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Synthesis and ⁸³Kr NMR spectroscopy of Kr@C₆₀†

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Synthesis of Kr@C₆₀ 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 C60 using 'molecular surgery' and Kr@C₆₀ 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 C₆₀ than for free Kr in solution. This is the first characterisation of a stable Kr compound by 83Kr 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. $\overline{^{1a-d}}$ The noble gas endofullerenes of C_{60} and C₇₀ (denoted e.g. Ng@C₆₀ 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 Ng@C60 compounds relied upon direct encapsulation by exposure of C₆₀ 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 C60 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 Kr@C₆₀ with 90–99% purity, ^{8,9} and *ca.* 0.3 mg Xe@ C₆₀ with 50% purity.^{7b} Resulting ¹³C NMR, UV-visible absorption, infrared, Raman, X-ray absorption and ¹²⁹Xe 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 H₂@C₆₀ and ⁴He@C₆₀ 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 HF@C60, $H_2@C_{60}$ and $H_2O@C_{60}$ (1), $Ar@C_{60}$ and $CH_4@C_{60}$ (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 ³He@C₆₀, ⁴He@C₆₀ and Ne@C₆₀. ¹⁸ Incorporation of approx. 50-60% of the noble gas was accomplished, and enrichment of Ne@C60 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

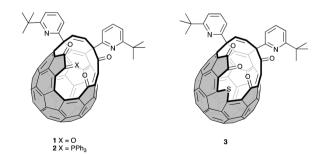
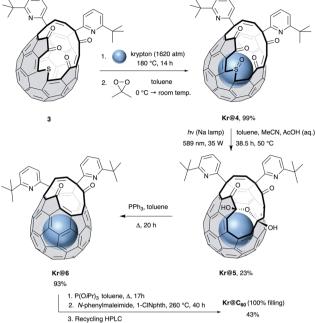


Fig. 1 Open-cage fullerenes **1–3** are key precursors to 'filling' by a single atom or molecule in reported syntheses of $H_2O@C_{60}$, $HF@C_{60}$, $H_2@C_{60}$ $(\mathbf{1})$, 11,16,17 HD@C₆₀, D₂@C₆₀, 3 He@C₆₀, 4 He@C₆₀, Ne@C₆₀ (**2**), 18 CH₄@C₆₀, Ar@C₆₀ (**3**). 14,15

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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 $CH_4@C_{60}^{15}$ 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 $\Delta H_{\rm entry}^{\dagger}$ = 87 kJ mol⁻¹ and $\Delta H^{\rm bind}$ = -57 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 kJ mol⁻¹ and $\Delta H^{\text{bind}} = -56 \text{ kJ mol}^{-1}$, and attempted preparation of Xe(a)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_a exit = 138.5 \pm 5.6 kJ mol⁻¹, ΔH^{\ddagger} = 134.8 \pm 5.6 kJ mol⁻¹, $\Delta S^{\ddagger} = -40.1 \pm 14.6$ J K⁻¹ mol⁻¹, $(\log)A = 11.3 \text{ and } \Delta G^{\ddagger} = 152.4 \pm 0.1 \text{ kJ mol}^{-1} \text{ at } 165 \,^{\circ}\text{C},$ 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 $(iPrO)_3P$. 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@ C_{60} {Ni II (OEP)} $2C_6H_6$. 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-d₄ has a chemical shift of δ_c = 143.20 ppm at 298 K, deshielded by $+0.390 \pm 0.001$ ppm relative to empty C₆₀ (Fig. 2a). Yamamoto et al. reported a consistent value of $\Delta \delta$ = +0.39 ppm in benzene d_{6} , 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 $^{1}\Delta_{HP}$ = 12.45 \pm 0.01 ppb and $^{1}\Delta_{HH}$ = 19.77 \pm 0.02 ppb, shielded relative to the main Kr@C60 peak, are smaller than those measured for empty C_{60} (${}^{1}\Delta_{HP}$ = 12.56 \pm 0.01 ppb and $^{1}\Delta_{\mathrm{HH}}$ = 19.98 \pm 0.02 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

