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OBSERVED SPECTROSCOPIC LINE SHAPE OBTAINED BY USING A LOCK-IN AMPLIFIER AND ITS SIMULATION BY A COMPUTER

By

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Abstract

This paper describes the use of a computer simulation method for analysing modulation-broadened spectroscopic lines which have been observed by means of a spectroscopic system involving a lock-in amplifier. Its application to analysis of NMR absorption lines of hydrogen adsorbed on powdered tungsten surfaces is reported.

§ 1. Introduction

Nowadays lock-in amplifiers are easily available and are being used widely in research laboratories, especially in connection with spectroscopic studies such as NMR, ESR and AES. They are very useful for detecting weak signals buried under noise. The principle of their operation is well-known (see below); by some means, we give periodic modulation to signals to be detected and the lock-in amplifier picks out and amplifies these periodically modulated signals.

If the signal level is high enough as compared with the noise level, it suffices to apply only weak modulation to signals, in which case distortion of the signal lines (absorption lines in the case of spectroscopies) by the modulation (modulational broadening) will be negligible. However, in the case where the signal is so weak that the maximum sensitivity of the lock-in amplifier must be invoked, strong modulation whose amplitude is comparable to the width of the signal line is required to observe the signal. As a result, the lines observed suffer from modulational broadening. To find out the true line shape from the observed one we may resort to the extrapolation to zero amplitude of the modulation provided that the line in question consists of a single line. On the contrary, a similar method can not be applied to composite lines.

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The author has been engaged in NMR spectroscopic studies of adsorbed species on metal surfaces, in which case he had to observe absorption lines which are weak, modulation-broadened, and frequently of composite structure. In order to determine the structure and the true width of such lines, the author has successfully used computer simulation.[1] Since this kind of method should be of wider utility and may be used in other spectroscopic studies, the method and its application will be briefly explained below.*)

§ 2. The action of a lock-in amplifier

The action of a lock-in amplifier in a spectroscopic measurement system is explained referring to the case of NMR experiments. A block diagram of a typical experimental system using a lock-in amplifier is shown in Fig. 1. The oscillator generates a periodic voltage $R(t)$ whose frequency is f_m. This $R(t)$ is used to modulate, by means of the modulator, the magnetic field in the detection system which consists of a sample, magnetic pole pieces, a radio frequency coil, a receiver coil, *etc.* The modulated magnetic field in turn modulates the NMR absorption signal $S(t)$, which is amplified by the preamplifier and supplied to the lock-in amplifier. This signal $S(t)$ is always accompanied by random noise $N(t)$.

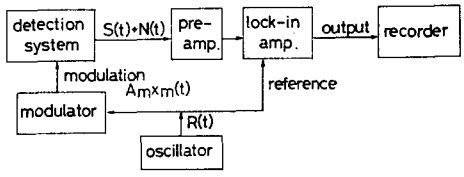

Fig. 1. Block diagram of a typical experimental system using a lock-in amplifier.

The heart of a lock-in amplifier is a phase sensitive detector. From the input signal the detector picks out only the Fourier component which has the same frequency as and is in a constant phase-angle relation with the reference signal $R(t)$. Thus the effect of the noise $N(t)$ is eliminated.

A typical case of observation is schematically shown in Fig. 2. The "true" absorption line as a function of the magnetic field x is represented by $F(x)$. The magnetic field x is a function of time t such as $x(t)=X(t)+A_m x_m(t)$, where $X(t)$ represents the sweep of the magnetic field with a constant rate and increases or decreases slowly and monotonically with time, and $A_m x_m(t)$ represents the modulation, where $x_m(t)$ is the periodic function $\sin(2\pi f_m t)$ with frequency f_m and A_m is the amplitude. As shown in Fig. 2, the shape of modulated signal $S(t)$ changes gradually as the center $X(t)$

*) After completion of the present work, the author found that Ono[2] had already used a similar method for analysing AES data obtained with a retarding field analyser.

of the modulation varies. The $S(t)$ is a periodic function which has a fundamental Fourier component of frequency f_m and its harmonics. The lock-in amplifier picks out only the fundamental component and puts out the coefficient of it as electric voltage. Provided that the amplitude of the modulation is small enough, the output gives the derivative curve of $F(x)$.*

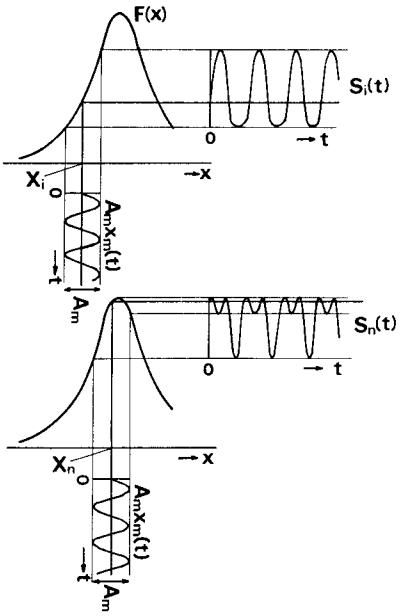

Fig. 2. Line shapes of the signal $S(t)$ obtained at different values of $X(t)$ (center of modulation), *i.e.*, X_i, ···, X_n, ···.

