

Jameson, Cynthia J.: Early Work on the Ranges of Chemical Shifts and Signs of Coupling Constants

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When I came to the University of Illinois at Urbana-Champaign as a graduate student, Herb Gutowsky's group had the only computer program in existence for the computation of high-resolution NMR spectra of a general six-spin system. It was written by Geneva Belford and ran on that marvelous machine (for its time) the Illiac I. I was using it to compute the proton spectrum of the $-\text{CH}_2\text{CH}_2-$ groups in [2.2] metacyclopentane (in which the methylene groups are locked in virtually symmetrical staggered positions, with tetrahedral bond angles), an AA'BB' spectrum which at 60 Mc s⁻¹ looked almost of the A₂X₂ type. The quality of the spectra, calibrated by the usual audiofrequency sideband method, was such that even at this high field I could distinguish between sets of chemical shift and coupling constant parameters by focusing on the relative intensities and splittings between two sets of small peaks. I came to the conclusion that it was impossible to fit the spectrum using uniformly positive coupling constants. Jim Shoolery at Varian Associates kindly ran a low-field spectrum for us (15.083 Mc s⁻¹) and this was definitely AA'BB'. There was excellent agreement with the assignment $J_{\text{trans}} = +12.3$, $J_{\text{gem}} = -12.0$, $J_{\text{gauche}} = +4.0$, and $J_{\text{gauche}'} = +3.2$ Hz and, of course, with the other set in which all the signs are reversed. The key finding was that J_{trans} and J_{gem} , the two largest coupling constants were opposite in sign.¹

I was convinced that I had logically exhausted all the possible combinations of the parameters to test against the spectra, but Herb did not have confidence in my results at that time. After all, Martin Karplus (with Anderson, Farrar, and Gutowsky) had calculated these coupling constants in CH₄ and the H-C-C-H fragment in two classic papers,^{2,3} the latter being the original paper about what was to become known as the Karplus relationship. Both papers were considered to be in good agreement with experiment, and in CH₄ itself the calculated magnitude of the coupling constant was right on. My results went into a hole for several months until Herb (with Dave Grant) started looking into the nature and analysis of A₂B₂ and A₂X₂ spectra in general, and became convinced that I was right after all. The implications of this finding were unfortunate, or so we said then, for it meant that one of the two calculations was in error. It turned out that it would be decades later before the J_{gem} value could be calculated properly, but the H-C-C-H fragment calculation lives on.

The synthesis of the xenon fluorides generated a lot of excitement during this time and there was a great deal of speculation about the nature of the bonding in these molecules. Tom Brown told Herb about the ¹²⁹Xe chemical shifts that he and Whipple obtained indirectly by INDOR on the ¹⁹F well before the paper came out in *Science*.⁴ The shifts were very large, Xe was deshielded by 5785 ppm in XeF₄ compared

to the Xe in xenon gas, for example, and among the three fluorides XeF₂, XeF₄, and XeOF₄ the spread was very nearly 2000 ppm. Were the shifts as large as they were because the bonding in these new compounds was highly unusual, i.e. drastically different from ordinary compounds? Herb asked me to 'explain' the very large Xe chemical shifts. I figured that I could not 'explain' the large magnitudes of the chemical shifts of Xe in these compounds in isolation. It would only be a credible explanation if at the same time I could explain why some nuclei have large chemical shifts while others were much smaller in the regular compounds for which the nature of the bonding was not in question. After collecting the entire chemical shift data known at that time (a mere handful of nuclei) and putting the ranges of their chemical shifts in the Periodic Table, I thought I could see a Z-dependence that might possibly be periodic. I look back on the very fragmentary information on which I based this leap of faith and think that it's amazing how graduate students have no fear. What could be causing this periodic behavior? If I could find a logical reason for the chemical shifts to behave that way then there is no problem with Xe, for I could almost see the rising trend in going from left to right in a row of the Periodic Table and within a group, from top to bottom, so that Xe would logically be at a peak in the row and also in the column of rare gas nuclei.

Well, I did not find the answer immediately. I got married and left to join my husband out east. While browsing around in the library in Columbia University, looking at the paper on chemical shifts of xenon in the gas phase at high pressures by Carr and the explanation of the relaxation of ¹²⁹Xe in xenon gas by Torrey, I happened upon the paper by Barnes and Smith in the same volume of the *Physical Review* (with computerized information retrieval this would never have happened). This paper was entitled 'Electric Field Gradients of Atomic p Electrons'.⁵ Off-hand one would not think that this had anything to do with chemical shifts, but I was just browsing. So I read about the determination of the spin-orbit coupling constants for the atoms from the term energies and the calculations of the average value of $1/r^3$ for the p electron from these constants. And there it was, the periodicity that I was looking for. The $1/r^3$ term that appears in the operator for the paramagnetic part of the nuclear magnetic shielding in Ramsey's formulation has an average value for the free atoms that was periodic in the way that I imagined the ranges of chemical shifts were periodic. It did not take long after I made this serendipitous discovery to write it up and send it off to Herb, and we polished it up during a two-week visit I made to Urbana.⁶ Of course, now that most nuclei in the Periodic Table have been observed extensively, the ranges of the chemical shifts of the nuclei show the periodic behavior very beautifully, tracking the periodic behavior in the average values of $1/r^3$ for the atoms.⁷

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Biographical Sketch

Cynthia J. Jameson. *b* 1937. B.S., University of the Philippines, Ph.D., 1963, University of Illinois at Urbana-Champaign. Introduced

to NMR by Herb Gutowsky. Faculty in Chemistry, University of Illinois at Chicago, 1968–present. Approx. 130 publications. Research interests include theoretical and experimental studies of the chemical shift, in simple systems in the gas phase and in molecules absorbed in microporous solids, with particular emphasis on intramolecular and intermolecular shielding surfaces and averages therein; also, spin relaxation in gases and their connection with the anisotropy of intermolecular potentials and molecular dynamics.