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Physics 518 - Quantum Mechanics III

The Mössbauer Effect

The Mössbauer effect was first described by Rudolf Mössbauer in 1957. The effect describes how nuclei can emit or absorb gamma-rays without recoiling under certain circumstances. When a free nuclei emits or absorbs gamma-rays, it recoils as a result of energy and momentum conservation. As a result, if a free nucleus undergoes a transition from an excited state to its ground state by emitting gamma-rays, the energy of the gamma-rays will be slightly less than the energy difference between the nucleus' ground and excited states. Gamma-rays emitted in this fashion will not have enough energy to excite other nuclei of the same isotope from their ground states to the initial excited state of the emitter nucleus. When gamma-ray emission or absorption is accompanied by the recoil of the emitting or absorbing nucleus, the condition of nuclear resonance can not be achieved. However, nuclei bound in a solid or some other form can undergo recoil-free emission and absorption of gamma-rays provided the recoil energy of the nuclei is too small to displace it from its position relative to other nuclei in the system. Under these conditions, the energy carried by the gamma-rays is equal to the energy difference between the excited and ground states of the nuclei and nuclear resonance can be achieved. The Mössbauer effect is the description of recoil-free nuclear resonances.

The Mössbauer effect can also be used to study the absorption and emission of gamma-rays in a wide variety of materials, usually by Mössbauer spectroscopy. Mössbauer spectroscopy can provide information on how a material chemically binds with other materials. It can also provide information on the magnetic and electric properties of nuclei. The Mössbauer effect has been used effectively in studying the structure and function of hemoglobin, a protein containing iron atoms that transports blood in the body, among other biologically important molecules.

Background

When a nucleus is in an excited state it will undergo a transition to its ground state by the emission of a gamma particle, or highly energetic photon. For many years, it was expected that the emitted photon would have energy equal to the energy difference between the excited and ground states of the emitting nucleus. It was reasoned that the emitted photon could be absorbed by a nearby nucleus of the same isotope exciting it from its ground state to the same excited state as the emitter nucleus. This process is called nuclear resonance. However, this process was not always observed. The reason being that when a nucleus in an excited state emits a gamma particle, the nucleus experiences a small recoil. This nuclear recoil effectively decreases the energy of the emitted photon so that it does not have the required amount of energy to excite a nucleus in its ground state to the excited state of the emitter nucleus.

If an excited nucleus with mass M is at rest with energy E above its ground state and emits a photon with energy E_γ, then by energy conservation the recoil energy of the nucleus, E_R, is given by [eq. 1].

$$E_R = E - E_\gamma \qquad \text{[eq. 1]}$$

Thus, the nucleus gains a recoil velocity, v_R ,leading to [eq. 2]

$$E_R = (M/2)v_R^2 = p_n^2/(2M) \qquad \text{[eq. 2]}$$

where $\mathbf{p}_n$ is the recoil momentum on the nucleus. From conservation of momentum, $\mathbf{p}_n$ must be equal in magnitude but opposite in direction to $\mathbf{p}_\gamma$, the momentum of the emitted photon given by [eq. 3] where k is the magnitude of the wave vector of the photon.

$$p_\gamma = \hbar k = (E_\gamma/c) \qquad \text{[eq. 3]}$$

Therefore, the recoil energy of the nucleus can be written in the form of [eq. 4].

$$E_R = p_\gamma^2/(2M) = E_\gamma^2/(2Mc^2) \qquad \text{[eq. 4]}$$

As a result, the energy of the emitted photon is less than the energy difference, E, between the ground state and excited state of the emitter nucleus as given in [eq. 5]

$$E_\gamma = E - E_R \qquad \text{[eq. 5]}$$

Therefore, if the photon were absorbed by another nuclei of the same isotope in its ground state the photon would not have enough energy to excite the absorber nuclei to the same initial excited state of the emitter nuclei. However, if the emitting nuclei were moving with velocity v, then the energy of the emitted photon can be shifted by a first-order Doppler effect. From conservation of energy, the energy of the emitted photon would have energy given by [eq. 6]

