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*Original Scientific Paper*

# Dipole Polarizabilities of Fluorinated Hydrocarbons*

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*Abstract.* Dipole polarizabilities of fluorinated C2 and C3 hydrocarbons have been studied using Coupled Cluster theory including single, double and non-iterative triple substitutions (CCSD(T)) – in conjunction with three basis sets: Pol, Z3Pol and HyPol. All molecular geometries were optimized at the MP2/aug-cc-pVTZ level. We have found only small effects of electron correlation on electric properties in fluorinated species. The dipole polarizabilities increase slightly with the increasing fluorination of ethene and propene. For fluorinated ethenes Pol and Z3Pol basis sets give polarizabilities in very good agreement with the literature data.

*Keywords:* quantum chemistry, dipole polarizability, coupled clusters, hydrocarbons, fluorine

## INTRODUCTION

Organic materials play an increasing role in the electronics industry which is dominated by semiconductors and metals.[1] Organic semiconductors are an attractive alternative for new materials due to their potential in optoelectronic devices, switches and modulators.[2–9] Their principal advantages are: versatility and easy processing, tuneable conjugation in the system of π-bonds that can affect the ability to transmit electro-optic signal, large nonlinear optical (NLO) response and the possibility to tailor their physico-chemical properties by the manipulation of the molecular structure of the NLO chromophore.[10] One of the key parameters for the transmittance of the signals are polarizabilities and hyperpolarizabilities. It is known that fluorination of the chromophores improves the photochemical stability and leads to lower optical loss in the active material.[1,5,6,11] Theoretical quantum chemical calculations can assist in the choice of the suitable building blocks of the potential chromophore providing reliable data on electric properties like electric moments and polarizabilities of fluorinated hydrocarbons. Since the currently tested chromophores are often large molecules possessing complicated dentritic structure, the viable route in molecular modelling of their electric properties is to use specifically designed basis sets that strongly reduce the computational demands but still provide useful data for the experimentalists.

The aim of this paper is investigate the dipole polarizabilities of two series of fluorinated alkenes – ethenes and propenes using highly correlated quantum chemical *ab initio* methods with variety of basis sets used to build the wave function. Our particular goal is to check the performance of the property-tailored basis set designed especially for the calculations of electric properties of larger molecules and to suggest the optimal computational strategy for longer alkene-chains. As model systems we have chosen ethene, propene and their fluorinated derivatives, the latter possessing highly polar C−F bonds. With this class of molecules we can avoid also the issues connected with conformational sampling. The experimental data on electric properties of these molecules are rather scarce. There are only dipole moments for *cis*-difluoroethene, *gem*-difluoroethene, propene reported in ref. 12, and for 3,3,3-fluoropropene in ref. 13, dipole polarizabilities for ethene in refs. 12 and 14, for propene and *gem*-difluoroethene in ref. 12. Electric properties were also studied for other fluorinated ethenes and propenes.[15–19] Closely related is also the electron scattering study on $C_3H_6$, cyclo-$C_3H_6$ and $C_3F_6$ by Makochekanwa *et al.*[20]

## METHODS

The dipole polarizabilities of difluoroethenes and trifluoropropenes were calculated using Coupled Cluster

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* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.
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theory including single, double and non-iterative triple substitutions, CCSD(T).[21–23] Our set of molecules contained also non-substituted $C_2H_4$, $C_2F_4$ and fully substituted $C_3H_6$, $C_3F_6$. All geometries were optimized at correlated level using the second order perturbation theory - MP2[24] and aug-cc-pVTZ basis set,[25] including the harmonic frequency check to confirm that the stationary points on potential energy surface are true minima. All geometries are deposited in the Supplement. The orientation of the molecules follows the convention adopted by Russel and Spackman,[26] *i.e.*, $\alpha_{xx}$ and $\alpha_{zz}$, are the in-plane components and $\alpha_{yy}$ is the out-of-plane component. The molecular plane is either CCH/CCF for ethenes or CCC for propenes. We have calculated the dipole polarizabilities within standard finite-field scheme. Briefly, following Buckhingham[27] one can expand the energy of the molecule embedded in the static homogeneous electric field $\boldsymbol{F}$ in the Taylor series and omitting the cubic and higher-order terms we get

$$E(\boldsymbol{F}) = E^0 - \mu_\alpha F_\alpha - \frac{1}{2!}\alpha_{\alpha\beta}F_\alpha F_\beta - ... \quad (1)$$

