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ESR Line Shape Analysis for Strongly Distorted Signals Due to an Intense Paramagnetic Sample: Application to Spin Polarized Atomic Hydrogen

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Abstract. We present a method suitable for a real time computer analysis of ESR signals strongly distorted due to an intense paramagnetic sample. This occurs typically in experiments with high Q cavities and narrow lines carried out at low temperatures. We have applied this method to ESR of gaseous spin polarized atomic hydrogen. During an experiment the density of gas atoms in a cavity may decrease a few orders of magnitude. Thus the ESR line shape evolves correspondingly from a regime of heavily distorted signals to that of undistorted ones. We have compared our analysis with independent measurements of the hydrogen density by a sensitive pressure gauge.

1. Introduction

If the number of paramagnetic moments in the sample is high enough so that an absorption of microwave power becomes comparable with the ohmic losses in the cavity, then one faces a problem of analyzing distorted ESR line shapes. This is the case in ESR experiments we have carried out both in Moscow and in Turku on spin polarized atomic hydrogen (H↓) at low temperatures using a 2 mm wave spectrometer [1]. In this Introduction we briefly state some facts about ESR of H↓ and give an overview how to handle line shape distortions. Also we describe the construction of a 2 mm wave homodyne spectrometer.

A gas of atomic hydrogen can be stabilized against a recombination into molecules by polarizing the electron spins in a high magnetic field ($B > 4$ Tesla) at temperatures below 1 K [2]. In such conditions H↓ populates the two lowest (a and b) hyperfine states, see Fig. 1. The atoms in states a

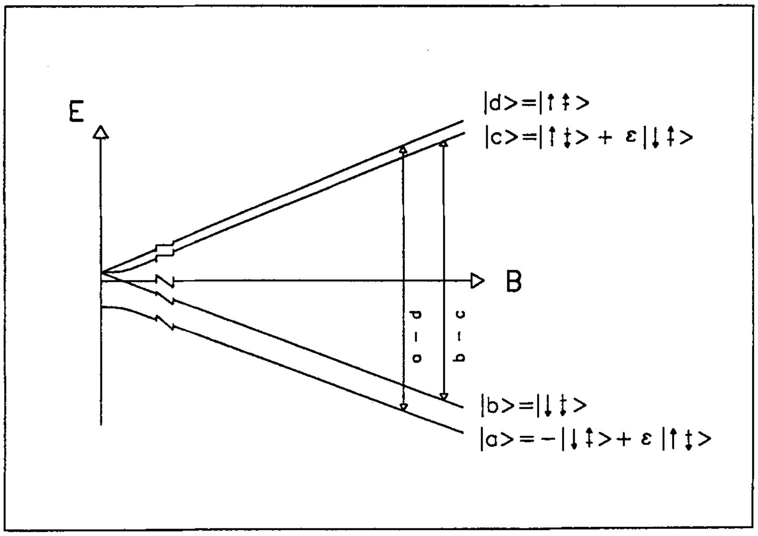

Fig. 1. Hyperfine energy levels of a hydrogen atom in magnetic field. The allowed ESR transitions are $a \to d$ and $b \to c$, separated by 507 Gauss. At 4.7 T resonance frequency is 127 GHz.

and *b* are high-field seekers and are confined in the maximum of the magnetic field, but the *c* and *d* state atoms are low-field seekers and are expelled out to zero field. Atoms may still recombine into molecules. The highest probability is in a collision between a spin down atom and a spin up atom. This fact has to be taken into account when designing a spectrometer. Exciting the electronic transitions $a \to d$ or $b \to c$ effectively means destroying atoms since the relaxation times are much longer than the characteristic time of recombination. Thus one has to work with very small microwave excitation levels. Using a high *Q* cavity is essential in achieving an acceptable signal to noise ratio.

In case of the gaseous sample of H↓ the line shape is determined by magnetic field inhomogeneities of the main solenoid and the sweep coil as well as by the configuration and the noise spectrum of the microwave field in the cavity. At low H↓ densities from a detection limit of about 10^{12} cm^{-3} to about 10^{14} cm^{-3}, the line shapes are undistorted. Both absorption and dispersion signals maintain their shapes within a scaling factor proportional to H↓ density. At higher densities up to the maximum recorded density of about 10^{16} cm^{-3}, the line shapes become gradually more and more distorted: the amplitude saturates, the wings broaden and the area under the line is no longer directly proportional to the atom density.

