Available online at www.sciencedirect.com
SCIENCE DIRECT®
Chemical Physics Letters 413 (2005) 272–279
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

The second hyperpolarizability of the N_2 molecule calculated using the approximate coupled cluster triples model CC3

Filip Pawłowski [a,*], Poul Jørgensen [a], Christof Hättig [b]

[a] Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark
[b] Forschungszentrum Karlsruhe, Institute of Nanotechnology, P.O. Box 3640, D-76021 Karlsruhe, Germany

Received 31 March 2005; in final form 24 June 2005
Available online 18 August 2005

Abstract

The static and frequency-dependent hyperpolarizabilities of the N_2 molecule have been calculated using the coupled cluster approximate triples model CC3. The CC3 basis-set limit of the hyperpolarizability has been estimated. Considering the zero-point vibrational correction and neglecting the relativistic contributions (which are found to be small) the best estimate of the static hyperpolarizability is 912.9 ± 4.3 a.u. (the uncertainty of 4.3 a.u. does not account for correlation effects beyond CC3). The effect of triples is important and increases with frequency. The hyperpolarizabilities calculated at the CC3 level agree well with experiment, the discrepancies being of 0.1–2.2%. The largest CC3 calculations employed 326 basis functions.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

The accurate determination of electric (hyper)polarizabilities plays an important role in the analysis and interpretation of many experiments. The most important fields include non-linear optics [1], scattering [2], and intermolecular interactions [3]. The prediction of electric properties is also a stimulating factor for the progress in technologically important applications. The design of new optical materials serves as one example when we realize that many non-linear optical processes are mediated by the third-order non-linear susceptibility, which in terms of molecular properties corresponds to the second dipole hyperpolarizability.

The determination of the second hyperpolarizability of atoms and molecules to high accuracy is a challenge for both experiment and theory. The history of the static hyperpolarizability of the Ne atom, which we have recently reviewed [4], is probably the best example. Another example is the theoretical value of the static second hyperpolarizability of the N_2 molecule – the property we focus on – for which 10 years ago there still existed the uncertainty of about 20% [5].

The introduction of the hierarchies of the correlation-consistent basis sets by Dunning and co-workers [6–9] and the hierarchies of coupled cluster (CC) wavefunction models [10] have made it possible to approach the exact solution of the Schrödinger equation in a systematic manner by controlling the one- and N-electron errors at each level of approximation. In particular the coupled cluster singles-and-doubles (CCSD) method with the perturbative treatment of triple excitations [CCSD(T)] [11] has turned out to become a very accurate tool for the calculation of static molecular properties [10].

While very successful for the accurate prediction of static properties, CCSD(T) cannot be used for the calculation of frequency-dependent properties, due to its non-iterative nature [12]. Unlike CCSD(T), the approximate triples model CC3 is iterative and may be used for the calculation of both static and frequency-dependent properties. CC3 is a member of the coupled cluster hier-

* Corresponding author. Present address. Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern N-0315 Oslo, Norway. Fax: +47 22855441.
E-mail address: filip.pawlowski@kjemi.uio.no (F. Pawłowski).

0009-2614/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2005.06.130

archy CCS, CC2, CCSD, CC3, CCSDT, which is designed to systematically improve the description of molecular response properties for single configuration dominated systems [13]. In CCS all single excitations are treated, in CCSD all doubles are added and in CCSDT all triples are further added. CC2 [14] and CC3 [15] are approximations to CCSD and CCSDT where the doubles and the triples, respectively, are treated in an approximate fashion and where the scaling of the computational cost with system size is reduced compared to, respectively, CCSD and CCSDT.

The aim of the present investigation is a systematic study on the convergence of the static and frequency-dependent second hyperpolarizability of the N_2 molecule in the one- and N-electron space. For this purpose we employ the correlation-consistent basis sets of Dunning and coworkers and the CCS, CC2, CCSD, CC3 hierarchy of wavefunction models. We report here the first CC3 calculations of the frequency-dependent second hyperpolarizability for a molecular system. We expect similar reductions in the errors from CCSD to CC3 for the static and frequency-dependent hyperpolarizabilities of N_2 as observed for the static properties when going from CCSD to CCSD(T). Very recently [4] we have calculated, using the CC3 model, the static and frequency-dependent hyperpolarizability for the Ne atom and obtained an uncertainty of about one atomic unit (about one per cent), an accuracy which for the first time has been obtained for a many electron system in ab initio calculations of frequency-dependent second hyperpolarizabilities.

The second hyperpolarizabilities of N_2, both static and frequency-dependent, have been studied before by many authors at different levels of theory [5,16–19]. The results we present are complementary to [19], where the hyperpolarizabilities of N_2 were studied at the CCSD level.

