1734 *J. Am. Chem. Soc.* **1983**, *105*, 1734-1737

Nuclear Quadrupole Interaction of the Excited Nuclear State ($^{19}F^*$, $I = {}^5/_2$) of Fluorine in Fluorobenzenes

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Received May 10, 1982

Abstract: Nuclear quadrupole coupling constants and asymmetry parameters associated with the excited state $^{19}F^*$ ($I = {}^5/_2$) of the fluorine nucleus have been obtained by the nuclear radiation technique referred to as the time differential perturbed angular distribution (DPAD) technique in fluorobenzene systems. The experimental results are explained successfully using the self-consistent charge extended-Hückel procedure to obtain the electronic wave functions of these systems. The results provide support for the recent revision of the nuclear quadrupole moment of this excited level of the fluorine nucleus.

I. Introduction

The nuclear quadrupole interaction tensors of the halogen nuclei^{35,37}Cl, ^{79,81}Br, and ^{127,129}I have provided valuable insights[1-3] into the electron distributions in halobenzenes. Such data were not available in the past for the fluorobenzenes because of the fact that the ground state of the ^{19}F nucleus has spin $^1/_2$ and hence zero quadrupole moment which precluded the possibility of obtaining field gradient tensor data by conventional nuclear magnetic resonance and quadrupole resonance methods. Recently, however, through the nuclear radiative technique, referred to as the time-dependent angular distribution (DPAD) technique,[4] an increasing amount of nuclear quadrupole interaction data is being obtained for the $\tau = 129$ ns isomeric state of the excited $^{19}F^*$ nucleus. In view of the fact that this state of $^{19}F^*$ has spin $^5/_2$, it is possible to obtain[1,2] both the quadrupole coupling constants (e^2qQ) and asymmetry parameters (η) in fluorine compounds. In the present paper we present such data for a number of fluorobenzenes obtained through DPAD measurements and analyze them from the point of view of the electronic structures of these compounds. There are four features of the data that are subjected to theoretical test in the present work. These are the absolute values of the quadrupole coupling constants, the trend of variation of these quadrupole coupling constants among the fluorobenzenes, the absolute values of the asymmetry parameters, and the trend in their variations over the fluorobenzenes. Recently, a value of the quadrupole moment Q of $^{19}F^*$ has been obtained[5] within a confidence limit of 5% from a combination of the calculated field gradient in the diatomic FCl molecule using an accurate first-principle Hartree–Fock procedure with the observed $^{19}F^*$ quadrupole coupling constant.[6] The interpretation of the absolute values of the fluorobenzene quadrupole coupling constants therefore provide a consistency test of this new value of the quadrupole moment.[5] Unfortunately, the sizes of the fluorobenzene molecules make first-principle calculation of the field gradient at $^{19}F^*$ nuclei rather laborious and expensive in terms of computer time.

We have therefore utilized the self-consistent charge extended-Hückel (SCCEH) procedure[7] for obtaining the electronic wave functions and utilized them to calculate the field gradient tensors at the $^{19}F^*$ sites in the fluorobenzenes. Analysis of this type allows semiquantitative tests of the electron distributions over the molecules by their ability not only to explain the values of the $^{19}F^*$ quadrupole coupling constants but also the other three features of the quadrupole interaction data. The SCCEH procedure has been successful in the past for analysis of nuclear quadrupole interactions in a number of systems, among them solid halogens[8] and ^{125}Te nucleus in[9] tellurium, selenium, and sulfur. Section II provides a brief description of the experimental procedure and presents nuclear quadrupole interaction data. Section III describes the procedure of calculation of the electronic wave functions and field-gradient tensor. Section IV presents the theoretical results for the quadrupole coupling and asymmetry parameters, their comparison with experiment, and discussion. The last section presents the main conclusions of the present work and possible future investigations that are suggested by it.

