



Cite this: *Chem. Commun.*, 2022, 58, 11284

Received 16th June 2022,
Accepted 11th September 2022

DOI: 10.1039/d2cc03398d

rsc.li/chemcomm

Synthesis and ^{83}Kr NMR spectroscopy of $\text{Kr}@C_{60}$ †

Gabriela Hoffman, George R. Bacanu, Elizabeth S. Marsden, Mark C. Walkey, Mohamed Sabba, Sally Bloodworth, Graham J. Tizzard, Malcolm H. Levitt and Richard J. Whitby*

Synthesis of $\text{Kr}@C_{60}$ is achieved by quantitative high-pressure encapsulation of the noble gas into an open-fullerene, and subsequent cage closure. Krypton is the largest noble gas entrapped in C_{60} using 'molecular surgery' and $\text{Kr}@C_{60}$ is prepared with >99.4% incorporation of the endohedral atom, in ca. 4% yield from C_{60} . Encapsulation in C_{60} causes a shift of the ^{83}Kr resonance by -39.5 ppm with respect to free ^{83}Kr in solution. The ^{83}Kr spin-lattice relaxation time T_1 is approximately 36 times longer for Kr encapsulated in C_{60} than for free Kr in solution. This is the first characterisation of a stable Kr compound by ^{83}Kr NMR.

Endohedral fullerenes (endofullerenes) are compounds in which atoms or small molecules are encapsulated inside fullerenes, providing a unique opportunity for study of the confined species in the isolated cavity.^{1a-d} The noble gas endofullerenes of C_{60} and C_{70} (denoted e.g. $\text{Ng}@C_{60}$ for the former case) are a specific group that have been the subject of sustained research activity, as compounds of great interest for study of the interactions between the encapsulated species and the encapsulating cage,^{2,3} the quantised energy level structure of the endohedral noble gas atom,² and the effect of the noble gas upon the properties and reactivity of the fullerene cage.^{4a,b} Many theoretical studies have addressed these areas,^{5a-h} and our interest in the practical synthesis of noble gas endofullerenes is motivated by both the opportunity for direct study of these materials, and the value of resulting data as a test of theoretical models.

Early methods for preparation of $\text{Ng}@C_{60}$ compounds relied upon direct encapsulation by exposure of C_{60} to the gas under high temperature and pressure, and led to approximately 0.1% incorporation of a single endohedral atom of He, Ne, Ar or Kr, and just 0.03% of Xe.⁶ Under similar conditions, an improved level of direct encapsulation into C_{60} ground with KCN was

achieved, of 1% He and approx. 0.3% Ar, Kr or Xe.^{7a-c} Enriched samples have been obtained using recycling HPLC, of ca. 0.1–1.0 mg $\text{Kr}@C_{60}$ with 90–99% purity,^{8,9} and ca. 0.3 mg $\text{Xe}@C_{60}$ with 50% purity.^{7b} Resulting ^{13}C NMR, UV-visible absorption, infrared, Raman, X-ray absorption and ^{129}Xe NMR studies have confirmed a weak interaction between the noble gas atom and interior cage surface,^{7b,8} and observed the endohedral atom to influence cage vibrational and rotational properties.^{5d,9}

With the development of the 'molecular surgery' method of endofullerene synthesis, high incorporation to facilitate spectroscopic studies on a macroscopic (multi-milligram) scale has become possible, the synthesis of $\text{H}_2\text{O}@C_{60}$ and $^4\text{He}@C_{60}$ being early examples.^{10,11} Murata's open-fullerenes **1** and **3** (Fig. 1)^{12,13} are key intermediates for 'filling' in the syntheses of $\text{HF}@C_{60}$, $\text{H}_2\text{O}@C_{60}$ and $\text{H}_2\text{O}@C_{60}$ (**1**), $\text{Ar}@C_{60}$ and $\text{CH}_4@C_{60}$ (**3**),^{13–17} and we recently developed a one-pot filling and partial closure of a phosphorous ylid derivative **2** that enabled efficient synthesis of noble gas endofullerenes $^3\text{He}@C_{60}$, $^4\text{He}@C_{60}$ and $\text{Ne}@C_{60}$.¹⁸ Incorporation of approx. 50–60% of the noble gas was accomplished, and enrichment of $\text{Ne}@C_{60}$ to >99.5% encapsulation of the noble gas atom was achieved by recycling preparative HPLC.

