Foreword

The year 2014 marks the 20th Anniversary of the publication (appearing in *Nature* and co-authored by me and several others) that first reported the magnetic resonance imaging of a hyperpolarized noble gas in a biological sample—^{129}Xe in the lungs of a mouse. The study of optical pumping, spin-exchange, and angular-momentum-transfer in atomic systems rather suddenly had a quite visible, interesting, and viable application that had potential clinical relevance. MRI with hyperpolarized noble gases is being pursued now by many groups worldwide and has continued to develop, if a bit methodically, toward clinical relevance. All the while a smaller group of scientists, mostly physicists and a few chemists, have continued to pursue the basic physics of spin-exchange optical pumping, which has its roots in the early work of Kastler and co-workers in Paris in the late 1940s and is absolutely crucial to the success of the various applications. I have worked both in the MRI application and on the basic physics, and while the former often pays the bills, the latter (as exemplified by a portion of this thesis) is probably a bit closer to my heart. My group has worked on longitudinal nuclear spin relaxation of ^{129}Xe in frozen hyperpola-rized xenon for some time, since it relates to how one generates and stores large quantities of hyperpolarized ^{129}Xe for various applications, such as lung MRI.

With this work, Dr. Limes has made the only truly reproducible T_1 measurements of solid ^{129}Xe near 77 K, the temperature at which hyperpolarized ^{129}Xe is usually cryogenically accumulated. His experiments have demonstrated differences in relaxation dependent upon how the solid is condensed (polycrystalline "snow" or "ice" that passes through the liquid phase prior to freezing), and he has also shown why previous results by our own and other groups were less consistent and reproducible. To do all this, Dr. Limes used a glass-dewar/NMR probe that can condense hyperpolarized ^{129}Xe gas as a polycrystalline snow, but can also manipulate the sample through the liquid phase and back to the solid state. The NMR spectrum is used to determine the amount of each phase in the sample. Mark also worked to thoroughly understand the Raman-phonon scattering relaxation theory for a spin-1/2 lattice (developed by Happer from earlier work by van Kranendonk) and its potential limitations. He has proposed modifications that may explain both the longer T_1 values that he now consistently observes compared to the published theory, as well as an observed linear component to the T_1 temperature dependence that would not be predicted by the

Raman mechanism alone. At once, one sees in this work Dr. Limes' ability to conduct elegant experiments, provide the needed theoretical background, and to pursue doggedly a difficult measurement problem that has previously produced inconsistent or inexplicable results.

Another significant portion of this thesis came out of collaborative work of our group with that of Christoph Boehme, under the aegis of the Utah Materials Research Science and Engineering Center (MRSEC), awarded by the U.S. National Science Foundation in 2011. Prof. Boehme had been trying for more than a year to get a student to do computational modeling of the nature of the Rabi nutation spectrum for two coupled spins (as with electron-hole charge carriers in a semiconductor) in different regimes of dipolar-coupling and exchange-coupling strengths. Dr. Limes' was able to properly implement a Liouville-superoperator formalism to solve the problem numerically and to generate the complicated two-spin spectra across the multi-dimensional parameter space; the work was done in a matter of a couple of months. These computational results have been validated by others from both an analytical perspective and through experimental work. The ongoing work of this particular collaborative group within the Utah MRSEC is to understand spin-dependent carrier transport in organic semiconducting devices, such as organic LEDs. Although use of the spin degree of freedom in these materials is an emerging field, the promise of cheap, easily synthesized organic semiconductors has already been realized in modern portable electronics (cell phones, tablets, *etc.*) The problem Dr. Limes' addresses here is relevant precisely because weak spin-orbit coupling in these materials provides for weak, coulombically bound electron-hole pairs (polaron pairs—precursors to exciton pairs), for which the spin-permutation symmetry is both non-trivial and alterable with microwave fields.

Finally, the third major portion of this thesis addresses a problem in nuclear magnetic resonance (NMR) that has potential far-reaching implications for the broad study of two-level systems. Dr. Limes led the experimental effort to validate the theoretical predictions having to do with beats in the Rabi precession pattern in the presence of a small longitudinal modulation field (added on top of the main applied Zeeman field). The predictions stem from the analysis of a weakly driven two-level system *with* such modulation, which can be mapped onto a strongly driven system *without* such modulation, and suggest that different regimes of spin dynamics, previously known for a strongly driven system (i.e., multi-photon resonances) can be realized under easily accessible (conventional NMR) conditions with proper choice of modulation frequency and amplitude. The theoretical work was done by Prof. Mikhail Raikh in our department (also as a collaborative MRSEC effort), along with his graduate student, Rachel Glenn. Mark brought Dr. Glenn into the laboratory and had her help with the design and execution of these experiments. This work has stimulated ongoing experiments in our laboratory, first to convert this experiment to one in which the radiofrequency field is modulated instead of the applied magnetic field, and ultimately to employ these techniques to perform useful NMR spin manipulations in solid materials.

I believe it is relatively rare for a graduate student to work so closely and productively with three different faculty members on three separate but related projects in pursuit of a Ph.D. It speaks to Dr. Limes breadth and versatility as a physicist that he was able to generate and validate important results in each of the three main areas of his thesis.

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Abstract

Several studies in magnetic resonance experiment and theory are presented. The longitudinal relaxation of solid ^{129}Xe is shown to have an unexpected structural dependence through experiments that provide previously unattainable reproducibility; also, groundwork is laid for theories that describe the observed data. A history of the field is given, including a theory of nuclear spin relaxation due to the coupling of the spins to the phonon bath, as well as the description of an extension of this theory. Theoretical work is also presented that involves nontraditional methods of magnetic resonance detection, such as optically and electrically detected magnetic resonance in semiconducting material. This work confirms, using computational and theoretical methods, the presence of dipolar coupling between two paramagnetic spin-half states to account for observed behavior in Rabi oscillations resulting in an increase of the Rabi frequency by a factor of $\sqrt{2}$; however, it is also shown that a strong presence of exchange coupling is required. Additional Rabi oscillation studies are given that involve experimental NMR water data, which confirm predictions of Rabi oscillation beat envelopes in three different regimes of longitudinal field modulation during a magnetic resonance experiment. Ancillary material include results from: a theoretical study of Rb atomic transition strengths, transverse relaxation in dilute-spin solid ^{129}Xe, and longitudinal relaxation of gaseous ^{129}Xe with regards to practical hyperpolarized ^{129}Xe storage.

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