

# Vibrational Overtone Spectroscopy of Metallocenes and “Half-Sandwich” Organometallic Complexes

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The FTIR spectra of ferrocene, ruthenocene, cyclopentadienyl manganese tricarbonyl (CPMT), cyclopentadienyl titanium trichloride (CPTT), and cyclopentadienyl iron dicarbonyl iodide (CPIDI)  $\text{CCl}_4$  solutions are presented at the first and second overtone region ( $\Delta\nu = 2, 3$ ). The gaseous ferrocene, ruthenocene, and CPMT spectra are also presented at the third overtone region ( $\Delta\nu = 4$ ) recorded by intracavity photoacoustic spectroscopy. Assignments for the observed transitions are suggested for the liquid and reevaluated for the gas-phase spectra. The influence of the metal and other ligands attached to the metal on the vibrational behavior of the cyclopentadienyl ring is also discussed.

## Introduction

Metallocenes<sup>1</sup> are “sandwich” organometallic complexes containing two cyclopentadienyl rings bound to a transition metal. Changes in the ligand geometry are induced when the hydrocarbon binds to a transition metal. Elucidation of these changes is important for understanding the catalytic activity of organometallic complexes. Vibrational overtone spectroscopy, in addition to infrared spectroscopy, brings a new dimension to the study of these geometry changes by examining the molecules at high internal energies. The vibrational overtone spectra display absorptions, which can be understood in terms of local mode theory.<sup>2</sup>

The infrared and Raman spectra of many sandwich and half-sandwich compounds have been investigated, providing information about the fundamental transitions in these molecules. The normal mode symmetry of sandwich compounds has been studied,<sup>3</sup> and the infrared spectra of gaseous,<sup>4</sup> solution,<sup>5</sup> and solid<sup>7</sup> ferrocene; gaseous<sup>4</sup> and solution<sup>5</sup> ruthenocene; solid manganocene;<sup>6,7</sup> solid chromocene;<sup>7</sup> and gaseous, liquid, and solid cyclopentadienyl manganese tricarbonyl<sup>9–12</sup> can be found in the literature. In addition, the Raman spectra<sup>8</sup> of manganocene and chromocene were reported.

Only a few reports of vibrational overtone spectra of organometallics have been published.<sup>13–17</sup> The third CH overtone spectrum of gaseous ferrocene was reported,<sup>13</sup> extending the work of Lewis<sup>14</sup> who recorded the fundamental ( $3080\text{ cm}^{-1}$ ) and first CH overtone ( $6105\text{ cm}^{-1}$ ) transitions for ferrocene in addition to five combination bands below  $5000\text{ cm}^{-1}$ . Because the cyclopentadienyl ligand becomes aromatic in the complex, local mode theory would predict only one peak in the overtone spectrum at each overtone level. A comparison of the third overtone spectrum of cyclopentadiene to those of ferrocene, ruthenocene, and related compounds indicated that the peak attributed to the CH olefinic stretch in cyclopentadiene splits into four peaks in the complex. This observation was interpreted as coupling of the CH stretch to other vibrations.<sup>15</sup>

The third overtone spectrum of butadiene iron tricarbonyl was compared to the spectrum of *trans*-1,3-butadiene.<sup>16</sup> The spectrum of the complex exhibited six transitions, three arising from the different CH oscillators of the ligand and the additional peaks arising from vibrational coupling initiated by the metal. By

scaling the vibrational overtone absorption frequency to the ab initio bond lengths of the free and complexed ligand the CH bond length change with complexation could be determined. In a similar study of the third overtone spectra of gaseous benzene chromium tricarbonyl and cycloheptatriene chromium tricarbonyl,<sup>17</sup> one additional absorption was observed in the benzene complex but none in the cycloheptatriene complex. According to the interpretation of the overtone spectra, complexation increases the CH bond lengths for both ligands.

