

Chemical Shift in RFR (Paper 84)

As for ESR, NMR and MRI, the chemical shift is the most important part of RFR. In the context of the IFE, this was first considered by:

R.A. Harris and I. Tinoco, J. Chem. Phys., 101, 9289 (1994).

using second order perturbation theory of the Schrodinger level:

$$E = \sum_n \langle 0 | H | n \rangle \langle n | H | 0 \rangle / (\hbar \omega_n) \quad (1)$$

The classical perturbation Hamiltonian is:

$$H = \frac{1}{2m} (\underline{p} + e(\underline{A} + \underline{A}_N))^2 + V \quad (2)$$

where:
$$\underline{A}_N = \frac{\mu_0}{4\pi r} m_N \times \underline{r} \quad (3)$$

is the vector potential due to the nuclear magnetic dipole moment m_N . As shown by Harris and Tinoco, the dominant perturbation term is the single photon off resonance population term, coming from the transition electric dipole moment:

$$\langle 0 | \underline{\mu} | n \rangle = \frac{e}{m \omega_n} \langle 0 | \underline{p} | n \rangle \quad (4)$$

The potential \underline{A} is a general complex, so the dominant chemical shift term is:

$$E = \frac{ie^3}{m^2 \hbar \omega_n} \sum_n \langle 0 | \underline{p} \cdot \underline{A} | n \rangle \langle n | \underline{A}_N \cdot \underline{A}^* | 0 \rangle \quad (5)$$

2) Units Check

$$E = \frac{e^3 p A^3}{n^3 \hbar \omega} = C^3 \text{kgmms}^{-1} (\text{Jsc}^{-1}\text{m}^{-1})^3 / (\text{Jkgm}^{-1}\text{m}^{-1})$$

$$= \text{ms}^{-1} \text{J}^2 \text{s}^3 \text{m}^{-3} / \text{kgm}$$

$$= \text{kgm}^2 \text{m}^4 \text{s}^{-4} \text{m}^{-2} \text{s}^2 / \text{kgm} = \text{J}$$

Now use the vector relations:

$$\underline{\mu} \times (\underline{m}_N \times \underline{r}) \cdot (\underline{A} \times \underline{A}^*)$$

$$= (\underline{\mu} \cdot \underline{A}) ((\underline{m}_N \times \underline{r}) \cdot \underline{A}^*) - (\underline{\mu} \cdot \underline{A}^*) ((\underline{m}_N \times \underline{r}) \cdot \underline{A})$$

- (6)

and

$$\underline{\mu} \times (\underline{\mu}_N \times \underline{r}) = (\underline{\mu} \cdot \underline{r}) \underline{\mu}_N - (\underline{\mu} \cdot \underline{\mu}_N) \underline{r}$$

- (7)

Basic Definitions in NMR

Before proceeding to complete chemical shift theory in RFR it is necessary to review the basics of chemical shift theory in ESR and NMR. The basic property of NMR is that different nuclei resonate at different values of the applied field. This is expressed as a shielding factor σ , such that:

$$\hbar \omega = g_N \mu_N B_{loc} = g_N \mu_N (1 - \sigma) B \quad - (8)$$

where:

$$\mu_N = \frac{e \hbar}{2m_p} \quad - (9)$$

is the nuclear magneton. ($5.05082 \times 10^{-27} \text{JT}^{-1}$)

3) The nuclear magnetic dipole produces a vector potential \underline{A}_N , used in eq. (2). Its form is (Albis page 397):

$$\underline{A}_N = \frac{\mu_0}{4\pi r^3} \underline{m}_N \times \underline{r} \quad (10)$$

as used in eq. (3). The nuclear magnetic dipole moment

is:

$$\underline{m}_N = \gamma_N \hbar \underline{I} = g_N \frac{e \hbar}{2m_p} \underline{I} \quad (11)$$

where \underline{I} is the nuclear spin quantum number and g_N is the nuclear g factor.

Units Check

$\underline{A}_N = \text{Js}^{-1} \text{m}^{-1}$, $\mu_0 = \text{Js}^2 \text{C}^{-2} \text{m}^{-1}$, $\hbar = \text{Js}$
 so: $\underline{m}_N = \text{Cm}^2 \text{s}^{-1}$ from eqs. (10) and (11) ✓

RFR Shielding Factor

The same principle applies in RFR. The nuclear resonance frequency is different for each nucleus. So RFR can be used as a new type of nuclear resonance spectroscopy. A whole new theoretical and experimental area of physics can be developed. In order to demonstrate the chemical shift in RFR the perturbation expression (5) is first written as:

$$b) \quad E = -\gamma \frac{e^2}{2m} \underline{\sigma} \cdot \underline{A} \times \underline{A}^* \quad - (12)$$

Instead of using the perturbation theory of Harris and Turoso, it is first seen that the RFR term is given by:

$$E = -\frac{ie^2}{2m} \underline{\sigma} \cdot (\underline{A} + \underline{A}_N) \times (\underline{A}^* + \underline{A}_N^*) \quad - (13)$$

by using the minimal prescription:

$$\underline{p} \rightarrow \underline{p} + e(\underline{A} + \underline{A}_N) \quad - (14)$$

where \underline{A} is the electromagnetic potential:

$$\underline{A} = \frac{A^{(0)}}{\sqrt{2}} (\underline{i} - i\underline{j}) e^{i\phi} \quad - (15)$$