2. Computational details

Most electric-field-induced second-harmonic generation (ESHG) experiments measure the parallel isotropic average component, which we will denote in the following as $\gamma_{\parallel}(\omega)$. For a diatomic homonuclear molecule $\gamma_{\parallel}(\omega)$ becomes

$$\gamma_{\parallel}(\omega) = \frac{1}{15}(8\gamma_{xxxx} + 4\gamma_{xxzz} + 4\gamma_{zzxx} + 2\gamma_{zxxz} + 2\gamma_{xzzx} + 3\gamma_{zzzz}), \tag{1}$$

where $\gamma_{\mu\nu\eta\xi} \equiv \gamma_{\mu\nu\eta\xi}(-2\omega;\omega,\omega,0)$. In the static limit, $\omega = 0$, $\gamma_{\parallel}(\omega)$ in Eq. (1) reduces to

$$\gamma_{\parallel}(0) = \frac{1}{15}(8\gamma_{xxxx} + 12\gamma_{xxzz} + 3\gamma_{zzzz}). \tag{2}$$

Occasionally in this Letter, $\gamma_{\parallel}(0)$ is denoted as γ_0.

Static and frequency-dependent second hyperpolarizabilities, $\gamma_{\parallel}(0)$ and $\gamma_{\parallel}(\omega)$, of N_2 will be reported for the basis sets cc-pVXZ augmented with diffuse functions with cardinal numbers $X = $ D, T, Q, 5, 6 and singly (s), doubly (d), triply (t), and quadruply (q) augmentation [6–8]. If not stated otherwise an internuclear distance of $R_{N-N} = 2.074$ a.u. was used (this is the equilibrium geometry obtained experimentally in [20]; the same geometry has been used in [19]). No orbitals were frozen in the calculations and in the coupled cluster response calculations orbitals were not allowed to relax.

To estimate the SCF basis-set limit we employed in addition two basis sets denoted in the following as F and G. The F basis has been constructed similar to the basis used in [4] to investigate the SCF basis-set limit of the neon hyperpolarizability: Starting from the t-aug-cc-pV6Z the g, h and i functions were discarded, while the s, p, d and f shells where decontracted. To this basis 3d and 2f functions were added with tight exponents taken from the core-correlation part of the cc-pwCV5Z basis [9]. This basis (F1) was further extended by: (1) a primitive (18s12p10d8f) set with exponents interpolated even-tempered between the exponents of basis F1; (2) a (2s2p2d2f) set of tight functions extrapolated even-tempered from the largest exponents of basis F1; (3) a (1s1p1d1f) set of diffuse functions taken from the q-aug-cc-pV6Z basis. The resulting uncontracted (40s28p24d20f) basis F should be virtually complete up to f functions, which is sufficient for an atom, but not for a molecule. To test for the effect of higher angular momenta in the basis set we constructed basis G by extending basis F with 16 primitive g functions. Seven of the exponents were taken from the t-aug-cc-pV6Z basis and the core-correlation part of the cc-pwCV5Z basis. These were augmented by six even-tempered interpolated and two tight even-tempered extrapolated exponents and the additional diffuse g function of the q-aug-cc-pV6Z basis. The uncontracted (40s28p24d 20f16g) basis G consists for N_2 of 1056 basis functions and should be virtually complete up to g functions.

All calculations were carried out with the DALTON program [21]. The implementation of analytic second hyperpolarizabilities for CC2 and CCSD has been described in [18] and the implementation for SCF wavefunctions in [22]. CC3 analytic second hyperpolarizabilities have recently been implemented by us [4,23] in the coupled cluster code [15,24] which is a part of the DALTON package [21]. The largest CC3 calculations carried out in the present study involved 326 basis functions (d-aug-cc-pV5Z basis).

3. Results

In Table 1, we present the values of the static second hyperpolarizability of N_2 calculated at the CCSD level

Table 1
The basis-set convergence of the electronic contribution to the isotropic average of the static hyperpolarizability γ_0 (a.u.) for N_2 calculated with the SCF, CCSD and CC3 models and the *n*-aug-cc-p(C)V*X*Z basis-set family (no frozen core approximation has been used)

Cardinal number *X*Z	SCF				CCSD					CC3
	n-aug-cc-pV*X*Z				*n*-aug-cc-pV*X*Z				d-aug-cc-pCV*X*Z	d-aug-cc-pV*X*Z
	Augmentation level *n*				Augmentation level *n*					
	s	d	t	q	s	d	t	q		
DZ	456.0	672.0	669.2	679.7	684.4[a]	937.6[a]	935.4[a]	943.4[a]	929.8	956.3
TZ	560.0	697.1	710.1	716.9	745.1[a]	895.3[a]	903.0[a]	908.8[a]	890.0	923.7
QZ	654.2	709.9	713.2	714.9	822.0[a]	880.7[a]	882.7[a]	884.3	876.1	912.6
5Z	684.5	713.9	714.3	714.2	844.1[a]	873.2[a]	873.3		870.8	906.9
6Z		714.4	714.7		855.2	869.2				
F basis		714.6								
G basis		714.7								
Limit[b]		714.7 ± 0.2				863.3 ± 3.3				898.9 ± 4.3

Calculations have been carried out at the equilibrium distance of $R_e = 2.074$ bohr.
[a] Calculations reported in [19].
[b] See text for details of extrapolations.

using the *n*-aug-cc-pV*X*Z basis-set family. It is clear from this table – as also observed in [19] – that singly augmentation does not provide enough diffuseness to assure a fast convergence of the hyperpolarizability towards the basis-set limit. At the doubly augmented level the convergence is much faster. Further augmentation becomes less important, especially for the higher cardinal numbers. Indeed, for $X = 5$ the difference between the doubly and triply augmented basis is for CCSD only 0.1 a.u. Smooth but slow convergence of electric properties within the hierarchy of the correlation-consistent basis sets towards the basis-set limit has been observed in many studies. The present results for γ_0 of N_2, Table 1, are another example of this trend. The hyperpolarizability calculated (using CCSD) in the largest basis, d-aug-cc-pV6Z, appears to be converged within a few a.u.

