Materials Properties Evaluated by Nuclear Magnetic Resonance (NMR) Relaxation Studies

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Abstract

Nuclear Magnetic Resonance (NMR) spectroscopy is a well-known analytical technique that uses the excitation of nuclear spins for solving chemical structures. Relaxometry is an emerging field of NMR spectroscopy where information is gained about interactions of nuclear spins with their surroundings. In NMR relaxometry investigations, the time it takes to lose the correlation between excited spins provides insight into viscosity, local mobility, or other properties based on molecular motion and intermolecular forces. The CPMG (Carr-Purcell-Meiboom-Gill) relaxation technique is the most common method for extracting relaxation time constants with NMR spectroscopy. Several sets of CPMG experiments are used to support ongoing research projects at S&T.

Introduction

Excited nuclear spins can lose their energy by a relaxation process called spin-lattice relaxation, which ultimately leads to the re-establishing of thermodynamic equilibrium. The time constant of spin-lattice relaxation is T_1. To measure T_1, nuclear spins are excited in an external magnetic field by an inversion pulse (180° pulse), after which a time τ is granted to allow for spins to turn back to equilibrium. At the conclusion of τ, a 90° pulse is used to measure the remaining magnetization.

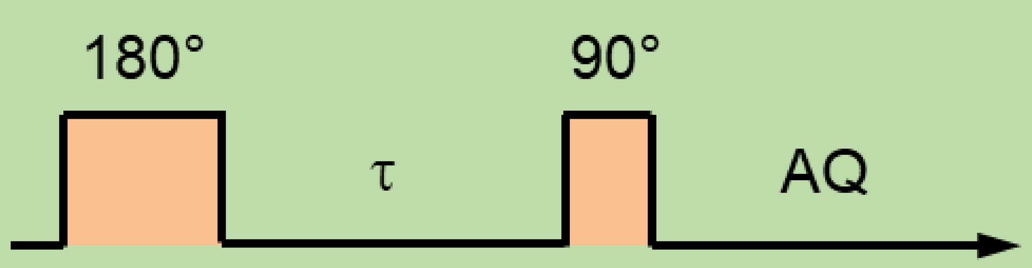

Fig.1: Pulse protocol for the measurement of T_1 relaxation time constants, where τ is the variable relaxation delay and AQ is the signal acquisition period.

By gradually increasing the relaxation delay τ, an NMR signal intensity is recorded, which exponentially approaches the signal intensity of thermodynamic equilibrium.

Transverse Relaxation of Phase-Correlated Nuclear Spins

While T_1 relaxation is typically measured by the 180°- τ - 90° inversion-recovery experiment, another relaxation time constant, T_2, refers to the phase correlation of nuclear spins after a 90° excitation. This relaxation is called spin-spin relaxation and refers to a loss of phase correlation. Some of the phase correlation can be refocused in a 180° pulse spin-echo experiment. The CPMG spin-echo experiment (Fig.2) measures the loss of spin-spin correlation that cannot be refocused. The spin-spin correlation that cannot be refocused is due to random motion and molecular interactions.

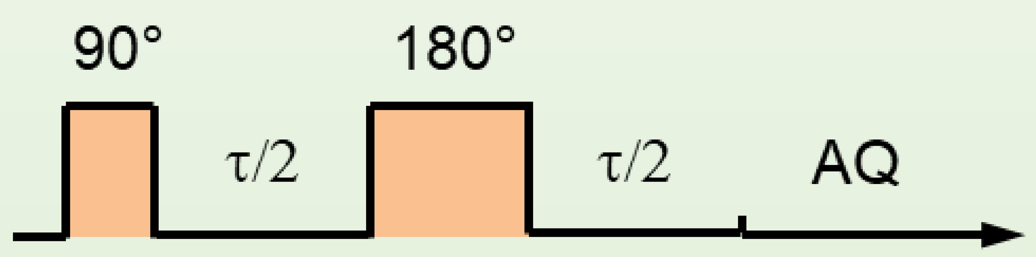

Fig.2: Pulse protocol for the measurement of T_2 relaxation time constants, where the variable relaxation delay τ is separated into two equal time segments that are interleaved with a 180° refocusing pulse.

