Vibrational Overtone Spectroscopy of Cycloheptatriene Chromium Tricarbonyl, Benzene Chromium Tricarbonyl, and Corresponding Hydrocarbon Ligands

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The vibrational overtone spectra of gaseous cycloheptatriene chromium tricarbonyl (CHTCT) and benzene chromium tricarbonyl (BCT) were recorded at the third overtone region using photoacoustic spectroscopy and compared to the spectra of the nonbonded ligands, cycloheptatriene (CHT) and benzene. Analysis of the spectra leads to the conclusion that the metal−ligand bonding lengthens the CH bond by 0.007 Å in the cycloheptatriene complex and by 0.003 Å in the benzene complex. The spectrum of BCT exhibits an additional transition which is absent in the spectrum of free benzene. The experimental peaks are assigned to the pure CH overtones and combination bands. The structural information obtained from the spectra is discussed and compared to the results of gas-phase electron diffraction and microwave spectroscopic studies. Analysis of experimental data indicates that μ_6-bonding is more favorable for cycloheptatriene chromium tricarbonyl.

Introduction

The catalytic activity of organometallic complexes in chemical processes is well-known.[1,2] For many catalyzed reactions the metal d-orbitals interact with π-orbitals of the organic ligand, forming an organometallic complex. In the stable complexes the presence of the metal atom induces changes in the ligand. These changes can be considered as the initial steps in activating the hydrocarbon toward reaction in the catalytic processes. Oligomerization of dienes,[1] double-bond migration reactions,[2] and transition-metal-catalyzed polymerization[1] serve as examples of such processes.

Vibrational overtone spectroscopy probes molecules at high internal energies close to the activation energy of catalytic reactions. At these high energies the XH bond stretch (X = C, O, N) exhibits local mode behavior,[3] where vibrational energy is localized in one of the XH oscillators. The absorbed energy, initially localized in the XH oscillators, redistributes over the molecule through the coupling of the XH stretch with other vibrations. The study of vibrational overtone spectra of organometallic complexes may help to elucidate the role of vibrational excitation in certain types of metal-catalyzed reactions. The effect of the metal can be studied by comparing the overtone spectra of organometallic complexes to the corresponding free hydrocarbon ligands. Changes in the bond length can be estimated from the shifts in the absorption features. Changes in vibrational coupling may result in new absorptions. In this paper we focus our attention on the vibrational spectra of two organometallic complexes—cycloheptatriene chromium tricarbonyl (CHTCT) and benzene chromium tricarbonyl (BCT).

Several organometallic complexes have been investigated by vibrational overtone spectroscopy.[4−9] The PAS spectra of solid BCT[4,5] have been recorded up to the second overtone region. Two effects were reported on the benzene ring upon metal coordination: redistribution of the electron density and lowering of the local symmetry. The first factor shifted the fundamental and overtone CH stretches. The second effect resulted in the appearance of three additional bands: at 3953, 4264, and 4464 cm^{-1}. The first two peaks were assigned to combinations of the CH stretch with the ring deformations. The assignment for the last peak was less certain. It was suggested that this combination may arise from bands that are infrared-inactive.

The high vibrational overtone spectrum of π-bonded cyclopentadienyl was recorded in ferrocene.[7] Because the cyclopentadienyl ligand becomes aromatic in the complex, the overtone spectrum was expected to display only one peak at each overtone level. A comparison of the spectrum of cyclopentadiene to those of ferrocene, ruthenocene, and related compounds in the third overtone region indicated that the peak attributed to the CH olefinic stretch in cyclopentadiene splits into four peaks in the complex. This was interpreted[8] as coupling between the CH stretch and other vibrations of the cyclopentadienyl ring induced by the metal complexation.

The third overtone spectrum of butadiene iron tricarbonyl has been recorded and compared to the spectrum of *trans*-1,3-butadiene.[9] The spectrum of the complex exhibited six transitions. Three of these absorptions were due to the different CH oscillators[10] of the butadiene ligand. The additional peaks in the spectrum must arise from vibrational coupling initiated by the metal. Changes in the CH bond lengths for the butadiene ligand were determined using an empirical formula developed for the bond length changes observed in local mode spectra of butadiene-type molecules.

