

Spectroscopy of endofullerenes and superconducting endofullerides

George R. Bacanu¹, Murari Soundararajan¹, Marina Carravetta¹, Richard Bounds¹,
Richard J. Whitby¹, Malcolm H. Levitt¹

¹Department of Chemistry, University of Southampton, UK

Fullerenes consist of symmetrical cages of pure carbon. Endofullerenes are substances in which the fullerene cages completely encapsulates a single atom, or a single molecule. Recent advances in organic chemistry have made a wide variety of endofullerenes available in relatively large quantities, including [1-3]:

- Noble gas endofullerenes such as He@C₆₀, Ne@C₆₀, Ar@C₆₀ and Kr@C₆₀
- Diatomic endofullerenes such as H₂@C₆₀, HD@C₆₀, N₂@C₆₀, HF@C₆₀
- Triatomic endofullerenes such as H₂O@C₆₀
- Organic molecule endofullerenes such as CH₄@C₆₀ and CH₂O@C₆₀.

In most cases a variety of isotopomers are available, such as ³He@C₆₀ and ⁴He@C₆₀.

The encapsulated molecules display spatial quantization (particle-in-a-box) as well as the spin degrees of freedom, including spin isomer states (such as the ortho and para states of water). In the case of H₂O@C₆₀ the ortho and para spin isomers display different electrical characteristics in the bulk solid [4].

Fulleride salts such as Rb₃C₆₀ become superconducting when cooled below ~ 30 K, although the mechanism of the superconductivity is not completely understood. We have synthesized fulleride salts in which the fulleride cages encapsulate single molecules, such as Rb₃(H₂@C₆₀) and Rb₃(HD@C₆₀). The superconducting transition is essentially unperturbed by the presence of the endohedral molecules. However, magnetic resonance of the ¹H nuclei provides a means to spy upon the electronic and magnetic dynamics of the fullerene cages, providing unique information on what happens when the material goes superconducting. In Rb₃(H₂@C₆₀), the spin-lattice relaxation rate constant (R₁) of the endohedral proton nuclei exhibits a very sharp transition at the superconducting transition. Very different behaviour is observed for Rb₃(HD@C₆₀). I will speculate on a possible mechanism of the unusual sharp transition in relaxation rate constants for Rb₃(H₂@C₆₀), and its absence for Rb₃(HD@C₆₀), arguing that this indicates a decisive change in the phonon spectrum of the material at T_c.

- [1] A. Krachmalnicoff *et al.*, Nature Chem. 8, 953 (2016).
[2] S. Bloodworth *et al.*, Angew. Chem. 58, 5038 (2019).
[3] G. Hoffman *et al.*, Chem. Commun. 58, 11284 (2022).
[2] B. Meier *et al.*, Nature Commun. 6, 8112 (2015).