

## Finite Electric Field Valence-Shell Calculations of Molecular Hyperpolarizabilities

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Using the Finite Electric Field CNDO/II method discussed previously (Chem. Physics Letters 5, 507, (1970)), components of the first hyperpolarizability tensor  $\beta_{ijk}$  are calculated for a series of linear molecules, for H<sub>2</sub>O and NH<sub>3</sub> and for methane and its fluorinated derivatives. These are compared, where possible, with results of previous calculations and with experimental results.

Mit Hilfe der zuvor diskutierten CNDO/II-Methode, bei der endliche Werte des störenden elektrischen Feldes Verwendung finden (Chem. Physics Letters 5, 507 (1970)), werden die Komponenten des ersten Hyperpolarisierbarkeitstensors  $\beta_{ijk}$  für eine Reihe von linearen Molekülen, für H<sub>2</sub>O, NH<sub>3</sub> und für Methan und seine fluorierten Derivate berechnet. Soweit möglich, werden die Ergebnisse mit früheren Rechnungen und experimentellen Werten verglichen.

In a previous communication [1a] concerned mainly with electronic polarizabilities, we mentioned briefly preliminary calculations of components of the first hyperpolarizability tensor [2]  $\beta_{ijk}$  for the diatomic molecules CO and NO. These have now been extended.

Several sets of *ab initio* calculations of hyperpolarizabilities have previously been reported. O'Hare and Hurst [3], using an uncoupled Hartree-Fock perturbation scheme calculated hyperpolarizability tensor components for a series of First-Row polar diatomic molecules using several sets of zero-order wavefunctions. The finite-field technique has been employed by McLean and Yoshimine [4, 5] for a number of linear molecules, while Moccia *et al.*, [6], used a coupled Hartree-Fock perturbation method for H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub> and CH<sub>3</sub>F.

One fact which the results of these calculations reveal is the sensitivity of the hyperpolarizability components to the form of the basis set used and to the form of the zeroorder wave-function employed. A critical evaluation of the theoretical results is difficult at present due to the paucity of experimental data<sup>1</sup>. Where values are available, the experimental difficulties often allow only order of magnitude estimates to be made.

It is of interest to see whether semi-empirical calculations, with a valence orbital basis set, are capable of yielding useful predictions of hyperpolarizabilities. Using the Finite-Electric-Field CNDO/II method described earlier [1] we have extended our previous work to include calculations of first hyperpolarizability components for several linear ( $C_{\infty v}$ ) molecules, for H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub> and its fluorinated derivatives.

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<sup>1</sup> For a comprehensive survey of experimental methods and results the reader is referred to the review by Buckingham and Orr [2].

The perturbed SCF equations in the CNDO/II approximation are given in Ref. [1a] and these are used to calculate the perturbed dipole moment  $\mu$ . The latter is expanded in the familiar Taylor series in powers of the external field  $F$ :

$$\mu_i = \mu_i^0 + a_{ij}F_j + \frac{1}{2}\beta_{ijk}F_jF_k + \dots \quad (1)$$

where  $\alpha_{ij}$  is the electronic polarizability tensor. The nonzero components of  $\beta_{ijk}$  are determined by the molecular point group symmetry and are listed elsewhere [2]. For example, in the case of a  $C_{\infty v}$  molecule the non-zero components are  $\beta_{zzz}$  and  $\beta_{xxz} = \beta_{yyz}$  where  $z$  is the highest symmetry axis. In the finite field method, the components of the perturbing electric field are chosen to induce the component of the dipole moment appropriate to the  $\beta_{ijk}$  component it is required to calculate.

Thus to calculate  $\beta_{xxz}$  for a  $C_{\infty v}$  molecule the field is applied purely in the  $x$  direction and, since  $\beta_{ijk}$  is symmetric in the suffices,  $\frac{1}{2}\beta_{xxz}$  is then the coefficient of  $F_x^2$  in the expansion of  $\mu_x$ . The components of  $\beta$  were determined in this way by calculating the appropriate dipole component for several values of the field and obtaining the quadratic coefficients from a least-squares analysis. The results are discussed in the sections below.