The BCT structure was examined by both electron diffraction (ED)[11] and microwave spectroscopy (MW).[12] The analysis of the gas-phase ED data obtained at 140 °C indicated that BCT exists as a mixture of several conformations. In addition to the expected staggered and eclipsed forms, other conformers may exist, making the complex a nearly free rotor. The values for the CH bonds obtained from ED varied from 1.105 Å for staggered form to 1.090 Å for the eclipsed form. The CH bond lengths for the other conformers fell between these two values. These CH bonds are all longer than in free benzene (1.083 Å, ED[13]). The CC bond in BCT was reported to be longer than in the free ligand (1.417 vs 1.397 Å).

No evidence for the relatively free rotation was found in the MW spectra.[12] The barrier for internal rotation was estimated to be 1.6 kJ/mol. All CC bonds for BCT were reported to be longer (by 0.02 Å) than for the unbound benzene; however,

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the MW CH bond length (1.080 Å) was shorter than the value for benzene (1.0815 Å[14]). The CH bonds in the complex are bent 2.8° toward the Cr atom.

Although cycloheptatriene transition-metal complexes have been known for more than 30 years, this ligand has been studied very little compared to the cyclopentadienyl and aryl ligands. The structural determination of cycloheptatriene Mo tricarbonyl[15] showed that the olefinic part of the cycloheptatriene ring is approximately planar with alternating single and double CC bonds. The structure of the cycloheptatriene complex of Cr[16] indicated that the C_1C_2 and C_5C_6 were identical in length. (In this notation C_7 is the carbon with two hydrogens.) The C_2C_3 and C_4C_5 were slightly longer than the single bonds of the free ligand. The C_3C_4 bond was longer than expected, approaching a single CC bond length. The structure appeared to be a flattened boat conformation with a lengthening of the C_3C_4 double bond and a shift of Cr from the center of the ring toward the C_3C_4 bond. This lead to the suggestion that the ring can be described equally as μ^4/μ^2-bound rather than μ^6-bound. However, this question remains open and requires further theoretical and experimental investigation.

The IR vibrational spectrum of cycloheptatriene chromium tricarbonyl was studied by several research groups.[17−19,21] Three transitions were reported for the CO stretch region.[16] The assignment of all metal−ligand vibrations (CO stretch, MCO bend, MC stretch, M-ring stretch, ring tilt, CMC bend) for (cycloheptatriene)M$(CO)_3$ (M = Cr, Mo, W) in the 100−250 cm^{-1} (FIR) and 100−2200 cm^{-1} (Raman) regions was complete.[18] Three CH stretch transitions at 3003, 2890, and 2786 cm^{-1} were reported for the $(cycloheptatriene)_2V$ complex.[19] These transitions are shifted to the red compared to the unbound cycloheptatriene CH fundamentals (3060, 3027, 3015 cm^{-1}).[20] The IR spectrum of (cycloheptatriene)Mo$(CO)_3$ also exhibits three transitions in the CH stretch region.[21] In all these reports, no normal-mode analysis was reported for (cycloheptatriene)M$(CO)_3$ (M = Cr, Mo, W) for the fundamental CH vibrations.

The most recent and complete studies of the BCT IR spectrum were conducted by Armstrong and colleagues.[22] Four transitions belonging to the different symmetry species were reported at the CH stretch region (2957, 3070, 3090, and 3102 cm^{-1}).

In this work the third overtone ($\Delta v = 4$) spectra of (cycloheptatriene)Cr$(CO)_3$ and (benzene)Cr$(CO)_3$ will be presented and compared to the spectrum of cycloheptatriene and benzene at the same region in order to study the effect of Cr metal on the vibrational properties of the hydrocarbon ligands. In addition, the interpretation of the overtone spectrum will be used to elucidate the structure and bonding of the complex.

