Department of Chemistry
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M.Sc Chemistry

Inorganic Special Paper
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Course – 4101 B
Course Title – Spectral Techniques in Inorganic Chemistry

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NMR Studies of Exchange Reactions between Ligands and Metal ions

- As we saw in chemical exchange, the presence of paramagnetic ions in aqueous solution causes a broadening of the line in NMR spectrum.

- Both Longitudinal, T_1, and Transverse, T_2, relaxation times are affected.

Explanation:

Water molecules in the system can be broadly divided into :

- Molecules in the coordination sphere

- Bulk solvent molecules

Coordinated molecules are:
- Held more firmly in place
- Less free to undergo proton exchange by the water-water exchange mechanism as compared to bulk molecules

On the other hand, the magnetic filed of the ion has a greater effect on the coordinated solvent molecules and hence on relaxation induced by the ion.

Line width will depend upon the following relaxation mechanism:

1) $1/\tau_B$, the exchange rate constant for the reaction between coordinated and bulk water molecules (τ_B is the lifetime of a coordinated water molecule).

2) $1/T_{2A}$, the relaxation rate for a bulk solvent molecule

3) $1/T_{2B}$, the relaxation time constant for a coordinated water molecule, which is not same as (2) because of the relatively greater effect of the magnetic field of the metal ion

4) $1/\tau_A$, the spin relaxation time, for the unpaired electrons.

In most instances, there is a very rapid exchange for the electron and no appreciable line broadening from this effect.

Experimentally:

The line width, $1/T_2$, observed for H_2O is given by the following expression:

$$1/T_2 = P_A/T_{2A} + P_B/(T_{2B} + \tau_B)$$

Where, P_B is the fraction of protons on coordinated water molecules, P_A the fraction of protons on the bulk solvent molecules (which is approximately one), and the other terms have been defined above. For a metal ion concentration of M moles liter^{-1} and a coordination number of six:

$$P_B = 6M/55$$

If $T_{2B} \gg \tau_B$, relaxation is rate determining and becomes:

$$1/T_2 = 1/T_{2A} + P_B/T_{2B} \qquad \ldots (1)$$

Under these conditions, $1/\tau_B$ is large (i.e., rate of exchange is fast) and the rate of relaxation slow. Nearly all solvent molecules will be influenced by the ion in a short time and the relaxation is said to be rate-controlling.
If $\tau_B \gg T_{2B}$, the exchange is line-width determining and the line width is given by:

$$1/T_2 = 1/T_{2A} + P_B/\tau_B \qquad \ldots (2)$$

When $\tau_B \gg T_{2B}$,the rate of exchange is controlling ($1/\tau_B$ is small), and the effect of paramagnetic ion is limited because a limited number of water molecule will be subjected to the field of the ions.

When τ_B » T_{2B},the rate of exchange is controlling ($1/\tau_B$ is small), and the effect of paramagnetic ion is limited because a limited number of water molecule will be subjected to the field of the ions.

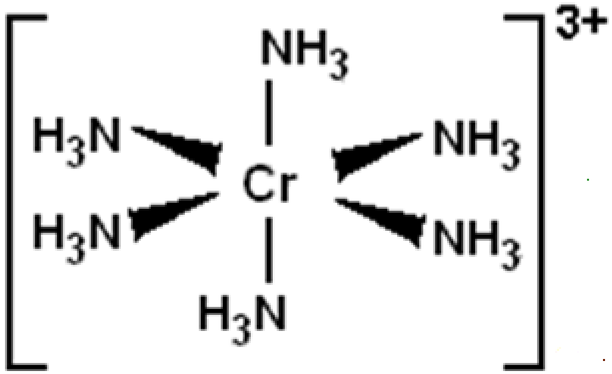
If the rate of exchange is studied as function of temperature, it can be determined whether τ_B or T_{2B} is greater. Since $1/\tau_B$ is the rate constant for a chemical process, it will increase with temperature, while $1/\tau_{2B}$ will increase with temperature. If the electron spin relaxation, τB is controlling, $1/T_{2B}$ increases slightly with temperature. These considerations indicate whether equation (1) or (2) should be employed. The quantity $1/T_2$ is measured from the line width, and PB can be easily determined. Evaluation of T_{2A} by the following procedure permits calculation of either τ_B or T_{2B}, the information being sought. The quantity, $1/T_{2A}$, the relaxation rate constant for the bulk solvent, cannot be evaluated from the pure solvent because water molecules in the second, third, etc., solvent layers around the ion are not in the same environment as water molecules in pure solvent. The relationship between $1/T_{2A}$ and $1/T_{2A}^0$, where T_{2A}^0 is the relaxation time constant for pure solvent, is:

