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J. Phys. E: Sci. Instrum., Vol. 15, 1982. Printed in Great Britain

A cryogenic RF oscillator, the heart of a new NMR dispersion spectrometer

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Received 15 July 1981, in final form 26 November 1981

Abstract. We describe a new CW–NMR dispersion spectrometer based on the detection of the frequency shift of a cryogenic tunnel diode oscillator, in which the inductance of the coil is influenced by the magnetic resonance phenomenon. Besides the design, the details of the construction and the operation of the oscillator, an outline of the performances and the major advantages and disadvantages of this spectrometer are given. The performances are compared with those of conventional NMR absorption (and dispersion) spectrometers.

1. Introduction

During the last ten years, HF oscillators have been extensively used as transducers for all kind of measurements of various physical quantities (Van Degrift 1975, Van Degrift *et al* 1978, Clover and Wolf 1970, Boschi *et al* 1973, Van Degrift and Love 1981, Lengeler 1974, Robinson 1977, Aslam and Weyhmann 1973) because of the great precision with which frequency may be measured. Measurements of the frequency of a LC oscillator can be used, indeed, to detect extremely small changes in the inductance or capacitance of the resonant circuit.

In the case of the study of properties at low temperatures one major difficulty arises. Not only has the LC circuit to be put in the cryostat, but also the entire HF oscillator. Otherwise, stability, signal-to-noise ratio, and the frequency itself are limited by the parasitic inductance and capacitance of the long transmission line from the resonant circuit to the rest of the oscillator at room temperature: e.g., changes of the dielectric constant of the transmission line, due to changes of the helium level, would give undesirable changes of the frequency. Consequently, the choice of active and passive components is strongly limited.

In this paper we describe the design, construction and operation of a *cryogenic LC oscillator*, driven by a tunnel diode, and, based upon it, the performance of a new kind of NMR spectrometer, the *NMR dispersion spectrometer*. An outline of the major advantages and disadvantages of this method is given.

2. The idea

In conventional CW–NMR spectrometers one uses the in-phase or out-of-phase voltage induced across the HF coil L_0, containing the sample, while the static magnetic field H_s is swept through resonance. Assuming the spectrometer to fulfil all classical conditions of a high-fidelity electronic device, the ultimately detected and observed quantities are voltages at the spectrometer 'output', given – if L_o is in a constant current parallel LC circuit – by:

$$\Delta V' = V\eta\chi' = L_o\omega_o Q_o K_o H_1 S\eta\chi' \tag{1}$$

$$\Delta V'' = V\eta\chi'' = L_o\omega_o Q_o K_o H_1 S\eta\chi'' \tag{2}$$

and – if L_o is in a constant current series LC circuit – by:

$$\Delta V' = V^*\eta\chi' = L_o\omega_o K_o H_1 S\eta\chi'$$

$$\Delta V'' = V^*\eta\chi'' = L_o\omega_o K_o H_1 S\eta\chi''$$

where†:

ω_o = the frequency of the spectrometer oscillator
Q_o = the quality factor of the LC circuit
K_o = an unknown HF coil coefficient
H_1 = the half amplitude of the HF magnetic field
S = a complex and variable sensitivity coefficient of the detection and amplification system, depending on the type of spectrometer (and on time)
η = the filling factor of the HF coil
$\chi = \chi' - j\chi''$ = the HF susceptibility of the sample.

Basically, equations (1) and (2) are derived from the variation $\Delta L_o = \eta L_o \chi$ in the induction coefficient L_o of the L_oC_o circuit as we sweep H_s through the resonance value $H_o \equiv \omega_o/\gamma$. The real part χ' of the HF susceptibility modifies the reactance X_o:

$$\Delta X_o = \eta L_o \omega_o \chi'. \tag{3}$$

Considering that in almost all cases $Q_o^2 \gg 1$, the eigenfrequency ω_e of the L_oC_o circuit is given by $\omega_e \equiv (L_oC_o)^{-1/2}$.

