Additivity and Transferability of Atomic Contributions to Molecular Second Dipole Hyperpolarizabilities

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Large basis set ab initio calculations of the dipole polarizabilities and second hyperpolarizabilities of a large set of organic molecules have been carried out and the results have been used to assess additivity and transferability of atomic contributions to the overall molecular response tensors. Reasonable estimates of the mean second hyperpolarizability response can be obtained from summing atomic parameters obtained here, though the reliability of the estimates is worse than what is found for dipole polarizabilities. Individual tensor elements are not as well determined from transferable, additive contributions, which means that the orientational nature of the response is more subject to local bonding features.

Introduction

Dipole hyperpolarizabilities are tensor properties that characterize the change in molecular energy with respect to the third and higher powers of an electric field. Nonlinear optical response develops from the frequency-dependent hyperpolarizabilities, and the zero-frequency values are a starting point for understanding the full nature of this type of molecular response. A chemical issue is how the response depends on which constituent atoms are in the molecule and then how bonding affects the response. And, do higher order response properties follow chemical similarities among different molecules? These are fundamental questions, but they can have a practical consequence in prediction of properties based on molecular structure and bonding. Ab initio calculations as reported here provide a means for a genuine assessment of how well such predictiveness develops.

There exist a number of models for dipole polarizabilities, the properties which represent the second-order response of the molecular state energy to an external field. Ideas have included bond contributions,[1,2] atomic contributions[3−5] and group contributions[6] in additive schemes,[7] sometimes for the isotropic response only and sometimes for the entire tensor. Ab initio calculations have revealed additivity,[8−11] and recently, we have investigated an additive atomic centers (AAC) model for the dipole polarizabilities based on ab initio values of the molecular tensors.[10,11] Nonadditivity in models[12−14] is a means for incorporating intramolecular polarization. In 1972, Applequist presented a nonadditive model[12] in which the polarization of one atom could be relayed to the next via its induced dipole moment, and so on. It is possible to use a nonadditive scheme of distributed dipole polarizabilities for implicit higher order response. Then, the mutual intramolecular polarization energy will necessarily depend on higher powers of the external field strength. This is an advantage in using such a model to describe phenomena that come about through higher order response, but there is an equivalent additive approach to modeling the higher order response. It is to represent the higher order properties, the hyperpolarizabilities, separately. In so doing, the number of model parameters grows with the number of separate properties, and the higher order response that is due to intrinsic higher order response at a center can be fully incorporated. That is the direction of this report. A further difference between additive and cerain nonadditive models of the dipole polarizability is that nonadditive models can achieve anisotropic molecular polarizabilities from isotropically polarizable atoms, but to do the same, additive models must have anisotropic polarizabilities for the constituent atoms. The same holds for higher order properties.

All odd-order dipole response proprties, such as the dipole moment and the first dipole hyperpolarizability, usually designated β, vanish for atoms and for centrosymmetric molecules. Even-order properties, such as the dipole polarizability α and the second hyperpolarizability, γ, have nonzero components for all atoms and molecules. Essentially for this symmetry reason, we examine the atomic contributions to γ, not β, in this first effort at decomposing contributions to molecular hyperpolarizabilities. Also, it has been argued[11] that from an additive perspective, properties that are zero by symmetry for an isolated atom develop into nonvanishing properties in a molecule through electronic density changes within a bonding region. Hence, a different scheme of representation may be better (e.g., bond sites instead of atomic centers) for those, the odd-order properties. Pioneering the atomic contributions to γ is work of Sundberg[15] that included fitting experimental mean γ values of 16 haloalkanes to atomic γ values of H, C, F, Cl, Br, and I.

The practical result of fundamental insight about molecular properties can include modeling that produces property values on the basis of chemical structure, the pattern of bond types,

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TABLE 1: Assumed Structural Parameters for the Molecules Studied

Bond Lengths (Å)

0.960	H−O	1.208	C═O	1.339	C═C
1.020	H−N	1.209	C═N	1.343	C−O
1.087	H−C	1.212	N═O	1.350	C−F
1.153	C≡N	1.251	N═N	1.368	C−N
1.206	C≡C	1.308	C═C(═)	1.459	C−C

Bond Angles[a] (deg)

104.5	H−O-X, C−O−C	119.0	X−C−N, X−N−C
106.7	H-N-X	120.0	H−N═C, X−C═N, O−C═C, H−N═O
108.6	X−N═O	120.3	C−C═C
109.5	H−C−X, C−C−O, C−C−C	121.3	H−C═C
110.0	H−N═N, C−N═N	123.5	F−C═C
110.2	H−C−C	124.5	X−C═O
111.0	F−C−C	128.0	X−N═C

[a] X is any other non-hydrogen atom.

and elements in a molecule. This requires a set of parameters associated with specific elements (atoms) and specific types of bonding. How well the modeling works is an assessment of the additivity (if invoked in the model) and the transferability of contributions to the overall molecular response.

