

# NMR SATELLITES AS A PROBE FOR CHEMICAL INVESTIGATIONS

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## ABSTRACT

Satellite lines in nmr spectra have, since their discovery, served conspicuously for the study of molecular structure and chemical bonding.

They can also be used for the determination of abundance ratios of isotopes; a comparison of the intensities of  $^{13}\text{C}$ —H satellite lines with that of the central line ( $^{12}\text{C}$ —H) gives the isotope ratio of  $^{13}\text{C}$ . This method is important in that it opens a way to determine the isotope abundance ratio in an individual functional group.<sup>1</sup>

Another application makes use of the difference in the spin-lattice relaxation times of the satellite and central lines. This difference reflects the relaxation of  $^{13}\text{C}$  spins and should give an insight into the  $^{13}\text{C}$  nuclear spin relaxation mechanisms.

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## 1. INTRODUCTION

Satellite lines of nmr spectra have extensively served as a useful probe to the investigation of molecular structure and chemical bonding. They can also be used for the determination of isotope abundance ratios and for the examination of the mechanisms of nuclear magnetic relaxation. This paper concerns the latter two applications, and, first, the background of the problem will be described briefly.

In 1961, the Committee of Atomic Weights of IUPAC revised the table of atomic weights of elements. In this revision, the chemical method which had so far been the main technique of atomic weight determination was replaced by mass spectroscopy. However, at the time of the revision, it was recommended by the Committee that efforts should be made in future to explore other methods in order to avoid relying on one method and to examine the bias error of mass spectroscopy. According to this requirement, the nmr satellite method has been proposed by which the isotope abundance ratio is obtained as the intensity ratio of the central and satellite lines of the proton resonance spectra.<sup>1</sup> By this method, the difference in the ionization efficiency among the molecules, which is always encountered in mass spectroscopy, is avoided, and it is moreover possible to measure the  $^{13}\text{C}$  concentration in each individual functional group of any organic molecule.

Before proceeding to its application, however, more detailed investigation of the satellite line itself has to be carried out. Two points are raised here as our main concern: the linearity of the response of the instrument, and the spin-lattice and spin-spin relaxation times. The first point comes up in

comparing the intensity of the central line with that of the satellite. All parts of the spectrometer, such as rf, narrow band and PSD amplifiers and so on, must have satisfactory linearity, which is not an easy problem in the case of  $^{13}\text{C}$  which is only 1 per cent of  $^{12}\text{C}$ . In so far as concerns the instruments we have examined, the situation is not completely satisfactory, and development on this particular point is awaited. The situation is assumed to be quite the same for mass spectroscopy. In the usual procedure of isotope abundance ratio measurement by mass spectroscopy, the sample compound is converted into carbon dioxide before measurement. Hence the problem of the yield of conversion occurs. In practice, all these difficulties are surmounted by the use of reference samples which are synthesized by mixing known amounts of isotopes. As a whole, it has been felt worthwhile to make efforts to develop other methods than mass spectroscopy.

The second subject of great importance in the investigation by the nmr satellite method is the difference in the relaxation times between the central and satellite lines. This problem itself is very interesting, and some investigations have been carried out<sup>2</sup>. The relaxation mechanisms of  $^{12}\text{C}-\text{H}$  and  $^{13}\text{C}-\text{H}$  protons differ only in the point that the latter has the contribution from the dipole-dipole interaction between  $^{13}\text{C}$  and proton.

## 2. SPIN-LATTICE RELAXATION

A sample of  $^{13}\text{C}$ -enriched (to 40%) formic acid was vacuum degassed by repeated freeze-pump cycles. This sample contains approximately 3 per cent of water as an impurity. Measurements were made at 23.5°C on a JEOLCO

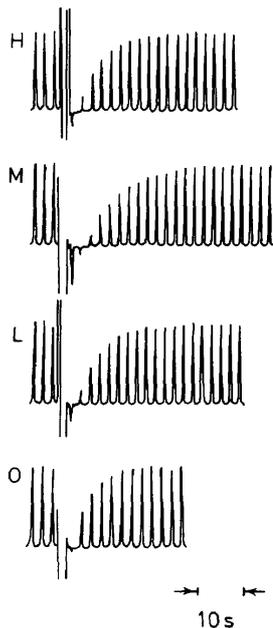


Figure 1. Transient recovery of the longitudinal magnetizations after adiabatic inversion for the  $^{13}\text{C}-\text{H}$  high-field (H),  $^{12}\text{C}-\text{H}$  (M),  $^{13}\text{C}-\text{H}$  low-field (L) and O—H (O) protons of formic acid.

