

The sign and magnitude of the vicinal ^{13}C - ^1H and long-range ^1H - ^1H coupling constant in acetone

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The natural abundance of ^{13}C (nuclear spin $\frac{1}{2}$) is 1.1 per cent. Therefore acetone contains the isotopic species $^{13}\text{CH}_3^{12}\text{CO}^{12}\text{CH}_3$ (II) and $(^{12}\text{CH}_3)_2^{13}\text{CO}$ (III) with an abundance of 2.2 and 1.1 per cent respectively in $(^{12}\text{CH}_3)_2^{12}\text{CO}$ (I). The possibility of two ^{13}C in the same molecule is small. We studied species (II) in natural abundance, which gives rise to an A_3M_3X spectrum. The nature of the ^1H and ^{13}C -resonance is given in figure 1, where first-order spectra are assumed. It should be noted that the M part of the spectrum is normally hidden under the main ^1H resonance due to (I).

The experiments were performed on a Varian HA-60 spectrometer. For heteronuclear double resonance the probe was modified as described in [1]. Further a 15.08 MHz crystal-controlled oscillator, built in this laboratory, with audio-frequency modulation was used for irradiation of the ^{13}C frequencies. A liquid sample of 0.5 molar acetone in benzene was used.

The relative signs of $^1J_{\text{CH}}$ and $^3J_{\text{CH}}$ were determined by weak irradiation in the M region whilst observing the A part of the ^1H spectrum. The satellite

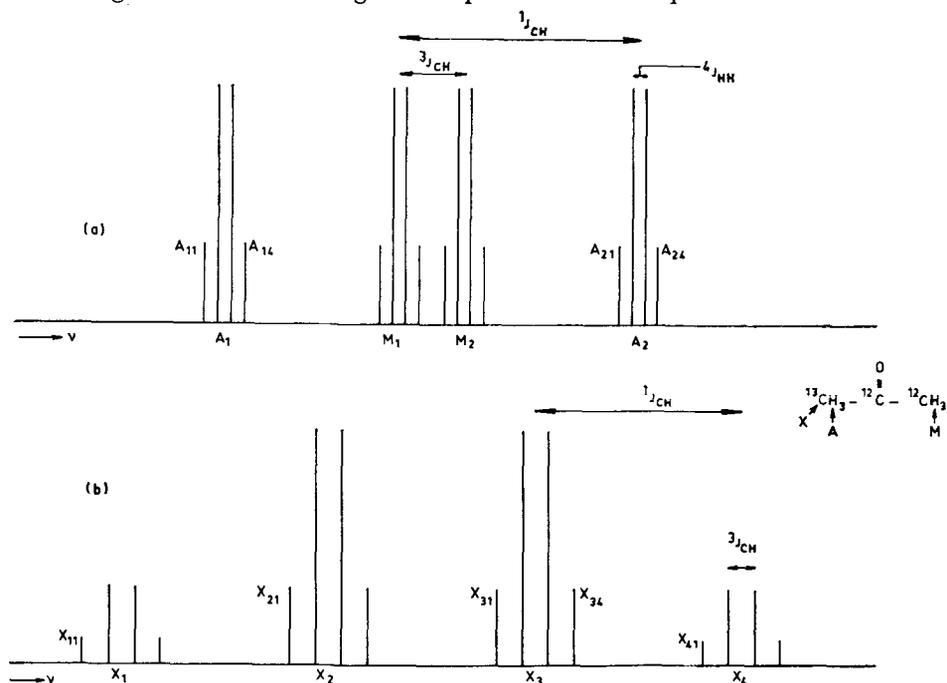


Figure 1. ^1H spectrum (a) and ^{13}C spectrum (b) of acetone species (II). Scale (a) is expanded twice compared with (b).

A_2 (figure 2 (a)) becomes a singlet on irradiation of M_2 (figure 2 (b)); A_1 becomes a singlet on irradiation of M_1 . So ${}^1J_{CH}$ and ${}^3J_{CH}$ have the same positive sign, as ${}^1J_{CH}$ is positive [2]. From the same experiment the magnitude of ${}^3J_{CH}$ could be determined to be 2.2 Hz.

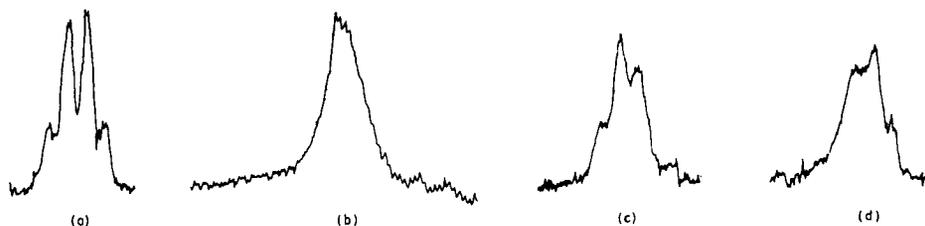


Figure 2. Satellite A_2 ; (a) normal; (b) at irradiation of M_2 ; (c) at irradiation of X_{34} ; (d) at irradiation of X_{31} .

The relative signs of ${}^3J_{CH}$ and ${}^4J_{HH}$ can be determined by irradiation of the outer lines of X_1 , X_2 , X_3 or X_4 whilst observing A_1 or A_2 . For a theoretical discussion see [2]. For instance at irradiation of X_{34} , A_{24} is affected (figure 2 (c)) and at irradiation of X_{31} , A_{21} is affected (figure 2 (d)). So ${}^4J_{HH}$ and ${}^3J_{CH}$ have the same (positive) sign. The magnitude of ${}^4J_{HH}$ is already known to be 0.55 Hz [3-5]. So the coupling constants for acetone species (II) are:

$${}^1J_{CH} = +126.7 \pm 0.2 \text{ Hz,}$$

$${}^3J_{CH} = +2.2 \pm 0.3 \text{ Hz,}$$

$${}^4J_{HH} = +0.55 \pm 0.02 \text{ Hz.}$$

It is interesting to note that the same type of experiment did not give results in the case of mercury dimethyl [6, 7]. In this case the ${}^{199}\text{Hg}$ transitions had to be used.

There has been considerable interest in the origin of long-range coupling constants. Holmes and Kivelson [3] interpreted ${}^4J_{HH}$ in acetone as due to interactions via the π electrons. As this leads to a negative sign for ${}^4J_{HH}$, it cannot be the only contribution. Moreover the increase of $|{}^4J_{HH}|$ in hydrogen-bonding solvents [5, 8] cannot be explained on this basis. De Jeu *et al.* [8] tried to explain this effect by assuming an additional positive through-space contribution to ${}^4J_{HH}$. Their interpretation is still based on a total negative sign of ${}^4J_{HH}$, so it cannot be correct.

The simplest rationalization of ${}^4J_{HH}$ in acetone is probably: (a) a negative contribution via the π electrons of about -0.5 Hz [3]; (b) a positive contribution through the σ bonds and possibly through space of about $+1.0$ Hz. The latter assumption agrees with some preliminary calculations [9] using Pople-Santry theory [10, 11]. The increase of $|{}^4J_{HH}|$ with hydrogen bonding can be explained by the expected decrease in absolute magnitude of contribution (a), while contribution (b) remains approximately constant [9]. More extensive theoretical calculations are in progress in this laboratory.

Note added in proof.—Recently we learnt that similar results have been obtained independently by H. Dreeskamp, 1968, *Z. phys. Chem.*, **59**, 321.

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