Calculational Approach

The ab initio calculations were done at the SCF level with analytical evaluation of the hyperpolarizabilities via the derivative Hartree−Fock method.[17] With a typical effect of electron correlation on multipole polarizabilities of covalent molecules amounting to 5−15%,[18−24] the neglect of correlation effects probably leaves an error source that could be 10% and even 50% for individual tensor elements, especially for the smaller valued elements; however, the objective of this study was to assess the extent to which the second hyperpolarizability response of small to intermediate sized organic molecules develops from additive atomic contributions, a feature which is not likely to be altered by correlation effects, as we have previously found for the dipole polarizabilities.[11]

For the ab initio calculations, the geometries of the molecules were set to chosen standard bond lengths and bond angles as shown in Table 1. This was also done in previous work,[10,11] and the idea is to remove variations in properties that are associated with the differences that might be found across a set of molecules due to small differences in the lengths of their carbon−carbon double bonds, for instance. The orientations of each molecule relative to the x, y, z axis system used to evaluate the tensor properties were such that the line between atoms with the highest bond order was coincident with the x axis. Except for a few linear molecules, all the molecules studied were planar or have a planar backbone, and we used the x−y plane for the molecular plane.

Very important in the evaluation of polarizabilities and hyperpolarizabilities, sometimes even more important than correlation effects, is the use of extended basis sets that include multiple diffuse polarization functions. We began by comparing the evaluation of the second hyperpolarizabilities of five small molecules with several basis sets. The results, as shown in Table 2, indicate that enlargement of the basis beyond that of the ELP basis sets of Liu and Dykstra[25] has a small effect (2−5%), but reducing that basis slightly produces more sizable changes in values (∼10%). Hence, in the subsequent calculations we used the ELP basis, a triply polarized basis with augmenting diffuse functions built on a Dunning−Huzinaga triple-ζ core-valence basis.[26]

The properties calculated from the ab initio calculations were fitted to a set of parameters by linear least squares minimization of the deviations. Under the assumption of additivity, a given element of a molecule's γ-tensor is expressed as a function that is linear in the γ-tensor elements of the contributing atoms, these being the parameters. The parameter tensor elements are for atoms of different types, and we tested different sets of atom types, retaining those that made a noticeable improvement in the fitting, while combining those that were close in value. We also inforced local symmetry on the parameter set according to the symmetry of the bonding environment, and thus, for example, an atom that was bonded to the next atom by a triple bond (e.g., −C≡) would be taken to be axially symmetric. This leads to symmetry constraints on the parameters, and for the specific case of an axially symmetric center and x as the bond axis, only the elements γ_{xxxx}, γ_{yyyy}, γ_{zzzz}, γ_{xxyy}, γ_{xxzz}, and γ_{yyzz} are nonzero and there is an equivalence of γ_{yyyy} with γ_{zzzz} and of γ_{xxyy} with γ_{xxzz}. In one case, we tested additivity by removing all molecules which included a fluorine center and found that the parameters of the other centers were only slightly affected. The parameter determination steps were also done for the dipole polarizabilities, repeating and extending to a much larger set of molecules the work of Stout and Dykstra.[10]

Results and Discussion

All the molecules in the data set were composed of H, C, N, O, and F atoms. We found that the best concise fits of the tensor properties were obtained with 14 atom types as shown in Table 3. Carbon required seven types, nitrogen four, oxygen two, and fluorine one. Hydrogen atoms will tend to have a smaller effect in view of how many more electrons the other atoms have. We have not found improvement[10] in the modeling of the response properties from assigning parameters to hydrogen centers; however, hydrogens do play a role in differentiating the response among certain species, and they are effectively included in our model parameter set by certain distinctions among the atom types, such as for nitrogen in an sp^3 bonding environment (Table 3).

The tensor elements obtained from fitting for the 14 atom types can be combined to obtain the isotropic contributions, which are themselves parameters for modeling the isotropic responses. These isotropic parameters, which are related to individual tensor elements (parameters) by

$$\alpha_{\mathrm{iso}} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \tag{1}$$

$$\gamma_{\mathrm{iso}} = [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]/5 \tag{2}$$

are given in Table 3. These are values which can be added together to estimate the isotropic α or isotropic γ for an organic molecule composed of H, C, N, O, and F atoms with the bonding environments listed. There are certain interesting features seen in these two sets of parameters.

(1) Except for an allenic carbon center, the isotropic contribution of any carbon atom to the dipole polarizability is within the range of 10.6−13.4 au. There tends to be an intrinsic atomic contribution with only a share affected by the bonding.

(2) The isotropic contributions to the dipole polarizability roughly decrease across the row of the periodic table from carbon to fluorine, with fluorine having a negligible contribution.

(3) The atomic, isotropic second-order hyperpolarizability parameters tend to follow the trends of the isotropic dipole polarizabilities in that among a pair of center types, mostly the one with the bigger γ_{iso} is the one with the bigger α_{iso}. However,

TABLE 2: Basis Set Effects on the Calculated Second Hyperpolarizability (Γ) Tensor Elements (in au)