In [19] the CCSD basis-set limit for γ_0 was estimated to 867 ± 7 a.u., a value obtained by combining the d-aug-cc-pV5Z result, 873.2 a.u., with a correction accounting for the fact that the all electron calculation had been carried out using a valence basis set. This correction has been evaluated in [19] to −6.7 a.u. by subtracting the value of γ_0 calculated in t-aug-cc-pVTZ basis (903.0 a.u.) from the one calculated in t-aug-cc-pCVTZ (896.3 a.u. [19]).

To investigate in more details the error that arises carrying out all electron calculations using the valence basis set, we have calculated γ_0 for N_2 at the CCSD/d-aug-cc-pCV*X*Z level with all electrons correlated and $X = $ D, T, Q, 5 (see the 10th column of Table 1). The differences between the CCSD/d-aug-cc-pCV*X*Z and the CCSD/d-aug-cc-pV*X*Z results are −7.8, −5.3, −4.6 and −2.4 a.u. for $X = $ D, T, Q, and 5, respectively. The error thus decreases with *X*. At the $X = 6$ level it may be expected to be about one a.u. and may thus safely be neglected for the accuracy we are aiming at.

To estimate the CCSD basis-set limit for γ_0 of N_2 we will combine the Hartree–Fock limit with the basis-set limit for the CCSD correlation contribution. The Hartree–Fock limit for γ_0 of N_2 has been estimated in [19] to 715 ± 2 a.u. This value is in agreement with a recent value of 715 ± 4 a.u. estimated by Maroulis [16] who used a basis of 290 contracted Gaussian-type functions (see [16] for details). Luo et al. [17] obtained in a [8s6p4d3f] basis (denoted in [17] as A3) the value of 716 a.u.

Looking at the trends in the basis-set convergence for the SCF hyperpolarizability (Table 1), one can expect that the results obtained with the basis sets F and G (see Section 2 for the description of these basis sets) begin a series which converges from below towards the basis-set limit. The value of 714.7 a.u. (G basis) may thus be regarded as a lower bound for the basis set limit and should be very close to it. This is confirmed by the results obtained in the t-aug-cc-pV*X*Z series (see Table 1), which also converges from below towards the basis-set limit. The hyperpolarizability obtained in the t-aug-cc-pV6Z basis is essentially equal to the one obtained in the G basis. We thus estimate the Hartree–Fock basis-set limit to 714.7 ± 0.2 a.u., where the uncertainty of 0.2 a.u. is half the difference between the SCF/t-aug-cc-pV6Z and SCF/t-aug-cc-pV5Z results. Note that the SCF basis-set limit obtained in this way agrees well with the previous estimates (715 ± 4 a.u. [16] and 715 ± 2 a.u. [19]), but has much smaller uncertainty.

The CCSD correlation contribution to γ_0 may be obtained as the difference between the CCSD results in the d-aug-cc-pV*X*Z basis set series from Table 1 and the Hartree–Fock results obtained in the same basis sets (column 3 in Table 1). We note that at the QZ and 5Z level the correlation contribution is (almost) the same for double and triple augmentation and that the SCF

contribution is close to convergence in these basis sets. Thus, the correlation contribution to γ_0 can be expected to converge in a similar way as the correlation energy – as it has been found in previous study for the hyperpolarizability of the Ne atom [4] – and the basis-set limit of the correlation contribution may be estimated by applying the two-point linear extrapolation formula from [25] (originally designed for correlation energies). Applicability of this formula is also confirmed by the results: the extrapolated values for the correlation contribution converge much faster with the cardinal number than the non-extrapolated values (e.g., for the d-aug-cc-pVXZ series original results are in a.u. 170.8 (QZ), 159.3 (5Z) and 154.8 (6Z), while the extrapolated correlation contributions are 150.8 (TZ/QZ), 147.2 (QZ/5Z) and 148.6 (5Z/6Z)). We thus estimate the basis-set limit of the CCSD correlation contribution to γ_0 as 148.6 ± 3.1 a.u. (5Z/6Z extrapolation), where the uncertainty of 3.1 a.u. is half the difference between the result for $X = 6$ (154.8 a.u.) and the extrapolated value (148.6 a.u.).

