

Pines, Alexander: Solid State NMR: Some Personal Recollections

Alexander Pines

University of California at Berkeley, Berkeley, CA, USA

I was born in 1945, the same year as NMR. I grew up in Rhodesia and then went to Israel to pursue my undergraduate studies in mathematics and chemistry at the Hebrew University of Jerusalem.

In 1968 I journeyed to the United States and entered the Massachusetts Institute of Technology (MIT) as a graduate student. There I was fortunate to work under the tutelage of John Waugh in the Department of Chemistry and the Research Laboratory of Electronics. It was an exciting time to be at MIT, and Waugh as well as postdoctoral co-workers from those days—among them Robert Griffin, Ulrich Haeberlen, Michael Mehring, and Won-Kyu Rhim—have remained my colleagues and friends for more than 25 years.

The MIT group's primary efforts at that time were directed toward the new area of multiple pulse and high-resolution NMR spectroscopy in solids. Waugh's accomplishments in average Hamiltonian theory and line narrowing were establishing much of the basis and the very language of modern pulsed NMR. The idea was to manipulate the spins by trains of pulses in order to average the spin interactions selectively—for example to eliminate dipole–dipole couplings while retaining the underlying chemical shifts, a sort of spin alchemy.

Participating in the study of coherent averaging and the challenging experimental techniques of multiple-pulse spectroscopy, including the magic sandwich time-reversal experiments (which appeared to violate the spin temperature hypothesis), was a stimulating educational experience for me, but it was natural to wonder if there might be an alternative way to observe chemical shifts in solids. An appealing prospect was the organic chemists' nucleus, carbon-13, which offered the possibility of resolved Fourier transform spectra in solids, owing to the isotope's low natural abundance and correspondingly weak dipole–dipole couplings. There would be no need for the demands of homonuclear multiple pulse sequences, and high power proton spin decoupling would suffice to eliminate the relevant heteronuclear couplings, but we anticipated that sensitivity might pose a problem. Here, however, we could capitalize upon the double resonance scheme of Hartmann and Hahn, whereby two different resonant frequencies are matched in the rotating frame, allowing the exchange of magnetization between different spin species. The process of cross polarization (CP) from abundant hydrogen to dilute carbon-13 combined with spin decoupling would allow us to enhance the sensitivity and resolution of the directly observed carbon signal.

The idea seemed promising, and we proceeded to design and construct a double resonance spectrometer with a PDP-12 controlled pulse programmer and data system. The experiments also required a novel probe that would allow cross polarization and direct observation of the enhanced carbon-13 signal in the presence of high power proton spin

decoupling. What we needed now was an appropriate model sample. It so happened that the late Henry Resing (known affectionately as Mr. Adamantane because of his work on plastic crystals) was visiting, and I asked him what would be an inexpensive compound (solid at room temperature) with at least two inequivalent carbon sites, but with the molecules reorienting rapidly and isotropically (in order to eliminate the chemical shift anisotropy) to yield laboratory and rotating frame spin–lattice relaxation times of about one second. He suggested adamantane.

Indeed, we were elated to observe resolved isotropic carbon-13 chemical shifts in solid adamantane, with ample signal/noise. We subsequently obtained resolved spectra allowing the measurement of carbon-13 chemical shift anisotropy in solid benzene and many other compounds, as well as signals from other dilute isotopes such as nitrogen-15 and silicon-29, leading some innocent bystanders to believe that high resolution solid state NMR of dilute spins might actually become useful in chemistry. We termed the technique proton-enhanced nuclear induction spectroscopy (proton-enhanced NMR for short) as a salute to the early foundations of nuclear induction laid by physicists. Combined with magic angle spinning (MAS), a legacy of Andrew, Lowe, and co-workers, incorporated by Schaefer and Stejskal soon after, the cross polarization/magic angle spinning (CP MAS) procedure was subsequently implemented and used on commercial spectrometers. Recent applications of CP MAS have included the possibility of measuring carbon-13 isotropic–anisotropic shift correlations through variable angle correlation spectroscopy (VACSYS) as well as the measurement of carbon–carbon and carbon–hydrogen dipolar correlations for the purposes of distance and structure determination in solids.

