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PUBLICATION CREDITS

1. Temperature Dependence of 207Pb MAS spectra of Solid Lead Nitrate, an Accurate, Sensitive Thermometer for Variable Temperature MAS

Bielecki, Anthony; Burum, Douglas P.

Journal of Magnetic Resonance, Series A (1995), 116(2), 215-20.

The remarkably sensitive temp. dependence of the 207Pb chem. shift in magic-angle-spinning (MAS) spectra of lead nitrate provides an excellent method for thermometry in solid-state NMR. The temp. dependence is uniform over a range of at least -130 to +150°, and also the NMR sensitivity and linewidth are very favorable. Lead nitrate can be used in MAS probes to measure sample temp. changes, temp. gradients, MAS heating effects, and the dynamics of temperature jumps.

2. Quadrature detection of CRAMPS NMR data for Maximum Resolution and Sensitivity

Burum, D. P.; Cory, D. G.; Gleason, K. K.; Levy, D.; Bielecki, A.

Journal of Magnetic Resonance, Series A (1993), 104(3), 347-52.

A simple phase-cycling method for CRAMPS NMR data acquisition is described. It allows single-window complex date acquisition to be used without special instrument calibration of data handling.

3. WIMSE, A New Spectral Editing Technique for CPMAS Solid-State NMR

Burum, D. P.; Bielecki, A.

Journal of Magnetic Resonance (1969-1992) (1991), 95(1), 184-90.

A new spectral editing method, windowless isotropic mixing for spectral editing (WIMSE), is introduced, which utilizes the WIM-24 windowless multiple-pulse sequence (P. Caravatti et al., 1983) to unambiguously identify methylene carbon resonances in ^{13}C CPMAS spectra of solids. Illustrative WIMSE spectra of sucrose and polystyrene are presented.

4. An Improved Experiment for Heteronuclear-Correlation 2D NMR in Solids

Burum, D. P.; Bielecki, A.

Journal of Magnetic Resonance (1969-1992) (1991), 94(3), 645-52.

The technique of heteronuclear correlation 2D NMR spectrometry is described. The method is used to obtain well resolved proton chemical shift information for a variety of solids such as polymers or pharmaceutical products. The technique was illustrated by using p-dimethoxybenzene, aspirin and polysaccharides as samples.

5. Solid-state Two-Dimensional Carbon-13-Proton Correlation (HETCOR) NMR Spectrum of Amorphous Poly(2,6-dimethylp-phenylene oxide) (PPO)

Bielecki, A.; Burum, D. P.; Rice, D. M.; Karasz, F. E.

Macromolecules (1991), 24(17), 4820-2.

A two-dimensional ^{13}C-^{1}H NMR correlation spectrum is presented for glassy amorphous poly(2,6-dimethyl-p-phenylene oxide) (PPO). Correlation is obtained through a multiple-pulse selective cross-polarization using the sequence WIM-24 along with an improved ^{13}C-^{1}H multiple-pulse decoupling sequence during the evolution period. The 2-dimensional data presented provide evidence supporting the solid-state ^{13}C and ^{1}H assignments for PPO. Correlation intensities provide conformational information about the dihedral angles associated with the conformation of amorphous PPO.

6. Application of Fluorine-19 CRAMPS to the Analysis of Calcium Fluoride/Fluoroapatite Mixtures

Smith, Karen Ann; Burum, Douglas P.

Journal of Magnetic Resonance (1969-1992) (1989), 84(1), 85-94.

CRAMPS (combined rotation and multiple-pulse spectrometry) can be readily applied to 19F NMR of solids to obtain quant. information about the components. For inorganic minerals such as fluoroapatite and CaF_2, accuracies of better than 10% were achieved. If the spectral width is very great, it is useful to employ the multipulse quadrature detection technique. It is sometimes difficult to det. the exact cause of line broadening in CRAMPS experiments. In the present case, many possible causes were ruled out, but the line broadening mechanism remains undeleted. The variation in linewidth does not affect the quantitative nature of the results.

