Department of Chemistry
UNIVERSITY OF DELHI

M.Sc Chemistry

Inorganic Special Paper
Semester IV

Course – 4101 B

Course Title – Spectral Techniques in Inorganic Chemistry

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Chemical Exchange

- Cross relaxation can lead to exchange of magnetization between coupled spins *I* and *S*.
- However, uncoupled spins can manifest themselves as an apparent coupled spin systems, if the spins are engaged in chemical exchange.
- Consider spins A and B on two molecules undergoing chemical exchange with rate constants k_A and k_B respectively.

$$A \underset{k_B}{\overset{k_A}{\rightleftharpoons}} B \qquad \underbrace{1/\tau_{ex}}_{\text{Exchange time}} = \underbrace{k_{ex}}_{\text{Exchange rate}} = k_A/k_b$$

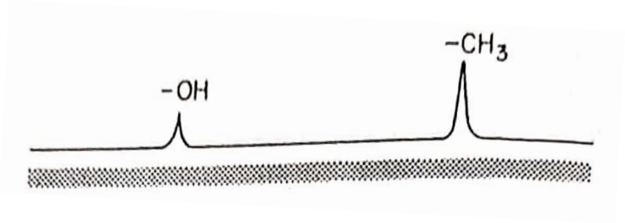
- We'll assume any transition from A to B is instantaneous, but happens at an average rate of $1/\tau_{ex}$

Effect of Chemical Exchange on Spectra

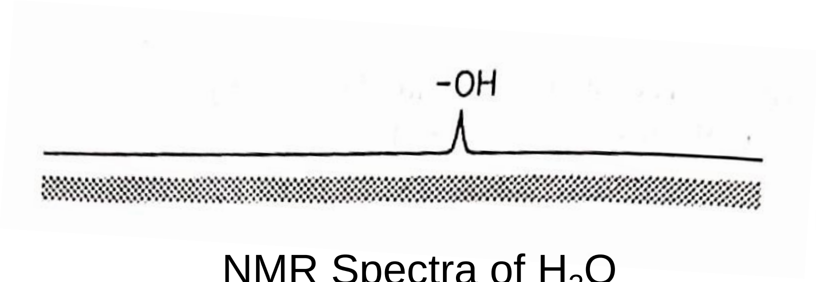
Chemical exchange in NMR is the change in magnetic environment of a nucleus, due to a chemical reaction. This changes the resonance frequency of the nucleus, and the observed effects on the NMR spectrum depend on the relative size of the frequency change and the reaction rate. The effects are classified according to whether the rate is slow, intermediate, or fast compared to the frequency difference. Each has different effects and different ways of measuring them, but they can be used together to study the dynamics of molecules over a wide range of rates.

Example of Chemical Exchange on Spectra

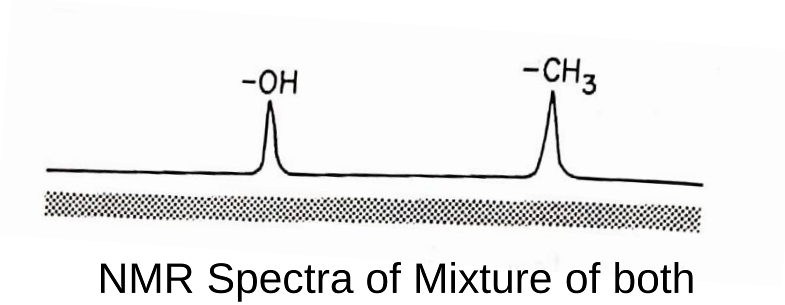
The NMR Spectrum gets drastically affected if the molecules being studied are undergoing rapid exchange reactions. For E.g.



