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SOLVENT DEPENDENCE OF ^{13}C -H AND H-H COUPLING IN ACETONE AND DIMETHYL SULFOXIDE

BY

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The coupling constants $J^{13}\text{CH}$ and J_{HH} for acetone and dimethyl sulfoxide were measured in a variety of solvents. $J^{13}\text{CH}$ for acetone was found to vary by up to 1.5 % and J_{HH} by up to 30 %. The magnitudes of these variations are in almost linear relationship with the carbonyl ^{13}C and ^{17}O chemical shifts in the same solvent. A reason for this is sought in polar structures caused by the formation of hydrogen bonds and favoured by the polarity of the solvent. $J^{13}\text{CH}$ for dimethyl sulfoxide also varies with the solvent but J_{HH} remains constant.

Introduction

During recent years several papers have been published on the dependence of the H-H coupling on the solvent.^{1,2,3} Little or no attention has been given to this aspect of ^{13}C -H coupling. As far as we know, only *Evans*⁴ has investigated this matter. The subject is important because variations in the coupling constants should correlate with differences in molecular charge distribution.

We have determined $J^{13}\text{CH}$ for acetone in water at four different concentrations and for pure acetone, and further for 0.20 or 0.35 molar fractions of acetone in 12 different solvents. $J^{13}\text{CH}$ for dimethyl sulfoxide was determined for a 0.35 molar fraction in three different solvents and for pure dimethyl sulfoxide. Both for acetone and for dimethyl sulfoxide J_{HH} was also determined in all cases.

Results

The results found for the acetone-water system are shown in Fig. 1.

The other results are given in Table I. Table I also shows the chemical shift values of ^{13}C and ^{17}O in the carbonyl group as measured by *Maciel*

- ¹ V. S. Watts, G. S. Reddy and J. H. Goldstein, *J. Mol. Spectry.* **11**, 325 (1963).
- ² B. L. Shapiro, R. M. Kopchick and S. J. Ebersole, *Ibid.* **11**, 326 (1963).
- ³ P. Bates, S. Cawley and S. S. Danyluk, *J. Chem. Phys.* **40**, 2415 (1964).
- ⁴ D. F. Evans, *J. Chem. Soc.* **1963**, 5575.

Table I
Results of measurements for acetone and dimethyl sulfoxide, alone and in various solvents.

Solvent	Acetone						Dimethyl sulfoxide		ϵ_r of the solvent
	molar fraction						molar fraction 0.35		
	0.20		0.35		0.20		unknown		
	J_{CH}^{13} in cps ^a	J_{HH} in cps ^b	J_{CH}^{13} in cps ^a	J_{HH} in cps ^b	$\tau_{13\text{C}}$ in ppm ⁶	$\tau_{17\text{O}}$ in ppm ⁷	J_{CH}^{13} in cps ^a	J_{HH} in cps ^b	
Acetone	126.6	0.51	126.6	0.51	0	0	137.6	0.44	20.7
dimethyl sulfoxide	126.6	0.58 ^c	126.7	0.52	1.3	-5	137.6	0.45	—
carbon disulfide	— ^d	0.53	127.0	0.52	-2.9	8			2.6
carbon tetrachloride	127.1	0.54	— ^d	0.54	-2.1	4			2.2
nitrobenzene				0.56	-0.7	2			35.7
ethyl alcohol				0.52	-2.3	6			24.3
acetonitrile				0.60		2			37.5
dimethylformamide				0.61		6			37.6
aniline				0.66		12			6.9
chloroform	127.5	0.60	127.4	0.56	-9.1	37	139.2	0.45	4.8
formamide	128.1	0.61	128.0	0.57	-8.7	20	138.9	0.45	109
water					-9.1	40			80.4
phenol					-8.7				9.8
formic acid	128.1	0.66			-9.1				58.5

^a Standard deviation 0.2 cps.

^b Standard deviation 0.02 cps.

^c The reason for this high value is not understood.

^d J_{CH}^{13} cannot be determined exactly here because one of the ^{13}C satellites falls under a main peak of the spectrum.

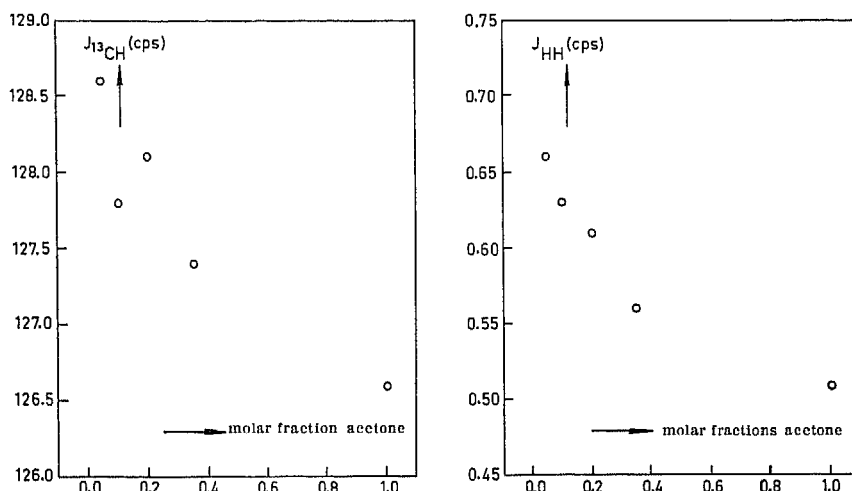


Fig. 1. $J_{^{13}\text{C}\text{H}}$ and $J_{\text{H}\text{H}}$ for acetone against concentration of acetone in water. Standard deviation is 0.2 cps for $J_{^{13}\text{C}\text{H}}$ and 0.02 cps for $J_{\text{H}\text{H}}$.