With the aim of elucidating the energy level structure of a confined noble gas atom and its interaction with the interior

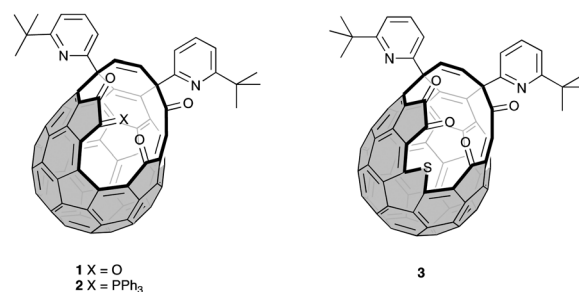
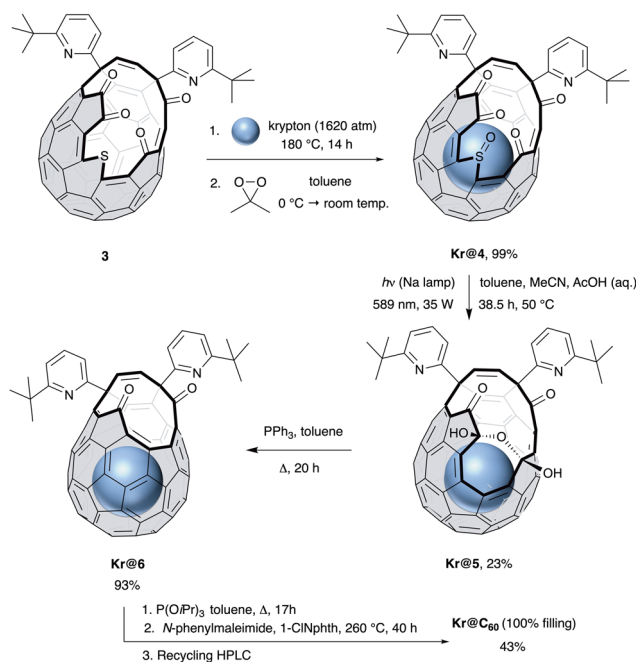


Fig. 1 Open-cage fullerenes **1–3** are key precursors to 'filling' by a single atom or molecule in reported syntheses of $\text{H}_2\text{O}@C_{60}$, $\text{HF}@C_{60}$, $\text{H}_2\text{O}@C_{60}$ (**1**),^{11,16,17} $\text{HD}@C_{60}$, $\text{D}_2@C_{60}$, $^3\text{He}@C_{60}$, $^4\text{He}@C_{60}$, $\text{Ne}@C_{60}$ (**2**),¹⁸ $\text{CH}_4@C_{60}$, $\text{Ar}@C_{60}$ (**3**).^{14,15}

Chemistry, Faculty of Engineering and Physical Sciences,
University of Southampton, Southampton, SO17 1BJ, UK. E-mail: rjw1@soton.ac.uk
† Electronic supplementary information (ESI) available. CCDC 2141931. For ESI
and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2cc03398d>



Scheme 1 Synthesis of Kr@C₆₀.

cage surface in detail, our syntheses of ³He@C₆₀ and ⁴He@C₆₀ have so far enabled characterisation of internuclear interactions in the form of the “non-bonded” *J*-coupling (⁰*J*_{HeC}) and experimental interaction potential – each evaluated against theoretical models.^{2,3} We now describe preparation of pure Kr@C₆₀ on a scale of tens of milligrams suitable for detailed study, including by ¹³C and ⁸³Kr NMR discussed herein. We also report upon current limitations to the application of molecular surgery methods for synthesis of Xe@C₆₀.