NMR Spectra of CH_3COOH



NMR Spectra of H_2O



NMR Spectra of Mixture of both

The NMR of mixture doesnot show two separate O-H resonances from the water and the acid but instead shows only one. The position of this one average resonance is the linear function of the mole fraction, N, of CH_3COOH in the mixture $\delta_{avg} = N_A\delta_A + N_B\delta_{B.}$ In the mixture, the –OH protons are exchanging positions very rapidly between the acid and the water. The time for the NMR transition is much longer than the time required for the proton exchange, and the method measures the average hydroxyl proton environment in the system. The proton exchange between water and acetic acid is always too fast to be studied by NMR techniques and is mentioned simply to illustrate the effects of fast exchange on the NMR spectrum.

Other examples of Rapid Chemical Exchange

- The protons in the system H_2O – H_2O_2 are found to undergo rapid exchange and to give rise to a single proton peak at room temperature under all conditions. From the width of the single peak (which varies with exchange rate), it is found that acids and bases catalyse the exchange reaction.

- The spectrum of N,N-dimethylacetamide, $CH_3C(O)N(CH_3)_2$ has three peaks at room temperature, two of which corresponds to the different environments of the two methyl groups on the nitrogen (one cis and one trans to oxygen). The C-N bond has multiple bond character and give s rise to an appropriate barrier to rotation about this bond. As a result of this barrier, the two non-equivalent N-CH_3 groups are detected. As the temperature is increased, the rate of rotation about the C-N bond increases and the N-methyl resonances merge, giving rise to a series of spectra. The lifetime of a particular configuration can be determined as a function of temperature nad the activation energy for the barrier to rotation evaluated.

Change in Spectra with Changes in Rate of a Nucleus Undergoing Exchange between two sites

Mathematical Expression

The hypothetical spectra obtained for the proton exchange in molecules A-H and B-H are indicated in the figure given below:

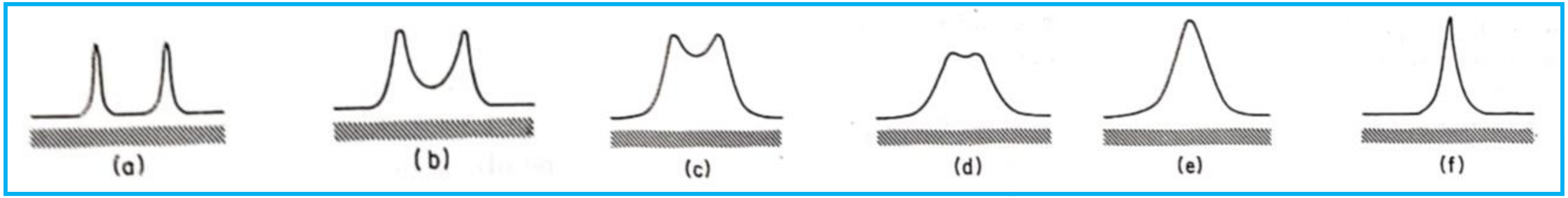


Fig: (a) Slow Exchange, (b) to (e) increasing rate, and (f) very rapid exchange

In (a) the mean lifetime of the protons on A and B is long compared to the NMR transition time. In the sequence (b) to (f), spectra are indicated for increasing rates of proton exchange between the two sites. In the regression of partial collapse [spectra (b) to (d)], the lifetime of the proton on A, τ_A', which is equal to the lifetime on B (there are two equally populated sites with equal lifetimes), τ_B', can be obtained from the expression:

$$\boxed{\frac{(\nu_A - \nu_B)_{obs}}{\nu_A{}^0 - \nu_B{}^0} = \left[1 - \frac{1}{2\pi^2\tau^2(\nu_A{}^0 - \nu_B{}^0)^2}\right]^{1/2}}$$

where $(v_A{}^0 - v_B{}^0)$ is the separation of peaks for long mean lifetimes, as in (a); $(v_A - v_B)_{obs}$ is the separation of peaks which has begun to coalesce as in (b), (c) and (d), and τ' equals $\tau'_A/2$ (the values of $v_A - v_B$ are expressed in cps).

