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SPIN-LATTICE RELAXATION TIMES OF CARBON-13 NUCLEI IN ORGANIC COMPOUNDS

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A. ОЛИВСОН, Э. ЛИПМАА, Я. ПАСТ. СПИН-РЕШЕТОЧНЫЕ ВРЕМЕНА РЕЛАКСАЦИИ
УГЛЕРОДА-13 В ОРГАНИЧЕСКИХ СОЕДИНЕНИЯХ

It has generally been assumed that the spin-lattice relaxation time of carbon-13 nuclei in organic compounds is rather long [1], particularly in deuterated compounds [5]. These relaxation times have never been actually measured, but it has been found that at 8.5 Mc the spin-lattice relaxation time T_1 is of the order of one minute in unenriched oxygen-free carbon disulfide and much longer in carbon tetrachloride [1-3]. The relaxation times of carbon-13 nuclei are of considerable practical importance, since good signal to noise ratio can only be achieved if the condition for adiabatic rapid passage [3-4] is fulfilled

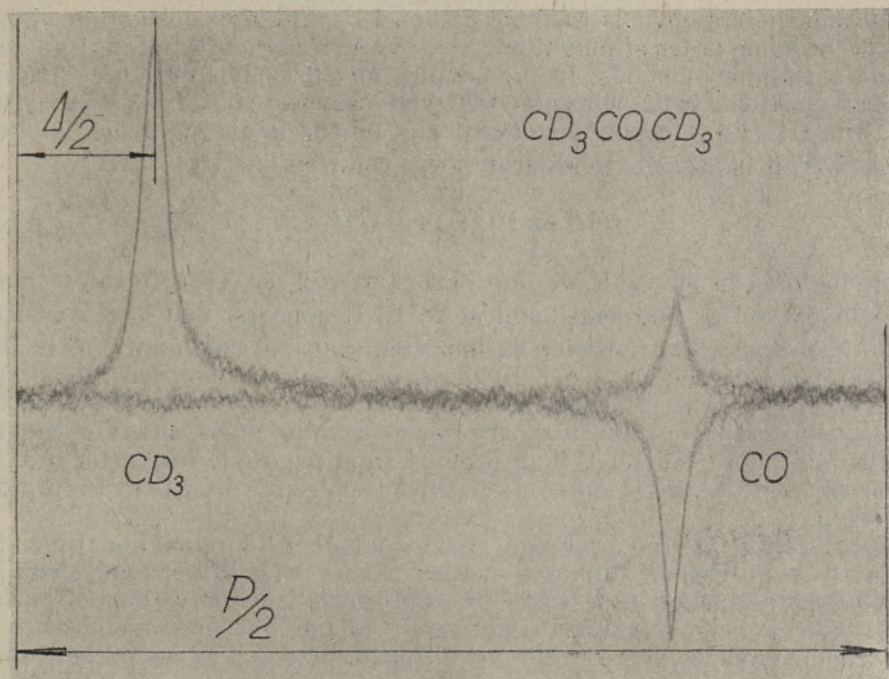
$$1/T_1, 1/T_2 \ll dH_0/dt \ll \sqrt{H_1^2}, \quad (1)$$

and this is difficult if these times are short. The carbon-13 relaxation time T_1 can also provide insight into the details of molecular motion [2].

Since the carbon-13 signal is very weak, the adiabatic fast passage method of Drain [4-8] was used to measure the spin-lattice relaxation time T_1 of various single lines in carbon-13 spectra with natural (1.1 per cent) abundance of this isotope. Very good zero and sweep stability as well as sensitivity is needed. The necessary zero stability was achieved through the use of time sharing with 4 kc pulse repetition rate [10] and the line position was stabilized with a 40/60 Mc proton sideband spin generator [11]. The spectra were registered in the linear frequency sweep mode, using 5 kc and in a few cases 2.5 kc sweep width and a $P=40$ to 150 sec sweep period. The X-Y recorder, Omnigraphic HR-100 (Bellaire, Texas) was used as a memory device. In all cases from 5 to 20 traces were recorded and the mean value showed up well (see Fig.). The relaxation times T_1 were found from the equation

$$\frac{\Delta}{P} = \frac{T_1}{P} \ln \left[\frac{2}{1 + e^{-P/T_1}} \right] \quad (2)$$

where Δ is the shorter time, spent below or above the resonance [4-8]. Due to this particular method of measurement, the error in T_1 is fairly constant and does not exceed ± 2 sec. All measurements were performed at 15.09 or 10.07 Mc and room temperature (26 to 28°C). Pure argon gas was bubbled