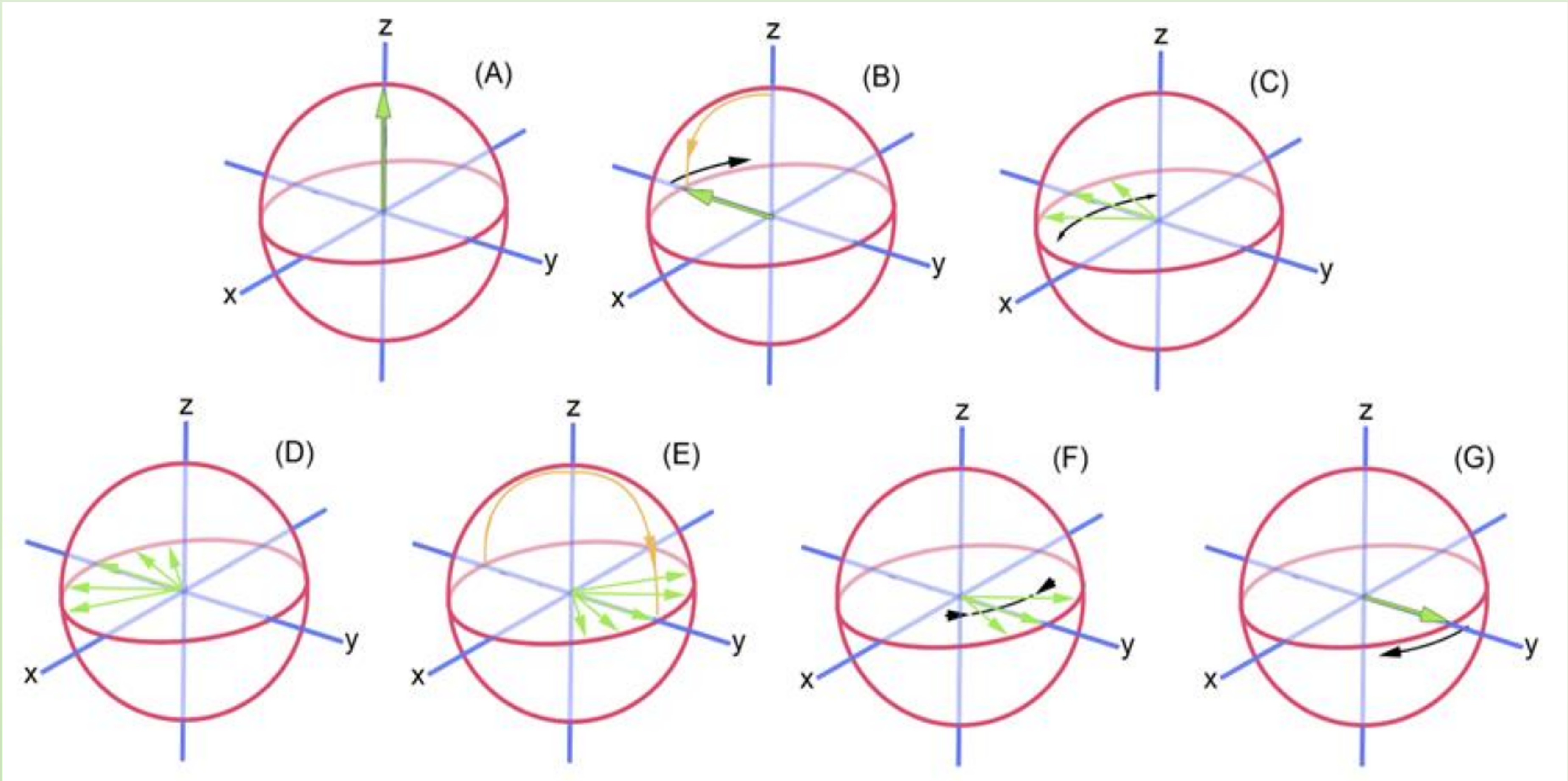

Fig.3: Path of nuclear magnetization during a CPMG pulse sequence (Fig.2). After a 90° pulse, transverse magnetization loses its phase correlation. Some of the lost correlation is refocused by a 180° pulse.

