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Vibrational overtone spectra of metallocenes: effect of the coordinating metal on the CH bond lengths

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Received 6 September 2002; revised 3 December 2002; accepted 12 December 2002

Abstract

The first through third overtone spectra of ferrocene, ruthenocene, nickelocene, cobaltocene, dicyclopentadienyl magnesium and sodium cyclopentadienyl are examined with particular attention to the CH stretching of the cyclopentadienyl. Using semi-empirical correlations between CH bond length and CH stretching frequencies in each overtone region, we have determined that the type of metal atom within a metallocene complex has little effect on the CH bond length in the cyclopentadienyl. The only exception is cobaltocene where there is evidence that the Jahn-Teller effect results in several different CH bond lengths. Evidence that bis(cyclopentadienyl) magnesium is not ionic has been observed.

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Keywords: Metallocenes; Overtones; Organometallic; CH bond length

1. Introduction

Overtone spectroscopy is generally described using the local mode (LM) theory [1], wherein vibrations are localized to R–X bonds, X is some light atom and R is some heavy atom. Overtone spectra may be interpreted to provide bond specific information and thus are very useful for the study of the C–H bonds of metallocenes. Two cyclopentadienyl rings bound to a metal atom characterize these organometallic compounds, widely used in synthetic chemistry [2]. In the present work, overtone spectroscopy is used to elucidate the role of the metal atom on the geometry

of the cyclopentadienyl rings and, in particular, on the C–H bonds lengths.

There are few reports of vibrational overtone spectra of organometallics in the literature. In 1982, Lewis published the first overtone spectrum of ferrocene [3]. Most of the studies on the overtone spectra of organometallic compounds that followed were done by Snively et al. [4–9], two of which were focused on ferrocene, ruthenocene and related compounds [5,8]. One notable observation in the spectra of the metallocenes is the appearance of combination bands that are not present in cyclopentadiene.

D.C McKean et al. [10–13], as well as other authors [14], have shown that there is an excellent correlation between the CH bond length and the fundamental vibrational frequency of CH bonds isolated by replacing all other hydrogens with deuterium. In these papers, McKean draws attention

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to the existence of Fermi resonances (FR) that may cause significant error in any attempt to correlate frequency to bond length. The relationship between vibrational frequency and bond length has been extended to the CH stretch overtone frequencies [15–18]. The higher overtone vibrations are LM in character, that is, the bonds behave as individual uncoupled anharmonic oscillators, and hence the requirement for deuterium isolation is eliminated. A number of studies of the vibrational spectra of metallocenes in the fundamental region [19–29] provide useful information on the symmetry and the normal modes of vibration, since combinations of LM and normal modes often are observed along with the dominant pure LM. Even in the overtone region, attention must be paid to FR if any meaningful correlation is to be found [30–35].

In this work, we reexamine the spectra of both ruthenocene and ferrocene in addition to the previously unexamined nickelocene, cobaltocene, bis(cyclopentadienyl) magnesium and sodium cyclopentadienyl. Particular attention is paid to the CH bond vibrational energies and their relationship to bond length. In the metallocenes, two separate geometries are possible: eclipsed and staggered. However, calculations have shown that there is no difference in the geometry of the cyclopentadienyl groups in the two conformations [36]. This simplifies many of our considerations since concerns about changes during internal rotation are eliminated, though it also precludes any determination of the preferred geometry from overtone spectra. There is some question as to whether bis(cyclopentadienyl) magnesium is ionic or covalently bonded. The nature of the metal-ligand bond will affect the ligand structure, and therefore the spectrum of this compound. This study will help clarify the nature of bis(cyclopentadienyl) magnesium. Cobaltocene is of spin multiplicity 2, therefore it is expected to manifest the Jahn-Teller effect [36,37], with distortion of the cyclopentadienyl ring, reducing the symmetry to C_2 with three separate sets of CH bonds with different lengths [36]. In this case, we would expect three separate bands instead of one in the overtone spectrum of cobaltocene.

