LBL-13332 Rev.
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

FEB 22 1982

LIBRARY AND
DOCUMENTS SECTION

Submitted to the Journal of Chemical Physics

HIGH RESOLUTION PROTON NMR OF DILUTE SPINS IN SOLIDS

Richard Eckman

September 1981

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

LBL-13332 Rev. c.2

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.

LBL 13332 Revised

HIGH RESOLUTION PROTON NMR OF DILUTE SPINS IN SOLIDS

Richard Eckman

Department of Chemistry, University of California, Lawrence Berkeley Laboratory, Berkeley, California 94720

This work was supported by the Assistant Secretary of Fossil Energy, Office of Coal Research, Liquefaction Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48 through the Pittsburgh Energy Center, Pittsburgh, Pa.

Recent advances in NMR multiple pulse line narrowing have provided measurement of proton chemical shift tensors in solids[1]. Similarly, the approach of Pines, Vega, and Mehring to obtain proton chemical shift powder patterns by isotopic dilution of protons in a deuterated solid with deuterium double quantum decoupling has been successful[2]. However, the overlapping of powder patterns of chemically or crystallographically distinct sites is a serious limitation. Combination of multiple pulse methods with magic angle sample rotation has demonstrated a solution by observation of only the isotropic chemical shift[3]. Unfortunately, the relatively small size of proton isotropic shifts has limited the resolution obtainable since the residual proton homonuclear dipole linewidth is substantial. Recent work has shown significant improvement in this situation by use of high magnetic fields to increase the absolute magnitude of the chemical shift[4]. An alternative approach has been to obtain isotropic chemical shift spectra of deuterium in solids. Quadrupole and dipole broadening are removed by precise magic angle spinning combined with rotation synchronized data acquisition and narrow single and double quantum resonances have been observed[5]. However, a high magnetic field is useful for reduction of higher order quadrupole effects.

In this communication, high resolution proton NMR in solids is demonstrated by isotopic dilution of protons in a deuterated solid combined with magic angle spinning. Isotropic chemical shift spectra are obtained with greater resolution than all other methods to date. The technical difficulties of multiple r.f. pulse sequences and synchronous data acquisition are removed and heteronuclear r.f. decoupling is not required. This is accomplished by removal of the proton homonuclear dipole coupling, H^d_{SS}, and heteronuclear dipole coupling, H^d_{IS}. Dilution

of the proton spins (S) reduces H^d_{SS} to a very small value. Then in the absence of the homonuclear dipole coupling, H^d_{II}, of the abundant spins (I), H^d_{IS} is inhomogeneous and can be spun away at the magic angle. A striking demonstration of this fact is the retrieval of ^1H - ^{13}C J couplings in ^{13}C-MAS spectra by off resonance proton decoupling[6]. For deuterium, the small gyromagnetic ratio and large quadrupole couplings cause H^d_{II} to be inhomogeneous, i.e. the ^2H-^2H dipole flip-flop terms are quenched[7]. Thus $[H^d_{II}, H^d_{IS}] = 0$ at almost all times and magic angle spinning alone suffices to remove the effects of both even when the spinner frequency $\omega_r < \omega^d_{II}, \omega^d_{IS}$.[8]

Experiments were performed on a homebuilt spectrometer with superconducting solenoid operating at $\omega_L/2\pi(^1H) = 361$MHz. Samples were rotated with a cylindrical gas bearing spinner for which the basic design was described previously[5a]. For observation of dilute protons, a single $\pi/2$ pulse was applied followed by normal data acquisition. Spectra were taken at room temperature.

In Figure 1 is shown the isotropic proton spectrum of 98.8% deuterated p-di-tert-butylbenzene powder rotated about the magic axis at 3677±4Hz. The ^1H concentration in this sample was 1.2% of the total number of deuterons and protons. The intense line is assigned to the methyl groups with FWHM = 0.53 ppm. The smaller resonance 6.63 ppm downfield is due to the ring protons with FWHM = 0.45 ppm. The -1 spinning sideband of the methyl line also appears at 10.2 ppm. Total accumulation time was 3.7 minutes.