7. **High Resolution CPMAS and Solution NMR Studies of Polysaccharides.** Part 1: starch
By Dev, S. B.; Burum, D. P.; Rha, C. K.
Extensive high resolution. NMR measurements, both in the solid-state and in solution, of starch are reported. Starch samples were in the form of wheat starch and sol. starch from potato. Both wheat starch and whole wheat grain samples were run in the CPMAS experiments. Apart from the normal ^{13}C spectra, 50.29 MHz for the CPMAS and 67.89 MHz for the solution, proton T_1 and $T_{1\rho}$ and ^{13}C T_1 were also measured in the CPMAS experiments. Slightly different chemical shifts are obtained in the solution work for different solvents (water, NaOH and LiBr) from those reported earlier. All the carbon resonances were assigned. In CPMAS the wheat starch samples, both powder and grain, show three well-resolved resonances almost of equal intensities for the C-1 carbon, around 100 ppm, as opposed to only one in the soln. These results exactly match xray data for starch A. The NMR results also indicate that there is a difference in the solid-state and solution conformation. Proton T_1 of starch, 0.7 s, is nearly one order of magnitude shorter than the corresponding α-D-glucose. The ^{13}C T_1 values for the carbon peaks in the CPMAS spectra of wheat starch, corresponding to 62, 73 and 100 ppm relative to TMS, are 17.4, 27.7 and 14.5, respectively. It is suggested that the resolution enhancement technique can indicate polysaccharide branching residues in CPMAS experiments.

8. **Optically Detected Nuclear Resonance of Excited And Ground States of Praseodymium(3+)-Doped Yttrium Phosphate (YPO4)**
Shelby, R. M.; Burum, D. P.; Macfarlane, R. M.
Language: English, Database: CAPLUS,
The hyperfine structure and nuclear magnetic moments of Pr_{3+}:YPO_4 in the ground state and lowest component of the $1D_2$ excited state were measured by using laser hole-burning and optically-detected nuclear resonance. For the ground state, and excited state, the quadrupole coupling constants and the magnetic splitting factors are given. Model calculations of the splitting factors assuming pure $4f_2$ electron states agree with the ground state values but rather poorly with those in the excited state.

9. **Heteronuclear correlated 2D NMR Spectroscopy of Spins Greater Than 1/2. Application to Decaborane**
Burum, D. P.
The technique of 2D (2-dimensional) heteronuclear correlated spectroscopy is extended to the case of protons coupled to nuclei with spins >1/2. The method is applied to decaborane, with the result that even the weakly coupled bridging proton correlations are elucidated, and simplified, B-decoupled proton spectra are obtained without the use of B decoupling.

10. **Hyperfine Structure and Nuclear And Electronic Zeeman Effect of the 1D2 $\leftrightarrow$ 3H4 Transition of Praseodymium(3+)-Activated Calcium Fluoride**
Macfarlane, R. M.; Burum, D. P.; Shelby, R. M.
The electronic and nuclear magnetic moments and the effective nuclear-quadrupole interactions of the ground and excited states of the 5940.97-Å $1D_2 \leftrightarrow 3H_4$ transition of Pr_{3+} ions in tetragonal sites of CaF_2 were measured using spectral hole burning, radio-frequency (rf) and microwave-optical double-resonance and laser-excited fluorescence excitation spectroscopy. The ground state is an electronic doublet of E symmetry whose electronic magnetic moment tensor is given by $g\beta/h = 5.44$ MHz/G and g = 0. The nuclear magnetic splitting factor parallel to the C_4 axis is $\gamma_g/2\pi = 1.65$ kHz/G, and the effective quadrupole coupling const. $D_8 = +1.39$ MHz is dominated by pseudoquadrupole effects. The excited state is an electronic singlet, and rf-optical double resonance was used to det. the nuclear Zeeman splittings and obtain a very precise value for the nuclear magnetic moment of $141Pr$, i.e., $4.2754(5)\mu_N$. For fields parallel to the C_4 axis, γ_e is unenhanced: $\gamma_e/2\pi = 1.2924 \pm 0.0001$ kHz/G. However, $\gamma_e/2\pi = 2.12 \pm 0.05$ kHz/G shows modest enhancement due to 2nd-order admixture of other $1D_2$ electronic levels. This result is used to assign the symmetry of the excited state as A_1 in the point group C_{4u}, and to locate the E level $\sim$200 cm$_{-1}$ higher. Unlike that of the ground state, the excited-state quadrupole coupling is dominated by real elec. quadrupole interactions, and the const. is $D_e = -0.44$ MHz.

11. **Temperature Dependence of Aluminum-27 NMR in Yttrium Aluminate (YAlO3)**
Burum, D. P.; Macfarlane, R. M.; Shelby, R. M.; Mueller, L.
The nuclear quadrupole tensor for $27Al$ in $YAlO_3$ orthoferrite was detected at 30 and -150°. The coupling constant e^2qQ/h varies linearly from 1.44 to 1.56 MHz, whereas the asymmetry parameter of drops rapidly from 0.748 toward an asymptotic value of 0.663.

