Angewandte Chemie

DOI: 10.1002/ange.201307389

Spin Isomers

Nuclear Spin Isomers of Ethylene: Enrichment by Chemical Synthesis and Application for NMR Signal Enhancement**

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The existence of distinct nuclear spin isomers of molecules (NSIMs) is the direct manifestation of the laws of quantum mechanics and thus has fundamental significance in science.[1] In addition, the use of NSIMs is highly promising for the development of powerful research tools in various scientific disciplines. In astrophysics, measurements of the ortho/para ratio (OPR) for molecules such as H_2, H_2O, H_2CO, and NH_3 in objects of the interstellar medium are used to gain knowledge about when and how these objects were formed.[2] In NMR spectroscopy, the use of parahydrogen in homogeneous[3] and heterogeneous[4,5] catalytic hydrogenations can provide an enhancement of observed signals by three to five orders of magnitude, thus advancing significantly the studies of the mechanisms of such reactions, the development of novel applications of MRI,[6] NMR spectroscopy in ultra-low and zero magnetic fields,[7] and more.

However, the only NSIMs that can be readily produced in arbitrary quantities and with maximum enrichment is parahydrogen.[8] Owing to the unusually large rotational constant of H_2, the enrichment can be done by simply cooling normal H_2 to cryogenic temperatures over a paramagnetic material. For larger molecules, different enrichment techniques (by synthesis, separation, destruction, or conversion) are needed.[9] One of the most efficient methods is the light-induced-drift (LID) approach,[9,10] which was successfully used to separate the NSIMs of CH_3F and $^{13}CH_3F$,[10,11] as well as ethylene[12] and ^{13}C-labeled ethylene.[13] Separation in cold molecular beams was used recently to produce spin-polarized focused beams of NSIMs for water and methane.[14] Unfortunately, all production approaches for NSIMs demonstrated so far provide enriched NSIMs in very limited quantities, which are insufficient for many scientific and practical applications. In particular, their use for NMR signal enhancement will be practical only when much larger amounts of enriched NSIMs become available. In addition, a facile and abundant production of enriched NSIMs will undoubtedly have a dramatic impact on the studies of their fundamental properties and behavior in various processes such as interconversion,[9,15,16] chemical reactions,[17] scattering of particles, interaction with external fields, etc.

In this study, the enrichment NSIMs of ethylene is achieved by chemical synthesis in quantities sufficient to successfully utilize it for NMR signal enhancement and to interrogate interconversion of NSIMs at ambient pressure. To perform the enrichment of NSIMs of ethylene ($H_2C{=}CH_2$), acetylene ($HC{\equiv}CH$) is catalytically hydrogenated with parahydrogen-enriched H_2 (pH_2). The reaction is performed continuously by flowing the acetylene/pH_2 mixture over a Pd/TiO_2 catalyst (Figure 1a). It was established earlier[18] that hydrogenation of alkynes and alkenes over such catalysts proceeds to some extent in a pairwise manner, that is, that both H atoms of pH_2 can end up in the same ethylene molecule and the correlation of their nuclear spins is preserved in the reaction, at least partially. Such a reaction should yield a nonstatistical mixture of NSIMs of ethylene. Indeed, similar to H_2, normal acetylene is a 3:1 mixture of ortho (with the total nuclear spin $I=1$) and para ($I=0$) NSIMs. Thus, the reaction of normal acetylene with parahydrogen ($I=0$) can only produce ethylene molecules with $I=0$ or 1, while ethylene molecules with $I=2$ will be missing in the reaction product. The four NSIMs of ethylene and their relative quantities produced in this reaction are discussed in more detail later.