Synthesis of Kr@C₆₀ was carried out according to the methods we have reported for preparation of CH₄@C₆₀¹⁵ and Ar@C₆₀,¹⁴ and is described in Scheme 1. The bis(hemiketal) hydrate of open fullerene **1** was prepared from C₆₀ using our recent optimisation¹⁸ of the cage-opening steps earlier described by Murata and co-workers,^{13,19} before dehydration to give **1** and insertion of sulfur to furnish **3**.¹² DFT calculations (see ESI†) indicated $\Delta H_{\text{entry}}^{\ddagger} = 87 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{bind}} = -57 \text{ kJ mol}^{-1}$ for encapsulation of krypton by **3**, similar to the values for CH₄. Accordingly, heating powdered **3** under >1500 atm of krypton gas for 14 h gave Kr@**3** with >99% filling estimated from the ¹H NMR and ESI+ mass spectra.

Encapsulation of xenon by **3** was calculated to have $\Delta H_{\text{entry}}^{\ddagger} = 152 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{bind}} = -56 \text{ kJ mol}^{-1}$, and attempted preparation of Xe@**3** by heating **3** at 212 °C under 1850 atm of xenon gas for 17 h gave <1% xenon incorporation, from the ESI+ mass spectrum. Higher temperature or a longer reaction time led to substantial decomposition, so xenon ‘filling’ of **3** does not constitute a viable route for the synthesis of Xe@C₆₀ for which a larger cage opening is needed.

The rate of first-order thermal dissociation of Kr@**3** was measured between 433 and 453 K. Arrhenius and Eyring plots are shown in the ESI.† All parameters for loss of krypton from

the fullerene ($E_{\text{a exit}} = 138.5 \pm 5.6 \text{ kJ mol}^{-1}$, $\Delta H^{\ddagger} = 134.8 \pm 5.6 \text{ kJ mol}^{-1}$, $\Delta S^{\ddagger} = -40.1 \pm 14.6 \text{ J K}^{-1} \text{ mol}^{-1}$, $(\log)A = 11.3$ and $\Delta G^{\ddagger} = 152.4 \pm 0.1 \text{ kJ mol}^{-1}$ at 165 °C, closely matched those for loss of CH₄ from **3**.²⁰

Oxidation of Kr@**3** gave sulfoxide Kr@**4** cleanly, and photochemical desulfinylation of Kr@**4** led to the ring-contracted product Kr@**1**, isolated as its hydrate Kr@**5** with >99% encapsulation. Separation of Kr@C₆₀ and H₂O@C₆₀ is possible using recycling preparative HPLC so it was unnecessary to conduct exhaustive drying of Kr@**5** or to use conditions for the following step that avoid re-encapsulation of traces of water (*cf.* our Ar@C₆₀ synthesis).¹⁴ The final ring-closure steps for conversion of Kr@**5** to Kr@C₆₀ were therefore conducted under the conditions we originally reported for the synthesis of H₂O@C₆₀,¹⁷ involving dehydration to Kr@**1**, intramolecular Wittig reaction of the phosphonium ylid Kr@**2** to give Kr@**6**, then similar Wittig closure of a phosphite ylid upon heating Kr@**6** with (*i*PrO)₃P. Reaction with *N*-phenylmaleimide in a final step that involves sequential [4 + 2], retro[4 + 2] and [2 + 2 + 2] cycloaddition completed the cage closure. Removal of H₂O@C₆₀ and enrichment of the krypton encapsulation, was achieved by recycling preparative HPLC.^{8,21a,b} Overall, Kr@C₆₀ was recovered with >99.4% incorporation of the noble gas, and in 3.6–4.1% yield from C₆₀ over repeated batch syntheses. A crystal structure of the nickel(II) octaethylporphyrin/benzene solvate of Kr@C₆₀ was obtained, in which the noble gas atom is centred in the cage (see ESI†) as in the previously reported structure of *ca.* 9% filled Kr@C₆₀ {Ni^{II}(OEP)} 2C₆H₆.^{21a}

