A Nuclear Resonance Modulation Correction*

M. M. PERLMAN AND M. BLOOM†
Radiation Laboratory, McGill University, Montreal, Canada

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A theoretical modulation correction with experimental justification is derived. It is found that the experimentally measured value of the second moment is always larger than the true value by an amount $\frac{1}{3}Hm^2$ where Hm is the modulation amplitude. The correction holds even for amplitudes close to the line width and gives consistently good results when applied to the analysis of line shapes.

IT is well known that the effect of low temperatures on solids is to reduce the amount of molecular rotation present and hence to produce a correspondingly wider magnetic resonance signal. Indeed, this fact has been used in many investigations on the structure and internal properties of liquids and solids.

However, the wider the resonance line, the weaker it becomes. For detection purposes then, it becomes necessary to use comparatively large values of modulation amplitude in order to obtain an observable signal. As has been demonstrated,[1] this often results in experimentally measured values of the second moment of the absorption line being in error by as much as 20 percent. Because of the difficulties involved in obtaining an adequate signal and accurate and detailed plots of line shape, no experimental attempts have as yet been made to account quantitatively for this effect.

If one considers the function of the modulation as being mainly an averaging of the line shape over the range of modulation, one can derive a first-order theoretical correction using the following simple considerations:

We have

$$G(H)=\frac{1}{2Hm}\int_{H-Hm}^{H+Hm}g(H')dH'=\frac{F(H)}{2Hm}, \tag{1}$$

where

$g(H)$ = true line shape function,

$G(H)$ = experimental line shape function,

for a modulation field of the form $Hm\sin wt$. We want

$$(\Delta H_2{}^2)_{\text{true}}=\frac{\int_{-\infty}^{\infty}H^2g(H)dH}{\int_{-\infty}^{\infty}g(H)dH}=\frac{A}{C}, \tag{2}$$

where $\Delta H_2{}^2$ denotes the second moment over the absorption line. We know

$$(\Delta H_2)^2_{\text{exp}}=\frac{\int_{-\infty}^{\infty}H^2G(H)dH}{\int_{-\infty}^{\infty}G(H)dH}=\frac{\int_{-\infty}^{\infty}H^2F(H)dH}{\int_{-\infty}^{\infty}F(H)dH}=\frac{X}{Y}. \tag{3}$$

We expand $g(H')$ in a Taylor series in the neighborhood of H, i.e., we put

$$g(H')=g(H)+(H'-H)\left(\frac{dg}{dH'}\right)_H+\frac{(H'-H)^2}{2!}\left(\frac{d^2g}{dH'^2}\right)_H+\cdots. \tag{4}$$

Substituting (4) into (3) and integrating, we obtain

$$(\Delta H_2)^2_{\text{exp}}=\frac{\int_{-\infty}^{\infty}H^2g(H)dH+\frac{Hm^2}{6}\int_{-\infty}^{\infty}H^2\left(\frac{d^2g}{dH'^2}\right)_H dH}{\int_{-\infty}^{\infty}g(H)dH+\frac{Hm^2}{6}\int_{-\infty}^{\infty}\left(\frac{d^2g}{dH'^2}\right)_H dH}=\frac{A+B}{C+D}=\frac{A}{C}\frac{1+B/A}{1+D/C}, \tag{5}$$

neglecting derivatives of order 4 or greater;

$$\frac{A}{C}=(\Delta H_2{}^2)_{\text{true}}\simeq(\Delta H_2)^2_{\text{exp}}\left(1+\frac{D}{C}-\frac{B}{A}\right). \tag{6}$$

For most lines $D/C\ll B/A$ (this may be shown experimentally), and $B/A\simeq\frac{1}{3}Hm^2Y/X$ (assume $g(H)=G(H)$ to first order and perform two partial integrations).

To first order, we have

$$(\Delta H_2{}^2)_{\text{exp}}=(\Delta H_2{}^2)_{\text{true}}+\tfrac{1}{3}Hm^2. \tag{7}$$

The proton resonance in NH_4NO_3 at room temperature is ideally suited for a study of the effect of modulation on the second moment. The signal is strong, and the line width fairly narrow ($\sim$4 gauss), so that the effect on the second moment of a modulation amplitude of 2 gauss or more should be easily detectable. (For wider lines of $\sim$10 gauss, the statistics on the evaluation of the second moment are such that they mask the effect of amplitudes of less than about 3 gauss.)

Fourteen room temperature absorption curves were plotted and found suitable, two for each of $2Hm=1$, 3, 4.4, 5, 6, 8, and 10 gauss, where Hm is the modulation amplitude. The true second moment, that is, its value at zero modulation amplitude, was taken as 3.0 gauss.[2] The statistics on the second moment are in all cases better than ±3 percent.

The experimental results are plotted in Fig. 1. The solid line, drawn to fit the experimental points was

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† Now at University of Illinois, Urbana, Illinois.

