

# Enhancement of $^{13}\text{C}$ NMR signals in solid $\text{C}_{60}$ and $\text{C}_{70}$ using laser-polarized xenon

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## Abstract

NMR signals emanating from surface nuclei of solids may be enhanced by the transfer of spin polarization from laser-polarized noble gases via SPINOE (spin polarization induced nuclear Overhauser effect). The present contribution describes experiments in which the spin polarization is transferred under magic angle spinning (MAS) from laser-polarized  $^{129}\text{Xe}$  to  $^{13}\text{C}$ , a nuclear spin with a low gyromagnetic ratio in the fullerenes  $\text{C}_{60}$  and  $\text{C}_{70}$ , polycrystalline materials with a low surface area. In  $\text{C}_{70}$ , differential enhancement of the NMR is observed for the different atomic sites in the molecule. © 1998 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Noble gas nuclei, especially  $^{129}\text{Xe}$ , have found numerous applications as probe molecules in surface NMR spectroscopy (see, e.g., Refs. [1–5]). There is increasing interest in the enhancement of NMR using laser-polarized noble gas nuclei such as  $^3\text{He}$  or  $^{129}\text{Xe}$  [6,7] for MRI [8,9] and materials science [10,11]. At high magnetic field two pathways for the transfer of enhanced spin polarization from laser-polarized noble gas nuclei to other nuclei have been exploited: (1) cross relaxation, a mechanism dubbed SPINOE [12,13] and (2) cross polarization (CP, [14]), which requires a static magnetic dipole interaction between

the  $^{129}\text{Xe}$  spins and the nuclei to be polarized. The  $^1\text{H}$  NMR signals of surface hydroxyl groups of  $\text{SiO}_2$ , as well as the  $^{13}\text{C}$  NMR signals of  $\text{CO}_2$  adsorbed on  $\text{SiO}_2$ , were enhanced by SPINOE from laser-polarized  $^{129}\text{Xe}$  [13]. These studies can also be accomplished under conditions of a circulating flow of laser-polarized  $^{129}\text{Xe}$  through the sample [15]. Furthermore, it was shown that such investigations can be carried out under conditions of MAS [16–18]. A constant stream of laser-polarized  $^{129}\text{Xe}$  is brought into contact with the spinning sample via a capillary directed into the MAS rotor. Under steady-state conditions, the macroscopic magnetization  $M_S$  of the spins  $S$  on the sample surface may deviate from its equilibrium value  $M_S^0$ . According to the Solomon equations [19],  $M_S$  approaches an equilibrium value

$$\langle M_S \rangle - M_S^0 \propto \frac{\sigma_{IS}}{\rho} (\langle M_I \rangle - M_I^0). \quad (1)$$

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$I$  denotes the  $^{129}\text{Xe}$  spin  $^1$ ,  $\langle M_I \rangle$  the steady-state magnetization of the  $^{129}\text{Xe}$  atoms adsorbed on the sample,  $M_I^0$  is the equilibrium magnetization of  $^{129}\text{Xe}$ ,  $\sigma_{IS}$  denotes the cross relaxation rate and  $\rho$  the longitudinal relaxation rate of the  $S$  spins.

In the present Letter we show that this new methodology is useful for spin polarization transfer to surface nuclei with a low gyromagnetic ratio, especially  $^{13}\text{C}$ , even in low surface area materials. Fullerenes are suitable model compounds since their longitudinal relaxation times ( $T_1$ ) are relatively long at low temperatures [20–23]. In such samples, large enhancements of the spin polarization should be possible for those surface  $^{13}\text{C}$  nuclei that experience dipolar interactions with the adsorbed laser-polarized  $^{129}\text{Xe}$  nuclei (cf. Eq. (1)), provided that the  $^{129}\text{Xe}$  layer remains polarized during a time of the order of  $T_1$  ( $\sim 80$  s for  $^{13}\text{C}$  in  $\text{C}_{60}$  at 150 K [21]). The application of a continuous flow of laser-polarized  $^{129}\text{Xe}$  is an attractive approach for such long polarization times.

## 2. Experimental

The experimental setup used for these experiments, described in detail in Ref. [17], consists of an optical pumping apparatus similar to the one designed by Driehuys et al. [7] together with a modified variable-temperature MAS probe. Laser-polarized  $^{129}\text{Xe}$  is inserted into the spinning rotor via a glass capillary using helium as a carrier gas. A similar setup was used for in situ NMR spectroscopic investigations of chemical reactions [24,25]. The spin polarization of the  $^{129}\text{Xe}$  gas signal in the rotor was measured to be  $\sim 1$ –2%, about three orders of magnitude higher than the equilibrium spin polarization at 293 K.

