NMR

The suggestion is also made that CO_2 may be strongly dissociated by the metastable Xe atoms (and H_2O somewhat less strongly), thus producing oxygen atoms which combine to form the O_2 molecules; ($D(CO_2)=5.5$ v, $D(H_2O)=5.0$ v). If so, the fact that CO did not yield the bands would indicate that the dissociation energy of CO is greater than the energy of the upper metastable state of Xe, namely 9.4 volts. (Energy of lower metastable state equals 8.3 v.) This appears to be direct evidence in favor of the 9.6-volt value of D(CO) as determined by Hagstrum and Tate[1] from appearance potentials in the mass spectrograph, or for the 11.11 v-value obtained in a recent spectral analysis by Gaydon and Penney,[2] but against the 9.14-volt value determined from certain predissociation data.[3] The higher value appears to be more in accord also with thermochemical data as brought out by Hagstrum and Tate,[1] and also by Asundi and Samuel.[4]

[1] H. D. Hagstrum and J. T. Tate, Phys. Rev. **59**, 355 (1941).
[2] A. G. Gaydon and W. G. Penney, Proc. Roy. Soc. **A183**, 374 (June, 1945).
[3] For a review see G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), Chap. VIII.
[4] R. K. Asundi and R. Samuel, Ind. Acad. Sci. **3A**, 267 (1936).

Resonance Absorption by Nuclear Magnetic Moments in a Solid

E. M. Purcell, H. C. Torrey, and R. V. Pound*
Radiation Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts
December 24, 1945

IN the well-known magnetic resonance method for the determination of nuclear magnetic moments by molecular beams,[1] transitions are induced between energy levels which correspond to different orientations of the nuclear spin in a strong, constant, applied magnetic field. We have observed the absorption of radiofrequency energy, due to such transitions, in a *solid* material (paraffin) containing protons. In this case there are two levels, the separation of which corresponds to a frequency, ν, near 30 megacycles/sec., at the magnetic field-strength, H, used in our experiment, according to the relation $h\nu=2\mu H$. Although the difference in population of the two levels is very slight at room temperature ($h\nu/kT\sim 10^{-5}$), the number of nuclei taking part is so large that a measurable effect is to be expected providing thermal equilibrium can be established. If one assumes that the only local fields of importance are caused by the moments of neighboring nuclei, one can show that the imaginary part of the magnetic permeability, at resonance, should be of the order $h\nu/kT$. The absence from this expression of the nuclear moment and the internuclear distance is explained by the fact that the influence of these factors upon absorption cross section per nucleus and density of nuclei is just cancelled by their influence on the width of the observed resonance.

A crucial question concerns the time required for the establishment of thermal equilibrium between spins and lattice. A difference in the populations of the two levels is a prerequisite for the observed absorption, because of the relation between absorption and stimulated emission. Moreover, unless the relaxation time is very short the absorption of energy from the radiofrequency field will equalize the population of the levels, more or less rapidly, depending on the strength of this r-f field. In the expectation of a long relaxation time (several hours), we chose to use so weak an oscillating field that the absorption would persist for hours regardless of the relaxation time, once thermal equilibrium had been established.

A resonant cavity was made in the form of a short section of coaxial line loaded heavily by the capacity of an end plate. It was adjusted to resonate at about 30 mc/sec. Input and output coupling loops were provided. The inductive part of the cavity was filled with 850 cm³ of paraffin, which remained at room temperature throughout the experiment. The resonator was placed in the gap of the large cosmic-ray magnet in the Research Laboratory of Physics, at Harvard. Radiofrequency power was introduced into the cavity at a level of about 10^{-10} watts. The radiofrequency magnetic field in the cavity was everywhere perpendicular to the steady field. The cavity output was balanced in phase and amplitude against another portion of the signal generator output. Any residual signal, after amplification and detection, was indicated by a microammeter.

