NMR Investigation of the Thermolysis of Citric Acid

JOHN W. FISCHER, LAWRENCE H. MERWIN,* and ROBIN A. NISSAN

Research Department, Chemistry and Materials Division, Naval Air Warfare Center, Weapons Division, China Lake, California 93555

The thermolytic decomposition of citric acid in the presence of tin/lead solder has been investigated. The solid reaction products were first examined by solid-state ¹³C NMR. The samples were then dissolved in D_2O , and ¹H and ¹³C 1D and 2D (HMQC, TOCSY) spectra were obtained. Results indicate the presence of a series of compounds including 3-hydroxyglutaric, citraconic, itaconic and aconitic acids, and anhydrides. Solution- and solid-state NMR data are provided for citric acid and a number of metal and alkali metal citrate salts. Results of this work are related to the use of citric acid as a solder flux and to the elimination of chlorofluorocarbon cleaning processes in the electronics industry. Index Headings: NMR; Solid-state NMR; Citric acid; Thermolysis.

INTRODUCTION

The ozone-depleting chemical (ODC) cleaning solvents, methyl chloroform and freons [chlorofluorocarbons (CFCs)], have been in use in the electronics industry for decades. The relative stability, low toxicity, and nonflammability of these ODCs made them easy to use, while their ability to clean thoroughly and leave little or no residue made them the ideal cleaning agent for military and aerospace applications. Unfortunately, the identification of the role of these materials in the depletion of the earth's stratospheric ozone layer has led to a ban on their production in the United States beginning in 1996. Depletion of the ozone layer has been implicated in an increase in the number of cases of skin cancer and cataracts and in crop damage. In early 1992, a NASA study was published indicating that the erosion of the earth's ozone laver, as a result of the widespread uses of several ODCs, was occurring faster and extending farther than had previously been believed. The ban on these substances is having a significant impact on the electronics manufacturing industry as a whole and the manufacture of high-reliability electronics components in particular.^{1,2}

In standard wave soldering processes, the circuit board and components are pretreated with a flux. As the board is soldered, the flux serves to remove or break down the oxide layer present on the surface of the circuit board and component leads. This process results in faster solder wetting (higher manufacturing volume) as well as a stronger and more reliable solder joint. Traditionally, the flux compound of choice has been rosin moderately activated (RMA). This pine-pitch-based material is a complex mixture of terpenoids with a quaternary alkyl amine hydrohalide activator. While this material works well as a solder flux, the chemical residues are corrosive to electronics and *not* water soluble. RMA flux requires an efficient cleaning system such as that which has been provided by ODC solvent cleaning and degreasing.

Received 22 June 1994; accepted 30 September 1994.

One option for the manufacture, rework, and repair of electronics that does not require the use of an ODC solvent cleaning system is the implementation of a process using only water-soluble fluxes. Water-soluble fluxes have traditionally not been allowed on high-reliability systems because of the highly corrosive nature of these materials. Recently, however, aqueous citric acid (CA) has received attention as a flux because it is chemically active, yet very easy to remove after soldering. CA is readily available and inexpensive, and it has taken the early lead in the area of "environmentally green" fluxes. Since only warm water is required for cleaning and disposal of the rinsates, it is cost-effective on both large and small scales. CAbased fluxes have been shown to exhibit excellent soldering properties. However, an understanding of the fundamental chemistry of these materials and their thermal degradation products is required before they can be certified for high-reliability applications.

CA has been one of the most studied alternatives to rosin-based fluxes by industry as well as the military. Preliminary investigations have concluded that CA performs at least as well as, if not better than, conventional rosin flux technology.³ However, CA and other organic acids that are presently under investigation are new ingredients in soldering processes and, therefore, must be studied thoroughly prior to large-scale utilization. This paper details the study of the interaction of CA with metals likely to be found in the soldering process as well as the decomposition pathways of CA under typical soldering conditions. It is essential that a good understanding be obtained of the contaminants likely to be found and of the potential for these contaminants to cause problems with long-term reliability.

GENERAL EXPERIMENTAL APPROACH

Before CA will gain widespread approval as a soldering flux for high-reliability applications, several questions must be answered. These include:

- 1. What products are formed during the thermolysis of CA at solder liquidus?
- 2. Are any tin, lead, or other metal citrates formed?
- 3. What is the chemical composition of these residues?

