

The hyperpolarizability of *trans*-butadiene rerevisited

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It has been stated that TDHF results for the dynamic second hyperpolarizability $\gamma_{||}$ of *trans*-butadiene provide superior results to those obtained with electron correlation [P. Norman *et al.* *J. Chem. Phys.* **106**, 1827 (1997)]. Using the newly developed correlated frequency dependent EOM-CCSD method we critically address this question. Using three geometries and three basis sets to assess the importance of the right choice of these parameters, and estimating orbital relaxation, triple excitations and vibrational contributions, unlike TDHF, the EOM-CCSD method provides excellent agreement with experiment. The average $\gamma_{||}$ at the experimental geometry in our best basis is 20.3 at $\omega=0.043$ a.u. and 28.0 at $\omega=0.0656$ a.u. compared to experimental values of 20.2 ± 0.1 and 27.7 ± 1.6 , respectively. © 1998 American Institute of Physics. [S0021-9606(98)01715-2]

I. INTRODUCTION

Trans-butadiene has served for many years as the prototype system for polyenes which have attractive intrinsic non-linear optical properties (NLO). Clearly, if quantum chemistry is to play a role in the design of NLO materials, it must be able to correctly account for butadiene's hyperpolarizability.

However, it has been pointed out in several papers¹⁻³ that *trans*-butadiene's theoretically determined hyperpolarizability behaves differently compared to several other molecules.^{4,3} Whereas for N₂, CO, CO₂, H₂, HF, HCl, NH₃, H₂O and others, correlation effects evaluated with MBPT or CC theory provides substantial improvement compared to experiment,^{4,3} as they should, for butadiene correlation appears to hurt the agreement, as the uncorrelated TDHF value for $\gamma_{||}$ for butadiene (and to a lesser extent ethylene) appears to give very good agreement with experiment while MBPT(2) and CCSD appears to change this value dramatically.^{1,2} Furthermore, recently, Norman *et al.*⁵ made the statement with reference to TDHF that "...None of the more sophisticated correlating methods are able to match this accuracy....," implying that TDHF applied to dynamic hyperpolarizabilities of *trans*-butadiene and other linear polyenes provide accuracy exceeding that of highly-correlated coupled cluster methods.

The history of quantum chemistry is checkered by many examples of excellent, but accidental agreement between theory and experiment, largely based on fortuitous cancellation of errors. If TDHF "gets the right answer for the right reason," then all correlation effects must effectively vanish, which seems highly unlikely. To answer this question, a more detailed study is necessary, taking into consideration basis set effects, vibrational corrections, higher excitation contributions, and molecular geometry. Although it has been possible to do MBPT and coupled cluster calculations of static hyperpolarizabilities for a long time,^{6,1,4} a consistent approach to dynamic processes has not been possible until recently.^{2,7,8} We can now calculate frequency dependent hyperpolarizabilities for any order and any process, recursively,

using the EOM-CCSD method.⁹⁻¹² Hence, we are now in a position to offer more definitive correlated results.

II. HYPERPOLARIZABILITIES

The average hyperpolarizability of *trans*-butadiene in C_{2h} symmetry for the dc-SHG process is defined as

$$\gamma_{||}(-2\omega; \omega, \omega, 0) = \frac{1}{5} (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + \gamma_{xxyy} + \gamma_{yyxx} + \gamma_{xxzz} + \gamma_{zzxx} + \gamma_{yyzz} + \gamma_{zzyy}). \quad (1)$$

