Frequency-dependent hyperpolarizabilities of the Ne, Ar, and Kr atoms using the approximate coupled cluster triples model CC3

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The frequency-dependent electric field-induced second harmonic generation (ESHG) second hyperpolarizabilities γ of neon, argon, and krypton are calculated using the approximate coupled cluster triples model CC3. Systematic basis set investigations are carried out to establish basis set limits, and scalar relativistic effects are accounted for by direct perturbation theory. To estimate higher-order correlation effects, full configuration-interaction results are used to benchmark the accuracy of CC3. The best theoretical estimates obtained thereby for the static second hyperpolarizabilities γ_0 are 107.4, 1159, and 2589 a.u. for neon, argon, and krypton, respectively. These values as well as the results for the dispersion curve of the parallel component $\gamma_\parallel$ agree well with the latest experimental values from electric field-induced second harmonic generation. In addition, the dispersion of the perpendicular component $\gamma_\perp$ and the hyperpolarizability ratios $\gamma_\parallel/\gamma_\perp$ has been studied for the first time on a consistently correlated *ab initio* level. The analysis of the results indicates that, in particular for neon and krypton, the presently available experimental values are flawed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2008211]

I. INTRODUCTION

Nonlinear optical properties are important for developments in many new areas of technology, as, for example, in the design of new optical materials such as optical switches.[1] Theoretical investigations of these properties play an essential role in this research, as they not only aid the understanding of the complicated process, but also—in particular, for small molecules—can be used to calibrate or check the calibration of the experiments. Indeed, absolute measurements of these properties are rarely feasible,[2] and results are normalized to reference samples—ultimately to helium, for which highly accurate calculations from explicitly correlated configuration-interaction exist.[3,4]

When calculated, nonlinear optical properties may be expressed in terms of response functions. The evaluation of response functions has gone through a rapid development during the last decades.[5–10] In particular, after the Lagrangian technique[5,11] was introduced, the evaluation of response functions for arbitrary wave-function models became straightforward. Today, linear and nonlinear response functions up to cubic order have been derived and implemented for most standard wave-function models.

The coupled cluster (CC) methods have been used very successfully to calculate accurate molecular properties. In particular, the coupled cluster singles and doubles (CCSD) model with the perturbative treatment of triple excitations [CCSD(T)] (Ref. 12) has become a very accurate tool for the calculation of static molecular properties. Indeed, CCSD(T) calculations often yield an accuracy that is similar to or even surpasses the one obtained experimentally.[13–15]

The effect of connected triples is even more important to obtain frequency-dependent molecular properties of high quality. Due to its perturbative nature, the CCSD(T) model can only be used to determine static molecular properties.[5,16,17] To calculate frequency-dependent molecular properties with a comparable accuracy, we may use the iterative approximate triples model CC3. CC3 is a member of the coupled cluster hierarchy CCS, CC2, CCSD, CC3, CCSDT, etc., which is designed to give a systematically improved description of molecular response properties for a single configuration-dominated system. In CCS all single excitations out of a reference configuration are treated, in CCSD (Ref. 18) all doubles are added, and in CCSDT all triples are also included. CC2 (Ref. 19) and CC3 (Ref. 17) are approximations to CCSD and CCSDT where the doubles and the triples, respectively, are treated in an approximate fashion, and the scaling of the computational costs (compared to CCSD and CCSDT) is reduced by one order.

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In this paper we use CC3 to calculate the electric field-induced second harmonic generation (ESHG) hyperpolarizabilities of neon, argon, and krypton. We consider both the isotropic parallel $\gamma_{\parallel}(-2\omega;\omega,\omega,0)$ and perpendicular $\gamma_{\perp}(-2\omega;\omega,\omega,0)$ hyperpolarizability components. Of all nonlinear optical experiments in the gas phase, ESHG experiments yield the highest accuracy, as, in particular for centrosymmetric molecules, the temperature and pressure dependences are negligibly small.[2] Additionally, for atoms the vibrational component of the hyperpolarizability vanishes, so comparison of the calculated and experimental results becomes straightforward and thus ideal for benchmark studies.

Calculations for the series of models CCS, CC2, CCSD, and CC3 were performed to establish the convergence pattern of the coupled cluster hierarchy. Furthermore, we compare with full configuration-interaction (FCI) results to account for correlation effects beyond connected triples. Finally, scalar relativistic effects on $\gamma_{\parallel}$ and $\gamma_{\perp}$ are accounted for by means of direct perturbation theory (DPT). Comparison is then made between the calculated hyperpolarizabilities and experimental ESHG hyperpolarizabilities[20–25] for both the isotropic averaged parallel and perpendicular components.

The static hyperpolarizabilities γ_0 of the noble gas atoms have been calculated previously with different coupled cluster models. For neon, Pawłowski *et al.*[26] reported 107.77 a.u. using CC3/t-aug-cc-pV6Z. Soldán *et al.*[27] obtained 106.5 a.u. for neon and 1186.6 a.u. for argon with CCSD(T)/t-aug-cc-pV6Z, and 2690 a.u. for krypton with CCSD(T)/t-aug-cc-pV5Z. Using the CCSD model Hättig and Jørgensen[28] reported a static hyperpolarizability of 110.2 a.u. for neon and 1179.0 a.u. for argon in the q-aug-cc-pV5Z basis sets. Relativistic effects for static hyperpolarizabilities have been calculated before by Nakajima and Hirao[29] for the noble gases neon through radon at the CCSD(T) level using the third-order Douglas-Kroll method. They reported relativistic corrections of +0.6 a.u. (neon), +9 a.u. (argon), and +28 a.u. (krypton). Likewise, Klopper *et al.*[30] have for neon reported a relativistic correction of +0.6 a.u. obtained at the CCSD(T)/q-aug-cc-pCV6Z level.

As already stated, the hyperpolarizability of helium is known very accurately from explicitly correlated configuration-interaction (CI) calculations,[3,4] and will therefore not be considered in the present study.

Coupled cluster calculations for frequency-dependent hyperpolarizabilities of noble gases have been reported in Ref. 26 for $\gamma_{\parallel}$ of neon at the CC3 level and earlier in Ref. 28 for $\gamma_{\parallel}$ of neon and argon at the CCSD level. We will extend these studies to include coupled cluster calculations on krypton. Furthermore, we will consider relativistic effects and higher-order correlation effects on the frequency-dependent hyperpolarizabilities.