Experiment

The gaseous overtone spectra of cycloheptatriene chromium tricarbonyl (97%, Aldrich), benzene chromium tricarbonyl (97%, Strem), cycloheptatriene (90%, Aldrich), benzene (99.9%, Aldrich), toluene(99%, Aldrich), and 1,3-cycloheptadiene (97%, Aldrich) were obtained by using intracavity laser photoacoustic spectrometer described previously.[9] The solid complexes, benzene and toluene, were used without further purification. CHT and 1,3-cycloheptadiene were distilled prior to use. The sample was transferred under argon atmosphere (complex) or vacuum-transferred (ligand) into a 20 by 1.5 cm photoacoustic cell equipped with 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 300 Torr in the case of the ligands and 150 Torr for the complexes. A specially designed intracavity oven heated the samples up to 120 °C to sublime the solid samples inside the cell.

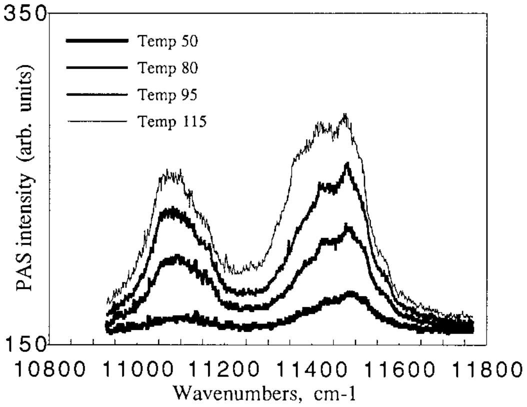

Figure 1. Vibrational third overtone spectra of CHTCT sample recorded at different temperatures.

The low-energy region of argon ion laser pumped CW Ti:sapphire laser (10 500−11 800 cm^{-1}) outfitted with the three-plate birefringent filter was used to obtain the spectra. The scanning monochromator was used to measure the initial and final wavelengths of the scanning region. Because the resolution of the monochromator is 0.3 cm^{-1}, the measurements were limited by the 2 cm^{-1} resolution of the birefringent filter. The positions of the peaks were corrected using a calibration procedure.

The pyrolysis of the complexes was conducted in the apparatus consisting of two connected Pyrex glass tubes. The complex was placed into the one tube, and the entire system was filled with argon to maintain the pressure of 150 Torr. The apparatus was placed in the oven and kept there at 120 °C for 6 h. At the end of the pyrolysis time period the gaseous contents were trapped in the other Pyrex tube using liquid nitrogen. Liquid nitrogen was also used to condense the gaseous contents of the PAS cell into the sidearm. In both cases the condensation products were analyzed by the Hewlett-Packard GCMS spectrometer.

Results and Discussion

Microcalorimetric studies[23−25] on thermal decomposition of various metal carbonyls including BCT, toluene chromium tricarbonyl (TCT), and CHTCT discovered decomposition beginning as low as 200 °C.[25] However, all complexes sublimed readily under reduced pressure in the temperature range 100−120 °C.[24] For example, for the molybdenum tricarbonyl complex of CHT, which is analogous to CHTCT, a 2−5% decomposition was reported during sublimation.[25] The enthalpies of sublimation were obtained for BCT (at 125 °C), TCT (at 120 °C), and CHTCT (at 95 °C), and it was concluded[24] that CHT is less strongly bound to the chromium tricarbonyl than benzene or toluene. In argon atmosphere BCT volatilizes at 100 °C and decomposes around 210 °C.[26] In air, however, BCT decomposes at 130 °C without sublimation. Given these facts, partial decomposition of the complexes is expected under our experimental conditions (150 Torr of Ar, 115−120 °C). Therefore, the presence of the complex decomposition products needs to be accounted for in our interpretation of the spectra.