Since, moreover, $\Delta\omega_e$, the variation of ω_e by the resonance phenomenon, is much smaller than ω_e, clearly $\Delta\omega_e/\omega_e = -\frac{1}{2}\Delta X_o/X_o$, and, using equation (3), we finally get:

$$\Delta\omega_e = -\tfrac{1}{2}\omega_e\eta\chi' \tag{4}$$

a relation analogous to relation (1). Indeed, an *eigen*frequency is not an *actual* frequency, a frequency of a signal, and therefore has to be determined, generally speaking – like an inductance or a capacitance – via a *voltage* measurement. So did the previous conventional NMR dispersion spectrometers.

What one should do – in fact a quite obvious thing – is to make the actual frequency ω_o of the oscillator identical to the eigenfrequency of the L_oC_o circuit, i.e. to incorporate the circuit as a tank circuit in a simple HF oscillator in such a way that

$$\omega_o \equiv \omega_e. \tag{5}$$

Now, relation (4) can be translated into:

$$\Delta\omega_o = -\tfrac{1}{2}\omega_o\eta\chi' \tag{6}$$

a 'sister' relation to relation (1), with V' and V replaced by ω_o. The major difference – and the major advantage – is that ω_o, as well as $\Delta\omega_o$, being *actual* frequencies, can be measured in a simple, absolute and accurate way. Recording the frequency shift $\Delta\omega_o$ of the oscillator yields directly the real term χ' of the HF susceptibility; the only unknown proportionality factor is the filling factor η.

Some striking differences with the conventional CW–NMR outputs (see relations (1) and (2)) appear.

(i) The frequency shift is independent from H_1. This has two consequences. First, we do not need to worry about the homogeneity of the HF field; we just need a component perpendicular to the static magnetic field. And secondly, it is much easier to compare intensities of two NMR lines (as long, of course, as we are in non-saturating conditions).

(ii) The quality factor Q_o of the L_oC_o circuit does not appear in the output of our spectrometer. Due to changes of this

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† Throughout this paper the subscript o stands for (o)scillator.

0022-3735/82/050558 + 04 $02.00 © 1982 The Institute of Physics

parameter, relative measurements at two different temperatures are almost impossible in conventional spectrometers.

(iii) Both the other coefficients K_0 and S depend upon the method used. They contain e.g. the coupling of the tank circuit to the oscillator, the gain of the HF amplifier, the level of oscillation of a marginal oscillator, the gain of the phase-sensitive amplifier, etc, and are difficult to determine and to keep constant.

All this together clearly indicates that *absolute* measurements of χ'' (and χ') are impossible with conventional CW–NMR methods, and that even *reproducible* and *comparable* measurements – *even when using calibrating samples* – are extremely difficult. Such measurements are possible and *easy* with our method.

3. The NMR spectrometer: design, construction, performance

Since we want to measure the oscillator frequency shift $\Delta\omega_0$ induced by the resonance dispersion, we have to avoid in such a spectrometer all other frequency shifts; so we need a *very stable* oscillator but not, of course, one locked to a crystal!

We have developed an extremely simple oscillator, driven by a tunnel diode, which operates in the whole temperature range from 300 K to 1.5 K, and even lower. A tunnel diode has proven to be an excellent low temperature active element in many applications (Van Degrift 1975, Van Degrift *et al* 1978, Lengeler 1974, Robinson 1977). The scheme is based on an article by Van Degrift (1975); it is shown in figure 1, as used in a typical 21 MHz spectrometer, which we will now describe.

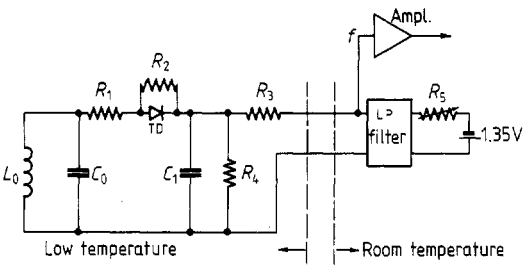

Figure 1. The scheme of our 21 MHz oscillator in the NMR spectrometer. $R_1 = 61.9\ \Omega$, $R_2 = 162\ \Omega$, $R_3 = 56.2\ \Omega$, $R_4 = 47.5\ \Omega$, all metal film resistors. R_5 is a 1 kΩ ten-turn potentiometer. $C_0 = 510$ pF, silvered mica capacitor; $C_1 = 1000$ pF, high Q ceramic capacitor. TD is a tunnel diode type TU301 from Siemens.