It is immediately seen at the classical level that the RFR resonance frequency is shifted. The original RFR resonance frequency is:

$$\hbar\omega = \frac{e^2 A^{(0)2}}{m} = -\frac{ie^2}{m} |\underline{A} \times \underline{A}^*| \quad - (16)$$

but the shielded and classically shifted RFR frequency is:

$$\hbar\omega_{\text{shifted}} = -\frac{ie^2}{m} |(\underline{A} + \underline{A}_N) \times (\underline{A}^* + \underline{A}_N^*)| \quad - (17)$$

5)

$$= \mathcal{L}\omega - i \frac{e^2}{m} (\underline{A} \times \underline{A}_N + \underline{A}_N \times \underline{A}^*) - (18)$$

So:

$$(\mathcal{L}\omega)_{\text{shifted}} = (1 + \sigma) \mathcal{L}\omega - (19)$$

where

$$\sigma = \frac{-ie^2}{\mathcal{L}\omega m} (\underline{A} \times \underline{A}_N + \underline{A}_N \times \underline{A}^*) - (20)$$

This is an example of a RFR shielding factor.
 This has been worked out at the classical level without the use of quantum perturbation theory. The factor σ is non-zero transiently, but over many cycles of the electromagnetic field averages to zero because:

$$\langle \underline{A} \rangle = \langle \underline{A}^* \rangle = \underline{0} - (21)$$

However, at low enough frequencies its effects may be detected transiently, giving a new type of spectroscopy.

In the quantum perturbation theory of eq. (1) with the Hamiltonian (13):

$$E = \frac{e^4}{4m^2 \hbar \omega_{on}} \sum_n \frac{\langle 0 | \underline{\sigma} \cdot (\underline{A} + \underline{A}_n) \times (\underline{A}^* + \underline{A}_n) | n \rangle}{\langle n | \underline{\sigma} \cdot (\underline{A} + \underline{A}_n) \times (\underline{A}^* + \underline{A}_n) | 0 \rangle} - (22)$$

After averaging over many electromagnetic field cycles:

$$E = \frac{e^4 \sum_n \langle 0 | n \rangle \langle n | 0 \rangle}{4m^2 \hbar \omega_{on}} (-i \underline{\sigma} \cdot \underline{A} \times \underline{A}^*) (-i \underline{\sigma} \cdot \underline{A} \times \underline{A}^*) - (23)$$

The original interaction Hamiltonian is:

$$E_0 = - \frac{i e^2}{2m} \underline{\sigma} \cdot \underline{A} \times \underline{A}^* - (24)$$

so this has been shifted by:

$$\gamma = - \frac{i e^2}{2m} \underline{\sigma} \cdot \underline{A} \times \underline{A}^* \frac{\sum_n \langle 0 | n \rangle \langle n | 0 \rangle}{\hbar \omega_{on}} - (25)$$

$$\boxed{\gamma = \frac{e^2 A^{(0)2}}{2m} \left(\sum_n \frac{\langle 0 | n \rangle \langle n | 0 \rangle}{\hbar \omega_{on}} \right) \underline{\sigma} \cdot \underline{k}}$$

The RFR resonance frequency is therefore shifted to:

$$7) \quad \omega_{res} = \frac{e^2 A^{(0)} (1 + \gamma)}{I_m} \quad - (26)$$

where: $\gamma = f(\omega_{on}) \quad - (27)$

Therefore for each ω_{on} of B atom or molecule the RFR shift is different. Using transient methods, such that:

$$\langle A \rangle = \langle A^* \rangle \neq 0 \quad - (28)$$

many more terms of eq. (25) contribute to the RFR spectrum.

Spin Up / Spin Down Chemical Shift of RFR

Another original feature of RFR is that the chemical shift γ in eq. (25) depends on the Pauli z matrix σ_z . The spin up shift and the spin down shift differ by:

$$\boxed{\gamma_+ - \gamma_- = \frac{e^2 A^{(0)} \sum_n \frac{\langle 0|k\rangle \langle n|l\rangle}{I \omega_{on}}}{m}} \quad - (29)$$

This means that a fermion at RFR resonance with spin up will be split in a way that depends on whether it is shifted up (γ_+) or down (γ_-)

2) This is a type of spin-spin splitting, eqn. (20) shows that there are four lines at second order in time-independent perturbation theory.

$\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow$

The energy in eq. (20) is of the type:

$$E = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad \text{--- (30)}$$

This is a schematic to show that there are two Σ Pauli matrices present, it does not mean the product of two Pauli matrices. It means

means $\begin{bmatrix} \text{spin up} & 0 \\ 0 & \text{spin down} \end{bmatrix} \begin{bmatrix} \text{spin up} & 0 \\ 0 & \text{spin down} \end{bmatrix}$
 and RFR can occur between the states of the first matrix while the second is spin up or while the second is spin down (ψ_+) or (ψ_-).

Finally if there are many nuclear protons and electrons present nuclear g_N factors must be brought into consideration, and A is different for each type of spin-spin coupling.

9) $S_{pi} - S_{pi}$ and $S_{pi} - \text{Orbit}$ Coupling 12
RFR

This is a very important feature of RFR because it gives the characteristic spectrum of ESR and NMR but without magnets. By following this perturbation energy terms such as:

$$E^{(2)} = \sum_n \left[\frac{-\lambda e^2 A^{(1)} \langle 0 | l_z | n \rangle \langle n | l \cdot s | 0 \rangle}{2m(E_0 - E_n)} + \langle 0 | l \cdot s | n \rangle \langle n | l_z | 0 \rangle \right] \quad (31)$$

So all ESR and NMR splitting theory can be used directly for RFR. The increased resolution comes from the fact that:

$$A^{(1)} \propto \frac{I}{\omega^2} \quad (32)$$

This then allows hyper-fine and super-hyperfine structure to be resolved where ESR or NMR cannot do so.