On completing my Ph.D. in 1972 I was awarded a Miller Fellowship in physics sponsored by Erwin Hahn at the University of California, Berkeley. Shortly afterwards, however, the Berkeley Chemistry Department offered me a faculty position, which I accepted, but not without some regret at passing up the opportunity to work directly with Hahn. Happily, Hahn, together with Mel Klein, has remained a mentor, colleague, and friend for more than two decades.

Over the years, our group at Berkeley (the so called Pinenuts) has been concerned with fundamental phenomena in NMR and chemical physics, hoping to develop techniques of some use in condensed matter chemistry and physics. Our work has involved a combination of concepts, theory, techniques, instrumentation, and applications to a variety of chemical systems and materials. Advances in spectral resolution, sensitivity and selectivity have remained consistent goals. I have been fortunate to work with, and learn from, a group of extremely talented and creative co-workers at Berkeley, including graduate students, postdoctoral fellows, and sabbatical visitors, some of whom are listed in Table 1; they were the ones who did the research and my story is largely theirs. In addition to research, I have devoted much time and effort to teaching. Beginning in the 1970s with advanced courses in physical chemistry, I was later persuaded by my colleague George Pimentel to take over the introductory general chemistry class which I have taught, on and off over the years, to many thousands of students. Both the freshmen and my research group, with their broad curiosity and their drive to understand the principles and beauty of science, have kept me alert and have enriched my academic experience. We

Table 1 Co-Workers at Berkeley

<i>Staff Scientist:</i> Gerard Chingas	<i>Administrative Assistant:</i> Dione Carmichael		
<i>Doctoral and Postdoctoral Students</i>			
Eric Abramson	Hideaki Fujiwara	Shigeru Matsui	Klaus Schmidt-Rohr
Jerome Ackerman	Holly Gaede	Thomas Meersman	Erika Schneider
Madis Alla	Sheryl Gann	Peter Meier	Athan Shaka
Stuart Allison	Joel Garbow	John Millar	Thomas Shatuck
Jay Baltisberger	Miriam Gochin	Karl Mueller	Jay Shore
Geoffrey Barrall	Philip Grandinetti	Luciano Mueller	David Shykind
Jean Baum	John Harwood	Michael Munowitz	Steven Sinton
Anthony Bielecki	Alfred Hohener	Eric Munson	Yiqiao Song
Angelo Bifone	Mei Hong	James Murdoch	Larry Sterna
Bruce Black	Shan Hsi	Alon McCormick	Boqin Sun
Russell Bowers	Hans Huber	Daniel Nanz	Dieter Suter
Stefano Caldarelli	Deidre Hugli-Cleary	Peter Neidig	Kiyonori Takegoshi
Daniel Caplan	Martin Hurliman	John Pearson	Jau Tang
James Chang	Thomas Jarvie	Zheng-Yu Peng	Ann Thayer
Jih-Wen Chang	Raz Jelinek	Dominique Petit	Karl Thier
Bradley Chmelka	Jonathan Jones	Tanja Pietrass	Malaine Trecocke
Herman Cho	Paul Jonsen	Marie Quinton	Robert Tycko
Chuck Connor	Marianne Koenig	Daniel Raftery	Shimon Vega
George Davenport	Andrew Kolbert	Linda Reven	Warren Warren
Charles de Menorval	Juergen Kritzenberger	Toomas Room	Daniel Weitekamp
Susan DePaul	Bernard Lamotte	Mark Rosen	David Wemmer
Gary Drobny	Russell Larsen	David Ruben	Ulrike Werner
Margaret Eastman	Chang-Jae Lee	Steven Rucker	Wrenn Wooten
Richard Eckman	Young Lee	Ryong Ryoo	Yue Wu
Hommo Edzes	Shang-Bin Liu	Joseph Sachleben	Yu-Sze Yen
Lyndon Emsley	Antoine Llor	Ago Samoson	David Zax
Matthias Ernst	Henry Long	Kurt Schenker	Marcia Ziegeweid
Lucio Frydman	Gunter Majer	Claudia Schmidt	Kurt Zilm
			Josef Zwanziger
<i>Sabbatical Visitors</i>			
Yakir Aharonov	Jozef Kowalewski	Hiroshi Moriyama	Robert Vold
Ray Dupree	Raphael Levine	Shaul Mukamel	Jin-Feng Wang
Soemi Emid	Ze'ev Luz	Zbigniew Olejniczak	Chaohui Ye
Allen Garroway	Metka Luzar	Dietmar Stehlik	Dieter Ziessow
Gina Hoatson	Michael Mehring	Takehiko Terao	Herbert Zimmermann