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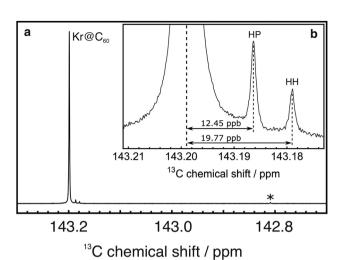


Fig. 2 (a) ^{13}C NMR spectrum of Kr@C $_{60}$ (99.44 mol% krypton) in 1, 2-dichlorobenzene- d_4 at a field of 16.45 T (13 C Larmor frequency = 176 MHz) and 298 K, acquired with 912 transients. An asterisk marks empty C₆₀ (0.56%). (b) Expanded view of the base of the Kr@C₆₀ resonance to show side peaks arising from minor isotopomers with two adjacent ¹³C nuclei that share either a hexagon-pentagon (HP) or hexagon-hexagon (HH) edae

offers the first opportunity for 83Kr NMR spectroscopy of a stable compound of krypton. The 83Kr NMR spectrum of Kr@C₆₀ in 1, 2-dichlorobenzene-d₄ solution with dissolved krypton gas at 298 K is shown in Fig. 3. The δ = 0 origin of the ⁸³Kr NMR chemical shift scale corresponds to low-pressure Kr gas on the unified IUPAC referencing scale, ²⁵ but using an updated Ξ parameter for ⁸³Kr as determined by Makulski (see ESI†).26

The 83Kr chemical shift for 83Kr@C₆₀ in 1,2-dichlorobenzene- d_4 solution is $\delta_{\rm Kr}$ = 64.3 \pm 0.1 ppm, shifted by -39.5 ppm with respect to the resonance of free 83Kr in solution. For comparison ³He@C₆₀ and ¹²⁹Xe@C₆₀ are reported at -6.04 and -16.5 ppm respectively from the dissolved gasses in this solvent. 27 In benzene- d_6 solution 83 Kr@C $_{60}$ is at $\delta_{\rm Kr}$ = 64.3 \pm 0.3 ppm, shifted by -32.7 ppm from the dissolved gas (see ESI†). The reported shifts of 129Xe@C60 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 CS2 with respect to either dissolved or free gas.²⁸

Simple (non-relativistic) calculations for ³He@C₆₀, ⁸³Kr@C₆₀ and ¹²⁹Xe@C₆₀ 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 ¹²⁹Xe@C₆₀ are in good agreement with the experimental shift.30 Whilst He observes the shielding effect of the cage on the field inside, for ⁸³Kr and ¹²⁹Xe 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 83Kr linewidths and relaxation times. The 83Kr peak of 83 Kr@C₆₀ has a linewidth of 2.7 \pm 0.1 Hz at half-height, which is much smaller than the linewidth of 10.8 \pm 0.1 Hz for free ⁸³Kr in solution (Fig. 3b and c). Similarly, the ⁸³Kr spin-lattice

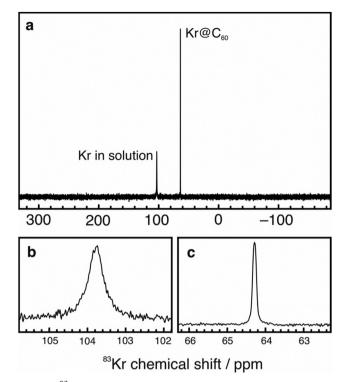


Fig. 3 (a) 83 Kr NMR spectrum of Kr@C₆₀ (99.44 mol% krypton) in 1, 2-dichlorobenzene- d_4 at a field of 14 T (83 Kr Larmor frequency = 23.1 MHz) and 298 K, acquired with 102400 transients. (b) Expanded view of the 83 Kr gas peak (dissolved in 1,2-dichlorobenzene- d_4). (c) Expanded view of the ⁸³Kr@C₆₀ peak. Horizontal axes in (b and c) both span 4 ppm, vertical axes are arbitrary.