One method to handle line shape distortions has been presented by Statt *et al.* [3], see also [4]. They used an undistorted reference line shape recorded at low H↓ density together with an iterative calculation based on Kramers-Kronig relations to obtain the true absorption signal from measured data. This method seems to be accurate but requires a lot of computing. Our aim was to develop a method to extract the H↓ density n_H from the line shape data immediately after having recorded the line. The method is based on using the wings of the dispersion signal where the absorption is zero. We have installed a sensitive pressure gauge in the H↓ sample cell to determine the total H↓ atom density whereas ESR gives separately the densities of the hyperfine states *a* and *b*.

2. The ESR Spectrometer

The high magnetic field necessary to stabilize H↓ determines the value of resonance frequency to be above 100 GHz. The destructive effect of ESR on H↓ dictates a spectrometer scheme with a very small microwave power fed into the cavity [5]. The UBC group [3, 4] has chosen heterodyne detection which has a good sensitivity but is rather complicated and expensive. They were able to work with incident microwave power levels to the cavity of about 4 pW while destroying only about 0.07% of the H↓ sample per sweep. We have chosen a homodyne detection of ESR because it is relatively easy to be realized and its sensitivity can be almost as good as that of heterodyne spectrometer.

Typically we work with microwave power levels from 0.1 to 1 nW achieving a sensitivity comparable to heterodyne detection. The increased loss of atoms is compensated by using a buffer volume (~ 30 times bigger than the cavity volume) of H↓ atoms connected to the microwave cavity through a small iris. Since H↓ is stabilized only at low temperatures, in our case from 0.08 K to about 0.6 K, a detection with a magnetic field modulation is not applicable due to eddy current heating of the sample cell. Instead, we employ microwave power modulation with fast PIN diode switches. Power reflected from the H↓ cavity is detected with an InSb detector cooled by liquid ^{4}He.

Figure 2 shows schematically the construction of the spectrometer. As a microwave source we use either a cavity stabilized backward wave oscillator (BWO) or a phase locked Gunn oscillator. Microwave power is split into two parts in a magic-T. One half of the power goes through the signal channel comprising an attenuator, a phase shifter, a PIN diode modulator and a directional coupler into the H↓ cavity, while the other half of the power goes through an attenuator and a phase shifter of the bias (or reference) arm. The signal reflected from the cavity is summed to the bias power in a directional coupler. This power is fed into the InSb detector. The purpose of the bias power is to bring the detector to a range of the highest conversion gain. Phase shifters serve to tune the spectrometer to absorption or dispersion. A

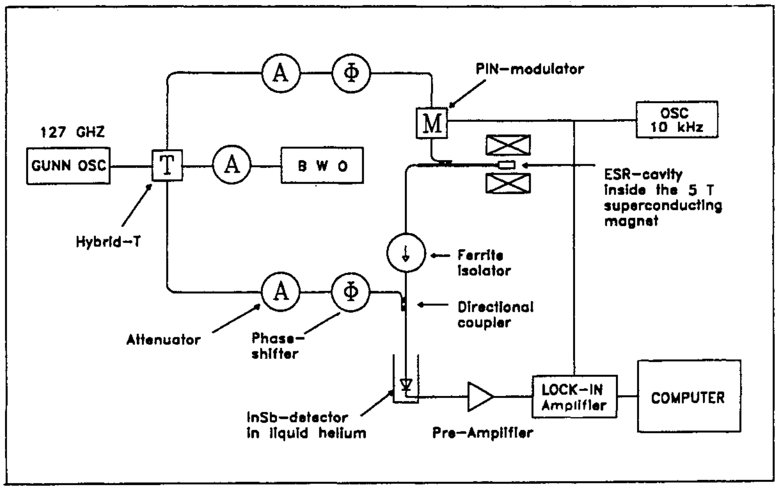

Fig. 2. Block diagram of the homodyne ESR spectrometer.

Ferrite isolator prevents bias power from leaking into the H↓ cavity. The responsivity of the InSb single crystal detector is of about 1500 V/W, the noise at the output being of about 3–10 $\mathrm{nV \cdot Hz^{-1/2}}$. The optimal bias power fed to the crystal is of about 10 μW. The signal is amplified by a low noise pre-amplifier and a lock-in detector. A desktop computer performs the magnetic field sweep across the resonance lines and reads the data through an AD converter. Examples of recorded absorption and dispersion line shapes are shown in Fig. 3 (next section).