Krypton is the largest noble gas so far encapsulated in C₆₀ by the ‘molecular surgery’ methods described here, enabling synthesis on a suitable scale for detailed NMR characterisation. The ¹³C NMR resonance of Kr@C₆₀ in 1,2-dichlorobenzene-*d*₄ has a chemical shift of $\delta_{\text{c}} = 143.20 \text{ ppm}$ at 298 K, deshielded by $+0.390 \pm 0.001 \text{ ppm}$ relative to empty C₆₀ (Fig. 2a). Yamamoto *et al.* reported a consistent value of $\Delta\delta = +0.39 \text{ ppm}$ in benzene-*d*₆,⁸ and it has been previously noted that deshielding of the cage ¹³C NMR resonance in the noble gas@C₆₀ series, with respect to C₆₀, becomes greater with the increasing van der Waals radius of the trapped atom.^{1a,18}

We observe a pair of side peaks to the main ¹³C NMR resonance (Fig. 2b), due to minor isotopomers of Kr@C₆₀ that each contain two adjacent ¹³C nuclei separated by either a hexagon–pentagon (HP) or shorter hexagon–hexagon (HH) bond, present in a 2:1 ratio respectively. One-bond secondary isotope shifts of $^1A_{\text{HP}} = 12.45 \pm 0.01 \text{ ppb}$ and $^1A_{\text{HH}} = 19.77 \pm 0.02 \text{ ppb}$, shielded relative to the main Kr@C₆₀ peak, are smaller than those measured for empty C₆₀ ($^1A_{\text{HP}} = 12.56 \pm 0.01 \text{ ppb}$ and $^1A_{\text{HH}} = 19.98 \pm 0.02 \text{ ppb}$)²² and are the smallest secondary isotope shifts yet measured for atomic or molecular endofullerenes.^{3,14,18,22}

The only stable krypton isotope with a nuclear spin is ⁸³Kr (*I* = 9/2, 11.58% natural abundance) and ⁸³Kr NMR has been used to study the surface and void adsorption properties of porous nanomaterials.^{23a,b} Hyperpolarised ⁸³Kr gas is used for MRI imaging of the lungs, despite the relatively short spin-lattice relaxation time of the quadrupolar ⁸³Kr spin.^{24a,b} To our knowledge, Kr@C₆₀



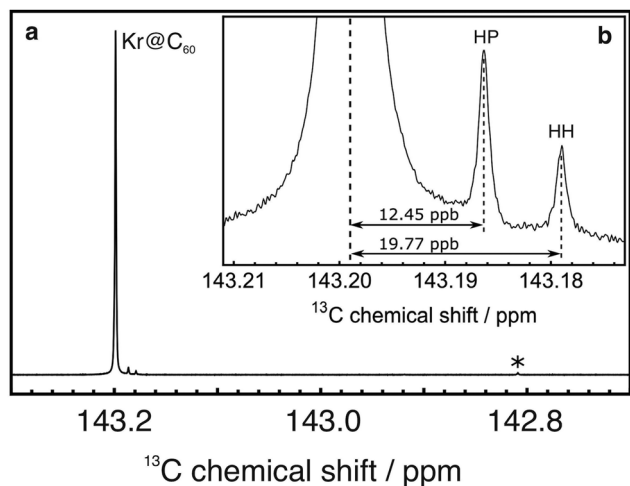


Fig. 2 (a) ^{13}C NMR spectrum of Kr@C_{60} (99.44 mol% krypton) in 1, 2-dichlorobenzene- d_4 at a field of 16.45 T (^{13}C Larmor frequency = 176 MHz) and 298 K, acquired with 912 transients. An asterisk marks empty C_{60} (0.56%). (b) Expanded view of the base of the Kr@C_{60} resonance to show side peaks arising from minor isotopomers with two adjacent ^{13}C nuclei that share either a hexagon–pentagon (HP) or hexagon–hexagon (HH) edge.

offers the first opportunity for ^{83}Kr NMR spectroscopy of a stable compound of krypton. The ^{83}Kr NMR spectrum of Kr@C_{60} in 1, 2-dichlorobenzene- d_4 solution with dissolved krypton gas at 298 K is shown in Fig. 3. The $\delta = 0$ origin of the ^{83}Kr NMR chemical shift scale corresponds to low-pressure Kr gas on the unified IUPAC referencing scale,²⁵ but using an updated Ξ parameter for ^{83}Kr as determined by Makulski (see ESI†).²⁶

