Lawrence Berkeley National Laboratory

Recent Work

Title

NEW APPROACH TO HIGH RESOLUTION PROTON NMR IN SOLIDS: DEUTERIUM SPIN-DECOUPLING BY MULTIPLE-QUANTUM TRANSITIONS

Permalink

<https://escholarship.org/uc/item/9kq6c41s>

Author

Pines, A.

Publication Date

1975-10-01

0 0 3 0 4 4 3 7 0 2 8

Submitted to Physical Review Letters

RECEIVED
LAWRENCE
BERKELEY LABORATORY

LBL-4525
Preprint c1

DEC 3 1975

LIBRARY AND
DOCUMENTS SECTION

NEW APPROACH TO HIGH RESOLUTION PROTON NMR
IN SOLIDS: DEUTERIUM SPIN-DECOUPLING
BY MULTIPLE-QUANTUM TRANSITIONS

A. Pines, D. J. Ruben, S. Vega, and M. Mehring

October 1975

Prepared for the U.S. Energy Research and
Development Administration under Contract W-7405-ENG-48 •

For Reference

Not to be taken from this room

LBL-4525
c1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

New Approach to High Resolution Proton NMR in Solids:
Deuterium Spin-Decoupling by Multiple-Quantum Transitions

A. Pines[†], D. J. Ruben and S. Vega

Department of Chemistry, University of California
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
Berkeley, California 94720

and

M. Mehring

Institute for Physics, University of Dortmund
Dortmund, West Germany

Abstract

Deuterium spin-decoupled by double-quantum transitions in the manner of Meiboom and co-workers, is applied for the first time to solids, opening the way for a new approach to high resolution proton nmr. Using this approach, the first resolved proton nmr spectrum of polycrystalline ice is presented and the chemical shielding tensor elements are determined. A simple treatment of the double-quantum process shows why decoupling is possible even though the deuterium spectral width is ~ 200 kHz due to quadrupolar broadening.

[†] Alfred P. Sloan Fellow.

New Approach to High Resolution Proton NMR in Solids:
Deuterium Spin-Decoupling by Multiple-Quantum Transitions

It is well known that nuclear magnetic resonance lines in diamagnetic solids are dominated by magnetic dipole-dipole interactions between the nuclear spins. Hidden in these broad lines is a wealth of information derived from much smaller interactions of interest to physicists and chemists, in particular chemical shifts. Two primary approaches have been adopted recently for the effective elimination of the dipolar couplings and the extraction of the smaller interactions. The first is applicable to abundant isotopes such as ^1H and ^{19}F , and involves selective modulation of the spin interactions by multiple-pulse sequences.¹ The second approach, applicable to dilute isotopes (e.g. ^{13}C , ^{15}N , or artificially or chemically dilute) involves spin-decoupling by strong resonant radio-frequency irradiation of an abundant isotope while observing the resonance of the isotope of interest.²

There are several reasons why the second approach is more attractive than the former. Firstly, it is considerably simpler technically, since the stability requirements for modulating first rank tensor interactions are more modest than those for their second rank counterparts. Secondly, there is a possibility for isotopic labelling, thus extending the technique to larger molecules. This is particularly clear for the case of the important abundant nucleus ^1H , which poses a serious challenge for multiple-pulse techniques due to its small chemical shifts and strong dipolar interactions. Indeed,

only a relatively small number of systems has been studied, confined mostly to small molecules.³ As a striking example of the difficulties, one of the simplest and most 'desirable' of proton containing solids, ice, has eluded such studies, due to its strong dipolar interactions and extremely short T_2 .⁴