The dispersion of the perpendicular component $\gamma_{\perp}$ and the ratios $\gamma_{\parallel}/\gamma_{\perp}$ has not yet been calculated for any of these noble gases at a truly correlated level. This is related to the fact that the calculation of $\gamma_{\perp}$ is only of interest for nonzero frequencies, since for atoms in the static limit, $\gamma_{\parallel}/\gamma_{\perp}=3$.

II. COMPUTATIONAL DETAILS

In this paper, we report calculations of the ESHG second hyperpolarizability tensors of the atoms neon, argon, and krypton. The quantity measured in most ESHG experiments is the isotropic hyperpolarizability, which, if all applied fields are parallel, is given by[2]

$$\gamma_{\parallel}(-2\omega;\omega,\omega,0)=\frac{1}{15}\sum_{\xi\eta}(\gamma_{\xi\xi\eta\eta}+\gamma_{\xi\eta\eta\xi}+\gamma_{\xi\eta\xi\eta}),$$

$$\xi,\eta=x,y,z, \tag{1}$$

where ω is the frequency of the incident laser light. Some experiments[20,21,23] also measure the perpendicular isotropic tensor component, which is the measured quantity if the optical field is polarized perpendicular to the static field

$$\gamma_{\perp}(-2\omega;\omega,\omega,0)=\frac{1}{15}\sum_{\xi\eta}(2\gamma_{\xi\eta\eta\xi}-\gamma_{\xi\xi\eta\eta}),$$

$$\xi,\eta=x,y,z. \tag{2}$$

For atoms, Eqs. (1) and (2) reduce to

$$\gamma_{\parallel}=\gamma_{zzzz}, \tag{3}$$

$$\gamma_{\perp}=\gamma_{zxxz}, \tag{4}$$

and in the static limit we have

$$\gamma_{zzzz}=3\gamma_{zzxx}=3\gamma_{zxxz}=3\gamma_{zxzx}. \tag{5}$$

An interesting quantity is the ratio $\gamma_{\parallel}/\gamma_{\perp}$, which may be expressed in terms of a polynomial in ω^2 as[31]

$$\gamma_{\parallel}(\omega)/\gamma_{\perp}(\omega)=3[1+A\omega^2+B\omega^4+\cdots]. \tag{6}$$

Its deviation from 3 is solely determined by the different dispersions of the two isotropic hyperpolarizability components, i.e., the deviation from Kleinmann symmetry.[20,21]

The static and frequency-dependent parallel and perpendicular components of the hyperpolarizability have been calculated for the coupled cluster model hierarchy CCS, CC2, CCSD, and CC3 and for FCI. We have considered the three frequencies 0.042 823 a.u. (1064.0 nm), 0.088 559 a.u. (514.5 nm), and 0.093 368 a.u. (488.0 nm). The coupled cluster calculations have been carried out with the DALTON program.[32] The implementation of the cubic response functions for the CCS, CC2, and CCSD models is described in Refs. 7 and 33, while the CC3 implementation has recently been done by Pawłowski,[34] and will appear in the next release of the DALTON program. The FCI calculations have been performed with the LUCIA program.[35]

Dunning's correlation consistent basis sets[36–38] augmented with diffuse functions[39,40] are used throughout. We employed the basis sets *n*-aug-cc-pV*X*Z with the double, triple, and quadruple augmentation levels, n=d, t, q, and cardinal numbers X=D, T, Q, 5, 6.

All electrons were correlated for neon and argon, while in the calculations on krypton, a frozen-core approximation was employed, with the $1s^22s^22p^63s^23p^6$ orbital occupation

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TABLE I. Neon. Deviation (in a.u.) of the ESHG hyperpolarizabilities $\gamma_{\parallel}$ and $\gamma_{\perp}$ in the coupled cluster models from the FCI hyperpolarizability ($\gamma^{\mathrm{FCI}}-\gamma^{\mathrm{CC}}$), using the d-aug-cc-pVDZ basis ($1s^2$ frozen core).

	$\gamma_{\parallel}$					$\gamma_{\perp}$				
ω	CCS	CC2	CCSD	CC3	FCI	CCS	CC2	CCSD	CC3	FCI
0.0	+21.90	-21.20	-4.97	-0.17	78.97	+7.30	-7.07	-1.66	-0.059	26.32
0.042 823	+22.97	-22.18	-5.17	-0.19	81.43	+7.66	-7.39	-1.72	-0.064	27.15
0.088 559	+26.98	-25.89	-5.92	-0.26	90.37	+8.96	-8.62	-1.96	-0.089	30.11
0.093 368	+27.66	-26.44	-5.99	-0.22	91.80	+9.18	-8.80	-1.99	-0.077	30.58

kept fixed. In the FCI calculations, however, only the eight valence electrons were correlated for neon, argon, and krypton.

Relativistic corrections using the scalar relativistic approximation have been calculated using DPT as implemented by Klopper *et al.*[30] The corrections are obtained by adding the relativistic perturbations to the nonrelativistic Hamiltonian and using the central difference formula to determine the relativistic correction Q' to property Q

$$Q' = \frac{Q(\lambda) - Q(-\lambda)}{2\lambda}. \tag{7}$$

We have used the perturbation strength parameter $\lambda=0.1$ for neon and argon, and $\lambda=0.05$ for krypton. Picture-change effects are accounted for in this approach.[30]

For the relativistic corrections we have used the augmented correlation consistent core-valence basis sets t-aug-cc-pCVTZ and t-aug-cc-pCVQZ.[36,41] However, it is not optimal to use these core-valence basis sets since the (contracted) inner-core orbitals might not be flexible enough to respond properly to the (finite) scalar relativistic perturbation. To examine the deficiencies of using core-valence basis sets we have constructed basis sets of uncontracted basis functions for neon, argon, and krypton in the following manner: we started out with the uncontracted TZV basis sets.[42] Functions of higher angular momenta were added with exponents β_b according to the formula[43]

$$\beta_b = \beta_a \frac{2l_b+3}{2l_a+3}, \tag{8}$$

where β and l are the orbital exponents and angular quantum numbers ($l_a=1$ for neon and argon and $l_a=2$ for krypton). The basis sets were then augmented by adding diffuse functions, giving the basis sets $14s9p7d6f5g$, $17s12p10d9f8g$, and $20s16p10d9f8g7h$ for neon, argon, and krypton, respectively. For computational reasons the largest exponents of highest angular momentum were removed for argon and krypton, giving the final basis sets $14s9p7d6f5g$, $17s12p10d5f5g$, and $20s16p10d5f5g5h$. Removing these functions had very little effect on the values of the hyperpolarizabilities.

