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THE VIBRATIONAL SPECTRUM OF THE h^5-CYCLOPENTADIENYL LIGAND

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Summary

The assignment of the fundamental vibrations of the h^5-coordinated cyclopentadienyl ligand is discussed on the basis of new data from the vibrational spectra of cyclopentadienyl complexes with a different type of metal—ligand bonding. The assignment of some vibrations is revised.

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1. Numerous studies have been published on the vibrational spectra of h^5-coordinated cyclopentadienyl ligands in metal derivatives. The spectra of Cp_2M (Cp = C_5H_5-ligand) metallocenes in which the Cp—M bond is mainly covalent such as ferrocene, ruthenocene, etc., have been studied in great detail. The interpretation of the Cp-ligand spectrum was first proposed in [1] where the spectra of ferrocene, ruthenocene are compared with the spectra of carbocyclic systems, in particular with benzene. Since then the results obtained in [1] were repeatedly revised [2—6]. At present, the refined assignments of Cp-ligand frequencies given in [1] are generally accepted and are used for analysis of the spectra of Cp-complexes in the form that was proposed in [6].

The frequency values of the Cp-ligand vibrations are important when applying methods of vibrational spectroscopy to the study of the structure of such a common type of compounds as the Cp-complexes of metals. Bearing this in mind and the fact that in the last few years new data has been obtained on the vibrational spectra of many Cp-complexes [3—17] including Raman spectra of several complexes, we decided to analyse the available spectral data with the aim of substantiating or revising the accepted interpretation of the vibrational spectrum of the h^5-coordinated Cp-ligand.

2. Consideration of the data from the vibrational spectra of Cp-complexes, of both homoligand and heteroligand types, leads to the conclusion that the vast majority of Cp-ligand frequencies vary in a relatively narrow range (10—30 cm^{-1}). This does not hold for the frequencies of the out-of-plane bending vibrations of the CH bonds of the Cp-ring, ρ(CH), which vary in quite a wide range

(150—200 cm^{-1}). These frequencies are low in compounds with an ionic or predominantly ionic Cp—M bond and are high in covalent Cp-complexes (see, for instance [2]). Another feature of the ρ(CH) vibrations is the wide interval in intensity variation of the corresponding bands in the IR spectra: these bands are very strong in the spectra of ionic complexes and become less and less intense in the spectra of compounds with a Cp—M bond covalent in nature [16]. Another vibration of the Cp-ligand with a wide range of frequency variation (50—60 cm^{-1}), is the breathing vibration of the ring at about 1100 cm^{-1}.

On account of the constancy of Cp-ligand frequencies the following technique can be used in spectra interpretation. We shall proceed from a model with a purely ionic Cp^-M^+ bond, the spectra of which should evidently conform with the selection rules of the D_{5h} group (symmetry of $C_5H_5^-$) and we shall then turn to a CpM model (C_{5v} symmetry) with less rigid selection rules. It is logical to assume that for real compounds the spectral features expected for the covalent CpM model will be displayed more vividly the stronger the covalent nature of the Cp—M bond.

It is evident that analysis of experimental data can be based not only on CpM compounds but also on Cp_nM compounds. Indeed, if a certain vibration is forbidden by selection rules for $C_5H_5^-$, the appearance of formally allowed vibrations in the Raman or IR spectrum, for instance for the $Cp_2^-M^{2+}$ model (in-phase in Raman spectrum and out-of-phase in IR spectra) does not have any serious consequences: the corresponding transitions in fact will either be very weak or undetectable. This is especially important when studying spectral data of weak covalent Cp_nM complexes; evidently vibrations forbidden for $C_5H_5^-$ and weakly displayed in Cp^-M^+ complexes, due to distortion introduced by the metal, will be weak in the corresponding spectra of Cp_nM complexes. Further on, without restricting the applicability of the conclusions, we shall concern ourselves only with sandwhich compounds of the Cp_2M type. The correlation of Cp-ligand vibrations of various types of symmetry for Cp^-M^+ (D_{5h}), CpM (C_{5v}) and Cp_2M (D_{5d}) * models is presented in Table 1.