$$E_\gamma = E - E_R - E_D \qquad \text{[eq. 6]}$$

where E_D is the energy of the Doppler shift. [eq. 6]

$$E_D = (v/c)E_\gamma \qquad \text{[eq. 7]}$$

This Doppler shift may offset the effect of the nuclear recoil, thus allowing nuclear resonance to occur. Of particular interest are Doppler shifts caused by the thermal motion of nuclei. If nuclei are undergoing thermal motion, their velocities follow the Maxwell velocity distribution. Therefore, the energy of the Doppler shift and thus the energy of the emitted photons would be proportional to the velocity of the emitting nuclei. Because the velocity of the emitting nuclei follow a Maxwell distribution, the energy of the emitted photons would have a broadened energy distribution and thus the probability of nuclear resonance is increased. Similar effects are observed for the absorbing nuclei. Therefore, by adjusting the motion of the absorbing and emitting nuclei either by thermal or mechanical means, nuclear resonance can be achieved.

The Mössbauer Effect

In 1957, Rudolf Mössbauer discovered that a nucleus in a solid can emit or absorb gamma rays without nuclear recoil under certain circumstances. In a solid, the positions of atoms are determined by the attractive and repulsive forces exerted by surrounding atoms. To model the structure of a solid, the interactions between atoms can be represented by springs connecting an atom to all of its nearest neighbors in a lattice. In this model of solids proposed by Einstein, thermal motion of the composite atoms can be described as vibrational oscillations with angular frequency $\omega_{E.}$ According to this simple model, the average kinetic energy of an atom in a solid can be expressed in terms of the energy of the oscillators where $<x^2>$ is the mean square vibrational amplitude [eq. 8].

$$E_t = M\omega_E <x^2> \qquad \text{[eq. 8]}$$

In quantum mechanics, the energy of each oscillator is described by phonons with energies given by [eq. 9] where n is an integer greater than or equal to zero.

$$E_t = \hbar\ \omega_E (n+1/2) \qquad \text{[eq. 9]}$$

The energy distribution of the phonons is then defined by the population of the energy levels corresponding to different values of n. For the lowest oscillator level, $n = 0$, $<x^2>$ is given by [eq. 10].

$$<x^2> = \hbar / (2M\omega_E) \qquad \text{[eq. 10]}$$

If an atom bound in a solid undergoes gamma-emission, there are several possible results. If the recoil energy of the nuclei is high enough, the emitting atom can be displaced from its position in the solid completely leaving a vacancy in the lattice. If the recoil energy is not enough to knock the emitting atom from its lattice site, it may still be energetic enough to slightly displace the atom. This happens when the recoil energy is higher than the energy spacing $\hbar\omega_E$ between phonon levels. If a single atom is displaced due to the recoil associated with emitting a photon, higher energy phonon levels are excited and the energy will be transferred to the surrounding lattice very quickly reaching thermal equilibrium. However, if the recoil energy is less than the energy separation of the vibrational levels of the solid, i.e. $E_R < \hbar\omega_E$, then the photon is released without the excitation of phonons in the lattice.

The emission of gamma-rays from an atom bound in a solid without excitation of phonons corresponds to a recoil-free emission. This recoil free emission is the Mössbauer effect. In quantum mechanics it can be shown that the mean energy transferred to the lattice in the emission of a single photon is equal to the recoil energy of the emitting atom. In the case of single-phonon processes, the recoil energy transferred to the lattice is given by [eq. 11] where f is the probability of a recoil-free emission.

$$E_R = (1 - f)\,\hbar\omega_E \qquad \text{[eq. 11]}$$

From [eq. 4] and [eq. 10], the fraction of recoil-free emissions can be written in several forms shown in [eq. 12].

$$f = 1 - ((\hbar k)^2/(2M\,\hbar\omega_E)) = 1 - k^2\langle x^2\rangle \qquad \text{[eq. 12a]}$$

$$\approx \exp(-k^2\langle x^2\rangle)\ (\text{for } k^2\langle x^2\rangle << 1) \qquad \text{[eq. 12b]}$$