The ^{83}Kr chemical shift for $^{83}\text{Kr@C}_{60}$ in 1,2-dichlorobenzene- d_4 solution is $\delta_{\text{Kr}} = 64.3 \pm 0.1$ ppm, shifted by -39.5 ppm with respect to the resonance of free ^{83}Kr in solution. For comparison $^3\text{He@C}_{60}$ and $^{129}\text{Xe@C}_{60}$ are reported at -6.04 and -16.5 ppm respectively from the dissolved gasses in this solvent.²⁷ In benzene- d_6 solution $^{83}\text{Kr@C}_{60}$ is at $\delta_{\text{Kr}} = 64.3 \pm 0.3$ ppm, shifted by -32.7 ppm from the dissolved gas (see ESI†). The reported shifts of $^{129}\text{Xe@C}_{60}$ in benzene are 179.2 ppm from Xe gas, and -8.89 ppm relative to dissolved gas.^{7b} The shift of $^3\text{He@C}_{60}$ is -6.3 ± 0.15 ppm in 1-methylnaphthalene or CS_2 with respect to either dissolved or free gas.²⁸

Simple (non-relativistic) calculations for $^3\text{He@C}_{60}$, $^{83}\text{Kr@C}_{60}$ and $^{129}\text{Xe@C}_{60}$ predict cage induced shifts of -7.0 , 29.9 and 71.7 ppm, consistent with the relative order, if not absolute values, observed.²⁹ Recent calculations on $^{129}\text{Xe@C}_{60}$ are in good agreement with the experimental shift.³⁰ Whilst ^3He observes the shielding effect of the cage on the field inside, for ^{83}Kr and ^{129}Xe the shift is dominated by an increasing direct interaction between the atomic orbitals and the π -electron orbitals of the cage.

The protective effect of the cage is revealed by measurement of ^{83}Kr linewidths and relaxation times. The ^{83}Kr peak of $^{83}\text{Kr@C}_{60}$ has a linewidth of 2.7 ± 0.1 Hz at half-height, which is much smaller than the linewidth of 10.8 ± 0.1 Hz for free ^{83}Kr in solution (Fig. 3b and c). Similarly, the ^{83}Kr spin-lattice

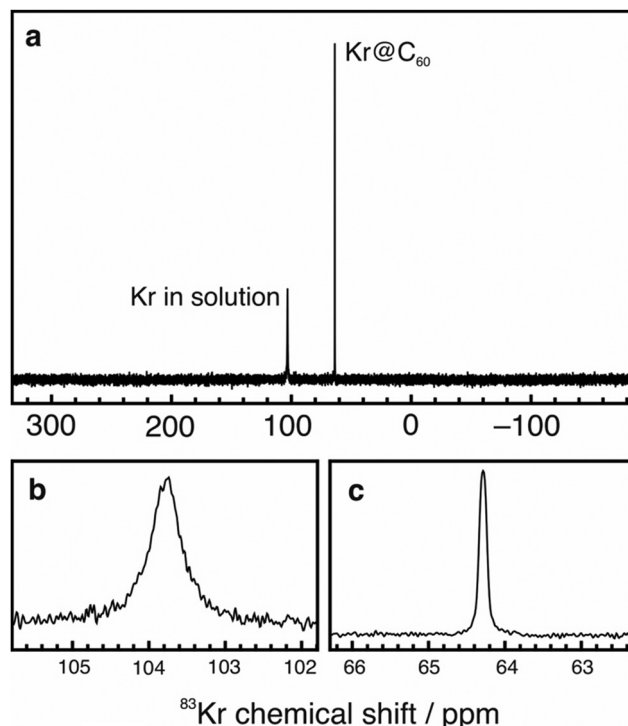


Fig. 3 (a) ^{83}Kr NMR spectrum of Kr@C_{60} (99.44 mol% krypton) in 1, 2-dichlorobenzene- d_4 at a field of 14 T (^{83}Kr Larmor frequency = 23.1 MHz) and 298 K, acquired with 102 400 transients. (b) Expanded view of the ^{83}Kr gas peak (dissolved in 1,2-dichlorobenzene- d_4). (c) Expanded view of the $^{83}\text{Kr@C}_{60}$ peak. Horizontal axes in (b) and (c) both span 4 ppm, vertical axes are arbitrary.