3. Extraction of H↓ Density from the Line Shapes

When recording the ESR line shape we measure the changes δ of the cavity reflection coefficient Γ_0, $\delta = (\Gamma - \Gamma_0)/\Gamma_0$. To extract the H↓ atom density from this we introduce the normalized susceptibility [3] $\gamma = \mathrm{i}\gamma' + \gamma'' = 4\pi\mathrm{i}Q_\mathrm{L}(\chi' - \mathrm{i}\chi'')$, where Q_L is the loaded quality factor of the cavity, χ is a magnetic susceptibility of a uniform sample completely filling the cavity. The density n_H of hydrogen atoms can now be written as

$$n_\mathrm{H} = \frac{4}{\pi \hbar \gamma_\mathrm{e}} \int \chi''(H)\,\mathrm{d}H = \frac{1}{\pi^2 \hbar \gamma_\mathrm{e}} \int \gamma''(H)\,\mathrm{d}H\,, \tag{1}$$

where the integration is performed over the magnetic field sweep interval. Here γ_e is the gyromagnetic ratio of electron. Calculating the reflection coefficient for a cavity loaded with a paramagnetic sample, denoting $\eta = 1 - 1/\Gamma_0$ the cavity coupling parameter, we obtain δ using the normalized susceptibility γ as

$$\delta = \frac{\eta\gamma}{1+\gamma}, \tag{2}$$

or writing separately the imaginary and real parts

$$\delta_{\rm Im} = {\rm Im}(\delta) = \frac{\eta\gamma'}{(1+\gamma'')^2 + \gamma'^2},$$

$$\delta_{\rm Re} = {\rm Re}(\delta) = \frac{\eta(\gamma'' + \gamma''^2 + \gamma'^2)}{(1+\gamma'')^2 + \gamma'^2}. \tag{3}$$

When $|\gamma| \ll 1$, δ is proportional to γ and the density is found by integrating the line shape $\delta_{\rm Re}$. But as γ increases one can see that absorption and dispersion become intermixed in δ and the lines become distorted, see Figs. 3 and 4. Even at strong distortions one can find the spin density by integrating the true absorption γ''. However, to obtain γ'' from $\delta_{\rm Re}$ or $\delta_{\rm Im}$ is a rather complicated iterative procedure using Kramers-Kronig relations. This requires a substantial amount of computing time and thus it does not suit well data monitoring in real time. This method is well described in [3] where it was used for data analysis.

The true ESR line shape of gaseous atomic hydrogen is determined by inhomogeneous broadening corresponding to the magnetic and microwave field configuration in the cavity. Thus outside a certain region $\varDelta_0$ around the center of line, absorption is zero to a good approximation. In this case we may write the imaginary part of δ as

$$\delta_{\rm Im} = \frac{\eta\gamma'}{1+\gamma'^2}, \qquad |\Delta H| > \varDelta_0. \tag{4}$$

It is clearly seen that $|\delta_{\rm Im}|$ has maxima of $\eta/2$ at $\gamma' = \pm 1$ as the reflected power cannot be bigger than the incident one. This allows one to determine a coupling parameter η simply by recording a strong enough signal.

Considering the part of the dispersion wings where $|\gamma'| < 1$ and the function $\gamma'(\delta_{\rm Im})$ is well defined, one can obtain the atom density $n_{\rm H}$. As in [3] we also make use of a low density reference signal. It is recorded for both *a* and *b* lines at a density where distortions are still negligible. Using Eq.(4) we find $\gamma'_{\rm Ref}$. For this case we obtain the density from the corresponding absorption signal. Then for all subsequent line shapes we find γ' using Eq.(4) and then obtain the corresponding density from