With the r-f circuit balanced the strong magnetic field was slowly varied. An extremely sharp resonance absorption was observed. At the peak of the absorption the deflection of the output meter was roughly 20 times the magnitude of fluctuations due to noise, frequency, instability, etc. The absorption reduced the cavity output by 0.4 percent, and as the loaded Q of the cavity was 670, the imaginary part of the permeability of paraffin, at resonance, was about $3\cdot 10^{-4}$, as predicted.

Resonance occurred at a field of 7100 oersteds, and a frequency of 29.8 mc/sec., according to our rather rough calibration. We did not attempt a precise calibration of the field and frequency, and the value of the proton magnetic moment inferred from the above numbers, 2.75 nuclear magnetons, agrees satisfactorily with the accepted value, 2.7896, established by the molecular beam method.

The full width of the resonance, at half value, is about 10 oersteds, which may be caused in part by inhomogeneities in the magnetic field which were known to be of this order. The width due to local fields from neighboring nuclei had been estimated at about 4 oersteds.

The relaxation time was apparently shorter than the time (one minute) required to bring the field up to the resonance value. The types of spin-lattice coupling suggested by F. Waller[2] fail by a factor of several hundred to account for a time so short.

The method can be refined in both sensitivity and precision. In particular, it appears feasible to increase the sensitivity by a factor of several hundred through a change in detection technique. The method seems applicable to the precise measurement of magnetic moments (strictly, gyromagnetic ratios) of most moderately abundant nuclei.

electric accelerating fields are to be obtained by replacing the usual "dee" assembly and acceleration chamber by a cavity resonator, similar to types now commonly employed in radar. The use of such a cavity becomes practical only in an iron-less device, because of the limitation imposed by the air-gap in present accelerators.

The maximum orbit radius is to be small. This requires a large guiding magnetic field, but at the same time greatly reduces the volume through which this field must be maintained. It, therefore, appears practicable to immerse the entire accelerator in a liquified gas, such as hydrogen or nitrogen. Cooling the assembly materially reduces ohmic resistance losses in the field windings, and thus simplifies the problem of passing large current pulses. It has also the advantage of increasing the "Q" of the resonator.

Although many of the commoner types of cavity resonators[3] exhibit electric field configurations adapted to producing resonance acceleration, the type describable as a "sphere (or spheroid) and re-entrant cones"[4] seems particularly suitable. In such a cavity, the electric field lines appear as arcs of circles, terminating on the surfaces of the re-entrant cones. Small slots are to be made at points in the conical surfaces, through which the accelerated particles are to pass in their circular orbits. Injection may conveniently be accomplished from a point external to the accelerating fields by placing the injector gun within one of the cones. A target may also be conveniently located within the cones. It will probably be necessary to partially "open-circuit" the cavity walls for low frequency currents generated by the guide field. This can readily be done.

Within a resonator such as described, it should be possible to obtain exceptionally high accelerating potential drops, of the order of several hundred thousand volts. This follows from the fact that a cavity resonator is an extremely efficient device, often exhibiting an electrical "Q" greater than 100,000 and consequently requiring a relatively small energy input to produce large internal fields. The upper limit of attainable electric fields within an evacuated cavity should be very high, and will probably be imposed by field emission effects. In the use of such a resonator, it is convenient to employ the cavity itself as the frequency controlling element of a power oscillator, thus eliminating problems of accurate frequency control.

Some small advantage may also be gained from enclosing the particle orbits within a closed conducting surface, in that this will minimize that part of the radiation losses contributed by low order harmonics. It has been shown,[5] however, that these harmonics contribute only slightly to the total radiative dissipation.

The conditions for "resonant" increase of energy[6] can be satisfied at all times during an acceleration cycle, provided the amplitude of the resonance electric field is increased simultaneously with the rise of the magnetic field. It can be shown that under these conditions the effect of the magnetic component of the cavity field will be negligible throughout the cycle, provided adequate focusing forces are established by the guide field.

To provide the necessary pulses of current through the field windings, three methods could be employed: (a) a "pulse transformer" excited from a d.c. source, (b) a short-circuited d.c. generator (following Kapitza's technique), or (c) a bank of high capacity storage batteries of the type used in submarines. A large ignitron and delay-line extinguishing circuit would serve as the switching element. The limits on the particle yield of the accelerator will be set by the available power and by the allowable rate of heat dissipation from the field windings.

