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Институт химии и Институт кибернетики
Академии наук Эстонской ССР

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E. LIPPMAA, S. RANG, O. EISEN, J. PUSKAR

KÜLLASTUMATUTE SÜSIVESINIKE TUUMARESONANTS-SPEKTROSKOOPIA. I.

Alkeenid, alküünid ja asendatud tsüklohekseenid.

E. LIPPMAA, S. RANG, O. EISEN, J. PUSKAR

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF UNSATURATED COMPOUNDS. I.

Alkenes, alkynes and cyclohexenes with alkyl substituents.

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E. LIPPMAA, M. ALLA

MODULATION TRANSFER IN NUCLEAR MAGNETIC DOUBLE RESONANCE OF NITROGEN COMPOUNDS

Modulation transfer from ^{13}C nuclei to ^1H nuclei has been described by Freeman and Anderson [1] who have developed the necessary theory and used it to determine ^{13}C chemical shifts and the signs of spin-spin coupling constants J (^{13}CH). This method depends upon local periodic magnetic field changes that are transmitted through nuclear spin-spin coupling from the nuclei perturbed by a very strong frequency modulated rf field H_2 to the nuclei being investigated. Modulation transfer appears to be quite a promising method for indirect determination of chemical shifts. Chemical shifts of nitrogen are very important but are hard to determine directly, particularly if only small samples can be used. Since nitrogen compounds show sharp J (^{14}NH) multiplets only in special cases [2, 3], it is essential to show whether modulation can be transferred from ^{14}N to hydrogen nuclei that have only broad lines in proton spectra. A saturated acidified solution of ammonium nitrate in water and some organic compounds were used in these experiments. The proton spectrum of ammonium ions is a well-resolved triplet of equal lines, and modulation transfer proceeds smoothly in this case. The signals are as strong as ordinary proton signals of NH_4^+ (Fig. 1).

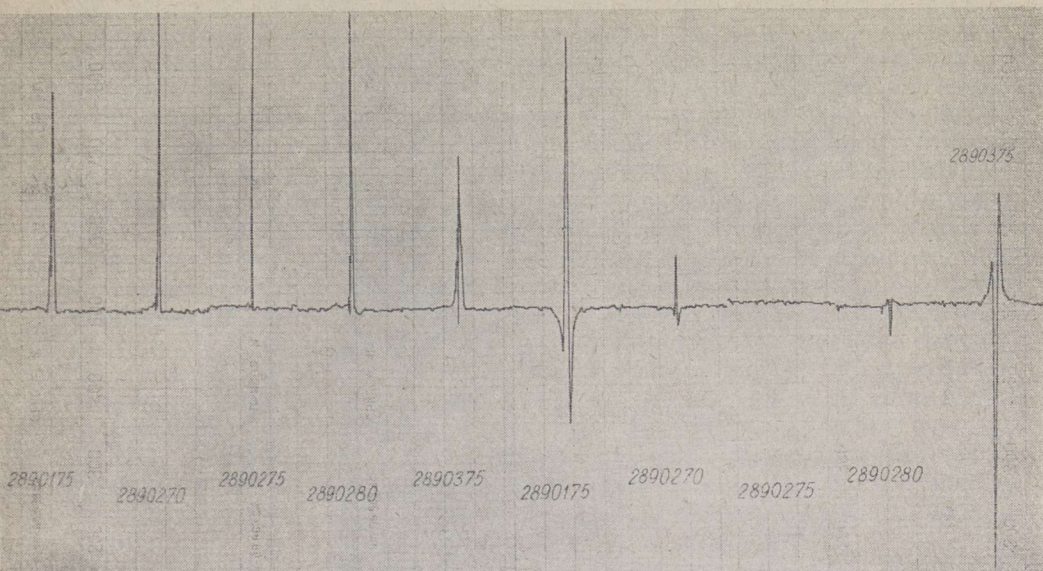


Fig. 1. Saturated acidified solution of ammonium nitrate in water. Double resonance spectra are given on the left, modulation transfer spectra on the right. The perturbing frequency $\omega_2/2\pi$ is given in cps and the central value 2890275 cps corresponds to exact resonance of the ^{14}N nucleus and total collapse of the hydrogen triplet. The frequency scale of each spectrum corresponds to that used in Fig. 2 and the line distance $J(^{14}\text{NH})=46$ cps can serve for calibration purposes.

Although tickling (Fig. 2) is a better method for chemical shift determination in this particular case, the shift could also be determined from modulation transfer spectra; the ratio of nitrogen resonance frequency of NH_4^+ ions to that of tetramethylsilane (TMS) protons was found to be 0.0722463 ± 0.0000001 . No modulation transfer could be effected in aniline, pyridine and their derivatives (neat liquids), but it was successful with formamide (Fig. 3) where the nitrogen nucleus causes only some broadening of the lines in ^1H spectrum without any $J(^{14}\text{NH})$ fine structure[4]. As in Fig. 1,

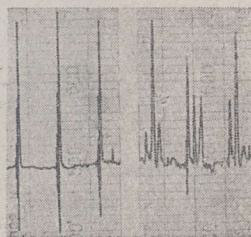


Fig. 2. Proton spectra of NH_4NO_3 in a saturated acidified solution. Monoresonance on the left, tickling on the right. The tickling pattern is most sensitive to small deviations (± 1 cps) of ω_2 from exact resonance of the ^{14}N nucleus.

modulation transfer spectra are presented alongside with double resonance proton spectra, while the strength of the frequency modulated perturbing field γH_2 was the same in all cases. The very strong perturbing field caused after $250\times$ attenuation a 5 cps splitting of NH_4^+ proton lines in a tickling experiment. A high modulation index was used and the strength of each sideband was equal to 0.7 of the centreband. Quite strong modulation transfer spectra were produced and the nitrogen chemical shift could be determined from the crossover frequency between 2890500 and 2890600 cps (2890530 ± 10 cps by interpolation). The ratio of nitrogen resonance frequency to the resonance frequency of TMS protons is $0.0722527 \pm \pm 0.0000002$. The ratio is slightly higher than was reported previously [4].

