JOURNAL OF MAGNETIC RESONANCE **52**, 35–41 (1983)

Proton Chemical Shifts in Polycrystalline Solids Determined by Off-Resonance Decoupling ^{13}C CP–MAS NMR

AD BAX, THOMAS A. EARLY,* AND GARY E. MACIEL†

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received July 26, 1982; revised October 26, 1982

A ^{13}C CP–MAS method is described which uses off-resonance decoupling in order to correlate directly bonded ^{13}C–^{1}H pairs in the solid state. An analysis of the experimental results gives ^{1}H chemical shifts by inspection while at the same time separating various ^{1}H resonances via the paired ^{13}C resonance. An example is shown using *p*-diethoxybenzene.

INTRODUCTION

In liquid-state NMR a commonly used method for determining which proton and carbon-13 resonances correspond to directly bonded ^{13}C–^{1}H pairs is the double-resonance experiments (*1*, *2*). One can selectively irradiate the proton resonance at the position of the various proton multiplets with a rather weak, coherent rf field and observe which ^{13}C multiplet coalesces. Another method is to irradiate the proton resonance with a strong, coherent rf field that is off resonance; the reduction of the ^{13}C multiplet splitting is then related to the difference in frequency between the proton transmitter and the proton resonance and to the strength of the proton rf field (*2*). More sophisticated liquid-state methods utilize two-dimensional Fourier transformation to correlate proton and carbon-13 chemical shifts (*3–6*). Several workers have attempted to apply two-dimensional heteronuclear shift correlation spectroscopy in correlating proton and carbon-13 chemical shifts in polycrystalline solids, but experimental problems appear to be severe. Recently, Caravatti, Bodenhausen, and Ernst (*7*) have succeeded in recording a heteronuclear chemical shift correlation spectrum of a nonspinning, single crystal in two cases. In this paper we demonstrate that methods relying on the same idea as the liquid-state coherent off-resonance decoupling can be used straightforwardly in solid-state NMR, and that they allow an accurate determination of the proton chemical shifts. Technically, these experiments are much simpler to perform than the heteronuclear two-dimensional shift correlation

---

* Present address: Nicolet Magnetics Corp., 255 Fourier Ave., Fremont, CA 94539.

† Author to whom correspondence should be addressed.

0022-2364/83 $3.00

experiment (*7*), although, if the state-of-the-art instrumentation of solid-state NMR is improved significantly the two-dimensional experiment would be superior.

THEORY

Off-Resonance Decoupling

Details about the theory of off-resonance decoupling in solids have been discussed by Mehring (*8*) and in a more pictorial way by VanderHart *et al.* (*9*). Coherent irradiation of the proton resonances as commonly used for proton decoupling of ^{13}C spectra in solids appears to be rather different from coherent decoupling in liquid-state NMR spectroscopy, mainly because of the rapid proton spin diffusion in solids. This spin diffusion can be viewed as a kind of noise modulation of the coherent decoupling, making the decoupling process very effective over a wide range of proton chemical shifts. In addition, VanderHart *et al.* point out that the magic-angle spinning can also improve the decoupling process in the case where proton spin diffusion rates are of the order of the magic-angle spinning frequency or slower (*9*).

Mehring (*8*) has shown that for the case of off-resonance decoupling in solids the line broadening of the ^{13}C resonance at half-height, $\Delta\nu$ (in Hz) for small deviations from resonance is given by

$$\Delta\nu = \pi^{-1/2}\nu_H^{-2}(\Delta\nu_H)^2 M_{CH}^{(2)}\tau_d. \qquad [1]$$