3. Four vibrations of the Cp-ring are allowed for $C_5H_5^-$ in the IR spectrum: E'_1 $\nu(CH')\nu(CC')\beta(CH')$ and A''_2 ρ(CH), in the Raman spectrum seven vibrations are allowed: A'_1 $\nu(CH')\nu(CC)$; E''_1 ρ(CH); E'_2 $\nu(CH')\nu(CC)$, $\beta(CH')\gamma(CCC)$. Extensive data are available on the IR spectra of cyclopentadienyl compounds in which the predominantly ionic nature of the Cp—M bond is obvious, such as Cp-derivatives of alkaline, alkaline-earth and of certain other metals. The IR spectra of these compounds, indeed, display only four absorption bands in the frequency range characteristic of the expected types of vibrations. Typical examples are shown in Table 2. Occasionally additional weak absorption bands with frequencies close to the frequencies of vibrations forbidden in the IR spectra for $C_5H_5^-$ are observed in such compounds. Weak bands have been observed in the IR spectrum of Cp_2Ca, which has recently been thoroughly reexamined [14], and in other compounds. This nonconfirmity with the selection rules for $C_5H_5^-$ is evidently due to the distorting effect of the metal and it increases with

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* For sandwich Cp_2M complexes the model with D_{5d} symmetry was selected. Since for both models, D_{5h} and D_{5d}, the selection rules are the same, this will obviously not have any significant effect.

TABLE 1

SYMMETRY CORRELATION OF VIBRATIONS FOR $C_5H_5^-$ ION AND CpM AND Cp_2M MODELS OF COMPLEXES

N^0, N^0 (D_{5h}, C_{5v})	$C_5H_5^-$ ion (D_{5h})		CpM (C_{5v})		Cp_2M (D_{5d})						Assignment
	Symmetry	Selection rules	Symmetry	Selection rules	in-phase vibrations			out-of-phase vibrations			
					N^0, N^0	Symmetry	Selection rules	N^0, N^0	Symmetry	Selection rules	
$\nu(1)$	A'_1	Raman	A_1	IR, Raman	$\nu(1)$	A_{1g}	Raman	$\nu(8)$	A_{2u}	IR	$\nu(CH)$
$\nu(2)$	A_1	Raman	A_1	IR, Raman	$\nu(2)$	A_{1g}	Raman	$\nu(9)$	A_{2u}	IR	$\nu(CC)$
$\nu(3)$	A''_2	IR	A_1	IR, Raman	$\nu(3)$	A_{1g}	Raman	$\nu(10)$	A_{2u}	IR	$\rho(CH)$
$\nu(4)$			A_1	IR, Raman	$\nu(4)$	A_{1g}	Raman	$\nu(11)$	A_{2u}	IR	$\nu(M-L)$
$\nu(5)$	A'_2	n.a.	A_2	n.a.	$\nu(5)$	A_{2g}	n.a.	$\nu(6)$	A_{1u}	n.a.	$\beta(CH)$
								$\nu(7)$	A_{1u}	n.a.	torsion
$\nu(6)$	E'_1	IR	E_1	IR, Raman	$\nu(12)$	E_{1g}	Raman	$\nu(17)$	E_{1u}	IR	$\nu(CH)$
$\nu(7)$	E'_1	IR	E_1	IR, Raman	$\nu(13)$	E_{1g}	Raman	$\nu(18)$	E_{1u}	IR	$\nu(CC)$
$\nu(8)$	E'_1	IR	E_1	IR, Raman	$\nu(14)$	E_{1g}	Raman	$\nu(19)$	E_{1u}	IR	$\beta(CH)$
$\nu(9)$	E''_1	Raman	E_1	IR, Raman	$\nu(15)$	E_{1g}	Raman	$\nu(20)$	E_{1u}	IR	$\rho(CH)$
$\nu(10)$			E_1	IR, Raman	$\nu(16)$	E_{1g}	Raman	$\nu(21)$	E_{1u}	IR	$\nu(M-L)$
								$\nu(22)$	E_{1u}	IR	$\delta(CpMCp)$
$\nu(11)$	E'_2	Raman	E_2	Raman	$\nu(23)$	E_{2g}	Raman	$\nu(29)$	E_{2u}	n.a.	$\nu(CH)$
$\nu(12)$	E'_2	Raman	E_2	Raman	$\nu(24)$	E_{2g}	Raman	$\nu(30)$	E_{2u}	n.a.	$\nu(CC)$
$\nu(13)$	E'_2	Raman	E_2	Raman	$\nu(25)$	E_{2g}	Raman	$\nu(31)$	E_{2u}	n.a.	$\beta(CH)$
$\nu(14)$	E'_2	Raman	E_2	Raman	$\nu(26)$	E_{2g}	Raman	$\nu(32)$	E_{2u}	n.a.	$\gamma(CCC)$
$\nu(15)$	E''_2	n.a.	E_2	Raman	$\nu(27)$	E_{2g}	Raman	$\nu(33)$	E_{2u}	n.a.	$\rho(CH)$
$\nu(16)$	E''_2	n.a.	E_2	Raman	$\nu(28)$	E_{2g}	Raman	$\nu(34)$	E_{2u}	n.a.	$\chi(CCC)$