This current work is a return to the vibrational overtone spectra of the metallocenes in order to complete the overall vibrational pattern of these highly symmetric compounds. In addition, the spectra of several half-sandwich compounds are included in this study. Comparisons of these spectra further elucidate the effect of metal and carbonyl or halogen ligands on the vibrational behavior of cyclopentadienyl in organometallic complexes. The comparison between tricarbonyl and trichloride complexes will elucidate the influence of the ligand type on the cyclopentadienyl properties. Specifically, the vibrational spectra of carbon tetrachloride solutions of ferrocene ( $\Delta\nu = 2, 3$ ); ruthenocene ( $\Delta\nu = 2, 3$ ); CPMT ( $\Delta\nu = 2, 3$ ), CPTT ( $\Delta\nu = 2$ ), and CPIDI ( $\Delta\nu = 2$ ); and gaseous CPMT ( $\Delta\nu = 4$ ), ferrocene ( $\Delta\nu = 4$ ), and ruthenocene ( $\Delta\nu = 4$ ) are presented.

## Experimental Section

Ferrocene (98% purity), ruthenocene (97% purity), CPTT (97% purity), and CPIDI (97% purity) were obtained from Aldrich. CPMT (98% purity) was purchased from Strem Chemicals. All samples were sublimed prior to use using standard sublimation techniques.

The first and second overtone spectra of the complexes in carbon tetrachloride solution were recorded at  $4\text{ cm}^{-1}$  resolution on a Mattson FT-near-IR spectrometer with a tungsten lamp and quartz beam splitter. A PdSe detector was used to record the spectra in the  $4000\text{--}10000\text{ cm}^{-1}$  region. Solvents were degassed with bubbling nitrogen for 2 h. The complex was dissolved in  $\text{CCl}_4$  under inert atmosphere and the 1-cm cell was kept airtight during the experiment. The complex concentrations varied depending on the solubility and the amount of the complex available.

**TABLE 1: Transition Wavenumbers (cm<sup>-1</sup>) and Vibrational Assignments for the Studied Organometallic Complexes**

| quantum no. | Fe(Cp) <sub>2</sub> | Ru(Cp) <sub>2</sub> | CPMT           | CPTT               | CPIDI          | assignments   |
|-------------|---------------------|---------------------|----------------|--------------------|----------------|---|
| 2           | 5688                | 5690                | 5721           | 5723               | 5686           | 1ν <sub>CH</sub> + ν <sub>CCstr(as)</sub> + ν <sub>CHbend</sub> |
|             | 5748                | 5759                | 5782           | 5805               | 5796           | 1ν <sub>CH</sub> + ν <sub>CCstr(as)</sub> + ν <sub>CHbend</sub> |
|             | 5854                | 5856                | 5890           | 5903               | 5881           | 1ν <sub>CH</sub> + ν <sub>CCstr</sub> + ν <sub>CHbend</sub>     |
|             | 5912                | 5911                | 5952           | 5985               | 5950           | 1ν <sub>CH</sub> + 2ν <sub>CCstr(as)</sub>                      |
|             | 6072                | 6083                | 6102           | 6106               | 6106           | 2ν <sub>CH</sub>  |
|             | 6201                | 6208                | 6224           | — <sup>a</sup>     | — <sup>a</sup> | 1ν <sub>CH</sub> + 2ν <sub>CCstr</sub>                          |
| 3           | — <sup>a</sup>      | — <sup>a</sup>      | — <sup>a</sup> | — <sup>a</sup>     | — <sup>a</sup> | 2ν <sub>CH</sub> + ν <sub>CCstr(as)</sub> + ν <sub>CHbend</sub> |
|             | 8735                | — <sup>a</sup>      | 8789           | — <sup>a</sup>     | — <sup>a</sup> | 2ν <sub>CH</sub> + ν <sub>CCstr(as)</sub> + ν <sub>CHbend</sub> |
|             | 8839                | — <sup>a</sup>      | 8901           | — <sup>a</sup>     | — <sup>a</sup> | 2ν <sub>CH</sub> + ν <sub>CCstr</sub> + ν <sub>CHbend</sub>     |
|             | 8891                | — <sup>a</sup>      | 8961           | — <sup>a</sup>     | — <sup>a</sup> | 2ν <sub>CH</sub> + 2ν <sub>CCstr(as)</sub>                      |
|             | 8957                | 8968                | 9009           | 8997               | 9024           | 3ν <sub>CH</sub>  |
|             | 9006                | — <sup>a</sup>      | — <sup>a</sup> | — <sup>a</sup>     | — <sup>a</sup> | 2ν <sub>CH</sub> + 2ν <sub>CCstr</sub>                          |
| 4           | 11519               | — <sup>a</sup>      | 11580          | — <sup>a</sup>     | — <sup>a</sup> | 3ν <sub>CH</sub> + ν <sub>CCstr(as)</sub> + ν <sub>CHbend</sub> |
|             | 11589               | 11609               | 11666          | — <sup>a</sup>     | — <sup>a</sup> | 3ν <sub>CH</sub> + ν <sub>CCstr(as)</sub> + ν <sub>CHbend</sub> |
|             | 11650               | 11666               | 11726          | 11658 <sup>b</sup> | — <sup>a</sup> | 3ν <sub>CH</sub> + ν <sub>CCstr</sub> + ν <sub>CHbend</sub>     |
|             | 11705               | 11728               | 11787          | 11723 <sup>b</sup> | — <sup>a</sup> | 4ν <sub>CH</sub>  |
|             | 11782               | 11799               | — <sup>a</sup> | 11800 <sup>b</sup> | — <sup>a</sup> | 3ν <sub>CH</sub> + 2ν <sub>CCstr(as)</sub>                      |
|             | 11851               | 11860               | — <sup>a</sup> | 11861 <sup>b</sup> | — <sup>a</sup> | 3ν <sub>CH</sub> + 2ν <sub>CCstr</sub>                          |