(Cycloheptatriene)Cr$(CO)_3$. The spectrum of CHTCT recorded at different temperatures is presented in Figure 1. For all temperatures two intense absorptions centered at 11 100 and 11 450 cm^{-1} were present. The first step in the analysis of the

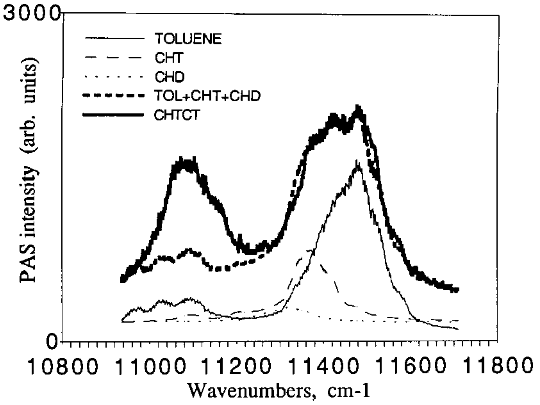

Figure 2. Comparison of CHTCT sample spectrum recorded at 115 °C (darker line) and combined spectrum of the CHTCT decomposition products (lighter lines) recorded at elevated temperatures (115−120 °C).

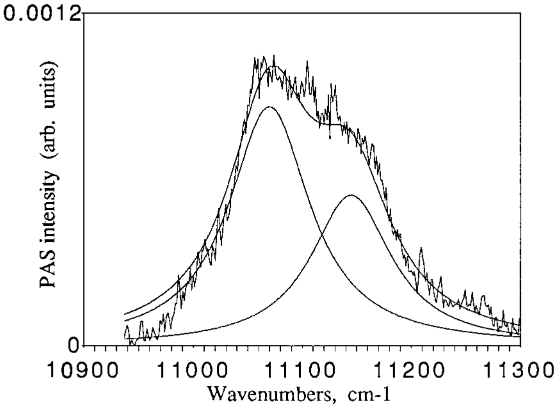

Figure 3. Vibrational third overtone spectrum of CHTCT obtained by subtraction of combined decomposition products spectrum from the CHTCT sample spectrum.

CHTCT spectrum was to eliminate the influence of CHTCT decomposition products. To detect decomposition products, both the products of a 6 h CHTCT pyrolysis and the contents of the PAS cell after recording the spectra were analyzed by GCMS. Three major decomposition products were observed in both cases. CHT was the result of the metal−ring bond cleavage.[27] Toluene was the result of CHTCT isomerization into TCT with further cleavage of the metal−ring bond.[27] In both cases 1,3-cycloheptadiene (CHD) was also present as a minor decomposition product.

The vibrational overtone spectra of CHT, toluene, and CHD at the third overtone region were recorded at elevated temperatures. The hydrocarbon spectra were added together in order to match the experimental spectrum of the CHTCT sample. The results are presented in Figure 2. The combined decomposition product spectrum matches the high-energy absorption of the CHTCT spectrum located around 11 450 cm^{-1}. For each independent trial spectrum, different relative intensities of the decomposition products absorptions were needed to match the sample spectrum. This confirms that different amounts of decomposition products were formed during each run. Nevertheless, for all runs the low-energy absorption around 11 100 cm^{-1} of the CHTCT sample was more intense than the peaks of CHT, toluene, and CHD in this region.

The pure overtone spectrum of CHTCT can be obtained by subtracting the spectra of the decomposition products. This spectrum is shown in Figure 3. Deconvolution of the results yields two absorptions located at 11 070 and 11 145 cm^{-1}.

TABLE 1: Peak Positions and Vibrational Assignments for CHTCT, BCT, and Corresponding Hydrocarbon Ligands