II. Experimental Procedure and Results

The fluorobenzene data have been obtained by the DPAD technique[4] in which probe nuclei are implanted into a host material as recoil nuclei from the nuclear reaction F(P,P′)F*. A fraction of these recoils are left in an isomeric state for subsequent γ decay. The quadrupole interaction of the probe and environment then gives rise to the modulation of the γ-decay intensity, when the γ-rays are recorded at a fixed angle with respect to the beam axis and time-correlated to the initiating reaction. The modulation pattern takes the form[10]

$$G_{22}(t) = A_{20}(\eta) + \sum_{i=1}^{3} a_{2i}(\eta) \exp[-{}^1/_2(n_i(\eta)\omega_0\delta t)^2] \times \cos\,(n_i(\eta)\omega_0 t) \quad (1)$$

which applies to the case of fluorine. For $I = {}^5/_2$, one has[2]

$$\omega_0 = \frac{3\pi}{10}e^2qQ/\hbar$$

where q is the largest principal component of the field-gradient tensor. The coefficients a_{2i} and n_i are known functions of the asymmetry parameter η. For axial symmetry ($\eta = 0$) n_i becomes equal to i (= 1, 2, 3). The δ parameter of the exponential damping term accounts for the Gaussian distribution in the components of the electric field gradient, an effect of the damage produced

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(2) T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy", Academic Press, New York, 1958.

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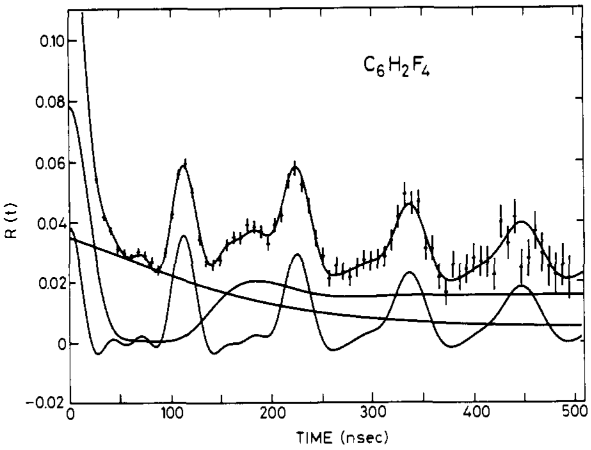

Figure 1. Illustration of the three-component fitting of $R(t)$ (see text).

in the target during bombardment. It also accounts approximately for the superposition of field gradients from the different fluorobenzenes produced in the sample. For example, in a target of monofluorobenzene, one expects that the $^{19}F^*$ recoil nuclei will be substituted according to the statistical weights of the various available position on benzene including the position of the normal ^{19}F nucleus already present, yielding a sample of $^1/_6C_6H_5F^*$ + ($^1/_3$ortho + $^1/_3$meta + $^1/_6$para)$C_6H_4FF^*$, and that the measured quadrupole frequency represents the corresponding average value. At high beam doses one may expect secondary effects of radiation-induced accumulated changes in the target composition (except for the case of C_6F_6). Since no significant changes in the modulation spectra were observed for a factor of ten increase in dose from 10^{14} to 10^{15} protons per cm^2, this is not expected to be a major effect in our data.

A typical time spectrum is shown in Figure 1, which also illustrates the least-squares fitting of the experimental ratio function

$$R(t) = \frac{N(0°) - N(90°)}{\frac{1}{2}N(0°) + N(90°)}$$

Here $N(\theta)$ is a number of coincidence counts of γ decay and beam burst at angle θ between beam direction and the direction of the detectors. Three modulation terms have been included in the fit, the first two being a weakly damped unique benzene component and a strongly damped component, which may represent superposition of signals from radiation-induced molecular fragments or radicals. Both of these are represented by eq 1. The third decaying term is needed to produce good fits; it could represent F recoils in a nonstatic environment, or it could have a similar origin to that of the second component but with weaker average quadrupole interaction. The crucial parameters η and e^2qQ of the benzene signal are not influenced significantly by its exact shape. The initial (t = 0) amplitude is expected to be 0.15, in good agreement with the sum over all three terms. All measured and fitted benzene components are shown in Figure 2.