The actual working equation for a single component of the dc-SHG process is quite simple when based upon the standard perturbation expression.^{12,7} For a nonpolar molecule

$$\begin{aligned} \gamma_{zzzz}(-2\omega; \omega, \omega, 0) &= P(\omega) [\langle 0 | (1 + \Lambda) \tilde{q}_z R(-2\omega) \tilde{q}_z R(-\omega) \tilde{q}_z R(0) \tilde{q}_z | 0 \rangle \\ &\quad - \langle 0 | (1 + \Lambda) \tilde{q}_z R(-2\omega) \tilde{q}_z | 0 \rangle \\ &\quad \times \langle 0 | (1 + \Lambda) R(-\omega) \tilde{q}_z R(\omega) \tilde{q}_z | 0 \rangle \\ &\quad - \langle 0 | (1 + \Lambda) \tilde{q}_z R(-2\omega) \tilde{q}_z | 0 \rangle \\ &\quad \times \langle 0 | (1 + \Lambda) \tilde{q}_z R(-\omega) R(\omega) \tilde{q}_z | 0 \rangle], \end{aligned} \quad (2)$$

where the permutation operator $P(\omega)$ permutes the frequencies $(-2\omega; \omega, \omega, 0)$ with their associated spatial subscripts (here: z, z, z, z). Similarly, we can readily evaluate the THG, IDRI, and EOKe processes. In the above expression $R_0(n\omega)$ is a frequency-dependent resolvent,

$$R_0(\pm n\omega) = |\mathbf{h}\rangle \langle \mathbf{h} | E_{cc} - \bar{H} \pm n\omega | \mathbf{h}\rangle^{-1} \langle \mathbf{h} |. \quad (3)$$

In our current calculations we employ three sets of basis functions: that previously used in *trans*-butadiene calculations^{13,1,2} 6-31G+(P, D) basis [$3s3p1d/2s$], obtained by augmenting the standard 6-31G set by one p and one d Gaussian with the exponent $\zeta=0.05$, the standard POL1 set¹⁴ [$5s3p2d/3s2p$] and finally, the doubly augmented POL1 set [$5s4p3d1f/5s4p1d$], denoted POL1++ (Ref. 7) here. The geometry plays an important role in these calculations, especially the TDHF ones. We choose the three

TABLE I. Geometry of the *trans*-butadiene molecule at various levels of optimization.

Variable	SCF (I)	CCSD (II)	Expt ^a (III)
C ₂ -C ₃	1.465Å	1.481Å	1.467Å
C ₁ -C ₂ =	1.327Å	1.361Å	1.343Å
C ₃ -C ₄			
C ₁ -C ₂ -C ₃	124.3°	124.0°	122.8°

^aReference 15.

sets of coordinates in Table I, that obtained by the SCF optimization in 6-31G basis (geometry I) previously used, that obtained by a CCSD optimization in the 6-31G+(*P,D*) basis (geometry II), and the “experimental” geometry from Haugen and Traetteberg.¹⁵

III. RESULTS AND DISCUSSION

In the small basis set originally used, 6-31G+(*P,D*) (Refs. 1, 2) the static EOM-CC averaged hyperpolarizability is 19.61 (here we assume the units of 10³ a.u.), whereas the corresponding SCF result is 13.62. Our previous studies⁷ show a large effect of including the Cartesian component of the *d* shell in smaller basis sets. Introducing this component the EOM-CC and SCF hyperpolarizabilities are 20.17 and 14.81, respectively.

The essence of the controversy is that for dc-SHG the TDHF results in the 6-31G+(*P,D*) Cartesian basis, at $\omega = 0.0430$ a.u. and $\omega = 0.0656$ a.u. are 18.2 and 24.9, which are in reasonable agreement with experiment (20.2 and 27.7, respectively). The above static MBPT(2) correlated results in this basis augmented by the percentage TDHF dispersion to estimate the correlated dc-SHG results, were substantially in error at 25.3 and 34.8, respectively.¹ Of course, there are many potential sources of error in such a calculation, particularly the dispersion estimates, and a different estimate of the dispersion,² based upon the relation of Bishop,¹⁶ plus CCSD instead of MBPT(2), reduced the correlated value to 24.3 and 29.7, in better agreement with experiment. However, neither of these results is satisfactory, as the proper result comes from a correlated, frequency dependent calculation. In order to obtain a more definitive result, we consider much larger basis sets and geometry effects, as well as the correlated frequency dependence.