Fast passage nuclear resonance lines of C^{13} in natural abundance in deuterioacetone through the neat liquids for degassing. This method proved to be just as effective as repeated freeze-pump-thaw cycles for oxygen removal. All measured spin-lattice relaxation times are given in the following table:

Compound	Measured carbon-13 nucleus	Sample with dissolved oxygen (T_1) ¹⁵	Degassed sample without dissolved oxygen	
			(T_1) ¹⁵	(T_1) ¹⁰
Carbon disulfide	CS ₂	19	30	42
Carbon tetrachloride*	CCl ₄	—	<6	—
Hexadeuterioacetone	CD ₃	22	33	32
	C=O	17	26	25
Tolane**	C≡C	32	52	66
Acetonitrile	C≡N	5	7	10
β-Bromopropionitrile	C≡N	6	—	—
Adipic acid dinitrile	C≡N	—	12	—
Acetone cyanhydrine	C≡N	17	—	—
	>C<	11	—	—
Acetic acid	COOH	—	32	—
Benzoyl chloride	COCl	34	49	—
Acetone	C=O	20	—	—
Acetophenone	C=O	27	34	—
Thienyl methyl ketone	C=O	24	30	—
Dicyclopropyl ketone	C=O	23	25	—
Hexadeuterobenzene	C ₆ D ₆	22	—	—
Tetradeproto methyl alcohol	CD ₃	23	—	—
Trideuproto ethyl alcohol	CD ₃	9	—	—
Pentadeuproto ethyl alcohol	CD ₂	20	—	—

* The relaxation time is very short and the signal very weak. Only the upper limit of T_1 could be measured.

** Saturated solution in CS₂.

It is immediately obvious that the carbon-13 spin-lattice relaxation times are of the same order of magnitude as proton relaxation times in degassed liquid organic compounds. In the simplest of all compounds investigated, carbon disulfide, both spin-rotational and chemical-shift relaxation operate. Since $1/(T_1)_\sigma$ depends quadratically on the intensity of the applied field H_0 [3], it is possible to separate these contributions [2]

$$1/T_1 = 1/(T_1)_J + 1/(T_1)_\sigma. \quad (3)$$

From the data in the table we find that $(T_1)_J = 62$ sec, $(T_1)_\sigma^{10} = 131$ sec and $(T_1)_\sigma^{15} = 58$ sec for the neat liquid at 28°C. It appears that the chemical shift anisotropy [7] can provide an important, but not dominant part in the relaxation of carbon-13 nuclei. In the case of carbon disulfide in equilibrium with atmospheric molecular oxygen the chemical-shift, spin-rotational and dipole-dipole relaxation are about equally important. The carbon nuclei are more shielded than protons from magnetic interactions with other molecules and the effect of dissolved oxygen is less than in proton spectra.

Deuteration has no profound effect on carbon-13 relaxation time. In contrast with earlier findings, neither a very long [5] nor very short [6] spin-lattice relaxation time could be confirmed. Isolated carbon-13 nuclei can have a long relaxation time, as in toluene, but substituents with a quadrupole moment, like chlorine or nitrogen, diminish it. Scalar spin-spin coupling with these nuclei can serve as efficient relaxation mechanism for carbon-13 nuclei [9]. Carbon tetrachloride has an especially low spin-lattice relaxation time, contrary to earlier assumptions [1]. The spin-lattice relaxation times of carbon-13 nuclei in various functional groups of a molecule are in general not equal and can provide additional information about molecular structure and motion.

REFERENCES

1. McConnell H. M., Holm C. H., *J. Chem. Phys.*, **25**, 1289 (1956).
2. Waugh J. S., in *Molecular Relaxation Processes*, Academic Press, London, 1966.
3. Abragam A., *Principles of Nuclear Magnetism*, Oxford Univ. Press, Oxford, 1961.
4. Drain L. E., *Proc. Phys. Soc.*, **62**, 301 (1949).
5. Spiess H., Schneider W. G., *J. Chem. Phys.*, **35**, 731 (1961).
6. Pugmire R. J., Grant D. M., Robins R. K., Rhodes G. W., *J. Am. Chem. Soc.*, **87**, 2225 (1965).
7. Pople J. A., *Mol. Phys.*, **7**, 301 (1963/64).
8. Anderson W., in *NMR and EPR Spectroscopy*, Pergamon Press, Oxford, 1960.
9. Freeman R., Ernst R. R., Anderson W. A., *J. Chem. Phys.*, **46**, 1125 (1967).
10. Липпмаа Э., Паст Я., Оливсон А., Салувере Т., *Изв. АН Эст. ССР, Серия физ.-матем. и техн. наук*, **15**, 58 (1966).
11. Lippmaa E., Pehk T., Past J., *this issue*, p. 345 (1967).