The fraction of the $^{19}F^*$ recoil nuclei that enters in a particular position in the benzene ring is found to be largely independent of the benzene derivative used, showing that the substitutional process is statistical to first order, not favoring the replacement of F over the replacement of H or vice versa. This conclusion is supported by similar results in Teflon,[11] which demonstrate that the substitution mechanism in this case is radiation-chemical in nature and requires the accumulation of broken bonds trapping the $^{19}F^*$ recoil nuclei. All data in Table I refer to molecular crystals, that is, fluorobenzenes condensed on a cold finger held at liquid nitrogen temperature. It is seen that the shifts between the sample components are smaller than δ, indicating that environmental effects on the coupling constant which have been enchanced by radiation damage are a major contribution to δ.

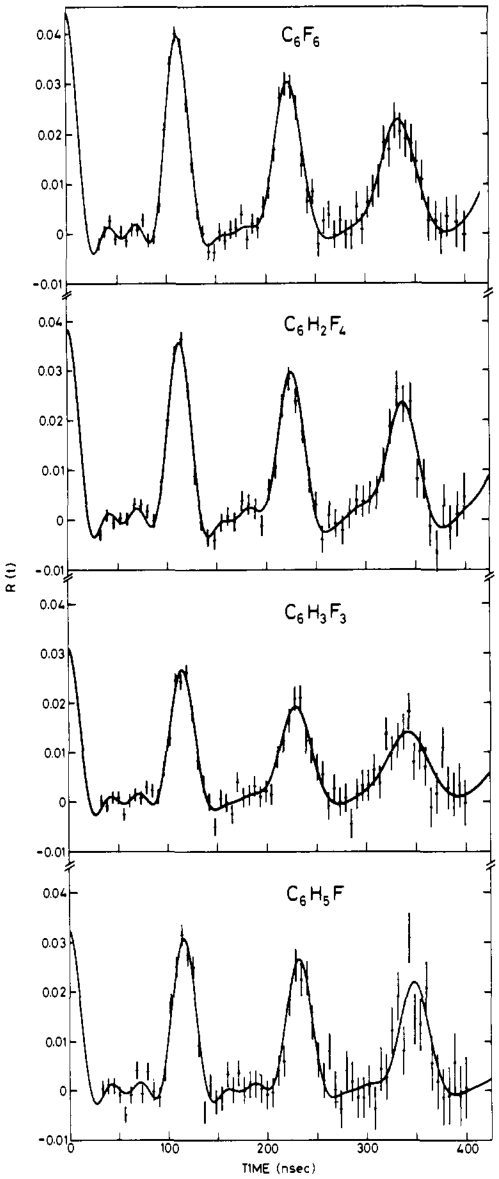

Figure 2. Experimental and fitted time spectra. Damped and decaying components subtracted (cf. Figure 1).

Table I. Experimental Quadrupole Coupling Parameters Obtained for Frozen Fluorobenzene Targets

target	sample	e^2qQ/h, MHz	η^b	δ^b
C_6H_5F	$^1/_6C_6H_5F$ + $^5/_6C_6H_4F_2{}^a$	57.1 ± 0.2	0.11 ± 0.03	0.03 ± 0.005
1,2,4-$C_6H_3F_3$	$^1/_2C_6H_4F_2{}^a$ + $^1/_2C_6H_3F_3{}^a$	57.5 ± 0.3	0.14 ± 0.03	0.05 ± 0.007
1,2,4,5-$C_6H_2F_4$	$^1/_3C_6HF_5{}^a$ + $^2/_3C_6H_2F_4$	58.7 ± 0.2	0.15 ± 0.02	0.04 ± 0.007
C_6F_6	C_6F_6	59.3 ± 0.2	0.11 ± 0.02	0.04 ± 0.003

[a] Average over three possible F* substitutional positions. [b] The presence of a finite δ might lead to a slight overestimate of η^{10} by 10%.