JNM 4H-100 spectrometer operating at 100 MHz. The spin-lattice relaxation times were measured by the adiabatic rapid passage method. The recovery of the magnetizations was sampled using the sawtooth modulation provided by the linear sweep unit. Transient nuclear Overhauser effects were observed employing the usual double-resonance technique.

Formic acid gives four kinds of proton signals,  $^{13}\text{C}$ -H high-field,  $^{12}\text{C}$ -H,  $^{13}\text{C}$ -H low-field and O-H, which are denoted by  $H, M, L$  and  $O$ , respectively. Figure 1 shows the recovery of the longitudinal magnetization after adiabatic inversion. Apparent relaxation times obtained are 4.9, 7.5, 4.9 and 3.5 s (accurate to 0.1 s) for the  $H, M, L$  and  $O$  protons, respectively.

The transient recoveries of the longitudinal magnetizations of the  $^{12}\text{C}$ -H and O-H protons are expressed by linear equations

$$-\frac{dM(M)}{dt} = \frac{M(M) - M_0(M)}{T_1(M)} \quad (1a)$$

and

$$-\frac{dM(O)}{dt} = \frac{M(O) - M_0(O)}{T_1(O)} \quad (1b)$$

Here,  $M(M)$  is the longitudinal magnetization for the  $M$  protons and  $M_0(M)$  is its thermal equilibrium value;  $T_1(M)$  is the spin-lattice relaxation time for the  $M$  system. The symbols  $M(O)$ ,  $M_0(O)$  and  $T_1(O)$  have equivalent significance in the  $O$  system. After adiabatic inversion, the magnetizations  $M(M)$  and  $M(O)$  recover to their thermal equilibrium values exponentially with time constants  $T_1(M)$  and  $T_1(O)$ , respectively.

Flip of the  $^{13}\text{C}$  spin would result in interchange of the two  $^{13}\text{C}$ -H proton signals. With this effect taken into account, the spin-lattice relaxation for the  $^{13}\text{C}$ -H protons may be represented by a set of linear equations

$$-\frac{dM(H)}{dt} = \frac{M(H) - M_0(H)}{T_1(H)} + \frac{M(H) - M(L)}{\tau} \quad (1c)$$

and

$$-\frac{dM(L)}{dt} = \frac{M(L) - M_0(L)}{T_1(L)} + \frac{M(L) - M(H)}{\tau}, \quad (1d)$$

where notations other than  $\tau$  are equivalent to those in equations 1a and 1b. Equations 1c and 1d are similar to those given by Forsén and Hoffman,<sup>3</sup> who discussed a contribution to a change in longitudinal magnetization from proton exchange between the keto and enol forms of acetylacetone and interpreted their results in terms of the residence time  $\tau$ . In equations 1c and 1d,  $\tau$  is a measure of the rate of *population transfer* between the two side bands  $H$  and  $L$  due to flip of the  $^{13}\text{C}$  spin. The second terms of equations 1c and 1d would affect the relaxation for the  $H$  and  $L$  magnetizations only when there is a difference in population between these two magnetizations. The recovery of the  $H$  magnetization is governed by the sum of two exponential functions with time constants  $(1/T_1(H) + 2/\tau)^{-1}$  and  $T_1(H)$ ; in practice, it is governed by the former constant. The transient recovery of the  $L$  magnetization can be treated in a similar way.

It is assumed that  $^1\text{H}$  and  $^{13}\text{C}$  relaxations are governed by their mutual dipolar interaction. The validity of this assumption is discussed later. Then it is shown from the calculation of transition probabilities for a coupled system of two unlike spins that in the limit of extremely narrow case  $\tau$  is related to  $^{13}\text{C}$  spin-lattice relaxation time  $T_1(^{13}\text{C})$  by a simple relation

$$\tau = \frac{16}{3} T_1(^{13}\text{C}). \quad (2)$$

Since both  $^1\text{H}$  and  $^{13}\text{C}$  have spin  $1/2$ ,  $T_1(^{13}\text{C})$  is equal to  $T_d^p$ , the dipolar relaxation time for the proton, which is given by

$$\frac{1}{T_d^p} = \frac{1}{T_1(H)} - \frac{1}{T_1(M)} = \frac{1}{T_1(L)} - \frac{1}{T_1(M)}. \quad (3)$$

