30 January 1998

ELSEVIER

Chemical Physics Letters 283 (1998) 109–113

CHEMICAL PHYSICS LETTERS

Estimate of the experimental static hyperpolarizability of neon based on coupled cluster response calculations

Christof Hättig, Poul Jørgensen

Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

Received 13 October 1997; in final form 4 November 1997

Abstract

The frequency-dependent electric field induced second harmonic generation (ESHG) hyperpolarizability of neon is calculated using coupled cluster singles doubles (CCSD) response theory. The CCSD dispersion curve shows that the most recent fit through the experimentally measured ESHG data is too flat due to the fact that one of the measured points in the infrared region is incorrect. Based on the CCSD dispersion curve, we suggest an adjusted extrapolation of the experimental ESHG data to a static limit result of $\gamma_0 = 106.4 \pm 2$ au. This estimate is corroborated by a CCSD(T) calculation using a large one-particle basis set and including core correlation effects that gives 107.1 au. © 1998 Elsevier Science B.V.

1. Introduction

The determination of hyperpolarizabilities of atoms and small molecules is a field that can benefit strongly from an interplay between experiment and theory, first because the determination of absolute hyperpolarizabilities, static or frequency-dependent, within an accuracy of a few percent is difficult both experimentally and in ab initio calculations, and second because theory and experiments provide partly complementary information. In particular, the second hyperpolarizability of neon has been the subject of intensive theoretical and experimental investigations [1–10]. For this atom the first reported experimental dispersion curve obtained from a fit through electric field induced second harmonic generation (ESHG) measurements for five different frequencies [5] gave an anomalous negative dispersion for small frequencies. In disagreement with the experimental observation, ab initio calculations at the MCSCF [3,7] and MP2 [8] level of theory obtained a normal positive dispersion, challenging the abnormal experimental curve. A reinvestigation of the experimental ESHG data for neon by Shelton and Donley [11] showed that the earlier ESHG experiments encountered large systematic errors for three of the frequencies and a new dispersion curve based on a fit through measurements for four frequencies gave a positive dispersion in agreement with the ab initio calculations. The static limit for the hyperpolarizability γ_0 and the first dispersion coefficient A from this fit were also in qualitative agreement with SCF [8], CASSCF [7] and MP2 [8] results. The second dispersion coefficient B was not obtained from a least square fit, but was arbitrarily set to a value between the MP2 and CASSCF results of Refs. [8,7].

However, for two experimental ESHG points in the infrared region at 1319 nm and 1064 nm the error bars do not overlap with the fitted dispersion curve of Shelton and Donley (cf. Table 1 and Fig. 1). Thus at least one of the two measurements must have a larger inaccuracy than indicated by its statisti-

0009-2614/98/$19.00 © 1998 Elsevier Science B.V. All rights reserved.
PII S0009-2614(97)01309-2

Table 1
Electric field induced second harmonic generation hyperpolarizability for neon

λ / nm	ω / au	$\gamma_{\parallel}^{\mathrm{ESHG}}(\omega)$ / au		
		CCSD	MP2 [a]	exp. [b]
∞	0.000000	110.2	110	
1319	0.034544	112.4	112	111.0 ± 0.8
1064	0.042823	113.6	113	109.9 ± 0.5
694.3	0.065625	118.3		126.5 ± 4.1 [c]
590.0	0.077226	121.7		
514.5	0.088558	125.7	123.6	122.2 ± 0.4
488.0	0.093368	127.7		123.5 ± 0.5

[a] Ref. [8,9]. [b] Refs. [5,19,11]. [c] Ref. [20].

cal uncertainty. Due to this disagreement between the two ESHG measurements in the infrared region, the uncertainties of the experimental estimates for the static limit γ_0 and of the dispersion coefficient A were reported as 2% and 10%, respectively and are thus much larger than the uncertainties of the individual measurements of 0.3%–0.8%.

