University of Babylon

College of Science

Department of Chemistry

Course No. Chsc 424

Undergraduate Studies

Physical chemistry
Fourth year - Semester 2
Credit Hour: 3 hrs.
Scholar units: 3 units

Lectures of Molecular Spectroscopy

Second Semester, Scholar year 2024-2025

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Lecture No. Six: Magnetic Resonance Spectroscopy

Introduction:

- Magnetic Resonance Spectroscopy is a branch of spectroscopy that deals with the phenomenon found in large number of nucleus (chemical species) that possess both "magnetic moments" and "angular momentum"; when it subjected to external magnetic field.

- Resonance – Implies that in tune with a natural frequency of the nuclear magnetic system in the magnetic field.

What is Spin for a rotating object?

A rotating object possesses a quantity is called angular momentum given by the right hand thumb rule. Spin is a type of angular momentum that does not vanish even at absolute zero! Therefore, a physical motion to represent this type of angular momentum is not without error. Spin is a fundamental property of electron and nucleus like mass, electric charge, and magnetism.

General properties:-

- Magnetic resonance spectroscopy technique gives a new pathway of energy levels production, where energy levels difference is occurred by the effect of outer magnetic field presence.

- Magnetic resonance are comes due interaction between outer magnetic field with the nuclear moment of spin for chemical species.

- The radiation energy at radio frequencies is absorbed (is directed to be perpendicular into magnetic field) by resonance of active chemical species to promotion into high energy levels.
- They found two general techniques in this area; there are Nuclear magnetic resonance spectroscopy (NMR) and Electron spin Resonance spectroscopy (ESR) or Electron para magnetic resonance spectroscopy (EPR).
- The radio frequency radiation limits in NMR reached 10m-100cm. The radio frequency radiation limits at ESR reached 100cm-1cm. Both of them techniques are physical change and not chemical change.

Theory of resonance

Imagine a charge travelling circularly about an axis. As a current that flows through a conducting loop. Such a circular current builds up a magnetic Moment μ whose direction is perpendicular to the plane of the conducting loop. The faster the charge travels the stronger is the induced magnetic field. In other words, a magnetic dipole has created.
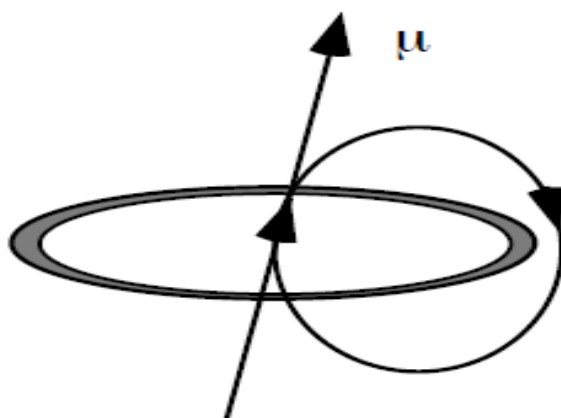

Such dipoles, when placed into a magnetic field, are expect to align with the direction of the magnetic field.

The case of a dipole moment that has created by a rotating charge this force is proportional to the strength of the field (**B**) and to the charge (**m**). The torque that acts to rotate the small magnate is described as:

$$T = \frac{\delta J}{\delta t} = r * F \quad \dots\dots 1$$

J is define as the *angular momentum* that is the equivalent for rotational movements of the linear momentum.


$$p = m \, v$$

$$J = r \times p$$
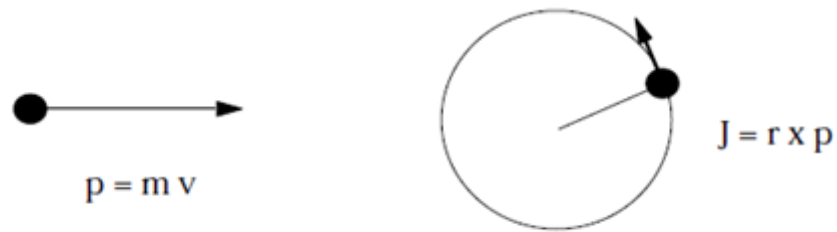
linear momentum. Right: angular momentum

Note that the direction of the momentum is tangential to the direction along which the particle moves. The torque is form by the vector product between the radius and the momentum and is describe by a vector, which is perpendicular to both radius and momentum. In fact, it is the axis of rotation, which is perpendicular to the plane. The corresponding potential energy is:

$$E_{Pot} = -\int_0^\varphi T d\varphi \quad \dots\dots 2$$

In contrast to the behavior of a compass needle, the nuclear spin does not exactly align with the axis of the external field:
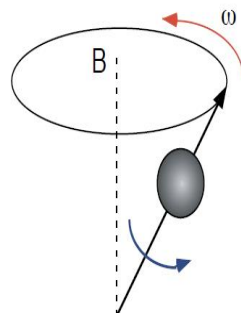
Rotation of the nuclear momentum about its own axis (blue) and about the magnetic field axis (red).