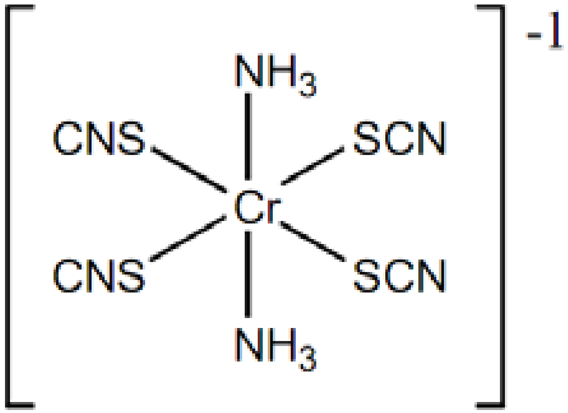
$$1/T_{2A} = 1/T_{2A}^0 + P_B/T_{2A}'$$

Where $1/T_{2A}'$ is the average contribution to $1/T_{2A}$ from solvent molecules estimated from the effects of substitution-inert complexes on the line width of pure solvent. In general, $1/T_{2A}$ is only one-tenth $1/T_{2B}$ so the crude estimate from the above experiment suffices.

Example of Exchange Reactions

In terms of Rate of exchange of at which OH^- removes a proton from the coordinated sphere