$E^0$ denotes the energy of the unperturbed system, $\boldsymbol{\mu}$ is the permanent electric dipole moment vector, $\alpha$, stands for the second rank tensor of the static electric dipole polarizability, $F_\alpha$ means the component of electric field applied in the $\alpha$-direction. The Greek indices represent the summation in Einstein convention over the Cartesian axes $x$, $y$, $z$. This convention is utilised throughout this paper unless stated otherwise. Since the orientationally averaged electric quantities are the measures achievable from experiment we can evaluate also the orientationally averaged electric dipole polarizability $<\alpha>$ defined as

$$<\alpha> = \frac{1}{3}\alpha_{\lambda\lambda} \quad (2)$$

Within the finite-field scheme the components of the dipole moment and the dipole polarizability for the planar systems are determined through numerical differentiation of the energy perturbed by an external electric field (1). The electric field magnitudes adopted in numerical differentiations must be carefully examined to avoid contamination from higher-order terms truncated in the expansion (1) and numerical noise for the higher order moments/polarizabilities. Appropriate attention should also be paid to the applied electric field strengths, we have tested the fields ±0.001, ±0.002, ±0.004 a.u. The numerical stability of the finite-field model turned out to be very good. For the propene and fluorinated propenes we have adopted the formulas from ref. 28 and tested also simple central difference formulas with the field ±0.002 a.u. Since the differences were small, for the ethene and fluorinated ethenes we have used only simple formulas. Alternatively, instead of numerical scheme one can also use methods based on analytical derivatives.

For the smaller difluorethenes we have used the following series of the basis sets Pol,[29,30] Hypol[31] and Z3Pol,[32,33] while for the larger trifluoroethenes we used only Pol and Z3Pol basis sets. For the latter we have used the Z3Pol contractions C,F: (10s6p3d)/[4s3p1d], H: (6s3p)/[3s1p]. The Pol and Z3Pol basis sets were designed especially for electric properties calculations on larger systems. The construction of these basis sets is based on a simple physical model of the polarization effect of the external electric field which leads to very economical subset of polarization functions added to the chosen initial basis set. These polarization function are still diffuse enough to describe properly the response properties as well as highly polar bonds C−F. These basis sets are not expected to produce extremely accurate results but are considered as the minimal sets for acceptable electric properties of large molecules[34] mainly for economical reasons. Z3Pol basis sets are rougly 3 times smaller than aug-cc-pVTZ and more than 5 times smaller than aug-cc-pVQZ. This ratio represents more than two orders of magnitude saving in the computational effort in coupled cluster steps. In addition, Z3Pol basis are small enough to avoid most of the difficulties connected with large and diffuse basis sets (convergence problems in SCF or linear dependencies). Benková, Sadlej and Oakes[32,33] have shown for the series of small molecules containing the first- and the second-row atoms that the MP2/Z3Pol results are competitive with the results obtained with more demanding aug-cc-pVXZ basis set.

Our goal is to compare the results for C2 and C3 hydrocarbons and their fluorinated analogs obtained with Pol and Z3Pol sets with both experimental dipole polarizabilities and with the other theoretical data. In addition, for the Z3Pol basis we present also SCF and CCSD(T) dipole moments as a check of the electric field strengths adopted in the finite field scheme. Although the HyPol set was devised primarily for hyperpolarizabilities,[31] we have included it in our series because we plan to calculate also the higher polarizabilities of larger fluorinated chains in the future.