[1] E. Andrew, J. Chem. Phys. 18, 607 (1950).

found to follow the formula $(\Delta H_2^2)_{exp}=(\Delta H_2^2)_{true}+\frac{1}{3}Hm^2$, exactly as determined above. Thus, the experimentally measured value of the second moment is always larger than the true value.

In the Van Vleck[2] formula for the second moment the internuclear distances appear to the inverse sixth power. Thus, an error of 10–20 percent in the determination of the second moment results in an error of only 1–3 percent in the evaluation of the internuclear parameters. A further check on Eq. (7), however, is provided by an analysis of the compound KH_2PO_4, where the calculated second moment (assuming that the hydrogens lay midway along the O−H−O bond, and taking an O−H−O bond distance of 2.54A as determined from Raman spectra experiments) of the proton resonance is 3.3 gauss.[2] The average uncorrected experimental second moment on the basis of 6 runs at −183°C was found to be 4.8±0.4 gauss[2] (an error of ~45 percent). A modulation amplitude of 2 gauss was used, thus yielding a corrected second moment of 3.5±0.4 gauss[2] in agreement with the calculated result.

[2] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

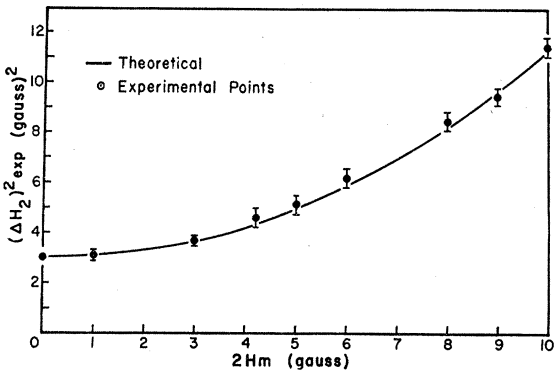

FIG. 1. The experimental modulation correction.

The experimentally observed line is the derivative of the true absorption line. When the modulation amplitude becomes nearly equal to the line width, small amounts of higher odd order derivatives are admixed. However, these effects are small, and a reasonably faithful first derivative may be obtained even in this region. In any case, the correction has been found to hold when the amplitude approaches the line width.

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Energy Levels in Light Nuclei*

J. C. ARTHUR,† A. J. ALLEN, R. S. BENDER, H. J. HAUSMAN,‡ AND C. J. MCDOLE§
University of Pittsburgh, Pittsburgh 13, Pennsylvania

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Targets of beryllium, Nylon, lead fluoride, sulfur, and lead sulfide were bombarded with 8-Mev protons from the University of Pittsburgh cyclotron. Energy levels were observed in Be^9, C^{12}, N^{14}, O^{16}, F^{19}, and S^{32} by inelastic scattering at 150° from thin targets. Single levels were assigned in Be^9 and C^{12}; two levels were assigned in N^{14}; nine levels were assigned in F^{19}; and seven levels were assigned in S^{32}.

I. INTRODUCTION

THE present investigation was undertaken to look for additional low-lying levels in some light nuclei. Similar work has been done at this laboratory by Ely *et al.*,[1] Reilley *et al.*,[2] and Hausman *et al.*[3] The 8-Mev proton beam from the University of Pittsburgh cyclotron was used to bombard targets of beryllium, Nylon, fluorine, and sulfur. The incident and reaction particle momenta were analyzed magnetically. Inelastic scattering was used to determine energy levels in Be^9, C^{12}, N^{14}, O^{16}, F^{19}, and S^{32}.

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† Now at Project Lincoln, Massachusetts Institute of Technology, Cambridge, Massachusetts.

‡ Now at the Ohio State University, Columbus, Ohio.

§ AEC Predoctoral Fellow.

[1] Ely, Allen, Arthur, Bender, Hausman, and Reilley, Phys. Rev. **86**, 859 (1952).

[2] Reilley, Allen, Arthur, Bender, Ely, and Hausman, Phys. Rev. **86**, 857 (1952).

[3] Hausman, Allen, Arthur, Bender, and McDole, following paper [Phys. Rev. **88**, 1296 (1952)].

II. APPARATUS

The apparatus used is essentially the same as that described previously.[4,5] It was modified by placing the detector inside the vacuum system to permit the observation of lower energy scattered particles. The target holder was remodeled to provide a means for calibration of the reaction particle analyzer without losing the vacuum.

A beam of 8-Mev protons from the cyclotron was focused by a sector magnet into a shielded scattering room. Within the scattering room the incident beam was analyzed magnetically by a 40° sector magnet and the spread in energy adjusted by appropriate slits. Charged reaction particles were momentum analyzed by a 60° sector magnet and detected by a scintillation counter using a ZnS crystal. Both analyzing magnets were calibrated with polonium alpha-particles using

[4] Bender, Reilley, Allen, Ely, Arthur, and Hausman, Rev. Sci. Instr. **23**, 542 (1952).

[5] University of Pittsburgh Radiation Laboratory Precision Scattering Report No. 2, May (1952) (unpublished).