		calculated values with different basis sets[b]					
molecule	γ element[a]	ELP/1f	ELP+	ELP	A	B	C
HCCH	*xxxx*	3124	3196	3144	3026	3040	2099
	yyyy = *zzzz*	5239	5689	5310	4229	3675	2774
	xxyy = *xxzz*	1587	1629	1610	1487	1409	1154
	yyzz	1746	1896	1770	1410	1225	925
	isotropic γ	4689	4977	4749	4050	3695	2822
HCC−CH$_3$	*xxxx*	7597	7627	7586	7613	7605	6812
	yyyy = *zzzz*	5624	5996	5569	4813	4520	3683
	xxyy = *xxzz*	2185	2215	2167	2038	1983	1631
	yyzz	1875	1999	1856	1604	1507	1228
	isotropic γ	6267	6495	6221	5720	5518	4631
HCC−CCH	*xxxx*	19279	19105	19662	19694	19399	18561
	yyyy = *zzzz*	6321	6684	6341	5707	5505	5241
	xxyy = *xxzz*	3564	3651	3488	3303	3204	3002
	yyzz	2107	2228	2114	1903	1835	1747
	isotropic γ	10078	10307	10105	9625	9379	8909
FCC−CCH	*xxxx*		14007	14073	14053	13890	13483
	yyyy = *zzzz*		5433	5193	4846	4680	4613
	xxyy = *xxzz*		2544	2493	2408	2354	2272
	yyzz		1811	1731	1615	1560	1538
	isotropic γ		7734	7579	7321	7158	6975
HCC−CC−CHO	*xxxx*			39700	39739	39354	38647
	yyyy			6194	5997	5908	5454
	zzzz			5546	5318	5115	4951
	xxyy			2893	2821	2773	2612
	xxzz			3155	3064	2987	2879
	yyzz			1887	1843	1787	1692
	xxxy			1222	1202	1195	1239
	xyyy			−356	−359	−343	−283
	isotropic γ			13462	13302	13094	12684

[a] The indicated equivalence of tensor elements is by symmetry. [b] The ELP basis[25] used for the calculations on the full set of molecules consists of the Dunning−Huzinaga[26] triple-ζ core-valence set plus (i) a set of one diffuse s and two diffuse p functions on each non-hydrogen center, (ii) one diffuse s function on each hydrogen, (iii) two sets of p-polarization functions on hydrogens, and (iv) three sets of d-polarization functions on atoms other than hydrogen. The ELP+ basis was the ELP basis augmented with one extra set of polarization functions: For C, N, O and F, the ELP d-function exponents were reset from 0.9, 0.13, and 0.02 to 0.9, 0.15, and 0.025, and the exponent of the added d-function was 0.004. For H, the ELP p-function exponents were reset from 0.9 and 0.1 to 0.9 and 0.18 with the exponent of the added p-function being 0.0036. The ELP/1f basis was the ELP basis augmented with one set of f-polarization functions for the non-hydrogen centers, and the exponent was 0.3. As in previous work on dipole polarizabilities,[10] bases A, B, and C corresponded to reductions from the ELP basis in the augmentation of the core/valence TZ basis. Basis A relative to the ELP set had two d-polarization functions for every three in the ELP set and lacked the diffuse s-function on the non-hydrogen centers. Relative to A, B had one diffuse p-function on the non-hydrogen centers for every two in A. Relative to B, basis C lacked the diffuse s-function on hydrogen centers and had one p-polarization function for hydrogen centers.

TABLE 3: Model Parameters for Isotropic Properties (au)

center type[a]	α_{iso}	γ_{iso}	center type[a]	α_{iso}	γ_{iso}
(O)=C=	10.581	459	N (sp)	3.434	−1843
(O)=C (sp^2)	11.274	998	N (sp^2)	8.748	1149
(H)C (sp)	11.476	2303	(H$_2$)N (sp^3)	8.912	1784
C (sp^3)	12.296	1688	(H)N (sp^3)	10.058	2028
C (sp)	12.344	2899	O=	3.131	206
C (sp^2)	13.383	2746	−O−	3.497	−53
(C)=C=(C)	16.837	2544	F	0.163	−1033

[a] Atoms in parentheses are specific adjacent atoms for the given center type.

the second dipole hyperpolarizabilities show much greater variation and very much more dependence on the bonding environment than on the atomic number. This may reflect that the fourth-order response to a field (i.e., γ) develops more in the outer, fringe regions of the electron distribution and involves the inner part of the electron density, the part less subject to changes from bonding, less than the second-order response (i.e., α).

(4) Both fluorine and a triply bonded nitrogen tend to diminish the fourth-order response.

Table 4 provides an assessment of the isotropic parameters by comparing the ab initio isotropic values and the model values. It is clear that the idea of additive, transferable contributions is more workable for α than for γ. The mean of the absolute percentage error for the set of 58 molecules is about 4 times greater for the isotropic γ values than for the isotropic α values. The range in percentage error is about 3−3.5 times greater for γ than α. The additive atomic centers (AAC) model reproduces the ab initio isotropic α values to within 12% and the isotropic γ values to within 42%, and to within 8% and 25%, respectively, if the four worst cases (HOCN, HCOOH, (CH$_3$F)$_2$, NH$_2$CH$_3$) are excluded. Therefore, AAC is moderately reliable for predicting the dipole polarizability but can give only a coarser level of prediction for the second dipole hyperpolarizability. The value of the model for γ values, though, is in identifying the chemical features that add to or diminish the overall γ response. Even to a 30% overall accuracy, the parameter values in Table 3 show, for instance, that fluorine substitution of a hydrogen will mostly reduce the size of the fourth-order (γ) response.

