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New values of quadrupole moments of fluorine nuclei

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The increasing availability of $^{19}F^*(I=\frac{5}{2})$ and $^{20}F(I=2)$ quadrupole interaction data by nuclear radiation techniques has crystallized the need for accurate values of Q for these nuclei. From accurate self-consistent-field calculations on the FCl molecule we have obtained $|Q(^{19}F^*)|=0.072\pm0.004$ barns and $|Q(^{20}F)|=0.043\pm0.002$, respectively, which are only two-thirds of earlier semiempirical estimates.

Nuclear quadrupole interactions of the halogen nuclei chlorine, bromine, and iodine, have provided a valuable tool to study[1] both structural effects and electron distributions in a wide range of solid-state systems, ranging from ionic crystals like the alkali halides to molecular crystals such as the solid halogens. Unfortunately, it has not been possible in the past to similarly employ fluorine quadrupole interactions because the ground state of the stable isotope ^{19}F has a quadrupole moment of zero. This situation has now been remedied by the development of nuclear radiative resonance techniques such as perturbed angular correlation (PAC)[2] and asymmetric β decay[3] which allow one to study, respectively, the excited state[4] of ^{19}F with $I=\frac{5}{2}$ and the ground state[5] of ^{20}F with $I=2$. Both of these nuclei have finite quadrupole moments. These techniques not only allow the extension of quadrupole interaction studies to the entire halogen series but have the added bonus of allowing such studies at impurity nuclear sites which are too difficult to study by conventional nuclear magnetic and quadrupole resonance techniques. To utilize the full potential of the new data for determining the electric field gradients (EFG) at the fluorine nuclear sites, accurate values of the quadrupole moments of the nuclei $^{19}F^*(\frac{5}{2})$ and $^{20}F(2)$ are needed. We report here a determination of these two moments accurate to within 5%.

$^{19}F^*$ nuclear quadrupole interaction data are available from PAC measurements[6] on FCl in the form of a molecular solid. Experimental data on other halogen nuclei in solid halogens[7] and recent theoretical investigations[8] have demonstrated that intermolecular interactions in these systems do not influence the field gradients by more than 5%. Consequently quadrupole interaction data are available in essentially the relatively simple isolated molecule FCl to an accuracy of better than 5%. We have carried out SCF (Gaussian) electronic structure calculations[9] for this molecule, and from the wave functions we have determined the EFG at both nuclei. On combining the PAC data[6] with the field gradient at the fluorine site we deduce $|Q(^{19}F^*)|=(0.072\pm0.004)$ b. We utilized this result and the experimental ratio[5] of the quadrupole coupling constants for ^{20}F and $^{19}F^*$ in MgF_2, the former being measured by β-decay asymmetry techniques, to obtain $|Q(^{20}F)|=0.043\pm0.002$ barns.

The various contributions to the EFG at the nuclei in FCl are listed in Table I. The molecular orbitals 1σ, 3σ, 4σ, 6σ, and 1π have primarily chlorine $1s$, $2s$, $2p_z$, $3s$, and $2p_{x,y}$ character, respectively, while the orbitals 2σ and 5σ primarily fluorine $1s$ and $2s$ orbitals. The molecular orbitals 7σ is a bonding orbital involving fluorine $2p_z$ and chlorine $3p_z$ atomic orbitals. The other occupied orbitals are 2π and 3π and these represent, respectively, the bonding and antibonding orbitals composed of fluorine $2p_{x,y}$ and chlorine $3p_{x,y}$ orbitals. Of these, the 2π bonding orbitals has relatively more fluorine character while the 3π antibonding orbitals has relatively more chlorine character.

TABLE I. Electric-field-gradient contributions from the molecular orbitals in FCl (in units 10^{16} esu/cm^3).

