A First-Principles Study of the Influence of Fluorine–Fluorine Interactions on the Nuclear Quadrupole Parameters in Fluorobenzenes

S. Swingle Nunes,† N. Sahoo,† F. Hagelberg,† T. P. Das,*,† and K. Bonde Nielsen‡

Contribution from the Department of Physics, State University of New York at Albany, Albany, New York, 12222, and Institute of Physics, University of Aarhus, Denmark

Received March 12, 1992

Abstract: The nuclear quadrupole interaction parameters e^2qQ and η are calculated for fluorine nuclei in fluorobenzenes from wave functions obtained using a first-principles Hartree–Fock procedure utilizing linear combinations of atomic orbitals. Weighted averages of these individual parameters are used in an attempt to explain results obtained from time-dependent perturbed angular distribution measurements made earlier on various fluorobenzene samples implanted with $^{19}F^*$. Six different basis sets were used. Agreement between the calculated and experimental results for e^2qQ was within 16% in all cases and within 3% for two of the basis sets used, and the trend in e^2qQ with increasing fluorine substitution was successfully predicted. The asymmetry parameter calculations yielded results in good overall agreement with experiment.

I. Introduction

Results of quadrupole interaction studies involving the halogen nuclei have long served[1–3] as a means of investigating the electronic structures of numerous organic systems including some halobenzenes. Until the development of the time-dependent perturbed angular distribution (TDPAD) technique[4] which generates the excited $I = {}^5/_2$ $^{19}F^*$ nucleus and the β-decay nuclear magnetic resonance technique[5] which studies the ^{20}F nucleus with $I = 2$, it was not possible to obtain nuclear quadrupole data for molecules containing fluorine. As a result of TDPAD experiments, the coupling constants e^2qQ and asymmetry parameters η for various mixtures of fluorobenzenes became available.[6] At that time the semiempirical self-consistent charge extended Hückel (SCCEH) procedure was used[6] to understand the trends that were observed in the coupling constants. In the present work we have undertaken first-principles self-consistent Hartree–Fock calculations to make a quantitative analysis of both e^2qQ and η. Six different basis sets have been used to test the sensitivity of these calculations to the choice of basis set. The Hartree–Fock results obtained using the basis set which performed best in this study are presented for all unique fluorine sites in the molecules studied.

II. Review of Experimental Results

In TDPAD experiments, $^{19}F^*$ is generated as a recoil nucleus from the reaction F(P,P′)F* and is implanted into the sample of interest. The implanted $^{19}F^*$ nuclei emit γ-radiation during the process of relaxation to the ground state. The intensity of the resulting decay pattern is modulated[7] in a known manner by the quadrupole interaction of these $I = {}^5/_2$ nuclei with the surrounding electronic environment. Both e^2qQ and η are obtained from analysis of the resulting spectrum.

In the experiment on fluorobenzenes, four different solid fluorobenzene targets, C_6H_5F, 1,2,4-$C_6H_3F_3$, 1,2,4,5-$C_6H_2F_4$, and C_6F_6, were implanted with $^{19}F^*$. The implantation was accomplished in such a way as to insure that substitution was likely to occur only once in any given molecule. Furthermore, evidence was provided to indicate that implantation was equally likely to occur at any one of the six available positions in the fluorobenzene ring. The complete details of the original experiment are available in the literature.[6]

III. Theoretical Procedure

A self-consistent-field Hartree–Fock procedure (HF-LCAO) employing linear combinations of Gaussian atomic orbitals was used to obtain the molecular wave functions, ψ_μ for the fluorobenzenes. The procedure was implemented using the Gaussian 86 computer code.

The quadrupole interaction is characterized by two independent parameters,[1,2] the quadrupole coupling constant e^2qQ and the asymmetry parameter η both of which are dependent on the principal components V_{ii} of the electric field gradient (efg) tensor.