III. Procedure of Calculation and Theoretical Results

The self-consistent charge extended-Hückel (SCCEH) procedure[7] that we have used for calculation of the electronic wave functions of the molecules studied is described extensively in a number of places in the literature.[12] We shall review it very briefly

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[11] K. Bonde Nielsen and B. Toft, *Hyperfine Interact.*, **10**, 747 (1981).

[12] See R. Hoffman, ref 7; M. Zerner, M. Gouterman, and H. Kobayashi, *Theor. Chim. Acta*, **6**, 363 (1966); P. S. Han, M. F. *Rettig*, and T. P. Das, *ibid.*, **16**, 1 (1970).

here for the sake of completeness and because this description is necessary to point out adjustments of some of the parameters in the theory that we have made to fit one of the nuclear quadrupole interaction data and verified their correctness by comparing the results of theory with other available data. The SCCEH procedure utilizes a molecular orbital approximation involving a linear combination of atomic oribtals (LCAOMO) in which the molecular wave functions are expressed as

$$\psi_\mu = \sum C_{\mu i}\chi_i \tag{2}$$

where the χ_i are atomic orbitals belonging to the valence states of the atoms in the molecule. The coefficients are obtained by solving the secular equation

$$\det|\mathcal{H}_{ij} - S_{ij}E_\mu| = 0$$

to obtain the eigenvalues E_μ for the molecular orbitals and then substituting these eigenvalues in the set of linear equation

$$\sum_j C_{\mu j}(\mathcal{H}_{ij} - S_{ij}E_\mu) = 0 \tag{3}$$

with $\mathcal{H}_{ij}$ and S_{ij} representing respectively the matrix elements of the Hamiltonian and the overlap integrals over the atomic orbitals χ_i and χ_j. The matrix elements $\mathcal{H}_{ij}$ are obtained semiempirically using ionization energies ϵ_i corresponding to the atomic orbitals and the effective charges on the atoms they belong to. Thus

$$\mathcal{H}_{ii} = \epsilon_i^\circ + |\xi|(\epsilon_i^\pm - \epsilon_i^\circ) \tag{4}$$

$$\mathcal{H}_{ij} = \frac{K}{2}S_{ij}(\mathcal{H}_{ii} + \mathcal{H}_{jj}) \tag{5}$$

with ξ, the charge on the atom, given by

$$\xi = Z - \sum_i U_i \tag{6}$$

In eq 6, Z represents the formal charge on the atom, that is, the number of electrons from the atom used in the molecular orbital expansion in eq 2, and U_i is the Mulliken population[13] in orbital i given by

$$U_i = \sum_\mu (C_{\mu i}^2 + \sum_j S_{ij}C_{\mu i}C_{\mu j})n_\mu \tag{7}$$

n_μ being 0, 1, or 2 depending on whether the molecular orbital is empty or singly or double occupied. The charge convergence in the SCCEH procedure is brought about by using the set of $C_{\mu i}$ for any cycle of iteration to determine ξ from eq 6 and 7 and then to use them for obtaining the Hamiltonian matrix elements for the next cycle and carrying on the iterative process until the charges on the atoms in successive cycles agree within 5%. The quantity k is an adjustable parameter in the range 1.5 to 2.0 obtained usually by fitting some observed experimental data such as optical spectroscopic data.