and Ruben^{5, 6}, and Christ and Diehl⁷. A positive τ -value means a shift to a higher field. The results for pure acetone correspond very well with those found by Holmes and Kivelson⁸. The ^{13}C isotope effect⁹ has been measured but is not listed in Table I because the standard deviation ($0.3 \cdot 10^{-2}$ ppm) of the values measured (0 to $1.3 \cdot 10^{-2}$ ppm) does not allow of a conclusion being drawn.

Discussion

In the case of acetone, the largest variations in $J_{^{13}\text{C}\text{H}}$ and $J_{\text{H}\text{H}}$ with a change in solvent and concentration are 1.5% and 30%, respectively. Neither for acetone nor for dimethyl sulfoxide is there a correlation with the dielectric constant of the solvent as has been found in some instances for other substances^{1, 2}. In Fig. 2, the values of $J_{^{13}\text{C}\text{H}}$ and $J_{\text{H}\text{H}}$ for acetone-water are plotted against the values of τ_{170} as measured by Christ and Diehl⁷. An almost linear relation is found. It may be that a similar — if not identical — mechanism is responsible for the variations in $J_{^{13}\text{C}\text{H}}$ and in τ_{170} . Hydrogen bonds with the solvent and/or large solvent dipoles may increase the relative importance of polar resonance structures of the $\text{C}=\text{O}$

⁵ G. E. Maciel and G. C. Ruben, *J. Am. Chem. Soc.* **85**, 3903 (1963).

⁶ G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.* **42**, 2752 (1965).

⁷ H. A. Christ and P. Diehl, *Helv. Phys. Acta* **36**, 170 (1963).

⁸ J. R. Holmes and D. Kivelson, *J. Am. Chem. Soc.* **83**, 2959 (1961).

⁹ H. Dreeskamp and E. Sackmann, *J. Phys. Chem.* **27**, 136 (1961).

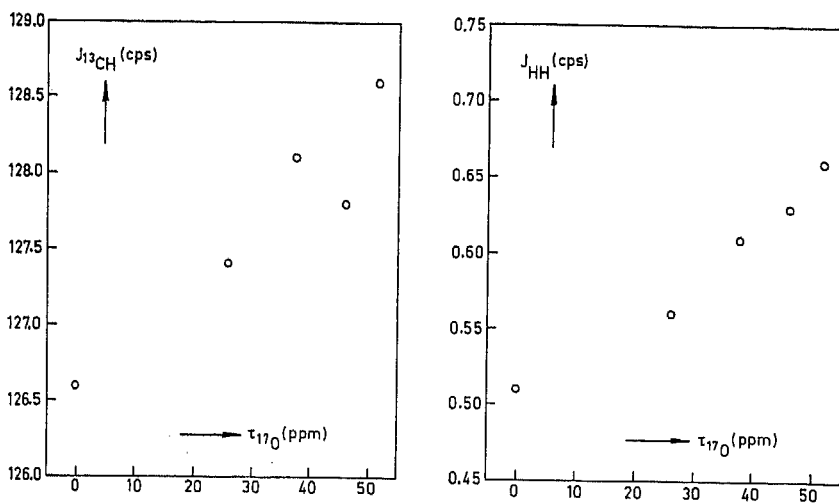


Fig. 2. J_{13CH} and J_{HH} for acetone against the chemical shift of ^{17}O with different concentrations in water.

group (Fig. 3). These will result in a larger electron withdrawal experienced by the CH_3 -groups and will cause the increase of J_{13CH} . The effect is similar to that due to the substitution of different groups of larger electro-negativity, which also leads to an increase in J_{13CH} ¹⁰. Similar arguments apply to the $S=O$ group in dimethyl sulfoxide.

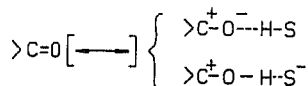


Fig. 3. Resonance structures of the carbonyl group ($H-S$ = solvent).

A comparison of the J_{13CH} values given in Table I with those of τ_{17O} and τ_{13C} seems to indicate the same tendency. All solvents used, which give a distinct change in chemical shifts and coupling constants, are capable of forming a hydrogen bond, except acetonitrile and nitrobenzene which, however, have a large electric dipole moment.

According to Fig. 2, the relationship between J_{HH} and τ_{17O} of acetone is also approximately linear, whilst the values of Table I again show the same tendency. We do not yet understand the underlying principle for this.

In this respect it is remarkable that in the case of dimethyl sulfoxide the value of J_{13CH} does change with the solvent (up to 1.5% just as for acetone) whereas J_{HH} remains constant (Table I).

¹⁰ N. Muller and D. E. Pritchard, *J. Chem. Phys.* **31**, 768 (1959); **31**, 1471 (1959).

Experimental

All spectra were taken with a Varian DP-60 spectrometer. The position of the ^{13}C satellites in the proton spectrum was measured by the side band modulation technique. The values of $J^{13}\text{C-H}$ and $J_{\text{H-H}}$ are averages of four spectra.

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