To verify experimentally the enrichment of the NSIMs of ethylene produced in the reaction, we exploit the ability of NSIMs to provide dramatic signal enhancements in NMR spectra when the symmetry of the molecule is broken. This has been convincingly demonstrated by using parahydrogen

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[**] This work was partially supported by the grants from RFBR (no. 11-03-00248-a, 12-03-00403-a, 12-03-31386-mol-a), RAS (no. 5.1.1), SB RAS (no. 60, 61, 57, 122), the program of support of Leading Scientific Schools (no. NSh-2429.2012.3), the Council on Grants of the President of the Russian Federation (MK-4391.2013.3), and the program of the Russian Government to support leading scientists (no. 11.G34.31.0045). We thank Prof. V. I. Bukhtiyarov and his group (Boreskov Institute of Catalysis) for providing the heterogeneous catalysts used in this work as well as Prof. A. V. Zibarev and Dr. A. Yu. Makarov (Novosibirsk Institute of Organic Chemistry) for providing PTSC and 5CB nematic liquid crystal samples, and Prof. T. Oka (University of Chicago) for commenting on the manuscript.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201307389.

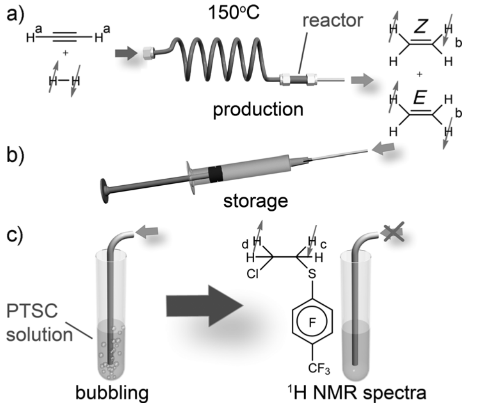

Figure 1. Experimental setup and sequence of events. a) The catalytic reactor for hydrogenation of acetylene with parahydrogen is made of copper tubing and consists of a spiral heat exchanger and a wider straight section packed with the Pd/TiO$_2$ solid catalyst. The reaction is performed by passing the acetylene/parahydrogen mixture heated to 150 °C through the catalyst layer. b) The product ethylene gas is collected and optionally stored for various time periods in a syringe. c) The ethylene gas produced in the reaction is bubbled through the PTSC solution in the NMR sample tube residing inside the NMR magnet at 7 T, thus leading to the formation of the ethylene/PTSC adduct and breaking the symmetry of ethylene.

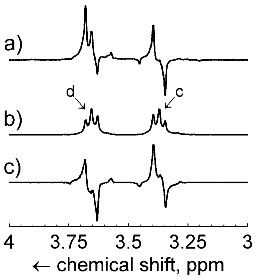

Figure 2. ^{1}H NMR spectra observed immediately after bubbling the produced ethylene through the PTSC solution (a,c) and 20 s after the bubbling was stopped (b). The spectrum in (c) was acquired using double-quantum filtering. The signal labels in (b) refer to the adduct structure in Figure 1.

in hydrogenation reactions in the context of parahydrogen-induced polarization (PHIP) studies.[3–5] For ethylene, we have chosen an efficient electrophilic addition reaction of arenesulfenyl chloride to an alkene.[19] This approach can provide hyperpolarization of nuclear spins leading to NMR signal enhancements of about 10^4 and more. Therefore, even the enrichments of approximately 0.1 % should be detectable, and the enrichments for the catalytic system used here are expected to be on the order of 1 %.[18] It is also essential that the use of NSIMs in NMR spectroscopy generates signals with the characteristic features (e.g., antiphase multiplets) which make them easily distinguishable from the conventional NMR signals of other gases, liquids, or solutes.[3–5]

In the experiment, the produced ethylene gas was bubbled through a CCl$_4$ solution of perfluoro(*para*-tolylsulfenyl) chloride (PTSC) in an NMR sample tube residing in the probe of an NMR instrument. This reaction yields an asymmetric PTSC/ethylene adduct (PTSCA; Figure 1 c). The ^{1}H NMR spectra detected immediately after the bubbling and 20 seconds later are shown in Figures 2 a and b, respectively. Their comparison clearly confirms the presence of the contributions with the characteristic antiphase character in the ^{1}H NMR signals of PTSCA in the spectrum (Figure 2 a), with emission and absorption components being present simultaneously. Control experiments performed with normal ethylene gave the usual thermal equilibrium NMR signals only, with no antiphase contributions. Therefore, the results indicate that before entering the reaction with PTSC, ethylene produced in the reaction of acetylene with pH$_2$ represented a nonstatistical mixture of its NSIMs.

