

NUCLEAR QUADRUPOLE RESONANCE OF Mn^{55} , Re^{185} , Re^{187} IN
CYCLOPENTADIENYLMANGANESE (RHENIUM) TRICARBONYLS

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The subject of this work is a study of Mn^{55} , Re^{185} and Re^{187} NQR spectra for a series of substituted cyclopentadienylmanganese (rhenium) tricarbonyls.

The NQR spectrum of Mn^{55} was first investigated in $C_5H_5Mn(CO)_3$ at room temperature by Voitländer et al [1].

The spectrum of $Mn_2(CO)_{10}$ measured by those authors was found to be erroneous [2].

The only known spectrum of Re^{185} , Re^{187} was the spectrum of $Re_2(CO)_{10}$ studied at room temperature [3].

The result of our investigation are listed in Table 1 and 2. We calculated quadrupole coupling constants eQq_{zz} and asymmetry parameters when we succeeded in watching transition ($\pm 1/2 \leftrightarrow \pm 3/2$) as well as ($\pm 3/2 \leftrightarrow \pm 5/2$) in Mn^{55} , Re^{185} and Re^{187} .

Of special interest is the study of the influence of a substituent on a metal atom. For this we applied the method of two parameter correlations of NQR spectral parameters of Mn^{55} with G - constants of the substituents. Supposing the influence of the substituents to be a function of the interaction reactivity according to the induction or conjugation mechanism, the expression

$$A = A_0 + \alpha G_I + \beta G_R \quad (1)$$

has been plotted, where

$$A = eQq_{zz} \quad \text{or} \quad \vee (\pm 3/2 \leftrightarrow \pm 5/2)$$

σ_I and σ_R are the induction and conjugation constants of substituents

α and β - the coefficients which determine the transmission properties of a system in relation to the induction and conjugation influence of the substituents.

After a least squares treatment the following equations have been obtained

$$eQq_{zz} = [(63.72 + 2.89 \sigma_I - 14.18 \sigma_R) \pm 0.42] \text{ Mc/S} \quad (2)$$

$$r = 0.971$$

$$\nu (\pm 3/2 \leftrightarrow \pm 5/2) = [(19.12 + 0.65 \sigma_I - 4.32 \sigma_R) \pm 0.12] \text{ Mc/S} \quad (3)$$

$$r = 0.973$$

The equation (2) was derived by making use of the compounds 1,3-8,11 (see Table 1) and the equation (3) by making use of the compounds 1,3-8, 11-13,16. The values of σ_I and σ_R , used in the calculations as the induction and conjugations constants, have been determined from the chemical shifts of F^{19} for some fluorobenzene derivatives in inert solvents [4].

The ratio of the constant terms and coefficients α and β in these equations is near to 0.3-0.4 which approximately coincides with the ratio $\frac{\nu}{eQq_{zz}}$ for the spin $I = 5/2$.

It is seen here that the equation (2) can be applied more widely than simply for the substituents which were used to obtain it.

It should be noted that in both equations the coefficient of σ_R is for greater than that of σ_I . This means that in the series in question the influence transmission from a substituent in the cyclopentadienyl ring to a metal atom occurs rather in accordance with the conjugation than the induction mechanism.

Attention must be called to the fact that the experimental value of eQq_{zz} for $C_5H_5Mn(CO)_3$ (this point was left out in the calculations) is about 1.5 Mc/S greater than the one calculated from the equation (2). It is possible to explain such a great difference by admitting a fulvene-like rearrangement of C_5H_5 -ring on introduction of the substituent X. In addition the

introduction of a substituent changes the symmetry of the ring: the five-fold axis as well as four symmetry planes out of five are lost.

It is worth noticing that the asymmetry parameters η for the substituents COR (R = CH₃, CF₃, C₆H₅) are appreciably greater than the asymmetry parameter η for C₅H₅Mn(CO)₃. It is possibly caused either by a direct interaction of the substituent (or more exactly by a lone electron pair on the oxygen atom) with the metal atom giving rise to a distortion of the ideal structure of the molecule C₅H₅Mn(CO)₃ or by a fulvene-like rearrangement of the cyclopentadienyl ring. Since all these points fit in with correlation equations it should be assumed that in spite of some slight distortions in the molecule there is no loss of the conjugation of a substituent with the ring.

An increase in the asymmetry parameter η for similar substituents in cyclopentadienyl rhenium tricarbonyls is more pronounced. In this case the distortion of a molecule is probably much greater than for the manganese compounds.

If one compares the quadrupole coupling constants of Mn⁵⁵ and Re¹⁸⁷ in the analogous compounds the difference between them appears to be of about an order of magnitude while their quadrupole moments [5] differ by about five or six times. It means that the electric field gradient at the nucleus of Re atom is about twice as high as that at the manganese nucleus.