12. Nonphotochemical Hole Burning and antihole production in the Mixed Molecular Crystal Pentacene in Benzoic Acid

Olson, R. W.; Lee, H. W. H.; Patterson, F. G.; Fayer, M. D.; Shelby, R. M.; Burum, D. P.; Macfarlane, R. M.

g experiments and picosecond photon-echo experiments on pentacene in benzoic acid are presented. On burning, several new discrete pentacene absorptions (antiholes) are created. These spontaneously revert to the unburned form at low temps., but may also be induced to revert by optical excitation. Deuteration of the host acidic protons markedly changes the pentacene fluorescence lifetime and hole-burning and recovery behavior, indicating the strong interaction of pentacene and the benzoic acid dimer H bonds. Hole burning and antihole formation are attributed to H bond tautomerism of benzoic acid dimers near excited pentacenes. Two mechanisms for this tautomerization are suggested. The homogeneous linewidth of the pentacene $S_0 \rightarrow S_1$ transition was measured by both photon-echo and hole-burning experiments. A preliminary study of the homogeneous linewidth measured by hole burning indicates that the transition broadens with an 11- cm_{-1} thermal activation energy, which differs from measurements made by other methods.

13. New Determination of the Nuclear Magnetic Moment Of Praseodymium-141

MacFarlane, R. M.; Burum, D. P.; Shelby, R. M.

A new value for the nuclear magnetic moment of ^{141}Pr was obtained as $\mu_{nucl}(^{141}Pr)$ = 4.2754(5)μ_N. This is 2 orders of magnitude more precise than the best previous (atomic beam) measurement. Major limitations of previous measurements were circumvented by a direct measurement of the moment in an electronically excited state ($_1D_2$ of the Pr_{3+} ion in CaF_2), where electronic contributions to the nuclear moment are only 3 parts in 10^4.

14. Perturbed Aluminum-27 Photon Echo ENDOR Double Resonance in Praseodymium(3+)-Doped Yttrium Aluminate and Europium(3+)-Doped Yttrium Aluminate

Burum, D. P.; Macfarlane, R. M.; Shelby, R. M.

Al pure quadrupole spectra measured by photon-echo ENDOR double resonance (PENDOR) are reported for crystals of $YAlO_3$ doped with Pr^{3+} and for crystals doped with Eu^{3+}. These spectra, which correspond to Al nuclei adjacent to a rare earth impurity, are compared with the results of a conventional NMR study of ^{27}Al in $YAlO_3$.

15. Hole Burning and Optically Detected Fluorine NMR in Praseodymium(3+)-Doped Calcium Fluoride

Burum, D. P.; Shelby, R. M.; Macfarlane, R. M.

The interactions between Pr^{3+} in a tetragonal site of 0.01-atomic % Pr^{3+}:CaF_2 and the surrounding nuclei are investigated, primarily by means of optically detected NMR (ODNMR). This technique is based on the fact that hole burning in the 5941-Å $_3H_4 \leftrightarrow _1D_2$ transition takes place due to coupling between the rare-earth ion and neighboring $_{19}F$ nuclear spins. ODNMR lines are identified which are due to nearest-neighbor (NN), next-nearest-neighbor (NNN), and interstitial (i) F. The distorted positions of the NNN F are detected from the ODNMR data, but this is impossible for the other near neighbors due to strong covalent-bonding effects. Phys. models for the hole-burning and refilling processes are proposed which agree qualitatively with the hole shapes and ODNMR line intensities, and with the observation of rf-assisted optical hole burning when a strong magnetic field H_0 is applied parallel to C_4.

16. Optical Hole Burning by Superhyperfine Interactions in Praseodymium(3+)-Doped Calcium Fluoride

Macfarlane, R. M.; Shelby, R. M.; Burum, D. P.

Optical hole burning was observed in the 5941-Å transition of Pr^{3+} in a charge-compensated tetragonal site of CaF_2. The Pr^{3+} ground state is doubly degenerate and shows a large 1st-order hyperfine splitting, which is clearly resolved because of the very narrow inhomogeneous linewidth of 650 MHz. The hole burning involves a new mechanism, in which optically induced spin flips of neighboring nuclei (here ^{19}F) shift the optical transition frequency outside its homogeneous linewidth. This mechanism was confirmed by optical rf double resonance.

17. Low-power Multipulse Line Narrowing in Solid-State NMR
Burum, D. P.; Linder, M.; Ernst, R. R.

Multipulse line narrowing sequences were investigated with regard to performance at low radio-frequency power, and a new class of multiphase sequences specifically designed for low-power requirements is introduced. Of all sequences tested, BR-24 leads to optimum performance. The pulse width in a BR-24 expt. can be increased to 6 μs and beyond with only a minimal increase in linewidth. Fully windowless pulse cycles form a promising new class of multipulse sequences. One of these new techniques, BLEW-48, nearly equals, but does not surpass, BR-24 in dipolar suppression capability at low radio-frequency power.