2. Computational methods

We applied the recently implemented CCSD cubic response approach [12] to reinvestigate the dispersion of the ESHG hyperpolarizability of neon. In coupled cluster response theory frequency-dependent second hyperpolarizabilities are obtained as derivatives of the real part of the coupled cluster quasienergy with respect to the field strengths of four electric fields:

$$\gamma_{ijkl}^{\mathrm{CCSD}}(\omega_i;\omega_j,\omega_k,\omega_l) = \left(\frac{\mathrm{d}^4\{\mathrm{Re}\mathscr{W}^{\mathrm{CCSD}}\}_T}{\mathrm{d}f_i(\omega_i)\,\mathrm{d}f_j(\omega_j)\,\mathrm{d}f_k(\omega_k)\,\mathrm{d}f_l(\omega_l)} \right)_0, \quad (1)$$

where $\omega_i = -\omega_j - \omega_k - \omega_l$ and the index 0 indicates that the derivative is taken at zero field strengths. The coupled cluster quasienergy is defined as [12]:

$$\{\mathscr{W}\}_T = \lim_{t_0\to\infty} \int_{-t_0}^{+t_0} \langle HF| \times \left(H - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\exp(T(t,f)) \right) |HF\rangle \,\mathrm{d}t, \quad (2)$$

where $T(t,f)$ is the time- and field-dependent cluster operator and $|HF\rangle$ is the SCF wavefunction for the unperturbed molecule. Thus nonrelaxed SCF orbitals are used in the coupled cluster response calculation and orbital relaxation is therefore accounted for through the single excitation part of the cluster oper-

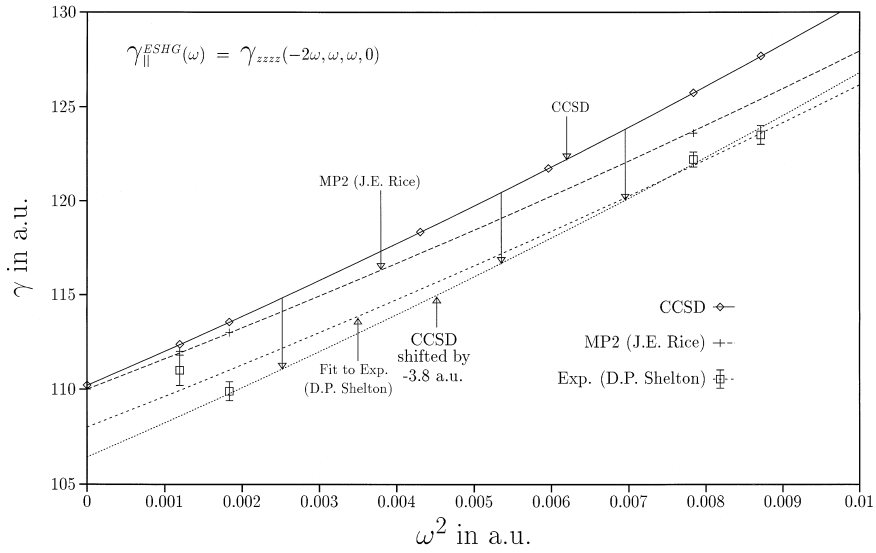


Fig. 1. The electric field induced second harmonic generation hyperpolarizability of neon as a function of frequency.

ator. Evaluation of the derivative in Eq. (1) using Lagrangian techniques and its implementation are detailed in Ref. [12].

