

THE UNIVERSITY OF MANITOBA

A DYNAMIC NUCLEAR MAGNETIC RESONANCE  
STUDY OF FLUORINE EXCHANGE IN  
TETRAPROPYLAMMONIUM METHYLTETRAFLUROSILICATE

by

RONALD KIRK MARAT

A THESIS

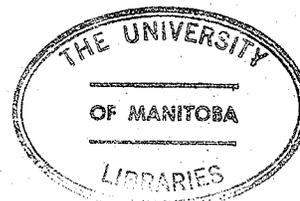
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A dissertation submitted to the Faculty of Graduate Studies of  
the University of Manitoba in partial fulfillment of the requirements  
of the degree of

MASTER OF SCIENCE

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ABSTRACT

A dynamic nuclear magnetic resonance lineshape analysis has been employed in a mechanistic study of the intermolecular fluorine exchange found in the methyltetrafluorosilicate moiety. The exchange is found to be second order in methanol and  $-0.2$  to  $-0.5$  order in the parent fluorosilicate salt. These results are shown to be inconsistent with the previously described mechanisms, and alternate mechanisms based on expansion of the coordination around silicon from five to six are presented. The exchange is found to be inhibited by Lewis-bases such as pyridine. The apparent exchange rate is sensitive to the fluorine spin-lattice relaxation time, under certain circumstances.

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"Synthesis of Phosphorus and Silicon Fluorides and Mechanisms of Ligand Exchange." R. K. Marat and A. F. Janzen, presented at the 58<sup>th</sup> Canadian Chemical Conference, May, 1975.

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CHAPTER 1 NATURE OF THE PROBLEM

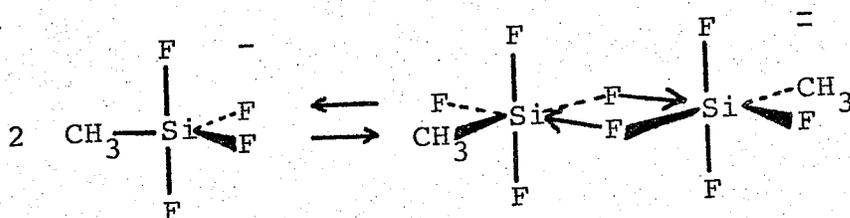
This study represents part of the continuing interest in this laboratory in the exchange mechanisms of the main group fluorides. (2-6) In particular, the work described in this thesis is a dynamic nuclear magnetic resonance (dnmr) study of the intermolecular fluorine exchange process in the five coordinate silicate salt tetrapropylammonium methyltetrafluorosilicate,  $[\text{CH}_3\text{SiF}_4]^-$   $[\text{N}(\text{C}_3\text{H}_7)_4]^+$ .<sup>†</sup> This salt was first prepared by Klanberg and Muettterties (1) in 1968, who found that the  $\text{CH}_3\text{SiF}_4^-$  ion underwent two distinct types of exchange processes: an intramolecular rearrangement of the fluorines which results in the four fluorines being magnetically and chemically equivalent, and an intermolecular exchange which proceeds at a rate fast enough to cause the loss of nuclear spin-spin coupling between the fluorines and the protons in the methyl group. The structure of the ion was assumed to be trigonal bipyramidal with the methyl group occupying one of the equatorial sites, analagous to the structure of  $(\text{C}_6\text{H}_5)_2\text{SiF}_3^-$ . (1) The intramolecular rearrangement of a trigonal bipyramid has been recently reviewed, and will not be of great concern to this study. (7)

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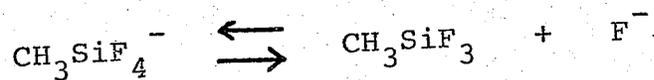
<sup>†</sup> For brevity, tetrapropylammonium methyltetrafluoro-silicate will often be referred to by the formula of the anion, viz  $\text{CH}_3\text{SiF}_4^-$ .

The intermolecular exchange, however, has been the subject of much speculation, but no kinetic studies have been carried out. The mechanisms proposed by the original authors were:

1. A bimolecular exchange involving fluorine bridged dimers.



2. A dissociative or ionization process.



The basis that they used for postulating these mechanisms was simple analogy to processes known or assumed to occur among the other main group inorganic fluorides (see section 2.1 and references therein for examples of these other mechanisms). For the  $\text{CH}_3\text{SiF}_4^-$  ion they favoured the dissociative mechanism, while for some of the other members of this series, notably  $\text{SiF}_5^-$ , the first mechanism was favoured.