Table II presents 6-31G+(*P,D*) TDHF and EOM-CCSD frequency dependent hyperpolarizabilities in the three different basis sets at geometry I. Since the POL1 and POL1++ sets do not show such large differences, we limit ourselves to the spherical components only. For TDHF the 6-31G+(*P,D*) dc-SHG results always lie below the experimental values and it appears that the POL1++ basis is converged since the difference between POL1 and POL1++ is

TABLE II. Static and dynamic hyperpolarizabilities of *trans*-butadiene (in 10³ a.u.) in geometry I. In parentheses, values obtained with all 6 Cartesian components of the *d* shell.

		THG	dc-SHG	IDRI	EOKE
TDHF					
0.0000	6-31G+(<i>P,D</i>)	13.62(14.81)	13.62(14.81)	13.62(14.81)	13.62(14.81)
	POL1	13.92	13.92	13.92	13.92
	POL1++	13.70	13.70	13.70	13.70
0.0430	6-31G+(<i>P,D</i>)	20.78(22.96)	16.53(18.2)	15.45(16.89)	14.49(15.80)
	POL1	22.33	17.29	16.02	14.91
	POL1++	22.37	17.14	15.84	14.71
	expt		20.18 ^a		
0.0656	6-31G+(<i>P,D</i>)	55.21(62.58)	22.46(24.93)	18.55(20.47)	15.80(17.28)
	POL1	64.49	24.44	19.73	16.42
	POL1++	74.50	24.60	19.67	16.25
	expt		27.70 ^a		
0.0882	6-31G+(<i>P,D</i>)	35.87	40.92	25.03	18.02
	POL1	140.14	49.24	28.14	19.03
	POL1++	40.72	51.67	28.59	18.94
EOM-CC					
0.0000	6-31G+(<i>P,D</i>)	19.61	19.61	19.61	19.61
	POL1	17.32	17.32	17.32	17.32
	POL1++	18.17	18.17	18.17	18.17
0.0430	6-31G+(<i>P,D</i>)	27.00	22.59	22.00	20.74
	POL1	39.27	20.57	19.55	19.11
	POL1++	36.74	22.45	20.56	19.29
	expt		20.18 ^a		
0.0656	6-31G+(<i>P,D</i>)	40.81	29.19	26.22	22.51
	POL1	36.46	26.63	23.32	20.77
	POL1++	39.31	27.76	24.57	20.99
	expt		27.70 ^a		
0.0882	6-31G+(<i>P,D</i>)	93.63	43.68	33.24	26.27
	POL1	101.31	36.82	29.48	23.04
	POL1++	104.40	45.50	31.35	24.76

^aReferences 19 and 20.

TABLE III. Static and dynamic hyperpolarizabilities of *trans*-butadiene (in 10^3 a.u.) in geometry II. Upper row, TDHF values; lower row, EOM-CCSD values.

Process	6-31G+(<i>P,D</i>)	POL1	POL1++	Exp ^a
static, $\omega=0$	16.42	15.46	15.29	...
	18.43	17.19	18.06	
dc-SHG, $\omega=0.0430$	20.41	19.54	19.47	20.18±0.11
	22.04	20.95	21.18	
dc-SHG, $\omega=0.0656$	29.01	28.66	29.04	27.70±1.60
	29.73	28.61	29.56	

^aReferences 19 and 20.

always quite small. On the other hand, the EOM values tend to oscillate with a minimum at the POL1 values.

In order to assess the geometry effect the dc-SHG values given in Table II for geometry I may be compared with those for geometries II and III given in Tables III and IV, respectively. [The TDHF values of $\gamma(0)$ in the 6-31G+(*P,D*) basis have a quite large range; from 14.81 at the SCF optimized geometry to 16.42 at the CCSD geometry.] The EOM results vary very little with geometry being 18.9 ± 0.5 . As the basis size increases from POL1 to POL1++, the TDHF static hyperpolarizabilities appear to be well converged, while EOM results increase by almost 5% in all geometries. Our EOM-CCSD values of $\gamma(0)$ in the POL1 basis are close to those obtained by finite differentiation of the CCSD energy by Kirtman *et al.*¹⁷ Our results of 17.32, 17.19, and 17.24 in geometries I, II, and III, respectively, are close to the value of 18.0 obtained therein. Hence, these numbers show very little effect of the non-Hellmann–Feynman terms, that are due to orbital and additional CC amplitude response,¹⁸ that are excluded here, but would be included in the numerical derivatives as discussed elsewhere.⁷