Crystalline  $\text{C}_{60}$  and  $\text{C}_{70}$  were ground in an agate mortar for  $\sim 30$  min, producing samples of mean crystallite diameter  $4 \mu\text{m}$  for  $\text{C}_{60}$  and  $2 \mu\text{m}$  for  $\text{C}_{70}$ , as determined by optical microscopy. Assuming a spherical shape of the particles one estimates specific surface areas of  $\sim 1$  and  $\sim 2 \text{ m}^2 \text{ g}^{-1}$  for  $\text{C}_{60}$  and

$\text{C}_{70}$ , respectively. The samples were evacuated at 373 K in high vacuum and then filled into the rotor in a glove box under nitrogen atmosphere. The rotor was then inserted into the probe and purged with a gas mixture containing 93.5% He, 5% Xe (natural abundance) and 1.5%  $\text{N}_2$  during the entire experiment. The sample was heated initially up to  $\sim 373$  K in order to remove water or oxygen which may have been adsorbed during the insertion of the rotor into the probe. After this procedure the sample was cooled down to 150 K. The temperature inside the rotor was calibrated by  $^{207}\text{Pb}$  NMR spectroscopy using the chemical shift temperature dependence of  $\text{Pb}(\text{NO}_3)_2$  [26–28]. The spatial temperature variation within the rotor was  $\sim 10$  K.  $^{129}\text{Xe}$  and  $^{13}\text{C}$  MAS NMR spectra were measured at resonance frequencies of 83.3 and 75.7 MHz, respectively, and at a sample spinning rate of  $\sim 3$  kHz. The  $^{13}\text{C}$  MAS NMR spectra were recorded using a saturation recovery sequence. The  $90^\circ$  pulse for  $^{13}\text{C}$  was measured to be  $15 \mu\text{s}$  at the used rf power level low enough to avoid arcing.

## 3. Results and discussion

Spin polarization transfer via SPINOE requires effective adsorption of laser-polarized  $^{129}\text{Xe}$  on the sample under study. Fig. 1 shows the  $^{129}\text{Xe}$  MAS NMR spectra of laser-polarized  $^{129}\text{Xe}$  adsorbed on fullerenes measured at 150 K. The spectra exhibit

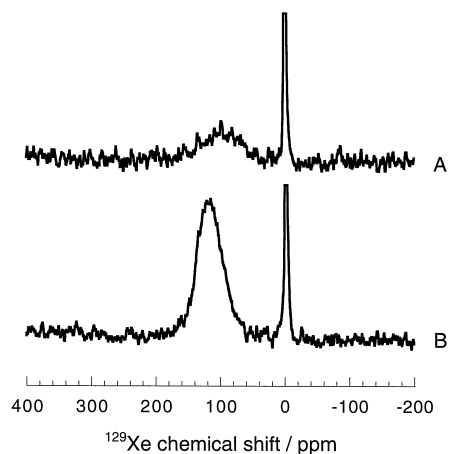


Fig. 1.  $^{129}\text{Xe}$  MAS NMR spectra of laser-polarized  $^{129}\text{Xe}$  adsorbed on  $\text{C}_{60}$  (A) and  $\text{C}_{70}$  (B), measured at 150 K. Note that the sharp signals at 0 ppm due to gaseous  $^{129}\text{Xe}$  are clipped to enlarge the scale.

<sup>1</sup> For consistency with the notation used for cross polarization in solid state NMR we use the convention that the nuclei constituting the source of polarization ( $^{129}\text{Xe}$ ) are denoted by  $I$  and the nuclei to be polarized are denoted by  $S$ .

narrow signals at  $\sim 0$  ppm due to gaseous xenon and broad signals centered at 100–120 ppm (50–80 ppm wide), characteristic of adsorbed xenon (see, e.g., Refs. [4,5,10,11]). The intensity of the latter signal is 4–5 times higher for  $C_{70}$  than for  $C_{60}$  because the specific surface of the  $C_{70}$  sample was approximately twice the specific surface of  $C_{60}$  and the mass of the  $C_{70}$  sample was 2.5 times the mass of the  $C_{60}$  sample. The fractional coverage of the surface with xenon was apparently the same for both samples.