The components V_{jk} of the efg tensor are related to the molecular wave functions by:[2]

$$V_{jk} = \sum_N \frac{\zeta_N(3X_{jN}X_{kN} - R_N{}^2\delta_{jk})}{\mathbf{R}_N{}^5} - \sum_\mu \left\langle \psi_\mu \left| \frac{3x_jx_k - r^2\delta_{jk}}{r^5} \right| \psi_\mu \right\rangle \quad (1)$$

In eq 1, $\mathbf{R}_N$ is the position vector locating the Nth nucleus with respect to the nucleus under study, ζ_N is the corresponding nuclear charge, and X_{iN} is the ith component of $\mathbf{R}_N$. In the second term, representing the electronic contribution, the ψ_μ are molecular orbital wave functions corresponding to the occupied states μ, r is the position vector of an electron with respect to the nucleus under study, and x_i are its components. The calculated ψ_μ are substituted into eq 1 to evaluate the field-gradient tensor components V_{jk}, and the resulting field gradient tensor is diagonalized to obtain the principal components. These components are denoted according to the convention[1,2] $|V_{zz}| > |V_{yy}| > |V_{xx}|$. The quadrupole coupling constant is then given by e^2qQ, where $q = V_{zz}$, and η by $(V_{xx} - V_{yy})/V_{zz}$. The quadrupole moment Q for the $^{19}F^*$ nucleus was taken to be[8] 0.072 b.

For each target we used the procedure described above to obtain e^2qQ and η at the site of each $^{19}F^*$ that would be present as a result of the

† State University of New York at Albany.
‡ University of Aarhus.

(1) Lucken, E. A. *Nuclear Quadrupole Coupling Constants*; Academic Press: New York, 1969.
(2) Das, T. P.; Hahn, E. L. *Nuclear Quadrupole Resonance Spectroscopy*; Academic Press: New York, 1958.
(3) Bersohn, R. *J. Chem. Phys.* **1954**, *22*, 2078.
(4) Haas, H. *Phys. Scr.* **1975**, *11*, 221. Raghavan, P.; Kaufmann, E. N.; Raghavan, R. S.; Ansaldo, E. J.; Naumann, R. A. *Phys. Rev. B* **1976**, *13*, 2835.
(5) Ackermann, H.; Dubbers, D.; Stockmann, H. J. In *Advances in Nuclear Quadrupole Resonance*; Smith, J. A. S., Ed.; Heyden: London, 1978; Vol. 3. Fujara, F.; Stockmann, H. J.; Ackermann, H.; Buttler, W.; Dorr, K.; Grupp, H.; Heitjans, P.; Kiese, G.; Korblein, Z. *Phys. B.* **1980**, *37*, 151.
(6) Bonde Nielsen, K.; Toft, B.; Mishra, K. C.; Mishra, S. K.; Duff, K. J.; Das, T. P. *J. Am. Chem. Soc.* **1983**, *105*, 1734.
(7) Forker, M. *Nucl. Instrum.* **1973**, *106*, 121. Budtz-Jorgensen, C.; Bonde Nielsen, K. *Hyperfine Interact.* **1975**, *1*, 81.
(8) Mishra, K. C.; Duff, K. J.; Das, T. P. *Phys. Rev. B* **1982**, *25*, 3389.

0002-7863/93/1515-5145$04.00/0 © 1993 American Chemical Society

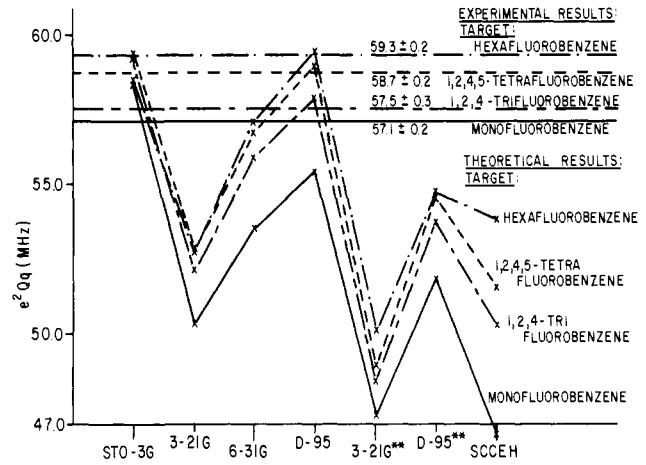

Figure 1. Electric quadrupole coupling constants, e^2qQ, obtained for four different fluorobenzene targets from Hartree–Fock theory using six different basis sets plotted together with the result of a self-consistent field extended Hückel calculation from a previous work. The horizontal lines represent experimental results from TDPAD measurements and are included for comparison.