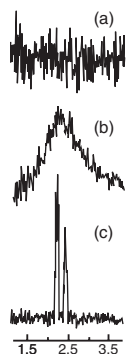
have continued to remind each other to refrain from the narrow path, not to hesitate to ask why and how, and never to accept simply on authority that something is impossible.

Our work at Berkeley in the early 1970s continued to deal with theoretical and experimental aspects of spin dynamics and solid state NMR, in particular the question of total adiabatic polarization transfer, the measurement of chemical shift tensors in single crystals, and the effects of symmetry-restricted motion on carbon-13 lineshapes in solids. The experiments required a homebuilt spectrometer (this time under the control of a new generation PDP-8 based pulse programmer and data system) as well as considerable effort in completing the superconducting joints, shim coils, and cryogenics of our primitive magnet. We also became intrigued by liquid crystals, for which we were able to use the carbon-13 tensors to study molecular ordering and phase transitions.

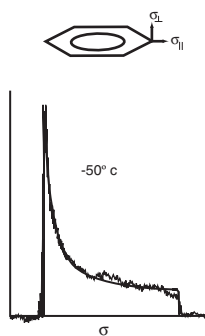
During that time, my colleague Charles Harris was also involved in magnetic resonance experiments that exploited the enormous sensitivity of optical detection to observe continuous wave electron paramagnetic resonance (EPR) microwave spectra in excited triplet states of molecular crystals. Because of the different rates of phosphorescence from the three triplet sublevels to the single ground state, microwave generated transitions between the sublevels could generate a change

in the phosphorescence signal by rearranging the sublevel populations, in analogy to continuous wave electron–nuclear double resonance (ENDOR). The detection of time domain signals, however, was a different matter—it was considered to be impossible because triplet sublevel coherences did not affect the populations and were therefore invisible to the phosphorescent emission; indeed, the detection of free induction decays and spin echoes in excited triplet states was traditionally performed only by direct microwave detection, with limited sensitivity. After pondering the possibility of applying optical detection to observe the spin coherence, we hit upon a solution that involved an additional read pulse, with which we were able to detect electron spin free induction decays and spin echoes through their effect on the optical emission. It was an early example of coherence transfer by transformation of the off-diagonal elements of the density matrix in order to map out the evolution of a perhaps invisible or hidden coherence, point by point.

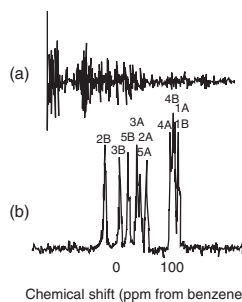
What we learned from these experiments soon proved useful in the multiple quantum NMR experiments that followed. Our original intention was to study hydrogen NMR in solids, to provide an alternative to homonuclear multiple pulse sequences, this time by diluting protonated samples with deuterium. The idea was reminiscent of the approach