III. RESULTS

A. Neon

In a recent paper[26] we calculated $\gamma_{\parallel}$ for neon using the t-aug-cc-pV6Z basis. A basis set investigation showed that the CC3 basis set limit result for $\gamma_{\parallel}(0)$ was about 0.8 a.u. below the CC3/t-aug-cc-pV6Z result. Relativistic effects added 0.6 a.u. to $\gamma_{\parallel}(0)$ and the correlation contribution beyond CC3 was estimated to be negligible, since a FCI calculation in the aug-cc-pVDZ basis deviated less than 0.2% from the CC3 result in the same basis.[44] Due to a cancellation of the relativistic and the basis set contributions beyond t-aug-cc-pV6Z, the CC3/t-aug-cc-pV6Z results for $\gamma_{\parallel}(-2\omega;\omega,\omega,0)$ were estimated to have an uncertainty of about 0.4 a.u. and thus to be significantly more accurate than the latest experimental results for this quantity.

In the present communication we extend the benchmarking of CC3 against FCI. This was necessary, as the calculations in the aug-cc-pVDZ basis yielded only about 26% of γ_0. The new FCI benchmark was obtained in a d-aug-cc-pVDZ basis where about 73% of γ_0 is recovered. In addition, the dispersion curve for both $\gamma_{\parallel}$ and $\gamma_{\perp}$ has been studied at the FCI level and compared to CC3. In Sec. III A 2, we present CC3/t-aug-cc-pV5Z results for $\gamma_{\parallel}$ and $\gamma_{\perp}$ and critically assess the accuracy of the experimental results for these quantities.

1. Convergence of $\gamma_{\parallel}$ and $\gamma_{\perp}$ in N-electron space

In Table I we report the FCI limit of the second hyperpolarizabilities in the d-aug-cc-pVDZ basis, and the deviations of the CCS, CC2, CCSD, and CC3 models. Comparison with Table II confirms that indeed a reasonable portion of γ is recovered in the d-aug-cc-pVDZ basis set. It should be noted that only the valence electrons were correlated in these calculations, the $1s^2$ core was kept frozen. A CC3 calculation in the same basis but with all electrons correlated showed that the core contribution to γ_0 is only 0.4%.

Inspecting the numbers in Table I, one finds that the CCS and CC2 models are not reliable enough for any quantitative assertion. Both models are off by about 30%—CCS underestimates the hyperpolarizability and CC2 overestimates it. The CCSD model, on the other hand, gives a good description of the hyperpolarizability with a deviation of only about 7%. With the CC3 model, clearly convergence in *N*-electron space is approached, with deviations from FCI of less than 0.3% all along the dispersion curve.

In Fig. 1 we have combined the results from Table I to obtain the hyperpolarizability ratio $\gamma_{\parallel}(\omega)/\gamma_{\perp}(\omega)$. For the frequency range considered, the hyperpolarizability ratio curve is well approximated with the terms of Eq. (6) that are linear and quadratic in ω^2. The CC3 curve is very close to the FCI result, emphasizing again that the CC3 model is approaching convergence in *N*-electron space.

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TABLE II. Neon. The ESHG hyperpolarizabilities $\gamma_{\parallel}$ and $\gamma_{\perp}$ (in a.u.) at frequency ω using the t-aug-cc-pV5Z basis.

	$\gamma_{\parallel}$					$\gamma_{\perp}$			
ω	CCS	CC2	CCSD	CC3	Expt.[a]	CCS	CC2	CCSD	CC3
0.0	78.2	134.7	109.3	108.0	108±2	26.07	44.89	36.43	35.99
0.042 823	80.1	139.1	112.6	111.3	109.9±0.5	26.70	46.39	37.54	37.08
0.088 559	87.0	155.3	124.6	123.2	122.2±0.4	28.93	51.88	41.53	41.06
0.093 368	88.0	157.8	126.5	125.1	123.5±0.5	29.26	52.73	42.14	41.67

[a]From Refs. 24 and 25.

2. High accuracy $\gamma_{\perp}$ calculations and comparison with experiment

Table II shows the parallel and perpendicular ESHG hyperpolarizabilities of neon calculated using the t-aug-cc-pV5Z basis. Experimental values are included for the parallel hyperpolarizabilities. The t-aug-cc-pV5Z basis was used because it gives hyperpolarizabilities that are only slightly above the t-aug-cc-pV6Z ones [0.2 a.u. for the CC3 static $\gamma_{\parallel}$ (Ref. 26)] and significantly reduces the computational time. Comparing the results in Tables I and II we note that the CC3 and CCSD results differ by about 6% in the d-aug-cc-pVDZ basis while this difference is reduced to about 1% in the t-aug-cc-pV5Z basis.

From the results in Ref. 26, the CC3/t-aug-cc-pV5Z static hyperpolarizability may be estimated to be about 0.97 a.u. above the CC3 basis set limit value. Relativistic effects at the CC3/t-aug-cc-pVQZ level add 0.58 a.u. to the hyperpolarizability, while the correlation contribution beyond CC3 may be estimated to −0.17 a.u. based on the FCI results in the d-aug-cc-pVDZ basis (Table I). Combining these numbers shows that the nonrelativistic CC3/t-aug-cc-pV5Z result is about 0.6 a.u. above the estimated relativistic FCI basis set limit. A similar analysis for the frequency-dependent hyperpolarizabilities shows that these values have about the same accuracy. The CC3/t-aug-cc-pV5Z results should therefore reproduce the experimental results with an uncertainty of about 0.5%.

In Fig. 2 we have plotted the hyperpolarizability ratio $\gamma_{\parallel}(\omega)/\gamma_{\perp}(\omega)$ based on the results from Table II. The CCS model overestimates, while the CC2 model underestimates the ratio. The CCSD and CC3 ratios are very close to each other. To a good approximation, the ratio $\gamma_{\parallel}/\gamma_{\perp}$ is linear in ω^2 in Fig. 2, as proposed by Shelton and Rice.[2] It is interesting to note the strong basis set dependence of the functional form of the hyperpolarizability ratios. In the t-aug-cc-pV5Z basis (Fig. 2) the linear term dominates, while in the d-aug-cc-pVDZ basis (Fig. 1) both the linear and the quadratic terms give significant contributions.