Cyclopentadienyl is an aromatic and, with the possible exception of cobaltocene, only one pure LM vibration is anticipated at each overtone; however,

this does not preclude the possibility of local-normal combination bands. These bands would be expected to have low intensity, particularly at higher overtones. However, FR may lead these bands to exhibit higher than expected intensities [38]. In previous work [5,8], the spectra of ferrocene and ruthenocene were compared to that of cyclopentadiene. The appearance of bands in the metallocenes that were absent in the cyclopentadiene spectra led the authors to suggest that these vibrations were brightened by the influence of the metal atom on the cyclopentadienyl ring [5,8]. However, since cyclopentadiene is not aromatic, it is also possible that the disparity is due to the structural differences between aromatic and diene, rather than to the effect of the metal atom. To investigate this possibility we have selected sodium cyclopentadienyl for comparison to the metallocene spectra. Sodium cyclopentadienyl is characterized as ionic and provides the best possible approximation to the spectrum of independent cyclopentadienide.

To study the effect of the metal atom on the CH bond length, we have determined correlations between the pure LM CH stretching vibration frequency and CH bond length calculated at several levels of theory. These correlations can then be used to estimate the relative CH bond lengths of the metallocenes. To this end, no scaling has been done on any of the calculated bond lengths. The results of this analysis are compared to bond lengths calculated with the BLYP level of theory, using the 6-311G(d,p) basis set for the carbon and hydrogen atoms and a 3-21G basis set for the metal atoms (hereafter referred to as BLYP/mixed), and bond lengths determined experimentally.

2. Experimental section

Sodium cyclopentadienyl (2 molar in THF), ferrocene (98% purity), ruthenocene (99% purity), bis(cyclopentadienyl) magnesium (99.9% purity), cobaltocene (98% purity) and nickelocene (99% purity) were obtained from Strem Chemicals. The sodium cyclopentadienyl solution was used directly. Saturated solutions of the pure compounds in carbon tetrachloride (99% purity, Aldrich) and THF (Fisher Scientific, purified using methods described by D.D Perrin and W.L.F Armarego [39]) were prepared under argon atmosphere. Concentration

varied depending on solubility. Solvent was degassed by repeated freeze thaw cycles.

All spectra were acquired using a Nicolet 870 FT-IR spectrometer with a white light source. The first and second overtones were acquired using a quartz beam splitter and MCT-A detector. For metallocenes, a 1 cm cell was used and 2048 scans were co-added. For the third overtone, a silicon detector and a 10 cm path length were used and 4096 scans were co-added. In all cases, spectra were ratioed against a carbon tetrachloride background. Sodium cyclopentadienyl spectra were acquired using the same parameters described above, except that a 3 mm cell was used and the spectrum was ratioed against the empty cell. The THF spectrum was subsequently subtracted.

2.1. CH bond length and wavenumber correlation

Correlations between overtone band maximum and ab initio geometry-optimized bond lengths are well known [15–18]. In order to evaluate relationships for the metallocenes, it was necessary to establish a bond length-frequency correlation based on compounds with well defined geometric and spectral parameters, for which the spectra have been recorded in the liquid phase. The spectra of *o*-xylene (Eastman), cycloheptatriene (J.T. Baker Chemical Co.), cyclooctadiene (J.T. Baker Chemical Co.), benzene (Aldrich), indene (Aldrich) and 1,4-cyclohexadiene (Aldrich) were chosen for the correlation, because they offered an appropriate range of CH bond lengths corresponding to well-defined LM vibrations. All spectra were collected in the liquid phase using a 3 mm path length; 2048 scans were collected for the first and second overtones and 4096 for the third overtone. The CH bond lengths used for the correlations were calculated at the HF/6-311G(d,p) and BLYP/6-311G(d,p) levels of theory. Calculations of the metallocene geometries were done with GAUSSIAN 98 software [40] using only BLYP/mixed, as the HF/6-311G(d,p) level of theory cannot be used for molecules containing heavy atoms.

3. Results

Figs. 1–3 show the overtone spectra of metallocenes for the first through third overtones, respectively.

Assignments for the peaks observed in these spectra were based on those made by Fedorov et al. on ferrocene [8] and are shown in Table 1. The pure LM vibrations used for the estimation of the CH bond length are in boldface.

The data from the molecules used in the determination of the CH bond length correlation are given in Table 2. This includes the band positions for the first, second and the third overtones and the lengths of the CH bonds to which they are assigned, calculated at both the HF/6-311G(d,p) and BLYP/6-311G(d,p) level of theory. In many cases the pure LM for the first overtone could not be assigned reliably due to significant normal mode character in that region.