TABLE 2

FREQUENCIES (cm^{-1}) OF THE IR-ACTIVE VIBRATIONS OF IONIC Cp-COMPLEXES [a]

Compound	ν(CH)	ν(CC)	β(CH)	ρ(CH)	References
KCp	3048	1455	1009	702	2
RbCp	3030	(1501)	1011	696	2
CsCp	3021	1494	1008	668	2
$MgCp_2$	3063	1428	1004	758	13
$CaCp_2$	3078	1437	1009	751	14
$SrCp_2$	3077	1464	1006	745	2
$BaCp_2$	3065	1435	1009	706	2
$MnCp_2$	3080	1427	998/1005	767	12
$EuCp_2$	3077	1435	1007	739	18
$YbCp_2$	3086	1433	1006	752	18
$TbCp_3$	3077	1435	1006	770	18
$HoCp_3$	3077	1435	1005	771	18
$TmCp_3$	3072	1439	1009	774	18
$LuCp_3$	3072	1438	1007	776	18
$PuCp_3$	3100	1447	1007	779/793	19
$PaCp_4$	3078	1445	1008	788/811	19
$NpCp_4$	3077	1447	1008	780/810	19

[a] Intensities of vibrations: ν(CH), weak, ν(CC), weak; β(CH), strong; ρ(CH), very strong.

the covalent nature of the Cp—M bond, reaching its highest point in the IR spectra of typical covalent complexes (Cp_2Fe, Cp_2Ru and Cp_2Os) [4,5,7,12].

Thus, the available data confirm the correctness of the assignment of the IR bands of Cp_2M in the frequency regions of about 800, 3070, 1420 and 1000 cm^{-1} to A_{2u} ($\nu(10)$ and E_{1u} ($\nu(17)$, $\nu(18)$, $\nu(19)$) respectively. The appearance of other vibrations of the same types of symmetry, that correlate with the Raman active vibrations of A'_1 and E''_1 symmetry types for $C_5H_5^-$, is determined by the distortion introduced by the metal. For instance, the bands of out-of-phase A_{2u} vibrations in Cp_2M corresponding in form to $\nu(1)$ and $\nu(2)$ vibrations of $C_5H_5^-$ are very weak or undetectable in the IR spectra of compounds with an ionic nature of the Cp—M bond, while in the spectra of covalent Cp_2M complexes they are sufficiently strong.

4. At present the only Raman spectrum of a Cp-derivative of an alkaline metal reported in the spectrum of CpK in ether solution [20]. The following assignments are proposed: A'_1 3043 cm^{-1} ($\nu(1)\nu(CH')$, 983 cm^{-1} ($\nu(2)$, $\nu(CC)$); E''_1 625 cm^{-1} ($\nu(9)\rho(CH)$; E'_2 565 cm^{-1} ($\nu(14)\nu(CCC)$), 1020 cm^{-1} ($\nu(13)\beta(CH)$), 1447 cm^{-1} ($\nu(12)\nu(CC)$) and 3096 cm^{-1} ($\nu(11)\nu(CH)$).