In this equation ν_H is the proton rf field strength (in Hz), $\Delta\nu_H$ is the frequency offset from proton resonance, $M_{CH}^{(2)}$ is the ^{13}C second moment due to dipolar interactions with protons, and τ_d is the dipolar fluctuation time appropriate to the ADRF cross-polarization experiment (*8*). It follows immediately from Eq. [1] that there is a linear relationship between the effect of off-resonance decoupling and the inverse square of the proton rf field strength, i.e., the lower the proton rf power, the more suitable for off-resonance decoupling experiments. However, as shown previously (*8*, *9*), even when the protons are irradiated exactly on resonance there appears to be a minimum rf field strength required to avoid broadening due to insufficient decoupling power (IDP). As it is the extra broadening due to off-resonance proton irradiation (ORPI) that is the center of our interest, the IDP broadening should be kept low. For typical organic solids the minimum rf field strength is usually somewhere between 6 and 10 gauss, i.e., $\nu_H \approx 24$ to 40 kHz. Further it is assumed that all residual broadening due to ORPI originates from the dipolar interaction between the ^{13}C and the proton(s) directly coupled to it, since all more distant protons exert much smaller dipolar interactions. From Eq. [1] it is clear that the higher the strength of the static magnetic field, the more accurate a determination of the proton shifts in ppm is possible using the ORPI technique.

A straightforward execution of a CP–MAS experiment with the proton power level set as low as possible (but still avoiding IDP), executed for a series of proton decoupling frequencies, gives a pseudo-two-dimensional spectrum with proton linewidths of the order of 3 kHz. Cross sections in the proton dimension show approximately Lorentzian shapes and the peak positions can be determined by using a Lorentzian curve-fitting routine, giving a reproducibility in the measured proton resonance frequency of about ±0.5 ppm.

Refocused Off-Resonance Decoupling

A significant enhancement in resolution in the proton frequency dimension can be obtained by using the sequence sketched in Fig. 1. The experiment starts out with a conventional Hartmann–Hahn cross-polarization, followed by a delay time, T, which has a length corresponding to an even integer number of spinner revolutions. A π pulse is applied in the center of this period, refocusing the effect of inhomogeneous broadening, e.g., due to a dispersion in chemical shifts or simply static magnetic field inhomogeneity. It is important that the π pulse is applied at an integer number of spinner revolutions after the end of the cross-polarization period, since otherwise distortions in the spectrum will occur due to nonrefocused chemical shift anisotropy (*10*). The period, T, is followed by an acquisition period with conventional high-power proton decoupling; if the spectrometer control permits, the ^1H decoupling irradiation during data acquisition should be close to the center of the proton spectrum. The initial amplitude of the detected signal depends on the decay due to transverse relaxation, IDP, and ORPI during the period, T. The setting of the decoupling power during this period is apparently a compromise between minimizing the effect of IDP and maximizing the effect of ORPI (Eq. [1]). An optimum is most conveniently found experimentally. If one assumes for the sake of convenience that the broadening due to off-resonance irradiation is Lorentzian, the intensity of a resonance detected in this experiment follows directly from Eq. [1]:

$$I = I_0 \exp(-T\pi\Delta\nu) \exp(-T/T_2), \qquad [2]$$

where I_0 is the intensity observed in a conventional cross-polarization experiment and $\Delta\nu$ is the broadening due to ORPI given in Eq. [1]. The T_2 value describes the effects of transverse relaxation and IDP. In comparison to a conventional CP experiment with ORPI, the main advantage of the scheme of Fig. 1 is that the line-broadening effects of ORPI are not obscured by inhomogeneous line-broadening mechanisms that could be manifested in the conventional experiment (*9*).

EXPERIMENTAL

The *p*-diethyoxybenzene was obtained from Chemical Services and used without further purification. The ^{13}C experiments were carried out at 50.3 MHz on a modified

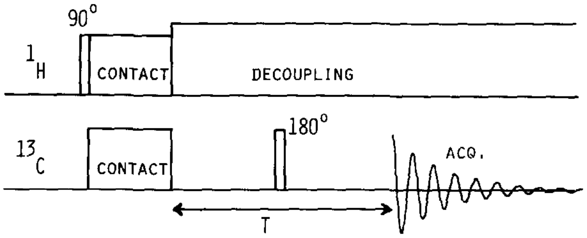

FIG. 1. The refocused off-resonance decoupling sequence is shown for the decoupling (^1H) and observe (^{13}C) frequencies. After the Hartmann–Hahn cross-polarization, the decoupler power is increased in order to prevent cross-polarization during the observe refocusing pulse.