The modeling scheme can generate specific tensor elements for each of the atom types, and these are given in Table 5. How well they work to yield the tensors for the 58-molecule set is shown by the data in Tables 6 and 7. For conciseness, these tables give values for a selection of half of the 58 molecules studied, but the selection includes the molecules with the worst percentage error and the most sizable difference between the model and the ab initio results. A comparison of the errors for fitting α-tensor elements and γ-tensor elements for the entire

TABLE 4: Error in the Additive Atomic Centers Model for Isotropic Response Properties

	isotropic α			isotropic γ		
molecule	ab initio	model	diff (%)	ab initio	model	diff (%)
CH_2NH	21.34	22.13	3.7	3167	3895	23.0
NH_2CH_3	24.13	21.21	−12.1	4734	3473	−26.6
C_2H_2	23.59	22.95	−2.7	4749	4607	−3.0
C_2H_4	28.12	26.77	−4.8	5778	5493	−4.9
C_2H_6	26.48	24.59	−7.1	3120	3378	8.2
cis-N_2H_2	18.14	17.50	−3.5	2278	2298	0.9
trans-N_2H_2	18.22	17.50	−4.0	2420	2298	−5.0
HNCO	21.78	22.46	3.1	1792	1815	1.3
HOCN	20.87	19.28	−7.6	1735	1004	−42.1
NH_2CN	25.24	24.69	−2.2	2932	2841	−3.1
HCOOH	20.29	17.90	−11.8	1970	1152	−41.5
NH_2CHO	24.90	23.32	−6.3	3447	2988	−13.3
$HN{=}CHOH$	25.71	25.63	−0.3	3950	3843	−2.7
CH_3NO	24.23	24.17	−0.2	2871	3044	6.0
trans-CH_3NNH	29.36	29.79	1.5	4315	3987	−7.6
CH_2CO	28.21	27.09	−4.0	4260	3412	−19.9
HCCOH	27.45	27.32	−0.5	4787	5150	7.6
CH_3CN	28.14	28.07	−0.2	2685	2745	2.3
NH_2CCH	32.79	32.73	−0.2	7987	6987	−12.5
$CH_3{-}CHO$	27.52	26.70	−3.0	3277	2893	−11.7
CH_3CH_2F	25.89	24.75	−4.4	2627	2344	−10.8
CH_3CCH	35.44	36.12	1.9	6221	6892	10.8
H_2CCCH_2	41.31	43.60	5.6	7694	8037	4.5
C_3H_6	39.10	39.06	−0.1	7093	7182	1.2
CO_2	16.78	16.84	0.4	885	872	−1.5
cis-CHOCHO	28.83	28.81	−0.1	3035	2408	−20.7
trans-CHOCHO	29.32	28.81	−1.7	2941	2408	−18.1
$F_2C{=}CH_2$	26.98	27.09	0.4	3079	3426	11.3
cis-$FHC{-}CHF$	26.73	27.09	1.4	3020	3426	13.5
trans-$FHC{-}CHF$	26.50	27.09	2.2	2748	3426	24.7
$NC{-}CH_2OH$	31.64	31.57	−0.2	3168	2693	−15.0
CH_3NCO	34.21	34.76	1.6	3460	3503	1.2
CH_3COOH	30.54	30.20	−1.1	2908	2840	−2.3
$HCO{-}O{-}CH_3$	30.04	30.20	0.5	2774	2840	2.4
$CH_2F{-}CH_2F$	25.41	24.92	−2.0	2108	1311	−37.8
$HCONHCH_3$	36.76	36.76	0.0	4802	4920	2.5
CH_3CONH_2	35.01	35.61	1.7	4408	4677	6.1
$HCC{-}CHO$	37.36	38.23	2.3	5360	6407	19.5
CH_2CCO	44.10	43.93	−0.4	5160	5956	15.4
CH_2CHCN	41.80	42.54	1.8	5698	6550	14.9
cis-CH_2CHCHO	40.18	41.17	2.5	6071	6697	10.3
trans-CH_2CHCHO	41.74	41.17	−1.4	5907	6697	13.4
$HCC{-}O{-}CH_3$	38.69	39.61	2.4	6753	6839	1.3
$HCCCH_2OH$	38.92	39.61	1.8	6866	6839	−0.4
CH_3CH_2CN	38.83	40.37	4.0	4050	4434	9.5
CH_3CCNH_2	44.45	45.90	3.3	8425	9272	10.1
CH_3COCH_3	37.97	39.00	2.7	4490	4581	2.0
HCCCCH	47.66	47.64	0.0	10104	10405	3.0
CH_2CCCH_2	61.50	60.44	−1.7	11150	10581	−5.1
$HCC{-}CHCH_2$	50.18	50.59	0.8	11165	10696	−4.2
$CH_2CHCHCH_2$	56.36	53.53	−5.0	14099	10986	−22.1
$CHO{-}COOH$	32.28	32.31	0.1	2732	2355	−13.8
$NH_2{-}CO{-}O{-}CH_3$	37.91	39.11	3.2	3968	4625	16.6
$CHO{-}O{-}CHCH_2$	44.84	44.67	−0.4	6723	6644	−1.2
$CH_2{=}CH{-}COOH$	42.88	44.67	4.2	5330	6644	24.7
$NH_2COCH{=}CH_2$	48.23	50.08	3.9	7390	8481	14.8
$HCC{-}CC{-}CH_3$	61.25	60.81	−0.7	12422	12690	2.2
$HCC{-}CC{-}CHO$	64.55	62.91	−2.5	13462	12205	−9.3
mean absolute error (%):			2.6			11.1

set of molecules is given in the Figure 1. For α values, the 58 molecules provide 205 unique tensor elements, and these are reproduced with a mean absolute percentage error of 18.6% using 27 tensor parameters for the 14 atom types (Table 5). The mean absolute percentage error for the diagonal elements, though, is only 5.1%. For γ values, the 58 molecules provide 429 unique tensor elements, and these are reproduced with a mean absolute percentage error of 71.5% using 70 tensor parameters for the 14 atom types (Table 5); however, the mean