An appealing idea would be to immerse the protons in a bath of deuterium nuclei thus rendering them isotopically dilute. The solid state ^1H high resolution spectrum could then be created by deuterium spin-decoupling. This has been used to observe ^1H dipolar spectra in selectively deuterated molecules dissolved in liquid crystals by Melboom and co-workers.⁵ Why then, has this not been attempted to date in solids? In order to appreciate the difficulty, let us examine the situation depicted schematically in figure 1. The ^1H linewidth is dominated by dipolar coupling to the deuterium. Imagine that we apply at the deuterium frequency a rotating field of intensity ω_1 (in angular frequency units). The criterion for spin-decoupling is that the rate of transitions between the deuterium magnetic sublevels induced by ω_1 must be comparable to the dipolar coupling.⁶ If the quadrupolar splitting were absent, this rate would be proportional to ω_1^2 , so this means:

$$\omega_1^2 \sim D^2, \quad (1)$$

an easily attainable experimental situation. However, with the quadrupolar splitting $Q/2\pi \sim 200 \text{ kHz} \gg D/2\pi$, the criterion for decoupling is that we need to 'cover' the spectral width of the

-3-

deuterium:

$$\omega_1^2 \sim Q^2 \quad (2)$$

i.e., a rotating field $H_1 \sim 300$ Gauss, which is quite simply prohibitive for continuous irradiation.

Nevertheless, as figure 2 demonstrates, the experiment is indeed possible, in clear violation of this logic. Shown is the Fourier transform spectrum of residual protons in a sample of $\sim 99\%$ deuterated water frozen to -90°C , with and without resonant irradiation at the deuterium frequency. The spectra were obtained on a homebuilt double-resonance spectrometer operating at 185 MHz for protons. This is, to our knowledge, the first proton nmr spectrum in a solid obtained with deuterium spin-decoupling and the first high resolution proton nmr spectrum of ice. The deuterium decoupling reveals a proton powder spectrum derived from a chemical shielding tensor with axial symmetry. The principal elements of the tensor relative to external tetramethylsilane (TMS) are:

$$\sigma_{\parallel} = 15 \pm 2 \text{ ppm}$$

$$\sigma_{\perp} = -19 \pm 2 \text{ ppm}$$

There is an isotropic shift of 2 ± 1 ppm from liquid water. We have also studied other materials in this manner, but have preferred to present here the results for ice--we believe it to be a particularly good prototype for these experiments, since:

- a) the proton dipolar couplings are large making the application of multiple-pulse techniques exceedingly difficult,
- b) the deuterium quadrupolar interaction is large (in excess of 200 kHz) making it an excellent test case for the spin-decoupling,
- c) the proton dynamics are of interest and controversy⁷ and can be studied by observing the high resolution lineshapes. Such a temperature-dependent study has indeed been carried out by us and will be described in detail in a separate paper.

We need now to understand why the experiment works. Figure 3 provides the basis for the discussion. The arguments given at the beginning for the transition probabilities and decoupling were based, of course, on the allowed deuterium transitions, $m = +1 \rightarrow 0$ and $m = 0 \rightarrow -1$, labeled ω_A and ω_B . As recognized by Meiboom and co-workers,⁵ decoupling might also be effected by the 'forbidden' transition $m = +1 \rightarrow -1$, which could occur by a double-quantum process at the unshifted frequency ω_0 . We can provide an extremely simple but illustrative argument to assess this effect. Consider again the applied field ω_1 at the central frequency ω_0 , with $Q \gg D$. The probability W for the double-quantum transition is easily calculated by second order perturbation theory:

$$W \sim \frac{\omega_1^4 |\langle 1 | I_x | 0 \rangle|^4}{(\omega_0 - \omega_A)^2} \sim \frac{\omega_1^4}{Q^2} \quad (3)$$

Employing again our spin-decoupling condition $W \sim D^2$ as before, this means we need:

$$\omega_1^2 \sim QD \quad . \quad (4)$$

This is considerably less than required by (2), is attainable in practice, and is indeed precisely what we observe experimentally. This, then, explains why the experiment is possible even with

$$Q \gg \omega_1 \gg D \quad .$$

Although the double-quantum process is inherently less probable than the allowed single-quantum processes (if both are induced on resonance), it is resonant for all the deuterium spins, whereas the allowed ones are not. Full details on our rigorous theory will be presented elsewhere.

To summarize, some final comments, which will be enlarged upon in a full paper:

1. The technique, with its technical simplicity (deuterium decoupling powers of only several hundred watts), opens the way for an alternative approach to high resolution proton nmr in solids. Samples can be selected from a wide and available range of pre-deuterated materials with observation of the residual protons. Where too many lines might render the spectrum intractable, isotopic labeling can be used to selectively emphasize particular nuclear sites.