Nicolet NT-200 spectrometer equipped with an 1180 data system. A Kel-F bullet type spinner, spinning at 1680 ± 2 Hz, was used. The experimental scheme sketched in Fig. 1 was employed using rf field strengths of 8.3 and 33 gauss for proton and carbon-13, respectively, during cross-polarization. During the delay period, T, and the acquisition period the decoupling field strength was increased to approximately 9.5 gauss, providing a mismatch for the Hartmann-Hahn condition during the application of the ^{13}C π pulse. The value of T employed was 23.4 msec and the delay time between experiments was optimized at 7 sec. Identical decoupler frequencies were used during the delay time T and during the acquisition period. The decoupler frequency was incremented in steps of 1.25 ppm and 31 different decoupling frequencies were used. The number of acquisitions for each decoupler setting was 200, giving a total measuring time of approximately 12 hours.

RESULTS AND DISCUSSION

Figure 2a shows the spectra obtained for the different decoupling frequency settings as a stacked trace plot in a two-dimensional way. (One should realize that this is *not* a 2D spectrum in the sense defined by Ernst and co-workers (*11*), involving Fourier transformations in two time domains.) In the ^{13}C dimension a large number of spinning sidebands occur for the aromatic carbons, due to the fact that the spinning speed is relatively slow compared to the width of the chemical shift anisotropy pattern. Figure 2b shows a contour plot from sections of Fig. 2a taken at the isotropic shift frequencies of the various ^{13}C nuclei. Several interesting features can immediately be seen from this spectrum. First, the solid-state carbon spectrum is more complex than the liquid-state spectrum, showing nondegeneracies for the protonated aromatic carbons as well as methylene carbons, with splittings of 4.9 and 1.2 ppm, respectively. This type of behavior has been reported previously for the aromatic carbons of *p*-dimethyoxybenzene and has been attributed to a frozen conformation with respect to rotation about the bond between the oxygen and aromatic carbon atoms (*12*, *13*). The corresponding proton frequency cross sections also show a similar splitting pattern. The nondegeneracies present in both the carbon-13 and proton spectra of Fig. 2 can be understood by examining the X-ray-determined crystal structure of this compound (*14*), which clearly shows the asymmetric environment of the *p*-diethoxybenzene molecule, even though the ethoxy groups adopt a *trans* conformation in the crystal. This asymmetric environment can cause the nondegeneracies through both intramolecular and intermolecular magnetic shielding effects in the crystal. Second, in the proton dimension the width of the methyl and quaternary resonances is much larger than the width of the methylene and aromatic resonances. This is due to a much smaller value for $M^{(2)}_{CH}$ for the latter two resonances. The second moment of the methyl group is significantly reduced due to its rapid rotation (*8*).

For an accurate determination of the proton resonance frequencies one can conveniently take cross sections through the spectrum of Fig. 2a parallel to the proton axis at the various carbon-13 resonance frequencies. A set of these cross sections is shown in Fig. 3. The computer-fitted chemical shifts and linewidths obtained from these and other cross sections are given in Table 1, together with the proton shifts measured in solution. As expected, the cross section at the sites of the quaternary carbon appears to have a blunt maximum at a proton frequency that is some weighted