The DC power is supplied by a mercury battery (1.35 V) at room temperature and delivered to the low temperature electronics through the same coaxial cable used to pick up the HF signal for frequency detection.

The tunnel diode provides a negative conductance to the L_0C_0 circuit and this sustains the oscillation. Resistor R_2 serves to decrease the level of oscillation in order to avoid saturation. R_1 suppresses the possible occurrence of higher frequencies. R_3, R_4 and R_5 provide the proper bias voltage to the tunnel diode. We choose this type of tunnel diode for its low junction capacity (typically 1.5 pF) because, as a general rule for tunnel diode oscillators, the main LC circuit capacitor C_0 should have a value much larger than the junction capacity: $C_0 > 100\ C_{junction}$. The copper coil is a typical HF coil of 4 turns ($L_0 \simeq 0.12\ \mu$H) made of 1.5 mm thick wire with a length of 35 mm and a diameter of 10 mm. Not only the coil, but the whole oscillator is carried out in a rigid way by building it into a heavy copper housing, to be free from vibrations and to protect it from stray electromagnetic radiation.

The frequency changes less than 1% from 300 K to 4.2 K. As one can see from figure 2, the TDO frequency $f(\equiv \omega_0/2\pi)$ becomes more and more temperature independent as the temperature is lowered: below 10 K the slope is less than 0.5 PPM K^{-1}. At liquid helium temperatures a typical frequency drift rate of 2 parts in 10^8 over one minute and 1 part in 10^7 over one hour is obtained. The data at liquid nitrogen are 5 parts in 10^8 and 1 part in 10^6 respectively. The magnetic field dependency up to 1 T at 4.2 K and 77 K is shown in figure 3.

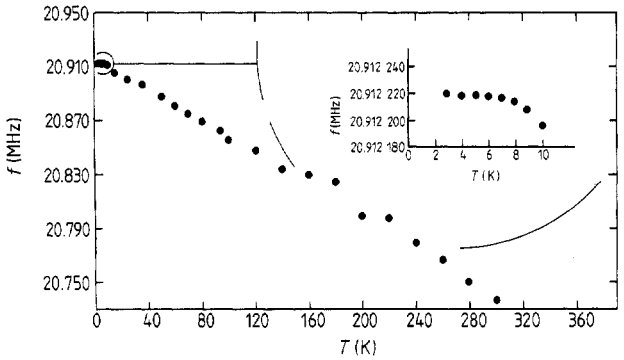

Figure 2. Temperature dependence of the frequency f of our 21 MHz tunnel diode oscillator.

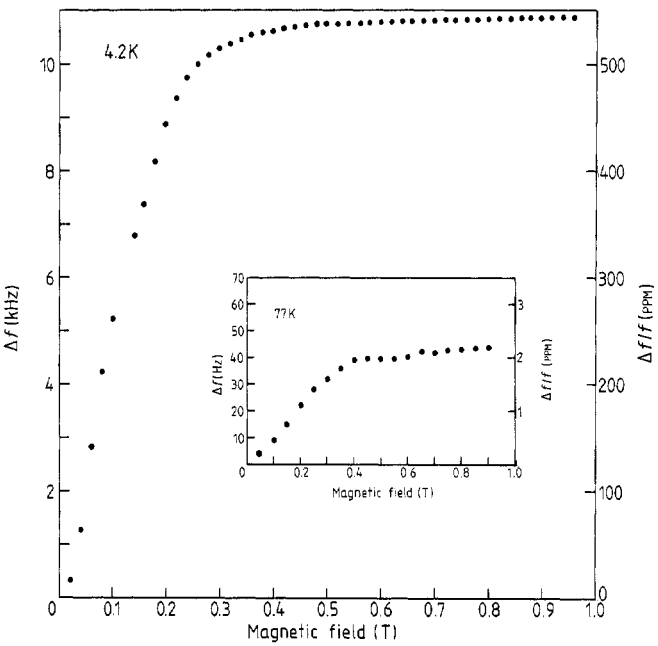

Figure 3. Magnetic field dependence of the frequency f of our 21 MHz tunnel diode oscillator at 4.2 K and 77 K.