The methodology presented above was further used to study the important issue of the interconversion of NSIMs as the ratio of different ethylene NSIMs returns to equilibrium. The produced ethylene gas was collected and stored for variable time intervals (Figure 1 b) before it was bubbled through the PTSC solution, and then monitored by ^{1}H NMR signal detection (see the Supporting Information for details). As the repetitive bubbling leads to a progressive accumulation of PTSCA, its thermal equilibrium signals rapidly become much stronger than the hyperpolarized signals of the freshly produced PTSCA, thus masking the antiphase contribution and making it difficult to quantify. Therefore, the double-quantum filtering (DQF) signal detection scheme[20,21] was employed, which suppresses the conventional equilibrium NMR signals and preserves only the antiphase signals in the spectrum (see Figure 2 c and the Supporting Information for details). This filtering made it possible to measure the equilibration curve for NSIMs of ethylene by monitoring the intensity of the antiphase signal of PTSCA as the function of the ethylene storage time, and is shown in Figure 3. It is important to stress that this curve does not reflect the relaxation of the polarized PTSCA signal, which is rapid once the asymmetric adduct is formed. Rather, the polarized signal

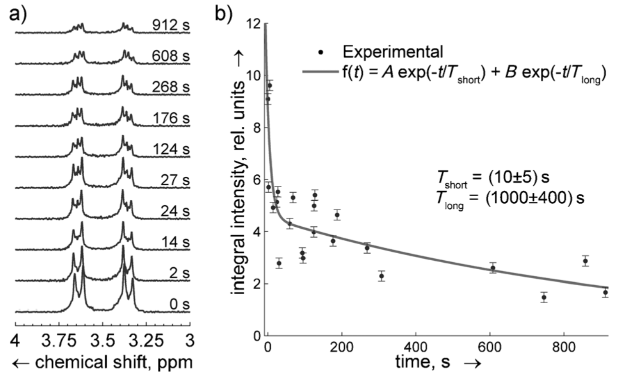

Figure 3. The dependence of the intensity of the polarized signals of the ethylene/PTSC adduct on the ethylene storage time. a) Selected absolute value DQF ^{1}H NMR spectra corresponding to various storage times. b) Kinetics of the equilibration of nuclear spin isomers in produced ethylene extracted from the set of spectra of the adduct, along with the double-exponential fitting curve. The $t=0$ point in this graph corresponds to the end of the syringe filling with ethylene. Note that the NMR signals in a) are polarized; the antiphase structure (see Figure 2) is apparently missing here because the spectra are presented in the absolute value (or magnitude) mode to simplify their integration.

of the adduct is measured repeatedly, using the same batch of ethylene for repetitive bubbling events and detecting the NMR signal right after the bubbling is stopped, and therefore reflects the interconversion of the NSIMs of ethylene as the function of ethylene storage time.

The equilibration curve of the produced mixture of NSIMs of ethylene is characterized by a rapid initial decay followed by a much slower decline. It was fitted with a biexponential function (solid line in Figure 3), yielding two time constants, $T_{\text{short}} = (10 \pm 5)$ s and $T_{\text{long}} = (1000 \pm 400)$ s. The relatively large uncertainties reflect the substantial scatter of the data points because all procedures were performed manually. This may have led to the variations in the ethylene yield in the hydrogenation reaction, bubbling conditions, dissolution of ethylene in the PTSC solution, etc., from one measurement to another. It is important to note, however, that complete equilibration of the NSIMs of ethylene results in the complete disappearance of the DQF signal of PTSCA, whereas a nonzero signal is clearly observed in the experiments with the storage time as long as 15 minutes. The measurement of the nuclear spin lattice relaxation time of ethylene under experimental conditions at 7 T yielded $T_1 = (270 \pm 20)$ ms. Therefore, as even the lower bounds of the estimated T_{long} and T_{short} times are much longer than T_1, we are clearly dealing with the long-lived nuclear spin states.[22]