The answers to these questions provide the basis for an understanding of the use of CA-based fluxes, their cleanability, and the ultimate effect on long-term circuit board reliability.

This study was focused on the use of nuclear magnetic resonance (NMR) spectroscopy to answer the above questions. NMR techniques were used to characterize neat CA, CA salts, and CA thermolyzed under the specific conditions noted below. Solid-state NMR was used to characterize the solids "as received" to avoid any inter-

^{*} Author to whom correspondence should be sent.



FIG. 1. Solder reflow process time/temperature profile.

ferences or solubility problems that may occur when the materials are being dissolved. Solution-state NMR was used to determine, as closely as is possible, the exact structure of the compounds formed.

Neat reference chemicals were obtained from a number of commercial sources. CA, the sodium and potassium salts of CA, and citraconic acid were purchased from Aldrich, Milwaukee, Wisconsin. Nickel citrate was obtained from ICN Biomedicals, Inc., Irvine, California. Stannous citrate and lead citrate were prepared by Polarchem, Garden Grove, California. Itaconic acid and anhydride were purchased from Pfizer & Co., New York, New York, and J. T. Baker, Phillipsburg, New Jersey, respectively.

INSTRUMENTATION

Solution-state NMR spectra were run on a Bruker AMX-400 NMR spectrometer operating at a magnetic field strength of 9.4 Tesla; this corresponds to ¹H and ¹³C frequencies of 400.1 and 100.6 MHz, respectively. Chemical shift values are reported [with respect to external tetramethylsilane (TMS) with the use of the high-frequency positive convention].⁴

Solid-state NMR spectra were run on a Bruker MSL-200 NMR spectrometer operating at a field of 4.7 Tesla with a corresponding ¹³C frequency of 50.3 MHz. All spectra were obtained with the use of magic-angle spinning at speeds of ~3 to 4 kHz. Both Bloch decay and cross polarization (CP) experiments were performed, and 90° pulse widths of 5 μ s were used throughout. For the CP experiments, contact times of 1 ms and recycle delays from 15 to 60 s were required. ¹³C shift values are reported with respect to TMS and were measured by replacing the sample with the secondary reference, adamantane (highfrequency line = 38.5 ppm with respect to TMS).⁵

SAMPLES

The amounts of decomposition products formed on a circuit board are relatively small. Therefore, a method was required for forming sufficient quantities of decomposition products for NMR analysis. At the same time, the CA had to be exposed to conditions similar to those of a typical wave solder process (Fig. 1). In a procedure to establish these conditions, a number of glass test tubes were prepared, each containing several grams of CA and



FIG. 2. ¹³C CP/MAS NMR spectrum of anhydrous CA.

a ~5-mm-diameter ball of military specification (QQ-S-571, 63/37 tin/lead) solder. The tubes were then immersed in a molten solder bath and allowed to remain for 5, 10, 15, 30, and 60 s past the point at which the solder in the tube liquified. The ends of the tubes were then sealed with parafilm until the decomposition products could be removed for analysis. (Note that the sample number CA5 denotes the residue of CA at 5 s past solder liquidus; CA10, 10 s; etc.) Samples were first examined by solid-state NMR. The samples were then dissolved in D₂O or d6-acetone for solution-state NMR analysis. Ultimately, D₂O was the solvent of choice since the residues were far more soluble and gave clear solutions with no turbidity as compared to the cloudy acetone solutions.

RESULTS AND DISCUSSION

Solid-State NMR Data for Known CA Reference Standards. Solid, anhydrous CA has a ¹³C NMR spectrum consisting of six lines (Fig. 2). The three lines at 179.5, 176.6, and 175.0 ppm arise from the carbon atoms of the carboxylic acid groups (Fig. 3). The sharp resonance at 72.9 ppm corresponds to the central carbon of the molecule, and the lines at 44.2 and 43.3 ppm may be assigned to the two methylene carbons. It will be noted that this line multiplicity reflects the fact that, in the solid, the carboxylic acid groups are crystallographically inequivalent. There also exists a solid form of CA in which the crystal lattice contains one molecule of water per molecule of CA. This spectrum is similar to that of the anhydrate in line multiplicity, but the chemical shift values are significantly different (Table I). No evidence of CA monohydrate was found in any other sample examined.