TABLE 5: Model Parameters (in au) for α and γ Tensors

	α tensor parameters[a]		γ tensor parameters[a]	
center type	element(s)	value	element(s)	value
C (sp^3)	*xx* = *yy* = *zz*	12.2956	*xxxx* = *yyyy* = *zzzz*	1522
			xxyy = *xxzz* = *yyzz*	646
C (sp^2)	*xx*	19.2020	*xxxx*	2103
	yy	11.5156	*yyyy*	1722
	zz	9.4305	*zzzz*	3383
			xxyy	1023
			xxzz	1306
			yyzz	933
(O)═C (sp^2)	*xx* = *zz*	13.4126	*xxxx*	949
	yy	6.9980	*yyyy*	1697
			zzzz	634
			xxyy	631
			xxzz	210
			yyzz	14
(C)═C═(C)	*xx*	35.5897	*xxxx*	2623
	yy = *zz*	7.4611	*yyyy*	1574
			zzzz	1372
			xxyy	1235
			xxzz	2001
			yyzz	339
(O)═C═	*xx*	17.7597	*xxxx*	1190
	yy = *zz*	6.9922	*yyyy*	−482
			zzzz	1601
			xxyy	−438
			xxzz	221
			yyzz	211
C (sp)	*xx*	24.8616	*xxxx*	9560
	yy = *zz*	6.0858	*yyyy* = *zzzz*	835
			xxyy = *xxzz*	676
			yyzz	281
(H)C (sp)	*xx*	15.3058	*xxxx*	303
	yy = *zz*	9.5618	*yyyy* = *zzzz*	2810
			xxyy = *xxzz* = *yyzz*	932
(H_2)N (sp^3)	*xx* = *yy* = *zz*	8.9117	*xxxx*	−114
			yyyy	1348
			zzzz	2442
			xxyy	697
			xxzz	1416
			yyzz	510
(H)N (sp^3)	*xx*	17.2036	*xxxx*	2921
	yy = *zz*	6.4847	*yyyy*	1002
			zzzz	1500
			xxyy	742
			xxzz	1872
			yyzz	−256
N (sp^2)	*xx*	11.9376	*xxxx*	1300
	yy	8.1553	*yyyy*	1410
	zz	6.1498	*zzzz*	416
			xxyy	806
			xxzz	286
			yyzz	218
N (sp)	*xx*	1.2229	*xxxx*	−6248
	yy = *zz*	4.5402	*yyyy* = *zzzz*	−379
			xxyy = *xxzz*	−442
			yyzz	−220
O═	*xx*	5.4717	*xxxx*	−186
	yy = *zz*	1.9600	*yyyy*	615
			zzzz	−327
			xxyy	440
			xxzz	−5
			yyzz	30
-O-	*xx* = *yy* = *zz*	3.4970	*xxxx*	−1934
			yyyy	259
			zzzz	660
			xxyy = *xxzz* = *yyzz*	125
F	*xx* = *zz*	0.6948	*xxxx*	−870
	yy	−0.9010	*yyyy*	−1019
			zzzz	−666
			xxyy = *xxzz*	−376
			yyzz	−553

[a] The tensor parameters are defined with respect to a reference orientation for each center. That reference orientation is with the highest order bond of the given center type aligned with the *x*-axis. Hence, the *x* axis is along the double bond of a carbon with sp^2 bonding environment. The *y* and *z* axes are equivalent for all but sp^2 centers (i.e., axial symmetry). For sp^2 centers, the *y* axis of the reference orientation is in the plane of the atoms to which the center is bound, whereas the *z* axis is perpendicular to this plane.

TABLE 6: Dipole Polarizability Tensor Elements (in au)