We have included in Fig. 2 the experimental values from Refs. 20 and 23. There are various discrepancies between the

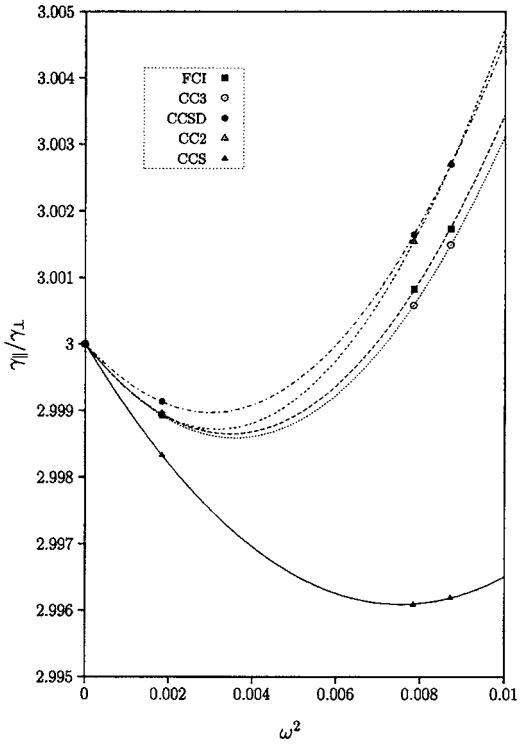


FIG. 1. $\gamma_{\parallel}/\gamma_{\perp}$ for neon with various wave-function approximations. Basis: d-aug-cc-pVDZ.

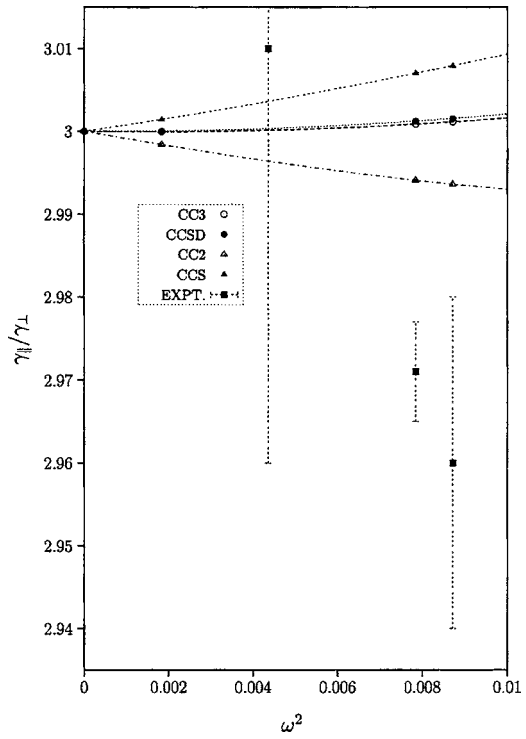


FIG. 2. $\gamma_{\parallel}/\gamma_{\perp}$ for neon with various wave-function approximations. Basis: t-aug-cc-pV5Z. Note the different scales of the abscissae in Figs. 1 and 2.

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TABLE III. Argon. Convergence of the CCSD static second hyperpolarizability $\gamma_\parallel$ (in a.u.) in the *n*-aug-cc-pV*X*Z basis set family.

Cardinal number	Augmentation level *n*			t-aug-cc-pCV*X*Z
	d	t	q	
DZ	992.50	977.41	978.13	967.95
TZ	1097.2	1224.2	1231.3	1193.07
QZ	1112.5	1181.2	1188.2	1154.12
5Z	1151.9	1169.4	1169.6	
6Z	1151.4	1157.2	1157.1	

TABLE IV. Argon. Basis set convergence (SCF and CC3) of the static second hyperpolarizability (in a.u.) in the t-aug-cc-pV*X*Z basis set family.

Cardinal number	SCF	Correlation contribution	
		CC3	Extrapolated
DZ	704.1	255.3	···
TZ	941.3	276.4	285.3(DT)
QZ	947.3	230.2	196.5(TQ)
5Z	959.0	213.4	195.8(Q5)
6Z	960.7	204.5	192.3 (56)

experimental results and the present calculations. The error bar of the older experiment (ω^2=0.004 356 a.u.) from Bigio and Ward[20] is too large for a meaningful comparison with the calculations, but also the values from Shelton and Lu[23] (ω^2 =0.007 842 5 and 0.008 717 6 a.u.) disagree strongly with the present results. As seen from Table II there is a very good agreement between the experiment and the CC3 results for $\gamma_\parallel(\omega)$. Since there is no reason why the calculations should be less accurate for $\gamma_\perp$, the large discrepancy between the CC3 and the experimental ratio must be due to the difficulties in the measurement of $\gamma_\perp(\omega)$ for neon.

B. Argon

The purpose of this section is to establish how accurately $\gamma_\parallel(\omega)$ and $\gamma_\perp(\omega)$ can be evaluated for argon. In Sec. III B 1 we carry out a basis set investigation in order to estimate the error in the one-electron space and determine the basis set that we will use in the calculations of $\gamma_\parallel(\omega)$ and $\gamma_\perp(\omega)$. In Sec. III B 2 we report FCI calculations to benchmark the accuracy of the CCSD and CC3 results. Calculations using the coupled cluster hierarchy CCS, CC2, CCSD, and CC3 in connection with large basis sets were performed to further investigate the convergence pattern in the *N*-electron space. The relativistic contribution to γ_0 is examined in Sec. III B 3, and finally in Sec. III B 4 we compare the obtained best theoretical estimates with the experimental results.

1. Basis set investigation

In Table III we present the basis set investigation for the static second hyperpolarizability for argon using the CCSD model and the *n*-aug-cc-pVXZ basis set family.[37,39] As for neon, it is obvious that a double augmentation is not sufficient, whereas going from triple to quadruple augmentation leads to very small changes. Core-valence basis sets were considered as well. For neon, it was found that for the larger cardinal numbers, the extension to core-valence basis sets leads to very small changes in the hyperpolarizabilities. For argon, it looks like the core-valence basis sets converge faster (see Table III), but no definite conclusions can be drawn, since core-valence basis sets of higher cardinal number than QZ do not exist for argon.

At the triply augmented level, we have investigated the basis set convergence of the self-consistent-field (SCF) contribution and the CC3 correlation contribution separately (Table IV). The SCF contribution is very close to being converged at the 6Z level. Furthermore, the remaining basis set errors for the SCF and the correlation contribution are oppositely directed. The correlation contribution to the static hyperpolarizability at the CC3 level is expected to converge in a similar fashion as the correlation energy, and the basis set limit of this contribution may therefore be estimated using an X^{-3} extrapolation.[45] This leads, for a two-point extrapolation using the t-aug-cc-pV5Z and the t-aug-cc-pV6Z results (hereafter denoted as 56-extrapolation), to 192.3 a.u. (see Table IV). Adding this correlation contribution to the SCF/t-aug-cc-pV6Z result gives 1153 a.u. as the estimate of the CC3 basis set limit for the static hyperpolarizability.