### 1) Linear ( $C_{\infty v}$ ) Molecules

For these molecules we have calculated the non-zero components  $\beta_{zzz}$  and  $\beta_{xxz}$  ( $=\beta_{yyz}$ ). These, along with available comparison calculations, are listed in Table 1. Also listed in Table 1 are the corresponding values of the anisotropy,  $\Delta\beta$ , of the hyperpolarizability tensor [2] defined as

$$\begin{aligned} \Delta\beta &= \beta_{zzz} - \frac{3}{2}\beta_{xxz} - \frac{3}{2}\beta_{yyz} \\ &= \beta_{zzz} - 3\beta_{xxz} \end{aligned}$$

for  $C_{00v}$  molecules.

We note firstly that agreement with the finite-field calculations of McLean and Yoshimine [5] is reasonably good (CO, LiF, FCCH and HF)<sup>2</sup>. The values for  $\beta_{zzz}$  obtained by O'Hare and Hurst [3] from different zero-order wavefunctions cover a wide range for each molecule studied; for CO and HF these ranges include the values obtained by us and McLean and Yoshimine. The general agreement is best for HF. For the molecule BF however, our value for  $\beta_{zzz}$  ( $-0.0624 \times 10^{-50} \text{C}^3 \text{m}^3 \text{J}^{-2}$ ) differs in sign from the range of values ( $0.289 - 1.834 \times 10^{-50} \text{C}^3 \text{m}^3 \text{J}^{-2}$ ) calculated by O'Hare and Hurst.

Our calculated values of  $\beta_{xxz}$  are also shown in Table 1, and compared with the calculations of O'Hare and Hurst for CO, HF and BF. The three sets of wavefunctions used by O'Hare and Hurst give reasonably consistent values of  $\beta_{xxz}$  for HF and BF whereas for both these molecules the CNDO wavefunctions yield a value with the opposite sign. For the other molecule where a comparison can be made, namely CO, the range of values quoted by O'Hare and Hurst ( $0.0794$  to  $-0.0698 \times 10^{-50} \text{C}^3 \text{m}^3 \text{J}^{-2}$ ) includes our value ( $-0.0635 \times 10^{-50} \text{C}^3 \text{m}^3 \text{J}^{-2}$ ).

<sup>2</sup> Comparison values have, wherever necessary, been converted to S.I. units.

Table 1. Hyperpolarizabilities of linear ( $C_{\infty v}$ ) molecules<sup>a</sup> (Units:  $\times 10^{-50} C^3 m^3 J^{-2}$ )

Molecule	$\mu$ (cm $\times 10^{30}$ ) (calc.) <sup>b</sup>	$\beta_{zzz}$		$\beta_{xxz} = \beta_{yyz}$		$\Delta\beta(\beta_{zzz} - 3\beta_{xxz})$	
		This work	Comparison	This work	Comparison <sup>c</sup>	This work	Comparison
CO	3.1986	0.0731	0.0705 [5] 0.9273 [3]	-0.0635	-	0.2603	-
					-0.0794		-0.6891
					-0.0698		-0.1692
NO	-0.0153	0.0831	-0.3648 [3]	-0.0120	-0.0564	0.1191	-0.1956
					-		-
					-		-
LiF	-16.0719	0.1980	-	0.262	-	-0.588	-
					-		-
					-		-
FCCH	3.1916	-0.1990	0.1002 [5]	0.157	-0.2969 [5]	-0.670	-
					-0.0275 [5]		-
					-0.1050 [5]		-
HF	-4.4968	-0.0865	-0.2342 [3]	0.0193	-	-0.1444	-
					-0.0434		-0.0963
					-0.0200		-0.1040
BF	7.4232	-0.0624	-0.0618 [3]	-0.2930	-0.1974	0.8166	1.2418
					0.1974		0.0018
					0.1221		0.0057
			0.289 [3]		0.0817	0.0439	

<sup>a</sup> Atoms lie along positive z axis, with atom on the left at origin (F at origin in FCCH)<sup>b</sup> Positive in sense A<sup>-</sup>B<sup>+</sup>.<sup>c</sup> Ref. [3]. All bond lengths as in Ref. [1b].