Adding to this value 714.7 ± 0.2 a.u. (the estimated Hartree–Fock limit) we obtain 863.3 ± 3.3 a.u. as best estimate for the CCSD basis-set limit for the static electronic hyperpolarizability of N_2 at $R_{N-N} = 2.074$ a.u.

To estimate the CC3 basis-set limit for the static hyperpolarizability we extrapolate – using the two-point formula of [25] – the *difference* between the CC3 and CCSD results obtained in the d-aug-cc-pV*X*Z basis (see Table 1). At the QZ/5Z level the extrapolated basis-set limit of the CC3 triples contribution is 35.6 ± 1.0 a.u., where the uncertainty has again been estimated as half the difference between the best basis set result ($X = 5$) and the extrapolated value. Adding this triples contribution to the estimated CCSD basis-set limit leads to 898.9 ± 4.3 a.u. as best estimate of the electronic contribution to the static hyperpolarizability of N_2.

An important issue in the correlated calculations of response properties is the relaxation of orbitals. As mentioned in Section 2, the CC results we present are obtained from unrelaxed calculations, i.e., the orbitals are not allowed to relax explicitly to the field. The unrelaxed approach is necessary, since for frequency-dependent properties the explicit treatment of orbital relaxation would lead to artificial non-correlated Hartree–Fock poles spoiling the pole structure of the coupled cluster response function [12]. In the static limit, however, both the unrelaxed and the relaxed coupled cluster hierarchies can be applied and will converge towards the same FCI limit. Indeed, in a very recent work [26] on the Cotton–Mouton effect of neon and argon we have shown that the orbital-relaxed CCSD(T) and the unrelaxed CC3 calculations led basically to the same static values. In [33] the polarizabilities and first hyperpolarizabilities calculated in the CCS–CC2–CCSD–CC3–CCSDT hierarchy were benchmarked against the FCI model for HF, Ne, and BH; it was found that the inclusion of orbital relaxation for the static properties gives results that are somewhat different from the unrelaxed results but are in general no improvement. Moreover, the numerical investigations of Salter et al. [27] and Kobayashi et al. [28] did not show any significant better performance of orbital-relaxed calculations compared to unrelaxed ones. In [19] γ_0 was calculated for N_2 at the orbital-relaxed CCSD(T)/d-aug-cc-pVTZ level leading to a value of 910.7 a.u. This value is 13 a.u. lower than the unrelaxed CC3 value calculated in the same basis (the last column of Table 1) – i.e., the differences between the relaxed CCSD(T) and the unrelaxed CC3 calculations point to an uncertainty of about 1% for γ_0 of N_2 due to the treatment of the orbitals in response calculations.

In [19] a 'best estimate' of the electronic contribution to γ_0 was obtained by combining the unrelaxed CCSD basis-set limit with the effect of connected triples and relaxation calculated using the CCSD(T) model (see [19] for details). This led to a value of 882 a.u. which is 17 a.u. lower than our unrelaxed CC3 best estimate of the electronic contribution to γ_0.

In Table 2 and Fig. 1 we have presented the frequency-dependent second hyperpolarizability, $\gamma_{\parallel}(\omega)$, calculated with the unrelaxed CC hierarchy, CCS, CC2, CCSD, CC3, using the t-aug-cc-pVTZ basis with all electrons correlated. We have used the set of frequencies commonly encountered in experimental studies. The highest frequency employed, 0.099505 a.u. or 457.9 nm, is below the first pole which occurs at the CC3/t-aug-cc-pVTZ level at 0.17 a.u. As observed before [4], the CCS model underestimates and CC2 model overestimates $\gamma_{\parallel}(\omega)$. The effect of triple excitations is significant and increases monotonically with the frequency. Between the static limit and the highest frequency employed here (457.9 nm) it varies between 28.8 a.u. (≈3%) and 60.9 a.u. (≈7%). The inclusion of connected triple excitations at the CC3 level improves the quality of the dispersion curve for $\gamma_{\parallel}(\omega)$ compared to CCSD and the improvement is especially pronounced for higher frequencies due to the more accurate description of the pole positions (excitation energies) at the CC3 level.

The experimental values of $\gamma_{\parallel}(\omega)$ obtained by Mizrahi and Shelton [29,30] are also shown in Table 2 and Fig. 1. However, no direct comparison of the calculated and experimental results can be carried out at this stage. Indeed, the theoretical results in Table 2 have been calculated using the t-aug-cc-pVTZ basis, which for γ_0 is still as far as 33 a.u. from the basis-set limit at the CC3 level (and 40 a.u. at the CCSD level). Moreover, the results presented in Table 2 represent the non-relativistic electronic contribution to the hyperpolarizability and for a direct comparison with the experimental data one must in addition account for vibrational averaging

Table 2
The parallel isotropic average of the frequency-dependent ESHG hyperpolarizability $\gamma_{\parallel}(\omega)$ (a.u.) for N_2