Table II contains the values for four fourth-order processes. Third harmonic generation (THG) $\gamma(-3\omega;\omega,\omega,\omega)$, dc induced second harmonic generation (dc-SHG) $\gamma(-2\omega;\omega,\omega,0)$, intensity dependent refractive index (IDRI) $\gamma(-\omega;\omega,-\omega,\omega)$, and the electro-optic Kerr effect (EOKE)

TABLE IV. Second hyperpolarizabilities of *trans*-butadiene at the experimental geometry (III). Upper row-TDHF values; lower row, EOM-CCSD values.

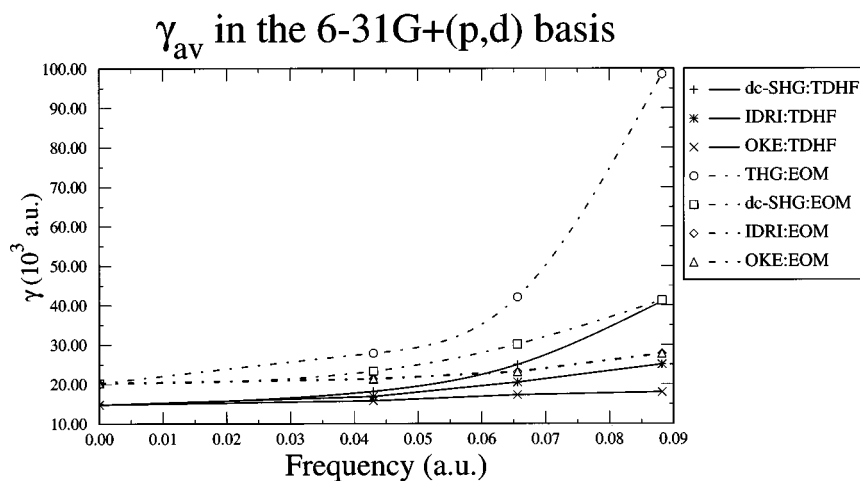
Process	6-31G+(<i>P,D</i>)	POL1	POL1++	Exp ^a
static, $\omega=0$	16.09	14.62	14.52	...
	18.60	17.24	18.13	
dc-SHG, $\omega=0.0430$	20.00	18.33	18.28	20.18±0.11
	22.09	20.26	21.27	
dc-SHG, $\omega=0.0656$	28.42	26.42	27.54	27.70±1.60
	30.23	27.96	29.63	

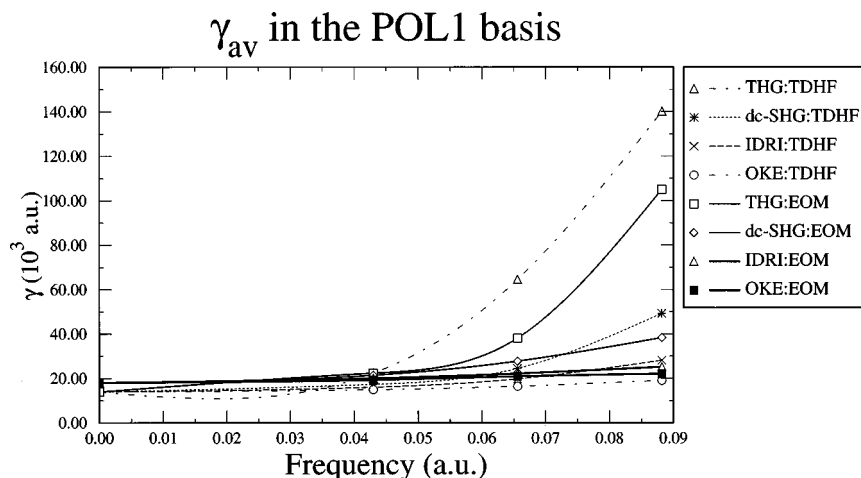
^aReferences 19 and 20.