Further analysis of the equilibration process requires a closer look at the properties of nuclear spin isomers of ethylene.[1,12,23–25] Ethylene in its ground electronic and vibrational state is known to have four nuclear spin isomers. They can be classified using the irreducible representations of the D_{2h}(M) symmetry group as A_g, B_{1u}, B_{2u}, and B_{3g} species with the nuclear multiplicities (degeneracies) of A_g:B_{1u}:B_{2u}:B_{3g} = 7:3:3:3. The A_g isomer includes the quintet ($I = 2$) and the two singlet ($I = 0$) spin states of the four hydrogen nuclei in ethylene, whereas the other three isomers all have $I = 1$. Upon heterogeneous hydrogenation of acetylene with pH_2, the two H atoms added to the two different carbon atoms can end up either on the same (*Z* ethylene) or on the opposite sides (*E* ethylene) with respect to the double bond of ethylene (Figure 1). The production of *Z* ethylene leads to the population of the two A_g singlet states and the B_{1u} and B_{3g} triplet states with the relative population ratio of A_g:B_{1u}:B_{2u}:B_{3g} = 2:3:0:3. In contrast, the formation of *E* ethylene yields A_g:B_{1u}:B_{2u}:B_{3g} = 2:3:3:0 (see the Supporting Information).

The equilibration process in the gas phase is the result of interconversion of the NSIMs induced by the mixing of states of different NSIMs, which are accidentally close in energy, by intramolecular interactions.[9,15,24,25] Several processes may contribute to the observed curve. The interconversion time within the u manifold ($B_{1u} \leftrightarrow B_{2u}$) of ethylene was measured as approximately 1800 s at the gas pressure of 1 torr.[12] Here, we always refer to the labeling of spin isomers as used in Ref. [25], which is different from that used in Refs. [12,24] simply because of a different labeling of molecular axes (see the Supporting Information). Calculations based on the direct dipolar interaction of nuclear spins[25] successfully reproduced this characteristic time, and also predicted that the time constant at atmospheric pressure should be approximately 10^3 s, which matches the value of T_{long} obtained here. No interconversion between the g and u manifolds could be observed experimentally at 1 torr.[12] Such transitions in ethylene imply a change in parity (symmetry of the full molecular wavefunction with respect to an inversion in space) and thus cannot be caused by intramolecular interactions.[1,12,24,25] Therefore, at present T_{long} can be tentatively assigned to the interconversion of B_{1u} and B_{2u} isomers.

To further demonstrate the key role of the high molecular symmetry of ethylene ($H_2C{=}CH_2$) in these studies, similar experiments were performed with [D_2]acetylene. Its hydrogenation with pH_2 produces [D_2]ethylene (DHC=CHD).The equilibration curve of this molecule (see Figure S4 in the Supporting Information) can be fitted using a single exponential term with the time constant of about (8 ± 3) s, which is comparable to T_{short} obtained for $H_2C{=}CH_2$. Moreover, the polarized signals for [D_2]ethylene can be observed in the gas or liquid phase directly, without the need to react it with PTSC (see Figure S3). This observation is the direct confirmation that addition of pH_2 to ethylene at least partially proceeds in a pairwise manner and preserves the nuclear spin correlation.[18] In contrast, for $H_2C{=}CH_2$ no PHIP effects were observed after the hydrogenation, as expected. This drastic difference between $H_2C{=}CH_2$ and DHC=CHD is a consequence of the differences in symmetry of the two molecules.