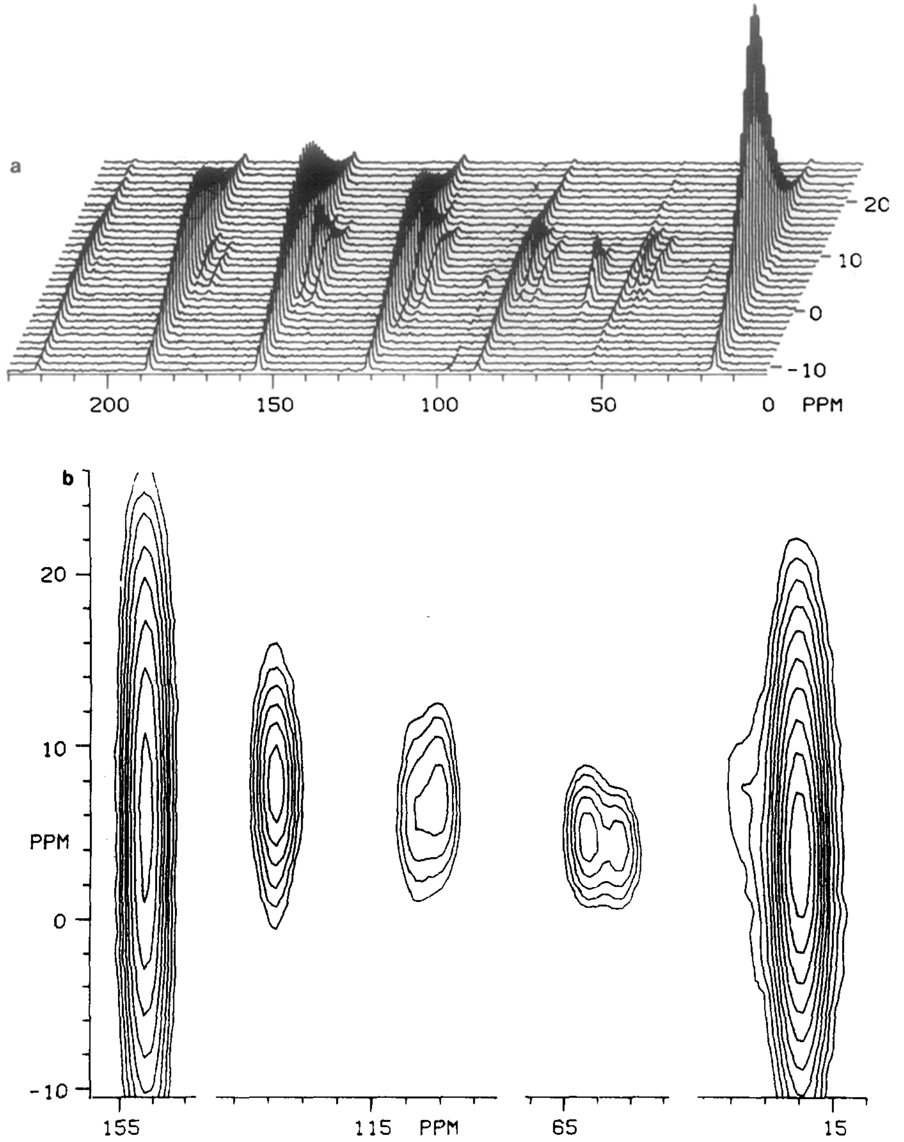

FIG. 2. The results of the refocused off-resonance decoupling experiment for *p*-diethoxybenzene. For details of the conditions, see under Experimental. (a) A stacked plot. (b) A contour plot of the spectrum of Fig. 2a is shown for the centerband (isotropic peak) of each carbon resonance.

average of the various proton resonance frequencies. The methylene ^{13}C nucleus has the largest second moment and, hence, according to Eqs. [1] and [2] displays the narrowest linewidth. The minimum decoupling power used during the delay time, T, is also determined by the methylene site. Higher proton resolution for the other sites can be obtained by lowering the decoupling power; but one then completely loses the resonance from the methylene site. The value chosen for T, together with

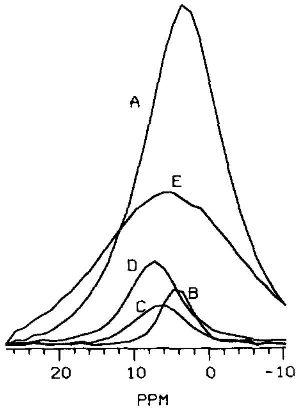

FIG. 3. Proton frequency cross sections for five different carbon chemical shifts. Cross sections A through E correspond to ^{13}C chemical shifts of 16.1, 64.4, 112.9, 117.8, and 154.2 ppm, respectively.

the proton rf power, determines the resolution in the proton dimension. It appears that one can get linewidths in the ^{1}H dimension as narrow as 800 Hz without a large sensitivity loss, but usually optimum conditions for the different sites in the molecule are different. In the work reported here the reproducibility of proton resonance frequencies was found to be about 0.2 ppm.