λ (nm)	ω (a.u.)	CCS	CC2	CCSD	CC3	Exp.[a]
∞	0.000000	825.2	975.1	903.0	931.8	917 ± 9[b]
1055.0	0.043188	870.1	1038.5	959.2	992.5	
694.3	0.065625	935.0	1131.2	1041.1	1081.1	1057.6 ± 6.4
632.8	0.072003	960.2	1167.6	1073.1	1115.7	1095.6 ± 4.6
590.0	0.077226	983.3	1201.5	1102.8	1147.9	1132.0 ± 4.2
514.5	0.088558	1042.7	1289.5	1179.6	1231.7	1208.7 ± 6.2
488.0	0.093368	1072.2	1333.8	1218.1	1273.7	1253.3 ± 6.3
457.9	0.099505	1114.2	1397.7	1273.4	1334.3	1327.5 ± 14.3

The theoretical results (pure electronic contribution) have been calculated using t-aug-cc-pVTZ basis (all electrons correlated) and the equilibrium bond distance $R_e = 2.074$ bohr.

[a] Experimental results from [29] and [30].

[b] Experimental static limit obtained by Shelton in [32] by extrapolation from results of [29] corrected for the pure rotational and vibrational contributions.

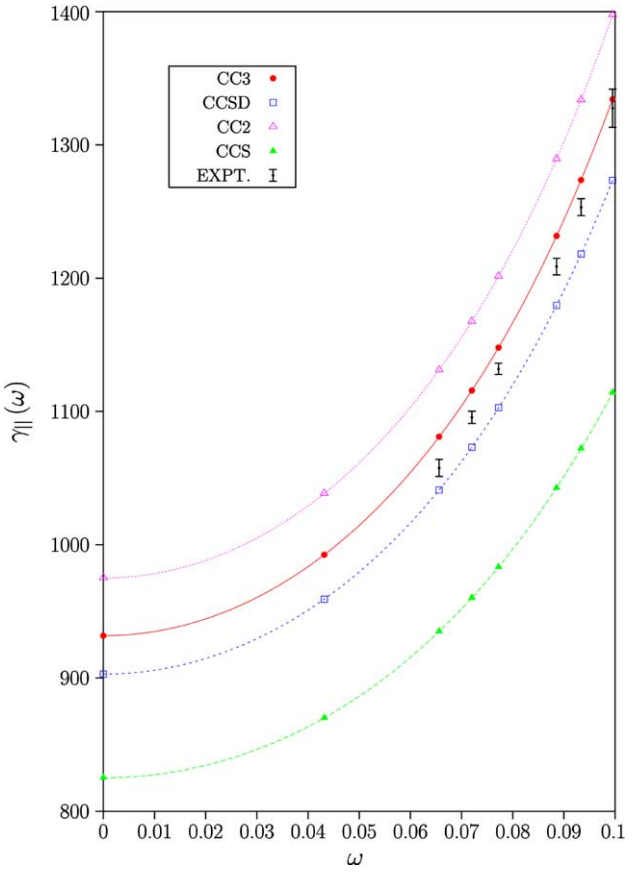


Fig. 1. Comparison of the electronic contribution to the parallel isotropic average of the ESHG hyperpolarizability, $\gamma_{\parallel}(\omega)$, of N_2 calculated with various wavefunction approximations using t-aug-cc-pVTZ basis set and the equilibrium bond distance $R_e = 2.074$ bohr. The experimental results from [29] and [30] are also plotted. All numbers in a.u.

and for the pure vibrational and rotational contributions, and also for the relativistic corrections.

The basis-set correction for static hyperpolarizability, $\Delta\gamma_0^{\text{basis}}$, has been calculated as the difference between the basis-set limit from Table 1 and the t-aug-cc-pVTZ result, which gives the correction of -39.7 a.u. for CCSD and -32.9 a.u. for CC3. To obtain the basis-set correction for the frequency-dependent hyperpolarizability, $\Delta\gamma_{\parallel}^{\text{basis}}(\omega)$, we have estimated the CCSD basis-set limit for $\gamma_{\parallel}(\omega)$ (applying the same two-point linear extrapolation procedure as in the static case and using the SCF frequency-dependent hyperpolarizabilities calculated in t-aug-cc-pV6Z basis) for two frequencies – 0.043188 a.u. or 1055 nm and 0.099505 a.u. or 457.9 nm – and obtained 915.2 and 1203.9 a.u., respectively. Subtracting from these values the corresponding CCSD/t-aug-cc-pVTZ $\gamma_{\parallel}(\omega)$ values we obtain for the two frequencies basis-set corrections of -44.0 and -69.5 a.u., respectively. For the remaining frequencies the basis-set correction has been interpolated with the formula

$$\Delta\gamma_{\parallel}^{\text{basis}}(\omega) \approx \Delta\gamma_0^{\text{basis}}\left(1 + a\omega_L^2 + b\omega_L^4\right), \tag{3}$$

where $\omega_L^2 = 6\omega^2$ and $a = 8.99$ a.u. and $b = 61.3$ a.u. The latter values where determined by fitting Eq. (3) to the results for $\omega = 0.043188$ and 0.099505 a.u. The CCSD basis-set corrections are collected in the fifth column of Table 3. To estimate the basis-set corrections to $\gamma_{\parallel}(\omega)$ for the CC3 model we applied the interpolation formula in Eq. (3) using for $\Delta\gamma_0^{\text{basis}}$ the CC3 value obtained above (-32.9 a.u.) and keeping for a and b the CCSD values. The CC3 basis-set corrections obtained in this way are collected in the sixth column of Table 3.