relaxation time constant of 83 Kr@C₆₀ ($T_1 = 860 \pm 24$ 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 ⁸³Kr dissolved in any other solvent at room temperature (Fig. 4).31 Presumably the high symmetry and rigidity of C₆₀ 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@C₆₀ is prepared in a yield of approx. 4% from C₆₀, 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@C₆₀ has enabled measurement of fine structure in the solution-phase 13C NMR spectrum, and characterisation by 83Kr NMR spectroscopy - the first example for a krypton compound (i.e., one in which the noble gas cannot escape without breaking covalent bonds). Endohedral 83Kr 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 83Kr in solution, presumably because the cage protects Kr from direct interactions with the solvent molecules. The ⁸³Kr spin-lattice relaxation for ⁸³Kr@C₆₀ is approximately 36 times slower than for free 83Kr in solution, indicating that

1.0 0.5 Peak area / a.u. 0.0 83 Kr@C₆₀ T_1 = 860 ± 24 ms -0.5⁸³Kr in solution $T_t = 31 \pm 2$ ms -1.02 8 4 $au_{\scriptscriptstyle \mathrm{EV}}$ / s

Fig. 4 Inversion Recovery relaxation curves fitted using a monoexponential curve, for $^{83}\mathrm{Kr}$ spin-lattice relaxation time (T_1) of free $^{83}\mathrm{Kr}$ (red) and 83 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 83Kr@C₆₀ points were acquired with 1024 transients.

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

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Conflicts of interest

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The authors declare no conflict of interest.

Notes and references

- 1 (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,
- 2 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. Rõõm, R. J. Whitby and M. H. Levitt, J. Chem. Phys., 2021,
- 3 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.
- 4 (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.
- 5 (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.

- 6 M. Saunders, H. A. Jiménez-Vázquez and R. J. Cross, J. Am. Chem. Soc., 1994, 116, 2193.
- 7 (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.
- 8 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.
- 9 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.
- 10 Y. Morinaka, F. Tanabe, M. Murata, Y. Murata and K. Komatsu, Chem. Commun., 2010, 46, 4532.
- 11 K. Komatsu, M. Murata and Y. Murata, Science, 2005, 307, 238.
- 12 T. Futagoishi, M. Murata, A. Wakamiya, T. Sasamori and Y. Murata, Org. Lett., 2013, 15, 2750.
- 13 K. Kurotobi and Y. Murata, Science, 2011, 333, 613.
- 14 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,
- 15 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.
- 16 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. Rõõm, M. Carravetta, M. H. Levitt and R. J. Whitby, Nat. Chem., 2016, 8, 953.
- 17 A. Krachmalnicoff, M. H. Levitt and R. J. Whitby, Chem. Commun., 2014, 50, 13037.
- 18 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.
- 19 Y. Hashikawa, M. Murata, A. Wakamiya and Y. Murata, J. Am. Chem. Soc., 2017, 139, 16350.
- 20 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. Rõõm, M. H. Levitt and R. J. Whitby, Chem. Phys. Chem., 2018, 19, 266.
- 21 (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.
- 22 G. R. Bacanu, G. Hoffman, M. Amponsah, M. Concistrè, R. J. Whitby and M. H. Levitt, Phys. Chem. Chem. Phys., 2020, 22, 11850.
- 23 (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.
- 24 (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.
- 25 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.
- 26 W. Makulski, Magn. Reson. Chem., 2014, 52, 430.
- 27 M. Frunzi, R. J. Cross and M. Saunders, J. Am. Chem. Soc., 2007, **129.** 13343.
- 28 M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross, S. Mroczkowski, D. I. Freedberg and F. A. L. Anet, Nature, 1994, 367, 256.
- 29 M. Bühl, S. Patchkovskii and W. Thiel, Chem. Phys. Lett., 1997, 275, 14,
- 30 S. Standara, P. Kulhánek, R. Marek and M. Straka, J. Comput. Chem., 2013, 34, 1890.
- 31 R. K. Mazitov, K. M. Enikeev and A. V. Ilyasov, Z. Phys. Chem., 1987,