Two important result of [eq. 12b] are: (1) the fraction of recoil-free emissions decreases as the energy of the gamma particle increases, i.e. increasing k; and (2) the fraction increases with decreasing temperature. The first result is logical because higher energy gamma-rays will produce higher nuclear recoil energies. The second result is a consequence of the relatively small energy separations between oscillation modes ($\hbar\omega_E$)in a substance at low temperatures. As a result fewer oscillator levels can be excited at low temperatures increasing the probability of recoil- free emission. The major importance of the existence of recoil-free emission of gamma-particles from a solid is its correspondence to a zero-phonon transition. A zero-phonon transition occurs without transferring any energy to the lattice meaning that the photon emitted will have the same energy as the energy difference between the ground and excited states of the emitter nucleus. The Mössbauer effect also applies to the recoil-free absorption of gamma particles under similar conditions. Thus, a photon emitted in a recoil-free fashion can be absorbed in a recoil-free fashion in solids leading to recoil-free nuclear resonances. Recoil-free nuclear resonance is the main feature of the Mössbauer effect and has many implications. This effect is used in several different spectroscopic methods used to study the properties of nuclei in a bound lattice.

Mössbauer Spectroscopy

The Mössbauer effect can be used to study several properties of solids and in some cases molecules. Mössbauer spectroscopy takes advantage of the recoil-free fashion of emission and absorption of gamma-rays in a strongly bound lattice. When one nuclei in the lattice is excited, its decay to its ground state will produce a gamma-ray that will then excite another nuclei in the lattice (nuclear resonance). In this case all gamma-rays that are emitted will be absorbed. However, if a small velocity shift between the emitting and absorbing nuclei is applied, the resulting Doppler shift in the gamma-ray's energy will bring the nuclei in and out of resonance. When not in resonance, gamma-ray's will not be completely absorbed in the lattice because their energy is insufficient to excite other nuclei. By observing the absorption of these gamma-rays over a range of different relative velocity differences, the exact energy of a gamma-ray neccessary for nuclear resonance in a solid can be determined.

The Mössbauer effect can also be used to study hyperfine interactions in a solid or other sample. Hyperfine interactions are the result of the interaction between a nuclear property and electronic or atomic properties of the sample. The three main hyperfine interactions that are studied are: (1) electric monopole interactions, (2) magnetic dipole interactions, and (3) electric quadrupole interactions.

The electric monopole interaction is the result of the nuclear charge distribution interacting with the electron-charge density at the nucleus. This interaction will change the energy levels of the ground and excited states of the nuclei. This will also change the transition energies in the emitting and absorbing nuclei. The difference between these transition energies is called the isomer shift. The isomer shift is a function of the relative change of nuclear radius between the excited state and ground state and the difference in the total electron density at the nucleus. Because electron density at the nucleus is a determining factor in an atom's highest electron valence state and therefore chemical bonding, Mössbauer spectroscopy can be used to study the chemical properties of a wide variety of substances.

The magnetic dipole interaction is the result of the nuclear dipole moment interacting with a magnetic field at the site of the nucleus. This interaction splits the nuclear states into sublevels determined by the nuclear spin quantum number. Each excited state of a nucleus has a different nuclear magnetic moment associated with it. Therefore, when a nuclei in an excited state emits a gamma particle to reach its ground state, its nuclear magnetic moment changes. Therefore, the energy splittings also change in this transition. This change in energy splitting provides information on the magnetic properties and allowed transitions of the material being studied.

The electric quadrupole interaction is the result of the interaction between the nuclear electric quadrupole moment and the principal component of the diagonalized electric field gradient tensor ($Vzz=\delta^2V/\delta^2z$). This interaction also splits the nuclear energy states into sublevels corresponding to different nuclear spin quantum numbers. Thus, a nucleus with an electric quadrupole moment in an excited state will emit gamma-rays in a pattern with a dependence on the angle between the direction of emission and the principal axis of the electric field gradient. This allows for studying the properties of nuclei in electric fields.