§ 3. Simulation of observed signals

The feature of the computer simulation is briefly described here. First, the true absorption line $F(x)$ is assumed. For example, it may be a Gaussian curve with certain width and intensity or a composite one which consists of two or more Gaussian curves. The modulated signals $S_1(t)$, $S_2(t)$, ··· which are expected to result from the absorption line $F(x)$ and the applied modulation $A_m x_m(t)$ are computed for fixed centers of modulation X_1, X_2, ···, respectively (see Fig. 2). Then these functions are expanded in the Fourier series, and thus the coefficient of the fundamental component is obtained as a function of the magnetic field x. This functional relation should simulate the output of the lock-in amplifier. The Fourier expansion is carried out on a computer by using the trapezoid formula for numerical integration, where one period of $S(t)$ is divided into 100 equal intervals. Actually division into 20 intervals is enough for practical use.

§ 4. Comparison between simulated and observed lines.

As an example, observed NMR absorption lines of Cu^{63} in copper powder are shown in Fig. 3. These lines suffer from modulational broadening by the sinusoidal modulation of the magnetic field. The true NMR line of

*) In the case that the lock-in amplifier picks out the second harmonic component, the output gives the second derivative of $F(x)$.

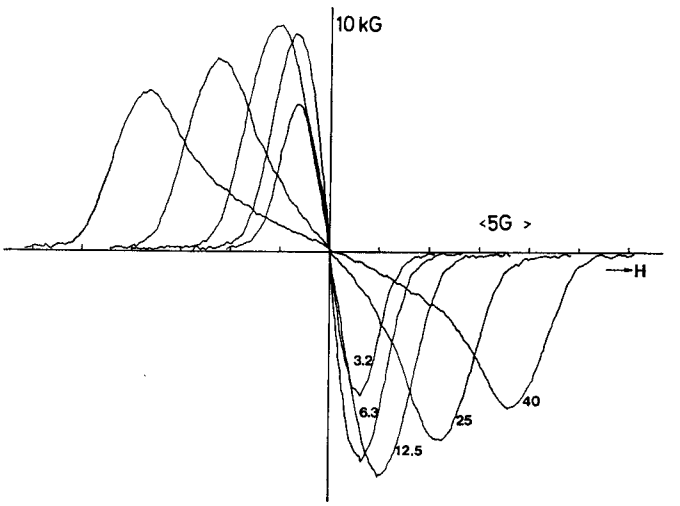

Fig. 3. Observed NMR lines of Cu^{63}. The amplitude of modulation (in Gauss) is attached on each line.

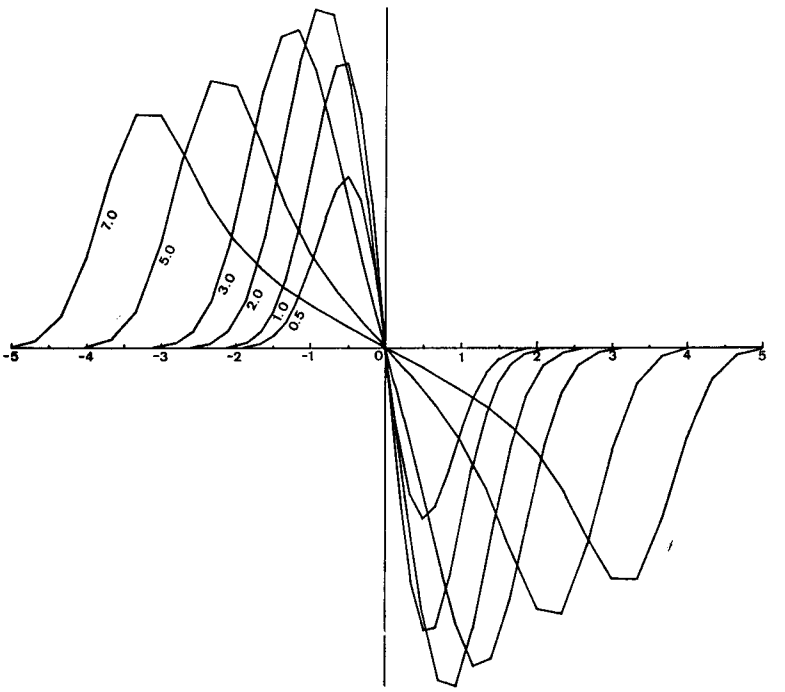

Fig. 4. Simulated lines by a computer. The assumed function $F(x)$ is Gaussian. Amplitude of modulation normalized to the width of the Gaussian curve is attached on each line.