$\gamma(-\omega;\omega,0,0)$. The dc induced optical rectification (dcOR) $\gamma(0;\omega,-\omega,0)$ after averaging is the same as EOKE so it will not be considered separately.

For 1,3-*trans*-butadiene the experimental values have been determined only for the dc-SHG process^{19,20} by the dc electric-field induced optical SHG experiment. The effect at the ruby-laser frequency (0.0656 a.u.) is 27.7 ± 1.6 while at 0.0430 a.u. it is 20.2 ± 0.1 . In the SCF optimized geometry (Table II) the TDHF values are consistently ~ 3 units too small compared to experiment, while EOM values are larger by about 1–3 units. At the CCSD and experimental geometry the EOM values for dc-SHG are systematically larger than experiment whereas the TDHF values may be either larger or smaller. Moving from the 6-31G+(*P,D*) basis to POL1 generally improves the EOM results. Adding extra functions to the POL1 basis increases the EOM-CCSD results by 1–2 units.

For *trans*-butadiene, the only previous correlated frequency dependent hyperpolarizability calculation was evaluated by finite field differentiation of the frequency dependent linear polarizability² to give values for the electro-optic Kerr effect (EOKE); they are 20.7, 21.9, and 23.7 at frequencies $\omega=0.0$, $\omega=0.0430$, and $\omega=0.0656$, respectively, in the 6-31+(*P,D*) basis. Our current results, 19.6, 20.7, and 22.5 are within 6% of the previous values and again show little importance of the non-Hellmann–Feynman terms that are

FIG. 1. Average dynamic hyperpolarizability of *trans*-butadiene in the 6-31 G+(*P,D*) basis set.

FIG. 2. Average dynamic hyperpolarizability of *trans*-butadiene in the POL1 basis set.

neglected in the analytical EOM-CC CI-like expression.⁷

Figures 1–3 show the frequency dependence of the relevant fourth-order processes of *trans*-butadiene in all three basis sets in the 6-31G+(*P,D*) optimized geometry. The TDHF dispersion is too high (27% in the POL++ basis compared to 17% for EOM at $\omega=0.0430$ a.u. and 90% compared to 64% at $\omega=0.0656$ a.u.), which would also cause an estimated percentage dispersion effect based upon TDHF superimposed on static correlated results to overshoot. That is primarily why the original MBPT(2) estimate of dc-SHG for butadiene was too large at 38.4,¹ or the CCSD result at 34.8.² The alternative estimate of dispersion provided by Bishop's formula¹⁶ based upon EOM-CCSD results for OKE (Ref. 2) led to a 29.7 value. The formula is

$$\gamma_{\parallel}(-\omega_{\sigma}; \omega_1, \omega_2, \omega_3) = \gamma(0)(1 + A\omega_L^2 + B\omega_L^4 + \dots), \quad (4)$$

$$\omega_L^2 = \omega_{\sigma}^2 + \omega_1^2 + \omega_2^2 + \omega_3^2.$$

For small frequencies we can set $B=0$ and evaluate A in a straightforward manner. For the EOM method, at $\omega=0.0656$ a.u., the A coefficient ranges from 18 to 22 depending on the process and basis set. The TDHF values are

on the other hand scattered widely, especially for multiphoton processes like THG. The TDHF A value for EOKE is 22 but for THG in the POL1++ basis it jumps to 86, making any predictions based on Eq. (4) with TDHF completely unreliable. A similar trend can be observed at any frequency studied; at $\omega=0.0430$ a.u. TDHF values of A range from 17 to 29 while EOM is more consistent placing them between 14 and 17. At the 0.0430 a.u. field strength A varies between 14 and 17, that is 18%, while TDHF varies between 17 and 29, giving a 70% error. This means that if we try to use the A coefficient extracted from the TDHF EOKE value (smallest A) and use Bishop's formula to calculate the third harmonic generation (largest value of A), we get an answer with such an error. The 18% error of EOM-CC is also large, but we would expect to reduce it by including the quartic term $B\omega_L^4$. For the higher frequency, $\omega=0.0656$ a.u. the inferior behavior of TDHF is even more evident; while the error in estimating the computed frequencies in the EOM-CCSD is 22%, TDHF variations of 22–86 units give 291% error for TDHF. Clearly, TDHF fails to deliver the accuracy expected from a modern *ab initio* method.