With these relations, the  $^1\text{H}$  and  $^{13}\text{C}$  spin-lattice relaxation times are determined at

$$\begin{aligned} T_1(H) &= T_1(L) = 5.4 \pm 0.2 \text{ s} \\ T_1(M) &= 7.5 \pm 0.1 \text{ s} \\ T_1(O) &= 3.5 \pm 0.1 \text{ s} \\ T_1(^{13}\text{C}) &= 19.4 \pm 1.8 \text{ s}, \end{aligned} \quad (4)$$

and the *population transfer time*  $\tau$  is calculated at about 100 s. In terms of the dipolar relaxation time  $T_d^p$ , the correlation time for the rotational Brownian motion of the molecule  $\tau_c$  is given by

$$\frac{1}{T_d^p} = \frac{\gamma_p^2 \gamma_c^2 \hbar^2}{r^6} \tau_c \quad (5)$$

where  $r$  is the C—H bond distance, and  $\gamma_p$  and  $\gamma_c$  are the gyromagnetic ratios of the  $^1\text{H}$  and  $^{13}\text{C}$  nuclei, respectively. Using equation 5 and assuming that  $r$  is equal to 1.09 Å, one obtains

$$\tau_c = (2.4 \pm 0.2) \times 10^{-12} \text{ s}. \quad (6)$$

When the  $L$  magnetization is saturated, the change in magnitude of the  $M$  and  $H$  magnetizations under steady-state condition is given by

$$\frac{M(M) - M_0(M)}{M_0(M)} = \frac{T_1(M) M_0(L)}{T_1(ML) M_0(M)} \equiv \eta(ML), \quad (7a)$$

$$\frac{M(H) - M_0(H)}{M_0(H)} = \frac{\frac{M_0(L)}{T_1(HL)} - \frac{M_0(H)}{\tau}}{\frac{1}{T_1(H)} + \frac{1}{\tau}} \frac{1}{M_0(H)} \equiv \eta(HL), \quad (7b)$$

where  $T_1(ML)$  and  $T_1(HL)$  are the cross-relaxation times between  $M$  and  $L$  and between  $H$  and  $L$  protons, respectively. The Overhauser enhancement parameters  $\eta(ML)$  and  $\eta(HL)$  are obtained by extrapolating the transient decay to  $t = 0$  when the irradiating field is cut off.

The enhancement parameter  $\eta(HL)$  was found to be zero within experimental error, indicating that  $\tau$  is of the same order of magnitude as  $T_1(HL)$ .

If other mechanisms than the dipolar interaction with the proton are dominant for the  $^{13}\text{C}$  relaxation,  $\tau$  should be much smaller than  $T_1(\text{HL})$ , which is inconsistent with the experimental result. When the  $^1\text{H}$  and  $^{13}\text{C}$  relaxations are solely due to their mutual dipolar coupling, it can be shown that  $\tau = \frac{7}{3}T_1(\text{HL})$ . The parameter  $\eta(\text{ML})$  was also too small to be detected. This shows that an intermolecular contribution to the proton relaxation is not important. In view of the above results it is concluded that the  $^{13}\text{C}$  relaxation is primarily determined by the intramolecular dipolar interaction with the proton.

### 3. LINE WIDTH

The line widths of  $^{12}\text{C}$ —H (central) and  $^{13}\text{C}$ —H (satellite) protons were examined for formic acid, chloroform, tetramethyl silane and other compounds with natural  $^{13}\text{C}$  abundance. The result was, contrary to our expectation, that the line width for the central line is always larger than that of the satellite line. The spin-lattice relaxation time of the  $^{13}\text{C}$ —H proton is shorter than that of the  $^{12}\text{C}$ —H proton, hence the observed fact cannot be interpreted in terms of the spin system alone. Linearity of the response of the spectrometer has been improved fairly satisfactorily by the modification of commercially available instruments, and any purely instrumental mechanism is also excluded. Thus it is assumed that the observed fact stems from some mechanism of coupling between the spin system and the instrument, such as radiation damping.<sup>4</sup>

This difficulty may be overcome by two methods: (1) integration of the spectral line because integrated intensity is proportional to the magnetization, and (2) addition of paramagnetic ions so that the effect of radiation damping may be neglected.

### 4. $^{13}\text{C}$ CONCENTRATION MEASUREMENT

$\text{Cu}(\text{acac})_2$  was added to a sample of chloroform (Guaranteed Reagent from Wako Pure Chemical Industries) to broaden the line width and  $^{12}\text{C}$ —H and  $^{13}\text{C}$ —H proton spectra were obtained after averaging. The  $^{13}\text{C}$  concentration was found at  $1.116 \pm 0.025$  per cent by comparison of the integrated areas of the signals. Though this value is tentative and may be revised by future investigation, it should be compared with the value  $1.108 \pm 0.004$  per cent determined by Niel<sup>5</sup> on limestones. In conclusion, the nmr satellite method is considered as a promising method of atomic abundance determination for suitable systems.

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