compound	peak positns, cm^{-1}	int^{a}	assignments
cycloheptatriene			
$v = 1$ liq	3060, 3027, 3015^{b}	s	v CH (A′, A″)
$v = 2$ sol. in CCl_4	5867^{c}	l.en.sh.	$2v$ $CH^{ol}_{2,3,4,5}$
	5905^{c}	s	$2v$ $CH^{ol}_{1,6}$
$v = 3$ sol. in CCl_4	8652^{c}	s	$4v$ CH^{ol}
$v = 4$ gas	11094^{c}	w	$4v$ CH^{ax}
	11216^{c}	w	$4v$ CH^{eq}
	11313^{c}	l.en.sh.	$3v$ $CH^{eq} + 2v$ $CH_{2\ \mathrm{bend}}$
	11366^{c}	s	$4v$ $CH^{ol}_{2,3,4,5}$
	11437^{c}	h.en.sh.	$4v$ $CH^{ol}_{1,6}$
CHTCT			
$v = 1$ solid	3000, 2860, 2800^{d}	s	v CH
$v = 2$			
$v = 3$			
$v = 4$ gas	11070	s	$4v$ $CH^{ol}_{2,3,4,5}$
	11145	h.en.sh.	$4v$ $CH^{ol}_{1,6}$
benzene			
$v = 1$ gas	3047^{e}	s	v CH
$v = 2$ liq (gas)	6025^{f} (5972^{e})	s	$2v$ CH^{arom}
$v = 3$ liq (gas)	8839^{f} (8786^{e})	s	$3v$ CH^{arom}
$v = 4$ gas (gas)	11500 (11498^{e})	s	$4v$ CH^{arom}
BCT			
$v = 1$ solid	3102, 3090, 3070, 2957^{g}	s	v CH (A′, A″, A′ + A″)
$v = 2$ solid	6090^{f}	s	$2v$ CH^{arom}
$v = 3$ solid	9000^{f}	s	$3v$ CH^{arom}
$v = 4$ gas	11363	s	$4v$ CH^{arom}
	11568	s	$3v$ $CH^{arom} + 2v$ CC_{str}

[a] w = weak, s = strong, l.en.sh. = low-energy shoulder, and h.en.sh. = high-energy shoulder. [b] Taken from ref 20. [c] Our previous work (ref 28). [d] Data for cycloheptatriene tungsten tricarbonyl taken from: King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966,** *5,* 1837. [e] Taken from: Reddy, K. V.; Heller, D. F.; Berry, M. J. *J. Chem. Phys.* **1982,** *76,* 2814. [f] Taken from ref 4. [g] Taken from ref 22.

The subtraction of the decomposition product spectrum allowed us to isolate the spectrum of CHTCT but also increased the error in determining the peak positions and line widths using deconvolution procedure. This would lead to the larger uncertainty in determining the band shifts and estimating the bond length changes. We believe, however, that despite the increased error, it is still possible to report the change in the bond length with 0.001 Å accuracy.

The overtone spectrum of free CHT was analyzed in our previous work.[28] The most intense transition at 11 366 cm^{-1} and high-energy shoulder of this peak (11 437 cm^{-1}) were assigned to the two different types of CH olefinic oscillators: $CH_{2,3,4,5}$ and $CH_{1,6}$. The spectral pattern observed for the complex is similar to that of the CHT ligand. Based on this observation, the two transitions observed for CHTCT can be assigned to $CH_{2,3,4,5}$ (11 070 cm^{-1}) and $CH_{1,6}$ (11 145 cm^{-1}) of CHT ligand bound to the $Cr(CO)_3$ fragment (Table 1). Significant flattening of the olefinic part[16] of the CHT ring due to bonding to the Cr metal seems to have no effect on the number of different types of CH olefinic oscillators (the same number of overtone transitions was observed for CHT and CHTCT) or the spectral spacing between the peaks (the peaks are 71 cm^{-1} apart in CHT and 75 cm^{-1} apart in CHTCT).

The CH olefinic bonds, however, become longer going from CHT to CHTCT. The complex transitions are shifted to the red by 296 cm^{-1} for $CH_{2,3,4,5}$ and by 292 cm^{-1} for $CH_{1,6}$ compared to the free ligand spectrum. Using the empirical formula developed for the substituted benzenes[29] ($\Delta r_{CH} = (\Delta v/11v)\cdot 0.001$, where Δv is the shift of the overtone transition in wavenumbers and v is the vibrational quantum number), the change in the bond length can be estimated. The lengthening

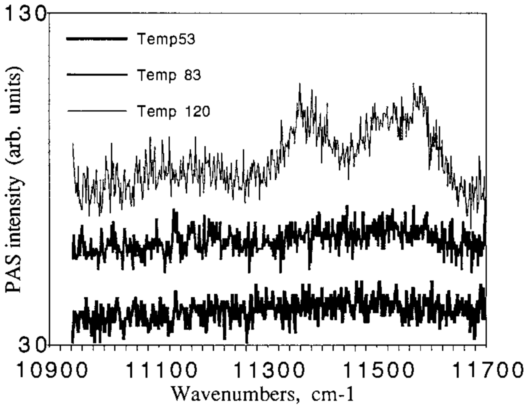

Figure 4. Vibrational third overtone spectra of BCT sample recorded at different temperatures.

for both $CH_{2,3,4,5}$ and $CH_{1,6}$ is about 0.007 Å. Because data for the first and second overtone of CHTCT were not available (Table 1), it was impossible to compare the results for CHTCT and CHT in these spectral regions.