18. A new "tune-up" NMR pulse cycle for minimizing and characterizing phase transients
Burum, D. P.; Linder, M.; Ernst, R. R.

A new pulse sequence, the flip-flip-flop cycle, which is useful for minimizing phase transients in a pulsed NMR spectrometer, is introduced. The cycle provides separate, quantitative measurements of the symmetric and antisymmetric parts of the phase transients, and virtually eliminates the need for an iterative tuning procedure. The flip-flip-flop cycle is analyzed using zeroth-order average Hamiltonian theory, and step-by-step guidelines for adjusting a 4-channel spectrometer are given.

19. Net Polarization Transfer Via a J-Ordered State for Signal Enhancement of Low-Sensitivity Nuclei
Burum, D. P.; Ernst, R. R.

An improved version is given of the heteronuclear coherence transfer expt. in NMR spectroscopy proposed by G. A. Morris and R. F. Freeman (1979). It permits uniform net polarization transfer via a J-ordered state in a wide variety of practical situation. Net polarization transfer by means of a short sequence of pulses is an attractive alternative to Overhauser polarization in many cases because the polarization transfer is much faster, leads to a stronger enhancement, causes almost no heating of the sample, and does not depend on cross-relaxation effects. In addition, the pulsed method can be used to selectively enhance lines in a decoupled spectrum which belongs to IS, I_2S, or I_3S multiplets.

20. Scaling of Heteronuclear Spin Interactions by Multipulse Sequences. Practical Guidelines
Aue, W. P.; Burum, D. P.; Ernst, R. R.

Multipulse sequences and their optimization are discussed for the scaling down of heteronuclear spin-spin interactions in the simplification of NMR spectra of rare spins; the discussion is limited to the scaling of proton-coupled ^{13}C spectra. The phase-alternated 2-pulse sequence is illustrated. The joined sequence special case is distinguished from the more general sepd. sequence. The following 3 criteria for determining optimum experimental parameters are considered: (1) offset insensitivity; (2) radiofrequency field insensitivity; and (3) radiofrequency field strength requirements.

21. Highly Flexible Pulse Programmer for NMR Applications
Dart, J.; Burum, D. P.; Rhim, W. K.

A pulse generator for NMR application is described. Eighteen output channels are provided to allow use in both single and double resonance experiments. Complex pulse sequences may be generated by loading instructions into a 256-word by 16-bit program memory. Features of the pulse generator include programmable time delays from 0.5 μs to 1000 s, branching and looping instructions, and the ability to be loaded and operated either manually or from a PDP-11/10 computer.

22. Proton Anisotropic Chemical Shift Spectra in a Single Crystal of Hexagonal Ice
Rhim, W. K.; Burum, D. P.; Elleman, D. D.

The proton anisotropic chem. shift spectra were obtained for the 1st time in a single crystal of hexagonal ice. Strong dipolar interactions between protons were averaged out by using an improved version of a multiple-pulse line-narrowing sequence, the 52-pulse cycle. The expt. was carried out in liquid-N_2 temperature so that no molecular motion was detectable in the spectra. This technique failed to confirm the orientational ordering of water molecules in the hexagonal ice. No hydrogen motion was observed at liquid-N_2 temperature

23. Analysis of Multiple Pulse NMR in Solids. III
Burum, D. P.; Rhim, W. K.

A 52-pulse cycle recently introduced in a communication, which has a substantially increased resolving power compared to previously available techniques, is analyzed in detail. Also, a new 24-pulse cycle which is essentially equiv. to the 52-pulse cycle in resolving power is introduced. These pulse cycles achieve their enhanced resolution compared to the REV-8 cycle by removing the effects of the homonuclear dipolar interaction in solids to higher orders of magnitude without reintroducing any dipolar terms eliminated by REV-8. Principles of pulse cycle decoupling are introduced which greatly simplify the systematic development of compd. multiple pulse cycles. Beginning with the 2-pulse solid echo sequence, how these principles could have been used in designing the WAHUHA and REV-8 cycles and the 14-pulse cycle recently introduced by Haeberlen is shown. The application of this method is further demonstrated by developing several new pulse cycles, such as a 12-pulse cycle equiv. to the 14-pulse cycle, the 24-pulse cycle, and the 52-pulse cycle. Finally, proton chem. shift tensor components for several org. solids which were measured using the 52-pulse cycle are reported without detailed discussion.

