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Solid-State nuclear magnetic resonance: performance of point-charge distributions to model intermolecular effects in ^{19}F chemical shifts

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Abstract. This contribution presents results from applying two different charge models to take into account intermolecular interactions to model the solid-state effects on the ^{19}F NMR chemical-shift tensors. The density functional theory approach with the B3LYP gradient-corrected exchange correlation functional has been used because it includes electron correlation effects at a reasonable cost and is able to reproduce chemical shifts for a great variety of nuclei with reasonable accuracy. The results obtained with the charge models are compared with experimental data and with results obtained from employing the cluster model, which explicitly includes neighboring molecular fragments. The results show that the point-charge models offer similar accuracy to the cluster model with a lower cost.

Key words: Chemical-shift tensors – Solid-state effects – Charge models

1 Introduction

NMR spectroscopy is now one of the most important tools for characterizing the structure of inorganic and organic materials, biological macromolecules and molecular crystals. Increasingly, researchers are using solid-state NMR to characterize a great variety of microscopic structures. The minor deviations of the solid state from the corresponding liquid spectrum may be modeled and used to investigate details in the solid-state spectra. Computer hardware and software have reached the point that modeling these effects may be an achievable goal [1–4].

Solid-state effects have been observed in both ^{13}C and ^{15}N chemical shifts, but in the latter they are an order of magnitude larger [5–7]. Existing quantum mechanical methods in use to predict NMR nuclear shielding do not use crystalline wave functions to evaluate the shift tensor components. Consequentely, the theoretical results do not include any intermolecular contribution to the shielding. Cluster and charge model methods have been used to model the intermolecular effects on shielding with some success [2, 8–12].

A common problem in using the cluster method is the selection of the “chemically significant” fragment to be included in the calculations. Models including the full unitary cell may prove to be computationally too expensive to be used routinely in the study of large organic crystals.

The simplest representation of the electrostatic properties of a system is through atom-centered point charges (monopole approximation). Atomic charges may be found from population analysis methods [13] or by adjusting them to values that generate an electrostatic potential previously obtained by ab initio calculations. The second method has proved to be superior [14] for studying intermolecular effects and so it is the one employed here.

In a recent article [15] one of us used charge models to calculate crystalline effects on ^{15}N chemical shifts in benzamide and imidazole and showed that those charge models improve the correlation between experimental and calculated values compared to those obtained using the cluster model.

There are considerable advantages in testing the charge models against NMR solid-state measurements. The molecular environment is well characterized when the neutron diffraction structures are available. The comparison between theoretical and experimental principal values of the chemical shifts is more complete than when including only the isotropic shift, which may average the anisotropic components of the intermolecular effects on the chemical shifts [6].

In the present contribution we investigate the performance of charge models to reproduce the experimental trends in the solid-state NMR spectra of ^{19}F in two organic crystals, *o*-fluorbenzoic acid and *p*-fluorbenzoic acid. These compounds are part of a series of organic molecular crystals for which we have taken the experimental solid-state ^{19}F chemical shifts from the literature.

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The charge model calculations show that, for at least these two examples, the ^{19}F solid-state NMR chemical shifts are not reproduced properly. We are extending the calculations to other members of the series to reach a final conclusion about the performance of charge models to describe the ^{19}F NMR spectra.

2 Charge models

The quantum mechanical model employed here consists of one central molecule, represented by atomic charges and atomic basis functions, surrounded by a finite set of point charges located in atomic positions generated in accordance with the space group symmetry of the crystal. That is a central molecule with charge field perturbation. The point charges were obtained by adjusting their values to fit the resulting electrostatic potential to that calculated using the electron density obtained from ab initio calculations. This means minimizing the residuals between the electrostatic potential derived from the discrete charge distribution and the electron density over a selected number of field points.

We employed two charge models, GRID [16] and SCREEP [17], to discuss the validity and efficiency of these kinds of methods to describe ^{19}F chemical shifts in the solid state.

2.1 GRID model

The GRID model [16] determines the point charges by adjusting their values to fit the resulting electrostatic potential to that calculated using the electron density obtained from ab initio calculations. This means minimizing the residuals between the electrostatic potential derived from the discrete charge distribution and the electron density over a selected number of field points.

The sampling algorithm is equivalent to the one adopted by Cox and Williams [18]. The selection of points for the fitting procedure implies the construction of a parallel piped-shaped grid of regularly spaced points. Points found to lie further than $R_{\max}$ (an arbitrary distance defining the grid boundaries) from any nucleus and points inside the van der Waals envelope are rejected before making the fit. We used $R_{\max} = 4.0$Å and a grid step of 0.5Å.