The Mössbauer Effect in Hemoglobin

Hemoglobin is a protein found in red blood cells that transports oxygen throughout the body. Hemoglobin is composed of four heme groups each of which contain an iron atom. The iron atoms in the heme groups exist as the ion Fe^{+2} allowing hemoglobin to bond to a number of different molecules (or ligands) such as oxygen (O_2), carbon monoxide (CO), and carbon dioxide (CO_2). The density of hemoglobin in red blood cells is so high that it can be modeled as an Einstein solid and exhibits the Mössbauer effect at low temperatures. In order to study the function of hemoglobin, Mössbauer spectroscopy can be used to study the transition of iron from its excited state with nuclear spin $I=3/2$ to its ground state with $I=1/2$ with the emission of a 14.4 keV gamma-ray. By attaching different ligands to hemoglobin and observing transitions in the iron atom, information about the properties of hemoglobin can be attained.

In 1965, an experiment conducted by U. Gonser and R. W. Grant used Mössbauer spectroscopy to study hemoglobin. In this experiment Cobalt-57 diffused in Platinum and kept at room temperature was used as a source of gamma-rays. These gamma-rays were then absorbed by red blood cell samples with various ligands attached to the hemoglobin. Mössbauer spectra were taken for each sample at a low temperature (5K) and used to infer some of hemoglobin's general properties. Table 1 contains information about the quadrupole splitting and isomer shift of each of the samples examined relative to those of Cobalt/Platinum source.

Absorber	Ligand	Quadrupole Splitting (mm/s)	Isomer Shift (mm/s)
Red Cells	O_2	2.25∓0.05	-0.08∓0.05
	H_2O	2.4∓0.1	0.59∓0.05
Red Cells O_2-atmosphere	O_2	2.25∓0.03	-0.08∓0.02
Red Cells CO_2-atmosphere	H_2O	2.35∓0.05	0.58∓0.03
Red Cells N_2-atmosphere	H_2O	2.36∓0.05	0.59∓0.03
Red Cells CO-atmosphere	CO	0.34∓0.05	-0.07∓0.03

Table 1. Quadrupole splitting and isomer shifts of several compounds.