For the electric-field induced second harmonic generation process the frequencies have to be chosen as $\omega_i = -2\omega$, $\omega_j = \omega_k = \omega$ and $\omega_l = 0$, where ω is the frequency of the laser light. For atoms the isotropic parallel component $\gamma_{||}$, which was measured in the ESHG experiments, is equal to the cartesian tensor components $\gamma_{zzzz} = \gamma_{yyyy} = \gamma_{xxxx}$. The CCSD dispersion curve was calculated using the triply-augmented correlation consistent polarized valence quintuple zeta (t-aug-cc-pV5Z) basis of Woon and Dunning [13]. This basis set is known to give accurate correlated energies for the unperturbed neon atom and due to the augmentation with three sets of diffuse spdfgh functions we expect a balanced description of the neon atom in electric fields. In the CCSD response calculations for the frequency-dependent hyperpolarizabilities we correlated only the eight valence electrons and kept the 1s electrons frozen.

The dispersion of the isotropic second hyperpolarizability for small frequencies below the first resonance can be described in terms of the coefficients A and B, which are defined by the expansion [14]:

$$\gamma_{||}^{\mathrm{ESHG}}(\omega) = \gamma_0\left(1 + A\omega_{\mathrm{L}}^2 + B\omega_{\mathrm{L}}^4 + \ldots\right), \qquad (3)$$

with $\omega_{\mathrm{L}}^2 = 6\omega^2$ for the ESHG process. While the coefficients A and B are usually found to be less basis set dependent than the static hyperpolarizability γ_0 [15], they are sensitive to the position of the first pole in $\gamma(\omega)$. For ESHG this pole occurs when ω approaches half the transition frequency of the first dipole allowed excitation. Smaller excitation energies will in general lead to larger values of A and B.

In numerous applications, the CCSD response approach has been found to give accurate excitation energies with errors which are often one order of magnitude smaller than at the time-dependent Hartree-Fock (TDHF) level [16,17]. MP2 frequency-dependent properties have poles at the same position as TDHF properties in addition to the poles that occur at the difference between two virtual and two occupied SCF orbital energies [18]. We therefore expect the CCSD cubic response method to give a much more accurate dispersion curve for the second hyperpolarizability than TDHF and MP2 calculations.

3. Results

In Table 1 and Fig. 1 we have compiled the results for the CCSD cubic response calculations compared with the experimental values [5,11,19,20] and the MP2 results of Ref. [8]. The latter results were obtained by combination of a frequency-dependent MP2 calculation with a CCSD(T)/CCSDT estimate for the static hyperpolarizability [9]. The CCSD response calculation gives 110.2 au for the static hyperpolarizability of neon, which is in close agreement to the CCSD(T)/CCSDT result of 110 ± 3 au obtained by Rice et al. [9] and also close to CCSD(T) results obtained by Woon and Dunning [13] (t-aug-cc-pVQZ: 107.3 au, q-aug-cc-pVQZ: 108.3 au). In contrast CCSD finite field calculations with relaxed SCF orbitals give significantly smaller results in the range of 98–103 au [9,13]. We note that the difference between the CCSD calculations with nonrelaxed and those with relaxed orbitals is not an error of the CCSD response approach. Coupled cluster calculations with relaxed and nonrelaxed orbitals define two different hierarchies which both approach the full CI limit, if the cluster expansion approaches completeness in the series CCS, CCSD, CCSDT, etc.

As discussed in the previous section, the slope and the curvature of the dispersion curves are expected to be sensitive to the accuracy of the excitation energy for the first dipole allowed transition. From excitation energy calculations [16] it is known that the predicted lowest excitation energy in neon ($^1\mathrm{S}^{\mathrm{e}} \leftarrow {}^1\mathrm{P}^{\mathrm{o}}$) decreases in the order TDHF $>$ CCSD $>$ full CI with small errors at the CCSD level. In the actual basis set we used, the excitation energy for the ($^1\mathrm{S}^{\mathrm{e}} \leftarrow {}^1\mathrm{P}^{\mathrm{o}}$) transition is obtained at the RPA or TDHF level as 18.34 eV and on the CCSD level as 16.74 eV, compared to the experimental value of 16.85 eV [21]. Accordingly, we expect an increase of the dispersion coefficients A and B if we go from TDHF or MP2 to a CCSD dispersion curve and the CCSD results are expected to overestimate only slightly the exact value. As can be seen from Fig. 1 and Table 2, the CCSD dispersion curve is indeed