## RESULTS AND DISCUSSION

In Table 1 we present as a by-product of our calculations the dipole moments for polar difluoroethenes and trifluoroethenes. The comparison of experimental and theoretical dipole polarizabilities of ethene is given in Table 2. Here we have included also the previous theo-

**Table 1.** Dipole moments (debye) of difluoroethenes and trifluoropropene obtained with Z3Pol basis set

| Molecule | $\mu$(SCF)(a) / D | $\mu(\mathrm{SCF_{FF}})$(b) / D | $\mu$(CCSD(T))(b) / D | $\mu_{\mathrm{exp}}$ / D |
|---|---|---|---|---|
| *cis*-difluoroethene | $2.691_5$ | 2.692 | $2.400_5$ | 2.42±0.02(c) |
| *gem*-difluoroethene | 1.658 | 1.657 | 1.489 | 1.3893±0.0002(c) |
| propene | 0.429 | 0.429 | 0.357 | 0.366±0.001(c) |
| 1,1,2-trifluoropropene | 2.297 | 2.297 | 2.047 | - |
| 1,1,3-trifluoropropene | 3.097 | 3.097 | 2.777 | - |
| *Z*-1,2,3-trifluoropropene | 1.828 | 1.828 | 1.624 | - |
| *E*-1,2,3-trifluoropropene | 1.748 | 1.748 | 1.558 | - |
| *Z*-1,3,3-trifluoropropene | 2.528 | 2.528 | 2.299 | - |
| *E*-1,3,3-trifluoropropene | 1.982 | 1.982 | 1.780 | - |
| 2,3,3-trifluoropropene | 3.547 | 3.547 | 3.152 | - |
| 3,3,3-trifluoropropene | 2.805 | 2.805 | 2.497 | 2.443±0.020(d) |
| hexafluoropropene | $1.014_5$ | 1.015 | 0.901 | - |

(a) Expectation value. (b) Finite field value. (c) From ref. 12. (d) From ref. 13.

**Table 2.** Comparison of experimental and theoretical dipole polarizabilities of $C_2H_4$. Theoretical data are without vibrational correction.

| | Exper. | ref. 26 | | ref. 35 | ref. 39 | Pol(f) | Hypol(f) | Z3Pol(f) |
|---|---|---|---|---|---|---|---|---|
| $\alpha_{xx}$ | 26.02(a) | 25.56 | (1.17)(c) | 25.29(d) | 24.88(e) | 24.99 | 25.10 | 25.28 |
| $\alpha_{yy}$ | 22.38(a) | 22.92 | (0.44)(c) | 22.64(d) | 21.93(e) | 22.02 | 22.24 | 22.26 |
| $\alpha_{zz}$ | 35.06(a) | 34.83 | (1.17)(c) | 34.33(d) | 34.04(e) | 34.06 | 34.11 | 33.60 |
| $\bar{\alpha}$ | 27.82(a) , 28.69(b) | 27.77 | (0.93)(c) | 27.42(d) | 26.95(e) | 27.02 | 27.15 | 27.04 |

(a) From ref. 14. (b) From ref. 12. (c) MP2/DZP-ANO2, data in parentheses are vibrational corrections. (d) MP2/ELP+. (e) CC3/t-aug-cc-pVTZ model. (f) this work - CCSD(T) data.

retical values reported by Russell and Spackman[26] and Zhou and Dykstra.[35] Table 3 contains the dipole polarizabilities of difluoroethenes calculated in all three basis sets (Pol, Hypol and Z3Pol), Table 4 those of trifluoroethenes calculated only with Z3Pol basis set. We have chosen Z3Pol because in comparison with polarized basis sets Pol, Z3Pol is reduced to 2/3 in size what leads to the order of magnitude computing time savings for large molecules. Simultaneously, the dipole moment and polarizability data remain at almost the same level of accuracy as in the case of the Pol sets.[32] This makes Z3Pol good candidate for the calculation of electric properties of larger molecular systems.