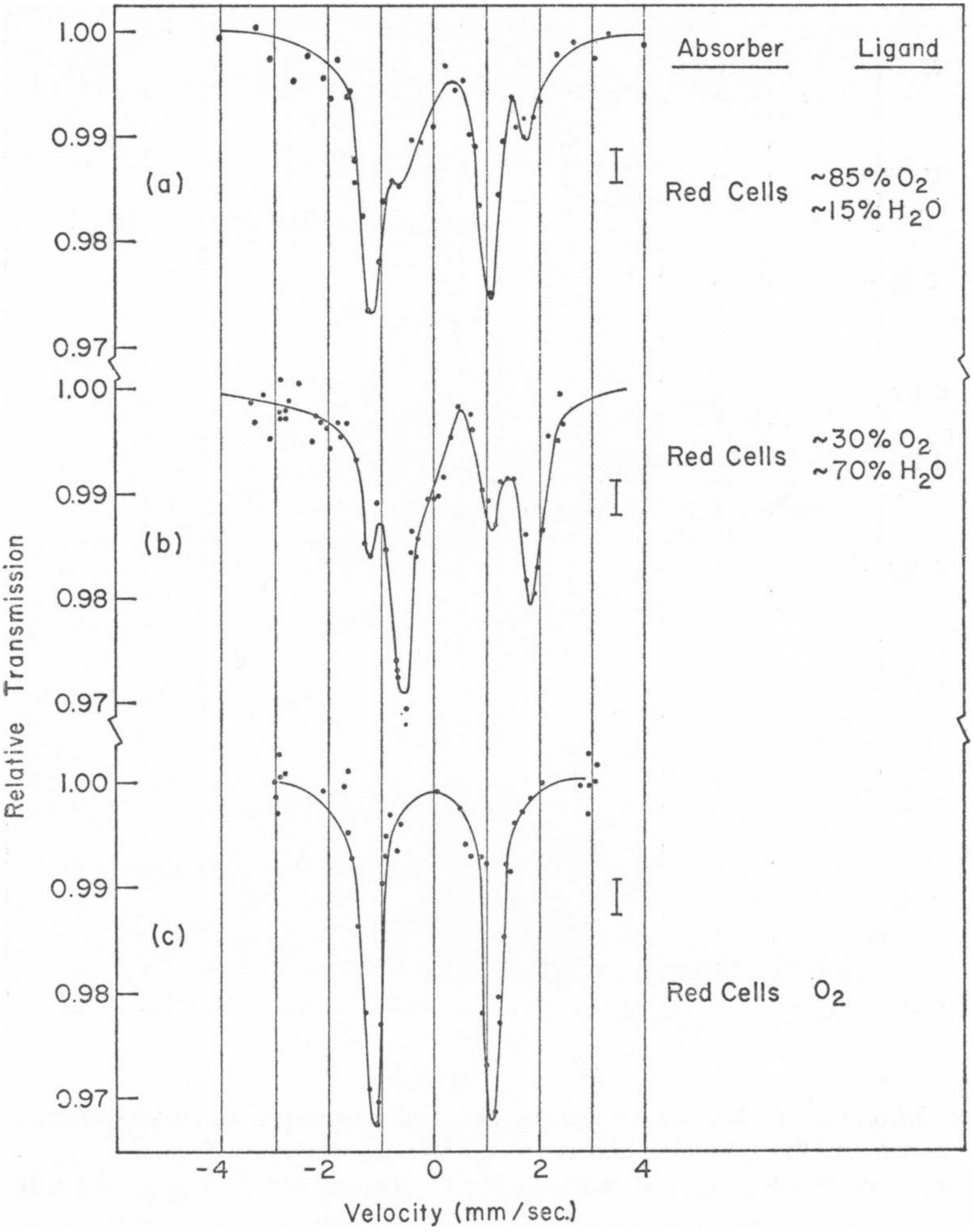
The actual spectra obtained by Gonser and Grant are included in Appendix A.