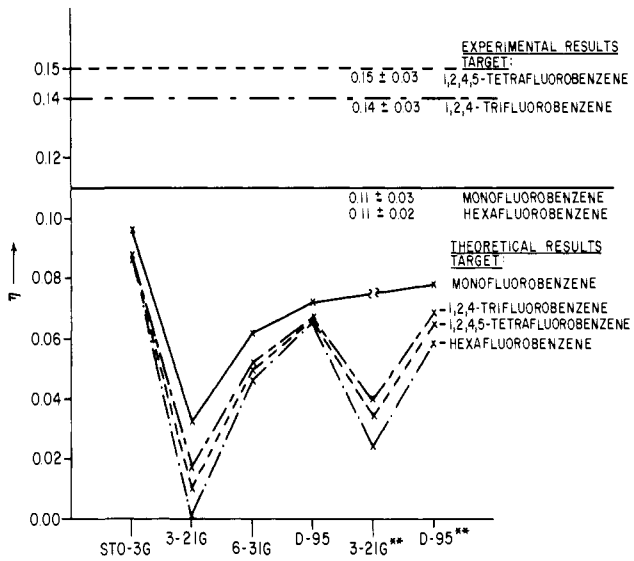

Figure 2. Asymmetry parameters, η, obtained for four different fluorobenzene targets from Hartree–Fock calculations using six different basis sets plotted together with the results of a self-consistent field extended Hückel calculation from a previous work. The horizontal lines represent the experimental results from TDPAD measurements and are included for comparison.

implantation process, using available structural data[9] for each molecule. In order to obtain the quadrupole coupling parameters for each target, the values of e^2qQ and η obtained for the individual substitution products were averaged according to the proportion of each one that would be present in the target after implantation. As mentioned earlier, it was assumed that substitution at each position in the fluorobenzene ring was equally probable. Thus, for example, in the case of the 1,2,4-trifluorobenzene target, three times out of six the result of the implantation process would be a 1,2,4-trifluorobenzene molecule with the excited nucleus located at positions 1, 2, and 4 with equal probability, i.e., in the ratio of 1:1:1. The remaining three times out of six substitution would produce a tetrafluorobenzene, the three products 1,2,3*,4-, 1,2,4,5*-, and 1*,2,3,5-tetrafluorobenzene occurring with equal probability.

Six different atomic orbital basis sets were employed in order to compare their suitability for field gradient calculations. The STO-3G[10] minimal basis set, the 3-21G[11] and 6-31G[12] split valence basis sets, and the double-ζ D-95[13] basis set were utilized. In addition, the 3-21G and D-95 bases were enhanced by the addition of d-orbitals on C and F and p-orbitals on H to incorporate possible polarization effects. These are subsequently referred to as 3-21G** and D-95**, respectively.

IV. Results and Discussion

The total energy was calculated for each molecule using all six basis sets, and the results were exactly as expected on the basis of the size and flexibility of each basis set. Of the four standard bases, the total energy calculated was in all cases lowest when the D-95 basis set was used, followed by 6-31G, 3-21G, and STO-3G. The addition of polarization orbitals to the 3-21G and D-95 bases resulted in lower total energies for all of the molecules.

Results of the coupling constant and asymmetry parameter calculations for all basis sets are presented graphically in Figures 1 and 2. The results[6] of both the TDPAD measurements and the SCCEH procedure are included for comparison.

