The Effect of the H-Bond Interactions on the First Hyperpolarisability of $(HF)_n$. A Comparative Study

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Z. Naturforsch. **45a,** 189–190 (1990); received November 13, 1989

The effect of H-bond interactions on the first hyperpolarisability (β) of $(HF)_n$ is discussed. The reported results confirm, computationally, the remarkable sensitivity of this property to intermolecular interactions, which has been found experimentally. Results for the second hyperpolarisability (γ) and the total energy (E) are also presented for comparative purposes. The analysis is based on data calculated by the CHF-PT-EB-CNDO method.

The molecular hyperpolarisabilities are of considerable importance because understanding of non-linear polarisation at the molecular level is essential for the design of materials with specific electric properties, which are required to construct various devices (e.g. switches for the modulation of waves carrying information, systems for the amplification of signals etc. [1]). Many questions related to these properties have not yet been fully answered. Among these problems are those concerning the effect of intermolecular interactions on the molecular hyperpolarisabilities. It is well documented experimentally, however, that they have a remarkable effect on the electric nonlinearities [2, 3]. Specific and very interesting examples of these interactions are those which may be found between H-bonded systems. In the present study we employ as model systems some hydrogen fluoride multimers $(HF)_n$ and analyse the effect of H-bond interactions on the first and second hyperpolarisability.

The properties (total energy and hyperpolarisabilities) have been determined by employing the CHF-PT-EB-CNDO [4] method, which relies on:

a) An extended basis (EB) CNDO wave function [5], the atomic orbitals of which are optimized, in general, with respect to some judiciously chosen property values. A detailed description of how this optimization is performed and its effect on the quality of the derived properties is given in [4]. The unperturbed wave function is computed by an upgraded version of the CNDO/2 program (QCPE 141). This part of the computations is in double precision.

b) McWeeny's et al. coupled Hartree-Fock perturbation theory (CHF-PT) [6]. The first and second order corrections to the density matrix are stored in single precision while all sums and inner products are computed in double precision.

The density matrices ($R^{(0)}$, $R^{(1)}$ and $R^{(2)}$), which appear in the expressions of the polarisability and hyperpolarisability components [6], were iteratively calculated. For their computation the following criteria have been used:

$$|{}_kR_{ij}^{(m)} - {}_{k-1}R_{ij}^{(m)}| < 10^{-n} N, \qquad (1)$$

where k is the iteration number, m the order of the density matrix R, and N the number of orbitals. We have for every ij:

for $m=0$, $n=4$ and
for $m=1, 2$, $n=6$.

In the present study the following basis set has been used [7a]:

H: 1s (1.0), 2s (0.9324), 2p (1.0),
F: 2s (2.6), 2p (2.6), 3s (0.6), 3p (0.8).

These orbitals have been optimized with respect to $\gamma(HF\ldots HF)=842$ a.u., which has been determined by an ab-initio method [7a].

In this work we employ normalized values for the properties, (total energy, E, first and second hyperpolarisabilities, β and γ [7b], respectively) since we are mainly interested in trends. In addition normalized

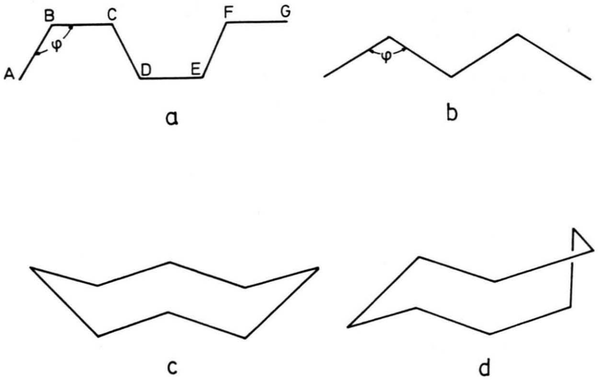

Fig. 1. The configurations of $(HF)_n$: a) Step form; b) Saw form; c) Extented crown; d) Boat-chair form.

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Table 1. The normalized[a] total energy E', the first and second hyperolarisabilities, β' and γ' of $(HF)_n$.

Cluster	Configuration[b]	E'	β'	γ'
$(HF)_3$	Linear form	1.00	1.00	1.00
$(HF)_4$	Linear form	1.3351	1.90	2.80
	Saw form	1.3385	0.91	1.30
	Step form	1.3393	0.63	1.25
$(HF)_5$	Linear form	1.6701	3.02	6.41
	Saw form	1.6749	1.42	2.68
	Step form	1.6760	0.76	2.61
$(HF)_6$	Linear form	2.0052	4.32	
	Saw form	2.0114	1.97	
	Step form	2.0131	1.44	
$(HF)_8$	Linear form	2.6753	7.72	
	Saw form	2.6843	3.44	
	Ext. crown form	2.6869	2.20	
	Boat form	2.6968	0.04	

[a] The values have been normalized with respect to the value of the linear $(HF)_3$ form.
[b] Figure 1.

values are much less affected by systematic errors (inherent to approximate methods like the present one), in comparison to the absolute values.

The employed configurations are shown Figure 1. The atoms of the hydrogen fluoride molecules in the linear configuration, which is not shown in Figure 1, lie on a straight line. The denotations for the configurations c and d have been taken from [8a]. Each side of every configuration (e.g. AB or BC) is 5.2723 a.u. (according to the experimental F…F distance [8b]). The angle φ in a and b is 108°, taken from the experimental geometry of $(HF)_2$ [8b], while c and d have the cyclooctane structure (the angles are given in [9]). For the calculation of the atomic coordinates a polar-to-cartesian conversion program has been used. This is similar to that which is included in the MINDO and MNDO programs (QCPE 309 and 353).

From the results in Table 1 we observe a much greater dependence of the hyperpolarisabilites, in comparison to the total energy, on the configuration and the size of the cluster. Comparing the first and second hyperpolarisability results, one notes that γ' is more sensitive than β' to the variation of n. It is also observed that the effect of varying the configuration ($n=$constant) is greater for the first hyperpolarisability than for the second. The same trend has been observed in the study of $(H_2O)_n$ [10]. For a given n the present hyperpolarisability values show the following dependence on configuration:

linear form > saw form > step form.

The present results also clearly demonstrate the cooperative effect [11] (each interaction enhances the next) of the intermolecular interactions on the hyperpolarisabilities.

In summary, the presented computations have provided evidence for the great sensitivity of the first hyperpolarisability of HF to intermolecular interactions. From the results presented here and others in the literature [10, 11], one may note the great sensitivity, in general, of the hyperpolarisabilities of molecules, which can form H-bonds, to environmental interactions. These remarks are supported by experimental evidence [2].

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[7] a) M. G. Papadopoulos and J. Waite, J. Chem. Soc., Faraday Trans., II, in press. b) The first and second hyperpolarisability (average values) are given by:
$$\beta=(3/5)\,(\beta_{zxx}+\beta_{zyy}+\beta_{zzz})$$
$$\gamma=(1/5)\,(\gamma_{xxxx}+\gamma_{yyyy}+\gamma_{zzzz}+2\gamma_{xxyy}+2\gamma_{xxzz}+2\gamma_{yyzz}),$$
where x, y, and z denote Cartesian components. One of the original references, where the above formulae are presented, is: A. D. Buckingham and B. J. Orr, Q. Rev. Chem. Soc. **21,** 195 (1967).

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