The zero-point vibrational (ZPV) corrections, $\Delta\gamma_{\parallel}^{\text{ZPV}}(\omega)$, to the CCSD values of the hyperpolarizability (both static and frequency-dependent) have been determined in [19] using a CCSD(T)/t-aug-cc-pVTZ potential energy curve and the CCSD/t-aug-cc-pVTZ values of the hyperpolarizability calculated at seven different bond distances (see Tables 12 and 13 in [19]). We used the ZPV corrections from [19] in the present study for the CCSD hyperpolarizabilities (the seventh column of Table 3).

To determine the ZPV corrections for the CC3 model we have calculated (at the CC3/t-aug-cc-pVTZ level) γ_0

Table 3
CCSD and CC3 results for the parallel isotropic average of the frequency-dependent ESHG hyperpolarizability $\gamma_{\parallel}(\omega)$ (a.u.) for N_2

λ (nm)	ω (a.u.)	Pure electronic		Basis-set correction		ZPV correction		Pure electronic + basis-set + ZPV		Exp.[a]
		CCSD	CC3	CCSD	CC3	CCSD	CC3	CCSD	CC3	
∞	0.000000	903.0	931.8	−39.7	−32.9	12.0	14.0	875.3	912.9	917 ± 9[b]
1055.0	0.043188	959.2	992.5	−44.0	−36.5	13.0	15.2	928.2	971.2	
694.3	0.065625	1041.1	1081.1	−50.6	−41.9	14.5	16.9	1005.0	1056.1	1057.6 ± 6.4
632.8	0.072003	1073.1	1115.7	−53.2	−44.0	15.1	17.6	1035.0	1089.3	1095.6 ± 4.6
590.0	0.077226	1102.8	1147.9	−55.6	−46.1	15.6	18.2	1062.8	1120.0	1132.0 ± 4.2
514.5	0.088558	1179.6	1231.7	−61.9	−51.3	17.1	20.0	1134.8	1200.4	1208.7 ± 6.2
488.0	0.093368	1218.1	1273.7	−65.0	−53.9	17.8	20.8	1170.9	1240.6	1253.3 ± 6.3
457.9	0.099505	1273.4	1334.3	−69.5	−57.6	18.8	21.9	1222.7	1298.6	1327.5 ± 14.3

The pure electronic CCSD and CC3 contributions from Table 2 have been corrected for incompleteness of the basis set and zero-point vibrational (ZPV) averaging. The relativistic contribution and the pure rotational and vibrational hyperpolarizability are neglected (see text for a detailed description of the corrections).

[a] Experimental results from [29] and [30].

[b] Experimental static limit obtained by Shelton in [32] by extrapolation from results of [29] corrected for the pure rotational and vibrational contributions.

at four different bond distances: 1.8, 1.9, 2.2 and 2.4 a.u., obtaining values of 724.0, 787.4, 1065.1 and 1330.4 a.u., respectively. Combining these values of γ_0 and the value for the equilibrium geometry (Table 2) with the CCSD(T)/t-aug-cc-pVTZ potential energy curve from [19] we obtained a value of 945.8 a.u. as the vibrational average of γ_0 at the CC3/t-aug-cc-pVTZ level. Subtracting from this vibrational average the value of electronic contribution to γ_0 calculated at the same level of theory (931.8 a.u.; see Table 2), one obtains a ZPV correction of 14 a.u. This should be compared with the ZPV correction obtained in [19] at the CCSD/t-aug-cc-pVTZ level as 12 a.u. The ZPV correction to γ_0 thus changes in this case only by 2 a.u. when going from CCSD to CC3. To estimate the ZPV correction for $\gamma_{\parallel}(\omega)$ at the CC3 level, we have applied a formula analogous to Eq. (3), where we have used for $\Delta\gamma_0^{\mathrm{ZPV}}$ the new value of 14 a.u. and for the coefficients a and b the CCSD results from [19]. The values of the CC3 ZPV corrections obtained in this way are collected in the eighth column of Table 3.

We have estimated the relativistic contribution to $\gamma_{\parallel}(\omega)$ at the CCSD/d-aug-cc-pCVQZ level using direct perturbation theory, following the procedure from [31]. The relativistic contribution is about 1.0 a.u. and is thus in this case negligible compared to remaining correlation and basis set errors.