Once the wave functions are obtained, one can in principle calculate[1,8] the components of the field gradient tensor at the nucleus under study in any coordinate system and then obtain the principal components by diagonalization, leading to the two important parameters q and asymmetry parameter η, where

$$q = q_{ZZ} \tag{8}$$

and

$$\eta = (q_{XX} - q_{YY})/q_{ZZ} \tag{9}$$

(X, Y, Z) referring to the principal axis system. Instead, in the spirit of the semiempirical procedure we have used for obtaining the electronic wave functions, we have made use of the Townes–Dailey procedure,[1,2,14] which has been found to be satisfactory for halogen nuclei, with q and η related to U_x, U_y, and U_z, the populations in the $2p_x$, $2p_y$, and $2p_z$ orbitals of fluorine atom as follows

$$\eta = \frac{1.5(U_x - U_y)}{U_z - (U_x + U_y)/2} \tag{11}$$

with q_0 in eq 10 representing the field gradient due to an electron in the p_z state. The field gradient parameter q is related to the observed quadrupole coupling constant by the relation

$$e^2qQ/h = 724.9(eq)(eQ)\ \text{MHz} \tag{12}$$

where eq is the field gradient is in units of 10^{16} esu and Q in units of barns, e^2qQ are being obtained from DPAD experiments as described in section II.

Table II. Quadrupole Coupling Constants and Asymmetry Parameters for Fluorobenzenes

	adjusted EH parameters		unadjusted EH parameters[a]	
molecule	e^2qQ, MHz	η	e^2qQ, MHz	η
C_6H_5F	44.63	0.088	26.13	0.357
p-$C_6H_4F_2$	46.13	0.113	26.05	0.389
o-$C_6H_4F_2$	47.42	0.095		
m-$C_6H_4F_2$	46.91	0.093		
1,3,5-$C_6H_3F_3$	49.31	0.102		
1,2,3-$C_6H_3F_3$	49.94	0.105		
1,2,4-$C_6H_3F_3$	49.02	0.126	26.89	0.398
1,2,3,4-$C_6H_2F_4$	52.37	0.116		
1,2,3,5-$C_6H_2F_4$	51.88	0.116		
1,2,4,5-$C_6H_2F_4$	50.66	0.141	26.95	0.429
C_6HF_5	53.04	0.159		
C_6F_6	53.84	0.168	28.02	0.447

[a] The quadrupole parameters for this choice were calculated for only a few systems, particularly for those needed for comparison with the experimental results for C_6H_5F target.

IV. Results from Theory, Comparison with Experiment, and Discussion

We have analyzed first the asymmetry parameters η to attempt to decide on a proper choice of the parameters in SCCEH theory. For the purposes of this decision it was considered more appropriate to use η rather than the quadrupole coupling constants, since the latter involve the quadrupole moment Q for $^{19}F^*$, and it was intended to check the recently revised value[5] of the latter by a comparison of theoretical and experimental coupling constants. Using the extended-Hückel parameter $\kappa = 1.75$ and the values of the effective ζ for the Slater oribtals commonly used[15] for C and F, namely 1.61 and 1.57 and 2.56 and 2.55 respectively for 2s and 2p orbitals, one obtains the values of η in the third column of Table II which are seen to be rather large compared with the experimental results in Table I. Since η is seen from eq 11 to depend on U_x, U_y, and U_z, the large value of η indicates that the covalent interaction between the π orbitals is overestimated in the wave-function calculation. To reduce this covalency, one needs to reduce the off-digonal matrix elements $\mathcal{H}_{ij}$ between C and F atoms. To accomplish this, we made the main adjustments in the Slater orbital exponents increasing the s and p orbital exponents for C by 0.25 and by 0.5 for F. The somewhat larger reduction for F is expected for two reasons, one of these being that F is a larger and more polarizable atom and therefore subject to more distortion from the isolated atom than C. The other reason is that the Slater parameter for carbon has been tested more extensively, especially for C–H bonds which also occur in the molecules under study. Further reduction of $\mathcal{H}_{ij}$ was accomplished by reducing κ to 1.5, which is in the range of values used in the literature[12] for κ. Using these choices, the asymmetry parameter η for the weighted combination ($^1/_6C_6H_5F + {}^5/_6C_6H_4F_2$) is seen from Table III to reduce to a value in good agreement with experiment. Further, with these choices of extended-Hückel (EH) parameters, the agreement of η with experiment for the other three weighted fluorobenzene systems in which data are available is also seen from Table III to show drastic improvement, providing a check of the choices for the modified extended-Hückel parameters. For these

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[13] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).