The basis set used for the CC3 calculations on the frequency-dependent hyperpolarizabilities of argon was t-aug-cc-pV5Z, which gives a reasonable balance between computation time and accuracy. From Table IV, the basis set error of the CC3/t-aug-cc-pV5Z calculations is about −19 a.u. (where the CC3 correlation contribution of −21 a.u., calculated as the difference between the 56-extrapolated and 5Z results, has been added to the SCF error of +2 a.u., calculated as the difference between the 6Z and 5Z results).

2. Convergence of the coupled cluster hierarchy

As for neon, we start with a comparison of the CC and FCI results for $\gamma_\parallel(\omega)$ and $\gamma_\perp(\omega)$ in a moderately sized basis. Again, the basis set chosen was d-aug-cc-pVDZ and only the eight valence electrons were correlated. The results are compiled in Table V. Comparing with the CC3 values obtained with the large t-aug-cc-pV5Z basis in Table VI, we find that still over 80% of the hyperpolarizabilities are recovered with the small basis, such that meaningful conclusions can be drawn from the FCI benchmark calculations. The core contribution in the d-aug-cc-pVDZ basis is only 0.7%, as inferred from the CC3 calculations of γ_0, justifying the frozen-core approximation in the calculations.

TABLE V. Argon. The deviation (in a.u.) of the ESHG hyperpolarizabilities $\gamma_\parallel$ and $\gamma_\perp$ in the coupled cluster models from the FCI hyperpolarizability ($\gamma^{\mathrm{FCI}}-\gamma^{\mathrm{CC}}$), using the d-aug-cc-pVDZ basis ($1s^2 2s^2 2p^6$ frozen core).

ω	$\gamma_\parallel$			$\gamma_\perp$		
	CCSD	CC3	FCI	CCSD	CC3	FCI
0.0	-19.9	-3.02	970.13	-6.64	-1.00	323.38
0.042 823	-20.7	-3.39	1044.00	-6.95	-1.17	351.76
0.088 558	-23.4	-4.96	1350.44	-8.04	-1.84	467.93
0.093 368	-23.9	-5.27	1405.51	-8.22	-1.97	488.51

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TABLE VI. Argon. The ESHG hyperpolarizabilities $\gamma_{\parallel}$ and $\gamma_{\perp}$ (in a.u.) at frequency ω using the t-aug-cc-pV5Z basis.

	$\gamma_{\parallel}$					$\gamma_{\perp}$			
ω	CCS	CC2	CCSD	CC3	Expt.[a]	CCS	CC2	CCSD	CC3
0.0	1152.4	1238.9	1169.4	1172.4	1167±20	384.1	413.0	389.8	390.8
0.042 823	1222.3	1322.4	1247.2	1252.3	1236.8±3.5	407.2	441.1	415.8	417.6
0.088 559	1503.0	1663.7	1564.0	1579.0	1559.2±8.2	499.0	555.8	521.4	526.6
0.093 368	1551.9	1724.1	1620.0	1636.9	1625.7±10.7	515.0	576.1	539.9	545.9

[a]From Refs. 24 and 21.

From Table V it can be seen that the difference between the CC3 and FCI results is only about 0.3% in the static limit. For both the parallel and the perpendicular component this deviation increases only slightly to about 0.4% for higher frequencies. For the CCSD model, the relative *N*-electron error is about 2%.

The convergence of CCS, CC2, CCSD, and CC3 hyperpolarizabilities in the large t-aug-cc-pV5Z basis is investigated in Table VI. The plot of these numbers (Fig. 3) clearly shows the convergence of the coupled cluster hierarchy. The CCS model underestimates while the CC2 model overestimates the correlation contribution to the hyperpolarizability, and they are both off by about 30%. As for neon, the CCSD and CC3 numbers are very close to each other in the t-aug-cc-pV5Z basis, while they differ significantly in the d-aug-cc-pVDZ basis. In summary, the above analysis suggests that correlation contributions beyond CC3 can be neglected.

3. Relativistic corrections

The relativistic DPT contributions to the static limit of $\gamma_{\parallel}$ are given in Table VII for both the uncontracted basis set (see Sec. II for a detailed description of the basis) and the t-aug-cc-pCVTZ basis. The relativistic corrections differ only by a few percent depending on whether the uncontracted basis or the t-aug-cc-pCVTZ basis is used. Furthermore, the difference between the relativistic corrections calculated at the CCSD level and the CC3 level is very small. In summary, relativistic effects add about 9 a.u. (0.7%) to the static hyperpolarizability of argon. The relativistic contribution has also been calculated for the frequency-dependent hyperpolarizabilities—it increases slightly with the frequency, but remains smaller than 1%.

Nakajima and Hirao[29] have calculated the relativistic contribution for the static hyperpolarizability of argon, using the third-order Douglas-Kroll method and a 10*s*9*p*9*d*9*f* basis set. At the CCSD(T) level, they obtained a relativistic correction of 9 a.u., which is in perfect agreement with the corrections we obtain with the DPT method. The total CCSD(T) hyperpolarizability reported by Nakajima and Hirao differs from the present result by about 100 a.u.—probably because these authors used a basis set with an insufficient number of diffuse basis functions.

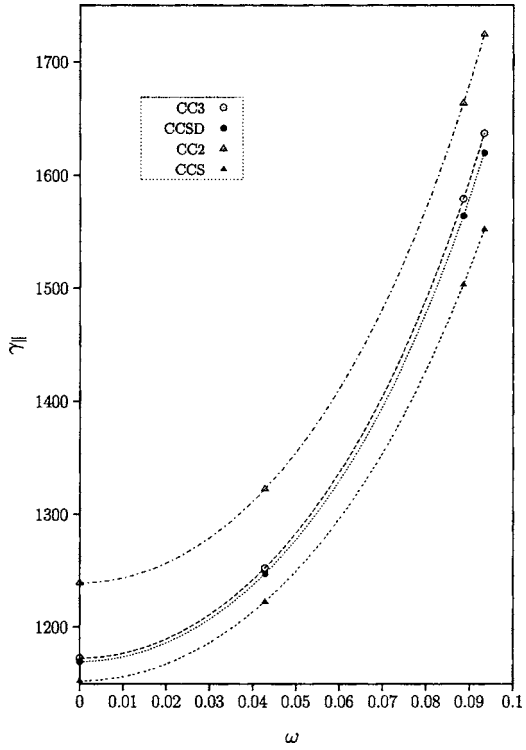


FIG. 3. The second hyperpolarizability dispersion for argon with various wave-function approximations. Basis: t-aug-cc-pV5Z.

