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Chain length dependence of static longitudinal polarizabilities and hyperpolarizabilities in linear polyynes

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Ab initio calculations of the static longitudinal dipole polarizability α_L and second dipole hyperpolarizability γ_L are reported for the linear $C_{2n}H_2$ polyynes up to $C_{44}H_2$. Basis set requirements diminish with increasing chain length. The intermediate neglect of differential overlap (INDO) method is able to mimic the *ab initio* results if the Ohno–Klopman parameterization is used. The values per acetylenic linkage, α_L/n and γ_L/n , converge very slowly with chain length; they are extrapolated to the infinite chain limit.

I. INTRODUCTION

Materials with relatively large linear and nonlinear response properties are of widespread interest particularly in connection with telecommunications and device technology.¹ Organic molecules with delocalized π electrons, such as conjugated chains, almost invariably have large dipole polarizabilities and hyperpolarizabilities.² The dependence of these electric properties upon the chain length needs to be better understood to aid the design of more promising optoelectronic materials. High accuracy *ab initio* calculations, using large one-particle basis sets and including the effects of electron correlation, could lead to such an understanding. Unfortunately such calculations are not feasible currently for long-chain molecules, and hence simpler models are used for the prediction of their polarizabilities and susceptibilities.³

Linear $C_{2n}H_2$ polyynes provide a particularly simple example of chains with conjugated π systems. Some *ab initio* studies of the electric properties of very short linear polyynes have already been published.^{4–9} Two heartening features have emerged from these and other studies. Electron correlation plays only a minor role in the dipole polarizabilities and hyperpolarizabilities of acetylene^{7,8} and butadiyne,^{7,9} and presumably the higher members of the $C_{2n}H_2$ series as well. Moreover as the chain length increases, intramolecular polarization becomes relatively more important and the basis set requirements for meaningful calculations of the longitudinal, but not transverse, polarizabilities decrease.^{6,9–12}

These two observations entice one to believe that coupled Hartree–Fock (CHF) calculations in a relatively small basis set may be adequate to study the chain length dependence of the longitudinal polarizabilities of the linear polyynes. The purpose of this paper is to report such a study of the linear polyynes from C_4H_2 to $C_{44}H_2$. We begin with a very brief review of polarizabilities and the finite-field method in Sec. II. The selection of a relatively small basis set that is adequate for the longitudinal polarizabilities of the $C_{2n}H_2$ polyynes is made and justified in Sec. III. The results and a discussion of the growth of the electric properties with chain length are given in Sec. IV. Hartree atomic units are used throughout.

II. METHOD

The energy E_p of a neutral centrosymmetric molecule in a weak, homogeneous electric field may be written¹³ as

$$E_p = E_0 - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{24}\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta + \cdots \quad (1)$$

in which F_α is the field strength, and E_0 , α , and γ , respectively are the energy, dipole polarizability, and second dipole hyperpolarizability tensors of the free molecule. The Greek subscripts denote Cartesian components (x , y or z) and a repeated subscript implies summation over the latter. We choose the z axis to coincide with the molecular axis and so the origin-independent α and γ tensors have two and three independent components, respectively. For simplicity of notation, the longitudinal components α_{zz} and γ_{zzzz} will be referred to as α_L and γ_L , respectively. Similarly, α_T and γ_T will denote the transverse components.

We use the finite-field method¹⁴ to calculate the response properties from energies of the molecule perturbed by various fields. Since the energies are obtained from self-consistent-field (SCF) solutions of the Roothaan–Hartree–Fock equations,¹⁵ using the GAUSSIAN 86 program,¹⁶ this method is equivalent to the coupled Hartree–Fock procedure.¹⁷ The accuracy of the finite-field calculations was controlled by choosing fields carefully and keeping enough terms in Eq. (1) to ensure that the calculated properties agreed with those obtained by using one less term in Eq. (1) and with values obtained from induced dipole moments.

The experimental r_0 geometry of butadiyne,¹⁸ and calculated geometries for hexatriyne¹⁹ and octatetrayne⁶ have been used as in our previous work.⁹ For the higher members of the $C_{2n}H_2$ sequence, we use an idealized geometry obtained from the calculated geometry of octatetrayne.⁶ This idealized geometry is defined by $R(C-H) = 107$ pm, $R(C-C) = 140$ pm, and $R(C\equiv C) = 118$ pm.