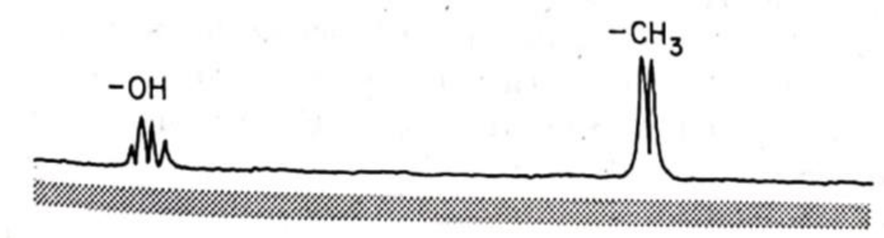
In the spectrum (e), where the two peaks have just merged, $(v_A - v_B)_{obs}$ equals zero and the following expression results:

$$\boxed{\tau' = \frac{\sqrt{2}}{2\pi(\nu_A{}^0 - \nu_B{}^0)}}$$

Equation 1

From these equations it can be seen that in order for two separate peaks to be observed at frequencies v_A and v_B, the lifetimes of the two states (A and B) must be greater than $1/(v_A - v_B)$; i.e., $1/(\Delta_A - \Delta_B)$. For smaller values of τ' (i.e., shorter lifetimes of a given state, as in (d)), the breadth of the merged peak can be used to calculate the lifetime. If the exchange rate falls outside the limit which permits measurement by this technique, the rate may possibly be measured if conditions (temperature, concentration) are changed to alter the rate. Sometimes, weak signals and large differences in Δ, rapid exchange ($\tau' \sim 1/\Delta$) results in such extensive broadening that a peak cannot be detected.

Effect of Chemical Exchange on Spin-Spin Splitting



Increasing field strength

Consider the spectrum of CH_3OH in the absence of exchange. The doublet methyl groups results from OH splitting and the quartet hydroxyl from the splitting by the three equivalent protons on carbon. The exchange of hydroxyl protons may result in a change in the nuclear spin state of the proton attached to the oxygen.

When rapid exchange occurs, this results in the presence on the oxygen of many different protons with both spin states and when the frequency of the exchange is greater than $\sqrt{2}\pi\ (v_A^0 - v_B^0)$ (see equation 1), only the average effect of the two spin states is observed. The spectrum obtained under conditions od rapid exchange consists of only two with no fine structure. The –O-H peak is a singlet because each hydroxyl proton spends some time on a large number of different molecules and the resonance is affected by an average of the methyl proton nuclear spins of all these molecules. The methyl group of each molecule experiences the effect of the nuclear spin of the many different hydroxyl protons on the oxygen. An average effect and single line results for the methyl group. As the exchange rate increases, the fine structure present in the spectrum obtained under conditions of no exchange gradually collapses to give a broad line and then sharpens. Since $J_{H\text{-}H}$ is the same for both the methyl and hydroxyl protons in methanol, both peaks will collapse to the same extent as the exchange reaction is catalysed. In the methanol-water system, the collapse of the methyl peak can be used to calculate the total proton exchange (i.e., CH_3OH with CH3OH and CH_3OH with H_2O). The broadening of the water line can be employed to calculate the exchange rate of methanol with water.

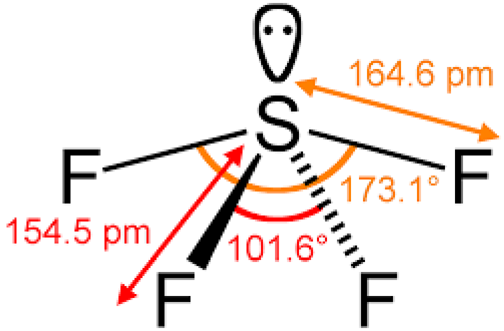
Proton Exchange for solutions of Methyl Ammonium Chloride in Water

In acidic medium (pH = 1.0) the NMR spectra of these solutions consists of a quadruplet methyl peak (split by the three ammonium protons), a sharp water peak, and three broad peaks from the ammonium protons. The triplet for the ammonium protons results from nitrogen splitting. No fine structure is observed in the ammonium proton peaks from the expected coupling to the methyl protons because of the quadrupole broadening by the nitrogen.

