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[Field Research Laboratory. Socony Mobil Oil Company. Inc.. Dallas. TX]

The nuclear spin relaxation times T_1 and T_2 are calculated for two identical atomic nuclei of spin ½ in an ellipsoid undergoing rotational Brownian motion in the motionally narrowed regime. Five correlation times are obtained for a completely asymmetric ellipsoid. For nonviscous liquids. $T_1 = T_2$. [The _SCI_® indicates that this paper has been cited in over 520 publications.]

NMR Relaxation and Nonspherical Molecular Rotation

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My continuing interest in relaxation times in NMR began when I was starting my thesis work in 1953 at Illinois under the direction of Professor H.S. Gutowsky, who pioneered high resolution NMR using homebuilt spectrometers incorporating specially manufactured permanent magnets. No commercial NMR machines were available at Illinois. One of the duties of a new student was to "shim" the magnet. This involved measuring the NMR frequency at various locations in the magnet gap with a small sample and then making the magnetic field more homogeneous by grinding down the magnet pole caps at regions of high NMR frequencies. Needless to say, this procedure was uninspiring. Then, when measuring the chemical shift of a liquid sample, I found that sudden frequency shifts of the radio frequency oscillator (quartz stabilized frequency synthesizers were far in the future) made the procedure conducive to ulcers.

I was given the opportunity to construct pulse NMR apparatus and make T_1 and T_2 measurements. I readily agreed to do this, and I built the first pulse NMR spectrometer in a university chemistry department (a pulse NMR spectrometer is a pulse PQR spectrometer with an added NMR magnet. I used this machine to carry out my thesis research on PQR

and NMR relaxation times and their relationships to structure and motions in the molecular framework of the sample, an exciting area of research.

Mobil recruited me to apply NMR relaxation to problems in petroleum exploration and production research. NMR was viewed as a potentially valuable tool in investigating the interactions of liquids with rock mineral surfaces, which can be important factors in the flow of water and oil in porous rocks. Previous NMR research at Mobil concentrated on molecular motions and interactions of approximately monomolecular layer coverage of water on silica gel (the surface of silica gel was assumed to be like that of quartz in sandstones). My assignment was to continue this research and extend it to clay mineral surfaces.

My relaxation time data did not agree with conventional theory based on isotropic molecular reorientation. Consequently, I became interested in anisotropic motion and its consequences on NMR relaxation times and spectra. The report[1] of doublet NMR spectra resulting from nonspherical symmetry of the proton-proton direction of rapidly moving water molecules in noncubic cages of zeolites confirmed its existence and importance. A highly cited paper[2] contains my first theoretical calculations on the topic and is the basis for interpreting my early experiments on water adsorbed on silica gel.[3]

My research at Mobil also entailed NMR relaxation measurements on liquids such as hydrocarbons. Since such molecules can be nonspherical, I reasoned that a proper interpretation of such data in terms of molecular motion must be based on rotational anisotropy. My earlier work was based on internal motion within a body reorienting isotropically, and I needed a more general model. In this work I used F. Perrin's elegant (but ignored) approach[4] to calculate in a simple fashion the rates of change of average values of orientational functions for ellipsoids subject to anisotropic rotational diffusion.

I tried to present the theoretical material in a form most useful to the experimentalist (many theoretical papers are incomprehensible to experimentalists). I think that is one reason this paper is highly cited. Actually, it was cited infrequently for many years, probably because few experimenters had the equipment capable of the measurements required to apply the theory. The frequency of citation rose greatly with the advent of pulse Fourier transform NMR spectrometers and with the application of NMR to medical research. Also, this work led, in part, to my receiving in 1975 the W.T. Doherty Award of the Dallas-Fort Worth Section of the American Chemical Society. Recently, this approach has been modified and generalized for the case of methyl groups in liquids.[5]

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