In terms of the basis set used, D-95 yielded results in the best overall agreement with experiment, although STO-3G did almost as well. For all targets, the values obtained for e^2qQ using these basis sets are within 3% of the observed values and the values obtained for η are also closest to the experimental values. The good agreement obtained using STO-3G may seem surprising; however, it is not without precedent.[14–16]

The split valence basis sets consistently yielded values of e^2qQ and η which were lower than both the observed values and those obtained using D-95 and STO-3G. Of the two, 6-31G, which yielded lower total energies, also gave results in better agreement with the observed results for each target. The addition of polarization orbitals affected the calculation of the two quadrupole parameters differently. The calculations involving D-95** and 3-21G** yielded lower coupling constants than the parent basis sets, resulting in theoretical values further from the experimental values. In contrast, they led to asymmetry parameters which were somewhat closer to the observed values.

In all cases the Hartree–Fock results for e^2qQ agree with the experimental results to within 16%, and the calculations predict the trend of increase in coupling constant which is observed experimentally as the average number of fluorine atoms in the ring increases. For the two best basis sets, as mentioned above, agreement was to within 3%. As expected, the results were in all cases significantly better than those obtained earlier[6] using the semiempirical SCCEH method.

In the case of the asymmetry parameter, there is overall agreement with the experimental values in terms of the small observed magnitudes and the small variation over the various targets studied. It is more difficult to assess the quantitative performance of the procedure with respect to the determination of η due to the greater degree of uncertainty in the experimental results. Results of the SCCEH calculations for η are not included here. Since the main objective of the earlier work[6] was to compare the calculated e^2qQ values to those of experiment, the experimental values of η were, in fact, used to adjust the extended Hückel parameters.

As mentioned earlier, to obtain the average values for comparison with TDPAD data the quadrupole interaction parameters, e^2qQ and η, for all possible positions of fluorine in the fluorobenzenes were evaluated using the Hartree–Fock procedure. The values which were obtained using the D-95 basis set for all unique fluorine positions are listed in Table I. It is interesting to observe that the predicted variation in both e^2qQ

(9) Madelung, O. *Numerical Data and Functional Relationships in Science and Technology*; Springer-Verlag: Berlin/Heidelberg, 1987; Vols. 15 and 16.
(10) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.
(11) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.
(12) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
(13) Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*; Plenum: New York, 1976.
(14) Huzinaga, S. *Comp. Phys. Rep.* **1985**, *2*, 279.
(15) Davidson, E. R.; Feller, D. *Chem. Rev.* **1986**, *86*, 681.
(16) Sauer, J. *Chem. Rev.* **1989**, *89*, 199.

Table I. Quadrupole Coupling Parameters For Individual Fluorobenzenes from Hartree–Fock Calculations Using the D-95 Basis Set

	fluorobenzene	e^2qQ (MHz)	η	no. ortho neighbors	no. meta neighbors
1	mono-	54.1	0.0729	0	0
	di-[a]	55.7	0.0733		
2	orthodi-	56.8	0.0656	1	0
3	metadi-	54.8	0.0820	0	1
4	paradi-	55.4	0.0723	0	0
	tri-[a]	56.8	0.0764		
	1,2,3-tri-[b]	58.3	0.0662		
5	1,3	57.6	0.0717	1	1
6	2	59.7	0.0553	2	0
	1,2,4-tri-[b]	57.0	0.0656		
7	1	57.5	0.0552	1	0
8	2	57.6	0.0718	1	1
9	4	55.6	0.0697	0	1
10	1,3,5-tri-	55.1	0.0975	0	2
	tetra-[a]	58.5	0.0659		
	1,2,3,4-tetra-[b]	59.3	0.0621		
11	1,4	58.1	0.0621	1	1
12	2,3	60.3	0.0621	2	1
	1,2,3,5-tetra-[b]	58.3	0.0709		
13	1,3	58.3	0.0792	1	2
14	2	60.4	0.0470	2	0
15	5	56.3	0.0782	0	2
	1,2,4,5-tetra-	57.8	0.0648	1	1
	penta-[b]	60.3	0.0630		
17	1,5	59.2	0.0685	1	2
18	2,4	61.0	0.0551	2	1
19	3	61.2	0.0677	2	2
20	hexa-	59.5	0.0651	2	2

[a] Averaged over all molecules of this type. [b] Averaged over all positions in the molecule.