Finally, we demonstrate that ethylene produced from acetylene and pH_2 can itself exhibit hyperpolarized NMR signals if placed in anisotropic environment, for example, a nematic liquid crystalline solvent. The use of partially oriented media leads to an incomplete averaging of anisotropic interactions, with the dominating contribution of residual dipolar couplings,[21,26] and results in a complex splitting pattern in the ^{1}H NMR spectrum of a solute. In contrast to the ^{1}H NMR spectrum of ethylene in isotropic liquid or gas phase where a single peak is observed, normal ethylene dissolved in nematic 4-cyano-4′-pentylbiphenyl (5CB) gives the complex spectrum shown in Figure 4a along with its modeling (Figure 4b). When ethylene produced in the reaction of acetylene and pH_2 is bubbled through 5CB for 3 s followed by an immediate detection of the ^{1}H DQF NMR spectrum, an antiphase pattern is observed for some of the spectral lines (Figure 4c). The observed effects can be reproduced quite well by mathematical modeling, assuming an equimolar mixture of *Z* and *E* ethylene (Figure 4d). For symmetry reasons, the residual dipole–dipole interactions only mix the quintet and the two singlet states belonging to the same A_g isomer of ethylene but cannot mix nuclear spin states of different NSIMs. Therefore, polarization for ethylene in the liquid crystal can be observed only if the relative abundance of these particular states is nonstatistical, which is indeed the case upon formation of both *Z* and *E* ethylene. However, once the equilibration within the manifold of A_g states is achieved, no polarization can be expected even if the A_g:B_{1u}:B_{2u}:B_{3g} ratio of the NSIMs is not at equilibrium. Therefore, this experiment provides unique access to the nuclear spin order associated with the imbalance of spin states belonging to the same nuclear spin isomer in a highly symmetric molecule. Importantly, the polarization in this experiment was observed only if the produced and collected

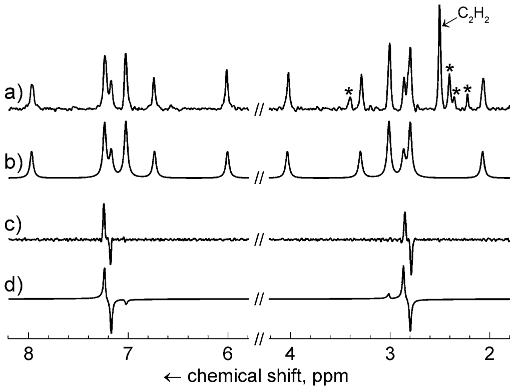

Figure 4. ^{1}H NMR spectra of ethylene dissolved in the nematic 5CB liquid crystal phase and their simulations. a) Thermal equilibrium spectrum at 28 °C and b) its simulation using the residual dipolar couplings $D_{cis} = -393.7$, $D_{trans} = -123.3$, $D_{gem} = 73.0$ Hz (anisotropic part of the J tensor was assumed to be zero). c) DQF spectrum measured immediately after bubbling the produced ethylene (an average of three similar spectra is shown) and d) simulation for ethylene molecule with two correlated protons in a nematic liquid crystalline phase assuming a 1:1 mixture of *Z* and *E* ethylene. * = impurities. The signal labeled C_2H_2 belongs to unreacted acetylene.

ethylene was immediately dissolved in 5CB, while no polarization was seen if ethylene was even briefly stored. These results show that equilibration within the A_g isomer is very rapid, and in particular is much faster than T_{short}, as can be expected from the quantum relaxation theory of nuclear spin conversion.[9]

Thus, the approach demonstrated here allowed us to 1) achieve an enrichment of nuclear spin isomers of a neutral molecule (ethylene) by chemical synthesis from enriched samples of isomers of another molecule (H_2), with enriched ethylene produced in large quantities and in a continuous mode; 2) demonstrate the possibility to use the enriched nuclear spin isomers of a molecule other than H_2 for NMR signal enhancement; 3) reveal the nuclear spin order which is normally not observable in a highly symmetric molecule by placing it in a non-isotropic environment rather than by breaking its symmetry in a chemical reaction; 4) experimentally address the interconversion of the NSIMs of a molecule other than H_2 at ambient pressure. To the best of our knowledge, none of this has been reported previously. Work is currently in progress to further improve the methodology and in particular to increase the levels of enrichment that can be achieved.

Received: August 22, 2013

Keywords: hydrogenation · long-lived spin states · NMR spectroscopy · nuclear spin hyperpolarization · nuclear spin isomers

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[1] L. D. Landau, E. M. Lifschitz, *Quantum Mechanics: Non-Relativistic Theory*, 3rd ed., Pergamon, Oxford, **1977**.