[14] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

[15] E. Clementi and D. L. Riamondi, *J. Chem. Phys.*, **38**, 2686 (1963); E. Clementi, D. L. Riamondi, and W. P. Reinhardt, *ibid.*, **47**, 1300 (1967); H, Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, **3**, 458 (1965).

Table III. Comparison of Theoretical and Experimental Quadrupole Coupling Parameters for Fluorobenzenes

	theory		experiment	
sample	e^2qQ, MHz	η	e^2qQ, MHz	η
$^1/_6C_6H_5F$ + $^5/_6C_6H_4F_2$	46.57	0.096	57.1 ± 0.2	0.11 ± 0.03
$^1/_2C_6H_2F_4$ + $^1/_2C_6H_3F_3$	50.32	0.125	57.5 ± 0.3	0.14 ± 0.03
$^1/_3C_6HF_5$ + $^2/_3C_6H_2F_4$	51.45	0.150	58.7 ± 0.2	0.15 ± 0.02
C_6F_6	53.84	0.168	59.3 ± 0.2	0.11 ± 0.02

modified choices, the values of the quadrupole coupling constants using the recently calculated[5] value of Q for $^{19}F^*$ are listed in Table II for all the individual systems studied as well as the corresponding values for a number of systems for the readjusted parameters. It is gratifying that the quadrupole coupling constant results for the individual molecules in Table II when weighted appropriately in Table III for comparison with experiment show that the overall agreement with experiment is satisfactory for the same choices of EH parameters that provide satisfactory agreement for the asymmetry parameters η. The smaller values of e^2qQ for the unmodified choice of EH parameters are a result of stronger covalent bonding obtained by this choice, the same overestimation being responsible for the substantially larger asymmetry parameters for this choice.

In Table III, the results of our calculation of e^2qQ and η in Table II with the adjusted EH parameter are combined according to the experimental weighting factors in Table I and compared with the experimental results. Considering first the absolute magnitudes of e^2qQ and η, we notice that there is very good overall agreement between theory and experiment. The asymmetry parameter η for the C_6H_5F target was used to adjust the parameters of the EH theory. Therefore the good agreement between experimental and theoretical results within the error range of the experimental results supports the choices made for the EH parameters. The agreement between theory and experiment is seen to be excellent for the systems in the second and third rows of Table III. For the case of C_6F_6, the experimental result including the upper limit of the error range is about 20% smaller than the theoretical value. We shall remark about this later in this section. It should be noted, however, that from Table III, without the adjustment of the EH parameters, the theoretical value would have been more than four times larger than experiment. As far as the absolute values of the coupling constants e^2qQ are concerned, the theoretical values are seen from Table III to be in all cases in agreement with experiment within the range of 10–15%. This lends support to the recently revised[5] value (0.072 ± 0.04) barns of the quadrupole moment of $^{19}F^*$ since the earlier value[16] of 0.12 barns would have led to theoretical results about 55% higher, leading to differences of about 45% from experiment.