2.2 SCREEP model

The SCREEP model [17] considers a region of the space, C, where the charge density is zero and the electrostatic potential in this region is produced by the charge distribution, $\rho(\mathbf{r})$, lying entirely outside C. In the SCREEP model, C is the region occupied by the cluster atoms (only one molecule in the present work) and $\rho(\mathbf{r})$ is the charge density in the environment. Using a well-known theorem from electrostatics it can be proved that no matter what the charge distribution outside C is, its electronic potential, V_{el}, over the boundary closed surface, $\mathbf{S}$, of volume C may be reproduced by a surface charge density, $\sigma(\mathbf{r})$, located on $\mathbf{S}$:

$$V_{\mathrm{el}}(\mathbf{r}) - \int_{\mathbf{S}} \frac{\sigma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}^2\mathbf{r} = 0 \qquad (1)$$

The potential generated by $\sigma(\mathbf{r})$ over $\mathbf{S}$ and inside the region C is $V_{\mathrm{el}}(\mathbf{r})$.

$\mathbf{S}$ is divided into M elements of area $\mathbf{S}_j$ and the surface charge distribution is represented by M point charges, q_j, localized in each center, $\mathbf{r}_j$, of the surface element, $\mathbf{S}_j$:

$$q_j \approx \sigma(\mathbf{r}_j)\mathbf{S}_j \ . \qquad (2)$$

The calculation of SCREEP charges, q_j, proceeds in three steps:

1. Construction of a discrete $\mathbf{S}$ around the cluster.
2. Calculation of Madelung potentials, V_j, on each surface element.
3. Solving the linear equations

$$V_j - \mathbf{A}_{ij} q_j = 0 \qquad (3)$$

with

$$\mathbf{A}_{ij} = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

for $i \neq j$ and

$$\mathbf{A}_{jj} = 1.07\left(\frac{4\pi}{\mathbf{S}_j}\right)^{\frac{1}{2}} \ . \qquad (4)$$

In the SCREEP implementation [17] $\mathbf{S}$ is generated by employing the gepol93 algorithm [19], and the Madelung potentials were calculated by using the Ewald summation technique.

To improve the accuracy of the SCREEP calculations, ions from the environment that are close to the quantum cluster and $\mathbf{S}$ are treated explicitly without approximation. Their potential is evaluated explicitly inside the cluster and is substracted from the potential vector, $\mathbf{V}$, in Eq. (3). A cutoff radius, R_{cut} ($R_{\mathrm{cut}} > R_{\mathrm{a}}$ = radius of the atomic spheres ≈2.5–3.0 Å), is selected and all the lattice ions in the environment lying within R_{cut} to the closest atom of the cluster are attributed to the explicit region.

3 Computational procedure

Shielding calculations were performed with the GAUSSIAN94 [20] suite of programs using the density functional theory approach proposed by Cheeseman et al. [21] with the B3LYP exchange correlation functional [22], gauge-including atomic orbitals [23] and direct Hartree–Fock methods [24].

The calculations were made by employing the experimental neutron diffraction structures for *o*-fluorbenzoic [25] and *p*-fluorbenzoic [26] acids. D95** [27] basis sets were employed in the calculations. The calculated shieldings, σ, were converted to the shift scale of ^{19}F, δ, by $\delta = -\sigma + 175.27$ ppm, where the reference is the ^{19}F shielding in CCl_3F calculated with the same basis set and functional (the δ calculations were also made by taking the experimental value of ^{19}F shielding in CCl_3F (189.9 ppm) as a reference signal [28] and their performance can judged in from the root mean square (RMS) difference between those results and the experimental data).

4 Discussion and conclusion

The calculated principal components of the ^{19}F shielding for *o*-fluorbenzoic and *p*-fluorbenzoic acids are reported in Tables 1 and 2. For completeness, the values calculated with the charge models are compared with those corresponding to calculations using the bare molecule and the cluster model. The trends of the experimental data are well reproduced by the charge models.

From the analysis of the results for *o*-fluorbenzoic acid (Table 1), it is evident that δ_1 and δ_2 are very sensitive to the charge configuration chosen and that δ_3 is much less sensitive. In particular, a comparison of the δ_1 principal value for the bare molecule and the charge models with the experimental data shows that the charge models provide a very good improvement to its representation.