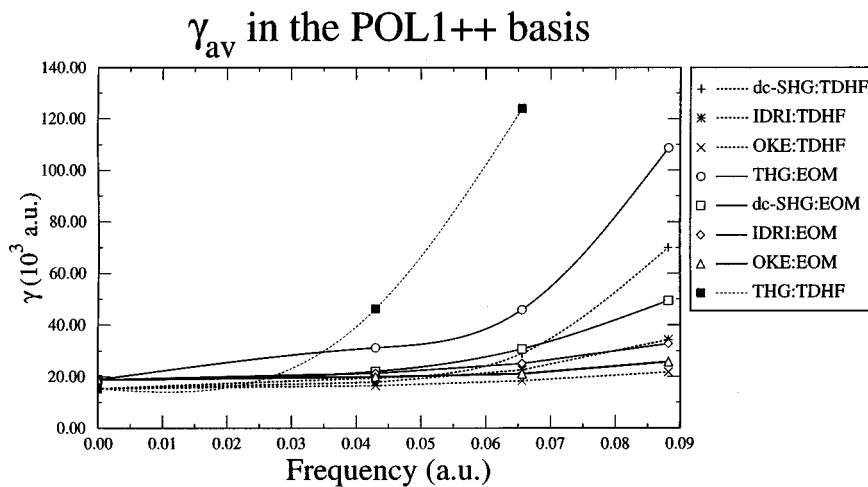
FIG. 3. Average dynamic hyperpolarizability of *trans*-butadiene in the POL1++ basis set.

TABLE V. Adjusted values of dynamic hyperpolarizabilities (dc-SHG) for *trans*-butadiene in the POL1++ basis.

	EOM-CCSD	Vibrations ^a	Triples ^b	Relaxation ^c	Total ^d
		geom I			
$\omega=0.0430$	22.45	-0.50	0.84	-1.55	21.24
$\omega=0.0656$	27.76	-0.40	1.09	-1.55	26.90
		geom II			
$\omega=0.0430$	21.18	-0.50	0.84	-1.55	19.97 ^e
$\omega=0.0656$	29.56	-0.40	1.09	-1.55	28.70 ^e
		geom III			
$\omega=0.0430$	21.27	-0.50	0.84	-1.55	20.06 ^e
$\omega=0.0656$	29.63	-0.40	1.09	-1.55	28.77 ^e

^aFrom B. Kirtman, J. L. Toto, C. Breneman, C. P. de Melo, and D. M. Bishop, *J. Chem. Phys.* (in press).

^bEstimated from the finite derivatives of the dipole moment in the 6-31G+(*P,D*) basis at geometry I, by the difference between μ for CCSD(T) and CCSD augmented by the EOM-CCSD percentage dispersion correction, 15.1% at 0.043 a.u. and 48.8% at 0.0656 a.u.

^cEstimated from the finite derivatives of the dipole moment in the 6-31G+(*P,D*) basis at geometry I, at CCSD.

^dThese should be compared to experimental values, 20.18 ± 0.11 at $\omega = 0.0430$ a.u. and 27.70 ± 1.60 at $\omega = 0.0656$ a.u.

^eIt has been pointed out to us by the authors of Ref. 17 that their estimates for the correlated values (using a slightly different geometry), are 21.2 and 29.8 at $\omega = 0.0430$ and at $\omega = 0.0656$, respectively. These results are in good agreement with ours.