III. SELECTION OF BASIS SETS

The requirements for small basis sets that can provide adequate longitudinal response properties of chains have been studied previously.^{6,11,12} In order to validate our results, we decided to conduct an extensive basis set study on linear butadiyne C_4H_2 for which accurate polarizabilities at the CHF level were calculated by Maroulis and Thakkar.⁹

TABLE I. Basis sets.

STO-3G from Refs. 15 and 16
3-21G from Refs. 15 and 16
4-31G from Refs. 15 and 16
6-31G from Refs. 15 and 16
SV = (9s5p/4s) contracted to [3s2p/2s], Ref. 20. H scale factor = 1
DZ = (9s5p/4s) contracted to [4s2p/2s], Ref. 21. H scale factor = 1
SV + Hs = SV + H:s(0.0483)
SV + Hp = SV + H:p(0.208)
SV + Cs = SV + C:s(0.05)
SV + Cp = SV + C:p(0.0365)
SV + CpHs = SV + C:p(0.0365) + H:s(0.0483)
SVp = SV + C:p(0.0365) + H:p(0.208)
SVpd = SVp + C:d(0.13)
B1 = [4s3p2d/3s2p1d] from Ref. 9
B3 = [5s3p2d/3s2p1d] from Ref. 9
B2 = [4s3p2d1f/3s2p1d] from Ref. 9

Table I lists 16 different basis sets of Gaussian-type functions (GTF), and Table II lists the longitudinal and transverse polarizabilities and hyperpolarizabilities obtained with these basis sets.

First consider the longitudinal properties. The minimal STO-3G basis¹⁵ recovers only 61% and 13%, respectively of the accurate CHF α_L and γ_L computed⁹ in the [4s3p2d1f/3s2p1d] basis B2. The split-valence 3-21G basis¹⁵ is already sufficient to obtain 88% of α_L but only 27% of γ_L . The 4-31G basis set¹⁵ does not provide any significant improvement over 3-21G. The 6-31G basis set¹⁵ is a bit better and gets 91% and 31%, respectively, of α_L and γ_L . The Dunning–Hay²⁰ split-valence (SV) basis set, which does not have the *sp*-shell constraint of the Pople split-valence sets,¹⁵ does noticeably better obtaining 94% and 47% of α_L and γ_L , respectively. Since the response properties are essentially valence properties, the Dunning

double-zeta²¹ basis leads to virtually the same results as the SV set.

Previous studies^{6,11,12} on unsaturated hydrocarbons have noted that diffuse *s*- and *p*-GTF on the carbon atoms are required to obtain response properties more accurate than those predicted by split-valence basis sets. However, in many of these studies the contributions of the diffuse *s*- and *p*-GTF on the carbons have not been separated, and diffuse *s*- and *p*-GTF on the hydrogens have not been considered. To clarify these issues, the SV basis was enlarged in four different ways by the addition of even-tempered diffuse *s*- or *p*-GTF shells on the carbon or hydrogen atoms. The γ_L values in Table II confirm that the most important of these diffuse functions is a *p*-GTF shell on the carbons just as it is for the $C_{2n}H_{2n+2}$ polyenes;¹¹ the SV + Cp basis set recovers 97% and 94% of the accurate α_L and γ_L , respectively, and is the smallest basis set that leads to a reasonable γ_L . However, the next most important diffuse function is a *p*-GTF shell on the hydrogens; this has not been noted in earlier studies^{6,11,12} which did not explore diffuse *p*-GTF on the hydrogens. Addition of both these *p*-GTF shells leads to our favoured SVp basis set that has a [3s3p/2s1p] composition. The addition of a *d*-GTF shell on the carbons, with an exponent taken from Ref. 9, leads to the SVpd set; this set may be unbalanced since it predicts a γ_L which seems a bit too large relative to the most accurate CHF value.⁹

Next consider the transverse properties. Table II confirms clearly that small basis sets which do reasonably well for the longitudinal properties are simply not flexible enough to handle the transverse properties. The SVp basis recovers only 59% and 42% of α_T and γ_T although it is quite good for the longitudinal properties. In fact, it is well known that *f*-GTF are needed to obtain accurate γ_T values for linear molecules.^{5,8,9} Thus, a comparison of the B2 and B3 sets shows that ~23% of γ_T for butadiyne comes from the addition of an *f*-shell on carbon. We do not calculate the transverse properties for the higher polyynes because we are unable to use large enough basis sets.