relaxation time constant of $^{83}\text{Kr@C}_{60}$ ($T_1 = 860 \pm 24$ ms) is much longer than that of free ^{83}Kr in 1,2-dichlorobenzene- d_4 solution ($T_1 = 31 \pm 2$ ms), and is longer than that reported for ^{83}Kr dissolved in any other solvent at room temperature (Fig. 4).³¹ Presumably the high symmetry and rigidity of C_{60} greatly reduces the magnitude of fluctuating electric field gradients at the location of the Kr nucleus, which are responsible for quadrupolar relaxation.

In summary, Kr@C_{60} is prepared in a yield of approx. 4% from C_{60} , with $>99\%$ krypton incorporation, using methods which overcome the severe limitation of only 0.1–0.3% direct krypton incorporation that results in very low mass recovery in the previously reported synthesis. An intermediate open-cage fullerene, **3**, encapsulates krypton under high pressure but was shown to have a cage opening too small for the entry of xenon gas. The larger scale synthesis of Kr@C_{60} has enabled measurement of fine structure in the solution-phase ^{13}C NMR spectrum, and characterisation by ^{83}Kr NMR spectroscopy – the first example for a krypton compound (*i.e.*, one in which the noble gas cannot escape without breaking covalent bonds). Endohedral ^{83}Kr has a chemical shift of 64.3 ppm in 1, 2-dichlorobenzene- d_4 , with respect to ^{83}Kr gas. This is less deshielded than ^{83}Kr in solution, presumably because the cage protects Kr from direct interactions with the solvent molecules. The ^{83}Kr spin-lattice relaxation for $^{83}\text{Kr@C}_{60}$ is approximately 36 times slower than for free ^{83}Kr in solution, indicating that



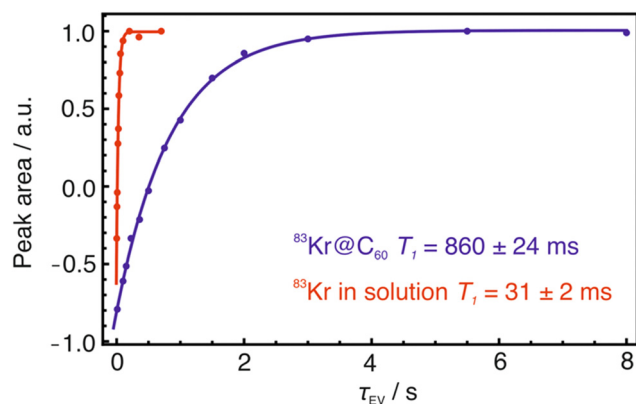


Fig. 4 Inversion Recovery relaxation curves fitted using a monoexponential curve, for ^{83}Kr spin-lattice relaxation time (T_1) of free ^{83}Kr (red) and $^{83}\text{Kr}@C_{60}$ approx. 26 mM (blue) in degassed 1,2-dichlorobenzene- d_4 at a field of 14 T (^{83}Kr Larmor frequency = 23.1 MHz) and 298 K. ^{83}Kr solution points were acquired with 2560 transients and $^{83}\text{Kr}@C_{60}$ points were acquired with 1024 transients.

the cage shields the endohedral atom from fluctuating electric field gradients.

This research was supported by EPSRC grants EP/P009980/1, EP/P030491/1 and EP/T004320/1. The authors acknowledge the use of the IRIDIS High Performance Computing Facility at the University of Southampton.

Conflicts of interest

The authors declare no conflict of interest.