On the other hand, Raman spectra of several Cp_nM complexes with a Cp—M bond predominantly ionic in nature, for instance of magnesocene [13], magnanocene (rose-coloured modification) [12] and tricyclopentadienyl complexes of lanthanides [10,11] have been obtained recently. In certain respects the spectra of these complexes differ significantly from the Raman spectrum of CpK (see Table 3):

(a) The line of the Raman breathing mode of the ring in the spectra of both ionic and covalent complexes (osmocene represents the latter in Table 3) is invariably displayed near 1100 cm^{-1}, whereas in [20] the unusually low frequency of 983 cm^{-1} is assigned to this vibration.

TABLE 3

RAMAN SPECTRA OF SOME CYCLOPENTADIENYL COMPLEXES IN MELTED STATE

$MgCp_2$ [13]			$MnCp_2$ [12]			$TbCp_3$ [11]			$HoCp_3$ [11]			$OsCp_2$ [12]		
(cm^{-1})	I	ρ	(cm^{-1})	I	ρ	(cm^{-1})	I	ρ	(cm^{-1})	I	ρ	(cm^{-1})	I	ρ
			620	1^{a}	dp?	618	vw	?	632	vw	?	599	1	dp
760	6	dp	749	6	dp	770	m	dp	769	m	dp	816	1	dp
778	1	p?	774	3	?				787	w	p?	831	2	p
832	4	?	843	1	dp?	841	vw	dp?	840	vw	dp			
						910	vw	dp				890	1	dp
1014	1	dp				1008	w	dp	1006	vw	dp	991	2	dp
1068	5	dp	1060	5	dp	1064	m	dp	1065	w	dp	1059	7	dp
1113	100	p	1109	100	p	1122	vs	p	1122	vs	p	1094	100	p
1264	1	p	1234	2	p	1230	w	p	1229	w	p	1180	1	p
1342	6	dp	1336	7	dp	1350	m	dp	1360	m	dp	1352	1	dp
			1442	1	dp	1435	w	dp	1432	w	dp	1401	5	dp
3077	2	dp	3077	w	dp							3095	m	dp
3105	7	p	3100	s	p							3110	s	p

[a] Relative photometric intensities.

(b) In all spectra presented in Table 3 a sufficiently strong Raman line is exhibited near 1350 cm^{-1}. The line near 1447 cm^{-1} is either weak or entirely absent in the spectra of complexes with an ionic nature of Cp—M bond, although $\nu(12)$, E'_2 vibration is allowed in the Raman spectrum for $C_5H_5^-$.

There is no clarity as to the position of the γ(CCC) vibration. In the Raman spectra of covalent Cp_2M complexes one of the weak lines in the 900 cm^{-1} region is usually assigned to the $\nu(26)$ (E_{2g}) vibration (see, for instance [1,6]). Similar lines are present in the spectra presented in Table 3. The Raman line in the region of 600 cm^{-1} is assigned to out-of-plane ring vibrations γ(CCC) ($\nu(16)$ for $C_5H_5^-$ and $\nu(28)$, E_{2g} for Cp_2M). As the frequency values in the Cp-ligand spectrum are hardly affected by the nature of Cp—M bond, these deviations can not be dismissed. Evidently additional investigation of the Raman spectra of Cp-derivatives of alkaline metals is required. For now we decided to use as a model of ionic complexes, compounds the spectra of which are given in Table 3 bearing in mind the predominantly ionic character of the Cp—M bond in these complexes and the fact that the spectra were recorded in the molten state so the effect of the solvent is excluded.

5. Let us start from the logical assumption that in the average the most intense Raman lines in the spectra of magnesocene, manganocene and lanthanide Cp-derivatives correspond to Raman active vibrations of $C_5H_5^-$. These include first of all lines at 750, 1060, 1110, 1350, 3080 and 3100 cm^{-1}, some of which do not have analogues in the IR spectra of ionic compounds. Taking into account polarization it is natural to assign the lines near 3080 and 3100 cm^{-1} to vibrations that correlate with the Raman active $\nu(11)$ (E'_2) and $\nu(1)$ (A'_1) vibrations of $C_5H_5^-$ and lines near 750 cm^{-1} corresponding to ρ(CH) ($\nu(9)$, E''_1) vibrations. The assignment of the 1100 cm^{-1} line to the breathing vibrations of Cp-rings ($\nu(2)$ for $C_5H_5^-$) was discussed above. The only suitable candidate for the 1060 cm^{-1} line, taking into account its location in the spectrum, is the β(CH) vibration, ($\nu(13)$, E'_2 for $C_5H_5^-$). The assignment of 1350 cm^{-1} line to ν(CC) vibrations ($\nu(12)$, E'_2 for $C_5H_5^-$) seems also self-evident. There is no evident candidate in the recorded spectra for the γ(CCC) vibration ($\nu(14)$, E'_2). The vibration, although allowed for $C_5H_5^-$ ion is probably weakly revealed in Raman spectra. We do not possess any evidence that would have enabled us to confirm or reject the accepted assignment of the Raman line in the 900 cm^{-1} region to this vibration.

