

# 3D Opal Nanosponge and Carbone-Fluorine Spectroscopy<sup>TM</sup>: The Emergence of Nanotronics<sup>TM</sup> as a Possible Nano-Fluoro-Theranostic Tool

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## Introduction

The practical use of <sup>13</sup>C resonance has been hindered by low natural abundance of this nucleus (1. 1%), low inherent sensitivity to nmr detection (1. 6% relative to protons at constant field) and long relaxation times. Various methods are used to overcome these difficulties. Isotopic enrichment increases the quantity of <sup>13</sup>C nuclei within the active sample volume. Furthermore, specific introduction of <sup>13</sup>C allows unambiguous assignments of the carbon resonances to be made. The foremost disadvantage of this technique is that the expense of preparing the labelled materials. The likelihood of using <sup>13</sup>C as a non-degradative tracer in labelling studies has received only limited attention thanks to the experimental difficulties in observing <sup>13</sup>C resonances (3). The INDOR technique developed by Baker (4) allows the <sup>13</sup>C resonances to be detected with the sensitivity of proton nmr. For observation of <sup>13</sup>C resonances by INDOR the world of the spectrometer is adjusted so as that a <sup>13</sup>C satellite resonance within the proton spectrum is on resonance. A weak rf field is then swept through the <sup>13</sup>C spectrum. When a transition within the <sup>13</sup>C spectrum is irradiated which has an energy level in common with the proton line, a perturbation of the proton resonance is seen. This technique demands excellent spectrometer stability and thus the clear observation of the <sup>13</sup>C satellites of the proton spectrum. Thanks to the complexity of the proton spectrum of giant molecules, the

technique is restricted to simple structures, then far has been mainly used for the magnetically equivalent protons of methyl groups. So on cash in of the utmost signal-to-noise from the direct observation of a given sample, high rf fields are used and to scale back difficulties with saturation, the world is swept rapidly and thus the spectra are observed within the dispersion mode. By adjusting the rf field so as that the trailing halves of the dispersion peaks are saturated and thus not seen, the spectrum resembles a typical absorption-mode spectrum. Trailing peaks in spin-spin multiplets are partly saturated thanks to magnetization transfer effects (which might better be termed cross-relaxation). Linewidths of true singlets are on the order of 10 Hz thanks to broadening associated with the rapid sweep rate. Small chemical shifts and long-range coupling cannot be resolved, but the resolution is adequate for a couple of studies. Most <sup>13</sup>C studies are administered during this way.

A major advance within the sector of natural abundance <sup>13</sup>C nmr was the appliance of complete proton decoupling during conventional field-sweep experiments. Grant and Paul found that the signal-to-noise was improved both by the collapse of the three proton induced multiplet structure and a positive nuclear Overhauser effect. Because the sensitivity was increased, slower passage conditions could be used resulting in higher resolution. Precision of measurement was also improved because the ratio of the decoupling

and thus the observing frequencies could be measured an order of magnitude more accurately than the peak separations in rapid-passage spectra. The spectra were easier to interpret because only singlets are seen for each unique kind of carbon. With linewidths on the order of 1 Hz long-range effects on the  $^{13}\text{C}$  chemical shifts could be studied for the first time. Although the spectra obtained using this technique are very useful within the study of chemical shifts, they suffer from the actual fact that every one proton spin-spin coupling information is lost. The sensitivity is kind of good when the proton decoupling frequency is optimized, but the frequency range over which the signal-to-noise improvement is seen is simply a few of Hz.

### Abstract

Photonic crystals, or 3D photonic crystals, are monodispersed nanostructures that can have a daily lattice of structural elements of a size comparable the wavelength of electromagnetic radiation within the visible range. One example of a 3D photonic crystal could also be a  $\text{SiO}_2$  amorphous material mentioned as "synthetic opal," which is usually made up of tightly and orderly packed  $\text{SiO}_2$  spherical globules of equal size. The spaces in synthetic opal are often full of various compounds including fluoroorganics (e.g. F-drugs, F-biomolecules, F-polymers).

We previously demonstrated that Carbon-Fluorine Spectroscopy (CFS<sup>TM</sup>) aka Spectro-Fluor<sup>TM</sup>, a member tool from our PLIRFA<sup>TM</sup> (Pulsed Laser Isochronic Raman and Fluorine/Fluorescence Apparatus) platform, could also be a green, non-destructive, non-invasive, reliable and disruptive analytical technology that matches various pharmaceutical and bio-medical applications. The key feature of CFS<sup>TM</sup> is based on the potential to specifically, sensitively and rapidly detect C-F bond(s) within the fingerprint spectral area of 550-850  $\text{cm}^{-1}$  allowing F-imaging also as qualitative and quantitative characterization of fluoroorganics either in vitro, ex-vivo or in-vivo.

In the present work, I aim to present and discuss CFS<sup>TM</sup>-derived applications valuable

for the pharmaceutical, biomedical and nanomedical segments, with a special emphasis on Nanotronics<sup>TM</sup> which allows the characterization of fluoro-organics loaded into nanostructures (e.g. size determination of ultra-dispersed fluoro-polymers, length determination of fluorinated molecules entrapped into nanoparticles). Indeed, we showed that the use of our developed synthetic 3D-photonic opal  $\text{SiO}_2$  nanosponge<sup>TM</sup> can considerably enhance the unique Fluoro-Raman light scattering effects (about 104-106 folds), therefore allowing rapid, sensitive, specific detection and characterization of nanosponge-loaded fluoro-analytes. Interestingly, preliminary data showed that, likewise CFS<sup>TM</sup>, Nanotronics<sup>TM</sup> could further synergize with other analytical tools (e.g. HTS, chromatography, microscopy, AFM) to implement theranostic strategies (eg. screening, drug delivery, imaging, molecular interactions).

Eventually, Nanotronics<sup>TM</sup> is emerging as an innovative tool application to detect and characterize fluoroorganics loaded into nanostructures.

### Conclusion

The chemical community took notice, beginning within the 1960s, of a sometime heated controversy surrounding the structural aspects of sort of carbocations, primarily the 2 - norbornyl (bicycloheptyl) cation. The so - called nonclassical carbocation controversy was extensively reviewed. In essence, the discussion centered on the question whether the structure of these interesting ions are often described using only the quality two - center, two - electron ( $2\text{c} - 2\text{e}$ ) valance bonds while involving rapid equilibration of the limiting carbenium ions through a carbon - bridged transition state (as argued by Herbert C. Brown) or, as suggests by Saul Winstein, these ions have carbon - bridged structures involving hypercarbon - containing higher coordinate three - center, two electron ( $3\text{c} - 2\text{e}$ ) carbon - carbon bonding interactions.

### References

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