4. Comparison to experiment

In Table VI, we have also given the experimental values of Shelton and co-worker.[21,24] The CC3/t-aug-cc-pV5Z numbers are all larger by 5–20 a.u. as compared to the experimental results, which can be explained by examining the remaining errors at this level. The static value for $\gamma_{\parallel}$ has a basis set error of −19 a.u., a correlation error of about −3 a.u., and misses a relativistic correction of 9 a.u. Adding these numbers the CC3 result the static hyperpolarizability $\gamma_{\parallel}$ is estimated to be about 13 a.u. too high. Our best estimate is thus 1159 a.u., which is in perfect agreement with the experimental value of 1167±20 (see Table VI and Fig. 4). The CC3/t-aug-cc-pV5Z values for the frequency-dependent $\gamma_{\parallel}$ may be expected to have an accuracy similar to the one for the static limit, in agreement with the above-mentioned ob-

TABLE VII. Argon. Relativistic corrections (in a.u.) to the static ESHG hyperpolarizabilities $\gamma_{\parallel}$ for the uncontracted basis set and t-aug-cc-pCVTZ.

	t-aug-cc-pCVTZ	Uncontracted
CCS	+8.10	+8.40
CC2	+10.4	+10.3
CCSD	+9.11	+8.99
CC3	+8.92	+8.90

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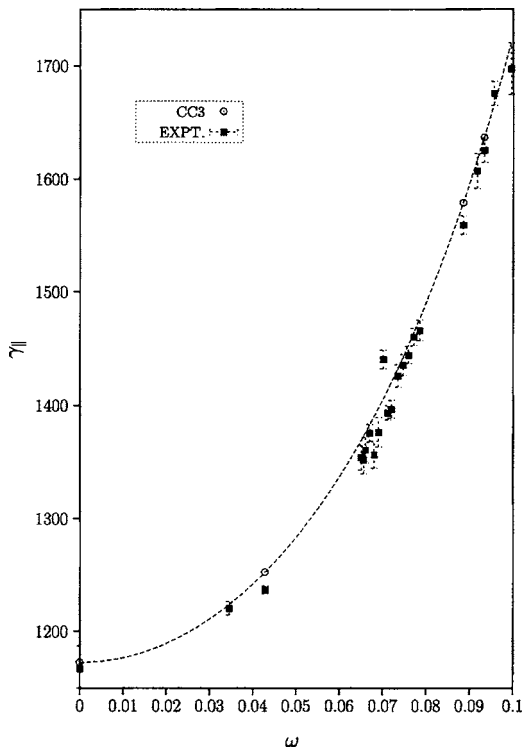


FIG. 4. The CC3 second hyperpolarizability dispersion for argon compared to the experimental results. Basis: t-aug-cc-pV5Z.

servation that the experimental values for $\gamma_{\parallel}$ are in general slightly below the CC3 results (see Table VI and Fig. 4).

In Fig. 5 the ratio $\gamma_{\parallel}(\omega)/\gamma_{\perp}(\omega)$ is plotted for the CCS, CC2, CCSD, and CC3 models including the experimental values of Bigio and Ward[20] (ω^2=0.004 356) and Mizrahi and Shelton[21] (ω^2=0.005 221, 0.007 843, 0.008 717 6). Note that, whereas for neon, the ratio in Eq. (6) is to a good approximation linear in ω^2 (Fig. 2), this is obviously not true for argon, where the term quadratic in ω^2 must clearly be included. As for neon, the older experiment[20] has a large error bar. The numbers from Mizrahi and Shelton,[21] on the other hand, agree well with our calculations, but the uncertainty is still too large to draw any conclusion on the functional form of the hyperpolarizability ratio curve based on the experimental results.

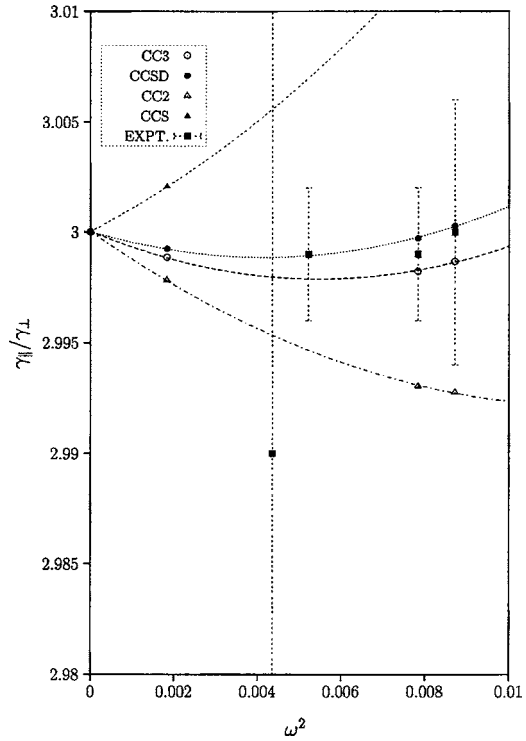


FIG. 5. $\gamma_{\parallel}/\gamma_{\perp}$ for argon with various wave-function approximations. Basis: t-aug-cc-pV5Z.

TABLE VIII. Krypton. Convergence of the CCSD static second hyperpolarizability (in a.u.) in the *n*-aug-cc-pV*X*Z basis set family ($1s^2 2s^2 2p^6 3s^2 3p^6$ frozen core).

	Augmentation level *n*		
Cardinal number	d	t	q
DZ	1875.7	2041.1	2059.4
TZ	2484.8	2770.1	2800.3
QZ	2545.9	2670.0	2674.9
5Z	2545.4	2601.4	2602.1

C. Krypton

We finally apply our computing method to the krypton atom. As in Sec. III B for argon, we start with a basis set investigation, Sec. III C 1, and try to estimate the CCSD basis set limit for the static second hyperpolarizability. In Sec. III C 2 we use again FCI calculations to benchmark the accuracy of the CCSD and CC3 results, and study the convergence of the dispersion curves in the coupled cluster hierarchy using large basis sets. The calculation of relativistic contributions to the static and frequency-dependent hyperpolarizabilities is described in Sec. III C 3, and finally we compare our best estimates to the experimental hyperpolarizabilities in Sec. III C 4.