Workers in this laboratory have found that other mechanisms might be the predominant mechanism of inter-

molecular fluorine exchange. Gibson,<sup>(2,3)</sup> in a study of the acceptor properties of the  $\text{SiF}_5^-$  ion, found that the exchange was caused by the presence of trace quantities of moisture. The addition of a drying agent (hexamethyldisilazane) reduced the rate of fluorine exchange, on a nuclear magnetic resonance time scale, to almost zero. Similar effects were noted for  $\text{CH}_3\text{SiF}_4^-$ , suggesting that a common mechanism was the cause of exchange in both ions. Many similar cases of catalysis by impurities exist among the other main group inorganic fluorides (section 2.2 and references therein).

In order to help clarify the mechanism of fluorine exchange in these salts, it was decided to undertake a thorough kinetic study of the exchange process in the  $\text{CH}_3\text{SiF}_4^-$  ion, this ion being particularly suitable for dnmr studies because of the nuclear spin-spin coupling between the fluorines and the methyl group.

To accomplish this it was necessary to generate proton magnetic resonance line shapes for a group of three equivalent protons coupled to a group of four equivalent fluorines undergoing intermolecular exchange. Since no examples of a similar system were available in the literature, and none of the generally available line-shape programs appeared capable of solving this problem, it was necessary to derive suitable expressions for the

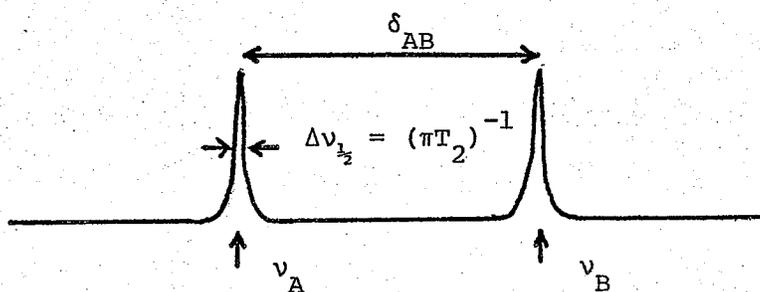
simulation of the spectra. The McConnell <sup>(14)</sup> formulation<sup>4</sup> on the Bloch <sup>(10)</sup> equations was chosen as being the most suitable for this study. The procedure employed was similar to that of Reeves and Shaw, <sup>(15)</sup> except that matrix manipulation yielded an analytical expression that could be used with the quantum mechanical lineshape programs available to the author. This method of describing the lineshape phenomenon has the advantage of being intuitively understood by someone not versed in the fine points of quantum statistics (such is the case with the author).

Methanol was chosen as the exchange catalyst because it is completely soluble in methylene chloride and the quantities required for exchange were easily measured by standard techniques.

## CHAPTER 2 INTRODUCTION

### 2.1 The dynamic nuclear magnetic resonance technique

Nuclear magnetic resonance spectroscopy provides a convenient method for the study of rate processes that have rates of  $10^{-1}$  to  $10^5 \text{ s}^{-1}$ . Consider a situation in which the members of an ensemble of nuclei can exist with equal probability in one of two magnetic environments, A or B, with a difference in Larmor (resonance) frequency of  $\delta_{AB}$ . If the lifetime in each site is long compared to  $T_2$ , the transverse relaxation time, the spectrum will consist of two lines at the resonance frequencies of A and B with line widths ( $\Delta\nu_{\frac{1}{2}}$ ) characteristic of the relaxation time of the nuclei in that situation.

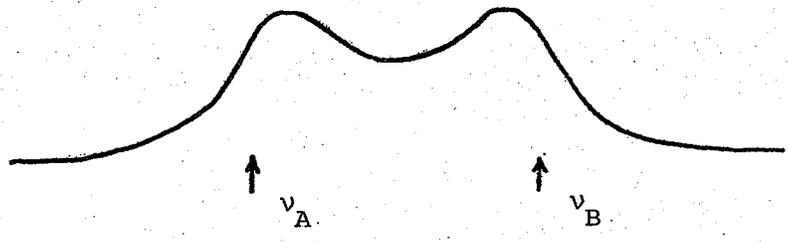


Now, if some mechanism can transfer some of the A type nuclei into site B at the same time that the B's are being transferred into A, a change in the lineshape will occur, the magnitude of which depends on the rate at which this exchange of sites can take place. As the exchange rate

approaches  $T_2^{-1}$  the lines will broaden due to a shortening of the lifetime in each site. This effect is a consequence of the uncertainty principle, and is known as "lifetime broadening". Since the lifetime in each site is still longer than the inverse of the frequency difference between the sites,  $\delta_{AB}^{-1}$ , all of the phase coherence acquired by the A nuclei will be lost by the time that the nuclei return to A. At this point the exchange may be thought of as another  $T_2$  process. This results in a line width of:

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2} + \frac{1}{\pi \tau}$$

where  $\tau$  is the mean lifetime between exchanges. If the exchange rate approaches the frequency difference between the sites, some of the phase coherence will be maintained between exchanges. The nuclei at site A will start to take on some of the characteristics of B and vice versa. At this point the lines become very broad, and a decrease in the peak separation is noticed. The following diagram provides an illustration of this concept.