molecule	α element	ab initio	model	% error
NH_2CH_3	*xx*	26.60	21.21	20.3
	yy	22.97	21.21	7.7
	zz	22.83	21.21	7.1
C_2H_2	*xx*	32.29	30.61	5.2
	yy = *zz*	19.23	19.12	0.6
C_2H_4	*xx*	36.87	38.40	−4.2
	yy	24.75	23.03	6.9
	zz	22.76	18.86	17.1
C_2H_6	*xx*	27.90	24.59	11.9
	yy = *zz*	25.76	24.59	4.5
cis-N_2H_2	*xx*	24.35	23.88	1.9
	yy	16.56	16.31	1.5
	zz	13.50	12.30	8.9
HNCO	*xx*	33.18	35.17	−6.0
	yy	16.32	17.11	−4.8
	zz	15.84	15.10	4.7
HCOOH	*xx*	26.77	22.38	16.4
	yy	19.20	18.87	1.7
	zz	14.91	12.46	16.5
HN=CHOH	*xx*	35.13	34.64	1.4
	yy	23.46	23.17	1.2
	zz	18.55	19.08	−2.9
CH_2CO	*xx*	42.24	42.43	−0.4
	yy	21.06	20.47	2.8
	zz	21.34	18.38	13.9
CH_3CN	*xx*	37.70	38.38	−1.8
	yy = *zz*	23.37	22.92	1.9
CH_3CCH	*xx*	49.27	52.46	−6.5
	yy = *zz*	28.52	27.94	2.0
H_2CCCH_2	*xx*	65.17	73.99	−13.5
	yy = *zz*	29.37	28.41	3.3
C_3H_6	*xx*	49.52	50.70	−2.4
	yy	36.25	35.33	2.6
	zz	31.53	31.16	1.2
CO_2	*xx*	25.58	28.70	−12.2
	yy = *zz*	12.39	10.91	11.9
$F_2C{=}CH_2$	*xx*	35.45	37.57	−6.0
	yy	25.01	23.45	6.2
	zz	20.48	20.25	1.1
cis-FHC−CHF	*xx*	35.16	37.57	−6.9
	yy	24.68	23.45	5.0
	zz	20.34	20.25	0.5
trans-FHC−CHF	*xx*	35.10	37.57	−7.0
	yy	24.45	23.45	4.1
	zz	19.94	20.25	−1.6
CH_3COOH	*xx*	34.48	34.68	−0.6
	yy	32.52	31.17	4.2
	zz	24.61	24.75	−0.6
HCC−CHO	*xx*	54.72	56.67	−3.6
	yy	32.06	33.41	−4.2
	zz	25.30	24.61	2.7
CH_2CCO	*xx*	78.39	78.02	0.5
	yy	28.20	27.93	1.0
	zz	25.71	25.84	−0.5
CH_2CHCN	*xx*	56.49	53.26	5.7
	yy	40.38	44.88	−11.1
	zz	28.54	29.49	−3.3
$HCC{-}O{-}CH_3$	*xx*	52.26	55.96	−7.1
	yy	32.52	31.44	3.3
	zz	31.30	31.44	−0.5
HCCCCH	*xx*	81.48	80.33	1.4
	yy = *zz*	30.74	31.30	−1.8
CH_2CCCH_2	*xx*	113.81	109.58	3.7
	yy	36.46	37.95	−4.1
	zz	34.23	33.78	1.3
$HCC{-}CHCH_2$	*xx*	71.10	67.11	5.6
	yy	45.65	50.14	−9.8
	zz	33.78	34.51	−2.2
$CH_2CHCHCH_2$	*xx*	85.44	76.81	10.1
	yy	46.58	46.06	1.1
	zz	37.06	37.72	−1.8
$NH_2\text{-}CO{-}O{-}CH_3$	*xx*	39.46	43.59	−10.5
	yy	43.95	40.08	8.8
	zz	30.30	33.66	−11.1
$HCC{-}CC{-}CH_3$	*xx*	103.96	102.19	1.7
	yy = *zz*	39.90	40.11	−0.5
HCC−CC−CHO	*xx*	113.31	106.39	6.1
	yy	43.49	45.58	−4.8
	zz	36.84	36.78	0.2

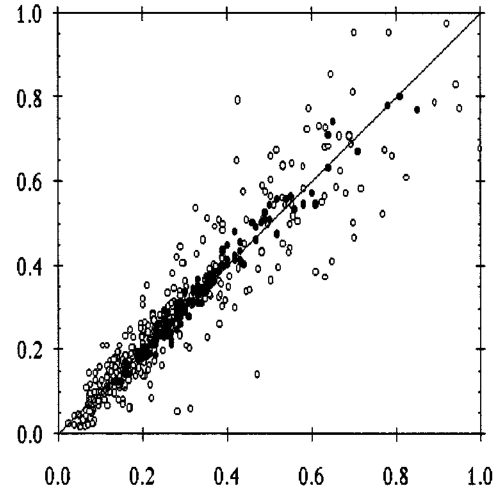

Figure 1. A comparison of model tensor values against ab initio values for the diagonal α-tensor elements (filled circles) and the γ-tensor elements γ_{xxxx}, γ_{yyyy}, γ_{zzzz}, γ_{xxyy}, γ_{xxzz}, and γ_{yyzz} (open circles) of the 58 molecules. To make for a comparison of the AAC scheme in application to α versus γ, α-tensor elements were multiplied by 10^{-2} and γ-tensor elements were multiplied by $10{-}^{4}$ before graphing. In so doing, most of the properties evaluated fall in the range shown, from 0 to 1. The vertical axis corresponds to the model values, whereas the ab initio values are the horizontal axis. The solid line is the line of perfect correspondence between the model and the ab initio results. The plot shows less scatter from this line for the major α elements than for the major γ elements.

absolute percentage error for the elements that contribute to the isotropic second hyperpolarizability (i.e., those in eq 2) is 21.1%. Thus, while certain of the elements have very substantial percentage errors, these are generally elements that are small with respect to others in the same tensor. In an application such as the evaluation of electrostatics interaction energetics, γ tensors predicted by this scheme will more reflect the errors in the diagonal elements, which are usually the most sizable elements, and this implies errors ∼20−30%.

Bond conjugation effects in larger molecular systems than treated here present certain difficulties. Large dipole polarizabilities and large hyperpolarizabilities arise from delocalized π bonding.[27−30] From one standpoint, these effects introduce nonlinearity[27−37] through more facile intramolecular polarization, that polarization growing with chain length until an asymptotic limit. From another standpoint, that of an additive scheme, bond conjugation introduces significant end effects which will require more atom types (end, next to the end, next in from the end, and so on); additivity is still workable since at the asymptotic limit of a long chain, an additional segment added to the chain gives an additive contribution to the response properties. Our parameter values are not based on a data set with long chain molecules and will not successfully model the response properties if there are significant conjugation effects. Thus, predictions for $H{-}(C{\equiv}C)_n{-}H$ using only values in Table 5 will likely worsen with increasing *n*. With a data set large enough to include many end types, the additive scheme could be as workable for conjugated systems, and this has been done for certain parts of the γ-response in a special case.[38] Also, within the AAC scheme, the effects of conjugation may involve end atoms that might not be considered conjugated. For instance, we carried out ab initio calculations on $FC{\equiv}C{-}C{\equiv}CH$, and including it in the data set altered the fluorine center's γ parameters somewhat, while the errors of the fit for all fluorine molecules were worsened. This did not happen with fluorine