The ¹³C spectrum of tin (stannous) citrate is similar in appearance to that of CA, but with the lines shifted somewhat by the presence of the tin (Fig. 4 and Table I). However, in the lead citrate there is a doubling of the number of lines in the carbon spectrum. This behavior



FIG. 3. Structure of citric acid.

TABLE I. ¹³ C NMR chemical shift data ^a for	CA	and re	elated (compounds
---	----	--------	----------	-----------

Compound	Solid-state ¹³ C shift values/ppm ^b (solution-state values in parentheses)			
	-COOH	С-ОН	-CH ₂ -	
CA (anhydrous)	179.5, 176.6, 175.0	72.8	44.2, 43.3	
CA (monohydrate)	177.9, 174.5, 174.0	75.9	45.7, 43.4	
CA (D_2O solution) ext. Tss reference	(178.4, 175.2 (2 C _s))	(75.1)	(44.9)	
Stannous citrate	184.7, 182.0, 178.7	80.1	51.3, 47.8	
Plumbous citrate	185.0, 184.3, 181.5, 180.7, 178.2, 177.5	78.9, 76.0	51.5, 48.3, 45.8	
CA monosodium salt	180.2, 173.4	73.3	49.9, 41.9	
CA disodium salt (\cdot 1.5 H ₂ O)	184.2, 181.5, 180.6, 179.6	74.3	48.9, 45.0	
CA (trisodium salt ($\cdot 2 H_2 O$)	186.1, 181.4, 178.1	75.8	47.5, 42.9	
CA tripotassium salt	182.2, 178.1	76.8	53.5, 51.6	
	C=O	Olefin C, CH, CH ₂	Alkane CH ₂ , CH ₃	
Aconitic acid in D ₂ O	(176.7, 171.4, 170.6)	(141.6(q), 132.6 (CH))	(35.3)	
Itaconic acid	180.0, 172.8	136.5, 132.2 (q)°	37.5	
Itaconic anhydride (D ₂ O solution)	(178.1, 172.2)	(135.8, 133.1)	(39.7)	
Citraconic acid	174.2, 172.6	135.9, 131.1 (q) ^c	20.2	
Citraconic anhydride (D ₂ O solution)	(175.5, 170.4)	(149.5, 122.5)	(22.0)	

^a NB: Both nickel and copper citrate gave no ¹³C result because of the paramagnetic nature of metal cation.

^{b 13}C shifts reported with respect to external TMS, error \pm 0.1 ppm.

c q = Quaternary.

apparently occurs because of the presence of two differing types of citrate anions in the lead citrate unit cell.

The ¹³C NMR data for three sodium salts and one potassium salt of CA are given in Table I. The trisodium and tripotassium salts have line multiplicity similar to that of CA but, again, significantly different shift values. The monosodium salt spectrum contains small resonances, the sources of which are not readily apparent. These may be either minor crystal phases or impurities; however, the shift values for the minor components do not correlate to any other CA compound examined in this study. The carbonyl region of the disodium salt spectrum consists of four lines in a 2:1:2:1 ratio. This pattern reflects the presence of 1.5 waters of crystallization (i.e., two molecules of water for every three CA molecules in the crystal lattice).

Several aspects of the data presented in the previous paragraph must be emphasized. First, the solid-state ¹³C NMR results for CA and its related compounds show assignable spectra that consist of narrow lines that are all well resolved. Furthermore, each compound examined has a unique set of resonances that may be used to identify the presence of that component.

Solid-State NMR Results of Thermolyzed CA. After thermolysis in the presence of solder, the sample CA5 appeared light brown in color and was of a viscous, amorphous consistency. A small amount of white, crystalline CA had apparently spattered upwards and coated the inside of the test tube. Samples CA10, CA15, and CA30 were similar in appearance. Samples CA45 and CA60 were a darker, red-brown in color with little or no remaining CA on the tube sides. Solid-state NMR spectra of the brown material from samples CA5, CA30, and CA60, along with the spectrum of CA as reference, are shown in Fig. 5. The spectra at 5 and 30 s past liquidus show only very minor changes from the spectrum of neat CA. The methylene region at \sim 45 ppm broadens, and the resonance associated with the central, guaternary carbon (72 ppm) shifts slightly. There is an increase in line multiplicity in the carbonyl region (175 to 185 ppm), but this is not accompanied by any new lines in the 0-80 ppm region, which one would expect to observe if new compounds or salts were being formed. This result suggests that the multiplicity in the carbonyl region is associated with changes in hydrogen bonding (possibly associated



FIG. 4. ¹³C CP/MAS NMR spectra of lead citrate and tin citrate.