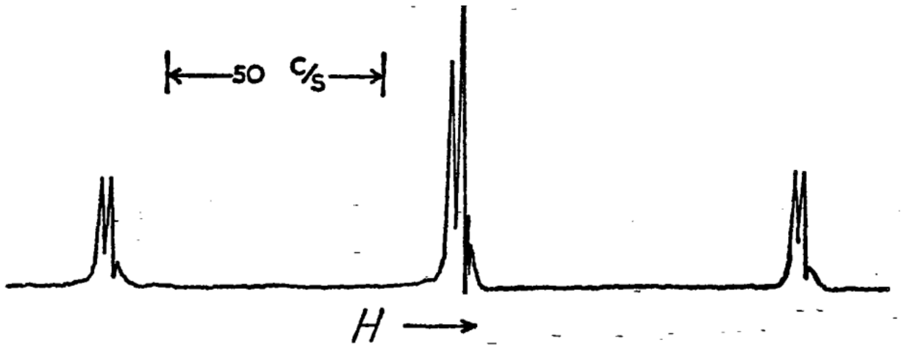
As the pH is increased, rapid proton exchange reactions begin to occur and the $-CH_3$, H_2O, and $-NH_3^+$ band begin to broaden. Eventually at about pH 5, two peaks with no fine structure remain, one from the protons on the $-CH_3$ group and the other a broad peak from an average of all other proton shifts.

As the pH is raised to 8, the broad proton peak sharpens again. The $-CH_3$ broadening yields the exchange rate of protons on nitrogen; the broadening of the water line measures the lifetime of the proton on water and the broadening of the $-NH_3^+$ triplet measures the lifetime of the proton on the nitrogen.

Fluorine NMR Spectrum of Sulphur Tetrafluoride



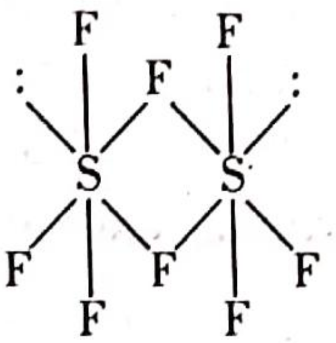
- C_{2v} structure
- 2 sets of non-equivalent fluorine atoms.
- Fluorine NMR – Sharp peak at room temperature - two triplets at -60 ^{0}



Low-field half of fluorine resonance of SF_4 at −101° C.

At -90°C all the peaks of both triplets were observed to split into doublets. The two halves of the spectrum are symmetrical about the center, and the low-field half of the spectrum is reproduced in Fig.

It was found that the exchange rate in solution was a function of SF4 concentration, supporting a bimolecular mechanism. It was proposed that the intermediate is involved.