Using a simple charged sphere model of a polar diatomic molecule, Buckingham and Orr [2] have shown that for this extreme limit  $\beta_{zzz} = 3\beta_{xxz}$  or  $\Delta\beta = 0$ . Such a model might roughly represent a highly polar molecule such as HCl but would form a poor representation of, for example, CO. From the values of  $\Delta\beta$  listed in Table 1 it is clear that in general for both the present and comparison calculations, this simple relationship is not well obeyed. However for two molecules, namely HF and BF, one of the values of  $\Delta\beta$  calculated by O'Hare and Hurst is indeed very small.

## 2) CH<sub>4</sub>(T<sub>d</sub>)

The only non-zero component of  $\beta_{ijk}$  in this case is  $\beta_{xzy}$  where the x, y and z axes are co-incident with the three twofold axes. Our calculated value can be compared with an approximate experimental one [2], and also with the theoretical values of Buckingham and Stephen [7] and Moccia *et al.* [6]:

This work	Previous calculations	Experimental	(Units: $\times 10^{-50} \text{C}^3 \text{m}^3 \text{J}^{-2}$ )
-0.00779 ( $r_{\text{C-H}} = 1.094 \text{ \AA}$ ; $\angle \text{HCH} = 109^\circ 28'$ )	-0.0779 [7] +0.0148 [6] +0.0071 [6]	$ \beta_{xzy}  \approx 0.0037$ [2]	

Moccia *et al.* calculate a positive sign for this quantity, in disagreement with the negative sign obtained in the present work and that of Buckingham and Stephen.

## 3) NH<sub>3</sub>(C<sub>3v</sub>)

With the reference frame such that the z-axis is the three-fold axis with the y-z plane one of the planes of symmetry, the non-zero components are  $\beta_{zzz}$ ,  $\beta_{yyy} = -\beta_{yxx}$  and  $\beta_{yyz} = \beta_{xxz}$ . Our values for these can be compared with those of Moccia *et al.* [6]. We can also compare values for the quantity  $\beta$  defined [2] as

$$\beta = \frac{3}{5}(\beta_{xxz} + \beta_{yyz} + \beta_{zzz})$$

for which an approximate experimental value has been quoted [2]. There is agreement of sign for both  $\beta_{zzz}$  and  $\beta_{yyz}$  but not for the  $\beta_{yyy}$  components. Both sets of calculated values of  $\beta$  have the same sign as the approximate experimental quantity but are smaller in absolute magnitude. It should also be noted that  $\beta$  is independent of  $\beta_{yyy}$ .

	This work	Moccia <i>et al.</i>	Expt.
$\beta_{zzz}$	-0.0488	-0.000798 -0.00854	
$\beta_{yyz}$	-0.00980	-0.00924 -0.0203	
$\beta_{yyy}$	-0.00490	+0.0173 +0.0283	
$\beta$	-0.0419	-0.0116 -0.0304	ca. -2.6

(Units:  $\times 10^{-50} \text{C}^3 \text{m}^3 \text{J}^{-2}$ )  
( $r_{\text{N-H}} = 1.016 \text{ \AA}$ ,  $\angle \text{HNH} = 107^\circ$ )

#### 4) $\text{H}_2\text{O}(\text{C}_{2v})$

The non-zero components here are  $\beta_{zzz}$ ,  $\beta_{xxz}$  and  $\beta_{yyz}$  with  $z$  as the two-fold axis and  $yz$  as the molecular plane. Again our results for these can be compared with Moccia *et al.* [6]. For the  $\beta_{xxz}$  component there is a disagreement in sign. The  $\beta_{zzz}$  values are in reasonable agreement and the  $\beta_{yyz}$  values agree in sign; however, there is a marked difference in Moccia's calculations performed with two different sized basis sets which emphasises the sensitivity of these calculations to choice of orbital basis.

	This work	Moccia <i>et al.</i> [6]	(Units: $\times 10^{-50} \text{C}^3 \text{m}^3 \text{J}^{-2}$ )
$\beta_{xxz}$	-0.1532	0.1086 0.8974	
$\beta_{yyz}$	-0.1232	-0.00006 -0.01026	
$\beta_{zzz}$	0.1274	0.06372 0.08032	

( $r_{\text{O-H}} = 0.958 \text{ \AA}$ ,  $\angle \text{HOH} = 104^\circ 27'$ )

#### 5) Fluorinated Derivatives of Methane

There is an unfortunate lack of experimental data for the molecules mentioned above; consequently appraisal of the various theoretical methods employed in the calculation of  $\beta$ 's is difficult. Recently however, experimental estimates of hyperpolarizability components for  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$  and  $\text{CHF}_3$  have become available through the work of Buckingham and Orr [8] on the temperature dependence of the first Kerr virial coefficient. The experimentally determined parameter is  $\beta$  (defined as in Section 3 above) and our calculated values for this quantity are compared with the experimental values in Table 2. Also included for comparison is a calculation by Moccia *et al.* [6] of  $\beta$  for  $\text{CH}_3\text{F}$ .