Notes and references

- (a) R. G. Lawler, *Nanostruct. Sci. Technol.*, 2017, 229; (b) M. H. Levitt, *Philos. Trans. R. Soc., A*, 2013, 371, 20120429; (c) M. H. Levitt and A. J. Horsewill, *Philos. Trans. R. Soc., A*, 2013, 371, 20130124; (d) A. A. Popov, S. F. Yang and L. Dunsch, *Chem. Rev.*, 2013, 113, 5989.
- G. R. Bacanu, T. Jafari, M. Aouane, J. Rantaharju, M. Walkey, G. Hoffman, A. Shugai, U. Nagel, M. Jiménez-Ruiz, A. J. Horsewill, S. Rols, T. Rööm, R. J. Whitby and M. H. Levitt, *J. Chem. Phys.*, 2021, 155, 144302.
- G. R. Bacanu, J. Rantaharju, G. Hoffman, M. C. Walkey, S. Bloodworth, M. Concistrè, R. J. Whitby and M. H. Levitt, *J. Am. Chem. Soc.*, 2020, 142, 16926.
- (a) S. Jalife, J. Arcudia, S. Pan and G. Merino, *Chem. Sci.*, 2020, 11, 6642; (b) M. Saunders, R. J. Cross, H. A. Jiménez-Vázquez, R. Shimshi and A. Khong, *Science*, 1996, 271, 1693.
- (a) V. V. Albert, J. R. Sabin and F. E. Harris, *Int. J. Quantum Chem.*, 2007, 107, 3061; (b) M. Y. Amusia and L. V. Chernysheva, *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2020, 28, 179; (c) S. K. Chaudhuri, R. K. Chaudhuri, P. K. Mukherjee and S. A. Chattopadhyay, *J. Chem. Phys.*, 2017, 147, 034111; (d) F. Cimpoesu, S. Ito, H. Shimotani, H. Takagi and N. Dragoe, *Phys. Chem. Chem. Phys.*, 2011, 13, 9609; (e) A. Jaworski and N. Hedin, *Phys. Chem. Chem. Phys.*, 2021, 23, 21554; (f) T. Kupka, *eMagRes*, 2016, 5, 959; (g) L. Pizzagalli, *Phys. Chem. Chem. Phys.*, 2022, 24, 9449; (h) H. Yan, S. Yu, X. Wang, Y. He, W. Huang and M. Yang, *Chem. Phys. Lett.*, 2008, 456, 223.
- M. Saunders, H. A. Jiménez-Vázquez and R. J. Cross, *J. Am. Chem. Soc.*, 1994, 116, 2193.
- (a) R. J. Cross, A. Khong and M. Saunders, *J. Org. Chem.*, 2003, 68, 8281; (b) M. S. Syamala, R. J. Cross and M. Saunders, *J. Am. Chem. Soc.*, 2002, 124, 6216; (c) A. Takeda, Y. Yokoyama, S. Ito, T. Miyazaki, H. Shimotani, K. Yakigaya, T. Kakiuchi, H. Sawa, H. Takagi, K. Kitazawa and N. Dragoe, *Chem. Commun.*, 2006, 912.
- K. Yamamoto, M. Saunders, A. Khong, R. J. Cross, M. Grayson, M. L. Gross, A. F. Benedetto and R. B. Weisman, *J. Am. Chem. Soc.*, 1999, 121, 1591.
- S. Ito, A. Takeda, T. Miyazaki, Y. Yokoyama, M. Saunders, R. J. Cross, H. Takagi, P. Berthet and N. Dragoe, *J. Phys. Chem. B*, 2004, 108, 3191.
- Y. Morinaka, F. Tanabe, M. Murata, Y. Murata and K. Komatsu, *Chem. Commun.*, 2010, 46, 4532.
- K. Komatsu, M. Murata and Y. Murata, *Science*, 2005, 307, 238.
- T. Futagoishi, M. Murata, A. Wakamiya, T. Sasamori and Y. Murata, *Org. Lett.*, 2013, 15, 2750.
- K. Kurotobi and Y. Murata, *Science*, 2011, 333, 613.
- S. Bloodworth, G. Hoffman, M. C. Walkey, G. R. Bacanu, J. M. Herniman, M. H. Levitt and R. J. Whitby, *Chem. Commun.*, 2020, 56, 10521.