Nuclear	Chlorine core-like orbitals					Fluorine core-like orbitals		Valence orbitals			Total		
site	1σ	3σ	4σ	1π	6σ	2σ	5σ	2π	7σ	3π	Electronic	Nuclear	Total
Cl	0.000	0.005	51.680	−52.027	0.002	0.045	0.131	−0.297	1.295	−3.241	−2.408	−0.200	−2.608
F	0.045	0.045	0.047	0.087	0.238	0.000	0.055	−3.203	2.006	−0.530	−1.212	−0.378	−1.591

From Table I, it is seen that for the EFG at both nuclei, the major contribution arises from the electrons, that from the nuclear charge on the adjacent atom being relatively weak. This is in keeping with the expectation[1,10] that the major source of the EFG is local in character, arising from the population hole in the σ state on each atom. An interesting feature is the Sternheimer shielding[11] of the EFG contributions from the valence electrons. The Sternheimer shielding factor R, for instance, in the case of the fluorine nucleus, is obtained by dividing the sum of th 2σ and 5σ contributions by the sum of the 7σ, 2π, and 3π, contributions, leading to $R=0.03$. The corresponding value of R for the chlorine nucleus is -0.13, which is antishielding in nature, the difference in signs of R in the two cases being a consequence of the presence of the $2p$ core shell in chlorine. The sum of the contributions from the 4σ and 1π chlorine corelike orbitals represents the unbalance of $2p_z$ and combined $2p_x$ and $2p_y$ contributions to the EFG due to the influence of the small but significant covalent bonding effects associated with the $2p$ core orbitals.

The net EFG at the fluorine nucleus from Table I is 1.591×10^{16} esu/cm^3. This is the value that we have utilized to obtain the quadrupole moments of ^{19}F* and ^{20}F given earlier, using the available quadrupole coupling data.[6] We have tested the accuracy of our calculated EFG in three ways: (a) the comparison of our calculated coupling constant for ^{35}Cl with experiment, using the known quadrupole moment[12] $Q(^{35}\mathrm{Cl})$; (b) the convergence of the calculated EFG with respect to the size of the basis set; and (c) the calculated electric fields at the nuclei whose exact values are zero.

The net EFG at the chlorine nucleus from Table I is seen to be 2.608×10^{16} esu/cm^3. On combining this with the accepted value[12] of $Q(^{35}\mathrm{Cl})=-0.079$ b, we obtain the quadrupole coupling constant $e^2qQ(^{35}\mathrm{Cl})$ to be 149 MHz in very good agreement with the experimental value[13] of 145.99 MHz for the free molecule, testifying to the accuracy of our wave functions from which the EFG have been calculated.

The molecular orbitals in our work were taken as linear combinations of primitive Gaussian orbitals[9] at the two atomic centers, the number of these orbitals being 12 s type and 9 p type on chlorine and 11 s type and 7 p type for fluorine. Examination of the changes in EFG produced by reducing the size of the basis set indicated that the convergence of the EFG with respect to the size of the basis set was better than 1% and 2%, respectively, for the F and Cl nuclei. We have also tested the influence of including d orbitals in the basis set and find that they produce changes of no more than 0.1% at the Cl nucleus and 4% at F. The incorporation of fluorine d orbitals is expected to be less important because of the relatively large energy difference between fluorine $2p$ and $3d$ orbitals. These convergence criteria and the possible influence of solid-state effects[8,14] on the EFG have led us to the confidence limit of 5% indicated in the values of $Q(^{19}\mathrm{F}^*)$ and $Q(^{20}\mathrm{F})$ we have given earlier.

The third test for the accuracy of our result was the comparison between the values predicted using our wave functions for the net electric fields at the nuclei with the zero result expected at the equilibrium separation. This zero result was expected out of the exact cancellations of the nuclear and electronic contributions to the fields. Our results showed cancellation of the individual contributions to better than 7% for the electric fields at both nuclei. Earlier calculations[15] with a limited size Slater-type basis set has provided poorer cancellations of the nuclear and electronic contributions. We were able to reproduce the EFG calculated with these wave functions[15] with a much smaller Gaussian basis set than we have used.