The most precise experimental value for  $\beta$  is that for  $\text{CH}_2\text{F}_2$  ( $-0.041 \pm 0.01 \times 10^{-50} \text{C}^3 \text{m}^3 \text{J}^{-2}$ ) and our calculated value of  $-0.0254 \times 10^{-50} \text{C}^3 \text{m}^3 \text{J}^{-2}$  is in fair agreement with this. For both  $\text{CH}_3\text{F}$  and  $\text{CHF}_3$  the experimental and calcu-

Table 2. Hyperpolarizabilities of fluorinated methanes (Units:  $-\times 10^{-50}\text{C}^3\text{m}^3\text{J}^{-2}$ )<sup>a</sup>

Molecule	$\mu_z(\text{cm} \times 10^{30})$ (calc.)	$\beta_{zzz}$	$\beta_{xxx}$	$\beta_{yyy}$	$\beta_{xyz}$	$\beta$ (calc.)	$\beta$ (expt.)
CH <sub>3</sub> F	-5.7310	-0.0186	-0.0067	-0.0067	0.0	-0.0192 <sup>b</sup>	-0.19 ± 0.1
CH <sub>2</sub> F <sub>2</sub>	6.6283	-0.0121	-0.0130	-0.0173	0.0	-0.0254	-0.041 ± 0.01
CHF <sub>3</sub>	5.7557	0.0221	0.0076	0.0076	0.0	0.0224	0.27 ± 0.1
CF <sub>4</sub>	0.0	0.0	0.0	0.0	0.0043	-	-

<sup>a</sup> Axis system is right-handed, with carbon at origin;  $z$  is the highest symmetry axis and the fluorine atom(s) always constitute the negative end of the dipole. In CH<sub>2</sub>F<sub>2</sub> the CH<sub>2</sub> fragment is in the  $yz$  plane.

<sup>b</sup> Moccia *et al.* [6] calculate  $\beta = -0.0594 \times 10^{-50}\text{C}^3\text{m}^3\text{J}^{-2}$

<sup>c</sup> Ref. [8].

Bond Lengths and angles:

CH <sub>3</sub> F: <HCH = 110°	$r_{\text{C-H}} = 1.109 \text{ \AA}$	$r_{\text{C-F}} = 1.385 \text{ \AA}$	
CH <sub>2</sub> F <sub>2</sub> : <HCH = 109.5°	<FCF = 108.5°	$r_{\text{C-H}} = 1.093 \text{ \AA}$	$r_{\text{C-F}} = 1.360 \text{ \AA}$
CHF <sub>3</sub> : <FCF = 108.8°	$r_{\text{C-H}} = 1.098 \text{ \AA}$	$r_{\text{C-F}} = 1.332 \text{ \AA}$	
CF <sub>4</sub> : $r_{\text{C-F}} = 1.317 \text{ \AA}$	<FCF = 109.5°		

lated  $\beta$  values have the same sign but even allowing for the appreciable uncertainty in the experimental value, the calculated  $\beta$  for CHF<sub>3</sub> is an order of magnitude different from that reported. The calculated  $\beta$  for CH<sub>3</sub>F is of the same order of magnitude as the upper estimated experimental limit for this molecule, as also is the calculated value of Moccia *et al.* [6].

It is clearly difficult at present to draw general conclusions from these results. Two points may however (with caution) be regarded as encouraging: these are firstly, the reasonable agreement for the axial hyperpolarizability components of linear molecules calculated by two finite-field methods (ours and that of Ref. [5]) and secondly, the quite good agreement for  $\beta$  with the best-established experimental value (i.e., that for CH<sub>2</sub>F<sub>2</sub>).

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