This behaviour is explained by the saturation of the ferromagnetic leads of the tunnel diode and possibly by some other, not so important factors. For a typical sweep of 0.01 T around 0.8 T the frequency changes less than 1 part in 10^7.

We use a FM demodulation technique to avoid the long gating times required by a conventional frequency counter (see figure 4). Because our detection system has to be extremely

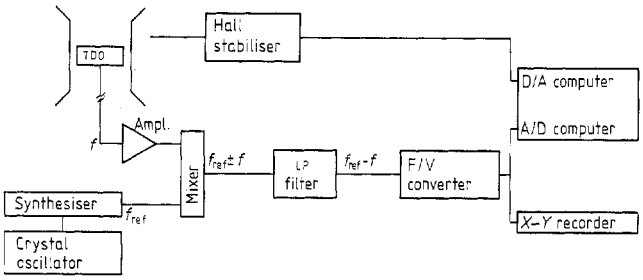

Figure 4. The block scheme of the NMR dispersion spectrometer with detection and registration.

weakly coupled to the HF oscillator, the HF output signal is first amplified and then heterodyned to below 10 kHz. At that point the frequency is converted to a voltage using a frequency-to-voltage converter (Analog Devices, model 451 J). The non-linearity is guaranteed to be less than 0.03%. The reference frequency for the heterodyne can be chosen from a frequency synthesiser in steps of 1 Hz. In order to improve the original frequency stability of the synthesiser, we have locked its clock to a 5 MHz crystal oscillator, type XSF, with an aging of less than 2×10^{-10} per day.

For determining experimentally the sensitivity of this type of spectrometer at liquid helium temperatures, we use a 0.3 g sample of γ-picoline (4-methyl-pyridine). Figure 5 presents a

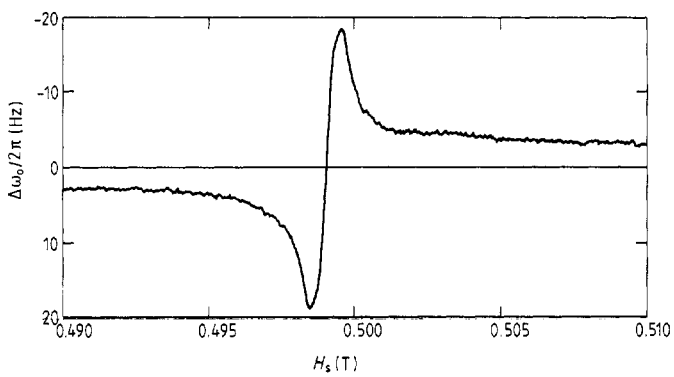

Figure 5. A typical proton NMR dispersion spectrum taken at $\omega_0/2\pi = 21$ MHz and $T = 4.2$ K in 0.3 g of γ-picoline. The field scan is 0.02 T.

typical dispersion spectrum taken at 4.2 K and 21 MHz after waiting long enough to get the spin system in thermal equilibrium. The spectrum $\Delta\omega_0$ against H_s is recorded in one minute; the field scan is 0.02 T broad. The peak-to-peak width of the resonance dispersion line is about 0.9 mT and the peak-to-peak frequency shift is 37 Hz. The 'noise' in our case is given by the unstability of the oscillator and the discriminator ($\sim$0.4 Hz), the synthesiser being two orders of magnitude more stable. One can see that changes of 0.02 PPM of the frequency ω_0 are easily recorded by this frequency detection method. In terms of a line width of 1 gauss we deduce from these experimental results a minimal detectable quantity of 10^{19} proton spins. Although this sensitivity is poor, it is nevertheless good enough for the study of most NMR properties at low temperatures.

Another point worth noting is the fact that the absolute frequency shift

$$\Delta\omega_0 = -\tfrac{1}{2}\omega_0 \eta \chi'(\omega_0) \tag{6}$$

is proportional to the square of the frequency ω_0 because χ' is also proportional to ω_0. Working at 60 MHz instead of 20 MHz would give an increase of one order of magnitude in the above mentioned sensitivity.