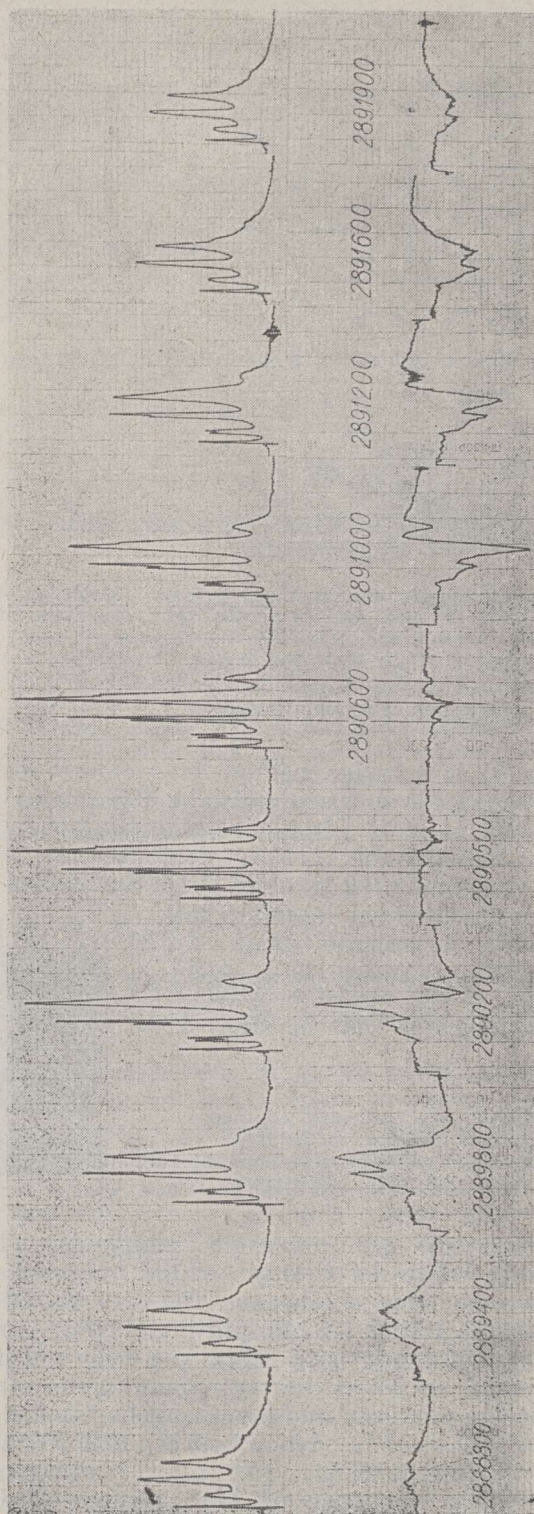


Fig. 3. Proton spectra of formamide. Double resonance spectra are given in the top row and modulation transfer spectra below. The perturbing frequency $\omega_2/2\pi$ is given in cps and the crossover frequency 2890530 cps corresponds to ^{14}N chemical shift in formamide and maximum collapse. A sharp peak on the low field side of the formamide spectrum is an impurity peak and no modulation is transferred to it.

The perturbing field was not strong enough for total decoupling as in [5]. It is important to note that modulation is transferred to all lines of the proton spectrum, but with unequal intensities. Double resonance spectra were recorded with field modulation at the same frequency ω_m used for modulation transfer, but γH_1 was diminished by 30 db in this case. The 40 Mc spectrometer was stabilized by spin generator [6] and frequency synthesis was used to generate the swept frequency ω_1 and the "frequency modulated" [7] perturbing frequency ω_2 . A special frequency modulator, incorporating a PDG-1 synthesizer (Messelektronik, DDR) was employed. A standard bridge-type NMR probe with 5 mm o. d. sample tubes was equipped with two concentric coils for H_1 and H_2 respectively. Time sharing at a 5 kc pulse repetition rate and 50 per cent duty cycle was used to decouple the transmitter from the *rf* amplifier and thus to eliminate spurious base-line drift [7]. The frequency ω_1 of the measuring field H_1 was displaced by ω_m to lower frequencies from the proton resonance frequency ω_0 . The modulation transfer signal was carried at the modulation frequency ω_m (599.1 cps for NH_4NO_3 and 546.1 cps for $HCONH_2$) after high-frequency synchronous detection in the *rf* (ω_1) amplifier as is usual in modulation experiments. The signal was recorded after audio-frequency synchronous detection and filtration.

It appears that modulation transfer is possible in nitrogen compounds possessing only broad lines without any visible fine structure, but it depends in a complicated manner upon the nitrogen-hydrogen spin-spin coupling constant $J(^{14}NH)$, and proton exchange frequency as well as nitrogen relaxation. The last two are sensitive to environment (pH, concentration, temperature, etc.).

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Academy of Sciences of the Estonian SSR,
Institute of Cybernetics

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E. LIPPMAA, M. ALLA

MODULATSIOONI ULEKANNE LÄMMASTIKUÜHENDITE MAGNETILISE TOPELTRESONANTSI SPEKTRITES

Э. ЛИППМАА, М. АЛЛА

ПЕРЕДАЧА МОДУЛЯЦИИ В СПЕКТРАХ ЯДЕРНОГО МАГНИТНОГО ДВОЙНОГО РЕЗОНАНСА СОЕДИНЕНИЙ АЗОТА