24. Proton NMR Study of Gypsum, CaSO4.2H2O, using an improved technique for Homonuclear Dipolar Decoupling in Solids
Burum, D. P.; Rhim, W. K.

A room-temperature NMR study of proton chem. shift anisotropy in gypsum was carried out by using a new multiple-pulse cycle which removes the dipolar interactions to 3rd order while retaining the advantages of REV-8 with regard to pulse imperfections. The power of the new sequence to decouple the homonuclear dipolar interaction is demonstrated by its ability to produce well-resolved chemical shift spectra for gypsum even at crystal orientations where the dipolar splitting is as great as 22 G. The new pulse cycle is made up of 12 4-pulse groups with 4 extra pulses inserted, giving a total of 52 $\pi/2$ pulses and a cycle time of 72 τ.

25. An Improved NMR Technique for Homonuclear Dipolar Decoupling in Solids: Application to Polycrystalline Ice
Burum, D. P.; Rhim, W. K.

A new multiple pulse NMR cycle is presented for decoupling the homonuclear dipolar interaction in solids; it has substantially more resolving power than currently available techniques. This pulse cycle removes the dipolar interaction to 3rd order and also eliminates those 1st-order cross terms which are removed by REV-8. A well-resolved chem. shift spectrum is presented for naturally abundant protons in polycrystalline ice which, when compared to the results of A. Pines et al.(1976) for 99% deuterated ice, reveals for the 1st time definite differences in dynamics and chem. shifts between the 2 cases.

26. New Technique for Single-Scan T1 Measurements Using Solid Echoes
Burum, D. P.; Elleman, D. D.; Rhim, W. K.

A simple technique for single-scan T_1 measurements in solids is proposed and analyzed for single exponential spin-lattice relaxation. In this technique, the direct spin heating caused by the sampling process is significantly reduced in comparison with conventional techniques by utilizing the solid echo to refocus the magnetization. The applicability of this technique to both the solid and liq. phases is demonstrated.

27. A Multiple Pulse Zero Crossing NMR Technique, and Its Application to Fluorine-19 Chemical Shift Measurements in Solids
Burum, D. P.; Elleman, D. D.; Rhim, W. K.

A simple, multiple pulse zero crossing technique for accurately determined the 1st moment of a solid state NMR spectrum is introduced. This technique was applied to obtain the ^{19}F chemical shift vs. pressure curves up to 5 kbar for single crystals of CaF_2 (0.29 ± 0.02 ppm/kbar) and BaF_2 (0.62 ± 0.05 ppm/kbar). Results at ambient temperature and pressure are also reported for a number of other F compounds. Because of its high data rate, this technique is potentially several orders of magnitude more sensitive than similar cw methods.

28. ADRF Experiments Using Near $N\pi$ Pulse Strings
Rhim, W. K.; Burum, D. P.; Elleman, D. D.
Physics Letters A (1977), 62A(7), 507-8.
An ADRF (adiabatic demagnetization radio frequency) and inverse repolarization phenomenon was obsd. in dipolar solids by applying a string of rf pulses in which the pulse angle was gradually varied past $n\pi$. This phenomenon, which is characteristic of discrete excitation schemes, is explained qualitatively.

29. Multiple-Pulse Spin Locking in Dipolar Solids
Rhim, W. K.; Burum, D. P.; Elleman, D. D.
Physical Review Letters (1976), 37(26), 1764-6.
Preliminary results are reported on a multiple-pulse spin-locking effect in dipolar solids. This effect has significant experimental advantages over prior techniques because of its high duty cycle for data collection. The spin temperature assumption can be applied to explain the rather long-term behavior of the spin system. It is demonstrated how this method can be applied to obtain magnetization curves almost instantly for $T1\rho$ decay and adiabatic demagnetization.

30. Extraction of Quadrature Phase Information From Multiple Pulse NMR Signals
Rhim, W. K.; Burum, D. P.; Vaughan, R. W.
Review of Scientific Instruments (1976), 47(6), 720-5.
A multiple pulse sequence (8-pulse sequence) used for high-resolution solid state NMR was analyzed with regard to the information available from each of the 4 wide sampling windows. It was demonstrated that full quadrature phase information can be obtained using only a single phase detector and that, for the commonly encountered situation where the spectral width is much less than the folding frequency, the signals from the various windows can be combined easily by using standard complex Fourier transform software. An improvement in the signal-to-noise ratio of 31/2 was obtained over either standard single or quadrature phase detection schemes. Procedures for correcting spectral distortions are presented.