In our detection and registration system, no field modulation is used and as a consequence no phase-sensitive technique whatsoever. The output gives us immediately χ' (not the derivative), free from any *modulation* or *detection distortion*. Further, due to the independency of the performances of our spectrometer – in particular the sensitivity – from H_1, we are allowed to use arbitrary values of H_1. In particular we may reduce H_1 to very low values – without reducing or distorting the signal – e.g. in order to avoid saturation and *saturation distortion*. A practical limit, of course, is, that at extremely low H_1 values the necessary oscillator frequency stability would no longer subsist.

Let us recall that, in order to keep a direct relation between χ' and the measured frequency shift, we do not use field modulation. Nevertheless, for some applications one could use this technique and improve the sensitivity in this way by a few orders of magnitude.

Our NMR dispersion spectrometer can be applied, like any dispersion spectrometer, to measure, via the theory based on asymptotic expansion of χ' as described by Talpe and Van Gerven (1966), the various coefficients of this expansion, in particular the static susceptibility of the nuclear spin system. This method has some advantages over the 'method of moments' based on the integrals of χ'', as e.g.: no integration, no null line problems, better convergence (Talpe and Van Gerven 1966).

Our spectrometer has, for these latter applications as well as for others, the major advantage that it yields *absolute data*. Indeed, from relation (6) one can see that we have the opportunity to perform *absolute measurements* – if η is known (see below) – or, at least, if η is not known, *strictly reproducible* measurements of χ'. This offers the possibility *i.a.* to measure absolute nuclear susceptibilities and also to compare spectra taken in different circumstances. The only adjustable spectrometer parameter indeed is H_1, which is controlled by R_5 (see figure 1).

Since η is independent from H_1 and also χ' is (as long as we are in the non-saturating regime), there is no spectrometer parameter whatsoever entering in relation (6). So, the relation between $\Delta\omega_0$ and χ' is absolute or quasi-absolute. For a specific application we refer to Van Riet and Van Gerven (1982).

To achieve really absolute measurements the only problem is the filling factor η, defined as:

$$\eta \equiv \int_{V_1} H_1^2 \, dV / \int_{V_2} H_1^2 \, dV$$

where V_1 = space taken by the sample, V_2 = space taken by the HF magnetic field.

It is extremely difficult to determine η experimentally without a reference sample, which, of course, we want to avoid in principle. Calculating the filling factor is also extremely difficult because of the boundary conditions imposed by the encapsulation of the sample space. The best solution for this problem is to increase η towards its maximum value of 1. This means that we have to fill up with sample all space where a HF magnetic field is present: $V_1 = V_2$. Such a procedure is not allowed in absorption spectrometers, because of the enormous inhomogeneity of H_1 outside the central part of the coil. In our case it is allowed just because the spectrometer output is independent from H_1. In practice, instead of putting the sample

in the coil (as usual!) we put the coil 'in' the sample which is contained in a small copper box. There is no HF field outside the shielding box; so $V_1 = V_2$. In fact we obtain a value not equal to 1 but very close to 1 (within 1%) because of skin effects and possible irregularities in the sample. Another solution is proposed by Van Degrift and Utton (private communication).

Let us emphasise that an important side-effect of this '$\eta = 1$'-procedure is another increase of the sensitivity by an order of magnitude.

4. Conclusion

The new type of CW-NMR spectrometer seems to be very promising because of the direct relation between the output and the real part of the HF susceptibility χ' as a consequence of the new concept of the spectrometer and the straightforward detection method. The sensitivity could easily be increased towards a minimal detectable quantity of 10^{17} proton spins by working at higher frequencies and by increasing the filling factor. We see two important applications.

One is determining very accurately and without any distortion NMR line shapes. The spectrometer output is free of modulation and detection distortion. Saturation distortion is very small. The oscillator, described above, has a H_1 of about 10^{-7} T, so that samples with a T_1 of a few minutes could be measured with only a slight saturation distortion.

The second application is the possibility of measuring χ' and nuclear susceptibilities in a strictly reproducible or even absolute way.

Acknowledgments

The authors want to thank the Belgian Interuniversitair Instituut voor Kernwetenschappen for its generous financial support in the framework of the project 'Nuclear Magnetism'.

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