Nuclear Magnetic Triple Resonance Spectrum of *N*-Methyl-acetamide

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The double resonance technique has proved to be a very promising method for obtaining well-resolved spectra of compounds with a nitrogen atom.1-3) If we can now supply a third r-f field to compounds which are already doubly irradiated, the spin-spin interaction between protons can be decoupled by this third r-f field in addition to decoupling of the ^{14}N-proton interaction.

The purpose of this note is to report on the successful development of a nuclear magnetic triple resonance and on the spectrum obtained by applying this triple resonance to the *N*-methyl-acetamide.

The JNM-3H-60 High Resolution Spectrometer (60 Mc) has been modified for this triple-resonance experiment.4) The unit for the second r-f field, which is designed to resonate to the ^{14}N nucleus, was constructed in our laboratory. The proton spin decoupler was used as the apparatus to supply the third r-f field for decoupling the proton-proton interaction. A detailed description of the whole apparatus has already been published.5) All the observations have been carried out by the field-sweep method.

The full spectrum, shown in Fig. 1(a), is a normal and undecoupled spectrum of *N*-methyl acetamide. Starting from the high-field side, the sharp singlet may be attributed to the protons in the acetyl group; the sharp doublet, to the proton in the *N*-methyl group, and the broad peak, to the amine proton. By the double-resonance technique the spectrum of the amine proton reveals its expected multiplet, the quartet, as is shown in Fig. 1(b). It was necessary to feed the strong r-f magnetic field, which was more than 3 gauss, to the ^{14}N nucleus in order to obtain a well-resolved multiplet like that shown in Fig. 1(b). No change in the peaks corresponding to other groups than the amine proton was observed by this second irradiation.

The quartet structure of the amine-proton spectrum suggests the coupling of the proton with three equivalent protons. Although it is quite reasonable to assign this quartet to the coupling with three protons of the *N*-methyl group, this assignment still needs confirmation. We could obtain this confirmation unambiguously by feeding the third r-f field so as to decouple the proton-proton coupling. The third r-f field was fed to the sample by using the spin decoupler system. The triple resonance spectra, which were obtained by the simultaneous resonance of protons of the

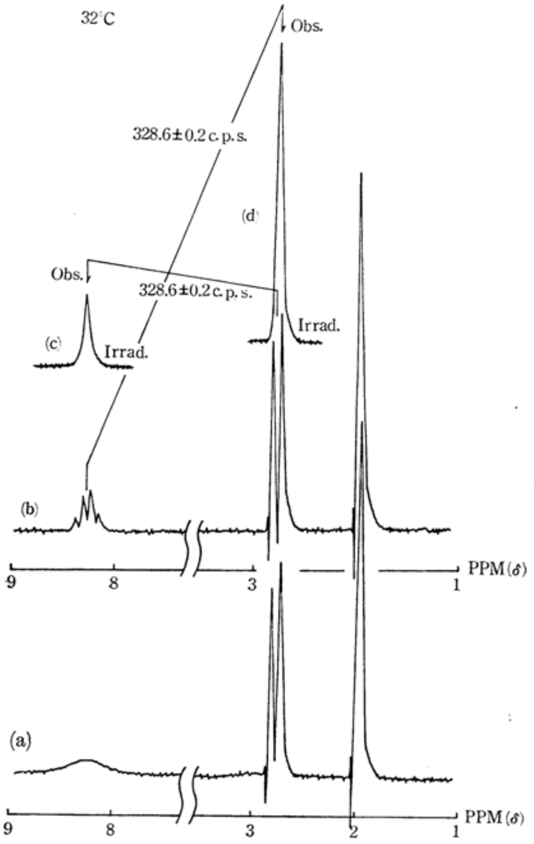

Fig. 1. Proton magnetic resonance spectra of *N*-methyl acetamide at 60 Mc. (a) Normal spectrum; (b) Double resonance spectrum being decoupled from ^{14}N; (c) Triple resonance spectrum observing amine proton decoupled from both ^{14}N and *N*-methyl protons; (d) Triple resonance spectrum, observing *N*-methyl proton decoupled from both ^{14}N and amine proton.

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two species and of ^{14}N, are shown in Figs. 1(c) and (d). By comparing these triple resonance spectra with the double-resonance spectrum, shown in Fig. 1(b), one can find collapses of the multiplets. It follows without question from the collapses that the origin of these multiplets is the spin-spin interaction between the amine proton and *N*-methyl protons. Thus, the chemical shift between these species of protons is the frequency difference between the first and the third irradiations, that is, 328.6±0.2 cps. The coupling constant, *J*, between these protons was found to be 4.7±0.2 cps.