At 25 ^{0}C
Rate constant = 2 X 10^6 litres mole^{-1} sec $^{-1}$

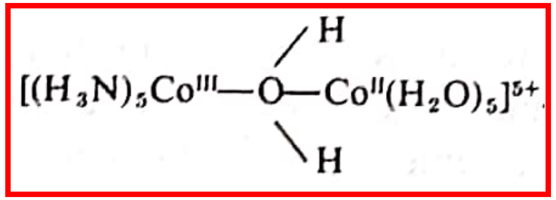
At 100 times slower rate

Reason - Negative Charge

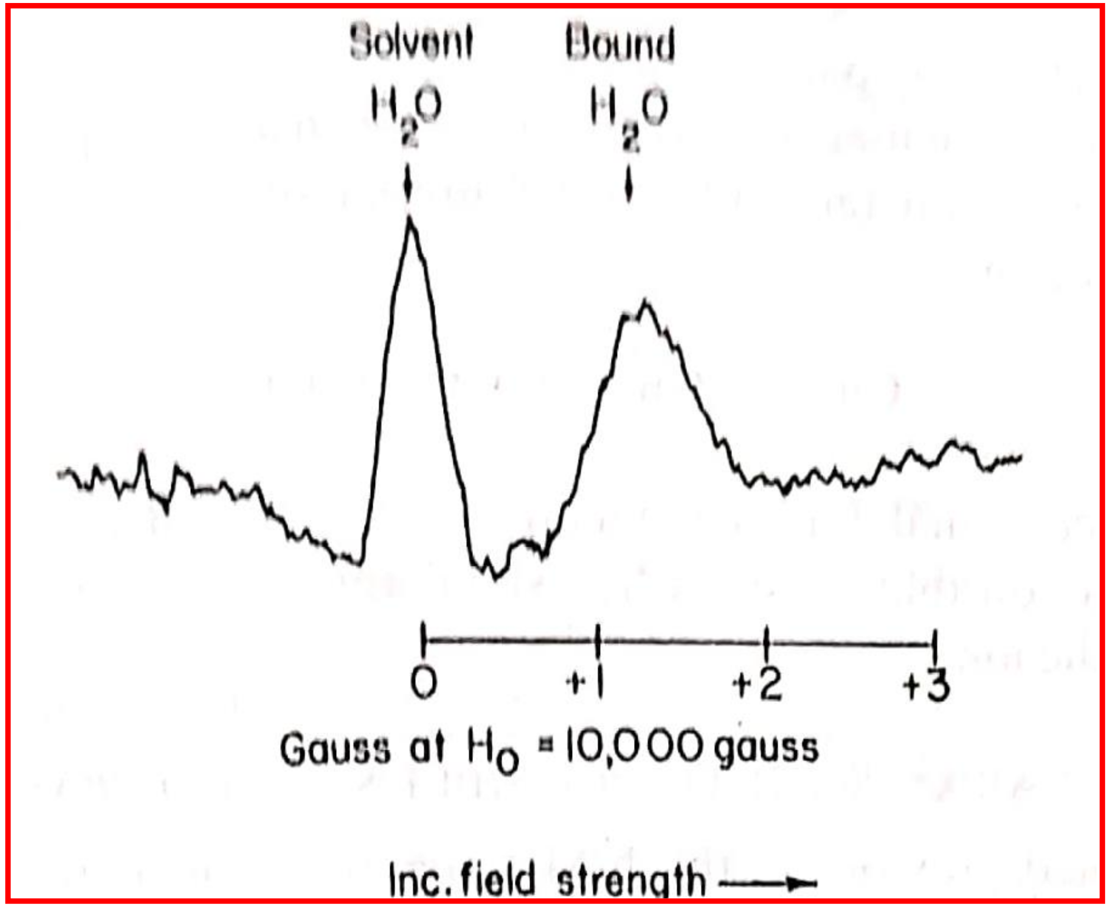
O^{17} NMR Spectrum

$[Co(NH_3)_5OH_2]F_3$

- A peak at +1.3 gauss in addition to the solvent peak.
- Addition of Co^{2+} ion caused a shift in the peak assigned to solvent water to -3.3 gauss, but the coordinated water peak (at +1.3 gauss) is not shifted.
- Shift in the solvent water peak is due to the coordination of water by Co^{2+} and rapid exchange of the water coordinated with Co^{2+} and solvent water.
- The water in $[Co(NH_3)_5O^{17}H_2]F_3$ doesn't not undergo rapid exchange with Co^{2+} and this peak is not shifted but is broadened slightly.
- The broadening is attributed to the species