<sup>a</sup> Transitions are expected to appear but were not observed experimentally. <sup>b</sup> Transition wavenumbers are taken from ref 15.

The gaseous overtone spectra of the organometallic complexes were obtained using an intracavity laser photoacoustic spectrometer described previously.<sup>16</sup> The sample was transferred under inert atmosphere into a photoacoustic cell equipped with a microphone and Brewster's angle quartz windows. To increase the signal-to-noise ratio, argon was added to the photoacoustic cell to obtain a total pressure of approximately 150 Torr. An intracavity oven heated the samples to 120 °C.

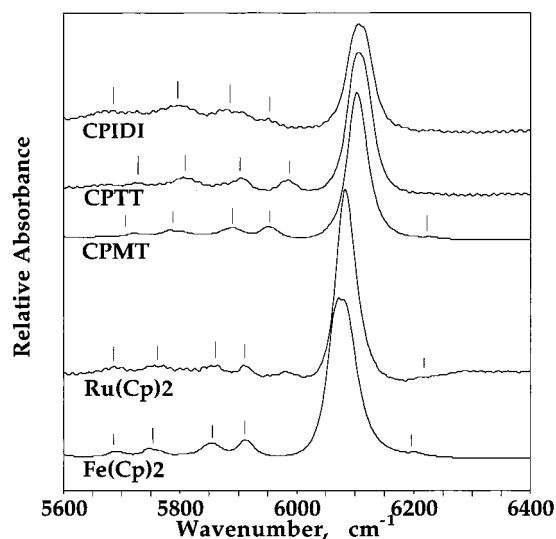
A Spectra-Physics series 2000 argon ion laser pumped a Spectra-Physics model 3900S CW Ti:sapphire laser outfitted with a three-plate birefringent filter. A 0.3 m McPherson monochromator with a scan control unit was used to measure the initial and final wavelengths. The positions of the peaks were corrected using a calibration procedure. Because the resolution of the monochromator is 0.3 cm<sup>-1</sup>, the measurements were limited by the 2 cm<sup>-1</sup> resolution of the birefringent filter. An optical chopper chopped the argon laser beam at 50 Hz, providing the reference signal for a lock-in amplifier.

## Results and Discussion

The spectra of ferrocene, ruthenocene, CPMT, CPTT, and CPIDI solutions in CCl<sub>4</sub> at the first overtone region are presented in Figure 1. The second overtone spectra of ferrocene, ruthenocene, and CPMT are shown in Figure 2. The gas-phase third overtone spectra of ferrocene, ruthenocene, and CPMT are displayed in Figure 3.

The spectral pattern is similar for all compounds. At the first overtone the strongest transition is accompanied by the group of less intense peaks to the red. At the second overtone region these less intense peaks appear to overlap the strongest transition, resulting in a series of partially resolved shoulders. At the third overtone the small transitions appear both to the red and to the blue of the strongest transition.