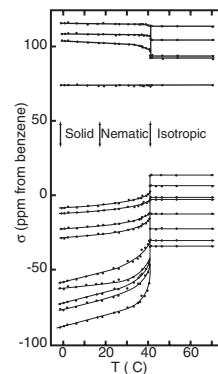
1. CP Adamantane



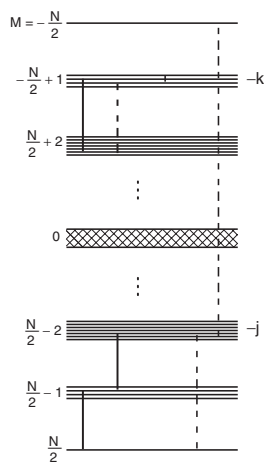
2. Benzene



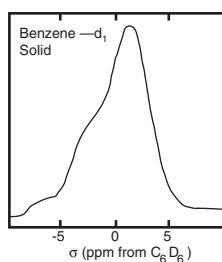
3. Durene Crystal



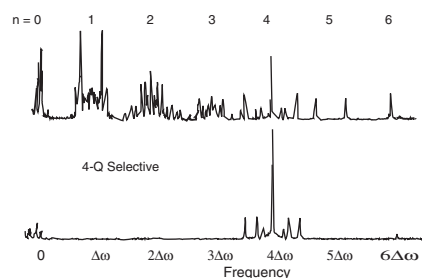
4. Liquid Crystal



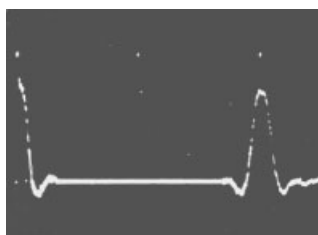
5. MQ Spectroscopy



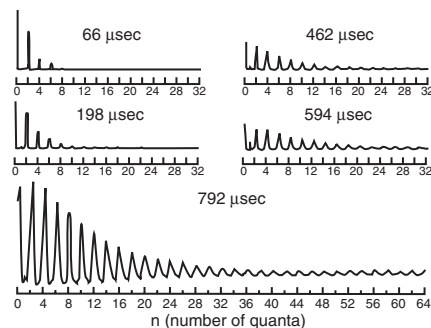
6. DQ Spectrum



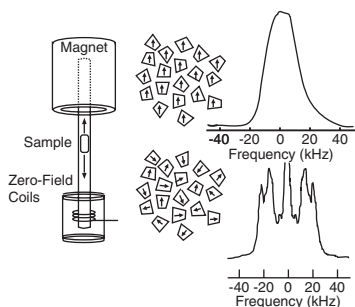
8. Benzene-LC MQ Spectra



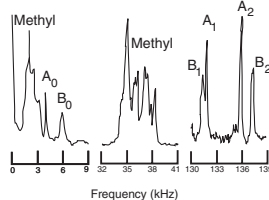
7. Magic Sandwich Echo



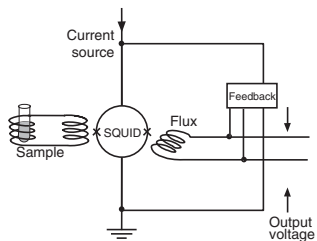
9. MQ Solids



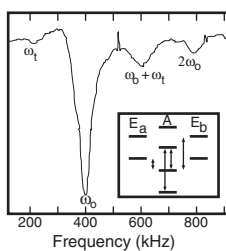
10. Zero-Field NMR



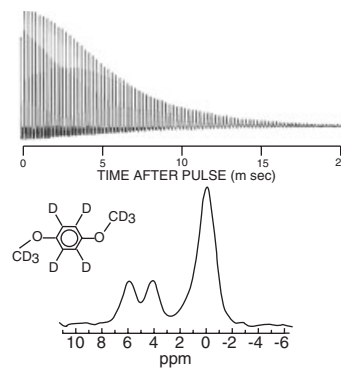
11. Deuterium Zero-Field



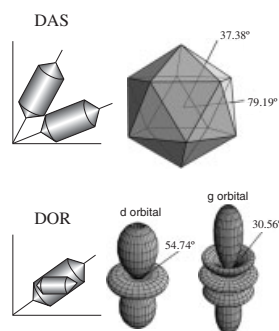
12. SQUID Spectrometer



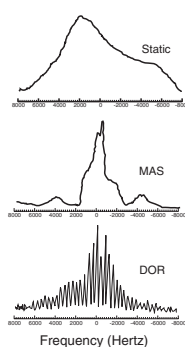
13. SQUID Methyl Tunneling



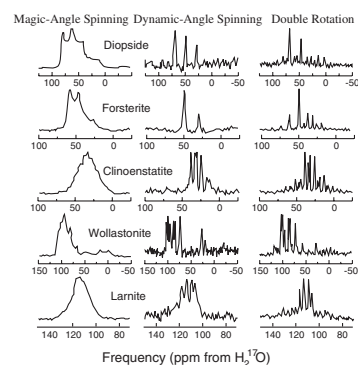
14. Deuterium MAS



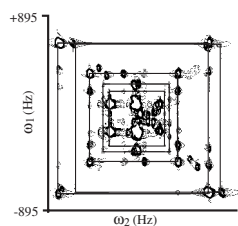
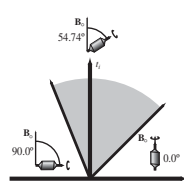
15. Quadrupolar Nuclei



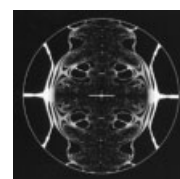
16. Sodium-23



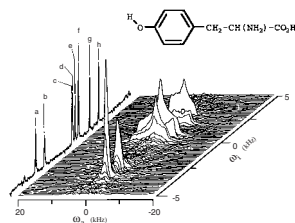
17. Oxygen-17



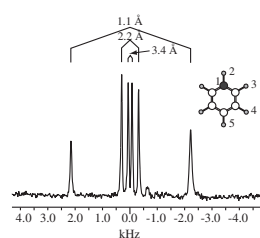
19. Dipole-Dipole Correlations



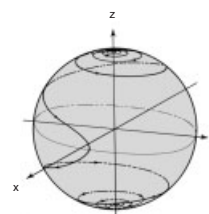