Before we discuss the results on dipole moments and polarizabilities, we will briefly comment on the geometries (see the Supplement). Choice of the appropriate geometry is of crucial importance for reliable predictions of static electric properties. Since we are interested in the trends in electric properties over a range of substituted alkenes, natural choice would be experimental geometries. These are not available for all the molecules, therefore we decided to optimize the geometries at MP2/cc-pVTZ and MP2/aug-cc-pVTZ levels, respectively. The latter combination of the method/basis set turned out to perform better and the differences between known experimental geometries[36] of ethene and some fluorinated ethenes and our MP2/aug-cc-pVTZ values usually did not exceed 1 %. The only exception was the $H_2C$=CH-group in 3,3,3-trifluoropropene, some differences between theoretical and experimental internal coordinates were above 1 %, in the worst case the theory underestimated the C(2)−H(3) bond length in the HC-bond adjacent to trifluorinated carbon by 2.7 %.

The SCF dipole moments obtained by finite field approach are in excellent agreement with the expectation values, which supports the use of field strengths adopted in the finite field scheme. The comparison of the SCF and CCSD(T) values in Table 1 documents that the effects of electron correlation are very small and uniformly reduce the dipole moments by less than 1 %. The overall agreement with the experimental dipole moments for the first three molecules in Table 1 is good, except for *gem*-difluoroethene where the CCSD(T)/Z3Pol dipole moment is overestimated by ~7 %. For this molecule, we have recalculated the dipole moment also in Pol basis set and the CCSD(T)/Pol gives $\mu$ = 1.323 D, a value lower by ~5 % than the experimental one. Very good agreement with the experimental dipole moment of Saito and Makino has been found also for 3,3,3-propene ($\mu$ (CCSD(T)/Z3Pol) is larger by ~2 %). Most probably, these deviations are caused by

**Table 3.** Dipole polarizabilities of difluoroethenes and tetrafluoroethene (atomic units)

| Method<br>basis | MP2[(a)]<br>ELP+ | Pol | CCSD(T)<br>Hypol | Z3Pol |
|---|---|---|---|---|
| | | *cis*-$C_2H_2F_2$ | | |
| $\alpha_{xx}$ | 27.13 | 27.17 | 27.31 | 27.15 |
| $\alpha_{yy}$ | 21.33 | 21.51 | 21.79 | 21.63 |
| $\alpha_{zz}$ | 35.21 | 36.38 | 35.98 | 36.24 |
| $\bar{\alpha}$ | 27.89 | 28.35 | 28.36 | 28.34 |
| | | *gem*-$C_2H_2F_2$[(b)] | | |
| $\alpha_{xx}$ | 27.32 | 26.73 | 26.86 | 26.70 |
| $\alpha_{yy}$ | 21.57 | 21.69 | 21.93 | 21.77 |
| $\alpha_{zz}$ | 35.57 | 35.63 | 35.71 | 35.10 |
| $\bar{\alpha}$ | 28.15 | 28.01 | 28.16 | 27.86 |
| | | *trans*-$C_2H_2F_2$ | | |
| $\alpha_{xx}$ | - | 26.99 | 27.11 | 26.96 |
| $\alpha_{yy}$ | - | 21.00 | 21.31 | 21.12 |
| $\alpha_{zz}$ | - | 34.72 | 34.86 | 34.10 |
| $\bar{\alpha}$ | - | 27.57 | 27.76 | 27.39 |
| | | $C_2F_4$ | | |
| $\alpha_{xx}$ | - | 29.12 | 29.30 | 29.06 |
| $\alpha_{yy}$ | - | 21.12 | 21.46 | 21.36 |
| $\alpha_{zz}$ | - | 37.03 | 37.12 | 36.57 |
| $\bar{\alpha}$ | - | 29.09 | 29.29 | 28.99 |

(a) From ref. 35. (b) Experimental value: 33.81 a.u. from ref. 12.