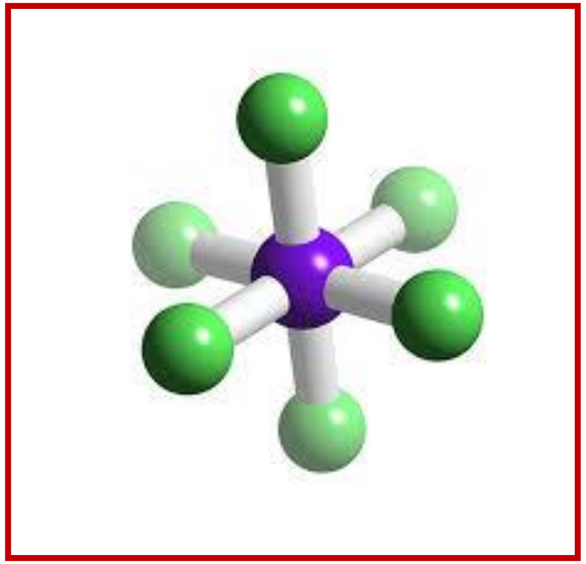


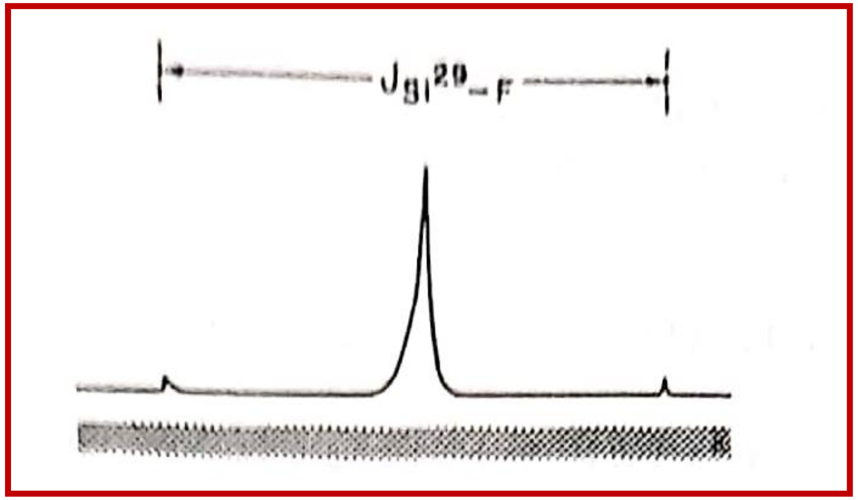
Increased rate of exchange

$SF_4 < SeF_4 < TeF_4$

https://www.nrcresearchpress.com/doi/pdf/10.1139/v63-139

Fluorine NMR Spectrum of SiF_6^{2-}





The main peak arises from fluorines on Si^{28} ($I = 0$), and the two small peaks result from spin-spin splitting of the fluorine by Si^{29} ($I = ½$). The appearance of the satellites corresponding to $J_{Si\text{-}F}$ indicates that the rate of exchange of fluorine atoms must be less than 10^3 sec^{-1}[$\tau' < 1/(\nu_A - \nu_B)$].

Also, the spectrum of solutions of SiF_6^{2-} containing added F^- contains two separate fluorine resonances. These are assigned to F^- and SiF_6^{2-}, There are satellites ($J_{Si\text{-}F}$) on the SiF_6^{2-} peak. When a solution of SiF_6^{2-} is acidified, rapid exchange occurs, the satellites disappear, and the central peak broadens. The following reactions are proposed:

$$SiF_6^{2-} + H_3O^+ \rightarrow HFSiF_5^- \xrightarrow{H_2O} H_2OSiF_5^- \xrightarrow{HF} SiF_6^{2-} + H_3O^+$$

https://www.nrcresearchpress.com/doi/pdf/10.1139/v77-543

C^{13} Spectrum of CO_2 in Water

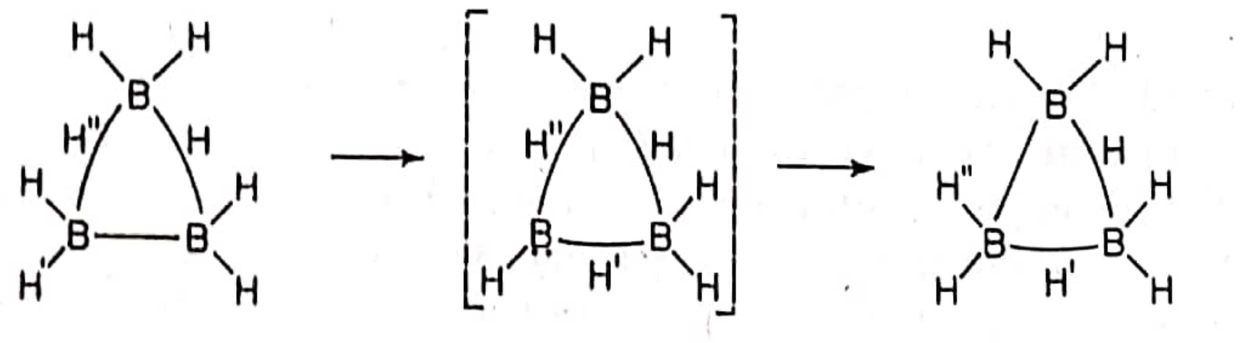
It gives rise to two peaks, one from dissolved CO_2 and a second for H_2CO_3, HCO_3^-, and CO_2. Rapid proton exchange gives rise to a single C^{13} peak for these latter three species. The reaction

$$\boxed{CO_2 + H_2O \longrightarrow H_2CO_3}$$

has a half-life of about 20 sec, so a separate peak for dissolved CO_2 is detected.