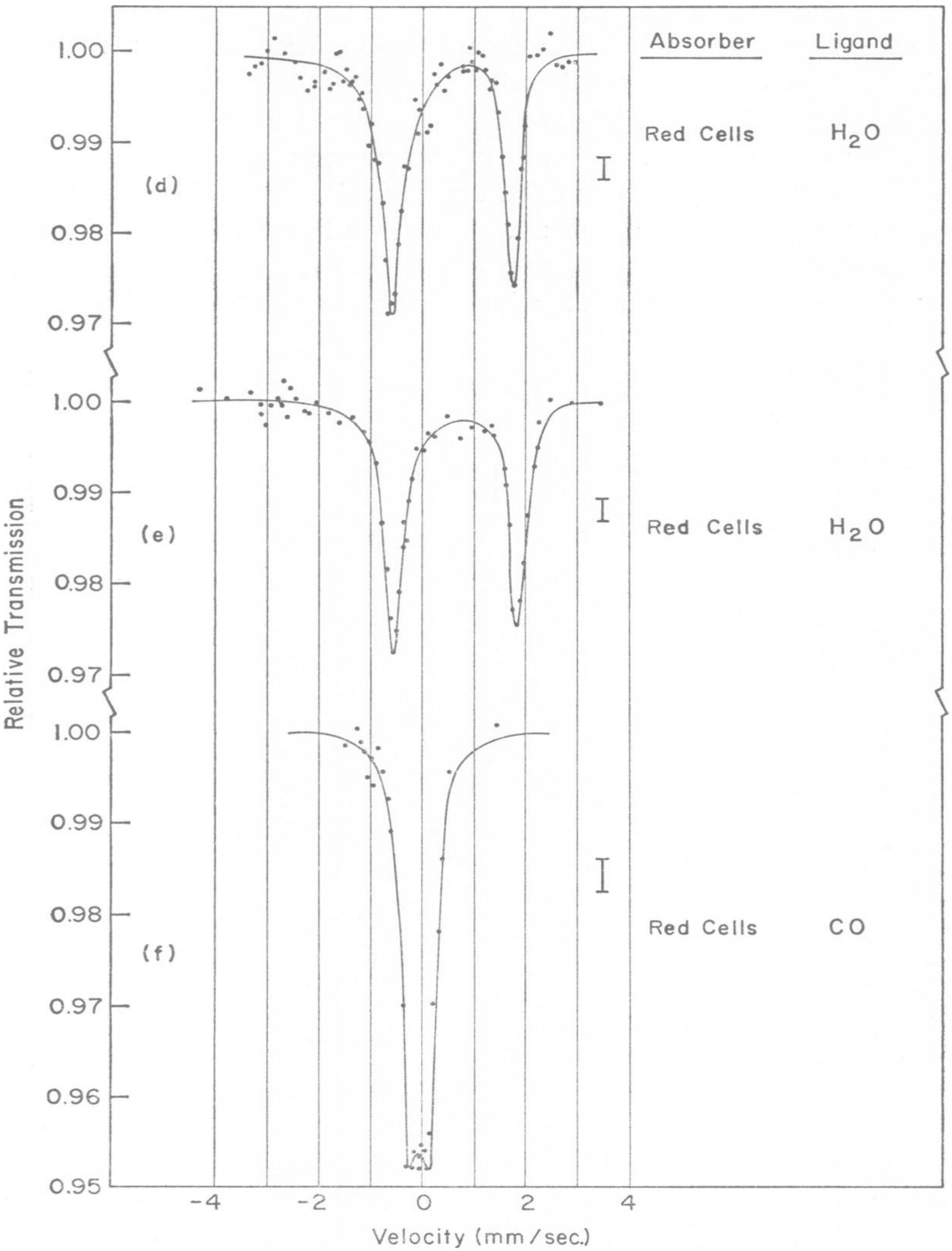
The results of the experiments contain large amounts of information about hemoglobin and how it binds to and releases different ligands. The small isomer shift of red cells in a CO-atmosphere with CO as the ligand means that the density of electrons around the iron nuclei in hemoglobin was approximately the same for the excited state and ground state. This suggests that CO bonds very well with hemoglobin. Whereas, the large isomer shifts observed for red cells with H_2O as the ligand suggests that H_2O will not bond very well with hemoglobin. Further information about the magnetic properties of hemoglobin can also be determined by measuring the quadrupole splitting as a function of the ligand attached to it. According to the data collected red cells with CO as the ligand experience much smaller quadrupole splitting when compared to all other ligands. This suggests that CO effectively prevents the interaction between the iron nuclei in hemoglobin with any present magnetic field. These are only a few of the many conclusions that can be made using Table 1.

Conclusion

The Mössbauer effect describes recoil-free nuclear resonances that occur in certain material. The Mössbauer effect has proven useful in studying the way in which hemoglobin, an iron-rich protein in red blood cells, will bond to a variety of ligands such as oxygen, carbon dioxide, and carbon monoxide. This information is useful when studying any disorder involving hemoglobin such as sickle cell disease. The Mössbauer effect also has many other applications in biological physics as well as almost every other field of science.

Appendix A


Relative Transmission
1.00
0.99
0.98
0.97
(a)
(b)
(c)
Absorber
Ligand
Red Cells
~85% O_2
~15% H_2O
Red Cells
~30% O_2
~70% H_2O
Red Cells
O_2
-4
-2
0
2
4
Velocity (mm/sec.)


Absorber
Ligand
Red Cells
H_2O
(d)
Red Cells
H_2O
(e)
Red Cells
CO
(f)
Relative Transmission
1.00
0.99
0.98
0.97
0.96
0.95
-4
-2
0
2
4
Velocity (mm / sec.)

References

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