TABLE II. Tests of various basis sets on response properties of butadiyne C_4H_2 . Conversion factors to SI units are $e^2 a_0^2 E_H^{-1} = 1.648\,778 \times 10^{-41} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$ and $e^4 a_0^4 E_H^{-3} = 6.235\,378 \times 10^{-65} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$ for α and γ , respectively.

	α_L	$10^{-4}\gamma_L$	α_T	$10^{-2}\gamma_T$
STO-3G	50.674	0.256	3.469	−0.1
3-21G	73.003	0.534	9.110	0.1
4-31G	73.960	0.584	10.429	0.3
6-31G	75.016	0.620	11.336	0.5
SV	77.942	0.944	15.249	5.5
DZ	77.947	0.945	15.308	5.5
SV + Hs	78.126	0.961	16.171	6.9
SV + Hp	78.516	1.061	16.455	6.2
SV + Cs	78.241	0.980	17.167	8.9
SV + Cp	79.806	1.888	16.589	29.3
SV + CpHs	79.961	1.905	17.613	41.4
SVp	80.456	2.049	17.870	30.9
SVpd	80.879	2.227	28.676	40.3
B1 ^a	82.624	2.083	30.253	57.3
B3 ^a	82.570	2.058	30.284	55.0
B2 ^a	82.646	2.014	30.451	74.0

^aReference 9.

IV. RESULTS AND DISCUSSION

We calculated α_L and γ_L for the higher polyynes with six basis sets, the SVp and SVpd sets recommended above and the smaller STO-3G, 3-21G, 6-31G, and SV sets. This allows us to check the basis set dependence of the response properties of the linear $C_{2n}H_2$ polyynes as a function of chain length. In a similar study Hurst, Dupuis, and Clementi¹¹ found that basis set requirements diminish with increasing chain length in the nonlinear $C_{2n}H_{2n+2}$ polyenes.¹¹ We demonstrate that this is the case in the $C_{2n}H_2$ chains as well.

The minimal STO-3G set contains “only” $10n + 2$ basis functions for $C_{2n}H_2$ in contrast with the split-valence 3-21G, 6-31G, and SV sets that each contain $18n + 4$ basis functions, and the SVp and SVpd basis sets that contain $24n + 10$ and $34n + 10$ basis functions, respectively. Thus, we were able to extend the STO-3G calculations to $C_{44}H_2$, the 3-21G calculations to $C_{26}H_2$, the 6-31G calculations to $C_{22}H_2$, the SV and SVp calculations to $C_{18}H_2$, and the

TABLE III. Longitudinal polarizabilities α_L for the $C_{2n}H_2$ polyynes calculated in various ways. See caption to Table II for conversion factors.

n	INDO(MN)	INDO(OK)	STO-3G	3-21G	6-31G	SV	SV _p	SV _{pd}
2	66.635	67.466	50.674	73.003	75.016	77.942	80.456	80.879
3	122.78	123.46	91.558	130.44	132.76	135.84	138.71	139.94
4	199.05	200.03	145.41	206.53	209.00	212.15	215.68	218.23
5	284.40	286.65	205.60	292.56	294.83	297.51	301.71	305.74
6	375.74	380.29	269.84	385.61	387.35	389.05	393.78	
7	471.50	479.22	336.95	483.87	484.84	485.20	490.46	
8	570.30	581.93	405.96	585.80	585.83	584.00	590.37	
9	671.24	687.36	476.25	690.31	689.29	686.23	691.09	
10	773.71	794.77	547.40	796.70	794.52			
11	877.30	903.62	619.16	904.44	901.04			
12	981.74	1013.5	691.34	1013.2				
13	1086.8	1124.3	763.84	1122.7				
14	1192.3	1235.6	836.56					
15	1298.3	1347.5	909.46					
16	1404.5	1459.7	982.49					
17	1511.0	1572.2	1055.6					
18	1617.6	1684.9	1128.8					
19	1724.4	1797.9	1202.1					
20	1831.4	1910.9	1275.5					
21	1938.5	2024.2	1348.8					
22	2045.6	2137.5	1422.2					
23		2250.9						
24		2364.4						

SV_{pd} calculations to $C_{10}H_2$. Convergence difficulties prevented us from carrying the 6-31G and SV computations out as far as the 3-21G calculations. Some of these computations were not small. The largest STO-3G calculation involved 222 basis functions constructed from 666 primitive GTF for $C_{44}H_2$, and the largest SV_p calculation involved 226 basis functions constructed from 518 primitive GTF for $C_{18}H_2$. For the sake of comparison, we include finite-field SCF calculations based on the semiempirical intermediate neglect of differential overlap (INDO) method,²² as implemented by Ridley and Zerner,²³ using both the Mataga–Nishimoto²⁴ (MN) and Ohno–Klopman^{25,26} (OK) parametrizations.