For the case of *p*-fluorbenzoic acid (Table 2) the behavior of the calculated principal values of the ^{19}F shielding verify the experimental trend, but the accuracy

Table 1. Experimental and calculated principal values of the chemical-shift tensor of fluorine in *o*-fluorobenzoic acid relative to $CFCl_3$ on the δ scale

Method	δ_1	δ_2	δ_3	δ_{iso}	RMS[b] difference	RMS[c] difference
Theoretical[a,b]						
Bare molecule						
Crystal structure	−3.07	−104.60	−209.61	−105.76	11.27	16.10
Optimized structure	−11.62	−83.53	−234.56	−109.91	11.11	14.67
Charge models						
GRID						
14 first neigbour molecules	−17.47	−113.92	−210.67	−114.02	9.42	11.84
40 first neigbour molecules	−18.94	−114.40	−211.07	−114.81	9.27	11.40
SCREEP						
R_{cut} = 3.0 Å	−20.12	−115.40	−211.30	−115.61	9.38	11.12
R_{cut} = 2.0 Å	−19.88	−114.72	−211.57	−115.39	9.20	11.09
Cluster[d]	−3.64	−99.47	−205.63	−102.92	10.85	16.53
Cluster[e]	−17.25	−106.60	−208.91	−110.92	7.66	11.85
Experimental[f]	−34	−91	−211	−112		

[a] All the calculations were made by employing Direct Hartree-Fock *D*95** gauge-including atomic orbital basis sets and B3LYP density functional theory
[b] Reference signal: 175.27 ppm for fluorine in CCl_3F calculated with the same basis set and functional
[c] Experimental reference signal: 189.90 ppm for fluorine in CCl_3F taken from Ref. [28]
[d] The explicit fragments are nine atoms belonging to the closest neighbours to the fluorine nucleus
[e] Cluster of four molecules of *o*-fluorbenzoic acid
[f] Experimental data taken from Ref. [29]

Table 2. Experimental and calculated principal values of the chemical shift tensor of fluorine in *p*-fluorobensoic acid relative to $CFCl_3$ on the δ scale

Method	δ_1	δ_2	δ_3	δ_{iso}	RMS[c] difference	RMS[d] difference
Theoretical[a,c]						
Bare molecule						
Crystal structure	−19.45	−119.15	−210.51	−116.37	13.34	13.65
Optimized structure	−26.15	−113.68	−199.91	−113.25	9.66	11.10
Charge models						
GRID						
40 first neigbour molecules	−26.13	−122.48	−212.08	−120.23	13.52	12.02
SCREEP						
R_{cut} = 3.0 Å	−27.99	−124.36	−212.30	−121.551	13.53	11.50
R_{cut} = 2.0 Å	−27.17	−123.37	−213.99	−117.85	14.93	12.16
Cluster[b]	−11.52	−117.37	−204.37	−111.09	13.23	15.06
Experimental[e]	−36	−118	−173	−109		

[a] All the calculations were made by employing Direct Hartree-Fock *D*95** gauge-including atomic orbital basis set and B3LYP density functional theory
[b] The explicit fragments are nine atoms belonging to the closest neighbors to the fluorine nucleus
[c] Reference signal: 175.27 ppm for fluorine in CCl_3F calculated with the same basis set and functional
[d] Experimental reference signal: 189.90 ppm for fluorine in CCl_3F taken from Ref. [28]
[e] Experimental data taken for Ref. [29]

of the results must be improved. We think that the improvement will not come from alternative point-charge configurations, the explicit inclusion of solid-state effects provided by the exact crystal wave function is needed.

For both compounds the principal components of the ^{19}F theoretical shieldings are given with respect to the calculated reference, 175.27 ppm, i.e. the shielding constant of ^{19}F in CCl_3F, and the RMS difference between the experimental data and the calculated values are also given for the experimental value of the same reference signal, 189.9 ppm [28]. The trend of the RMS difference shows that charge models are better than bare molecule results for *o*-fluorbenzoic acid, but there is no improvement for *p*-fluorbenzoic acid. The differences between the results obtained with the GRID and SCREEP models are quite minor.

The cluster model, i.e. calculations considering atomic charge and functions in the molecular fragments nearest to the fluorine nucleus for both compounds, do not improve the theoretical results with respect to those obtained from charge models. This means, to the authors' knowledge, that the intermolecular solid-state effects are not, at least for these compounds, a "through-space" effect. For *o*-fluorbenzoic acid we have also included (Table 1) the calculation for a cluster of four molecules in the unit cell. For this case the RMS difference is improved by nearly 30% with respect to calculations corresponding to charge models and the computation time of a Pentium-based computer increased from 10 hours to 3 days.

In conclusion, the results presented here clearly indicate that the charge models are not so useful to describe ^{19}F solid-state chemical shifts, at least for the two compounds analyzed, as they proved to be in the description of ^{15}N solid-state chemical shifts [15]. We are applying the GRID and SCREEP models to other compounds for which we have the solid-state NMR spectra of ^{19}F to determine if this conclusion must be extended to a general description of fluorine chemical shifts in the solid state. Charge models are attractive because the computational cost required to perform the calculations is similar to that corresponding to the isolated molecule. So, it is very important to determine for which nuclei they are good enough to be useful for typical applications in solids, such as spatial assignments or rationalization of multiple lines in magic-angle spinning spectra.

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