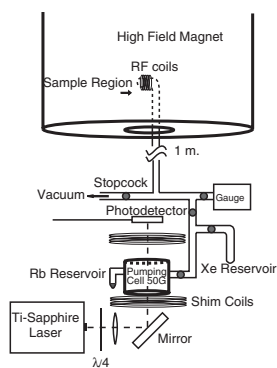
21. Iterative Sequence



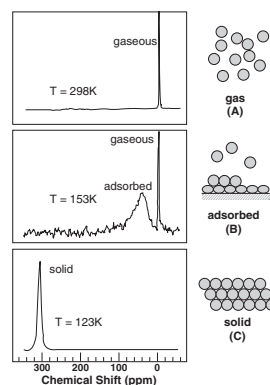
18. VACS



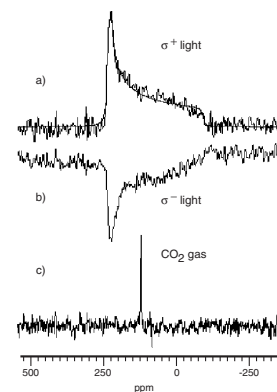
20. Resolved Local Fields

22. Sech π Pulse

23. Optical Pumping Spectrometer



24. OP Xenon-129 Surface

25. OP CP $^{129}\text{Xe} - ^{13}\text{CO}_2$

taken earlier with carbon, and here again there was a heteronuclear interaction that needed to be decoupled. The hydrogen–deuterium coupling, however, seemed futile to average because the wide, quadrupolar broadened deuterium line would require prohibitive radiofrequency power, but it was conceivable that we could exploit double quantum decoupling which had recently been used by Meiboom and co-workers in liquid crystals. Indeed, narrowband irradiation of the (+1, -1) transition of the deuterium with modest power yielded a resolved hydrogen spectrum, and in this way we could

observe the chemical shift anisotropy of hydrogen in ice—a notoriously difficult system for homonuclear multiple-pulse techniques. This approach has also been useful for obtaining resolved hydrogen dipole–dipole couplings and, combined with MAS, is an alternative approach to high-resolution hydrogen NMR in solids.