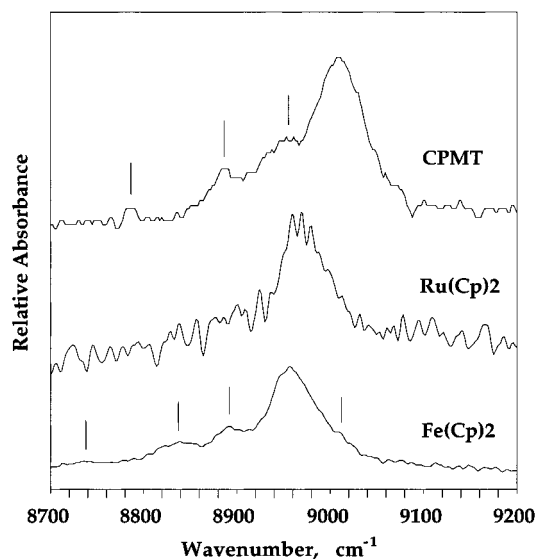
The results of the normal-mode analysis and IR vibrational frequencies for ferrocene,<sup>5</sup> ruthenocene,<sup>5</sup> and CPMT<sup>9</sup> were used to suggest the assignments for the observed transitions at the first, second, and third overtones. All of the suggested assignments are presented in Table 1. For the first and second overtone regions the strongest transitions are attributed to the pure CH stretch overtones. This assignment is supported by the reasonable fit of these transition energies in the Birge-Sponer plot (plot of  $E/v$  vs  $v$ ) and the typically large anharmonicities obtained from these plots (mechanical frequency: 3097 ± 8, ferrocene,



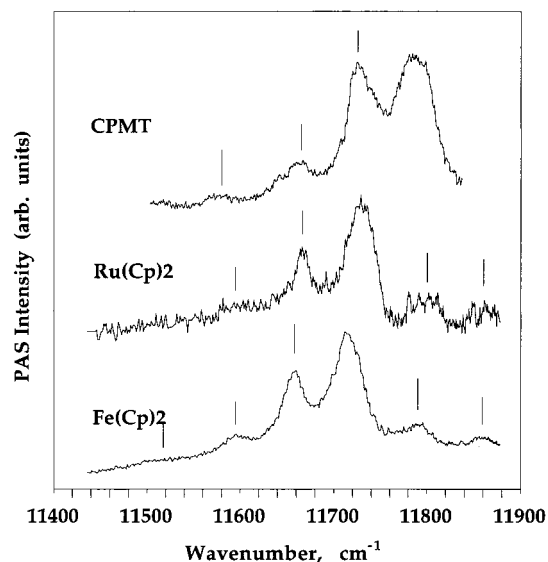
**Figure 1.** First overtone spectra of ferrocene, ruthenocene, CPMT, CPTT, and CPIDI in carbon tetrachloride solution (1 cm path length). The solutions are 0.5 M for ferrocene, ruthenocene, and CPMT and saturated for CPTT and CPIDI. All spectra are recorded at room temperature. Observed combination bands are indicated by vertical lines.

3103 ± 6, ruthenocene, 3117 ± 13, CPMT; anharmonicity: 57 ± 4, ferrocene, 58 ± 3, ruthenocene, 59 ± 6, CPMT). Only data for fundamental and liquid-phase (first and second overtone) transitions were included. These liquid-phase data aided in the reevaluation of the previous assignments<sup>15</sup> of the third overtone region. Following the spectral pattern established in the liquid spectra, the most intense peak of the gas-phase third overtone spectra is assigned to the pure CH overtone transition for all complexes. The inclusion of the gas-phase energies did not significantly change the mechanical frequency and anharmonicity (mechanical frequency: 3097 ± 7, ferrocene, 3102 ± 3, ruthenocene, 3115 ± 11, CPMT; anharmonicity: 57 ± 2, ferrocene, 57 ± 1, ruthenocene, 57 ± 4, CPMT).