Several relatively weak lines in the spectra presented in Table 3 should be commented on. The weak lines at 1010 and 1420 cm^{-1} are undoubtedly due to in-phase analogues ($\nu(14)$ and $\nu(13)$ for Cp_2M) of $\nu(8)$ and $\nu(7)$ vibrations of $C_5H_5^-$ allowed in the IR spectrum. It is interesting that the intensity of the "forbidden" vibration at 1420 cm^{-1} increases as compared with the 1350 cm^{-1} line in spectra of covalent complexes (see spectrum of osmocene in Table 3, a similar pattern is observed in the Raman spectra of ferrocene and ruthenocene). Thus, the measurement of relative intensities of spectral transitions provide interesting information about the character of Cp—M bond.

The considered data make it possible to assign the frequencies of practically all Raman active $C_5H_5^-$ vibrations (with the exception of γ(CCC)). This assignment differs from accepted one [6] only in one respect: we assigned the 1060 line to in-plane bending vibrations β(CH) ($\nu(13)E'_2$). Usually the spectral transi-

TABLE 4

ASSIGNMENT OF h^5-Cp LIGAND VIBRATIONAL FREQUENCIES IN CYCLOPENTADIENYL COMPLEXES

Frequency (cm^{-1})	Intensity		Assignment [6]	Assignment [this work]	Number of vibrations for Cp_2M complexes
	IR	Raman			
600	vw	vw	χ(CCC)	χ(CCC)	ν(28), ν(34)
660—860	m—vs	vw	ρ(CH)	ρ(CH)	ν(3), ν(15), ν(27), ν(20), ν(10), ν(33)
900	w	vw	γ(CCC)	γ(CCC)	ν(26), ν(32)
1000	vs	vw—m	β(CH)	β(CH)	ν(14), ν(19)
1060	vw	m	ρ(CH)	β(CH)	ν(25), ν(31)
1100	vw—m	vs	ν(CC)	ν(CC)	ν(2), ν(9)
1200 (Raman)		vw	β(CH)	overtone	2ν(28), 2ν(34)
1240 (IR)	vw		β(CH)	β(CH)	ν(5), ν(6)
1350	vw	m—s	ν(CC)	ν(CC)	ν(24), ν(30)
1420	m	vw—w	ν(CC)	ν(CC)	ν(13), ν(18)
3070	w	w	ν(CH)	ν(CH)	ν(12), ν(17), ν(23), ν(29)
3100		m	ν(CH)	ν(CH)	ν(1), ν(8)

tions in this region are assigned to ρ(CH) vibrations (ν(27) and ν(33) for Cp_2M), although the corresponding vibration of $C_5H_5^-$ (ν(15), E''_2) is forbidden both in the IR and Raman spectra (Table 1).

The weak lines in the Raman spectra of crystals in the 1180—1250 cm^{-1} region and the weak absorption bands in the IR absorption spectra in the same region are assigned to the ν(5) (A_{2g}) and ν(6) (A_{1u}) vibrations forbidden in both spectra. As our measurements of the Raman spectra of several complexes [10—13,15] have shown, the Raman line in the region of 1180—1250 cm^{-1} is also present in the spectra of liquids and is always polarised. Its frequency is approximately equal to the double value of the frequency of the 600 cm^{-1} frequency line. It was therefore assigned to the overtone of the γ(CCC) vibration strenghtened by Fermi resonance with ring breathing vibration [15].

The final results of this analysis of Cp-ligand vibrations are given in Table 4 where they are compared with literature data.

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