FIG. 5. 13 C NMR spectra of CA heated in the presence of tin/lead solder.



FIG. 6. 13 C NMR spectrum of CA heated in the presence of tin/lead solder for 45 s past solder liquidus.

with loss of water) for the carboxylic acid groups. There is also no evidence of resonances that could be correlated to tin or lead citrate.

At 45 s past liquidus, the ¹³C NMR spectrum clearly shows evidence of chemical changes in the sample (Fig. 6). The carbonyl region has broadened considerably, as has the quaternary resonance. The methylene resonance not only has broadened but also exhibits a considerable increase in relative intensity in the spectrum. Most notably, there is a new resonance that has appeared at ~ 132 ppm, indicating the presence of an olefinic carbon species. In the spectrum of the 60-s sample, the intensity of the CA quaternary carbon has significantly decreased, indicating that a significant portion of the CA has been converted to other compounds (Fig. 5). There is some structure to the carbonyl region. Three of the features in this region and the maximum of the broad resonance at ~ 40 ppm correspond to itaconic anhydride (see below). In addition, there is a resonance at 10.5 ppm which may correspond to the methyl group in citraconic acid or anhydride. Citraconic anhydride has a melting point of 8°C, but may form a eutectic in this type of system. It is interesting to note that, when a sample of the 60-s material was placed in a vacuum oven overnight at 80°C, this methyl resonance disappeared. This pattern would seem to suggest that the low-melting-point citraconic anhydride was present. There is no evidence for the presence of metal citrates or alkali metal citrate salts.

In conclusion, the solid-state NMR results suggest little or no reaction of the CA for times of 30 s or less. At 45 s, there is clear evidence of chemical changes taking place. The 60-s spectrum indicates the possible presence of itaconic and citraconic anhydrides. There is no evidence of metal or alkali citrate salts in any of the spectra recorded.

Solution-State NMR Results. Samples of CA and several samples of thermally aged CA (see above) were subjected to a battery of solution-state NMR experiments. Both ¹H and ¹³C solution-state NMR results will be discussed in this section. The goal of this work was to identify







FIG. 8. 'H NMR series for CA at solder liquidus.

the decomposition products that might be formed under standard wave solder conditions with CA-based fluxes. The bulk of the materials formed by thermal decomposition in the presence of liquid solder was water soluble, and solutions in D_2O were analyzed by NMR methods. The destructive distillation of CA is described in Ref. 6 and is shown in Fig. 7.

Figures 8 and 9 display the ¹H and ¹³C NMR spectra of CA and three samples of CA that were allowed to thermally decompose for 5, 30, and 60 s in the presence of liquid solder. The initial spectrum of CA is characterized as an AB quartet centered near 2.9 ppm assigned to the methylene protons of CA. The peak near 5.5 ppm is residual HDO from the solvent. After just 5 s at solder liquidus, several dramatic changes were observed in the ¹H NMR spectrum. Residual HDO now appears at near 4.9 ppm which is a result of the change in acidity of the solution. The growth of new resonances at 2.1, 3.1, 3.8, and 6.9 ppm is noted. The appearance of these resonances after 5 s at solder liquidus indicates that dehydration and decarboxylation steps are occurring in the early stages of CA decomposition. The CA30 sample is very similar to the 5-s sample with additional small peaks growing in the olefinic region (between 5 and 7 ppm). The sample that had been thermolyzed for 60 s at solder liquidus changed

FIG. 10. Expanded decomposition pathway for CA involving decarboxylation and dehydration.

dramatically. While there is still a small amount of CA present, the majority of product is represented by singlets or slightly broadened singlets in the aliphatic and olefinic regions.

The ¹³C NMR series yields further evidence that CA is present in large quantities after 5 and 30 s at solder liquidus (Fig. 9). The CA methylene (45 ppm), quaternary (75 ppm), and carboxyl resonances (178 and 175 ppm) in the ¹³C NMR spectrum are prominent in the CA5 and CA30 samples. Once again there are definite indications of new materials containing olefinic carbons (120 to 150 ppm) as well as some new aliphatic resonances (20 to 50 ppm) appearing in the early stages of thermal decomposition. After 60 s of thermolysis, the ¹³C NMR results indicate that a small amount of CA is still present and compounds containing olefinic carbons are dominating the spectrum, thus confirming the 1H NMR results. The major decomposition products have been identified with the use of an array of one- and two-dimensional NMR techniques.