$$[(H_3N)_5Co^{III}-\underset{H}{\overset{H}{O}}-Co^{II}(H_2O)_5]^{5+}$$



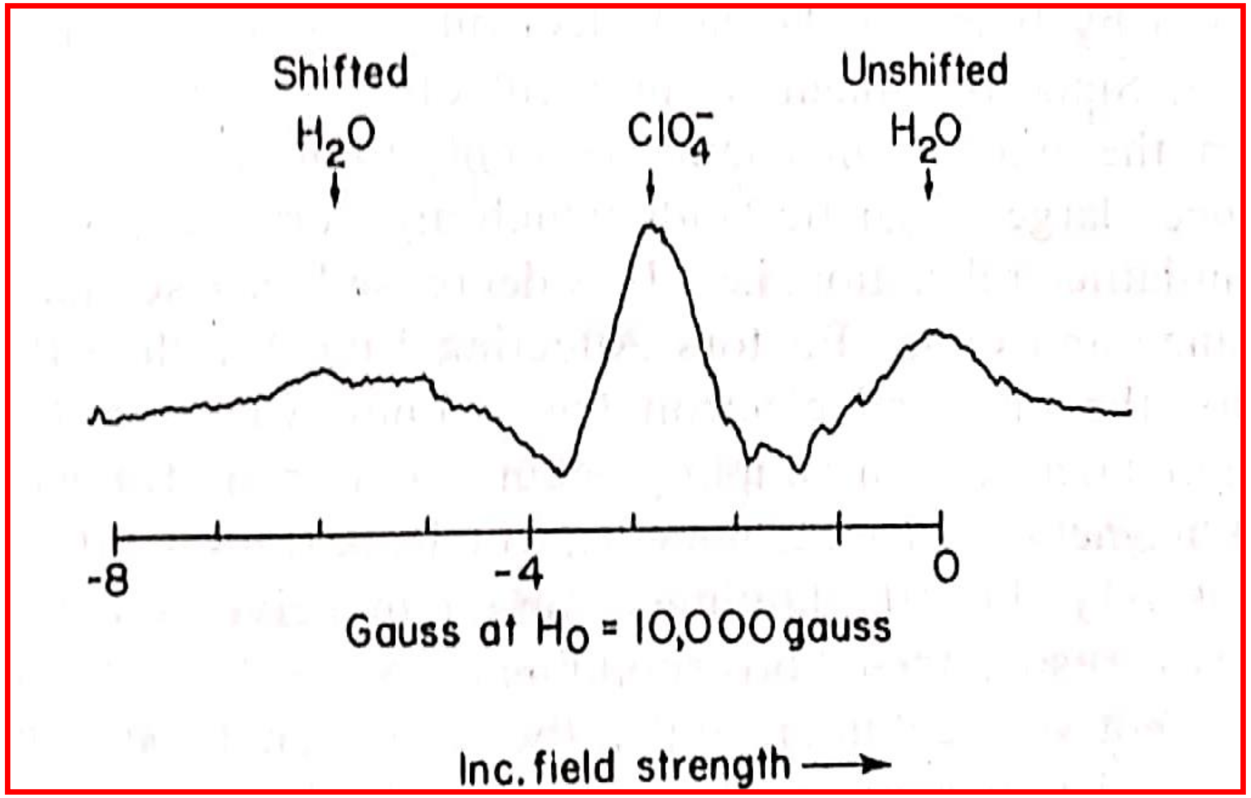
O^{17} NMR Spectrum of $[Co(NH_3)_5OH_2]F_3$ in H_2O^{17}

Hence, can be used as a technique for determining solvation number of ions

Another example for determining solvation number of ions

$Al(ClO_4)_3$ +$Co(ClO_4)_2$ in H_2O^{17}

- When aluminium (III) is dissolved in H_2O^{17}, only a single peak is found.
- The coordinated and free water resonances overlap.
- When Cobalt (II) is added, this peak is diminished in intensity and a second peak at higher field is observed for free water rapidly exchanging with cobalt (II).
- There is residual absorption at the same resonance position as in the solution containing only aluminium (III), and this is attributed to water coordinated to this ion.
- Separate resonances for bound and free water upon the addition of cobalt (II) were not observed when labile ions (e.g. Li^+) were substituted for aluminium (II)



$Al(ClO_4)_3$ +$Co(ClO_4)_2$ in H_2O^{17}

Applications of Exchange Reactions

- used as a technique for determining solvation number of ions
- Used for calculating coordination numbers
- Rate of substitution of coordinated water molecules by bulk water molecules from the broadening of the O^{17} resonance in H_2O^{17} by paramagnetic ions.
- Employed to measure the rate constant for the electron exchange reactions. For example

$$Cu^{2+} + Cu^{+} \longrightarrow Cu^{+} + Cu^{2+}$$

In the Cu^{63} Nuclear Magnetic Resonance Spectrum, the resonance signal for diamagnetic Cu^{+} is broadened by the rapid exchange reaction that occur when small amounts of Cu^{2+} are added to a solution of the ion.


Thank you!