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Authors

Mueller, Leonard J
Elliott, Douglas W
Kim, Kee-Chan
et al.

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Establishing Through-Bond Connectivity in Solids with NMR: Structure and Dynamics in HC$_{60}^{+}$

Leonard J. Mueller,*,[†] Douglas W. Elliott,[†] Kee-Chan Kim,[†] Christopher A. Reed,[†] and Peter D. W. Boyd[‡]

Department of Chemistry, University of California, Riverside, California 92521, and Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand

Establishing through-bond and through-space connectivity is essential to the role of nuclear magnetic resonance (NMR) in answering questions of molecular structure and dynamics. In NMR, it is the scalar or *J*-coupling interaction that signifies covalent through-bond contact, while the dipolar coupling provides through-space distance constraints. A variety of liquid-state NMR experiments have been developed that make use of scalar and dipolar couplings to transfer magnetization between pairs of nuclear spins and establish their through-bond and through-space connectivity, respectively, via cross-peaks in 2D NMR experiments.[1] While an array of experiments for determining through-space connectivity in disordered solids has also been developed,[2] relatively few correlation experiments in solids make use of scalar couplings.[3] Scalar coupling-driven correlation in solids is essential for two reasons. First, as in liquid-state NMR, delineating through-bond and through-space connectivity is a critical step for establishing structure. Second, unlike dipolar interactions, which can average to zero under molecular motion even in the solid state, scalar couplings are relatively insensitive to global molecular dynamics and can provide for correlation and spectral assignment in situations where dipolar-driven experiments fail. This is the case for HC$_{60}^{+}$, where significant (anisotropic) molecular motion renders dipolar-driven transfer ineffective for ^{13}C chemical shift correlation. To characterize the covalent bonding network in HC$_{60}^{+}$ we introduce a novel solid-state correlation method, which is a variant of the popular double-quantum-filtered correlation spectroscopy (2QF COSY) experiment in liquids.[4] This experiment maintains the many advantages of the 2QF COSY experiment but is also robust for solids (both dynamic and rigid) and is applicable under fast (>30 kHz) magic-angle-spinning (MAS) conditions. In HC$_{60}^{+}$ this through-bond correlation answers a significant structural question by accurately identifying the direct bond between the protonated sp^3 hybridized carbon site and the sp^2 hybridized cationic site.

The 2QF COSY provides through-bond connectivity via scalar coupling-driven coherence transfer and is often the first step in establishing the spectral assignment in any liquid-state NMR investigation. An important characteristic of the 2QF COSY experiment is the purely absorptive diagonal and cross-peaks, which provide considerably better resolution than earlier versions of the COSY experiment. The original liquid-state 2QF COSY experiment is not compatible with solid-state applications as the cross-peaks, which indicate the through-bond connectivity, have an anti-phase relationship in which the doublet components (split in frequency by the scalar coupling) have opposite signs. In solids, where scalar couplings are seldom resolved even under magic-angle-spinning

* To whom correspondence should be addressed. E-mail: leonard.mueller@ucr.edu.
† University of California.
‡ University of Auckland.

conditions[5] and high power proton decoupling,[6] considerable cancellation of the cross-peak is typical, and the through-bond correlation is difficult to ascertain. To provide a robust 2QF COSY experiment for solids it is necessary to transform the cross-peaks from anti-phase to in-phase, in which the doublet components have a uniform sign. This transformation can be accomplished through standard methods in multiple-pulse NMR[1] and we append these "refocusing" pulse sequence elements to the original pulse sequence to give a novel variant of the 2QF COSY (Figure 1a) with diagonal and cross-peaks of uniform algebraic sign. We call this variant the *u*niform-sign *c*ross-peak (UC) 2QF COSY. Introducing refocusing periods on the order of $1/(2J)$ into the pulse sequence may seem incompatible with solid-state NMR where one would expect significant intensity loss due to relaxation during this time. The relaxation rate under echo sequences, however, is governed by the homogeneous line width and is significantly slower than the relaxation rate of the directly observed signal, which is governed by the inhomogeneous line width.[7] Recently, Emsley showed that such refocusing periods have acceptable efficiency in solid-state NMR experiments.[3c]

The UC2QF COSY experiment is similar to the well-known refocused INADEQUATE experiment,[8] which has been successfully applied in both liquids and solids,[3c] but retains the direct chemical shift–chemical shift correlation of the 2QF COSY. A related but different approach used for resolving long-range scalar couplings in liquids is the SUPER COSY.[9]

HC$_{60}^{+}$ represents a challenge to structural studies in solids. The ^{1}H-decoupled 1D ^{13}C spectrum reveals distinct peaks at the expected frequencies for an sp^3 site and an sp^2 cationic site, in addition to a plethora of inequivalent sp^2 hybridized sites (Figure 2). Our attempts to make use of ^{13}C–^{13}C dipolar-driven correlation spectroscopy to determine spatial connectivity failed, however, suggesting that HC$_{60}^{+}$ is undergoing rapid molecular reorientation, causing the dipolar couplings to average. Such motion is consistent with the prior solid-state NMR observations of dynamics in C$_{60}$ and C$_{70}$.[10] The larger ^{1}H–^{13}C heteronuclear dipolar interactions could still be observed through ^{1}H–^{13}C cross-polarization experiments, and spinning sidebands due to the chemical shift anisotropy are still clearly visible in the MAS spectrum, although they are reduced in intensity from what would be expected for a rigid sp^2 hybridized site.[10] These imply that the molecular reorientation is anisotropic, leading to a distribution of partially averaged chemical shift anisotropies and dipolar couplings. The latter explain the distorted ^{1}H–^{13}C cross-polarization exchange dynamics previously observed, which led us to incorrectly suggest a 1,4 disposition of the cationic site.[11]