Table 2
Dispersion coefficients [a] for the ESHG hyperpolarizability for neon

Method	γ_0	A	B
SCF [b]	68.7	2.28	4.72
CASSCF [c]	96.6	2.55	5.94
MP2 [b]	110.4	2.40	5.33
CCSD [d]	110.2	2.70	5.58
fit to exp. [e]	108.1 ± 2.2	2.47 ± 0.25	–

[a] For the definition of A and B see Eq. (3).
[b] Refs. [9,8,15].
[c] Ref. [7].
[d] This work, obtained from a least square fit of the calculated seven points to $\gamma(\omega) = \gamma_0(1 + \mathrm{A}\,\omega_\mathrm{L}^2 + \mathrm{B}\,\omega_\mathrm{L}^4 + \mathrm{C}\,\omega_\mathrm{L}^6)$.
[e] Refs. [11], only γ_0 and A were obtained from a least square fit; B was arbitrarily set to a value between the CASSCF and MP2 results (5.50 au).

significantly steeper than the MP2 dispersion curve which itself is somewhat steeper than the SCF curve obtained with the same basis set [8]. The CASSCF dispersion curve of Ref. [7] has a slope and a curvature which are halfway between the MP2 and CCSD results.

Unexpectedly, the fit through the experimental points is significantly less steep than the CCSD dispersion curve and the A coefficient extracted from this fit is bracketed by the MP2 and CASSCF results. As mentioned in the introduction, the experimental value for A has a large uncertainty because the error bars for the infrared measurements do not overlap with the fitted curve. Shelton and Donley have also noted this and pointed out that this might be the result of possible unaccounted systematic errors in those measurements [11]. Although the CCSD calculation may be only accurate within an uncertainty of a few percent for the static hyperpolarizability, the slope and the curvature of the dispersion curve should be significantly more accurate than those of previous ab initio calculations and also more reliable than the value obtained from the fit through the four experimental points. Shifting the CCSD dispersion curve until it matches the two points measured in the visible at $\lambda = 514.5$ and 488.0 nm, therefore should give a more accurate extrapolation to the static limit. With a shift of -3.8 au we obtained a dispersion curve which matches not only the two points in the visible, but also the point measured at $\lambda = 1056$ nm within its statistical uncertainty, while the fourth point at $\lambda = 1319$ nm lies significantly above this curve. From this observation we conclude that it is the latter point which has a larger error than indicated by its statistical error bar.

Therefore, we suggest to exclude this point from a fit and to change the extrapolated static limit γ_0 from 108 ± 2 to 106.4 ± 2 au. We note, that this refined estimate for the static limit as well as the A coefficient from the CCSD dispersion curve are within the statistical uncertainties of the original fit. The extrapolated estimate of 106.4 ± 2 au for the static hyperpolarizability is slightly smaller than the results obtained in recent CCSD(T)/CCSDT calculations by Rice et al. (110 ± 3 au) [9] and Woon and Dunning (109.4 au as estimated x-aug-pVQZ limit) [13]. However, intensive basis set studies by Woon and Dunning show that basis sets obtained from triple or quadruple zeta basis sets by successive augmentation with diffuse functions tend to overestimate isotropic hyperpolarizabilities in correlated calculations and a more accurate description of the valence orbitals is needed to obtain results within one or two percent of the respective basis set limit result. To test the new extrapolation to the static limit, we performed CCSD(T) finite difference calculations in the t-aug-cc-pV5Z basis set, used for the CCSD response calculations. Correlating only the eight valence electrons, we obtained a result of 107.7 au. If in the same basis set also the $1s$ electrons are correlated, the result decreases to 107.2 au. The inclusion of core correlation functions changes the value for γ_0 to 107.1 au. Based on these calculations we expect that the CCSD(T) basis set limit for γ_0 is less than 107 au, in good agreement with the value obtained from the extrapolation of the experimental results using the CCSD dispersion curve.