The CCSD and CC3 results for $\gamma_{\parallel}(\omega)$ corrected for basis-set effects beyond t-aug-cc-pVTZ level and zero-point vibrational averaging are compiled in Table 3 in column nine and ten, respectively, and in Fig. 2. The experimental results of Mizrahi and Shelton [29,30] are also quoted. As expected, the effect of connected triples is crucial for a highly accurate description of the second hyperpolarizability and its dispersion: the CC3 results are in very good agreement with the experimental results, the agreement being much better than in the case of the CCSD model. The CC3 results are 0.1–2.2% smaller than the experimental results, the largest discrepancy occurring for $\omega = 0.099505$ a.u., where also the experimental result has the largest uncertainty. It

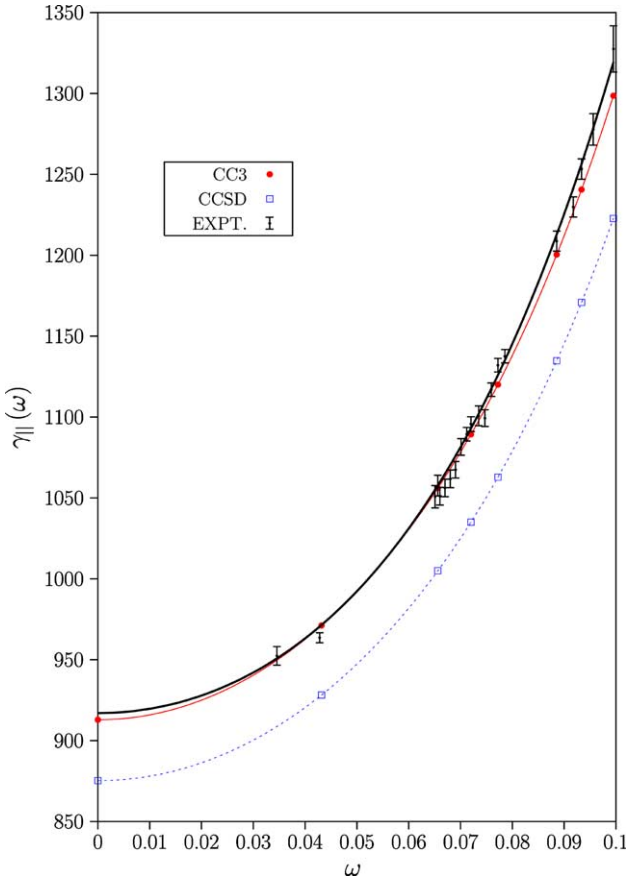


Fig. 2. Comparison of the CCSD and CC3 best estimates for the parallel isotropic average of the ESHG hyperpolarizability of N_2 (Table 3, columns nine and ten, respectively) with experimental results from [29] and [30]. The dispersion curve fitted to the experimental results in [29] corrected for the pure rotational and vibrational contributions [32] is also plotted (the thick line). All numbers in a.u.

should be noted that the experimental results in Table 3 and in Fig. 2 still contain the pure rotational and vibrational contributions which have not been accounted for in the CCSD and CC3 results. However, as shown by Shelton [32], these contributions are for N_2 much smaller than 0.1% and may be neglected.

In Fig. 2 we have also included the (weighted) fit [32] through the experimental results from [29], corrected for the pure rotational and vibrational contributions [32]. The CC3 dispersion curve is very close to the fitted experimental curve. We attribute the remaining discrepancies (of 0.1–2.2%) between the CC3 results and the experimental results to both inaccuracies of experiment and remaining uncertainties in CC3 values from the tenth column of Table 3.

This remaining uncertainty in the CC3 hyperpolarizabilities is mainly due to the higher correlation effects. No FCI results have been reported for the second hyperpolarizability of N_2. Comparison of CC3 and FCI polarizabilities and hyperpolarizabilities for HF, Ne, and BH [33] shows, however, that the CC3 results have very small errors in these benchmark calculations; in fact, the errors in these benchmark calculations were in all cases significantly smaller than one per cent. In [34] and [35] the excitation energies have been reported for the FCI model and cc-pVDZ basis sets augmented with diffuse functions. Comparison of the FCI excitation energies and the ones of the coupled cluster hierarchy CCS, CC2, CCSD, and CC3 showed that the errors in the excitation energies in general decreased by about a factor of 3 at each level. In particular, comparison with the FCI results showed that the error in the CC3 calculations of the lowest singlet transition in N_2 $1^1\Sigma_g^+ \rightarrow 1^1\Pi_g$ was as small as 0.001 a.u. (0.4%). This comparison with FCI results for small molecules as well as the remaining difference of 13 a.u. between the relaxed CCSD(T)/d-aug-cc-pVTZ and the unrelaxed CC3/d-aug-cc-pVTZ results for the static limit (see above) indicate that remaining correlation errors are in the order of 1%.

4. Summary

The electronic dynamic ESHG hyperpolarizabilities of N_2 calculated at the approximate coupled cluster singles, doubles and triples level CC3, corrected for the basis-set effects and zero-point vibrational averaging, are in a very good agreement with the experimental results, the discrepancy ranging from 0.1% to 2.2%. The largest contributions to this discrepancy come from the correlation effects beyond CC3 and uncertainties related to the experimental results. As the best estimate of the static hyperpolarizability of N_2 we obtain 912.9 ± 4.3 a.u. (the uncertainty of 4.3 a.u. accounts for remaining basis set errors, but not for correlation effects beyond CC3). This is within a 1% agreement with the value of 917 ± 9 a.u. extrapolated from the ESHG experiments [32].