Cu^{63} is nearly Gaussian with width of 6.3 Gauss determined from the peak-to-peak distance of the derivative curve. The corresponding simulated curves are shown in Fig. 4 which are now compared with the observed ones in Fig. 3. The agreement is very good, which fact shows that the simulation program is correct. The simulation has started with an assumed Gaussian absorption line,

$$F(x)=\frac{B}{(2\pi\sigma^2)^{1/2}}\exp\left(-\frac{x^2}{2\sigma^2}\right).$$

From these figures, it is easily seen that overmodulation introduces distortion of the curve and decrease of the peak height (intensity). In Fig. 5 the line width W_0 and peak height I_0 of the simulated line are plotted against the amplitude of modulation A_m. From this figure we can find two important facts. One is that observed line width W_0 is always larger than the true line width 2σ. It is to be noted that in the region of large modulation the width W_0 increases linearly with the modulation amplitude A_m but its asymptote is not $W_0=A_m$. The broadening when the amplitude of modulation A_m is equal to 2σ is only 13%. And the other fact is that the maximum peak height occurs at $A_m/2\sigma=1.85$.

Another example of application of this program is shown in Fig. 6, where an observed NMR absorption line of hydrogen adsorbed on powdered tungsten surfaces and a corresponding simulated line are compared.[1] The line consists of two component lines, narrow and broad ones. The narrow

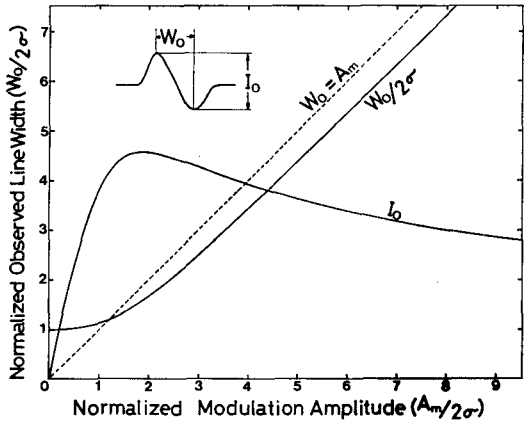

Fig. 5. Line width W_0 and peak height I_0, of the simulated line versus amplitude of modulation A_m. W_0 and A_m are normalized to the width of Gaussian curves. Units of I_0 is arbitrary.

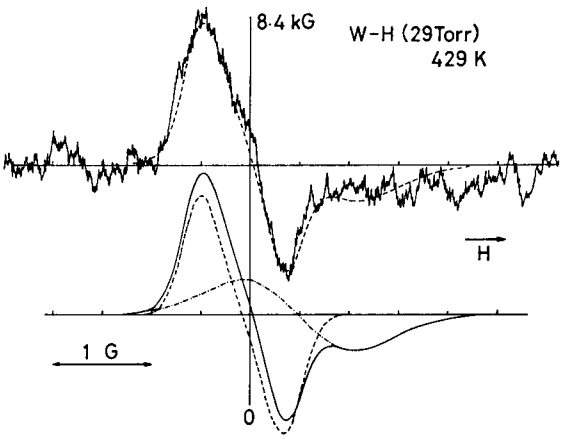

Fig. 6. Upper part is an observed NMR line of hydrogen adsorbed on powdered tungsten surfaces. Amplitude of modulation is 1 Gauss, which is indicated by arrows. "0" is the position of the reference. Dotted line superposed on this NMR line and solid line in lower part are the corresponding simulated line. In lower part dotted and dot-dash lines show the decomposition into two component lines.

one (left side) suffers from modulational broadening. From the analysis using the simulation the following conclusions have been drawn. Intensity ratio of the two lines is 1 : 1; their widths are 0.33 and 1.0 Gauss, respectively; the shifts of two lines are 0.0008 ± 0.0002 and $-0.006 \pm 0.002\%$, respectively.

The simulations described above have been performed by using an OKITAC 4300C mini-computer in the author's Insititute.

References

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2) M. Ono, Shinkū (Vacuum), **16**, 33 (1973).