$$n = n_{\rm Ref} \frac{\int \gamma'}{\int \gamma'_{\rm Ref}}, \tag{5}$$

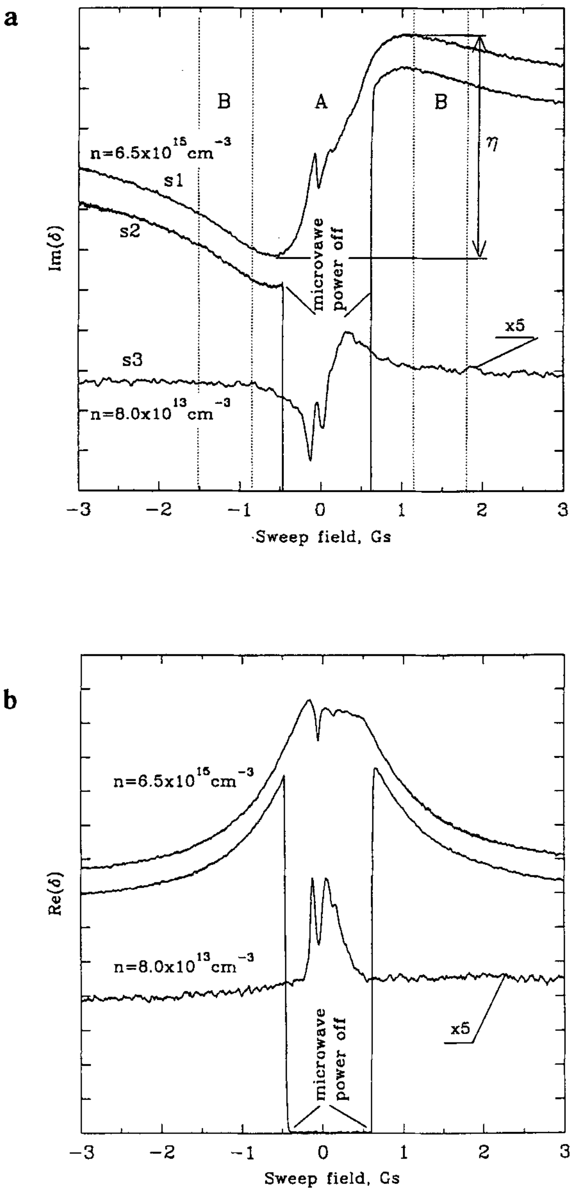

Fig. 3. ESR line shapes recorded using the Gunn oscillator microwave source: **a** – dispersion signals; s1 and s2 recorded at $n_H = 6.5 \cdot 10^{15}$ cm^{-3}; s2 shows the line shape when the microwave power fed into the cavity is switched off while passing through the center of the line; s3 shows an undistorted line at $n_H = 8 \cdot 10^{13}$ cm^{-3} (scaled by a factor of 5); **b** – the corresponding absorption signals.

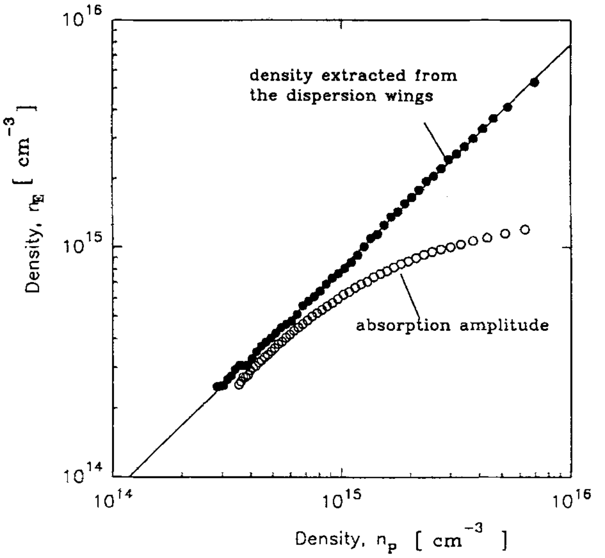

Fig. 4. Comparison of the H↓ densities n_p and n_E obtained respectively from the pressure gauge and ESR signals at the cell temperature 0.4 K. It is clearly seen how the height of the absorption line starts to saturate already at $n_H \sim 10^{15}$ cm^{-3}.

where the integration is carried out only in the region B (see Fig. 3). We assume that the true line shape scales linearly with density which is true for negligible saturation.

When integrating the dispersion wings we can suppress uncertainties in the zero line by using the line shape data symmetrically on both sides of the line center H_0. Instead of using simply $\delta_{\mathrm{Im}}(H)$ we calculate $\delta_{\mathrm{Im}}(H) = 1/2|\delta_{\mathrm{Im}}(H_0 + \Delta H) - \delta_{\mathrm{Im}}(H_0 - \Delta H)|$ and then find $\gamma'(H)$. This has a noticeable effect in reducing errors due to determining the zero line which is always a problem when integrating absorption. This also reduces an error from a small δ_{Re} admixture rising from the phase tuning inaccuracy. An additional advantage of the method described is the possibility to switch off a microwave power in the center of the line where the data are not being used anyhow. This allows one to reduce the ESR-induced destruction of H↓ sample when measuring its density.