1. Basis set investigation

The results of a basis set investigation at the CCSD level are given in Table VIII. Regarding the augmentation level, the same pattern as for neon and argon is observed: Triple augmentation is necessary and sufficient. With respect to the cardinal number of the basis sets, however, we are still far from convergence at the t-aug-cc-pV5Z level. In Table IX, we investigate the convergence of the SCF and CCSD correlation contributions separately. The core was not kept frozen in the SCF calculations, but the effect of this is expected

TABLE IX. Krypton. Basis set convergence (SCF and CCSD) of the static second hyperpolarizability (in a.u.) in t-aug-cc-pV*X*Z basis set family ($1s^2 2s^2 2p^6 3s^2 3p^6$ frozen core).

		Correlation contribution	
Cardinal number	SCF	CCSD	Extrapolated
DZ	1508.9	532.2	···
TZ	2221.6	548.5	555.3(DT)
QZ	2246.9	423.1	331.6(TQ)
5Z	2250.2	351.2	275.8(Q5)

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TABLE X. Krypton. The deviation (in a.u.) of the ESHG hyperpolarizabilities $\gamma_\parallel$ and $\gamma_\perp$ in the coupled cluster models from the FCI hyperpolarizability ($\gamma^{\mathrm{FCI}}-\gamma^{\mathrm{CC}}$), using the d-aug-cc-pVDZ basis ($1s^22s^22p^63s^23p^63d^{10}$ frozen core).

	$\gamma_\parallel$			$\gamma_\perp$		
ω	CCSD	CC3	FCI	CCSD	CC3	FCI
0.0	-50.0	-8.40	1824.99	-16.6	-2.80	608.33
0.042 823	-53.1	-9.66	2009.28	-17.9	-3.30	676.08
0.088 558	-65.0	-15.7	2837.57	-22.9	-5.65	969.87
0.093 368	-66.9	-16.9	2997.71	-23.7	-6.13	1024.75

to be minor, which has been confirmed by doing the same investigation with CCS and frozen core, where CCS replaced SCF. While the SCF contribution has practically converged at the SCF 5Z-level, the estimation of a basis set limit for the correlation contribution turns out to be difficult. Apparently, the correlation contribution does in this case not converge with X^{-3}, which is related to the fact that the cc-pVXZ basis sets are optimized for the correlation of the $4s4p$ valence shell only[40] and do not account in a systematic fashion for the correlation of the $3d$ subvalence shell. The latter contributes, however, significantly to the hyperpolarizability of krypton. Thus, it would have been interesting to investigate the core contribution systematically with core-valence basis sets (as for argon in Table III), but for the time being, no core-valence basis sets are available for krypton. Therefore, we have to content ourselves with the rough estimate that the t-aug-cc-pV5Z result is 50–100 a.u. above the basis set limit.

2. Convergence of the coupled cluster hierarchy

Again, the FCI model in connection with the d-aug-cc-pVDZ basis set was applied to assess the *N*-electron error of CCSD and CC3; the results are reported in Table X. As for neon and argon, the basis set is able to recover a relatively large part of the hyperpolarizability, 70%–75% as inferred from the CC3 results in Tables X and XI. For computational reasons the *d* electrons cannot be included in a FCI calculation. The restriction to pure valence-electron correlation may be expected to be more critical for krypton than for argon and neon. However, it turns out that the difference between the CC3/d-aug-cc-pVDZ calculations with and without the inclusion of *d* electrons amounts to less than 0.5%.

As for argon and neon, it can be concluded that the CC3 model is close to convergence in the *N*-electron space. The deviation of CC3 from FCI is for the static limit of $\gamma_\parallel$ about

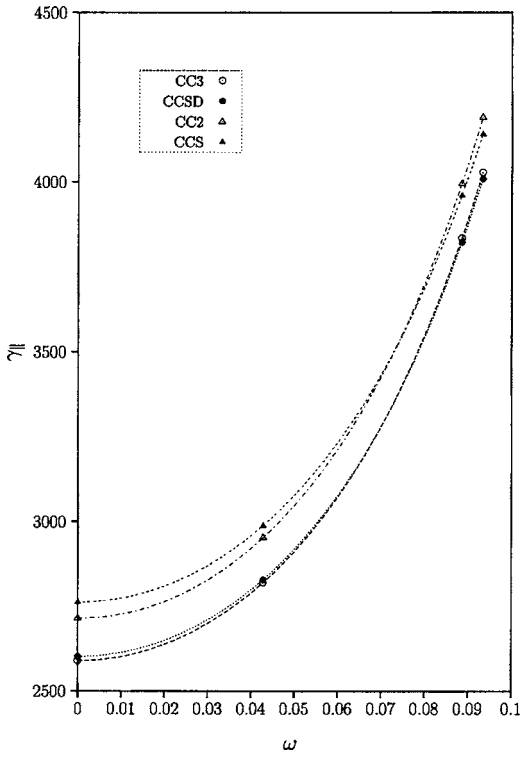


FIG. 6. The second hyperpolarizability dispersion for krypton with various wave-function approximations. Basis: t-aug-cc-pV5Z.

−8 a.u. and increases slightly with increasing frequency. The relative error is about 0.5%. A similar relative deviation is found for $\gamma_\perp(\omega)$. The deviation of the CCSD model from the FCI values amounts to less than 3%.

In Fig. 6, the dispersion curves have been plotted for the different CC models (see also Table XI). The CCS and CC2 results are in this case only off by about 5%, and both are larger than the CC3 results. As expected, CCSD is significantly closer to CC3 than either CC2 and CCS. As for neon and argon, the differences between the CCSD and CC3 results are much smaller in the t-aug-cc-pV5Z level than in the d-aug-cc-pVDZ basis.

3. Relativistic corrections

The relativistic DPT corrections to the hyperpolarizabilities of krypton have been calculated at the CCSD level in the uncontracted basis set described in Sec. II, and the results are listed in Table XII. The correction to the static $\gamma_\parallel$ is 29 a.u., which agrees well with the correction of 28 a.u. obtained at the CCSD(T) level by Nakajima and Hirao,[29] using the third-

TABLE XI. Krypton. The ESHG hyperpolarizabilities $\gamma_\parallel$ and $\gamma_\perp$ (in a.u.) at frequency ω using the t-aug-cc-pV5Z basis ($1s^22s^22p^63s^23p^6$ frozen core).