Fig. 2A shows the  $^{13}\text{C}$  MAS NMR spectrum of  $C_{60}$  with the characteristic single line at 144 ppm [20–22]. The SPINOE spectrum shown in Fig. 2B is obtained as the difference between the spectrum measured when the  $^{129}\text{Xe}$  flowing into the rotor is laser-polarized and the spectrum measured when the  $^{129}\text{Xe}$  exhibits its normal thermal equilibrium polarization. The intensity corresponds to  $\sim 15 \pm 5\%$  of the intensity of the spectrum observed when the  $^{129}\text{Xe}$  flowing through the sample is not laser-polarized. From the mean crystallite diameter of  $\sim 4 \mu\text{m}$  and the diameter of a  $C_{60}$  molecule ( $\sim 1 \text{ nm}$ ) one can estimate that only a fraction of  $\sim 0.0015$  of the  $C_{60}$  molecules is located at the surface of the particles. Assuming that effective polarization trans-

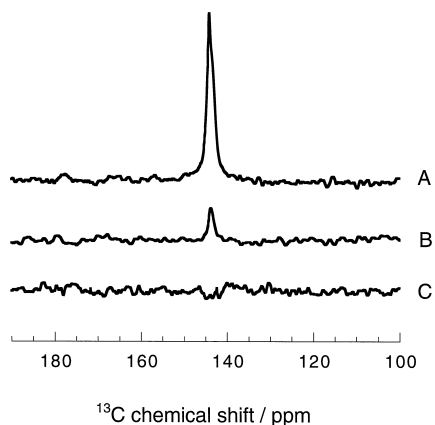


Fig. 2.  $^{13}\text{C}$  MAS NMR spectra of  $C_{60}$  acquired at 150 K. (A): Spectrum obtained when the gas stream is not laser-polarized (laser off). (B): Difference between the spectrum obtained when the gas stream is laser-polarized (laser on) and spectrum (A). This spectrum quantitatively represents the observed SPINOE intensity. (C): Difference between two succeeding recorded spectra obtained when the  $^{129}\text{Xe}$  flowing into the rotor is not laser-polarized. This demonstrates that the difference spectrum is free of artifacts.

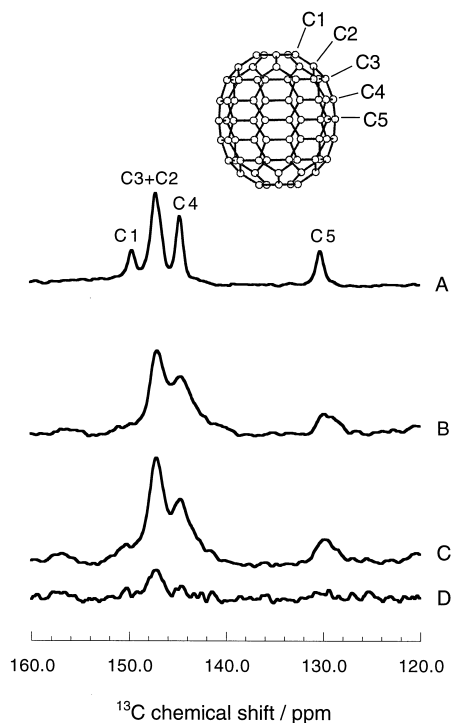


Fig. 3.  $^{13}\text{C}$  MAS NMR spectra of  $C_{70}$  acquired at room temperature (A) and 150 K (B–D). (B): Spectrum obtained when the  $^{129}\text{Xe}$  flowing into the rotor is not laser-polarized. (C): Spectrum obtained when the  $^{129}\text{Xe}$  flowing into the rotor is laser-polarized. (D): Difference between spectrum (C) and spectrum (B).

fer only occurs to  $C_{60}$  molecules located at the surface, one concludes that the observed signal enhancement of  $15 \pm 5\%$  corresponds to a polarization enhancement factor of  $\sim 100 \pm 30$ . However, it should be noted that this simple estimation neglects the influence of spin diffusion which can lead to a transport of spin polarization into the bulk, resulting in a lower surface enhancement factor (see below).

Fig. 3A and B shows the  $^{13}\text{C}$  MAS NMR spectra of  $C_{70}$  measured at room temperature and 150 K, respectively. The signal at 147 ppm arises from  $^{13}\text{C}$  nuclei at positions C2 and C3, whereas the nuclei located at C4 and C5 give rise to the signals at 144.5 and 130 ppm, respectively [23]. It should be noted that the signal at 150 ppm due to  $^{13}\text{C}$  nuclei located at C1 positions is clearly resolved at room temperature but it appears only as a ‘shoulder’ at 150 K since the residual linewidth of the  $^{13}\text{C}$  MAS NMR signals of  $C_{70}$  increases for decreasing temperature [23]. The