NMR Spectrum of $B_3H_8^-$

The B^{11} spectrum is a nonet which results from a splitting of three equivalent borons by eight equivalent protons.



The structure of $B_3H_8^-$ and a proposed step for the Intramolecular Exchange

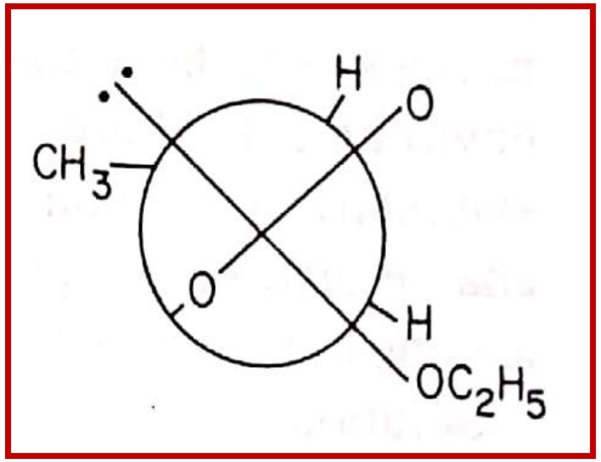
It is proposed that the frequency of steps similar to those in the figure is large, making the three borons equivalent and the eight protons equivalent in the NMR spectrum. In this example the eight hydrogens remain attached to the borons and cause splitting. Contrast this to rapid intermolecular exchange where a single boron resonance signal would result if exchange made all protons equivalent.

There is another possible explanation leading to the observed spectrum which does not involve exchange.When a particular set of nuclei are *strongly coupled together* (e.g. the eight hydrogens and also the three borons of B_3H_8), these nuclei can behave as single set of equivalent nuclei in coupling to nuclei outside the set. Stromg coupling of the eight protons would give rise to the observed nonet in the B^{11} resonance.

Example of system in which rapid rotation does not remove non-equivalence

Methylene protons of $(CH_3CH_2O)_2SO$

The two protons of a given methylene group are not stereochemically equivalent because of the lack of symmetry of the sulfur atom with respect to rotation about the S-O-C bonds. One of the possible rotamers is



The small dot in the center represents the sulfur with lines connecting the oxygen, the lone pair, and the ethoxyl groups. The large circle represents the methylene carbon with two hydrogens, an oxygen, and a methyl group attached.

The molecule is so oriented that we are looking along a line from sulfur to carbon. The non-equivalence of the two methylene hydrogens of a given -CH2- group is seen in this rotamer.

Non-equivalence in the chemical shift is said to arise if the populations of the different rotamers vary. If rapid interconversion between rotamers is taking place, non-equivalence can arise if the molecule spends a longer time in one of the lower energy confirmations, i.e., one must perform a time average to determine the chemical shifts of the non-equivalent protons.

However, the fact remains that symmetry considerations indicate the hydrogen can never be equivalent in any rotamer in this system.

Suggested Reading Links & PDFs

https://web.stanford.edu/class/rad226b/Lectures/Lecture6-2016-Chemical-Exchange.pdf

https://www.chemistry.mcmaster.ca/bain/Intro.pdf

https://web.stanford.edu/class/rad226b/Lectures/Lecture6-2016-Chemical-Exchange.pdf

http://baldwinlab.chem.ox.ac.uk/resources/pramodhNotes.pdf

http://mriquestions.com/chemical-exchange.html


Thank you!