A. *Ab initio* results

Table III lists our calculated α_L values. Our 3-21G results for C_6H_2 and C_8H_2 are essentially the same as those reported earlier by Bodart *et al.*⁴ and Chopra *et al.*,⁶ with very minor differences arising from the slightly different geometries used. The SV_{pd} results for C_6H_2 and C_8H_2 are within 2% of our previous values⁹ obtained in larger basis sets. The SV_p results are similar and hence we use them as the reference for the higher polyynes. The STO-3G values are too low by amounts decreasing from 37% to 31% as n increases from 2 to 9. By contrast, the 3-21G split-valence set is quite good; its prediction of α_L is too low by only 9% for C_4H_2 and this discrepancy decreases to 1% for $C_{14}H_2$. In fact, for $n > 5$, there are only small differences of <2% among the α_L values obtained from the three split-valence sets and the SV_p and SV_{pd} sets. Noting that electron correlation^{7–9} lowers α_L of C_2H_2 and C_4H_2 by only 1% and 4% of the respective SCF values, it is not far fetched to conclude that, for $n > 5$, even the 3-21G SCF results are adequate for the purposes of a study such as this one.

Table IV lists our calculated γ_L values. Our 3-21G results for C_6H_2 and C_8H_2 are in complete agreement with those reported by Chopra *et al.*⁶ The SV_p and SV_{pd} results for C_6H_2 and C_8H_2 are actually larger than our previous values⁹ of $10^{-5}\gamma_L = 0.634$ and 1.52 a.u., respectively obtained with larger basis sets. In the case of C_6H_2 we attribute this to imbalance in the SV_p and SV_{pd} bases. However, our previous γ_L value⁹ for C_8H_2 is probably too low because of a decision, unwise in retrospect, to jettison the diffuse *p*-GTF on the carbons. The SV_p values can be used as a reference for the higher polyynes because they are as good as the SV_{pd} ones. The STO-3G values are far too low, by amounts decreasing from 87% in C_4H_2 to 56% in $C_{18}H_2$. The 3-21G value is too low by 74% in C_4H_2 but this discrepancy decreases rapidly to a tolerable 24% for $C_{10}H_2$ and then to 6% for $C_{18}H_2$. The 6-31G and SV results are similar to the 3-21G values except for smaller n in which case they are noticeably better. Electron correlation^{8,9} lowers γ_L of C_2H_2 and C_4H_2 by only 13% and 17% of the respective SCF values. Hence, our longitudinal hyperpolarizabilities, except the STO-3G ones, should be useful at least in a qualitative sense.

B. Semiempirical INDO results

Since semiempirical calculations entail considerably less computational effort than *ab initio* calculations, it is important to examine how well the INDO results can mimic the *ab initio* calculations in the 3-21G and larger basis sets.

First, consider the longitudinal polarizabilities α_L . Both sets of INDO α_L are consistently lower than the SV_p results, although this discrepancy decreases as the chain length increases. Thus, the INDO(MN) α_L value is 17%

TABLE IV. Longitudinal hyperpolarizabilities $10^{-5}\gamma_L$ of the $C_{2n}H_2$ polyynes computed in various ways. See caption to Table II for conversion factors.

n	INDO(MN)	INDO(OK)	STO-3G	3-21G	6-31G	SV	SV _p	SV _{pd}
2	0.200	0.083	0.0256	0.0534	0.0620	0.0944	0.205	0.223
3	1.10	0.480	0.171	0.336	0.367	0.464	0.675	0.677
4	3.40	1.55	0.604	1.16	1.23	1.43	1.76	1.77
5	7.76	3.57	1.46	2.84	2.95	3.27	3.72	3.73
6	14.4	6.68	2.78	5.54	5.66	6.09	6.64	
7	22.9	10.9	4.56	9.29	9.42	9.92	10.6	
8	33.6	16.1	6.73	14.1	14.1	14.7	15.3	
9	45.6	22.2	9.23	19.7	19.7	20.2	21.0	
10	59.3	29.1	12.0	26.1	26.0			
11	73.7	36.5	14.9	33.2	32.8			
12	88.6	44.5	18.0	40.7				
13	105	52.8	21.2	48.6				
14	121	61.5	24.4					
15	138	70.4	27.8					
16	156	79.5	31.2					
17	173	88.9	34.6					
18	190	98.3	38.0					
19	208	108	41.5					
20	225	118	45.0					
21	243	127	48.5					
22	261	137	52.0					
23		147						
24		157						