The data shown in Table 2 were used to calculate correlations between bond length and frequency. Fig. 4 shows the correlation between CH bond length calculated at HF/6-311G(d,p) and BLYP/6-311G(d,p) level of theory and the pure LM CH stretching vibrational energy for the first, second and third overtones. The general relationship correlating bond length calculated at the HF/6-311G(d,p) or BLYP/6-311G(d,p) level to overtone position may be expressed as:

$$R_{\text{CH}}^{\text{Basis}} = I^{\text{Basis}} - S^{\text{Basis}} \times \bar{\nu}$$

where $\bar{\nu}$ is the wavenumber of the pure LM vibration, while I (intercept) and S (slope) have the values listed in Table 3 for the overtone considered; r^2 values of 0.9873, 0.9893 and 0.9874 were obtained for the first, second and third overtones, respectively for the HF calculations. The correlation of frequency to bond length calculated at the BLYP/mixed level of theory yielded r^2 values of 0.9632, 0.9877 and 0.9810 for the first through third overtones, respectively.

The parameters from the HF/6-311G(d,p) and BLYP/6-311(d,p) regressions and the experimental values for the frequency of the pure LM CH vibrations were used to estimate the CH bond lengths in the metallocenes and cyclopentadienide. Results of these calculations are given in Table 4, along with the CH bond lengths calculated for the metallocenes at the BLYP/mixed level of theory and the experimentally determined bond lengths from other sources where available.

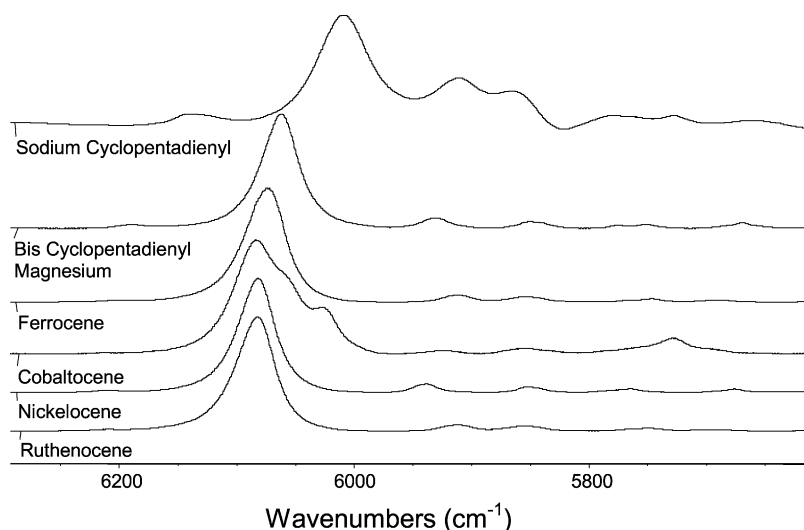


Fig. 1. First overtone spectra of metallocenes in carbon tetrachloride, and sodium cyclopentadienyl in THF. Spectra acquired at room temperature with a 1 cm path length.

4. Discussion

4.1. Assignments

In all of the overtones recorded (Figs. 1–3), significant similarities are observed between bis(cyclopentadienyl) magnesium, ferrocene, nickelocene and ruthenocene (hereinafter referred to as group 1). In the first overtone of all group 1

compounds, the dominant band at $\sim 6070\text{ cm}^{-1}$ is assigned to the pure LM CH stretching vibration. Several weak bands, observed in all of the group 1 compounds, have been assigned as combinations of CH stretching, CH bending and CC stretching. In the second overtone spectra all of the observed bands appear within a fairly narrow region. Since, at the second overtone, combination bands are not expected to have any significant intensity, it is reasonable to