In Figure 2 is shown the proton chemical shift spectrum of 98.7% deuterated diethyl terephthalate powder with ν_r = 3509±5 Hz. The ^1H concentration was 1.3% of the total number of deuterons and protons. Resonances are assigned from up to downfield to the methyl, methylene,

and aromatic protons with FHWM 0.61, 0.57, and 0.98 ppm respectively. The -1 spinning sidebands of each are also shown further downfield. Sample weight was 0.1 g and total accumulation time 3 minutes. The apparent splitting of 0.40 ppm in the aromatic peak is attributed to overlapping resonances of the 2,5 and 3,6 ring positions which are crystallographically inequivalent.

These results indicate that high resolution proton NMR of dilute spins in solids is feasible with greater resolution than other methods. An important feature is that currently obtainable spinner frequencies can "cover" the isotropic chemical shift range even at high field, thus spinning sidebands do not pose a large problem. Use of deuterium double quantum decoupling broadens the resonances since it is not completely efficient due to 1) small deuterium resonance offsets and 2) similar orders of magnitude of the decoupling frequency, $1/t_c$(dq-decouple) = $\omega_1^2/2\pi\omega_Q$, and the spinner frequency, ω_r. Correlation of the proton spectrum with the isotropic deuterium spectrum enhances the utility of both to study the solid state. A detailed study of high resolution proton NMR in dilute and semi-dilute solid materials is in progress.

The author is grateful to Professor Alex Pines for making this work possible. This work was supported by the Assistant Secretary of Fossil Energy, Office of Coal Research, Liquefaction Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48 through the Pittsburgh Energy Center, Pittsburgh, Pa.

References:

1. a) U. Haeberlen, High Resolution NMR in Solids, Selective Averaging, Supplement I in Advances in Magnetic Resonance, ed. J.S. Waugh (Academic Press, New York, 1976).

b) M. Mehring, High Resolution NMR Spectroscopy in Solids, in NMR-Basic Principles and Progress, eds. P. Diehl, E. Fluck and R. Kosfeld (Springer-Verlag, New York, 1976).

c) D.P. Burum and W.K. Rhim, J. Chem. Phys. 71, 944 (1979) and references therein.

2. A. Pines, S. Vega, and M. Mehring, Phys. Rev. B 18, 112 (1978).

3. a) U. Haeberlen and J.S. Waugh, Phys. Rev. 175, 453 (1968).

b) L.M. Ryan, R.E. Taylor, A.J. Paff, and B.C. Gerstein, J. Chem. Phys. 72, 508 (1980).

4. G. Scheler, U. Haubenreisser, and H. Rosenberger, J. Mag. Res. 44, 134 (1981).

5. a) R. Eckman, M. Alla, and A. Pines, J. Mag. Res. 41, 440 (1980).

b) R. Eckman, L. Müller, and A. Pines, Chem. Phys. Lett. 74, 376 (1980).

6. T. Terao, H. Mivra, and A. Saika, J. Chem. Phys. 75, 1573 (1981).

7. M. Alla, R. Eckman, and A. Pines, Chem. Phys. Lett. 71, 148 (1980).

8. M. Matti Maricq and J.S. Waugh, J. Chem. Phys. 70, 3300 (1979).

Captions:

Figure 1:

Isotropic chemical shift spectrum of 1.2% protons in 98.8% deuterated p-di-tert-butylbenzene solid powder. Fourier transform of fid obtained by magic angle spinning at ν_r = 3.7 kHz with a single proton $\pi/2$ pulse followed by normal data acquisition and without r.f. decoupling. Peak at 0 ppm is assigned to methyl groups and resonance at 6.6 ppm is due to ring protons. The -1 spinning sideband of methyl resonance appears at 10.2 ppm. Accumulation time 3.7 minutes.

Figure 2:

Isotropic chemical shift spectrum of 1.3% protons in 98.7% deuterated diethyl terephthalate solid powder. Resonances are assigned to methyl (0 ppm), methylene (2.4 ppm), and ring protons (5.5 ppm). The -1 spinning sidebands of each are also shown further downfield. Aromatic peak is broadened due to overlapping resonances of 2,5 and 3,6 ring positions with 0.40 ppm splitting due to their inequivalence in the solid state.