Acknowledgements

We thank Stinne Høst for carrying out the relativistic calculations. We acknowledge the support from the European Research and Training Network: 'Understanding Nanomaterials from a Quantum Perspective' (NANOQUANT), contract No. MRTN-CT-2003-506842, and from the Carlsbergfondet. This work was also partly supported by the Danish Natural Research Council (Grant No. 21-02-0467) and the Deutsche Forschungsgemeinschaft (Grant Ha 2588/3-1). We acknowledge the support from the Danish Center for Scientific Computing (DCSC).

References

[1] Y.R. Shen, Principles of Nonlinear Optics, Wiley, New York, 1984.
[2] N.F. Lane, Rev. Mod. Phys. 52 (1980) 29.
[3] G.C. Maitland, M. Rigby, E.B. Smith, W.A. Wakeham, Intermolecular Forces: Their Origin and Determination, Clarendon, Oxford, 1981.
[4] F. Pawłowski, P. Jørgensen, C. Hättig, Chem. Phys. Lett. 391 (2004) 27.
[5] E.F. Archibong, A.J. Thakkar, J. Chem. Phys. 100 (1994) 7471.
[6] T.H. Dunning, J. Chem. Phys. 90 (1989) 1007.
[7] D.E. Woon, T.H. Dunning, J. Chem. Phys. 103 (1995) 4572.
[8] R.A. Kendall, T.H. Dunning, R.J. Harrison, J. Chem. Phys. 96 (1992) 6796.
[9] K.A. Peterson, T.H. Dunning, J. Chem. Phys. 117 (2002) 10548.
[10] T. Helgaker, P. Jørgensen, J. Olsen, Molecular Electronic-Structure Theory, Wiley, New York, 2000.
[11] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1989) 479.
[12] O. Christiansen, P. Jørgensen, C. Hättig, Int. J. Quantum Chem. 68 (1998) 1.
[13] O. Christiansen, A hierarchy of coupled cluster models for accurate calculations of molecular properties, Ph.D. thesis, Aarhus University, Århus, Denmark, August 1997.
[14] O. Christiansen, H. Koch, P. Jørgensen, Chem. Phys. Lett. 243 (1995) 409.
[15] H. Koch, O. Christiansen, P. Jørgensen, A.M. Sanchez de Merás, T. Helgaker, J Chem. Phys. 106 (1997) 1808.
[16] G. Maroulis, J. Chem. Phys. 118 (2003) 2673.
[17] Y. Luo, O. Vahtras, H. Ågren, P. Jørgensen, Chem. Phys. Lett. 205 (1993) 555.
[18] C. Hättig, O. Christiansen, P. Jørgensen, Chem. Phys. Lett. 282 (1998) 139.
[19] C. Hättig, P. Jørgensen, J. Chem. Phys. 109 (1998) 2762.
[20] K.P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules, Van Nostrand, New York, 1979.
[21] T. Helgaker, et al., A Molecular Electronic Structure Program, Release 1.2. Available from: <http://www.kjemi.uio.no/software/dalton/dalton.html>, 2001.

[22] D. Jonsson, P. Norman, H. Ågren, J. Chem. Phys. 105 (1996) 6401.
[23] F. Pawłowski, Development and implementation of CC3 response theory for calculation of frequency-dependent molecular properties. Benchmarking of static molecular properties, Ph.D. Thesis, Aarhus University, Århus, Denmark, February 2004.
[24] K. Hald, P. Jørgensen, O. Christiansen, H. Koch, J. Chem. Phys. 116 (2002) 5963.
[25] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A.K. Wilson, Chem. Phys. Lett. 286 (1998) 243.
[26] A. Rizzo, M. Kállay, J. Gauss, F. Pawłowski, P. Jørgensen, C. Hättig, J. Chem. Phys. 121 (2004) 9461.
[27] E.A. Salter, H. Sekino, R.J. Bartlett, J. Chem. Phys. 87 (1987) 502.
[28] R. Kobayashi, H. Koch, P. Jørgensen, T.J. Lee, Chem. Phys. Lett. 211 (1993) 94.
[29] V. Mizrahi, D.P. Shelton, Phys. Rev. Lett. 55 (1985) 696.
[30] V. Mizrahi, D.P. Shelton, Phys. Rev. A 31 (1985) 3145.
[31] W. Klopper, S. Coriani, T. Helgaker, P. Jørgensen, J. Phys. B: At. Mol. Opt. Phys. 37 (2004) 3753.
[32] D.P. Shelton, Phys. Rev. A 42 (1990) 2578.
[33] H. Larsen, J. Olsen, C. Hättig, P. Jørgensen, O. Christiansen, J. Gauss, J. Chem. Phys. 111 (1999) 1917.
[34] H. Larsen, K. Hald, J. Olsen, P. Jørgensen, J. Chem. Phys. 115 (2001) 3015.
[35] O. Christiansen, H. Koch, P. Jørgensen, J. Olsen, Chem. Phys. Lett. 256 (1996) 185.