The next question, which emerged from our double quantum decoupling work and our previous experience with indirect detection of invisible microwave coherences, involved the possibility of preparing and observing, in the time domain,

the forbidden deuterium double quantum transition. Related work was being done independently by Hashi and co-workers. Having developed an appropriate spin-1 formalism involving fictitious spin-1/2 operators, we learned how to excite and detect the seemingly invisible two quantum coherence, point by point, by means of soft double quantum pulses (or pairs of hard pulses) combined with coherence transfer read pulses. Since the double quantum superposition should evolve independently of the quadrupole coupling, its spectrum would, in principle, reveal the deuterium chemical shift buried beneath the enormous quadrupolar broadening. By sidestepping rather than attempting to average the quadrupolar coupling, we were thus able to measure the chemical shift anisotropy of hydrogen in solid benzene. Various manifestations of double quantum coherence followed directly, including double quantum spin locking, cross polarization, spin diffusion, and magic angle spinning.

The spin-1 theory and experiments revealed the two-fold sensitivity of double quantum coherence to resonance offsets and radiofrequency phase shifts—double quantum spin locking, for example, was accomplished with a forty-five degree phase shift. Shortly thereafter, we provided an extension, namely the n quantum phase shift, to multiple quantum coherences in coupled spin-1/2 systems; this allowed a number of developments, including the separation of coherence orders (beginning with the progressively simplified spectra of orders zero through six in oriented benzene) by time proportional phase incrementation (TPPI), selective excitation of n quantum spectra (despite the arguments of some authorities that selective excitation was not possible), iterative multiple quantum sequences, multiple quantum filtering, imaging, relaxation and diffusion schemes, heteronuclear multiple quantum coherence experiments, bilinear rotation decoupling (BIRD), scalar (isotropic) recoupling, and total coherence transfer. The use of time-reversal sequences made it possible to produce two-dimensional schemes with symmetrized (conjugate) preparation and mixing propagators, yielding pure in-phase signals and allowing the observation of high n quantum spectra (sometimes in excess of one hundred quanta) and spin counting in liquid crystals and solids. We were delighted to see many of the multiple quantum ideas incorporated into high-resolution multidimensional liquid spectroscopy as well. For N spins, the high order ($N-1$ and $N-2$) spectra turned out to be particularly useful for the determination of molecular structures and conformations. Some of the experiments required the application of thousands of pulses, bringing to my mind the comment of Hahn when he heard about the original dipole–dipole time-reversal experiments—With that many pulses I could bring back the Messiah.

Three other areas that occupied our attention during the early 1980s were the magnetic isotope effect (through which we were able to obtain noticeable enrichments of carbon-13), broadband and selective excitation schemes involving iterative sequences and hyperbolic secant modulations, and the development of time domain zero-field NMR. Our long-standing interest in resolution and sensitivity led us to develop a pulsed version of nuclear quadrupole resonance (NQR) field cycling, by which it was possible to remove the orientational broadening from a powder spectrum while retaining resolved quadrupole and dipole–dipole couplings. The further development of Fourier transform zero-field spectroscopy included

various (sometimes surprising) analogs of multiple pulse techniques, spin decoupling, time reversal, spin diffusion, two-dimensional correlations, and chemical exchange. Eventually, too, we used a superconducting quantum interference device (SQUID) to detect the nuclear magnetic flux directly in zero field. Direct detection eliminated the restrictive requirements of field cycling and made it simple to obtain nitrogen-14 spectra and to study other low-frequency phenomena such as quantum tunneling in zero and low magnetic fields.

In the late 1980s, we were concerned with two aspects of the geometry of quantum mechanics and spin dynamics. On the one hand, the concepts of Berry's phase and holonomy made it possible to answer fundamental questions about quantum evolution without recourse to explicit solutions of the Schroedinger equation. Geometric concepts and gauge symmetry were sufficient to explain a number of effects that arise in systems undergoing cyclic evolution. Nuclear spins provided an ideal arena for the demonstration of geometric phases and related phenomena, and the behavior was consistent with a unification of other systems and phenomena as diverse as light, Jahn–Teller molecules, and the reorientation of falling cats.