Some design calculations have been made for a 300-Mev electron accelerator.

The author wishes to express his appreciation for counsel and suggestions given by Mr. H. F. Kaiser, Dr. Ross Gunn, and Mr. D. de Packh of the Naval Research Laboratory.

[1] Veksler, J. Phys. Acad. Sci. USSR **9**, 153 (1945).
[2] E. M. McMillan, Phys. Rev. **68**, 143 (1945).
[3] Terletsky, J. Phys. Acad. Sci. USSR **8**, 130 (1945).
[4] D. Ivanenko and I. Pomeranchuk, Phys. Rev. **65**, 343 (1944).
[5] Arzhelovich and Pomeranchuk, J. Phys. Acad. Sci. USSR **9**, 267 (1945).
[6] E. M. McMillan, Phys. Rev. **68**, 144 (1945).
[7] W. W. Hansen and R. D. Richtmyer, J. App. Phys. **10**, 189 (1939).
[8] Schelkunoff, *Electromagnetic Waves* (D. Van Nostrand Company, New York, 1943), p. 288.

Nuclear Induction

F. Bloch, W. W. Hansen, and Martin Packard
Stanford University, Stanford University, California
January 29, 1946

THE nuclear magnetic moments of a substance in a constant magnetic field would be expected to give rise to a small paramagnetic polarization, provided thermal equilibrium be established, or at least approached. By superposing on the constant field (z direction) an oscillating magnetic field in the x direction, the polarization, originally parallel to the constant field, will be forced to precess about that field with a latitude which decreases as the frequency of the oscillating field approaches the Larmor frequency. For frequencies near this magnetic resonance frequency one can, therefore, expect an oscillating induced voltage in a pick-up coil with axis parallel to the y direction. Simple calculation shows that with reasonable apparatus dimensions the signal power from the pick-up coil will be substantially larger than the thermal noise power in a practicable frequency band.

We have established this new effect using water at room temperature and observing the signal induced in a coil by the rotation of the proton moments. In some of the experiments paramagnetic catalysts were used to accelerate the establishment of thermal equilibrium.

By use of conventional radio techniques the induced voltage was observed to produce the expected pattern on an oscillograph screen. Measurements at two frequencies ν showed the effect to occur at values H of the z field such that the ratio H/ν had the same value. Within our experimental error this ratio agreed with the g value for protons, as determined by Kellogg, Rabi, Ramsey, and Zacharias.[1]

We have thought of various investigations in which this effect can be used fruitfully. A detailed account will be published in the near future.

[1] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, and J. R. Zacharias, Phys. Rev. **56**, 728 (1939).

Magnetyczny rezonans jądrowy Jądra wodoru ^{1}H o spinie I=1/2 (protony)

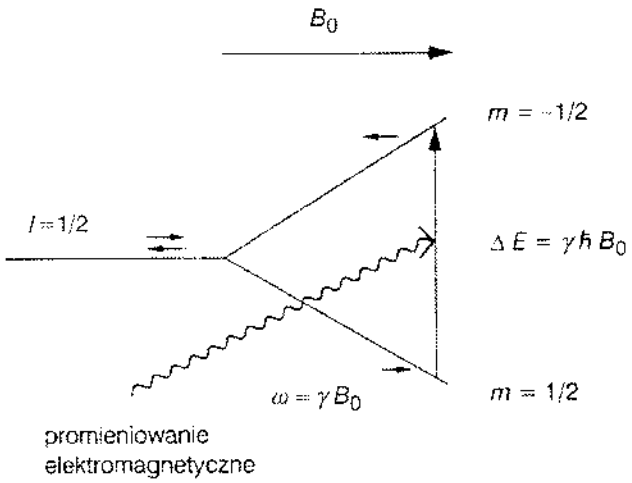
- W polu magnetycznym stan podstawowy jądra wodoru rozszczepia się tylko na dwa podpoziomy (m=1/2 i m=-1/2), których stosunek obsadzeń w danej temperaturze T opisuje prawo Boltzmanna