In conclusion it can be stated that the off-resonance decoupling method provides a simple way to determine proton resonance frequencies in solids with reasonable accuracy. The sensitivity and resolution are much lower than what can be obtained with the direct proton observation in combination with multipulse line narrowing (*15–18*), but as the various proton resonances are separated *via* ^{13}C chemical shifts, no overlap problems occur, apart from the case where magnetically different protons are attached to the same carbon nucleus. Care should be taken in interpreting the proton chemical shifts measured for rapidly rotating methyl groups, as for such car-

TABLE 1

^{13}C AND ^{1}H SPECTRAL DATA FOR *p*-DIETHOXYBENZENE

Site	^{13}C δ(solid)^a	^{1}H $\nu_{1/2}$(solid)^a	^{1}H δ(solid)^a	^{1}H δ(liquid)^{a,b}
CH_3	16.1	11.3	3.0	1.35
CH_2	63.2	4.2	3.5	3.90
CH_2	64.4	4.1	4.1	
Ortho	112.9	6.5	6.3	6.70
Ortho	117.8	7.1	7.1	
Substituted	154.2	19.3	5.0	—

[a] Chemical shifts (δ) and linewidths ($\nu_{1/2}$) are given in ppm.

[b] From "The Standard Spectra," Sadtler Research Laboratories, Philadelphia, PA.

bons the contribution to the dipolar second moment from more remote protons can be significant and, hence, the optimum decoupling frequency for the methyl groups is also determined by these protons; this may cause a systematic error in the measured methyl proton chemical shift. In principle the resolution in the proton dimension can be enhanced further by reducing proton spin diffusion while at the same time decoupling the protons from the carbon-13.

ACKNOWLEDGMENTS

The authors wish to thank Nick Szeverenyi for helpful discussions. The authors also gratefully acknowledge partial support of this research from the Colorado State University Experiment Station and the U.S. Department of Energy (Contract No. DE-AT20-81LC10652 from the Laramie Energy Technology Center.)

REFERENCES

1. W. A. ANDERSON AND R. FREEMAN, *J. Chem. Phys.* **37,** 85 (1962).
2. R. R. ERNST, *J. Chem. Phys.* **45,** 3845 (1966).
3. A. A. MAUDSLEY AND R. R. ERNST, *Chem. Phys. Lett.* **50,** 368 (1977).
4. A. A. MAUDSLEY, L. MULLER, AND R. R. ERNST, *J. Magn. Reson.* **28,** 463 (1977).
5. G. BODENHAUSEN AND R. FREEMAN, *J. Magn. Reson.* **28,** 471 (1977).
6. A. BAX, "Two-Dimensional Nuclear Magnetic Resonance in Liquids," Chap. 2, Reidel, Hingham, 1982.
7. P. CARAVATTI, G. BODENHAUSEN, AND R. R. ERNST, *Chem. Phys. Lett.* **89,** 363 (1982).
8. M. MEHRING, "High Resolution NMR Spectroscopy in Solids," Chap. 4, Springer-Verlag, New York, 1976.
9. D. L. VANDERHART, W. L. EARL, AND A. N. GARROWAY, *J. Magn. Reson.* **44,** 361 (1981).
10. M. M. MARICQ AND J. S. WAUGH, *J. Chem. Phys.* **70,** 3300 (1979).
11. W. P. AUE, E. BARTHOLDI, AND R. R. ERNST, *J. Chem. Phys.* **64,** 2229 (1976).
12. E. T. LIPPMAA, M. A. ALLA, T. J. PEHK, AND G. ENGLEHARDT, *J. Am. Chem. Soc.* **100,** 1929 (1978).
13. J. S. WAUGH, M. M. MARICQ, AND R. CANTOR, *J. Magn. Reson.* **29,** 183 (1978).
14. M. HAISA AND S. KASHINO, *Acta Crystallogr. B* **33,** 485 (1977).
15. J. S. WAUGH, L. HUBER, AND U. HAEBERLEN, *Phys. Rev. Lett.* **20,** 180 (1968).
16. W. K. RHIM, D. D. ELLEMAN, AND R. W. VAUGHAN, *J. Chem. Phys.* **59,** 3740 (1973).
17. D. P. BURUM AND W. K. RHIM, *J. Chem. Phys.* **71,** 944 (1979).
18. D. P. BURUM, M. LINDER, AND R. R. ERNST, *J. Magn. Reson.* **44,** 173 (1981).