

84(3): The Chemical Shift in RFR

The chemical shift in RFR is unique, and different from its counterpart in ESR and NMR. The essential reason for this is that ESR and NMR are quantum mechanical in origin, as RFR is classical in origin. This is revealed by the extra \hbar in the RFR resonance. For ESR and NMR:

$$\omega = \frac{e}{m} B \quad \text{--- (1)}$$

and the interaction energy is:

$$E = \frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{B}. \quad \text{--- (2)}$$

For RFR:

$$\omega = \frac{e^2 A^2}{2m} \quad \text{--- (3)}$$

and the interaction energy is classical:

$$E = -i \frac{e^2}{2m} \underline{\sigma} \cdot \underline{A} \times \underline{A}^*. \quad \text{--- (4)}$$

Before deriving the RFR chemical shift like ESR and NMR chemical shift is derived to illustrate the method.

ESR and NMR Chemical Shift

The basic method is to use the minimal prescription:

$$\underline{p} \rightarrow \underline{p} + e\underline{A} \quad \text{--- (5)}$$

where:

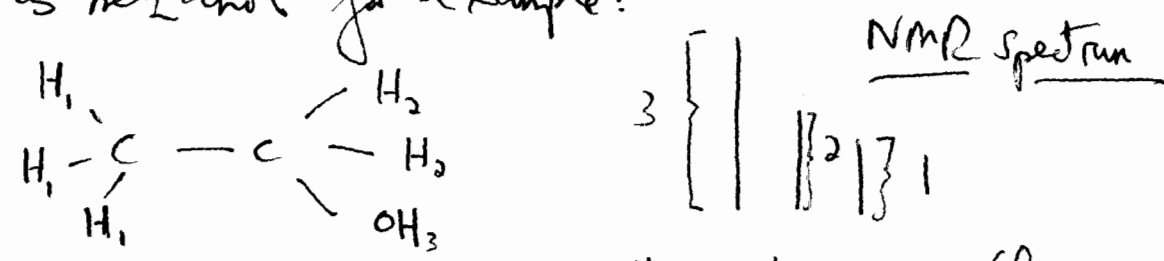
$$\underline{A} = \underline{A}_{\text{ext}} + \underline{A}_N. \quad \text{--- (6)}$$

Here $\underline{A}_{\text{ext}}$ denotes the vector potential associated with an externally applied static magnetic field and \underline{A}_N denotes the potential associated with a nucleus within an atom or molecule:

2)

$$\frac{A_N}{r} = \frac{\mu_0}{4\pi r^3} m_N \times r \quad - (7)$$

where m_N is a nuclear magnetic dipole moment. In a molecule such as methanol for example:



There is a characteristic 3:2:1 pattern because there are three distinct types of H. This is what is useful for chemists and others who use NMR.

The ESR and NMR chemical shift is most easily calculated from the Schrödinger Pauli equation using the Hamiltonian operator:

$$\hat{H} = \frac{1}{2m} \underline{\sigma} \cdot (\underline{p} + e\underline{A}) \underline{\sigma} \cdot (\underline{p} + e\underline{A}) \quad - (8)$$

The relevant part of the Hamiltonian for ESR and NMR is:

$$\hat{H}_{int} = \frac{i e}{2m} \underline{\sigma} \cdot (\underline{A} \times \underline{p} + \underline{p} \times \underline{A}) \quad - (9)$$

It is seen that classically:

$$\boxed{\hat{H}_{int}(\text{classical}) = 0} \quad - (10)$$

However in quantum mechanics:

$$\hat{H}_{int} \psi = E \psi, \quad - (11)$$

and

$$\underline{p}^n = i \hbar \nabla^n \quad - (12)$$

3) Here: $p^\mu = \left(\frac{E}{c}, \underline{p} \right), \quad d^\mu = \left(\frac{1}{c} \frac{d}{dt}, -\underline{\nabla} \right)$ — (13)

so: $E = i\hbar \frac{d}{dt}, \quad \underline{p} = -i\hbar \underline{\nabla}$ — (14)

signifying wave-particle duality. Therefore:

$\hat{H}_{int} = \frac{e\hbar}{2m} \underline{\sigma} \cdot (\underline{\nabla} \times \underline{A} + \underline{A} \times \underline{\nabla})$ — (15)

(NB) end: $\underline{\nabla} \times \underline{A} \psi$ acts on $\underline{A} \psi$

$\frac{e\hbar}{2m} \left(\underline{\sigma} \cdot \underline{\nabla} \times (\underline{A} \psi) + \underline{\sigma} \cdot (\underline{A} \times \underline{\nabla}) \psi \right) = E \psi$ — (16)

Thus: $E = \frac{e\hbar}{2m} \underline{\sigma} \cdot \underline{B}$ — (17)

because:

$(\underline{A} \times \underline{\nabla}) \psi = \underline{A} \times \underline{\nabla} \psi,$
 $\underline{\nabla} \times (\underline{A} \psi) = (\underline{\nabla} \times \underline{A}) \psi + \underline{\nabla} \psi \times \underline{A},$ — (18)

and $\underline{B} = \underline{\nabla} \times \underline{A}.$ — (19)

The ESR or NMR resonance frequency is:

$\hbar \omega = \frac{e\hbar}{m} B$ — (20)

i.e

$\omega = \frac{eB}{m}$ — (21)

where:

$B = \underline{B}_{ext} + \underline{B}_N$ — (22)

4) This is usually expressed as:

$$\omega = \frac{e}{m} \frac{B}{\text{ext}} (1 - \sigma) \quad - (23)$$

where σ is the shielding constant. Thus:

$$\sigma = - \frac{B_N}{B_{\text{ext}}} \quad - (24)$$

For each nucleus the shielding constant σ is different, so there is an NMR spectrum. The same fundamental principles apply to ESR and MRI. This is a greatly developed subject and now comprises about half of chemistry.