$$N_{1/2}/N_{-1/2}=\exp(\gamma\hbar B_0/k_B T)\approx 1+\gamma\hbar B_0/k_B T$$

- Dla B_0=1T i T=298 K różnica obsadzeń wynosi 6,857 $*10^{-6}$.
- Jeżeli próbka zawierająca protony, umieszczona w polu magnetycznym B_0 zostanie dodatkowo naświetlona promieniowaniem elektromagnetycznym o częstości $\nu=\omega/2\pi$ i indukcji magnetycznej $B_1<<B_0$ $\boldsymbol{B_1}$ prostopadle do $\boldsymbol{B_0}$ i jeżeli spełniony jest warunek rezonansu $\omega=\omega_0=\gamma B_0$, to wywołane zostaną przejścia pomiędzy sąsiednimi poziomami zeemanowskimi

$$\Delta E=h\nu=\gamma\hbar B_0$$

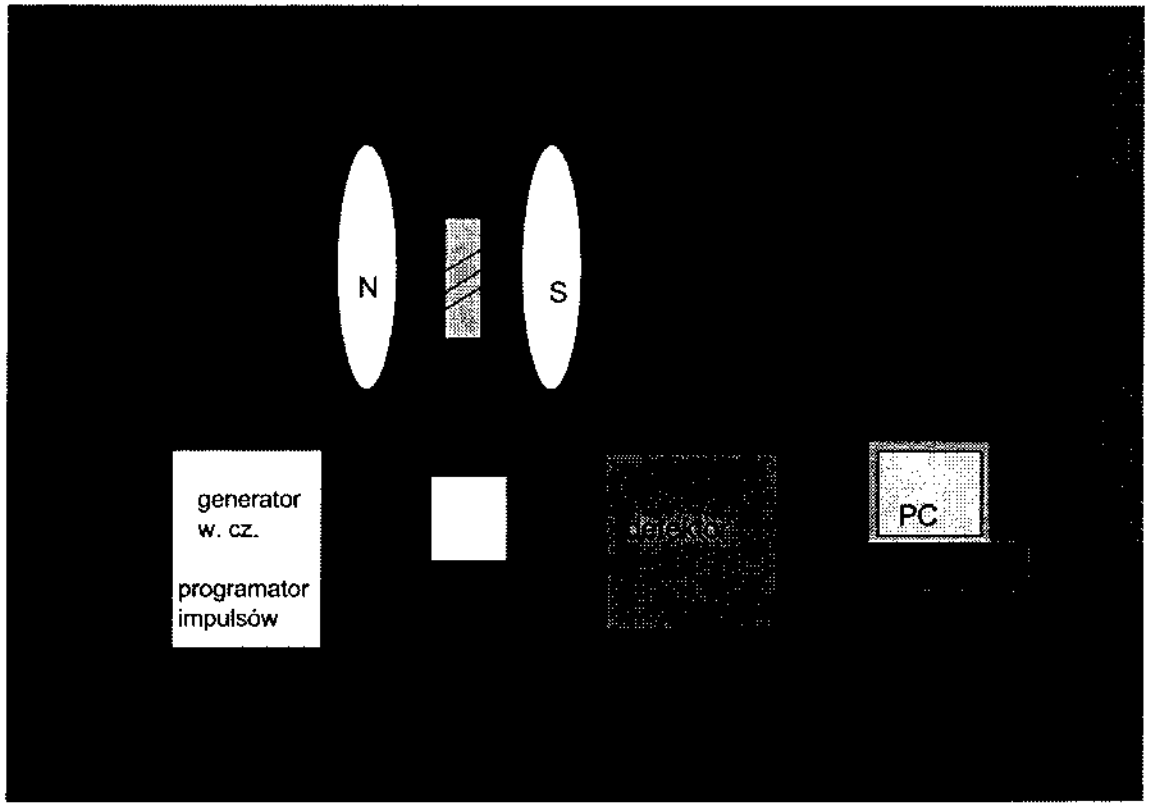
Magnetyczny rezonans jądrowy Jądra wodoru ^{1}H o spinie I=1/2 (protony)