spectrum shown in Fig. 3B was measured in the presence of a gas stream carrying unpolarized  $^{129}\text{Xe}$  (i.e., laser turned off). Turning the laser light on increases the signal intensity of the carbons in the C2 and C3 positions (147 ppm) by  $25 \pm 5\%$ , an effect that can also be seen in the difference spectrum (see Fig. 3C and D). The intensity of the ‘shoulder’ at 150 ppm also increases but a quantitative evaluation of this effect is difficult on the basis of the present data. The increase of the intensities of the signals at 144.5 and 130 ppm lies within the experimental error and is not considered to be significant. Identical  $T_1$  values of  $5 \pm 1$  s were measured for the  $^{13}\text{C}$  nuclei located at the positions C2, C3, C4 and C5 at 150 K, in agreement with the results of calculations and measurements presented in Ref. [23]. It is concluded, therefore, that the more intense SPINOE for  $^{13}\text{C}$  nuclei located at C2 or C3, or at both positions results from a higher cross relaxation rate  $\sigma_{IS}$  (see Eq. (1)). A plausible explanation for this selective enhancement would be better accessibility of xenon atoms to these sites and/or a higher heat of adsorption of xenon on these sites.

Since the build-up time of the SPINOE is of the order of  $T_1$  it has to be taken into account that spin diffusion caused by flip-flop processes may lead to a transport of non-equilibrium magnetization from the surface of the material into the bulk. Spin diffusion follows Fick’s second law [29]. It is assumed that the spin diffusion is spatially isotropic and that the penetration depth  $z$  of the non-equilibrium magnetization is small compared to the particle diameter. Adding the term  $(-\rho\Delta M_S) = -\rho(M_S - M_S^0)$  which describes the longitudinal relaxation of the non-equilibrium magnetization one can write

$$\frac{d(\Delta M_S)}{dt} = D \frac{d^2(\Delta M_S)}{dz^2} - \rho\Delta M_S. \quad (2)$$

The surface nuclei are located at  $z = 0$  and  $D$  denotes the spin diffusion coefficient. After a sufficiently long time the system will reach a steady state characterized by  $d(\Delta M_S)/dt = 0$  and the solution of Eq. (2) is then given by

$$\Delta M_S(z) = \Delta M_S(0)e^{-z/z_0},$$

$$z_0 = \sqrt{\frac{D}{\rho}} \approx a\sqrt{\frac{\sigma}{\rho}}, \quad (3)$$

where  $\sigma$  denotes the mean flip-flop rate [29] and  $a$  is the mean distance between neighboring  $^{13}\text{C}$  nuclei. This equation can be used in order to determine: (1) the upper limit of the mean penetration depth  $z_0$  of the non-equilibrium magnetization reached in steady state and (2) the non-equilibrium magnetization of the surface spins  $\Delta M_S(0)$ . The flip-flop rate can roughly be estimated [29] for static, i.e., non-spinning samples according to

$$\sigma \approx \frac{\sqrt{M_2^{SS}}}{30} \approx 0.089 \Delta\nu_{SS}, \quad (4)$$

where  $M_2^{SS}$  denotes van Vleck’s second moment due to the homonuclear magnetic dipole interaction and  $\Delta\nu_{SS}$  the corresponding homonuclear linewidth for a rigid lattice assuming a Gaussian lineshape. Blinc et al. [22] have measured the homogeneous linewidth of the  $^{13}\text{C}$  NMR signal of  $\text{C}_{60}$  and obtained a value of  $\sim 160$  Hz at 150 K which is less than the value of 334 Hz calculated for a rigid lattice. This behavior is interpreted by the presence of non-isotropic rapid thermal motions even at 150 K. For 160 Hz homonuclear linewidth Eq. (4) predicts a flip-flop rate of  $14 \text{ s}^{-1}$ . For a static  $\text{C}_{60}$  sample at 150 K where the longitudinal relaxation time of  $^{13}\text{C}$  nuclei amounts to  $\sim 80$  s [21] this would result in an upper limit for the mean penetration depth  $z_0$  of 30–40 nm (see Eq. (3)) corresponding to a lower limit of  $3 \pm 1$  for the magnetization enhancement factor of the surface  $^{13}\text{C}$  nuclei. It is, however, known that magic angle spinning strongly reduces the influence of spin diffusion provided that the sample spinning rate is fast compared to the homonuclear linewidth; a condition which is fulfilled since the samples were spun at  $\sim 3$  kHz. We also performed a so-called SPARTAN (selective population anti- $z$  and rate of transfer to adjacent nuclei [30,31]) experiment which revealed the absence of spectral spin diffusion in  $\text{C}_{70}$  at 150 K within  $T_1$  between the carbon positions C3/C2, C4 and C5. A detailed study of spin diffusion processes in fullerenes is in progress.

#### 4. Conclusions

The present Letter shows the feasibility of spin polarization transfer by SPINOE from laser-polarized

$^{129}\text{Xe}$  to surface  $^{13}\text{C}$  nuclei on low surface area materials in high-resolution solid state NMR experiments. This technique provides the basis for novel surface  $^{13}\text{C}$  NMR investigations, e.g., of surface coatings, supported catalysts and electrode materials.

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