The UC2QF COSY experiment provides a direct and accurate characterization of the through-bond connectivity in HC$_{60}^{+}$ as traced
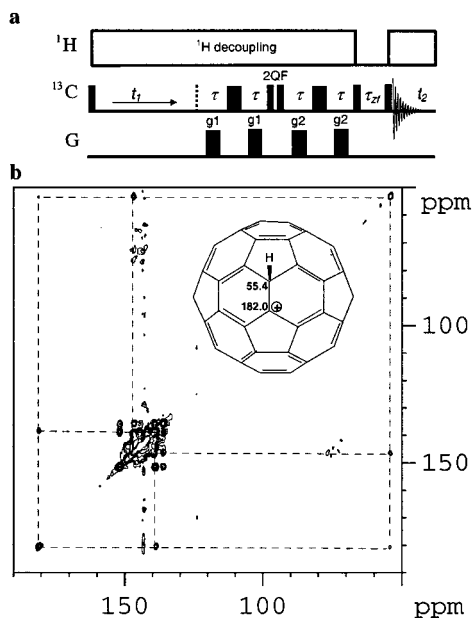
Figure 1. (a) UC2QF COSY experiment appends two $\pi-\tau-\pi$ refocusing elements about the double-quantum filter (2QF) to produce a correlation spectrum with in-phase cross-peaks. Thin vertical lines indicate $\pi/2$ pulses, and thick vertical lines indicate π pulses. The refocusing delay τ is set to an integral number of rotor periods to rigorously refocus the chemical shift interaction, and maximum signal intensity is obtained in two-spin systems for $\tau = 1/(4J_{IS})$. The final $\pi/2-\tau_{zf}-\pi/2$ and gated decoupling guarantee in-phase absorptive lines for multispin systems. (b) UC2QF COSY of HC_{60}^+. The direct bond between the protonated sp^3 and the $sp^2(+)$ sites is indicated by the cross-peaks between 55.4 ppm and 182.0 ppm. The dashed lines indicate correlations used for assigning peaks. Data were acquired using the pulse sequence from (a) on a 9.4 T (400.13 MHz ^{1}H) Bruker DSX spectrometer equipped with a double resonance 4-mm MAS probe spinning at a MAS rate of 7 kHz. The first three pulses were phase-cycled as a group for double quantum excitation, and gradient selection was applied to the π pulses.[13] Pure phase spectra were obtained using the method of States.[14] The random 10% ^{13}C-labeling of the C_{60} allows us to consider only effective two-spin pair interactions, making the choice of $\tau = 1/(4J_{IS}) = 5$ ms most efficient.
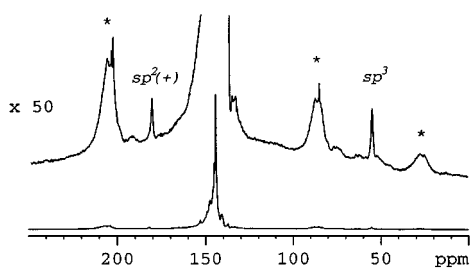

Figure 2. ^{1}H-decoupled ^{13}C MAS spectrum of HC_{60}^+ prepared from randomly 10% ^{13}C-labeled C_{60} reacted with the $H(CB_{11}H_6Cl_6)$ carborane superacid.[11] Spinning sidebands are labeled with asterisks.

out in the cross-peaks of the two-dimensional correlation spectrum (Figure 1b). Most importantly, the cross-peak between the protonated sp^3 hybridized carbon site at 55.4 ppm and the sp^2 hybridized cationic site at 182.0 ppm indicates that they are directly bonded. The additional cross-peaks from 55.4 to 148.2 ppm and from 182.0 to 140.0 ppm allow for the assignment of the neighboring ^{13}C resonances. As the sp^3 and $sp^2(+)$ hybridized peaks show only two cross-peaks each, their bond must lie along a molecular plane of symmetry and form the connection of two six-member rings as shown in Figure 1b.

Density functional calculations on the isolated HC_{60}^+ ion support our structural conclusions. Geometry optimization (B3LYP functional, 6-31G(d) basis, Gaussian98[12]) agrees with the 1,2 disposition

of the sp^3 hybridized site and the sp^2 hybridized cationic site. The 2 carbon is the least pyramidal and most positive carbon atom. The remainder of the positive charge is mainly distributed over the proton and the five-membered ring containing the sp^3 carbon atom. Calculated ^{13}C chemical shifts (B3LYP-6-311G(d,p)/GIAO method) versus TMS give excellent agreement with the experimental values with the sp^3 site at 54.8 ppm and the sp^2 site at 183.5 ppm.

The uniform-sign cross-peak method, UC2QF COSY, provides a powerful through-bond correlation spectroscopy for disordered solids, and we have successfully applied it in our laboratory to a number of rigid and dynamic solids. In the characterization of HC_{60}^+, where anisotropic molecular motion renders ^{13}C–^{13}C dipolar driven correlation ineffective and ^{1}H–^{13}C cross-polarization experiments lead to inaccurate structural conclusions, the scalar coupling-driven UC2QF COSY provides reliable experimental characterization of the direct bond between the sp^2 cationic site and the protonated sp^3 hybridized site.

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