- Dla protonów $\gamma/2\pi$=42,58MHz/T,
  przy polach B_0 z zakresu od 1 do 21,4 T częstość rezonansu protonowego ν~ 42,58 – 900 MHz (ultrakrótkie fale radiowe do mikrofal)
- Eksperymentalnie warunek rezonansu można spełnić albo poprzez zmianę indukcji pola B_0 lub poprzez dostrajanie do rezonansu częstości pola elektromagnetycznego B_1 (może być ciągłe albo impulsowe)

Magnetyczny rezonans jądrowy

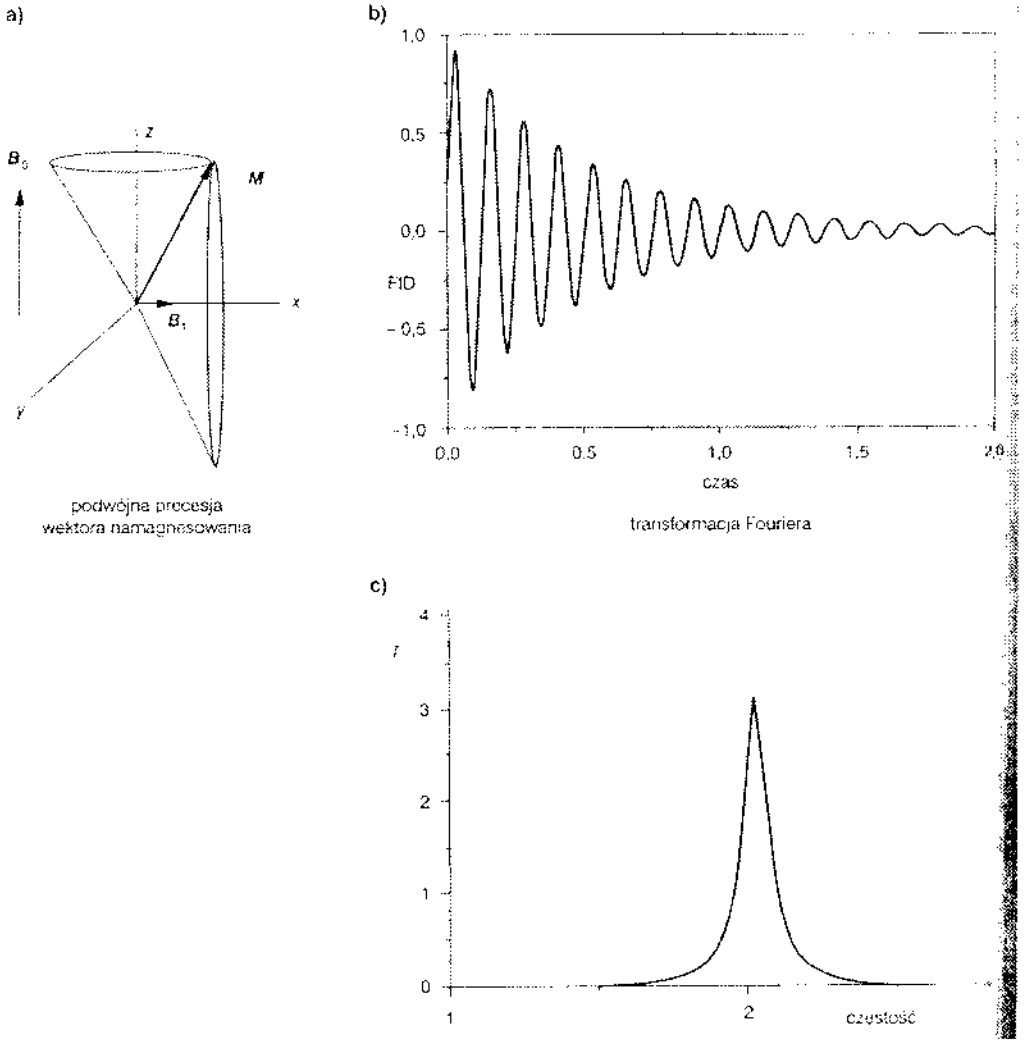
Schemat blokowy spektrometru NMR



- Pole magnetyczne musi być jednorodne (jednorodność rzędu ~ 10^{-10})
musi być również idealnie stabilne czasowo