This is a consequence of its rotation about its own axis. This property is call spin. It rotates (spins) about its own axis (the blue arrow) and processes about the axis of the magnetic field B (the red arrow). The frequency of the precession is proportional to the strength of the magnetic field:

$$\omega = \gamma \ \mathbf{B}$$

The proportionality constant γ is called the gyromagnetic ratio. The frequency ω is expressed in terms of angular velocity. It is specific for the kind of nucleus and therefore has a different value for ^1H, ^{13}C, ^{19}F …etc. The precession frequency is

$$\omega_0 = \nu_o 2 \ \pi$$

The relation is called the **Lamor frequency**. Of course, no observe single molecules but look at an ensemble of molecules (usually a huge number of identical spins belonging to different molecules).The sum of the dipole moments of identical spins is called **magnetization**:

$$M = \sum_j \ \mu i \quad ….3$$

Quantum-mechanical treatment:

The dipole moment μ of the nucleus is described in quantum-mechanical terms as:

$$\mu = \gamma \ J \ ……4$$

Therein, J is the spin angular momentum and γ the gyro magnetic ratio of the spin. When they looking at single spins, will have to use a quantum-mechanical treatment. There in, the z-component of the angular momentum J is quantized and can only take discrete values.

$$J_z = m * \frac{h}{2\pi} \quad …….5$$

Where m is the magnetic quantum number. The latter can adopt values of m = -I, -I+1, …,0,...,I-1, I ,since I being the spin quantum number.

4

Vectorial representation of the z-component of the angular momentum for a spin I=1/2 (left)
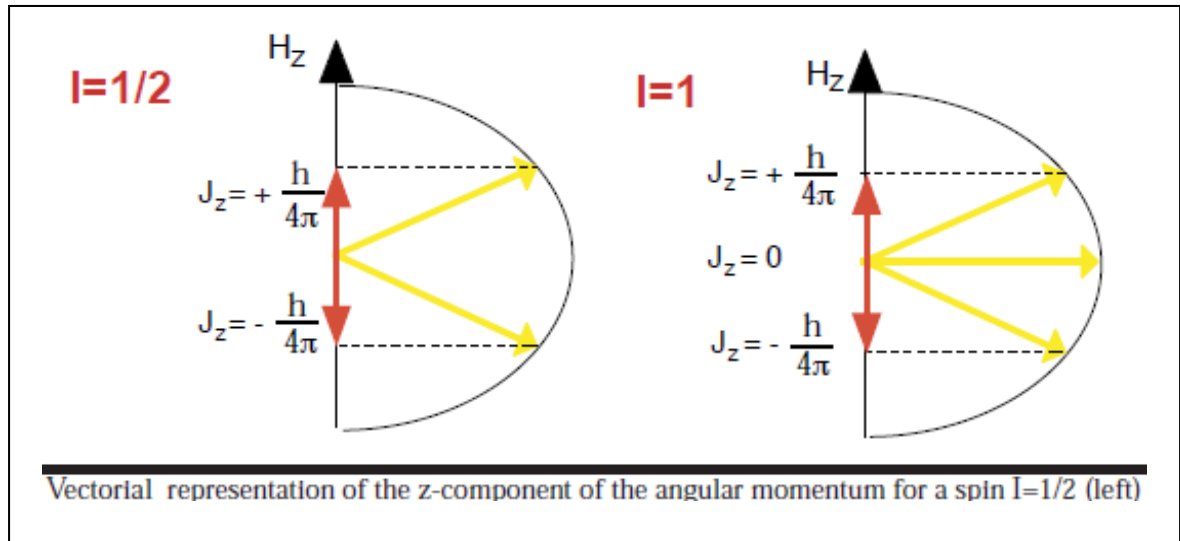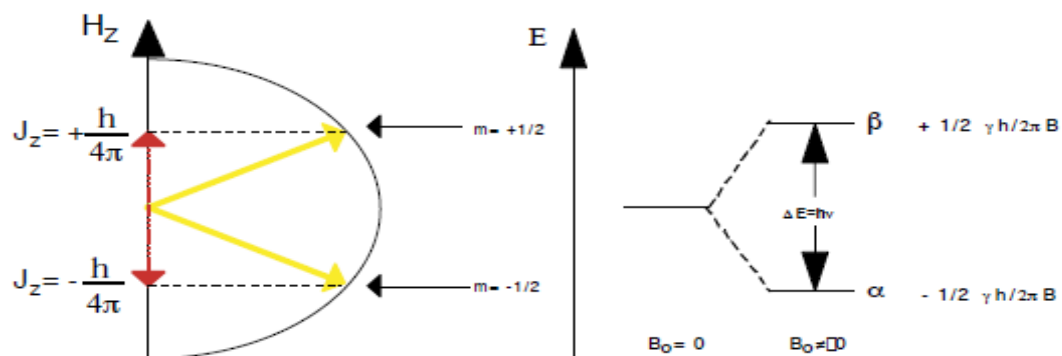
energy levels. For spins with I =1, nuclei will have three different values for J_z are allowed:

$$E_{pot}= \mu\, zB = \gamma\, J\, B \ldots\ldots 6$$

The energy difference ΔE_{pot}, which corresponds to the two states with m=±1/2, is then

$$E_{pot}= \gamma *\frac{h}{2\pi}*B \ldots\ldots 7$$

(The quantum-mechanical selection rule states that only transition with Δm=±1 are allowed):


Energy levels of the α- and β- states of I=1/2 nuclei

Active dipole magnetic moment:

The active dipole magnetic is represented by magnetic moment (**μ**).Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as ^{12}C) these spins are paired against each other, such that the nucleus of the atom has no overall spin. However, in some atoms (such as ^{1}H and ^{13}C) the nucleus does possess an overall spin.

The general rules for determining the net spin of a nucleus are as follows;

1. If the number of neutrons and the number of protons are both even, then the nucleus has NO spin.
2. If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)
3. If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, and 3).

The overall spin, I, is important. Quantum mechanics tells us that a nucleus of spin I will have $2I + 1$ possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a magnetic quantum number, m.

Energy levels for a nucleus with spin quantum number 1/2
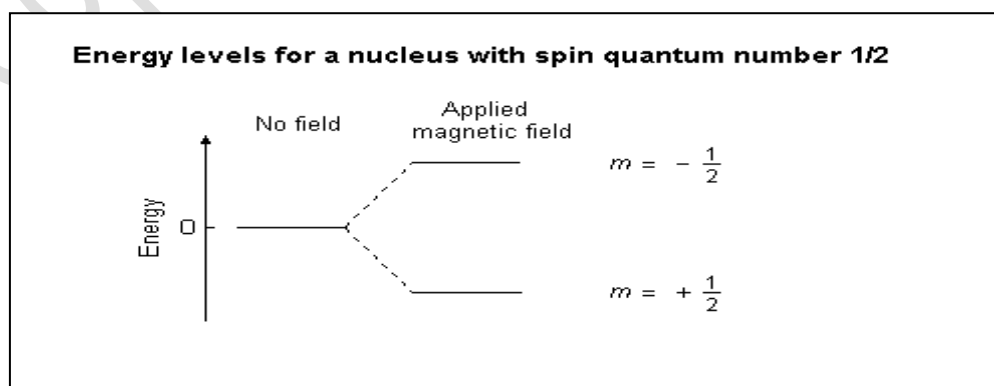
When the nucleus is in a magnetic field, the initial populations of the energy levels are determined by thermodynamics, as described by the Boltzmann distribution. This is very important, and it means that the lower energy level will contain slightly more nuclei than the higher level. It is possible to excite these nuclei into the higher level with electromagnetic radiation. The frequency of radiation needed is determined by the difference in energy between the energy levels.

Some characteristic properties of selected nuclei are given in the following table.

Isotope	Natural % Abundance	Spin (I)	Magnetic Moment (μ)*	Magneto gyro Ratio (γ)[†]
^1H	99.9844	1/2	2.7927	26.753
^2H	0.0156	1	0.8574	4,107
^{11}B	81.17	3/2	2.6880	--
^{13}C	1.108	1/2	0.7022	6,728
^{17}O	0.037	5/2	-1.8930	-3,628
^{19}F	100.0	1/2	2.6273	25,179
^{29}Si	4.700	1/2	-0.5555	-5,319
^{31}P	100.0	1/2	1.1305	10,840

* **μ** in units of nuclear magnetos = $5.05078 \cdot 10^{-27}$ JT^{-1}

[†] γ in units of $10^7 rad$ T^{-1} sec^{-1}