Transitions belonging to the CH_2 group of the CHT ring were not observed for the complex. The absorptions owing to the TCT species might also be present in the spectrum, but because of the low vapor pressure of this complex the TCT contribution is not significant.

In contrast to metallocenes[8] and butadiene iron tricarbonyl,[9] no additional absorptions initiated by the metal were recorded. This indicates that brightening of the dark states is not a general phenomenon for organometallic complexes, and the effect of the metal is different for each complex.

The similarity between the CH olefinic absorption pattern of CHT and CHTCT leads to the conclusion that the difference between the CH olefinic bonds in CHTCT is determined by the same steric factors as in the free CHT (i.e., $CH_{1,6}$ is closer to the CH_2 group of the ring than $CH_{2,3,4,5}$) rather than by the influence of the metal bonding. In addition, both types of olefinic CH's lengthen by the same amount. These observations suggest the μ^6-bonding for CHTCT in the gas phase in contrast to the μ^4/μ^2-bonding proposed from the X-ray diffraction studies.[16] The μ^4/μ^2-bonding in the complex would require two significantly different types of CH oscillators belonging to the μ^4- and μ^2-species appearing as two sufficiently separated peaks in the overtone spectrum. This situation was not observed in our studies.

(Benzene)Cr(CO)$_3$. The spectrum of the BCT sample recorded at different temperatures is shown in Figure 4. The BCT vapor pressure is much lower compared to that of CHTCT as can be seen from the signal-to-noise ratio of spectra from Figures 1 and 4. The high-temperature spectrum from Figure 4 displays three absorptions located at 11 363, 11 500, and 11 568 cm^{-1}. As in the case of CHTCT, the GCMS analysis for the decomposition products was conducted. Benzene was the only product as a result of the complex partial decomposition. The BCT spectrum was matched with the third overtone spectrum of benzene recorded at 115 °C. The results are shown in Figure 5. The subtraction of the benzene peak produces the spectrum of BCT displayed in Figure 6.

The low-energy peak at 11 363 cm^{-1} (fwhm 50 cm^{-1}) can be assigned to the $4v$ CH stretch of benzene ligand connected to the chromium (Table 1). The transition energy is shifted 135 cm^{-1} to the red compared to that of a free benzene. The effect of the metal is to lengthen the benzene CH bond by 0.003 Å (empirical formula from ref 29; see also CHTCT discussion).

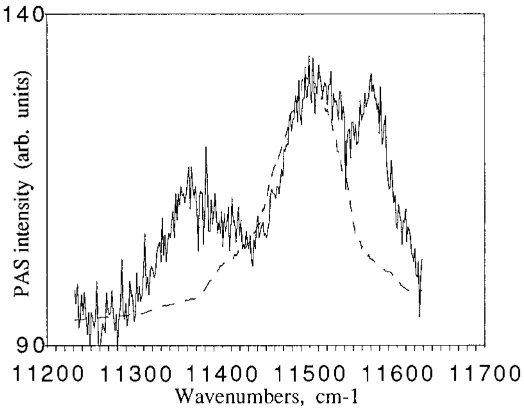

Figure 5. Comparison of BCT sample spectrum recorded at 120 °C (darker line) and benzene spectrum (lighter line) recorded at 115 °C.

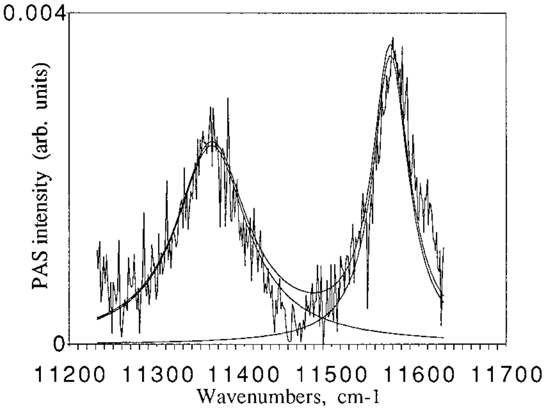

Figure 6. Vibrational third overtone spectrum of BCT obtained by subtraction of benzene spectrum from the BCT sample spectrum.

