [7s6p6d2f].

In conclusion, we have shown that the theoretical prediction of the static hyperpolarizability of the copper dimer represents a rather formidable task. The hyperpolarizability shows very strong basis set dependence. The electron correlation effects on the components of $\gamma_{\alpha\beta\gamma\delta}$ are unusually large, but the value of $\bar{\gamma}$ at R_e is unambiguously positive. In addition to the extensive study of basis set effects on SCF, post-Hartree−Fock, and B3LYP-DFT calculations, we have also examined the dependence of the calculated property values on the number of correlated electrons or the size of the frozen core. We have not considered the calculation of relativistic effects, as this is beyond the scope of the present investigation. It is worth mentioning that recent four-component Dirac−Coulomb Hartree−Fock calculations[59] show that the relativistic correction lowers the mean dipole polarizability by ≈6%. The B3LYP values differ from those obtained with conventional ab initio methods, but a more detailed investigation is needed in order to reach a valid conclusion for a wider class of DFT approaches. Such investigations have previously been reported; see, for instance, the model study on polyacetylene chains.[60] The extension of theoretical predictions to larger copper clusters demands the definition of very efficient computational strategies, as even for Cu_2 it is very difficult to obtain relatively small or medium-sized basis sets with a good peformance in hyperpolarizability calculations. Work toward this direction is in progress in our laboratory.

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(54) We mention also for the record the SCF/PA value for the energy of the free molecule at R_e: $E^\circ = -3277.93980757E_h$.

(55) This is further corroborated by a MP2/A4 calculation (10 MO frozen) which gave $\bar{\alpha} = 80.38$ and $\Delta\alpha = 52.66e^2a_0^2E_h^{-1}$, $\bar{\gamma} = (40 \times 10^3)e^4a_0^4E_h^{-3}$, quite close to the MP2/A4 (18 MO frozen) values listed in Table 1.

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