Table 1

Compound	Transition frequency (Mc/S)		Parameter asymmetry %	eQq _{zz} Mc/S	Notes
	($\pm 1/2 \leftrightarrow \pm 3/2$)	($\pm 3/2 \leftrightarrow \pm 5/2$)			
1. (CO) ₃ MnC ₅ H ₄ COCF ₃	9.09	17,736	13.9	59.35	
2. (CO) ₃ MnC ₅ H ₄ COOCH ₃	9.21	18,348	5.6	61.20	
3. (CO) ₃ MnC ₅ H ₄ COCH ₃	9.29	18,472	6.8	61.63	
4. (CO) ₃ MnC ₅ H ₄ COOH	9.34	18,682	0	62.27	
5. (CO) ₃ MnC ₅ H ₄ COC ₆ H ₅	9.50	18,672	11.8	62.41	
6. (CO) ₃ MnC ₅ H ₄ SO ₂ NH ₂	9.58	19,050	6.9	63.56	
7. (CO) ₃ MnC ₅ H ₄ CH ₃	9.75	19,452	4.4	64.86	
8. (CO) ₃ MnC ₅ H ₄ CH ₂ Cl	9.77	19,476	5.1	64.95	∪ Cl ³⁵ = 34.41 Mc/S
9. (CO) ₃ MnC ₅ H ₅	9.79	19,572	1.9	65.24	[1]
10. (CO) ₃ MnC ₅ H ₄ SO ₃ ⁻ Na	9.88	19,740	2.9	65.81	
11. (CO) ₃ MnC ₅ H ₄ J	10.07	20,094	4.3	67.00	
12. (CO) ₃ MnC ₅ H ₄ COCl	17,960	∪ Cl ³⁵ = 30.43 Mc/S
13. (CO) ₃ MnC ₅ H ₄ SO ₂ Cl	18,486	∪ Cl ³⁵ = 33.56 Mc/S
14. (CO) ₃ MnC ₅ H ₃ (CH ₂ Cl) ₂	18,820	∪ Cl ³⁵ = 34.58 = 33.79 Mc/S
15. (CO) ₃ MnC ₅ H ₄ SO ₃ C ₂ H ₅	19,300	
16. (CO) ₃ MnC ₅ H ₄ C ₂ H ₅	19,380 19,760	
17. (CO) ₃ MnC ₅ H ₄ COCH ₂ Cl	18,180	∪ Cl ³⁵ = 36.33 = 36.63 Mc/S
18. (CO) ₃ MnC ₅ H ₄ COCH ₂ Br	18,150	

Table 2

Compound	Isotope	Transition frequency		Parameter asymmetry 7 %	eQq _{zz} Mc/S	Notes
		Mc/S ($\pm 1/2 \leftrightarrow \pm 3/2$)($\pm 3/2 \leftrightarrow \pm 5/2$) at 77°K				
1. (CO) ₃ ReC ₅ H ₅	Re ¹⁸⁷	88.70	175.74	8.7	586.64	
	Re ¹⁸⁵	93.72	185.64	8.8	619.72	
2. (CO) ₃ ReC ₅ H ₄ COCH ₃	Re ¹⁸⁷	90.18	161.64	30.5	548.47	
	Re ¹⁸⁵	95.27	170.76	30.5	579.42	
3. (CO) ₃ ReC ₅ H ₄ COC ₆ H ₅	Re ¹⁸⁷	81.84	135.02	41.8	464.66	
	Re ¹⁸⁵	86.49	142.65	41.9	490.91	
4. (CO) ₃ ReC ₅ H ₄ COCl	Re ¹⁸⁷	82.75	139.50	39.1	478.25	} Cl ³⁵ = 30.59 Mc/S
	Re ¹⁸⁵	87.42	147.37	39.1	505.24	
5. (CO) ₃ ReC ₅ H ₄ COOH	Re ¹⁸⁷	83.86				
	Re ¹⁸⁵	88.60				
6. (CO) ₃ Re C ₅ H ₄ CH ₃ ^{x/}	Re ¹⁸⁷	94.55				
7. (CO) ₃ ReC ₅ H ₄ SO ₃ H · • 1.4 - NH ₂ C ₆ H ₄ CH ₃	Re ¹⁸⁷	{ 94.71				
		{ 99.02				
	Re ¹⁸⁵	{ 100.04				
		{ 104.63				
8. Re ₂ (CO) ₁₀ ^{xx/}	Re ¹⁸⁷	33.828	37.597	87.35	139.22	
	+/Re ¹⁸⁵	35.736	39.725	87.39	147.11	
9. (CO) ₃ ReC ₅ H ₄ SO ₂ Cl ^{+/}						} Cl ³⁵ = 33.84 Mc/S

^{x/} We obtain (CO)₃ ReC₅H₄CH₃ (m.p. 43-44°) by means of the interaction of Rhenium pentacarbonylchloride with sodium methylcyclopentadienyl.

^{xx/} The forbidden transition ($\pm 1/2 \leftrightarrow \pm 5/2$) Re¹⁸⁷ 71.51 Mc/S; Re¹⁸⁵ 75.45 Mc/S was observed. For the first time the spectrum of Re₂(CO)₁₀ at room temperature was observed in work [3].

^{+/} (CO)₃ Re C₅H₄SO₂Cl (m.p. 126.5-127.5) was obtained from the compound 7 (see Table 2). Its synthesis will be published later. All the remaining compounds in Tables 1 and 2 were prepared according to already known methods.

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