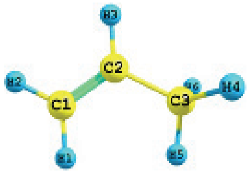
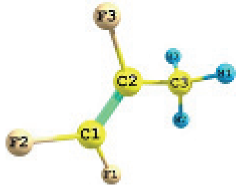
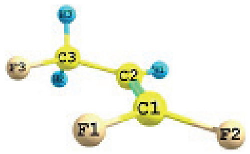
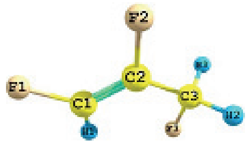
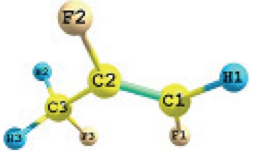
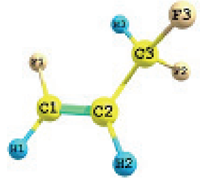
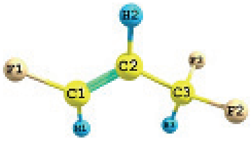
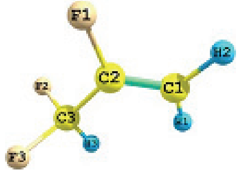
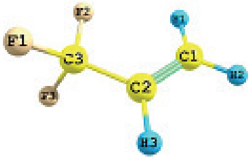
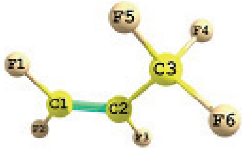
the interplay between possible basis set deficiency and missing vibrational correction.

The results for the dipole polarizabilities of ethene molecule are in Table 2. First, note that the vibrational correction to $\alpha$ is fairly small, as follows from the data reported by Russell and Spackman.[26] Our Pol, Hypol and Z3Pol results are very close to all three sets of the theoretical values, documenting very good performance of these "economical" basis sets. In Table 3 we can compare only the results for *cis*-difluoroethene and *gem*-difluoroethene with the data published by Zhou and Dykstra.[35] Again, the agreement is very good and gives the credibility to the polarizabilities of *trans*-difluoroethene and tetrafluoroethene. Overall, the fluorination of $C_2H_4$ does not bring dramatic changes in average dipole polarizability, for both bi- and tetra-substituted species. There is only moderate increase in *xx* and *zz* components, *i.e.* along the chain direction of (potentially) larger systems. The *yy* component is slightly lowered by fluorination. These trends are shared by all four species in Table 3.

Different trends can be observed in Table 4 for propene, trifluoropropenes and hexafluoropropene. First note that our $\bar{\alpha}$ for propene is lower than experimental value[12] by ~7 %, this is most probably due to the neglect of the vibrational correction. The out-of-CCC-plane $\alpha_{yy}$ components of the fluorinated species vary according to the position of the very electronegative fluorine atoms. If two fluorine atoms are attached directly to $sp^2$ carbons, there is a charge shift from >C=C< moiety towards fluorines, resulting in partial confinement of the electron density around CF groups. As a consequence the $\alpha_{yy}$ components are slightly lowered for 1,1,2-, 1,1,3-, *Z*-1,2,3- and *E*-1,2,3-trifluoropropene isomers.

If two or three fluorine atoms are attached directly to $sp^3$ carbon, there is a minor increase of the $\alpha_{yy}$ components of the dipole polarizability compared to $C_3H_6$ since the $\pi$-system on C=C double bond is less affected and there is probably also some back-donation from the fluorine lone pairs to C−C=C skeleton. In general, the $\alpha_{xx}$ and $\alpha_{zz}$ components tend to increase slightly upon fluorination. The overall changes in $\bar{\alpha}$ upon fluorination with respect to $C_3H_6$ are small, ranging from +1 % (*Z*-1,2,3- trifluoropropene) to 3 % (*E*-1,2,3-trifluoropropene). Full fluorination of $C_3H_6$ results only in 9 % increase of the total dipole polarizability. Small