TABLE 7: Second Dipole Hyperpolarizability Tensor Elements (in au)

molecule	γ element	ab initio	model	% error
NH_2-CH_3	*xxxx*	4709	1408	70.1
	yyyy	2257	2870	−27.2
	zzzz	5216	3963	24.0
	xxyy	1250	1343	−7.4
	xxzz	3118	2062	33.9
	yyzz	1376	1157	15.9
C_2H_2	*xxxx*	3144	607	80.7
	yyyy = *zzzz*	5310	5621	−5.8
	xxyy = *xxzz*	1610	1865	−15.8
	yyzz	1770	1865	−5.3
C_2H_4	*xxxx*	2796	4206	−50.4
	yyyy	2743	3444	−25.5
	zzzz	9997	6766	32.3
	xxyy	1789	2045	−14.3
	xxzz	2796	2613	6.6
	yyzz	2091	1866	10.7
C_2H_6	xxxx	3879	3044	21.5
	yyyy = *zzzz*	2618	3044	−16.3
	xxyy = *xxzz*	1186	1293	−9.1
	yyzz	873	1293	−48.2
cis-N_2H_2	*xxxx*	1952	2600	−33.2
	yyyy	2270	2820	−24.2
	zzzz	1431	833	41.8
	xxyy	1688	1612	4.5
	xxzz	668	571	14.4
	yyzz	513	436	15.1
HNCO	*xxxx*	1784	2303	−29.1
	yyyy	1385	1543	−11.4
	zzzz	1697	1690	0.4
	xxyy	752	808	−7.5
	xxzz	810	502	38.1
	yyzz	485	458	5.5
HCOOH	*xxxx*	2203	847	61.6
	yyyy	2153	1610	25.2
	zzzz	1339	967	27.8
	xxyy	959	668	30.4
	xxzz	593	331	44.3
	yyzz	524	169	67.8
$HN{=}CHOH$	*xxxx*	4466	3403	23.8
	yyyy	3825	2601	32.0
	zzzz	2890	4460	−54.3
	xxyy	2003	1382	31.0
	xxzz	1239	1717	−38.6
	yyzz	1044	1276	−22.3
CH_2CO	*xxxx*	2700	3106	−15.0
	yyyy	1947	1854	4.8
	zzzz	7008	4657	33.5
	xxyy	1104	1025	7.2
	xxzz	2133	1522	28.6
	yyzz	1586	1174	26.0
CH_3CN	*xxxx*	3892	4834	−24.2
	yyyy = *zzzz*	2133	1977	7.3
	xxyy = *xxzz*	961	881	8.3
	yyzz	711	708	0.4
CH_3CCH	*xxxx*	7586	11386	−50.1
	yyyy = *zzzz*	5569	5167	7.2
	xxyy = *xxzz*	2167	2255	−4.0
	yyzz	1856	1860	−0.2
H_2CCCH_2	*xxxx*	6329	6829	−7.9
	yyyy = *zzzz*	6996	6578	6.0
	xxyy = *xxzz*	3438	3947	−14.8
	yyzz	2199	2206	−0.3
C_3H_6	*xxxx*	4830	5887	−21.9
	yyyy	4860	5124	−5.4
	zzzz	9424	8288	12.1
	xxyy	2677	2533	5.4
	xxzz	3152	3259	−3.4
	yyzz	2347	2513	−7.1
CO_2	*xxxx*	836	817	2.3
	yyyy = *zzzz*	765	847	−10.7
	xxyy = *xxzz*	387	327	15.5
	yyzz	255	270	−5.9
$F_2C{=}CH_2$	*xxxx*	1447	2103	−45.3
	yyyy	1694	1456	14.1
	zzzz	5530	5434	1.7
	xxyy	873	1449	−66.0
	xxzz	1443	1615	−11.9
	yyzz	1047	1006	3.9
	xxzz	3155	3056	3.1
	yyzz	1887	1928	−2.2
cis-FHC−CHF	*xxxx*	1070	2103	−96.5
	yyyy	1974	1456	26.3
	zzzz	5368	5434	−1.2
	xxyy	883	1449	−64.1
	xxzz	1237	1615	−30.5
	yyzz	1223	1006	17.7
trans-FHC−CHF	*xxxx*	1153	2103	−82.3
	yyyy	1796	1456	19.0
	zzzz	5110	5434	−6.4
	xxyy	733	1449	−97.5
	xxzz	1169	1615	−38.1
	yyzz	938	1006	−7.2
CH_3COOH	*xxxx*	2684	2551	5.0
	yyyy	3852	3314	14.0
	zzzz	1957	2488	−27.2
	xxyy	1341	1132	15.6
	xxzz	892	977	−9.6
	yyzz	790	815	−3.2
HCC−CHO	*xxxx*	8488	12409	−46.2
	yyyy	5024	5635	−12.2
	zzzz	4275	3951	7.6
	xxyy	1435	1949	−35.9
	xxzz	1597	1704	−6.7
	yyzz	1476	1366	7.4
CH_2CCO	*xxxx*	4369	5729	−31.1
	yyyy	4537	3428	24.4
	zzzz	5049	6029	−19.4
	xxyy	2289	2260	1.3
	xxzz	2111	3523	−66.9
	yyzz	1522	1513	0.6
CH_2CHCN	*xxxx*	8924	7872	11.8
	yyyy	3269	5366	−64.1
	zzzz	5888	7222	−22.7
	xxyy	1151	1369	−18.9
	xxzz	2335	2302	1.4
	yyzz	1717	2473	−44.0
$HCC-O-CH_3$	*xxxx*	7000	9535	−36.2
	yyyy	6259	5509	12.0
	zzzz	7164	5827	18.7
	xxyy	1994	2298	−15.2
	xxzz	2188	2380	−8.8
	yyzz	2490	1985	20.3
HCCCCH	*xxxx*	19662	19728	−0.3
	yyyy = *zzzz*	6341	7290	−15.0
	xxyy = *xxzz*	3488	3217	7.8
	yyzz	2114	2427	−14.8
CH_2CCCH_2	*xxxx*	10382	9452	9.0
	yyyy	5048	6591	−30.6
	zzzz	10572	9511	10.0
	xxyy	4423	4516	−2.1
	xxzz	7908	6614	16.4
	yyzz	2544	2545	0.0
$HCC-CHCH_2$	*xxxx*	18233	14378	21.1
	yyyy	6462	8534	−32.1
	zzzz	9757	10411	−6.7
	xxyy	2629	2777	−5.6
	xxzz	5040	3665	27.3
	yyzz	3016	3636	−20.5
$CH_2CHCHCH_2$	*xxxx*	13075	8413	35.7
	yyyy	6934	6887	0.7
	zzzz	14003	13533	3.4
	xxyy	6486	4090	36.9
	xxzz	7701	5225	32.1
	yyzz	4053	3732	7.9
$NH_2-CO-O-CH_3$	*xxxx*	2996	4079	−36.1
	yyyy	4817	4318	10.4
	zzzz	3713	4930	−32.8
	xxyy	1436	1180	17.9
	xxzz	1313	1778	−35.4
	yyzz	1406	1941	−38.0
$HCC-CC-CH_3$	*xxxx*	30394	30507	−0.4
	yyyy = *zzzz*	6393	6836	−6.9
	xxyy = *xxzz*	3667	3607	1.6
	yyzz	2131	2422	−13.6
HCC−CC−CHO	*xxxx*	39700	31530	20.6
	yyyy	6194	7304	−17.9
	zzzz	5546	5621	−1.4
	xxyy	2893	3301	−14.1