The RFR Chemical Shift

The interaction hamiltonian is:

$$H = -i \frac{e^2}{2m} \underline{\sigma} \cdot \underline{A} \times \underline{A}^* \quad - (25)$$

which originates in eq. (8) when \underline{A} is complex valued. For an external electromagnetic field:

$$-i \frac{\underline{A}}{\text{ext}} \times \frac{\underline{A}^*}{\text{ext}} = A^{(0)2} \underline{k} \quad - (26)$$

and the conjugate product is real valued. In the presence of nucleus effects:

$$\underline{A} = \underline{A}_{\text{ext}} + \underline{A}_N \quad - (27)$$

$$\underline{A}^* = \underline{A}_{\text{ext}}^* + \underline{A}_N \quad - (28)$$

because \underline{A}_N from eq. (7) is real valued.

5) Thus:

$$-i \underline{A} \times \underline{A}^* = -i \left(\underline{A}_{\text{ext}} \times \underline{A}_{\text{ext}}^* + \underline{A}_{\text{ext}} \times \underline{A}_N + \underline{A}_N \times \underline{A}_{\text{ext}}^* \right) \quad - (29)$$

because:

$$\underline{A}_N \times \underline{A}_N = \underline{0} \quad - (30)$$

So:

$$\boxed{A^{(0)2} \underline{k} \rightarrow A^{(0)2} \underline{k} - i \left(\underline{A}_{\text{ext}} - \underline{A}_{\text{ext}}^* \right) \times \underline{A}_N} \quad - (31)$$

The resonance frequency:

$$\omega = \frac{e^2 A^{(0)2}}{\hbar m} \quad - (32)$$

is changed to:

$$\omega = \frac{e^2}{\hbar m} \left(A^{(0)2} + \sigma \right) \quad - (33)$$

where the RFR shielding factor σ depends on \underline{A}_N and is site specific. An example of eq. (31) can be used for plane waves:

$$\underline{A}_{\text{ext}} = \frac{A^{(0)}}{\sqrt{2}} (\underline{i} - \underline{j}) e^{i\phi} \quad - (34)$$

$$\underline{A}_{\text{ext}}^* = \frac{A^{(0)}}{\sqrt{2}} (\underline{i} + \underline{j}) e^{-i\phi} \quad - (35)$$

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$$\underline{A}_N = \frac{\mu_0}{4\pi} \frac{m_N}{\hbar} \times \underline{r} \quad - (36)$$

6) It is a matter of elementary algebra to work out the shielding factor, using the vector rule:

$$\underline{A} \times (\underline{B} \times \underline{C}) = (\underline{A} \cdot \underline{C}) \underline{B} - (\underline{A} \cdot \underline{B}) \underline{C} \quad - (37)$$

Denote:

$$\underline{m}_v = m_x \underline{i} + m_y \underline{j} + m_z \underline{k} \quad - (38)$$

$$\underline{r} = r_x \underline{i} + r_y \underline{j} + r_z \underline{k} \quad - (39)$$

Also:

$$\underline{A}_{\text{ext}} - \underline{A}_{\text{ext}}^* = \frac{A^{(0)}}{\sqrt{2}} \left((e^{i\phi} - e^{-i\phi}) \underline{i} - i(e^{i\phi} + e^{-i\phi}) \underline{j} \right) \quad - (40)$$

$$= \frac{2A^{(0)}}{\sqrt{2}} i \left(\underline{i} \sin \phi - \underline{j} \cos \phi \right),$$

so:

$$A^{(0)2} \underline{k} \rightarrow A^{(0)2} \underline{k} + \frac{A^{(0)}}{2\sqrt{2}\pi r^3} \left((m_y r_x - m_x r_y) \cos \phi \underline{i} + (m_y r_x - m_x r_y) \sin \phi \underline{j} \right)$$

i.e.:

$$A^{(0)2} \underline{k} \rightarrow A^{(0)2} \underline{k} + \frac{A^{(0)}}{2\sqrt{2}\pi r^3} (m_y r_x - m_x r_y) \left(\underline{i} \cos \phi + \underline{j} \sin \phi \right)$$

— (41)

The second term spins around the z axis of the applied electromagnetic field.

7) The magnitude $A^{(0)2}$ is changed to:

$$A_{\text{shifted}}^{(0)2} = \left(A^{(0)4} + \frac{A^{(0)2}}{16\pi^2 r^6} (m_y r_x - m_x r_y)^2 \right)^{1/2} \quad (42)$$

i. e.

$$A_{\text{shifted}}^{(0)2} = A^{(0)2} \left(1 + \left(\frac{(m_y r_x - m_x r_y)^2}{2\sqrt{2}\pi r^3} \right)^2 \right)^{1/2} \quad (43)$$

This equation means that the applied field potential amplitude squared is shifted by a factor that can be defined as:

$$\sigma_{\text{RFR}} := \left(\frac{(m_y r_x - m_x r_y)^2}{2\sqrt{2}\pi r^3} \right)^2 \quad (44)$$

This is the RFR chemical shift for an applied plane wave. In eq. (44):

$$r = (r_x^2 + r_y^2 + r_z^2)^{1/2} \quad (45)$$

The resonance frequency is thus shifted to:

$$\omega_{\text{res}} = \frac{e^2}{\hbar m} A^{(0)2} \left(1 + \sigma_{\text{RFR}} \right)^{1/2} \quad (46)$$

and the shift is site-specific (different for each nucleus) — ANALYTICALLY USEFUL