[2] a) L. Pagani, P. Lesaffre, E. Roueff, M. Jorfi, P. Honvault, T. Gonzalez-Lezana, A. Faure, *Philos. Trans. R. Soc. London Ser. A* **2012**, *370*, 5200 – 5212; b) B. P. Bonev, M. J. Mumma, G. L. Villanueva, M. A. Disanti, R. S. Ellis, K. Magee-Sauer, N. D. Russo, *Astrophys. J.* **2007**, *661*, L97; H. Kawakita, N. D. Russo, R. Furusho, T. Fuse, J.-I. Watanabe, D. C. Boice, K. Sadakane, N. Arimoto, M. Ohkubo, T. Ohnish, *Astrophys. J.* **2006**, *643*, 1337.

[3] a) C. R. Bowers, D. P. Weitekamp, *J. Am. Chem. Soc.* **1987**, *109*, 5541 – 5542; b) J. Natterer, J. Bargon, *Prog. Nucl. Magn. Reson. Spectrosc.* **1997**, *31*, 293 – 315; c) D. Canet, C. Aroulanda, P. Mutzenhardt, S. Aime, R. Gobetto, F. Reineri, *Concepts Magn. Reson. Part A* **2006**, *28*, 321 – 330; R. A. Green, R. W. Adams, S. B. Duckett, R. E. Mewis, D. C. Williamson, G. G. R. Green, *Prog. Nucl. Magn. Reson. Spectrosc.* **2012**, *67*, 1 – 48.

[4] a) I. V. Koptyug, K. V. Kovtunov, S. R. Burt, M. S. Anwar, C. Hilty, S. Han, A. Pines, R. Z. Sagdeev, *J. Am. Chem. Soc.* **2007**, *129*, 5580 – 5586; b) K. V. Kovtunov, V. V. Zhivonitko, I. V. Skovpin, D. A. Barskiy, I. V. Koptyug, *Top. Curr. Chem.* **2012**, *338*, 123 – 180.

[5] A. A. Lysova, I. V. Koptyug, *Chem. Soc. Rev.* **2010**, *39*, 4585 – 4601.

[6] a) V. V. Zhivonitko, V.-V. Telkki, I. V. Koptyug, *Angew. Chem.* **2012**, *124*, 8178 – 8182; *Angew. Chem. Int. Ed.* **2012**, *51*, 8054 – 8058; b) S. Månsson, E. Johansson, P. Magnusson, C.-M. Chai, G. Hansson, J. S. Petersson, F. Stahlberg, K. Golman, *Eur. Radiol.* **2006**, *16*, 57 – 67; c) P. Bhattacharya, E. Y. Chekmenev, W. F. Reynolds, S. Wagner, N. Zacharias, H. R. Chan, R. Bunger, B. D. Ross, *NMR Biomed.* **2011**, *24*, 1023 – 1028; d) N. M. Zacharias, H. R. Chan, N. Sailasuta, B. D. Ross, P. Bhattacharya, *J. Am. Chem. Soc.* **2012**, *134*, 934 – 943.

[7] a) S. Glöggler, M. Emondts, J. Colell, R. Muller, B. Blumich, S. Appelt, *Analyst* **2011**, *136*, 1566 – 1568; b) T. Theis, P. Ganssle, G. Kervern, S. Knappe, J. Kitching, M. P. Ledbetter, D. Budker, A. Pines, *Nat. Phys.* **2011**, *7*, 571 – 575; c) B. C. Hamans, A. Andreychenko, A. Heerschap, S. S. Wijmenga, M. Tessari, *J. Magn. Reson.* **2011**, *212*, 224 – 228.

[8] A. Farkas, *Principles of Nuclear Magnetic Resonance Microscopy*, Cambridge University Press, Cambridge, **1935**.

[9] P. L. Chapovsky, L. J. F. Hermans, *Annu. Rev. Phys. Chem.* **1999**, *50*, 315 – 345.

[10] P. L. Chapovsky, L. N. Krasnoperov, V. N. Panfilov, V. P. Strunin, *Chem. Phys.* **1985**, *97*, 449 – 455.

[11] a) B. Nagels, L. J. F. Hermans, P. L. Chapovsky, *Phys. Rev. Lett.* **1997**, *79*, 3097 – 3100; b) P. Cacciani, J. Cosleou, F. Herlemont, M. Khelkhal, J. Lecointre, *Phys. Rev. A* **2004**, *69*, 032704; c) B. Schramm, T. Worner, *Ber. Bunsen-Ges.* **1996**, *100*, 1684 – 1690.