4. Conclusions

We have calculated an accurate dispersion curve for the second hyperpolarizability of the neon atom using the CCSD cubic response approach and a large one-particle basis set. From a comparison of the CCSD dispersion curve with the results of recent ESHG measurements we conclude that one of the

points measured in the infrared region is less accurate than its statistical uncertainty indicates. Combining the remaining three ESHG measurements with the CCSD dispersion curve, we obtained a refined extrapolation to the static limit of 106.4 ± 2 au. This estimate is corroborated by the result of a CCSD(T) calculation using a large one-particle basis set and including core correlation which gives a result of 107.1 au.

After completion of the manuscript we became aware of a CCSD(T)-R12 benchmark finite field calculation by Müller et al. [22] for the static second hyperpolarizability of neon. Using an uncontracted (21s15p9d8f) basis set and correlating all electrons they obtained $\gamma_0 = 104.7$ au which is expected to be close to the CCSD(T) basis set limit. This result is in good agreement with our results and in particular with the extrapolation of the experimental values using the CCSD dispersion curve.

Acknowledgements

One of the authors (CH) thanks the European Commission for financial support through the Training and Mobility of Researchers (TMR) Programm (ERBFMBICT 96.1066). The work has been partly supported by the Danish natural research council (Grant No. 9600856).

References

[1] A.D. Buckingham, D.A. Dunmur, Trans. Faraday Soc. 64 (1968) 1776.
[2] J.F. Ward, G.H.C. New, Phys. Rev. 185 (1969) 57.
[3] M. Jaszuński, D.L. Yeager, Phys. Rev. A 40 (1989) 1651.
[4] P.R. Taylor, T.J. Lee, J.E. Rice, J. Almlöf, Chem. Phys. Lett. 163 (1989) 359.
[5] D.P. Shelton, Phys. Rev. A 42 (1990) 2578.
[6] D.M. Bishop, Phys. Rev. Lett. 65 (1990) 1688.
[7] H.J.A. Jensen, P. Jørgensen, H. Hettema, J. Olsen, Chem. Phys. Lett. 187 (1991) 387.
[8] J.E. Rice, J. Chem. Phys. 96 (1992) 7580.
[9] J.E. Rice, G.E. Scuseria, T.J. Lee, P.R. Taylor, J. Almlöf, Chem. Phys. Lett. 191 (1992) 23.
[10] O. Christiansen, P. Jørgensen, Chem. Phys. Lett. 207 (1993) 367.
[11] D.P. Shelton, E.A. Donley, Chem. Phys. Lett. 195 (1992) 591.
[12] C. Hättig, O. Christiansen, P. Jørgensen, Chem. Phys. Lett., accepted.
[13] D.E. Woon, T.H. Dunning, J. Chem. Phys. 100 (1994) 2975.
[14] D.M. Bishop, J. Chem. Phys. 90 (1989) 3192.
[15] D.P. Shelton, J.E. Rice, Chem. Rev. 94 (1994) 3.
[16] H. Koch, O. Christiansen, P. Jørgensen, Chem. Phys. Lett. 244 (1995) 75.
[17] O. Christiansen, H. Koch, P. Jørgensen, J. Olsen, Chem. Phys. Lett. 256 (1996) 185.
[18] C. Hättig, B.A. Heß, Chem. Phys. Lett. 233 (1995) 359.
[19] D.P. Shelton, Phys. Rev. Lett. 62 (1989) 2660.
[20] R.S. Finn, J.F. Ward, Phys. Rev. Lett. 26 (1971) 285.
[21] C.E. Moore, Natl. Bur. Stand. (US), Washington, 1949, Circ. 467.
[22] H. Müller, J. Noga, W. Kutzelnigg, to be published.