- S. Bloodworth, G. Sitinova, S. Alom, S. Vidal, G. R. Bacanu, S. J. Elliott, M. E. Light, J. M. Herniman, G. J. Langley, M. H. Levitt and R. J. Whitby, *Angew. Chem., Int. Ed.*, 2019, 58, 5038.
- A. Krachmalnicoff, R. Bounds, S. Mamone, S. Alom, M. Concistrè, B. Meier, K. Kouřil, M. E. Light, M. R. Johnson, S. Rols, A. J. Horsewill, A. Shugai, U. Nagel, T. Rööm, M. Carravetta, M. H. Levitt and R. J. Whitby, *Nat. Chem.*, 2016, 8, 953.
- A. Krachmalnicoff, M. H. Levitt and R. J. Whitby, *Chem. Commun.*, 2014, 50, 13037.
- G. Hoffman, M. C. Walkey, J. Gräsvik, G. R. Bacanu, S. Alom, S. Bloodworth, M. E. Light, M. H. Levitt and R. J. Whitby, *Angew. Chem., Int. Ed.*, 2021, 60, 8960.
- Y. Hashikawa, M. Murata, A. Wakamiya and Y. Murata, *J. Am. Chem. Soc.*, 2017, 139, 16350.
- S. Bloodworth, J. Gräsvik, S. Alom, K. Kouřil, S. J. Elliott, N. J. Wells, A. J. Horsewill, S. Mamone, M. Jiménez-Ruiz, S. Rols, U. Nagel, T. Rööm, M. H. Levitt and R. J. Whitby, *Chem. Phys. Chem.*, 2018, 19, 266.
- (a) H. M. Lee, M. M. Olmstead, T. Suetsuna, H. Shimotani, N. Dragoe, R. J. Cross, K. Kitazawa and A. L. Balch, *Chem. Commun.*, 2002, 1352; (b) T. Suetsuna, N. Dragoe, H. Shimotani, A. Takeda, S. Ito, R. J. Cross, M. Saunders, H. Takagi and K. Kitazawa, *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2002, 10, 15.
- G. R. Bacanu, G. Hoffman, M. Amponsah, M. Concistrè, R. J. Whitby and M. H. Levitt, *Phys. Chem. Chem. Phys.*, 2020, 22, 11850.
- (a) Z. I. Cleveland and T. Meersmann, *Magn. Reson. Chem.*, 2007, 45, S12–S23; (b) C. F. Horton-Garcia, G. E. Pavlovskaya and T. Meersmann, *J. Am. Chem. Soc.*, 2005, 127, 1958.
- (a) Z. I. Cleveland, G. E. Pavlovskaya, N. D. Elkins, K. F. Stupic, J. E. Repine and T. Meersmann, *J. Magn. Reson.*, 2008, 195, 232; (b) J. S. Six, T. Hughes-Riley, D. M. L. Lilburn, A. C. Dorkes, K. F. Stupic, D. E. Shaw, P. G. Morris, I. P. Hall, G. E. Pavlovskaya and T. Meersmann, *Magn. Reson. Imaging*, 2014, 32, 48.
- R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, P. Granger, R. E. Hoffman and K. W. Zilm, *Pure Appl. Chem.*, 2008, 80, 59.
- W. Makulski, *Magn. Reson. Chem.*, 2014, 52, 430.
- M. Frunzi, R. J. Cross and M. Saunders, *J. Am. Chem. Soc.*, 2007, 129, 13343.
- M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross, S. Mroczkowski, D. I. Freedberg and F. A. L. Anet, *Nature*, 1994, 367, 256.
- M. Bühl, S. Patchkovskii and W. Thiel, *Chem. Phys. Lett.*, 1997, 275, 14.
- S. Standara, P. Kulhánek, R. Marek and M. Straka, *J. Comput. Chem.*, 2013, 34, 1890.
- R. K. Mazitov, K. M. Enikeev and A. V. Ilyasov, *Z. Phys. Chem.*, 1987, 155, 55.