lower than the SV_p value at C_4H_2 , but this discrepancy is reduced to 3% for $C_{18}H_2$. Similarly, the INDO(OK) α_L is 16% lower than the SV_p value for C_4H_2 but this discrepancy decreases to 1% for $C_{18}H_2$. A comparison for somewhat longer chains can be made with the 3-21G results. Interestingly, the INDO(OK) α_L are lower than the 3-21G results for smaller chains but exceed them by increasing amounts in $C_{24}H_2$ and $C_{26}H_2$. Previous studies^{12(a),27} have found INDO α_L to be consistently lower than *ab initio* results obtained in split-valence or larger basis sets; this may be because of the INDO parametrization used or, more probably, because the chains examined were too short for the crossover to be seen.

Next, consider the longitudinal hyperpolarizabilities γ_L . The INDO γ_L results are extremely sensitive to the parametrization scheme as noticed earlier by Papadopoulos, Waite, and Nicolaides²⁸ for C_2H_4 . Using the SV_p values as the reference, we see that the INDO(MN) γ_L are too large, except by chance in C_4H_2 , by amounts ranging from 63% in C_6H_2 to 117% in $C_{18}H_2$. On the other hand, the INDO(OK) γ_L are too low for the smaller chains but are larger than the SV_p values for $n > 5$; however, they remain within 6% of the SV_p values for $n > 4$. Moreover, the INDO(OK) values exceed the 3-21G results by amounts decreasing steadily from 55% in C_4H_2 to only 9% in $C_{26}H_2$. These comparisons suggest that the INDO(OK) results can mimic the 3-21G and SV_p results out to much longer chain lengths.

C. Extrapolation to infinite chain length

Finally, it is interesting to consider the growth of the response properties with chain length, and their extrapolation to infinite chain length.²⁹ Such a study based on static polarizabilities and hyperpolarizabilities may not tell us

anything important about experimental susceptibilities because the magnitude of the dispersion depends not only on the optical frequency used but also the specific optical process. Nevertheless, studying the static limit is a start at understanding how these properties vary with chain length. Virtually all previous *ab initio* studies on extrapolation to infinite chain length have been carried out at the static limit.²⁹

Previous calculations^{6,9} on C_6H_2 and C_8H_2 had been used to determine that α_L and γ_L for $C_{2n}H_2$ were growing as $n^{1.5}$ and $n^{3.0}$, respectively. Similarly, the current SV_{pd} results for $n=4,5$ suggest that α_L and γ_L , respectively are growing as $n^{1.51}$ and $n^{3.3}$. It is not unreasonable to suppose that the growth slows down as the chain length increases. The data in Tables III and IV show precisely that sort of behavior. For example, for $n=8,9$ the growth of the SV_p α_L and γ_L , respectively, has slowed to $n^{1.34}$ and $n^{2.7}$, and for $n=12,13$ the 3-21G α_L and γ_L are growing as “only” $n^{1.28}$ and $n^{2.2}$, respectively.

For large enough n , one might expect both α_L and γ_L to grow linearly with n like the scalar quadrupole moment listed in Table V. Unfortunately, this leveling off of the α_L/n and γ_L/n curves is apparent only for the unreliable STO-3G and INDO(MN) data and the reasonably accurate INDO(OK) data which extend out to $C_{44}H_2$. Since the INDO(OK) data give us the best chance of extrapolation to the infinite chain limit, we extended the calculations to $C_{46}H_2$ and $C_{48}H_2$ (see Tables III and IV). The limiting values of the properties per acetylenic-linkage can be estimated from least squares fits of these quantities,^{27,29,30} or their logarithms,^{11,26} to power series in $1/n$. Thus,

$$A(n) = a_0 + a_1/n + a_2/n^2 + \cdots + a_k/n^k \quad (2)$$

TABLE V. Scalar quadrupole moments of the $C_{2n}H_2$ polyynes computed with various bases. The conversion factor to SI units is $ea_0^2 = 4.486\,554 \times 10^{-40} \text{ C m}^2$.