Because the less intense peaks, referred to above, are absent in the spectrum of cyclopentadiene, it was suggested<sup>15</sup> that these transitions might arise from combinations, which are dark in the ligand and become bright in the complex owing to the influence of the metal. The observed spectral pattern reveals that at each higher overtone the spectral pattern repeats itself but the intense transition and less intense peaks shift relative to



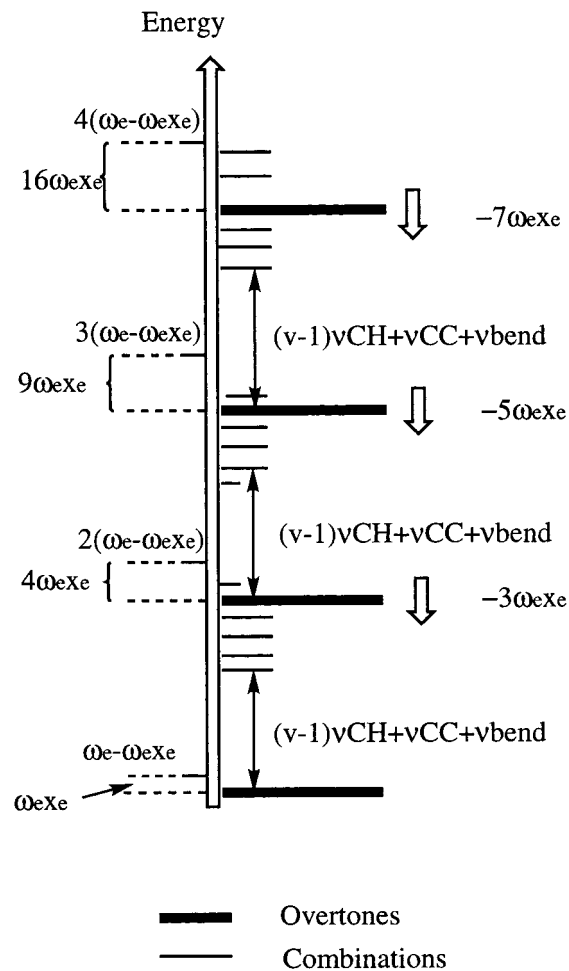
**Figure 2.** Second overtone spectra of ferrocene, ruthenocene, and CPMT in carbon tetrachloride solution (1 cm path length). All solutions are saturated. All spectra are recorded at room temperature. Observed combination bands are indicated by vertical lines.



**Figure 3.** Third (gas phase) overtone spectra of ferrocene, ruthenocene, and CPMT. Observed combination bands are indicated by vertical lines. The buffer gas (Ar) pressure is 150 Torr. All spectra are recorded at 120 °C.

one another. The observed situation is schematically represented in the Figure 4. This shifting pattern is a result of the larger anharmonicity for the CH stretch than for the combination bands.

In an attempt to identify the combination bands, only those involving CC stretch and CH bend were considered. This choice was motivated by theoretical work<sup>18–21</sup> describing the large bandwidths in the overtone spectrum of benzene where it was found that the highly energized CH oscillator primarily interacts with CC stretch and CH bend motions. A detailed assignment could not be made because the anharmonicities for all the normal mode vibrations of the metallocenes were not available. However, some symmetry considerations could be taken into account, and suggested assignments for this region are presented in Table 2. The normal-mode analysis for ferrocene,<sup>5</sup> for example, concluded that only transitions of  $A_{2u}$  and  $E_{1u}$  symmetry are allowed in the infrared. One of the possible assignments for the combination band in ferrocene observed at  $5688\text{ cm}^{-1}$  could be  $1\nu_{\text{CHstr}}(3099\text{ cm}^{-1} - A_{1g}) + 1\nu_{\text{CCstr}}(1411$



$$E = (\omega_e - \omega_e X_e)v - (\omega_e X_e)v^2$$

$$v=1 \quad E = (\omega_e - \omega_e X_e) - (\omega_e X_e)$$

$$v=2 \quad E = 2(\omega_e - \omega_e X_e) - 4(\omega_e X_e)$$

$$v=3 \quad E = 3(\omega_e - \omega_e X_e) - 9(\omega_e X_e)$$

$$v=4 \quad E = 4(\omega_e - \omega_e X_e) - 16(\omega_e X_e)$$

**Figure 4.** Schematic representation of vibrational pattern observed for metallocenes at the first, second, and third overtone regions. While combinations involving previous overtone CH stretch and other motions appear at the same relative energy from the previous overtone, the next overtone transition is getting closer to the previous one, which is indicated by an arrow pointing down, causing the change in the spectral pattern.