Relaxation Analysis

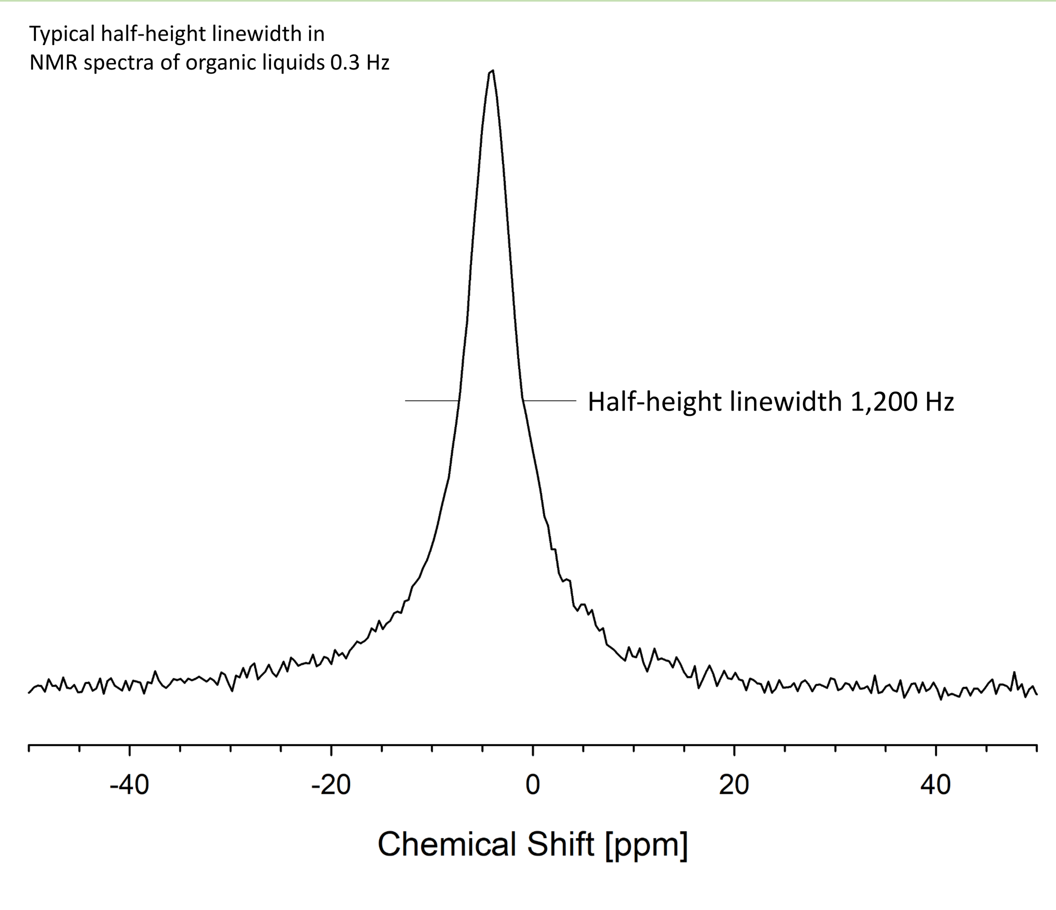

Fig.4: 200-MHz ^{1}H NMR spectrum of an asphalt binder sample (bitumen). Only one, very broad signal is observed, and no further structural information is identifiable on the chemical-shift axis.