Figure 3a shows three dispersion signals, one taken at the density of $8 \cdot 10^{13}$ cm^{-3} and the others at $6.5 \cdot 10^{15}$ cm^{-3}. The latter show clearly the presence of distortions. Region A in the line shapes corresponds to non zero absorption in the central part while near the edges $|\delta_{\mathrm{Im}}|$ is close to the maximum value of $\eta/2$ ($|\gamma| \sim 1$). Thus the region A is not used in density determination. Within the region B a signal to noise ratio is rather good and $|\delta_{\mathrm{Im}}| < \eta/2$ which enables one to determine γ' and to find the density. Outside the region B the signal is too small to give acceptable signal to noise ratio. Fig. 3b shows the corresponding absorption line shapes. These data were recorded by using the Gunn oscillator. The spectral purity of its frequency is clearly seen in the structure of the line shapes that display the distribution of transverse magnetic field of the cavity resonance mode TE_{012}.

One can easily estimate when the distortions become noticeable. It is seen from Eq.(1) that the number of paramagnetic centers in a sample should satisfy a relation:

$$N \,\mathrm{th}\, \frac{\hbar\omega}{kT} \sim \frac{4\Delta H}{\pi^2 \hbar \gamma_e Q_L} V_{\text{cavity}}, \qquad (6)$$

where ΔH is the line width of the absorption γ'' in Gauss, the temperature dependent factor $\mathrm{th}\,(\hbar\omega/kT)$ determines the equilibrium population difference between levels participating in ESR transitions. After a trivial calculation we obtain:

$$N \sim 2 \cdot 10^{19} \frac{\Delta H \cdot \lambda^3}{Q_L} \,\mathrm{cth}\, \frac{\hbar\omega}{kT}. \qquad (7)$$

Here λ and $\omega = 2\pi c/\lambda$ are the wave length and the frequency of the microwave field, $V_{\text{cavity}} \sim \lambda^3$. For example, in our case at $\Delta H \sim 0.5$ Gs, $\lambda \approx 2$ mm, $Q_L \sim 2000$ and $T \approx 0.5$ K we have $N \sim 5 \cdot 10^{13}$ spins. In case of $\lambda = 3$ cm, the other parameters being the same, considerable distortions appear at $N \sim 2 \cdot 10^{18}$ spins.

We have compared the density $n_E = n_a + n_b$ extracted from ESR data to the density n_p measured by a thin foil capacitive manometer calibrated against the ^{4}He vapor pressure. As mentioned in the Introduction the H↓ pressure gauge is located in the buffer volume (~ 1 cm^3) of the sample cell where H↓ is collected. Atoms from this volume enter the ESR cavity through a hole 0.3 mm long and 0.8 mm in diameter with the time constant less than 10 ms. It is short enough to guarantee an equilibrium between cavity and buffer volume. Fig. 4 shows a comparison between n_p (x-axis) and n_E (y-axis; solid points refer to the method described here and hollow points present the sum of the amplitudes of the a and b absorption lines). As can be seen the absorption amplitude saturates already at $n_H \sim 10^{15}$ cm^{-3}, but the dispersion wings provide a good result within a wide range of H↓ densities. Here the comparison is given in the region where the pressure gauge reads reliably. It has a density resolution of about 10^{14} cm^{-3}.

References

[1] Vasiljev S.A., Katunin A.Ya., Tjukanov E., Lukashevich I.I.: Soviet JETF Letters **48**, 131 (1988)

[2] Silvera I.F., Walraven J.T.M. in: Progress in Low Temperature Physics (Brewer D.F., ed.), vol.X. North-Holland, Amsterdam 1986.

[3] Statt B.W., Hardy W.H., Berlinsky A.J., Klein E.J.: J. of Low Temp. Phys. **61**, 471 (1985)

[4] Shinkoda I., Hardy W.N.: J. of Low Temp. Phys. **85**, 99 (1991); see also: Shinkoda I.: Ph. D. Thesis. University of British Columbia 1990.

[5] Feher G.: The Bell System Tech. J. XXXVI, 449 (1957)

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