Według: *„Fizyczne metody badań w biologii, medycynie i ochronie środowiska"* ,red. A.Z. Hrynkiewicz i E. Rokita, PWN Warszawa 1999

Makroskopowy opis zjawiska NMR

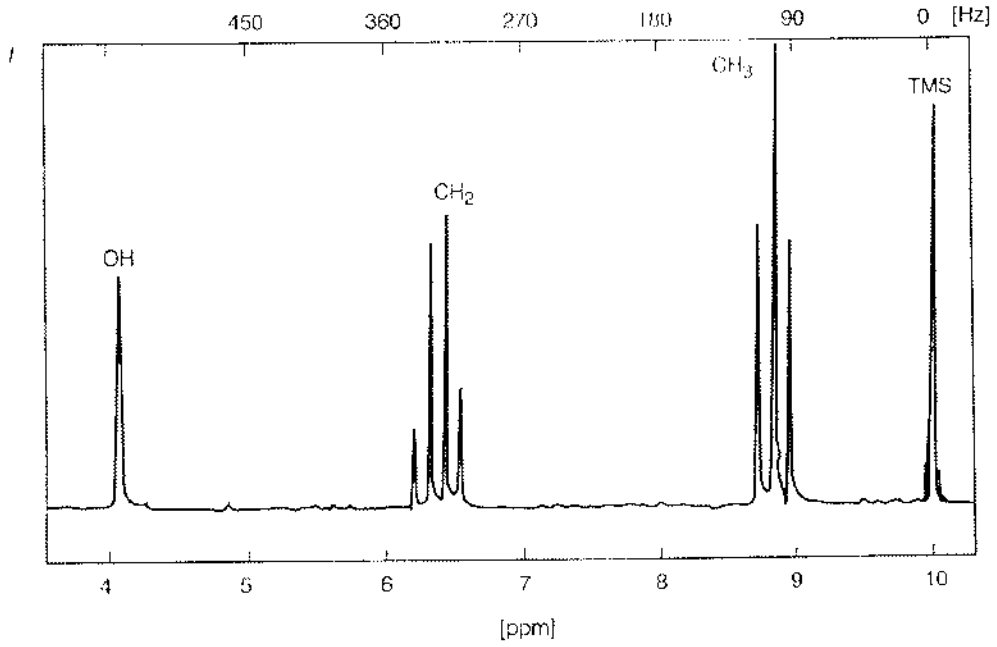


- W wyniku uporządkowania spinów jądrowych w zewnętrznym polu magnetycznym w próbce powstaje makroskopowy moment magnetyczny M, zwany namagnesowaniem.

  W wyniku działania pola B_1 wektor namagnesowania zostanie przeorientowany względem kierunku B_0.

  Zmiana kierunku precesującego namagnesowania M można zarejestrować. W cewce otaczającej próbkę indukowane jest zmienne napięcie – sygnał swobodnej precesji (FID- free induction decay)

Widma NMR



Widmo NMR alkoholu etylowego

Widma NMR

- Powierzchnia pod linią rezonansową jest proporcjonalna do liczby jąder dających wkład w tę linię
- Poszerzenie i rozszczepienie linii powodowane jest niejednorodnością zewnętrznego pola magnetycznego, ograniczonym czasem życia jądra na danym poziomie, wzajemnym oddziaływaniem jąder

Jądra rezonansowe wchodzące w skład rozmaitych związków chemicznych otoczone są przez chmury elektronowe, które ekranują pole magnetyczne w wyniku czego powstaje efektywne pole magnetyczne

$$B_{ef}=(1-\sigma)B_0$$

gdzie σ jest stałą ekranowania

Widma NMR

- Odległość danej linii od umownej linii wzorcowej nazywamy przesunięciem chemicznym

$$\delta=((\nu_{\text{danej linii}}-\nu_{\text{wzorca}})/\nu)10^6$$

- Jako wzorca przy pomiarach przesunięć chemicznych najczęściej używa się tetrametylosilanu $(CH_3)_4Si$