Our value for $Q(^{19}\mathrm{F}^*)$ is only about two-thirds of the earlier value[6] in the literature derived from an empirical estimate for the EFG in FCl molecule. This estimate was based on the Townes and Dailey semiempirical formula[1,10]

$$q=[1-s^2-I+\Pi)+Is^2]q_0\ , \tag{1}$$

where q_0 refers to the field gradient for a $2p_0$ electron in fluorine atom, namely, $q_0=4/5(-e)\langle 1/r^3\rangle 2p$ and s^2, I and Π refer to parameters describing the chemical bond between F and Cl atoms, the S hybridization, ionic character, and double-bond character, respectively. For these bond parameters, empirical values available in the literature[1,10] ($s^2=0.15$, $I=0.259$, $\Pi=0$) were employed. The value of $\langle 1/r^3\rangle$ was derived from empirical analysis[16] of fine-structure data which lead to 6.56 a_0^{-3}.

The discrepancy between our theoretical result for q and the semiempirical estimate[6] is not too disturbing because the latter was derived for the purpose of studying trends[17] in e^2qQ for small molecules involving halogen nuclei and not for accurate determinations of Q. However, since the semiempirical formula has been widely used in the past for study of e^2qQ for the other halogen nuclei, we have critically examined the parameters used[6] for fluorine in the semiempirical formula to resolve differences with our result. Thus, from our molecular wave functions, we have been able to obtain an ionic character of 0.29 which is only slightly larger than the value used in the earlier work. The S hybridization and Π character are difficult to characterize precisely in the framework of our SCF molecular calculations, but our calculated wave functions suggest that they are both less than 5%. Additionally, the value of $\langle 1/r^3\rangle$ obtained semiempirically from fine-structure data is $6.56a_0^{-3}$ which is significantly smaller than the Hartree-Fock value[18] of $7.45a_0^{-3}$. Using the value of $I=0.29$ from our work and $s^2=0=\Pi$ and the Hartree-Fock value of $\langle 1/r^3\rangle$, the relation (1) leads to $q=1.55\times10^{16}$ esu, in reasonable agreement with our accurate molecular orbital value. The major conclusions from this comparison then are that in using the semiempirical relation (1) for estimating q for molecular bonds involving fluorine, it is best to use zero S hybridization and the Hartree-Fock value of $\langle 1/r^3 \rangle$.

Before concluding, we would like to point out that the value of $Q(^{19}F^*)$ estimated from shell model[19] is -0.092 barns which compares reasonably well with our result, considering the approximations in the shell model. The influence of these approximations is manifested through the fact that the predicted ratio[19] of the magnitudes of $Q(^{20}F)$ and $Q(^{19}F^*)$ is 0.83 as compared to the experimental ratio[5] of 0.60 for the quadrupole coupling constants for these nuclei.

Further, we have used the same procedure as in FCl to study q in F_2 and obtain a value of 2.257×10^{16} esu/cm^3 which when combined with our $Q(^{19}F^*)$ leads to $a(\pm\frac{3}{2}, \pm\frac{1}{2})$ transition frequency of 17.67 MHz for this $I=\frac{5}{2}$ nucleus, the fundamental frequency[6] in PAC measurements. It is hoped that such measurements will be available for F_2 in the future to compare with our prediction.

In summary, we have obtained accurate values for $Q(^{19}F^*)$ and $Q(^{20}F)$ from SCF molecular calculations on FCl molecule. We trust that the availability of these values of Q will stimulate quantitative analysis of the EFG in the wide range of systems ranging from ionic crystals[20] and organic molecules[21] to metallic systems[22] in which fluorine nuclear quadrupole data are becoming increasingly available from PAC and β-asymmetry measurements, and in the process lead to valuable understanding of the electronic structures of these systems.

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[21] See, for instance, Bonde-Nielson and Toft in Ref. 4.

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