To assess two additional important effects, relaxation and triple excitations, we performed a series of finite field differentiations of the dipole moment (Table V). In the 6-31G+(*P,D*) basis at geometry I orbital relaxation in CCSD decreases the $\gamma(0)$ value by about 7.9% to 18.7. Calculating the CCSD(T) hyperpolarizability with relaxed orbitals gives 19.2, which is 5.4% smaller than the EOM-CCSD unrelaxed figure. For dynamic processes values of these effects only offer estimates. The triples correction was scaled by the percentage dispersion of the EOM-CCSD result to account for frequency dependence, while the orbital relaxation was left constant for all frequencies and geometries.

When the effect of relaxation and triples is included, along with the pure vibrational corrections,¹⁷ one gets the POL1++ values for dc-SHG (we exclude here any zero point vibrational correction) shown in Table V. The excellent agreement of these values with experiment is evident. TDHF hyperpolarizabilities already contain the relaxation effect,

TABLE VI. Excitation energies of *trans*-butadiene at the experimental geometry. Upper row, TDHF values; lower row, EOM-CC values.

Mode	6-31G(<i>P,D</i>)	POL1	POL1++	CCSD ^a	CCSDT-3 ^b	Expt ^c
2A _g	7.44	7.23	7.07			
	6.93	7.03	6.98	7.23	6.85	7.3
1A _u	6.85	6.54	6.47			
	6.41	6.59	6.57	6.61	6.59	6.66
1B _g	6.65	6.21	6.16			
	6.22	6.30	6.27	6.40	6.37	6.27
1B _u	6.07	5.94	5.92			
	6.62	6.37	6.34	6.42	6.35	5.92

^aIn an augmented ANO basis, Ref. 23.

^bIn an augmented ANO basis, Ref. 24.

^cReference 25.

while subtracting the pure vibrational contribution will give 16.6, 19.0, 17.8, and 24.2, 28.6, and 27.1 at the three geometries.

As an indirect measure of accuracy for hyperpolarizabilities, we can consider some of the low-lying excitation energies provided by different methods. Table VI contains the results; the upper (roman font) row contains uncorrelated TDHF values, the lower, italicized, corresponding to the EOM-CC energies. At the experimental geometry the TDHF seems to offer better agreement with the experiment than EOM-CCSD, especially in the smallest basis set, the 6-31G+(*P,D*). Even the notoriously difficult Rydberg-valence mixed B_u state²¹ has an error of only 0.15 eV, compared to 0.70 eV error on the EOM-CCSD level. Only one CC result obtains less than 6.0 eV [the two-determinant CCSD (TD-CCSD) result is 5.88 eV (Ref. 22) at a different geometry], but it is unlikely that TDHF gets this result for the right reason.

Watts *et al.*²³ have calculated partial triple excitation contributions to the excitation energies of *trans*-butadiene in an ANO basis set. These are shown in Table VI for the iterative EOM-CCSDT-3 method²⁴ to help assess any significant role for triple excitations. The best results ANO/CCSDT-3 and POL1++/CCSD are quite consistent.

IV. SUMMARY

In this paper we have presented EOM-CCSD correlated, frequency dependent results for four nonlinear optical processes and compared those to the corresponding TDHF results. We show dispersion curves up to 0.0882 a.u. Furthermore, we estimate the numerical effects of triple excitations while assuming constant orbital relaxation (this effect would be expected to differ at different frequencies and would vanish at the full CI limit), so we have to avoid claiming too high an accuracy in these calculations. However, the estimates affect the CCSD results by no more than ± 2 units, which seem to be a reasonable error for additional basis sets, geometry and correlation effects, too. Hence, at *any* estimated equilibrium geometry, the adjusted EOM-CCSD dc-SHG results average 20.4 ± 2 at $\omega = 0.0430$ a.u. compared to experiment, 20.18 ± 0.11 and 28.1 ± 2 at $\omega = 0.0656$ a.u. compared to 27.70 ± 1.60 . The corresponding TDHF results average 17.8 and 26.6, respectively, but are more accurate at the CCSD and experimental geometries.

Although the final averaged values are not too different, the TDHF being somewhat low and the EOM-CC being slightly high, compared to the rather old experimental value, the consistency of the EOM-CC with basis and geometry, and with it offering more consistent A factors in Eq. (4), attest to the greater reliability of the correlated result.

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