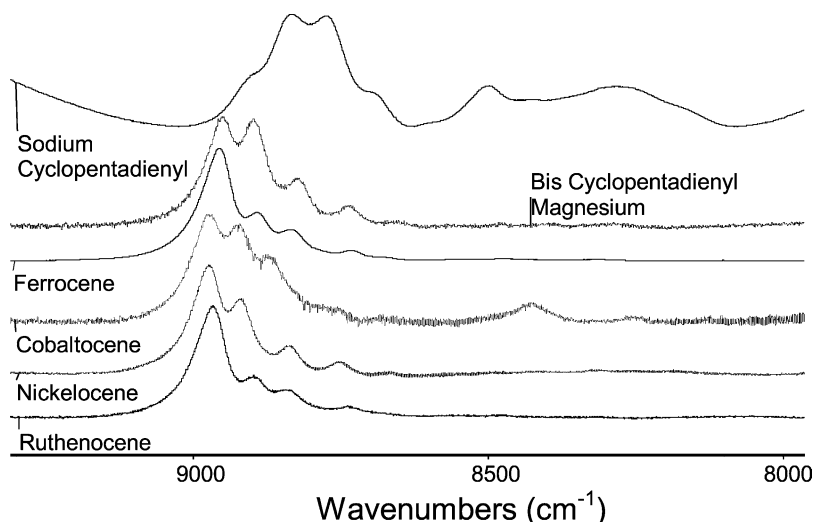


Fig. 2. Second overtone spectra of metallocenes in carbon tetrachloride, and sodium cyclopentadienyl in THF. Spectra acquired at room temperature with a 1 cm path length.

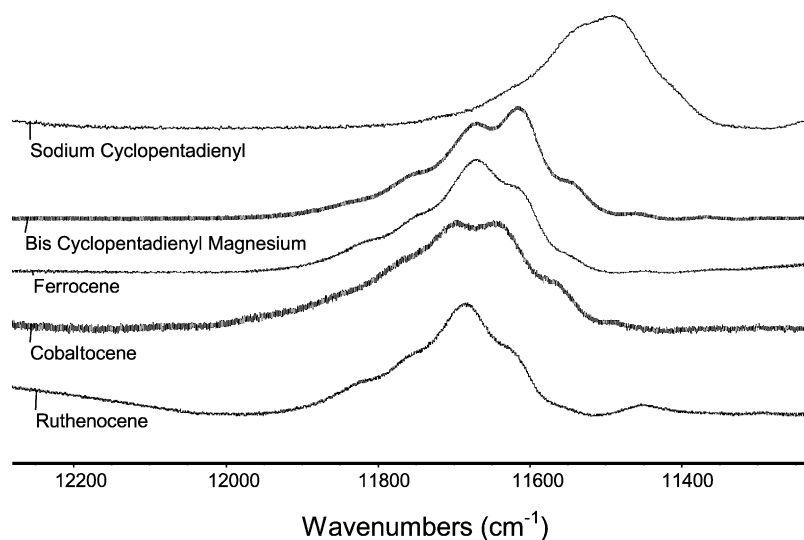


Fig. 3. Third overtone spectra of metallocenes in carbon tetrachloride, and sodium cyclopentadienyl in THF. Spectra acquired at room temperature with a 10 cm path length.

Table 1

Observed band positions (cm^{-1}) and assignments for metallocenes

Overtone	Mg(C ₅ H ₅) ₂	Fe(C ₅ H ₅) ₂	Co(C ₅ H ₅) ₂	Ni(C ₅ H ₅) ₂	Ru(C ₅ H ₅) ₂	Na(C ₅ H ₅)	Assignment
1 ^a		5503				5498	
		5555				Shoulder	
	5669	5686	Shoulder	5676	5698	5662	$\nu_{\text{CH}} + \nu_{\text{CCstr(as)}} + \nu_{\text{CHbend}}$
	5751	5746	5729	5766	5748	5727	$\nu_{\text{CH}} + \nu_{\text{CCstr(as)}} + \nu_{\text{CHbend}}$
	5775	Shoulder		Shoulder	Shoulder	5780	
	5849	5855	5856	5853	5854	5865	$\nu_{\text{CH}} + \nu_{\text{CCstr(as)}} + \nu_{\text{CHbend}}$
	5930	5911	5923	5938	5912	5910	$\nu_{\text{CH}} + 2\nu_{\text{CCstr(as)}}$
			6028				
			Shoulder				
	6062	6074	6084	6082	6082	6009	$2\nu_{\text{CH}}$
2 ^a	6190	6201	6211	6210	shoulder	6139	$\nu_{\text{CH}} + 2\nu_{\text{CCstr}}$
				8665			
	8734	8732		8758	8738	8693	$2\nu_{\text{CH}} + \nu_{\text{CCstr(as)}} + \nu_{\text{CHbend}}$
	8828	8833	8873	8837	8842	8776	$2\nu_{\text{CH}} + \nu_{\text{CCstr(as)}} + \nu_{\text{CHbend}}$
	8898	8891	8921	8922	8898	8903	$2\nu_{\text{CH}} + 2\nu_{\text{CCstr(as)}}$
	8949	8956	8977	8974	8967	8833	$3\nu_{\text{CH}}$
3 ^b	11363						
	11459						
	11542		11563				
	11610	11609	11636		11620	Shoulder	$3\nu_{\text{CH}} + \nu_{\text{CCstr(as)}} + \nu_{\text{CHbend}}$
	11675	11669	11698		11684	11489	$4\nu_{\text{CH}}$
	11756	11748	11763		11752		$3\nu_{\text{CH}} + \nu_{\text{CCstr}} + \nu_{\text{CHbend}}$
	11845	11821	11863		11822		$3\nu_{\text{CH}} + 2\nu_{\text{CCstr(as)}}$
ωx^c	56 ± 5	60 ± 5	59 ± 5		60 ± 5	66 ± 5	
ω^c	3090 ± 7	3100 ± 7	3104 ± 7		3104 ± 7	3139 ± 7	