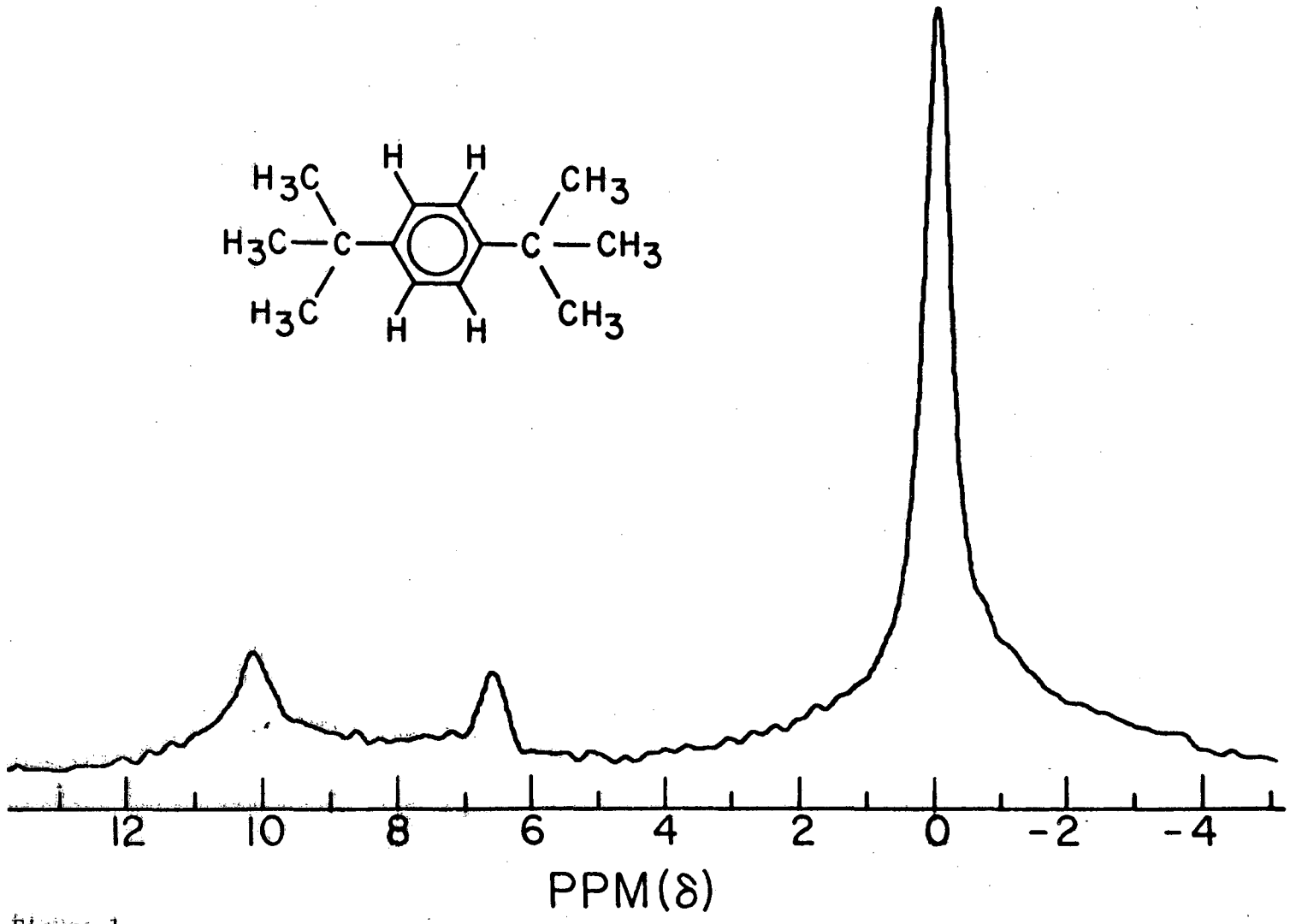

Figure 1

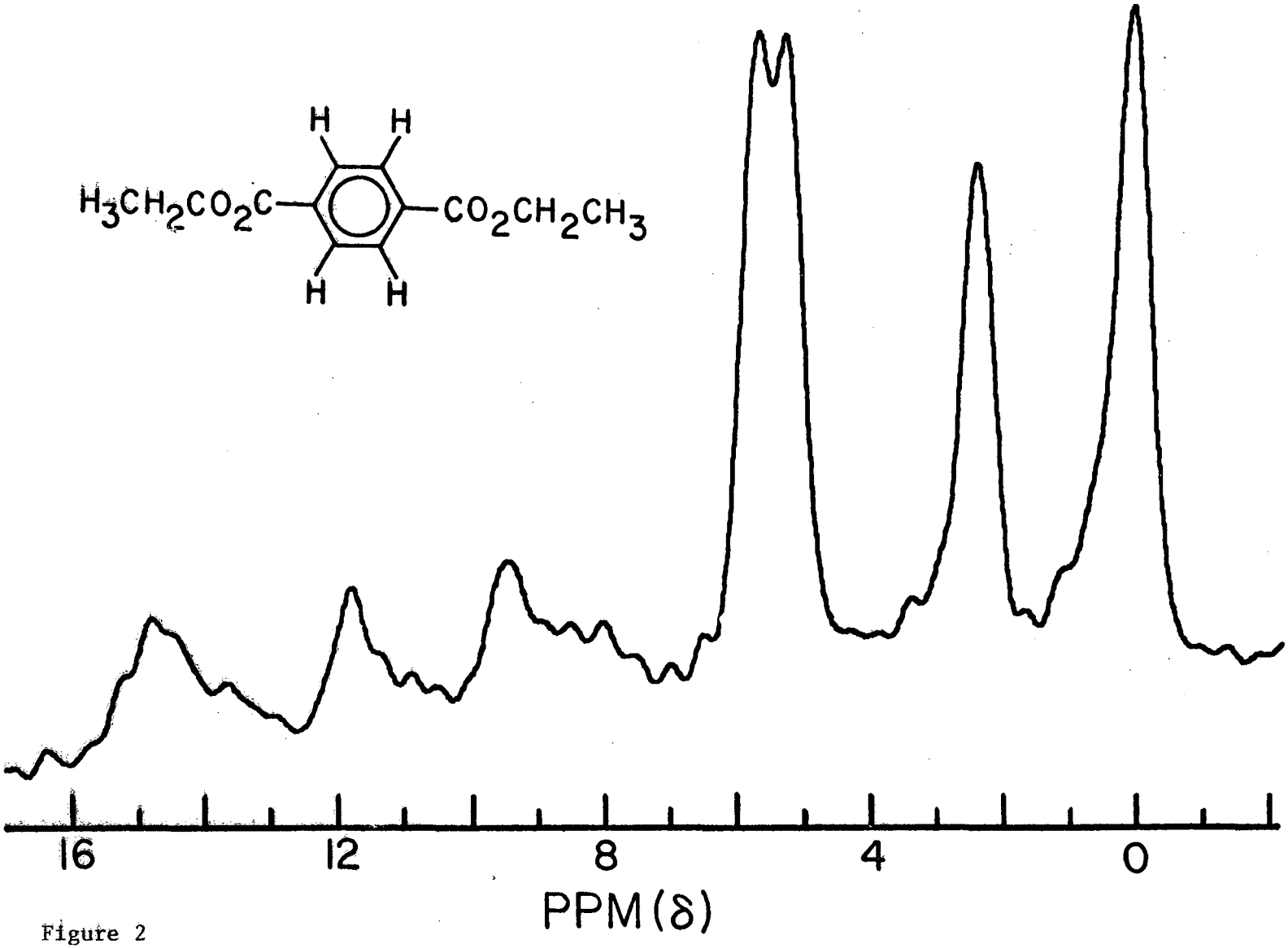

Figure 2

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

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