Next, considering the trends, the changes in both e^2qQ and η are determined primarily by the variation in the fluorine π-orbital population as discussed in the literature in earlier work[3] on other halobenzenes. Both e^2qQ and η are seen from Table II to have an overall trend of increases in magnitude as the number of fluorine substituents is increased, as would be expected from eq 10 and 11, due to increase in U_y resulting from the competition in covalent bonding of the fluorine electrons with those of the benzene ring. There are also significant variations among the others, *m*- and *p*-difluorobenzenes and similarly among the various trifluoro- and tetrafluorobenzenes due to differing competitions among the various substituent fluorine atoms in the different compounds. The results in Table III indicate that the experimental trend in the quadrupole coupling constants in going from the monofluorobenzene target results to the hexafluorobenzene target are well reproduced by theory, the results for the various systems being fairly close to each other from both theory and experiment and showing a slow but continuous increase although theory does predict a somewhat larger jump in going from the CH_5F to CH_3F_3 target than was observed. For the symmetry parameters, the significant increase observed from the monofluorobenzene target to the trifluorobenzene and tetrafluorobenzene targets is well explained by theory. On the other hand, in going from the tetrafluorobenzene target to the hexafluorobenzene target, experiment indicates a drop in η to a value comparable to the monofluorobenzene target results, while theory registers an increase. This is the main observed difference in the tend of the experimental and theoretical results and is a consequence of the difference in the absolute values of the asymmetry parameter results for hexafluorobenzene. In view of the good agreement between theory and experiment observed for the asymmetry parameters in the rest of the systems and the good overall agreement between both the absolute values and the trends in the quadrupole coupling constant results in all the measured systems, the difference between theory and experiment for η in hexafluorobenzene appears rather exceptional. It would be helpful to have experimental results for the pentafluorobenzene target to examine if the particular difference between experiment and theory for η in hexafluorobenzene is an isolated example or part of a trend in going from tetrafluorobenzene target to hexafluorobenzene. It is of course also possible that hexafluorobenzene, having no CH bonds but only CF bonds attached to the carbon atoms of the benzene ring, may be rather unique and the adjustments in the extended-Hückel parameters which apply to the rest of the systems which contain CH bonds may not be completely applicable to hexafluorobenzene. Further light could be shed on this situation by completely self-consistent calculations,[5] which would be rather laborious but obviate the need for any parametric adjustments.

V. Conclusions

The nuclear radiative DPAD technique has provided useful results for fluorine quadrupole coupling constants in a number of fluorobenzenes unavailable before. The analysis of the electronic structures of these systems by the self-consistent extended-Hückel procedure is able to successfully explain both the asymmetry parameters and quadrupole coupling constants in the $^{19}F^*$ ($I = {}^5/_2$) state of the fluorine nucleus, the latter agreement lending support to the recently verified value of the quadrupole moment of $^{19}F^*$. There is one main exception to this observed good agreement between experiment and theory and this is the case of the asymmetry parameter for hexafluorobenzene, where the theoretical result is about 30% higher than the highest limiting experimental value allowed by the observed range of error. As pointed out in the preceding section, the understanding of this situation could be enhanced on the experimental side by measurements on systems obtained from $^{19}F^*$ implantation on pentafluorobenzene and a further exploration of the substitution problematics of the DPAD technique. Also, more accurate and detailed theoretical analysis of the hexafluorobenzene as well as some of the other systems by Hartree–Fock self-consistent procedures[5,17] would be helpful. It will also be interesting to analyze other properties such as the ^{19}F chemical shifts[18] in magnetic resonance experiments using the electronic wave functions and energy levels available through the SCCEH procedure to see if they can also explain chemical shift data as well as the quadrupole interaction data observed in the present work.

Acknowledgment. This work was partially supported by grant HL15196 from the Heart, Lungs and Blood Institute of the National Institutes of Health.

Registry No. C_6H_5F, 462-06-6; *p*-$C_6H_4F_2$, 540-36-3; *o*-$C_6H_4F_2$, 367-11-3; *m*-$C_6H_4F_2$, 372-18-9; 1,3,5-$C_6H_3F_3$, 372-38-3; 1,2,3-$C_6H_3F_3$, 1489-53-8; 1,2,4-$C_6H_3F_3$, 367-23-7; 1,2,3,4-$C_6H_2F_4$, 551-62-2; 1,2,3,5-$C_6H_2F_4$, 2367-82-0; 1,2,4,5-$C_6H_2F_4$, 327-54-8; C_6HF_5, 363-72-4; C_6F_6, 392-56-3; fluorine, 7782-41-4.

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