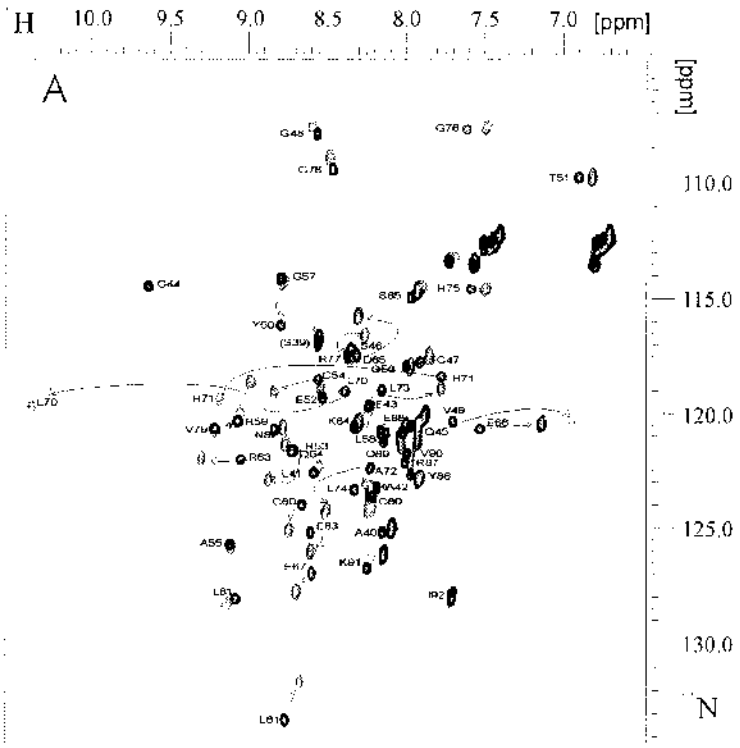
Magnetyczny rezonans jądrowy

Najważniejsze jądra rezonansowe występujące w materiale biologicznym

Jądro	Spin	Częstość rezonansu w polu B_0=1 T [MHz]	Naturalna abundancja [%]	Czułość względna [%]
^{1}H	1/2	42,58	99,98	1 (wzorzec)
^{2}H	1	6,53	$1,56 \cdot 10^{-2}$	$9,66 \cdot 10^{-3}$
^{13}C	1/2	10,71	1,11	$1,59 \cdot 10^{-2}$
^{14}N	1	3,08	99,63	$1,01 \cdot 10^{-3}$
^{15}N	1/2	4,31	0,37	$2,85 \cdot 10^{-6}$
^{17}O	5/2	5,77	$3,70 \cdot 10^{-2}$	$2,91 \cdot 10^{-2}$
^{19}F	1/2	40,07	100	0,83
^{23}Na	3/2	11,27	100	$9,25 \cdot 10^{-2}$
^{25}Mg	5/2	2,61	10,13	$2,67 \cdot 10^{-3}$
^{31}P	1/2	17,25	100	$6,63 \cdot 10^{-2}$
^{33}S	3/2	3,27	0,76	$2,26 \cdot 10^{-3}$
^{35}Cl	3/2	4,17	75,53	$4,70 \cdot 10^{-3}$
^{39}K	3/2	1,99	93,1	$5,08 \cdot 10^{-4}$
^{43}Ca	7/2	2,86	0,145	$2,10 \cdot 10^{-3}$

Źródło: *„Fizyczne metody badań w biologii, medycynie i ochronie środowiska”* ,red. A.Z. Hrynkiewicz i E. Rokita, PWN Warszawa 1999

Magnetyczny rezonans jądrowy



- Więcej fizyki na następnym wykładzie (precesja elektronu w polu magnetycznym)
- wielowymiarowy NMR