The high-energy transition at 11 568 cm^{-1} is much narrower (fwhm 25 cm^{-1}). There are two possible assignments for the this transition. First, it can be tentatively assigned to the combination of $3v$ CH stretch (9000 cm^{-1})[4] + $2v$ CC stretch (1314 cm^{-1})[22] = 11 628 cm^{-1}. The 60 cm^{-1} mismatch between the observed and predicted values can be accounted for by the CC stretch anharmonicity. This combination becomes bright in the BCT when Cr(CO)$_3$ is bound to the aromatic benzene. The second possibility is that the peak at 11 568 cm^{-1} might belong to the $4v$ CH stretch of the second rotamer of BCT (eclipsed). This possibility is based on the ED observations.

The first assignment is more favorable for several reasons. In addition to the staggered and eclipsed forms, other rotamers were suggested for BCT by the ED studies.[15] CH bond lengths for these rotamers were reported to be between the values for staggered and eclipsed BCT. Therefore, assuming that the observed peaks in the spectra belong to different rotamers of BCT, more than two peaks should appear in the overtone spectrum, but this did not happen. Second, the CH bond lengths for all rotamers of BCT are longer than that of free benzene according to the ED results. Based on these observations, the peaks belonging to the different CH oscillators of BCT rotamers should appear to the lower energy from the third overtone transition for free benzene (11 498 cm^{-1}), which contradicts the experimental observations (11 568 cm^{-1}). And, finally, transitions belonging to the third CH stretch overtone of BCT rotamers are expected to have similar bandwidths, contrary to the experimental observations (50 vs 25 cm^{-1}).

The trend between benzene and BCT for the first and second overtones is different than that observed in this work (Table 1). The transitions of the complex are shifted to the blue compared to the case of free benzene in the work of Lewis et al.[4] However, the comparison of our results to that of Lewis is inappropriate because he recorded the PAS of solid BCT, and shifts observed in his work represent the intermolecular interactions in the crystal lattice. Our gas-phase work only considers the influence of metal bonding within the single molecule.

The BCT spectrum indicates the lengthening of the CH bond in the complex (ΔCH = 0.003 Å), which is consistent with the ED results also predicting an increase of CH bond length in the complex (ΔCH = 0.022 Å, staggered BCT; ΔCH = 0.007 Å, eclipsed BCT) but does not agree with MW spectroscopic conclusions which predict shorter CH bonds in the complex (ΔCH= − 0.0015 Å). On the other hand, the presence of one CH overtone transition and one combination suggests only one type of CH oscillator in the gaseous BCT. Different CH bonds from different BCT conformers were not observed in our studies, in contrast to the ED observations.

Conclusions

The vibrational overtone spectra of cycloheptatriene chromium tricarbonyl and benzene chromium tricarbonyl were recorded at the third overtone region and compared to the spectra of free cycloheptatriene and benzene. The CHTCT spectrum displayed two partially resolved transitions assigned to the different types of CH olefinic oscillators in the complex. The effect of complex formation is to lengthen the CH olefinic bonds of CHT ring by approximately 0.007 Å. The similarity of the spectral patterns of CHT and CHTCT and the same increase in the CH olefinic bond lengths for different CH oscillators suggest the μ^6-bonding in the complex. No additional vibrational coupling initiated by the metal was observed for CHTCT, in contrast to the previously investigated complexes.

For the BCT two transitions were detected. In addition to the pure CH overtone peak, a new absorption was observed and tentatively assigned to the CH stretch−CC stretch combination in the complex. The effect of metal on BCT is to initiate the new channel for vibrational coupling and to make the CH bonds 0.003 Å longer. The lengthening of the CH bonds is consistent with the electron diffraction results.

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