^a Peak energies obtained based on center of gravity.

^b Peak energies estimated based on curve fitting.

^c ωx and ω determined from Birge-Sponer plots.

Table 2

Bond lengths (Å) and energies (cm⁻¹) used for correlations

Compound ^a		HF/6-311G(d,p)	BLYP	First overtone	Second overtone	Third overtone
Benzene ^b	ar	1.076	1.091	5983	8764	11438
Indene	ar	1.076	1.091/1.092 ^c	5954	8740	11426
	ol	1.074	1.088/1.089 ^c		8824	11548
	al	1.088	1.104	5669	8268	10784
1,4-cyclohexadiene	ol	1.078	1.092	5883	8658	11301
	al	1.090	1.109/1.110 ^c	5615	8126	10585
<i>o</i> -Xylene ^b	ol	1.076	1.092	5934	8740	11411
	ol'		1.091			
	al	1.087	1.102		8351	10889
	al'	1.083	1.098		8447	11030
Cycloheptatriene ^d	ol	1.078	1.094	5902	8653	11298
	ol'	1.077	1.093			
	al	1.083	1.098			11040
	al'	1.089	1.105			10615
Cyclooctadiene	ol	1.079	1.095			
	ol'	1.080	1.096	5837	8563	11176
	al	1.081	1.097			
	al'	1.089	1.105	5644	8229	10680
	al''	1.090	1.107			
	al'''	1.086	1.101			

^a All energies from liquid phase spectra. (ar = aromatic, ol = olefinic, al = aliphatic).^b Spectra of the second and third overtones of liquid benzene and *o*-xylene have been published by Henry et al. [41].^c Spectra of the third overtone of liquid cycloheptatriene have been published by Snavey et al. [42].^d In these cases BLYP/6-311G(d,p) gave two different bond lengths; for the correlation, the shorter bond length was used.

assume that the dominant vibration is the pure LM CH stretch, while the other bands are combinations that gain intensity through FR interactions with it. The bands are assigned to the same combinations as in

the first overtone, plus one quantum of CH stretch. The relative intensity of these bands is greater than that observed for the first overtone due to the stronger FR. This interaction increases at the second overtone