The CA60 sample was used for a series of NMR experiments to study the thermolysis of CA at solder liquidus. It is instructive to first consider how CA might decompose thermally. From these simple considerations, four materials were identified that appeared to be present in the thermally aged samples. Decarboxylation and dehydration are the most likely paths of decomposition for CA. Indeed, the destructive distillation of CA is known to lead to itaconic and citraconic anhydrides (Ref. 6, Fig. 7). If decarboxylation is considered first, there are two sites where a reaction could occur (Fig. 10). Decarboxylation at either of the two sites adjacent to a methylene group leads, after dehydration, to either itaconic or citraconic anhydride, 2 or 3. (For simplicity, it was assumed that anhydrides are formed that are later rehydrated when dissolved in D₂O for solution-state NMR experiments.) On the other hand, if decarboxylation is performed first at the central carbon of CA, then the result might be 3-hydroxyglutaric acid, 4, which could dehydrate to form a dehydroglutaric acid, 5. There is clear evidence for 4 in the ¹H and ¹³C NMR results, but evidence for 5 is not compelling. One last decomposition pathway for which there is clear evidence involves dehydration prior to any

FIG. 11. Decomposition of CA involving dehydration at the 2,3 position.

decarboxylation step. This pathway is depicted in Fig. 11 and the products, as shown, are *cis* or *trans* aconitic acid, **6**, or aconitic anhydride, 7. *Cis* aconitic acid is closely related to CA in the Krebs cycle.⁶ It is known that CA reacts with hydrochloric acid to give aconitic acid when heated.⁷

NMR evidence suggests that, under thermal conditions, CA undergoes both decarboxylation and dehydration to yield many of the products shown in Figs. 10 and 11. Data also show that the initial step in thermolysis of CA is dehydration to form aconitic acid derivatives, which are observed in the earliest stages of reaction.

Itaconic and citraconic anhydrides, 2 and 3, are seen in the CA60 sample, as is aconitic acid or anhydride 6 or 7 (see Table I). Citraconic anhydride is evident in the CA5 sample, but only at very low concentrations. However, an aconitic acid derivative can be clearly identified in the CA5 and CA30 samples. Heteronuclear multiple quantum coherence (HMQC)⁸ and total correlation spectroscopy (TOCSY)⁹ two-dimensional NMR experiments were performed in order to confirm our conclusions (Figs. 12A, 12B, and 13). The HMQC experiment allows direct correlation of 1H resonances with their directly bonded ¹³C resonances. Figure 12A displays the HMQC data for the aliphatic region, and Fig. 12B displays the olefinic region. Direct evidence for the presence of citraconic and itaconic acids or anhydrides is found in both regions of these two-dimensional data. The methyl carbon/protons for the citraconic derivative are observed near 2.1 and 22 ppm in the ¹H and ¹³C dimensions, respectively, and the olefinic CH is observed near 122 and 6.0 ppm (see Fig. 12A). Close examination of the ¹H resonance near 6.0 ppm reveals a quartet structure, ${}^{4}J_{H-H} = 1.6$ Hz from coupling to the methyl protons in the citraconic derivative (see inset Fig. 12B).

The evidence for an itaconic derivative is equally compelling, with a methylene resonance observed near 3.4 and 39 ppm in the ¹H and ¹³C dimensions and a pair of inequivalent olefinic protons near 5.9 and 6.4 ppm displaying a correlation to a carbon resonance near 133 ppm. This observation corresponds well to the expectation for itaconic acid or anhydride. The evidence for 3-hydroxy glutaric acid, **4**, as a decomposition product centers upon two multiplet resonances in the ¹H spectrum of the 60-s aged material. A quartet of doublets centered near 2.7 ppm and an apparent triplet centered near 3.2 ppm have the correct multiplicity and ratio of integrated areas to be assigned to the methylene and methine protons of **4**. Evidence for aconitic acid derivatives includes the res-

FIG. 12. HMQC spectrum for CA for 60 s at solder liquidus: (A) aliphatic regions, (B) olefinic regions.

onance near 7.0 and 133 ppm in Fig. 12B and also the resonance near 3.8 ppm and 36 ppm, which was assigned to the methylene group of aconitic acid or anhydride.