n	STO-3G	3-21G	6-31G	SV	SVp	SVpd
2	6.5	10.3	9.6	9.7	9.7	9.9
3	10.6	16.2	15.0	14.9	14.9	15.1
4	15.3	23.1	21.1	20.8	20.8	21.0
5	20.4	30.5	27.7	27.2	27.1	27.4
6	25.7	38.3	34.6	33.9	33.7	
7	31.2	46.4	41.8	40.8	40.6	
8	36.8	54.8	49.2	47.9	47.7	
9	42.6	63.4	56.8	55.2	54.8	
10	48.4	72.2	64.5			
11	54.3	81.1	72.4			
12	60.3	90.1				
13	66.3	99.2				
14	72.3					
15	78.3					
16	84.4					
17	90.4					
18	96.5					
19	102.6					
20	108.7					
21	114.8					
22	120.9					

in which $A(n)$ can be α_L/n or γ_L/n or their logarithms.

We fit α_L/n and γ_L/n using the INDO(OK), 3-21G, and SVp data. The INDO(MN) and STO-3G data are too poor to be worth fitting, the 6-31G and SV results are similar to the 3-21G ones and do not extend as far, and the SVpd results cannot be extrapolated because they extend only to $n=5$. The degree of each fit (k) was chosen to be the smallest that lowers the standard deviation to 85% of the estimated truncation error in our data (0.01 a.u. for α_L and $10^{-5}\gamma_L$), or to minimize the standard deviation in

cases where the former objective could not be met. A fit was also made with a polynomial containing one extra term. Both fits were repeated after discarding one or two short chains. The results are listed in Table VI. The scatter in the values can be used to estimate the uncertainty in the limits. Thus, it seems that in the infinite chain limit, the INDO(OK), 3-21G, and SVp values of α_L/n saturate to 114.5 ± 0.6 , 113.5 ± 1.5 , and 109 ± 3 a.u., respectively. Similarly, in the infinite chain limit, the INDO(OK), 3-21G, and SVp values of γ_L/n seem to saturate to (1.09 ± 0.01)

TABLE VI. Limiting values of α_L/n and $10^{-5}\gamma_L/n$. The range is the smallest and largest n included in the fit, k is the degree of the fitting polynomial, cf. Eq. (2), ν is the number of degrees of freedom in the fit, and σ is the standard deviation. See caption to Table II for conversion factors.

Range	α_L/n				$10^{-5}\gamma_L/n$			
	k	ν	σ	Limit	k	ν	σ	Limit
INDO(OK)								
2,24	5	17	0.023	114.7	4	18	0.014	10.9
2,24	6	16	0.002	113.9	5	17	0.013	11.0
3,24	4	17	0.035	115.2	4	17	0.013	11.0
3,24	5	16	0.003	114.1	5	16	0.007	10.7
4,24	4	16	0.011	114.6	3	17	0.009	10.8
4,24	5	15	0.002	114.0	4	16	0.009	10.9
3-21G								
2,13	5	6	0.018	114.4	4	7	0.019	10.4
2,13	6	5	0.002	112.2	5	6	0.004	11.5
3,13	3	7	0.015	115.1	3	7	0.040	9.5
3,13	4	6	0.016	115.0	4	6	0.004	11.1
4,13	3	6	0.016	115.1	3	6	0.012	10.3
4,13	4	5	0.002	113.8	4	5	0.004	11.2
SVp								
2,9	4	3	0.051	111.5	4	3	0.013	9.1
2,9	5	2	0.046	105.8	5	2	0.008	11.0
3,9	3	3	0.044	110.0	3	3	0.021	8.0
3,9	4	2	0.049	108.1	4	2	0.009	10.3

$\times 10^6$, $(1.05 \pm 0.10) \times 10^6$, and $(0.95 \pm 0.15) \times 10^6$ a.u., respectively. Clearly, the SVp extrapolations suffer from our inability to compute SVp polarizabilities beyond $n=9$. Considering all the above estimates together, we suggest that the Hartree–Fock limit values of α_L/n and γ_L/n saturate to 110 ± 10 and $(1.0 \pm 0.3) \times 10^6$ a.u., respectively.

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