Geometry and symmetry were also at the heart of our approach to averaging second-order anisotropic broadening effects in NMR, for example those due to quadrupolar couplings. Although MAS was very useful for the averaging of anisotropic interactions of spin-1/2 nuclei such as hydrogen, carbon-13, nitrogen-15, fluorine-19, silicon-29, and phosphorus-31, a long-standing problem in the field was what to do about the obviously important quadrupolar nuclei such as oxygen-17, sodium-23, and aluminum-27. In the presence of quadrupole couplings, the resolution was limited by second-order broadening, which is incompletely averaged by MAS.

The solution, for which we developed both the theory, with independent work by Llor and Virlet, and demonstrated the initial experiments (with the indispensable support of Berkeley's machine shop), involved motional averaging through sample spinning about two axes. Two techniques emerged—dynamic angle spinning (DAS) and double rotation (DOR)—which brought to quadrupolar nuclei the kind of resolution previously reserved for spins-1/2. During this period our laboratory often felt like a dental clinic, with the whizzing and whining sounds and rich harmonics of dynamic-angle and double rotor probes.

Whereas the geometry of MAS could be considered a dynamic implementation of cubic symmetry, an appropriate approximation to the sphere for the purpose of averaging second rank tensors, the new spinning techniques involved the next approximation to the sphere, namely icosahedral symmetry, necessary for the averaging of spherical harmonics or tensors up to fourth rank. The first experimental results were obtained for sodium-23, soon followed by high resolution spectra of boron-11, oxygen-17, aluminum-27, and rubidium-87. Applications of DAS and DOR have recently been demonstrated in a number of materials including polymers, minerals, oxides, zeolites, catalysts, and glasses, and commercial probes are now available from the instrument companies.

The most recent work in our laboratory concerns the possibility of surface NMR in samples with low surface area, a relevant interface between NMR and the realm of surface chemistry and catalysis. This poses a prominent challenge in terms of selectivity and sensitivity because of the low

concentration of surface spins in the sample. Our approach was inspired by the work of Happer and co-workers who spin-polarized xenon by means of optical pumping. We used laser-polarized xenon as a sensitive NMR spy of the surface, exploiting the sensitivity of xenon chemical shifts to chemical environment, as demonstrated by Fraissard and co-workers. The spin-polarized xenon was condensed onto the surface of a polycrystalline sample in high magnetic field where surface-specific NMR signals were observed with high signal/noise. In subsequent experiments it has been possible to transfer, by cross polarization, the high xenon spin polarization to adjacent spins, including hydrogen and carbon-13, giving rise to surface-selective and enhanced NMR spectra. With these experiments we appear to have come almost full circle—back to the original ideas of cross polarization and solid state NMR of dilute spins.

Over the last 25 years I have had the privilege of witnessing three of the major developments in NMR: magnetic resonance imaging, multidimensional spectroscopy, and high-resolution solid state NMR. Solid state NMR has progressed from the days of wide-line NMR, a curiosity for chemists, to the realm of modern high-resolution spectroscopy. These remain exciting times for solid state NMR as theory and experiments are further developed and used in many laboratories for chemistry and materials science; I look forward to the next generation of developments and surprises.

SELECTED PUBLICATIONS

Papers that illustrate our work in more detail and provide references to the relevant literature are listed below.

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17. NMR Study of Molecular Reorientation under Fivefold Symmetry: Solid Permethylferrocene, D. E. Wemmer, D. J. Ruben, and A. Pines, *J. Am. Chem. Soc.*, 1981, **103**, 28–33.
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Biographical Sketch

Alexander Pines. b 1945. B.Sc., 1967, Ph.D., 1972, Chemistry, M.I.T. (supervisor John Waugh). Faculty, University of California, Berkeley, and Materials Science, Lawrence Berkeley Laboratory, 1972–present, currently Professor and President's Chair, president ISMAR 1992–1995. Research specialty: solid state NMR theory and experiment.