	$\gamma_\parallel$					$\gamma_\perp$			
ω	CCS	CC2	CCSD	CC3	Expt.[a]	CCS	CC2	CCSD	CC3
0.0	2762.1	2713.9	2601.4	2589.0	2600	920.7	904.6	867.1	863.0
0.042 823	2987.7	2952.4	2828.9	2820.3	2845±8	995.0	984.8	943.1	940.4
0.088 559	3960.2	3994.4	3822.1	3835.5	3889±11	1312.8	1333.5	1272.9	1278.5
0.093 368	4141.4	4190.7	4009.1	4027.6	4080±11	1371.6	1398.8	1334.7	1342.0

[a]From Refs. 24 and 22.

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TABLE XII. Krypton. Relativistic corrections (in a.u.) to the ESHG hyperpolarizability $\gamma_{\|}$ at frequency ω using CCSD/uncontracted basis ($1s^2 2s^2 2p^6 3s^2 3p^6$ frozen core).

ω	CCSD rel. corr.
0.0	+29.3
0.042 823	+33.9
0.088 559	+57.8
0.093 368	+62.9

order Douglas-Kroll method and a 11*s*9*p*8*d*8f8*g* basis set. Compared to the total value of $\gamma_{\|}$, the relativistic correction amounts to 1% and increases slightly to 1.5% along the dispersion curve. Although no precise estimate of the basis set limit is available (see Sec. III C 1), we seem to have the same situation as for argon and neon, i.e., that the basis set error at the t-aug-cc-pV5Z level and the relativistic correction have the same size but opposite sign and thus largely cancel. It seems therefore justified to employ the CC3/t-aug-cc-pV5Z results directly for a comparison with the experiment.

4. Comparison to experiment

The static and frequency-dependent hyperpolarizabilities of krypton are shown in Fig. 7 in comparison with the experimental results by Shelton.[22,24] A very good agreement with the experiment is observed, suggesting that indeed the basis set error to a large degree cancels against the relativistic contributions (see Secs. III C 1 and III C 2).

Figure 8 displays the hyperpolarizability ratio $\gamma_{\|}(\omega)/\gamma_{\perp}(\omega)$ for the coupled cluster hierarchy compared to the experimental results.[20,21] The computed curves strongly suggest that the experiments contain a systematic error, as, in particular, for higher frequencies, the obtained ratio is too high. The calculated ratio develops very similar to argon. First, it drops slightly below 3, but begins to increase for larger frequencies, i.e., the term quadratic in ω^2 in Eq. (6) is important.

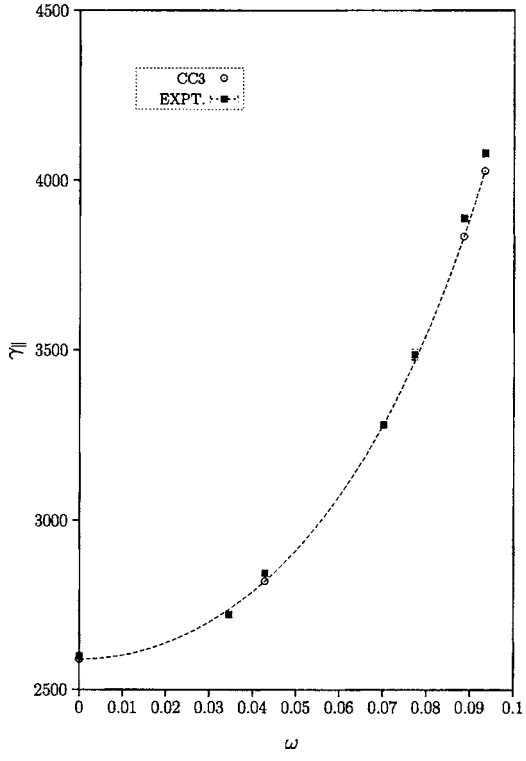


FIG. 7. The CC3 second hyperpolarizability dispersion for krypton compared to the experimental results. Basis: t-aug-cc-pV5Z.

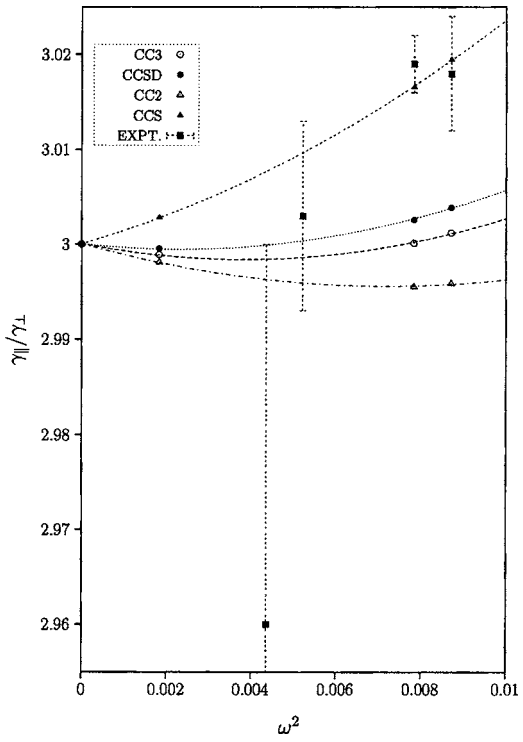


FIG. 8. $\gamma_{\|}/\gamma_{\perp}$ for krypton with various wave-function approximations. Basis: t-aug-cc-pV5Z.

IV. CONCLUDING REMARKS

We have presented CC3 calculations for the static and frequency-dependent second hyperpolarizabilities of neon, argon, and krypton. By studying in detail the convergence with respect to the one-electron (basis set) and *N*-electron space (correlation treatment) and accounting for relativistic effects by DPT we were able to obtain highly accurate results with reliable estimates for the remaining uncertainties. Benchmarking of the CC3 model against FCI in the d-aug-cc-pVDZ basis has shown that for the hyperpolarizabilities, the correlation contribution beyond CC3 is negligible for noble gas atoms. For argon and krypton, we obtain 1159 and 2589 a.u., respectively, for the static limit of $\gamma_{\|}$, which agrees perfectly with the experimental values of Shelton,[22,24] which are 1167 ± 20 a.u. (argon) and 2600 a.u. (krypton).

The calculations of the hyperpolarizability ratio $\gamma_{\|}(\omega)/\gamma_{\perp}(\omega)$, on the other hand, are in poor or no agreement with the presently available experimental results. The established accuracy of the CC3 model and the large error bars on the experimental values suggest that this disagreement is due to the difficulties in the measurements of $\gamma_{\|}(\omega)/\gamma_{\perp}(\omega)$, since there is no indication why the theoretical results for $\gamma_{\perp}(\omega)$ should be less accurate than for $\gamma_{\|}(\omega)$.

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