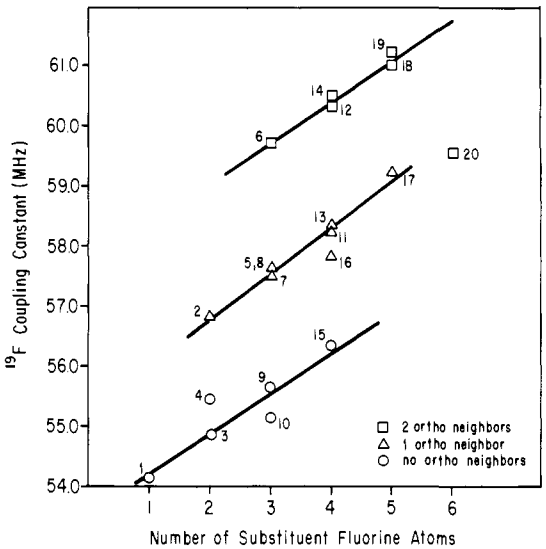

Figure 3. Theoretical quadrupole coupling constants, e^2qQ, obtained for the fluorine atoms of various fluorobenzenes using the D-95 basis set plotted against the total number of fluorine atoms in the rings. The numbers associated with the data points refer to the numbers used to identify the fluorine atoms in Table I.

and η from one site to another in a given fluorobenzene is often as great as the variation from one fluorobenzene to another. This is particularly striking in the case of η.

In Figure 3, the theoretically determined values of e^2qQ from Table I for each unique fluorine position are plotted against the number of fluorine atoms in the fluorobenzene ring. This plot is qualitatively similar to a plot of experimentally observed values of e^2qQ for chlorine nuclei in various chlorobenzenes which is presented elsewhere in the literature.[2] The plot in Figure 3 divides naturally into three distinct curves, each consisting of points

Table II. Comparison of Theoretical and Experimental Quadrupole Parameters for Fluorobenzene Targets

	HF-LCAO theory D-95 basis set		experimental[6]	
sample	e^2qQ (MHz)	η	e^2qQ (MHz)	η
$^1/_6C_6H_5F + {}^5/_6C_6H_4F_2$	55.4	0.0723	57.1 ± 0.2	0.11 ± 0.03
$^1/_2C_6H_3F_3 + {}^1/_2C_6H_2F_4$	57.8	0.0671	57.5 ± 0.3	0.14 ± 0.03
$^2/_3C_6H_2F_4 + {}^1/_3C_6HF_5$	58.9	0.0657	58.7 ± 0.2	0.15 ± 0.02
C_6F_6	59.4	0.0652	59.3 ± 0.2	0.11 ± 0.02

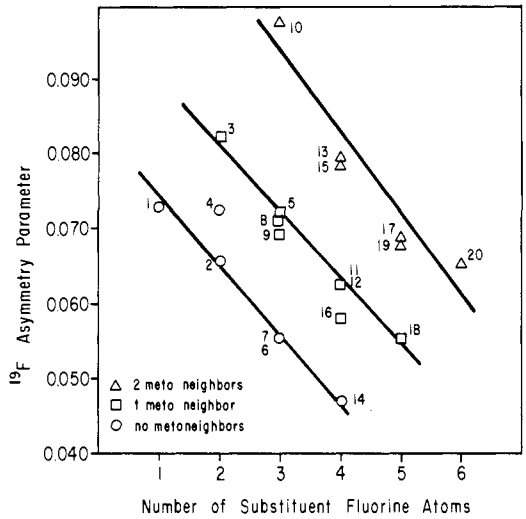

Figure 4. Theoretical asymmetry parameters, η, obtained for the fluorine atoms of various fluorobenzenes using the D-95 basis set plotted against the total number of fluorine atoms in the rings. The numbers associated with the data points refer to the numbers used to identify the fluorine atoms in Table I.

representing positions which have the same number of ortho fluorine neighbors. For those atoms with the same number of ortho neighbors, there is an approximately linear increase in the coupling constant as the number of fluorine atoms in the ring increases. This is in keeping with expectations,[3] since the inductive effect of the additional F atoms increases the competition for electrons from the ring, which in turn leads to a decrease in the ionic nature of the individual CF bonds. This shift in electron density away from the spherical symmetry characteristic of a purely ionic bond results in an increased e^2qQ.