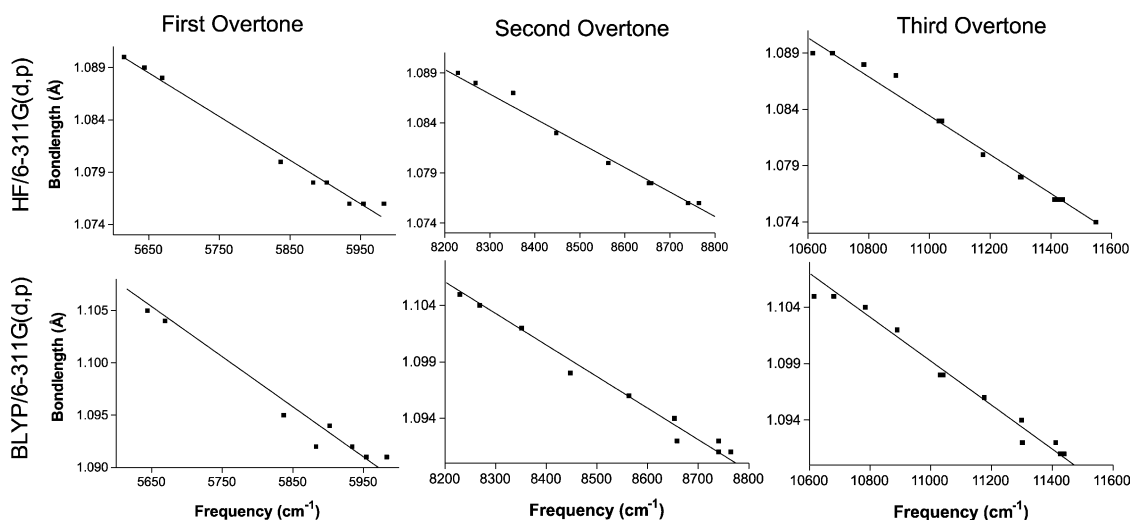


Fig. 4. Correlation between calculated bond lengths and CH stretching overtone vibration frequency.

Table 3
Constants for correlations

	$I(\text{\AA})$	Error in I	$S(\text{\AA}/\text{cm}^{-1})$	Error in S	r^2 of fit
First overtone	1.32	0.01	4.2×10^{-5}	0.2×10^{-5}	0.9873
Second overtone	1.290	0.007	2.6×10^{-5}	0.08×10^{-5}	0.9893
Third overtone	1.274	0.006	1.7×10^{-5}	0.06×10^{-5}	0.9874
BLYP					
First overtone	1.38	0.02	4.7×10^{-5}	0.4×10^{-5}	0.9632
Second overtone	1.336	0.008	2.8×10^{-5}	0.09×10^{-5}	0.9877
Third overtone	1.314	0.008	2.0×10^{-5}	0.07×10^{-5}	0.9810

due to the greater anharmonicity of the pure LM, which decreases the separation between the pure LM and the combination bands. Similar arguments apply to the third overtone, where different combinations appear as they become closer to the pure LM CH stretching energy and previously observed combinations fade as they shift away from it.

4.2. Bond lengths

As a general guideline, the first overtone should be avoided for the estimation of bond lengths since the spectra are still largely of normal mode character and are complicated by the presence of many combination bands. However, in the case of these metallocenes, the first overtone spectra typically do display a single, narrow, intense pure

LM peak that is generally free of interference from other vibrations. In the higher overtones, the greater anharmonicity of the CH stretching modes causes the pure LM CH vibration to shift in energy relative to the combination bands. As a result, many of the combination bands are closer to the pure LM band and their relative intensity is increased. The coupling between the pure LM band and the combination bands in question may shift the pure LM band and lead to errors in the estimation of the bond length. For this reason, the first through third overtones are considered so that any effects of coupling may be monitored.

Cobaltocene shows several differences when compared to group 1 molecules; two shoulders are observed at approximately 6028 and 6050 cm^{-1} . These peaks may be due to Jahn-Teller distortion of

Table 4
Metallocene CH bond lengths (\AA)

	From Standard Correlation						Calculated (BLYP/Hybrid)	Experimental
	First overtone		Second overtone		Third overtone			
	HF/ 6-311G(d,p)	BLYP/ 6-311G(d,p)	HF/ 6-311G(d,p)	BLYP/ 6-311G(d,p)	HF/ 6-311G(d,p)	BLYP/ 6-311G(d,p)		
Mg(C ₅ H ₅) ₂	1.071	1.085	1.071	1.085	1.072	1.086	1.087	
Fe(C ₅ H ₅) ₂	1.070	1.085	1.071	1.085	1.072	1.086	1.086	1.104 ± .006 [43]
Co(C ₅ H ₅) ₂	1.070	1.084	1.071	1.084	1.072	1.085	1.085	1.095 ± .006 [44]
	1.071	1.086					1.085	
	1.072	1.087					1.086	
Ni(C ₅ H ₅) ₂	1.070	1.084	1.071	1.085			1.085	1.083 ± .0095 [45]
Ru(C ₅ H ₅) ₂	1.070	1.084	1.071	1.085	1.072	1.086	1.086	1.130 ± .006 [46]
Na(C ₅ H ₅)	1.073	1.088	1.074	1.088	1.075	1.089	1.089	
Uncertainty	± 0.002	± 0.002	± 0.002	± 0.003	± 0.002	± 0.003		