2. The experiment can be combined with multiple-pulse techniques using partially deuterated materials. This reduces the requirement of short pulse cycle time and enhances the proton signal/noise. It also forms a useful way to solve the broadening induced by isotopic labeling as in 1 above. We have used this to observe fine splittings in crystal samples.

3. The arguments and experiments presented in this paper hold not only for deuterium-proton systems. The same reasoning exactly can be invoked for the spin-decoupling of two strongly dipolar coupled like spin - $\frac{1}{2}$ nuclei from a third unlike nuclear spin. Consider for example the case of two protons (I) coupled to a ^{13}C spin (S) as in high resolution ^{13}C spectroscopy. Here, double quantum transitions occur between the energetically lowest and highest proton triplet states: $|\alpha\alpha\rangle \leftrightarrow |\beta\beta\rangle$. This explains why proton-decoupling of ^{13}C is considerably simpler than might be guessed from the width of the proton lines, i.e., even when

$$\gamma ||H_{II}|| \gg \omega_1 \gg \gamma ||H_{IS}||$$

In methylene groups ($^{13}\text{CH}_2$) of liquid crystals, this fact was originally quite surprising⁸ since it might be expected that we require $\omega_1 \sim \gamma ||H_{II}||$.⁶

4. The treatment and experiments can be generalized to higher order multiple-quantum transitions. For example, for n equivalent coupled protons, or spin $\frac{n}{2}$ with axial symmetry, to be decoupled from an unlike spin, we need multiple-quantum transition of order $n, n-2, n-4 \dots$ etc.

Acknowledgments

We are grateful for support from the National Science Foundation, NATO, U. S. Energy Research and Development Administration, The Deutsche Forschungsgemeinschaft and the Herbert Quandt Stiftung. D. J. Ruben is an NSF Postdoctoral Fellow, and S. Vega holds a PRF Postdoctoral Fellowship administered by the American Chemical Society. We wish to thank D. Wemmer for help with the experiments. Finally, we thank E. L. Hahn, J. Jortner and R. A. Harris for helpful discussions on multiple-quantum processes, and R. Blinc for a helpful discussion on ice dynamics.

References

1. U. Haeberlen and J. S. Waugh, Phys. Rev., 175, 453 (1968).
2. A. Pines, M. G. Gibby and J. S. Waugh, J. Chem. Phys., 59, 569 (1973).
3. U. Haeberlen, in Advances in Magnetic Resonance, in press.
M. Mehring, in NMR: Basic Principles and Progress, in press.
4. D. E. Barnaal and I. J. Lowe, J. Chem. Phys., 46, 4800 (1967).
5. R. C. Hewitt, S. Meiboom and L. C. Snyder, J. Chem. Phys. 58, 5089 (1973); L. C. Snyder and S. Meiboom, J. Chem. Phys., 58, 5096 (1973).
6. A. Abragam, The Principles of Nuclear Magnetism, Oxford, (1961), Chapter XII; F. Bloch, Phys. Rev., 105, 1206 (1957).
7. L. Onsager and L. K. Runnels, J. Chem. Phys., 50, 1089 (1969);
H. Gränicher, in Physics of Ice, Plenum, N. Y., (1969).
8. A. Pines, D. J. Ruben and S. Allison, Phys. Rev. Lett., 33, 1002 (1974).

Figure Captions

1. Schematic representation of dipolar interacting proton and deuterium spins and nmr spectra. The dipolar coupling is D and the deuterium is characterized by quadrupolar splitting Q from an axially symmetric electric field gradient tensor. The problem with spin-decoupling deuterium comes from the large spread of frequencies (~ 200 kHz).
2. Fourier transform nmr spectrum of residual protons in 99% deuterated ice.
3. Energy level diagram for discussion of deuterium spin transitions. A double-quantum transition $1 \rightarrow -1$ occurs at the unshifted central frequency ω_0 .

Figure 1

XBL 758-6992 A

Figure 2

XBL 7511-7627

Figure 3

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720