**Table 4.** CCSD(T) dipole polarizabilities of $C_3H_6$, trifluoropropenes and $C_3F_6$ (atomic units)

| basis | Pol | Z3Pol | Pol | Z3Pol | Pol | Z3Pol | Pol | Z3Pol |
|---|---|---|---|---|---|---|---|---|
| | $C_3H_6$[(a)] | | 1,1,2- | | 1,1,3- | | Z-1,2,3- | |
| |  | |  | |  | |  | |
| $\alpha_{xx}$ | 42.49 | 42.36 | 44.47 | 44.16 | 44.53 | 44.35 | 44.35 | 44.02 |
| $\alpha_{yy}$ | 31.78 | 31.93 | 30.74 | 30.85 | 31.17 | 31.19 | 31.03 | 31.03 |
| $\alpha_{zz}$ | 43.66 | 43.73 | 45.42 | 45.26 | 45.33 | 45.18 | 44.77 | 44.51 |
| $\bar{\alpha}$ | 39.31 | 39.34 | 40.21 | 40.09 | 40.34 | 40.24 | 40.05 | 39.86 |
| | *E*-1,2,3- | | *Z*-1,3,3- | | *E*-1,3,3- | | 2,3,3- | |
| |  | |  | |  | |  | |
| $\alpha_{xx}$ | 46.55 | 46.15 | 43.85 | 43.56 | 42.29 | 42.11 | 45.01 | 44.77 |
| $\alpha_{yy}$ | 30.88 | 30.91 | 33.48 | 33.63 | 33.42 | 33.57 | 33.74 | 33.90 |
| $\alpha_{zz}$ | 43.06 | 42.90 | 43.73 | 43.68 | 46.04 | 45.95 | 42.81 | 42.77 |
| $\bar{\alpha}$ | 40.16 | 39.99 | 40.35 | 40.29 | 40.58 | 40.54 | 40.52 | 40.48 |
| | 3,3,3- | | $C_3F_6$ | | | | | |
| |  | |  | | | | | |
| $\alpha_{xx}$ | 43.49 | 43.42 | 48.08 | 47.95 | | | | |
| $\alpha_{yy}$ | 33.49 | 33.75 | 34.07 | 34.08 | | | | |
| $\alpha_{zz}$ | 43.19 | 43.43 | 46.61 | 46.63 | | | | |
| $\bar{\alpha}$ | 40.05 | 40.20 | 42.92 | 42.88 | | | | |

(a) Experimental value 42.24 a.u. from ref. 12.

changes in dipole polarizabilities are consistent with the rather small change of boiling points on fluorination, as well as surprisingly small changes in many other physical properties as documented by Liebman.[37] Our results are also relevant to the explanation of the "perfluoroalkyl effect" that suggests weak interactions between perfluorocarbons as contributing to the kinetic stability of strained perfluorocarbons over those of the parent species.[38]

## CONCLUSION

We have calculated dipole polarizabilities of fluorinated ethenes and propenes using CCSD(T) methodology and utilizing "economical" polarized basis sets. Their performance is very good, as far as the comparisons with the scarce experimental data and other theoretical calculations permit. Also the dipole moments for *cis*-difluoroethene, *gem*-difluoroethene and propene agree quite well with the available experimental ones. For the two lowest alkenes $C_2H_4$ and $C_3H_6$ we have found that the effect of fluorination on dipole polarizabilities is rather small and does not exceed +10 %. The increase of the average dipole polarizability is the result of the interplay between the $\alpha_{yy}$ component (perpendicular to CCC plane, prevailing minor reduction of dipole polarizability) and the $\alpha_{xx}$ and $\alpha_{zz}$ components (in the CCC plane, prevailing enhancement of the dipole polarizability). Our results demonstrate that the CCSD(T) method in conjunction with the Z3Pol basis set is suitable computational strategy for the calculations of the larger chains of fluorinated hydrocarbons. This combination is competitive to more demanding alternative for the calculations of electric properties using multiply-augmented cc-pVXZ basis sets.

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# SAŽETAK

## Dipolne polarizabilnosti fluoriranih ugljikovodika

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Dipolne polarizabilnosti fluoriranih C2 i C3 ugljikovodika proučavane su korištenjem *coupled cluster* teorije uz jednostruku, dvostruku i neiterativnu pobudu (CCSD(T)) – uz tri osnovna skupa: Pol, Z3Pol i HyPol. Sve molekulske geometrije optimirane su na MP2/aug-cc-pVTZ razini. Pronađen je samo mali efekt elektronske korelacije na elektronska svojstva flouriranih molekula. Dipolne polarizabilnosti su u malom porastu sa porastom broja fluoriranih atoma u etenu i propenu. Za fluorirane etene Pol i Z3Pol osnovni skupovi daju polarizabilnosti koje su u dobrom slaganju sa literaturnim podacima.