the cyclopentadienyl ring. From our correlation between experimental frequencies and bond lengths calculated with the HF/6-311 G(d,p) basis set, the positions of these peaks would suggest bond lengths of 1.070, 1.071 and 1.072 Å, respectively. The BLYP/6-311G(d,p) correlation suggests bond lengths of 1.084, 1.086 and 1.087 Å. Geometry optimization of cobaltocene at the BLYP/mixed level shows that the cyclopentadienyl ring is distorted from D_{5h} to C_2 symmetry and the CH bonds are predicted to have different lengths. The predictions show six CH bonds with a length of 1.085 Å and four at 1.086 Å. These lengths agree within experimental error with the predictions of the BLYP/6-311G(d,p) correlation. However, it should be noted that the lower basis set used for the cobalt might cause the effect of the metal to be underestimated. It should be noted that the relative intensities of the observed peaks do not appear to be 1:2:2 as might be expected; however, the true relative intensities are difficult to estimate due to the amount of overlap. It is also possible that there is some FR involved, but there is insufficient data for further conjecture. Using the equation correlating the CH bond length calculated at the HF/6-311G(d,p) and BLYP/6-311G(d,p) levels of theory and the pure LM band for CH stretch at the first overtone level, we find that the CH bond lengths for all the metallocenes are approximately the same (Table 4).

The results of the correlation for the second overtone are similar to those for the first overtone (Table 4), and we conclude that any FR coupling did not cause significant frequency shift. For cobaltocene, it is impossible to distinguish between possible combination bands and those attributed to LM from CH bonds of different lengths. However, had the bands observed in the first overtone actually been combination bands, at the second overtone they should have appeared at energies of $\sim 100\text{ cm}^{-1}$ above that of the pure LM. Such bands are not observed; therefore it is more likely that the bands observed in the first overtone are pure LM vibrations.

Similar observations are made for the third overtone, however the bond lengths obtained from the correlation equation are approximately 0.001 Å longer (Table 4). At the third overtone, strong coupling with the combination bands will have shifted the pure LM bands to lower frequencies.

The combination bands in the third overtone appear at higher frequency than the pure LM bands and have considerably more intensity than would be expected in the absence of coupling. In any event, this difference of 0.001 Å is within the error associated with the correlation, and is not significant.

4.3. Cyclopentadiene, cyclopentadienide and cyclopentadienyl

In evaluating the metallocene spectra, we must consider the possible differences between the parent molecule cyclopentadiene, the ionic cyclopentadienide, and the coordinated cyclopentadienyl ligand. Previously, the spectrum of ferrocene has been compared to that of cyclopentadiene [5]. This comparison led to the suggestion that the appearance of many of the combination bands was due to the influence of the metal on the ring. However, this theory fails to account for the change in geometry of the cyclopentadiene ring when it becomes cyclopentadienide.

Sodium cyclopentadienyl is characterized as essentially ionic and therefore the spectra should be interpreted as that of the cyclopentadienide. These spectra are quite different from those of group 1; however, the combination bands observed are quite similar. To determine whether the difference in solvents contributed to the observed dissimilarity between the sodium cyclopentadienyl and group 1 spectra, the spectrum of ferrocene in THF was acquired. No significant variation could be detected between the latter and its spectrum in carbon tetrachloride. We were unable to collect data on the other metallocenes in THF, due to their poor solubility, in conjunction with the strong absorptions of the THF in the same region. On the basis of the ferrocene results, we conclude that the differences observed for the sodium cyclopentadienyl are not solvent dependent, but are due to its essentially ionic character.

Very little similarity is observed between the overtone spectra of cyclopentadienide and those of cyclopentadiene obtained by Van Marter et al. [5]. There is only the one aromatic CH bond type in cyclopentadienyl, thus the aliphatic band at 8322 cm^{-1} is absent. The CC stretching and CH bending normal modes of vibration are the most likely

combination bands to appear in the overtone regions, however their probable location is shifted far from the pure LM CH stretching band because of significant differences between the frequencies of these modes for cyclopentadiene and cyclopentadienide. Thus, FR interaction is unlikely in cyclopentadiene. In the absence of FR, these combination bands would be expected to have very low intensity, and it is not surprising that they are not observed in the cyclopentadiene spectra.