At very high exchange rates all phase coherence will be maintained between exchanges, and furthermore, since the nuclei spend as much time in site A as in site B, a single peak at a frequency that is the average of the two site frequencies is observed. Several approaches have evolved in the attempt to provide a more quantitative description of this effect; a brief outline of these is given below:

a The Bloch-McConnell method

The equations of motion describing the nmr phenomenon were first derived by Bloch.<sup>(10)</sup> The effects of chemical exchange were first introduced by Gutowsky's group, who employed their modified Bloch equations to study the hindered rotation about the carbonyl-nitrogen bond in dimethylformamide and the related acetamide.<sup>(10-13)</sup> Piette and Anderson<sup>(34)</sup> generalized the method to account for multiple sites, with the restriction that the probability of a transfer from site A to site B was proportional to the fractional population of site B. This was applied to a study of bond rotation barriers in alkyl nitrates, and a similar technique was employed by Arnold in a study of proton exchange in ethanol.<sup>(35)</sup>

A direct introduction of exchange terms into the Bloch equations was proposed by McConnell in 1958.<sup>(14)</sup> When written in matrix form and solved for the usual steady-state conditions, this method may be generalized to account for

any number of sites with exchange occurring between any or all of the sites. (15,16,21) Many cases of both inter- and intramolecular exchange have been studied by this method, (17-20) and the list of references is by no means exhaustive. Several reviews on the use of the Bloch equations for the study of chemical exchange reactions have also appeared. (21-23,55,56) It must be noted, however, that the Bloch equations are subject to restrictions. At this point, a quotation from a paper by Reeves and Shaw (15) is appropriate: "the use of the modified Bloch equations is restricted to first-order spectra so that the nuclear spin isochromats associated with distinct sites of differing Larmor frequency may be considered to be independent except to chemical exchange effects."

b The density matrix (quantum mechanical) approach

An alternate method for the calculation of exchange broadened nmr spectra has been developed by several groups. (27-34,37) This technique employs a branch of quantum statistics known as "density matrix theory", which is a stochastic matrix representation of Markov probability chain. (57) This theory allows for spin-spin coupling of any magnitude between the sites, and provides for a simplification of the exchange process in terms familiar to chemists, that is: chemical shifts, coupling constants and permutations between nuclei. A detailed description of the

density matrix theory and its applications to nmr spectroscopy, including intramolecular exchange in an "ABX" spin system, has been given by Goodwin. (44)

Many refinements of this theory have been introduced in recent years. Two of these are: the extension of Alexander's work by Whitesides, (37) and the method developed by Jesson and Meakin for separating nmr distinguishable mechanisms by the application of group theory. (38)

The most notable development, however, has been the reformulation of the problem in Liouville space by Binsch and Kleier. (39) With appropriate symmetry and equivalence factoring this technique has enabled computer programs to be written that will handle systems of up to six tightly coupled spins with hundreds of lines. (42,43) These programs are quite simple to use, requiring only chemical shifts, coupling constants,  $T_2$  and a nuclear permutation vector which describes which nuclei become what after the exchange. They can also simulate the spectra in cases where the exchange is non-mutual. In this case the nuclei can exist in more than two configurations and the lifetimes in each situation are not necessarily equal (note that the concept of nuclear situation or configuration is distinct from the concept of "site" used in the Bloch equations). Unfortunately, these programs are of little use for prob-

lems involving intermolecular exchange.

c     Pulse methods

All of the methods described thus far have been a description of the spectrum in the frequency domain where the magnetization is plotted as a function of frequency. It is possible though, to study the process in the time domain, since the time interval between repetitive events and the frequency of the events are inversely related.

This approach was developed by Gutowsky's group, (45-52) who have applied the pulse sequence of Carr and Purcell (53) to the loss of transverse magnetization resulting from an exchange process. In the absence of exchange, the amplitude of the spin echoes following each pulse in the Carr-Purcell sequence decay in a purely exponential manner, characterized by a time constant  $T_2$ . If an exchange process can transfer magnetization among the various sites, an additional loss of magnetization can occur. The decay resulting from this process is not exponential. Both the Bloch (10,45) and the density matrix (47,50) methods have been employed in the mathematical analysis of this effect. The analysis gives values for the site frequencies,  $T_2$ , the site populations and the pre-exchange lifetime.

Advantages of the pulse methods include: separability of the various spectral parameters, making iterative fits to all parameters possible; and a greater dynamic range of