[12] Z.-D. Sun, K. Takagi, F. Matsushima, *Science* **2005**, *310*, 1938 – 1941.

[13] P. L. Chapovsky, J. Cosleou, F. Herlemont, M. Khelkhal, J. Legrand, *Chem. Phys. Lett.* **2000**, *322*, 424 – 428.

[14] T. Kravchuk, M. Reznikov, P. Tichonov, N. Avidor, Y. Meir, A. Bekkerman, G. Alexandrowicz, *Science* **2011**, *331*, 319 – 321.

[15] R. F. Curl, J. V. V. Kasper, K. S. Pitzer, *J. Chem. Phys.* **1967**, *46*, 3220 – 3228.

[16] a) M. Tudorie, P. Cacciani, J. Cosleou, F. Herlemont, M. Khelkhal, C. Puzzarini, S. Maret, C. Kahane, *Astron. Astrophys.* **2006**, *453*, 755 – 759; b) H.-H. Limbach, G. Buntkowsky, J. Matthes, S. Grundemann, T. Pery, B. Walaszek, B. Chaudret, *ChemPhysChem* **2006**, *7*, 551 – 554; c) M. Tudorie, M. Khelkhal, J. Cosleou, P. Cacciani, *Surf. Sci.* **2007**, *601*, 1630 – 1634.

[17] a) D. Uy, M. Cordonnier, T. Oka, *Phys. Rev. Lett.* **1997**, *78*, 3844; b) M. Cordonnier, D. Uy, R. M. Dickson, K. E. Kerr, Y. Zhang, T. Oka, *J. Chem. Phys.* **2000**, *113*, 3181; c) M. Quack, *Philos. Trans. R. Soc. London Ser. A* **1990**, *332*, 203 – 220.

[18] K. V. Kovtunov, I. E. Beck, V. V. Zhivonitko, D. A. Barskiy, V. I. Bukhtiyarov, I. V. Koptyug, *Phys. Chem. Chem. Phys.* **2012**, *14*, 11008 – 11014.

[19] G. H. Schmid, C. L. Dean, D. G. Garratt, *Can. J. Chem.* **1976**, *54*, 1253.

[20] J. A. Aguilar, R. W. Adams, S. B. Duckett, G. G. R. Green, R. Kandiah, *J. Magn. Reson.* **2011**, *208*, 49 – 57.

[21] M. H. Levitt, *Spin Dynamics: Basics of Nuclear Magnetic Resonance*, 2nd ed., Wiley, Chichester, **2008**.

[22] a) M. Carravetta, O. G. Johannessen, M. H. Levitt, *Phys. Rev. Lett.* **2004**, *92*, 153003; b) W. S. Warren, E. Jenista, R. T. Branca, X. Chen, *Science* **2009**, *323*, 1711 – 1714; c) G. Pileio, S. Bowen, C. Laustsen, M. C. D. Tayler, J. T. Hill-Cousins, L. J. Brown, R. C. D. Brown, J. H. Ardenkjaer-Larsen, M. H. Levitt, *J. Am. Chem. Soc.* **2013**, *135*, 5084 – 5088.

[23] P. R. Bunker, P. Jensen, *Molecular Symmetry and Spectroscopy*, 2nd ed., NRC Research Press, Ottawa, **2006**.

[24] J. T. Hougen, T. Oka, *Science* **2005**, *310*, 1913 – 1914.

[25] P. L. Chapovsky, V. V. Zhivonitko, I. V. Koptyug, *J. Phys. Chem. A* **2013**, *117*, 9673 – 9683.

[26] a) J. Kaski, P. Lantto, J. Vaara, J. Jokisaari, *J. Am. Chem. Soc.* **1998**, *120*, 3993 – 4005; b) J. Vaara, J. Jokisaari, R. E. Wasylishen, D. L. Bryce, *Prog. Nucl. Magn. Reson. Spectrosc.* **2002**, *41*, 233 – 304; c) J. W. Emsley. *Liquid Crystals: General Considerations*, eMagRes, **2007**.