We now compare the spectra of the sodium cyclopentadienyl, considering it to be the prototypical ionic form, to the remaining metallocenes of group 1. The principal difference is the red shift of the pure LM CH stretching band of sodium cyclopentadienyl. We conclude that the coordination of the metal ions to the ligand causes a shortening of about 0.003 Å in the CH bonds. Geometry optimizations at the BLYP/mixed level of theory agree with this.

The energies of the combination bands observed in sodium cyclopentadienyl are similar to those observed in the group 1 compounds and are ascribed to similar fundamental modes (Table 2). This is most evident for the first overtone. Since the pure LM CH stretching band is red shifted in sodium cyclopentadienyl, it lies closer to these combination bands and stronger FR interactions can occur. Thus, while the positions of the combination bands in the sodium cyclopentadienyl are similar to those in the group 1 spectra, they are more intense. Similar interpretations apply to the second and third overtones, where different bands are involved in FR interaction for the group 1 compounds and the sodium cyclopentadienyl.

We have assumed that sodium cyclopentadienyl is ionic and thus its spectra may be considered to be essentially that of cyclopentadienide. The combinations in sodium cyclopentadienyl spectra resemble those of the group 1 molecules, and both are quite different from the cyclopentadiene. It seems likely that the appearance of combination bands in the metallocenes, absent in the cyclopentadiene spectra, can be attributed to differences in structure between cyclopentadiene and cyclopentadienide rather than to the influence of the metal atoms, as had been suggested in earlier work [5,8].

It is also interesting to note that there has been some question as to whether bis(cyclopentadienyl)

magnesium is ionic in solution [2]. If the bis(cyclopentadienyl) magnesium were ionic, we would expect it to be more similar to the ionic sodium cyclopentadienyl. Instead, the spectrum of this compound in carbon tetrachloride is very similar to that of ferrocene, which is not ionic.

4.4. Comparison with X-ray crystal structure data

Bond lengths found using the method described here show little agreement to the CH bond lengths determined via X-ray crystallography (Table 4) [43–47]. The most significant explanation is likely the technique itself: it is very difficult to determine the position of hydrogen atoms using X-ray crystallography since hydrogen diffracts poorly. A second possible factor is the influence of crystal structure on the CH bond lengths, not present in solution. Differences in crystal packing could arise from the different relative sizes of these molecules. Third, the overtone spectroscopic method relies on the accuracy of *ab initio* calculations in the formulation of the correlation plots. The correlation is only as accurate as the level of theory used to determine the bond lengths and it is generally accepted that the relative bond lengths are more reliable than the absolute values, which also vary between levels of theory. Undoubtedly, these factors explain the large differences reported between the CH bond lengths within different metallocenes [43–47] that are not observed by the spectroscopic method used here.

5. Conclusions

From the correlation between the frequency of CH LM vibrations and *ab initio* calculated bond lengths, evidence has been found that the CH bonds of cyclopentadienyl are shortened by coordination to a metal atom in comparison to the cyclopentadienide studied via the sodium cyclopentadiene. However, the nature (i.e. the electronic structure, bonding, size etc.) of the metal atom does not have a significant effect on the magnitude of this shortening. The observed CH bond length of bis(cyclopentadienyl) magnesium is approximately

the same as those of the other metallocenes, indicating that it is not ionic.

The combination bands in the spectra of the metallocenes, previously postulated to arise from interactions with the metal atoms, are now ascribed to the aromatic nature of the cyclopentadienyl. There are significant differences between the spectrum of cyclopentadiene and that of sodium cyclopentadienyl, presumably due to the ionic nature of the latter compound. Differences in the structure, bond length and bond strength cause the combination bands to occur closer to the pure LM CH stretching band of the cyclopentadienide ion, allowing for increased FR.

While semi-empirical correlations such as those used here are heavily reliant on the accuracy of the ab initio calculations, they can be of great value in determining relative CH bond lengths, if proper care is taken in the selection of the basis set and level of theory. They are particularly helpful in cases such as this where there is a limited number of basis sets available that can handle heavy metals.

Acknowledgements

B.E. Billinghamurst is grateful to the University of Manitoba for a graduate fellowship. We are grateful to the National Sciences and Engineering Research Council for financial support.

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