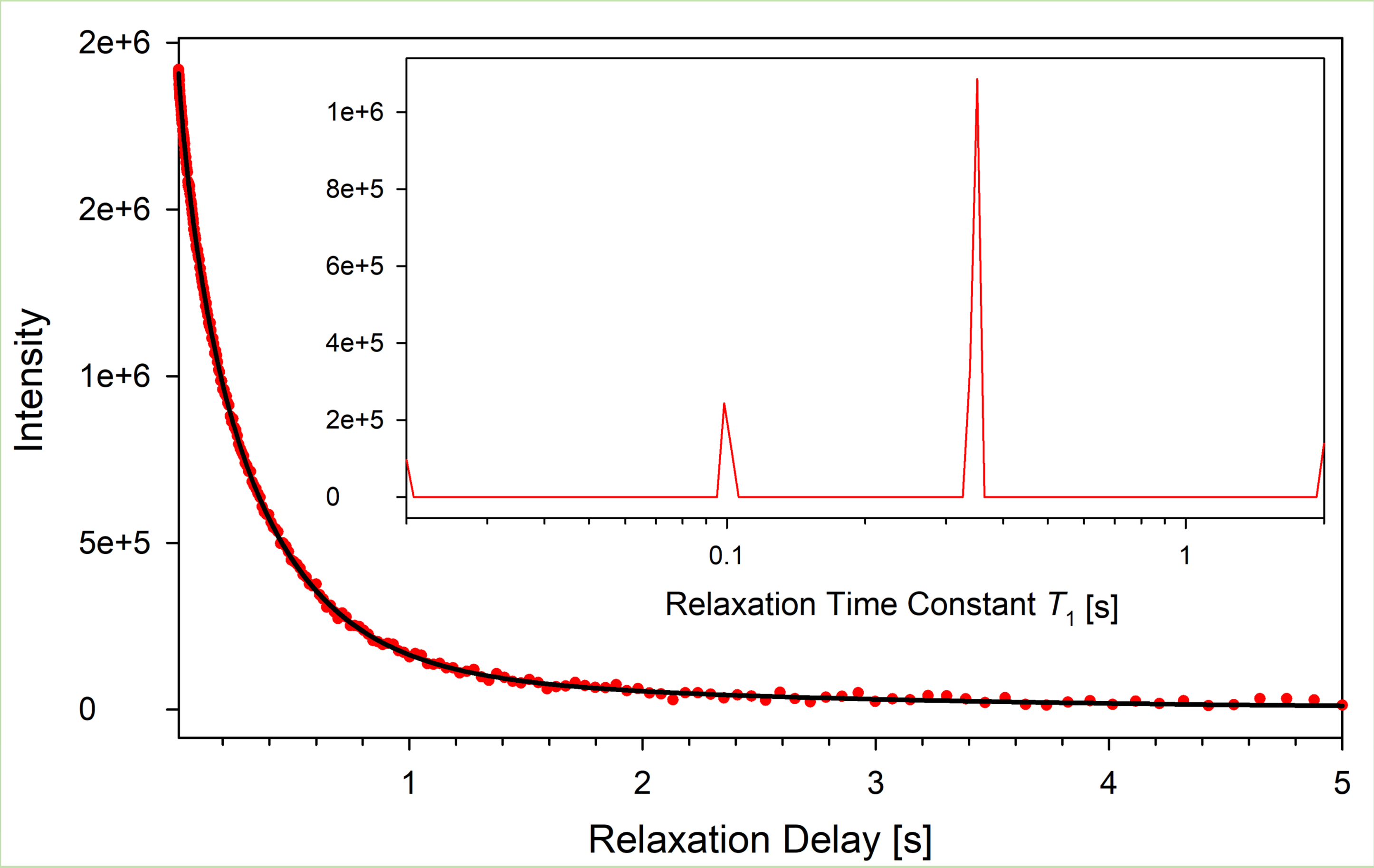

Fig.5: 200-MHz ^{1}H NMR relaxometry analysis of an aged asphalt binder sample (bitumen). The inset plot shows two relaxation time constants. The signal at 300 ms indicates regular asphalt behavior, while the signal at 100 ms points to degraded asphalt through oxidation and UV radiation.

Conclusion

Deterioration of asphalt is a major infrastructure problem and its rejuvenation an important field of research and development. In NMR relaxometry, it is known that, in solid materials, T_2 relaxation is faster than T_1 relaxation. However, we discovered that T_2 relaxation in asphalt samples is so fast ($T_2 \approx 200$ μs) that CPMG relaxation measurements fail to generate reliable results. Therefore, T_1 measurements using the traditional inversion-recovery technique may be the better choice to characterize aging asphalt. With T_1 analyses, we may be able to identify the progress of aging in asphalt samples.

Further Applications

The purpose of this research is to explore whether T_2 relaxation measurements will be a better way for identifying materials properties and their every-day performance. It was hypothesized that the utilization of T_2 relaxation would be a quicker way of recording relaxation times and being an efficient way of gathering meaningful data. Unfortunately, our first investigations with aged asphalt samples turned out not to be a good application for this technique.
Preliminary relaxation experiments were also conducted to investigate, for example, the industrial production of methanol from natural gas. Relaxometry results are expected to assist in improving the conversion yields of this large-scale industrial catalytic reaction. Further investigations are needed to determine the effectiveness of T_1 and T_2 relaxation measurements.

Acknowledgments

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