The plot also shows that when the total number of F atoms in the ring is fixed the coupling constant increases as the number of ortho neighbors increases. Since the inductive effect decreases with distance, the increase in e^2qQ with the number of ortho neighbors might be explained purely in terms of the inductive effect. It is, however, interesting to consider the theoretical values obtained for the difluorobenzenes. Based upon consideration of the inductive effect alone one would predict that $e^2qQ_{ortho} > e^2qQ_{meta} > e^2qQ_{para}$. The Hartree–Fock calculations predict, instead, $e^2qQ_{ortho} > e^2qQ_{para} > e^2qQ_{meta}$. An increase in fluorine π-character would also lead to a decrease[2] in e^2qQ. Ortho and para resonance structures would be expected to have qualitatively the same effect on the stability of this π-interaction, while meta resonance would have the opposite effect. The results of this work suggest that the ortho and para resonance destabilizes the fluorine π-interaction relative to that of the meta. Clearly, both inductive and resonance effects are important in determining e^2qQ in the fluorobenzenes.

A similar plot of the theoretical asymmetry parameters for the fluorobenzens is presented in Figure 4. The data again divide naturally into three distinct curves, but the division occurs on the basis of the number of meta fluorine neighbors of the nucleus under consideration. Each of these curves exhibits a distinct decrease in η as the number of fluorine atoms in the ring increases,

and in each instance the relationship is also approximately linear. The asymmetry parameter in a π-system such as this one is determined by the degree to which the F atom participates in π-bonding.[3] As electrons are drawn from one of the p orbitals perpendicular to the plane of the molecule, the electron distribution becomes less symmetric about the bonding axis and η increases. The increased competition for electrons which accompanies the addition of F atoms to the ring decreases the participation of individual F atoms in the aromatic system, and so η decreases.[2] The plot also shows that the asymmetry parameter increases as the number of meta neighbors increases when the total number of F atoms is fixed. Thus, the participation of fluorine electrons in the π-system seems again to be stabilized by a resonance effect when they are in the meta position. This conclusion is further supported by the Hartree–Fock values for η in the difluorobenzenes, i.e., $\eta_{meta} > \eta_{para} > \eta_{ortho}$.

V. Conclusions

In summary, the most reliable basis set, D-95, used for our SCF Hartree–Fock calculations provides good overall agreement with e^2qQ and η obtained from TDPAD measurements made on different fluorobenzene targets. This is demonstrated in Table II, where the values obtained for e^2qQ and η for all targets using the D-95 basis set are compared to the experimental results. The quantitative agreement is better for the coupling constant e^2qQ than for the asymmetry parameter η, and so it is worthwhile to remark on possible avenues of improvement. It might be useful to explore the possibility that these basis sets underestimate the extent to which the fluorine atoms are involved in π-bonding. One potential means of accomplishing this is suggested by the effect observed on the values of η when polarization orbitals were added to the standard basis sets. The addition of carefully optimized d-orbitals to the more saturated D-95 basis set might provide a means to better describe this π-interaction. However, as we have observed, the addition of this particular set of d-orbitals caused an increase in the departure of e^2qQ from the observed values. It would be interesting to determine whether increasing the flexibility of the basis set by using a larger set of d-states would improve the results of the calculations of η without diminishing the good agreement for e^2qQ. Also, molecule-optimized basis functions[14] are available in which the coefficients of σ-bonding p-orbitals are optimized separately from the π-bonding p-orbitals. Basis sets of this type might be more successful in quantitatively predicting the asymmetry parameters in aromatic systems such as the halobenzenes.

Finally, we look forward to the development of an experimental technique which would permit the measurement of e^2qQ and η at the site of all the individual F nuclei. Comparison of these theoretical results to the results of such experiments is necessary in order to more completely verify the conclusions of the theory than is currently possible with TDPAD which measures averages.