$\text{cm}^{-1} - E_{1u}) + 1\nu_{\text{CHbend}}(1178\text{ cm}^{-1} - E_{2g})$ . The direct product of  $A_{1g} \times E_{1u} \times E_{2g}$  is the sum of two symmetry species  $E_{1u} + E_{2u}$ , one of which is infrared active making this combination transition allowed from the symmetry considerations. Another combination observed at  $5912\text{ cm}^{-1}$  can be attributed to one quantum of CH stretch ( $3099\text{ cm}^{-1} - A_{1g}$ ) and  $2\nu_{\text{CCstr}}(1411\text{ cm}^{-1} - E_{1u})$ . The direct product of these normal modes leads to the sum of three symmetry components  $A_{1g} + A_{2g} + E_{2g}$ , none of which is allowed in the infrared. However, the replacement of CH stretch from ( $3099\text{ cm}^{-1} - A_{1g}$ ) to ( $3085\text{ cm}^{-1} - A_{2u}$ ) species yields the allowed  $A_{1u} + A_{2u} + E_{2u}$  combination. All of the suggested assignments for the combination region between the CH fundamental and first overtone listed in Table 2 are in accordance with these normal mode symmetry restrictions. This type of analysis was not conducted for the

**TABLE 2: Transition Wavenumbers (cm<sup>-1</sup>) and Vibrational Assignments for Ferrocene, Ruthenocene, and CPMT at the First Overtone Region**

| compd                          | transition wavenumber | intensity <sup>a</sup> | assignment   |
|--------------------------------|-----------------------|------------------------|--|
| ferrocene<br>v = 2             | 5503                  | w                      |  |
|                                | 5553                  | w                      |  |
|                                | 5688                  | w                      | $1\nu_{\text{CH}}(3099) + \nu_{\text{CCstr}}(1411^b) + \nu_{\text{CHbend}}(1178) = 5688$ |
|                                | 5748                  | w                      | $1\nu_{\text{CH}} + \nu_{\text{CCstr}}(1411) + \nu_{\text{CHbend}}(1200) = 5710$         |
|                                | 5854                  | w                      | $1\nu_{\text{CH}} + \nu_{\text{CCstr}}(1560) + \nu_{\text{CHbend}}(1200) = 5859$         |
|                                | 5912                  | w                      | $1\nu_{\text{CH}} + 2\nu_{\text{CCstr}}(1411) = 5921$                                    |
|                                | 6072                  | s                      | $2\nu_{\text{CH}}$   |
|                                | 6201                  | w                      | $1\nu_{\text{CH}} + 2\nu_{\text{CCstr}}(1560) = 6219$                                    |
| ruthenocene<br>v = 2           | 5690                  | w                      | $1\nu_{\text{CH}}(3104) + \nu_{\text{CCstr}}(1413^b) + \nu_{\text{CHbend}}(1193) = 5710$ |
|                                | 5759                  | w                      | $1\nu_{\text{CH}} + \nu_{\text{CCstr}}(1413) + \nu_{\text{CHbend}}(1200) = 5717$         |
|                                | 5856                  | w                      | $1\nu_{\text{CH}} + \nu_{\text{CCstr}}(1560) + \nu_{\text{CHbend}}(1200) = 5864$         |
|                                | 5911                  | w                      | $1\nu_{\text{CH}} + 2\nu_{\text{CCstr}}(1413) = 5930$                                    |
|                                | 6083                  | s                      | $2\nu_{\text{CH}}$   |
|                                | 6208                  | w                      | $1\nu_{\text{CH}} + 2\nu_{\text{CCstr}}(1560) = 6224$                                    |
| CpMn(CO) <sub>3</sub><br>v = 2 | 5721                  | w                      | $1\nu_{\text{CH}}(3120) + \nu_{\text{CCstr}}(1428^c) + \nu_{\text{CHbend}}(1152) = 5792$ |
|                                | 5782                  | w                      | $1\nu_{\text{CH}} + \nu_{\text{CCstr}}(1428) + \nu_{\text{CHbend}}(1267) = 5815$         |
|                                | 5890                  | w                      | $1\nu_{\text{CH}} + \nu_{\text{CCstr}}(1520) + \nu_{\text{CHbend}}(1267) = 5907$         |
|                                | 5952                  | w                      | $1\nu_{\text{CH}} + 2\nu_{\text{CCstr}}(1428) = 5976$                                    |
|                                | 6102                  | s                      | $2\nu_{\text{CH}}$   |
|                                | 6224                  | w                      | $1\nu_{\text{CH}} + 2\nu_{\text{CCstr}}(1520) = 6160$                                    |