TABLE 8: Parameter Transferability Analysis

	change (%) in parameter value from excluding F molecules	
center type	α_{iso}	γ_{iso}
(O)═C═	−1.2	−5.7
(O)═C (sp^2)	0.2	1.3
(H)C (sp)	−0.5	−3.7
C (sp^3)	−0.2	−1.7
C (sp)	−0.6	−8.9
C (sp^2)	0.3	0.7
(C)═C═(C)	−0.1	−0.2
N (sp)	0.4	1.5
N (sp^2)	1.4	4.4
(H$_2$)N (sp^3)	0.3	1.3
(H)N (sp^3)	1.2	−1.3
O═	2.0	19.4
−O−	0.9	−22.6

included in a molecule with four other non-hydrogen atoms but all single bonds.

An assessment of transferability is given by the values in Table 8. The table shows the percentage change in the parameter values from excluding fluorine molecules from the data set, and thereby excluding the F-center parameters from the fit. The changes are small, except for the γ parameters for the oxygen centers. However, oxygen's parameters (Table 3) are relatively small, and so the larger percentage change corresponds to roughly the same size of change as for the carbon centers. This clearly supports the idea that one can identify contributions from different types of atoms—that the parameters are transferable in part.

Additivity and transferability in the atomic origin of the second dipole hyperpolarizability response of organic molecules make for suitable predictions of the isotropic γ and even the entire tensor; however, the nature of this response is different from that of the induction of a dipole moment directly by an external field (i.e., the dipole polarizability response). From the fact that greater diffuseness in polarization functions is needed to carry out accurate ab initio evaluations of hyperpolarizabilities than polarizabilities, β, γ and so on, depend more on the outer regions of the electron distribution than does α. It is not surprising, then, that γ depends more on the bonding characteristics than does α, and hence, the AAC scheme does not work as well for γ as for α. Even so, the scheme has utility for estimating the second dipole hyperpolarizability of molecules that may be too large for ab initio calculations or for making comparison predictions within a series of compounds that may be too lengthy for ab initio calculations or laboratory measurement. To use the AAC scheme to find the γ-tensor elements of a chosen molecule, one must arrange the "building blocks", the atoms according to the types in Table 3, with respect to a chosen axis system for the molecule. Then, the individual tensors for each building block (Table 5) need to be transformed (rotated) by standard methods for fourth-ranked tensors from their reference orientation to their orientation in the chosen molecule. One then has a distributed representation of the molecular second dipole hyperpolarizability, and the complete γ tensor is the element-by-element sum of the rotated, atomic contributions.

Conclusions

The extensive collection of large basis ab initio results for the α and γ property tensors for 58 organic molecules shows that the major elements of these tensors are associated with atomic contributions. That is, they depend on additive and transferable contributions associated with the chemical composition and bonding types of the atoms. The predictive capability is judged to be around 10% for α and 40% for γ; however, the more important result from the AAC modeling of γ response is in showing the sizable influence of the bonding environment and distinguishing centers that tend to diminish the response. This may prove helpful in selecting substituents for the design of organic polymers for enhanced nonlinear response.

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