One further conclusion, based upon the ¹H spectra at 5- and 30-s thermolysis in Fig. 12 and comparison to the spectra of aconitic acid, is that the initial decomposition pathway involves dehydration at the 2,3 position of CA. The appearance of singlets at 7.0 and 3.9 ppm would indicate that aconitic acid derivatives are present in the earliest stages of thermolysis, and each of the six ¹³C resonances of aconitic acid in the ¹³C NMR spectra of CA5 and CA30 can be identified (Fig. 9).

The TOCSY experiment allows for correlation between all coupled proton spins within a molecule (Fig. 13). This technique is very helpful for looking at samples that contain mixtures of materials. Off-diagonal resonances correspond to coupled spin systems and must indicate resonances that are within the same molecule. There is a clear correlation (off-diagonal peak) between two olefinic peaks near 6.4 and 5.9 ppm, and each of these olefinic resonances has an additional correlation to a resonance near 3.4 ppm. This result corresponds exactly to what would be expected for itaconic acid. If focus is placed on the other major olefinic resonance near 6.0 ppm, a cor-

FIG. 13. TOCSY for CA decomposition for 60 s at solder liquidus.

relation with a resonance near 2.0 ppm can be identified. These resonances were assigned to the olefin and methyl resonances of citraconic acid. The evidence for 3-hydroxyglutaric acid, 4, is the off-diagonal resonance near 2.7 and 3.2 ppm, indicating a strong, probably vicinal, coupling between these two resonances. An authentic sample of 4 could not be found; however, comparison to malic acid, which contains similar methine and methylene protons, does indicate a similar coupling pattern. Finally, one other correlation is observed in the TOCSY experiment between protons near 7.0 and 3.9 ppm, and this can be assigned to the 4-bond coupling between olefin and methylene protons of an aconitic acid derivative.

CONCLUSION

In conclusion, the thermal decomposition of CA in the presence of liquid solder leads to many of the possible organic products associated with dehydration and decarboxylation. From the standpoint of the materials and processing questions raised in the introduction, we believe the identified thermolysis products will not pose any significant problems. The products have acid dissociation constants that are typically of the same order as citric acid; none are known to be particularly toxic; and, most importantly, all are water soluble. This latter point means that they should be removed in the cleaning procedures currently used in citric acid flux-based solder processes. and will then likely not be a source of future circuit board corrosion. (Indeed, citric acid itself is a strong enough acid to cause surface corrosion of circuit board components under given conditions. It is the fact that citric acid is easily removed in a hot water wash which allows its use in commercial wave solder applications.)

Thus far, these efforts have not led to the identification of any metal salts; however, their presence is not precluded by these investigations. Indeed, many of the anticipated citrate salts are only sparingly soluble in water or acetone and might not be observed by the techniques employed herein. A further extension of this work will be to monitor CA/solder flux products by atomic absorption methods.

ACKNOWLEDGMENTS

We would like to thank Loretta Lusk, Jerry Maurice, Roger Nickell, and Jim Smith for technical assistance in this effort.

- 1. T. S. Perry, IEEE Spectrum 30, 20 (1993).
- 2. P. S. Zurer, Chem. Eng. News 70 (25), 6 (1992).
- 3. R. L. Turner, in 17th Annual Electronics Manufacturing Seminar

Proceedings, Naval Air Warfare Center Weapons Division Technical Publication 8096 (Naval Air Warfare Center, China Lake, California, 1992), p. 137.

- 4. R. K. Harris and B. E. Mann, *NMR and the Periodic Table* (Academic Press, London, 1978).
- 5. S. Hayashi and K. Hayamizu, Bull. Chem. Soc. Jpn. 62, 2429 (1989).
- 6. L. F. Fieser and M. Fieser, Advanced Organic Chemistry (Rheinhold, New York, 1961).
- 7. G. A. Hill and L. Kelley, Organic Chemistry (The Blakiston Company, Philadelphia, 1943), p. 398.
- 8. A. Bax and S. Subramanian, J. Magn. Reson. 67, 565 (1986).
- 9. A. Bax and D. G. Davis, J. Magn. Reson. 65, 355 (1985).