<sup>a</sup> s-strong; m-medium; w-weak; vw-very weak; shld-shoulder. <sup>b</sup> Values for IR transitions are taken from ref 5. <sup>c</sup> Values for IR transitions are taken from ref 9.

higher energy combinations, owing to the increased complexity of symmetry considerations and failure of the normal-mode analysis.

The fundamental transition energies and normal-mode analysis were available only for three compounds listed in Table 2. However, on the basis of the same spectral pattern for all five complexes and the similarity between the combination band assignments from Table 2, it is possible that the observed peaks for all of the complexes follow a single pattern. For example, the combination band closest to the intense CH overtone peak ( $\Delta\nu = 2, 3$ ) could be assigned to the combination of the previous CH stretch overtone with two quanta of CC stretch for all complexes. These generalizations are presented in Table 1.

Despite the similar spectral patterns for these compounds, the transitions for CPMT ( $\Delta\nu = 2, 3, 4$ ), CPTT ( $\Delta\nu = 2$ ), and CPIDI ( $\Delta\nu = 2$ ) are shifted to the blue compared to those of ferrocene and ruthenocene. For example, the CH overtone transition of CPMT is shifted 82 cm<sup>-1</sup> to the blue compared to that of ferrocene at the third overtone region (Figure 3). Substitution of one cyclopentadienyl ligand with three carbonyls or chlorines preserves the vibrational pattern but alters the CH bond length (blue shift indicating a shortening of the bond).

The similarity of the spectra of CPMT and CPTT at the first overtone leads to some interesting observations. In CPMT the cyclopentadienyl ring is replaced by three carbonyls which are strong sigma donors supplying an electron pair to the metal and  $\pi$ -acceptors participating in a strong back-bonding overlap between the empty carbonyl  $\pi$ -orbitals and metal d-orbitals.<sup>22</sup> In CPTT three chlorines, known as poor  $\pi$ -acceptors (in some cases even  $\pi$ -donors),<sup>22</sup> provide only sigma bonding to the metal. The similar peak shifts in the CPMT and CPTT spectra compared to those in ferrocene indicate that sigma bonding of the other ligands is responsible for the CH bond length changes in cyclopentadienyl, with  $\pi$ -back-bonding having no effect. The similarity between the CPMT and CPTT spectra and the spectrum of CPIDI, where both carbonyls and iodine are present, provides additional confirmation of this suggestion.

Several attempts were made to study the overtone spectra of

chromocene and manganocene; however, the reactivity<sup>7,8</sup> and air sensitivity of both complexes made gas-phase photoacoustic spectroscopy difficult.

## Conclusions

Vibrational overtone spectra of ferrocene, ruthenocene, CPMT, CPTT, and CPIDI were recorded at the first (CCl<sub>4</sub> solutions), second (CCl<sub>4</sub> solutions), and third (gas phase) overtone regions. All complexes showed similar vibrational patterns at all overtones, where the intense CH overtone transitions were accompanied by less intense multiple peaks. This investigation confirmed that the pattern of weaker peaks observed in metallocenes also appears in the "half-sandwich" complexes. These weak peaks were assigned to combinations of CH stretch and CC stretch and/or CH bend. It was possible to assign the observed transitions to similar combinations for all complexes. The vibrational transitions were shifted to higher energies for the "half-sandwich" complexes. These shifts serve as a measure of the influence of the other ligands on the CH bond in the cyclopentadienyl ring.

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