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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 5/18/92		3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE Vibrational Overtone Spectroscopy of Gaseous Metallocenes				5. FUNDING NUMBERS N00014-88-K-0664 4131063	
6. AUTHOR(S) C. Olsen, T. Van Marter, S. Hassoon and D. L. Snavely					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Bowling Green State University Bowling Green, OH 43403				8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report No. 10	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT This document has been approved for public release and sale: its distribution is unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  The vibrational overtone spectra of ferrocene, acetylferrocene, ruthenocene and cyclopentadienyltitaniumtrichloride has been recorded in the third overtone region of the C-H stretch vibration. All of the spectra display four peaks in this region which, by comparison to the overtone spectrum of gaseous cyclopentadiene, appear where the C-H olefinic overtone vibration absorbs. The pattern of the absorption spectrum does not vary upon change of the metal (iron, ruthenium or titanium) or the ligand (chloride or acetylcyclopentadienyl).					
14. SUBJECT TERMS  Overtone Spectroscopy, Metallocenes				15. NUMBER OF PAGES 8	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT		18. SECURITY CLASSIFICATION OF THIS PAGE		19. SECURITY CLASSIFICATION OF ABSTRACT	
				20. LIMITATION OF ABSTRACT	

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## OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT N00014-88-K-0664

R&amp;T Code 4131063

Technical Report No. 10

Vibrational Overtone Spectroscopy of Gaseous Metallocenes

by

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Prepared for Publication

in

Chemical Physics Letters



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May 20, 1992

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## Vibrational Overtone Spectroscopy of Gaseous Metallocenes

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### Abstract

The vibrational overtone spectra of ferrocene, acetylferrocene, ruthenocene and cyclopentadienyltitaniumtrichloride has been recorded in the third overtone region of the C-H stretch vibration. All of the spectra display four peaks in this region which, by comparison to the overtone spectrum of gaseous cyclopentadiene, appear where the C-H olefinic overtone vibration absorbs. The pattern of the absorption spectrum does not vary upon change of the metal (iron, ruthenium or titanium) or the ligand (chloride or acetylcyclopentadienyl).

### Introduction

Metallocenes are sandwich compounds consisting of two cyclopentadienyl rings joined by a metal atom. The visible vibrational spectrum of ferrocene has been observed using laser vibrational overtone spectroscopy by Blackburn, Snavely and Oref<sup>1</sup>. Two peaks at 11,669 cm<sup>-1</sup> and 11,712 cm<sup>-1</sup> were observed and assigned to the third overtone of the C-H oscillator. The appearance of two peaks was not expected and it was hypothesized that these absorptions originated from the two conformations of ferrocene, staggered and eclipsed.

In our present study, with improved signal to noise ratio, we have reinvestigated the overtone spectrum of ferrocene and observed four transitions all belonging to the third overtone of the C-H. In order to further test the internal rotation hypothesis we have observed for the first time the overtone spectra of acetylferrocene, ruthenocene and cyclopentadienyltitaniumtrichloride.

### Experimental

Ferrocene and ruthenocene were purchased from the Aldrich Chemical Company. Acetylferrocene and cyclopentadienyltitaniumtrichloride were purchased from Strem Chemicals Inc. Samples were sublimed into a 20 by 1.5 cm vacuum cell equipped with a 1741 Knowles Electronics Inc. microphone. The cell was outfitted with quartz windows oriented at Brewster's angle. A special intracavity oven holds the cell in place at elevated temperatures. These spectra were recorded at temperatures ranging from 60°C for ferrocene and acetylferrocene to 120°C for ruthenocene. To increase our signal-to-noise ratio, argon was added to the photoacoustic cell to attain a total pressure of ~400 torr. The oven sits inside a Spectra-Physics Model 375B argon

pumped tunable Styryl 9 dye laser outfitted with a three plate birefringent filter which limits the laser bandwidth of  $2 \text{ cm}^{-1}$ . The rotation of the birefringent filter was controlled by an Oriel motor mike and control unit Model 18007. A Spex Industries Inc. Model 1401 double monochromator was used to detect the wavelength of the dye laser at intervals of about  $200 \text{ cm}^{-1}$ . The monochromator had a resolution of  $0.2 \text{ cm}^{-1}$  so the measurements were still limited by the  $2 \text{ cm}^{-1}$  resolution of the birefringent filter. A PTI Model 03-OC4000 optical chopper chopped (frequencies ranged from 230 to 300 Hertz) the argon laser and provided a reference signal for an EG&G Brookdeal Electronics Model 5207 lock-in amplifier.

## Results and Discussion

The spectra of ferrocene, ruthenocene, acetylferrocene and cyclopentadienyltitaniumtrichloride are shown in Figures 1, 2, 3 and 4, respectively. These spectra were recorded at temperatures ranging from  $60^{\circ}\text{C}$  for ferrocene and acetylferrocene to  $120^{\circ}\text{C}$  for ruthenocene. The transition wavenumbers are reported in Table 1.

Table 1 Transition Wavenumbers for Gaseous Metallocenes (in wavenumbers)

Ferrocene	Ruthenocene	Acetylferrocene	Cyclopentadienyl-Ti-Cl <sub>3</sub>
11,659 m	11,665 m	11,661 m	11,658 m
11,724 s	11,732 s	11,724 s	11,723 s
11,802 w	11,806 w	11,803 w	11,800 w
11,861 w	11,866 w	11,863 w	11,861 w

The overtone spectrum of gaseous cyclopentadiene in this same spectral region was measured using intracavity laser photoacoustic spectroscopy. A single peak was observed at  $11,654 \text{ cm}^{-1}$ . In addition we recorded the NIR spectrum in a multipass 20 m cell on a Mattson FTIR and found the next lower overtone transition at  $8,895 \text{ cm}^{-1}$ . Fitting these transitions to a Birge-Sponer plot leads to the assignment of this peak at  $11,654 \text{ cm}^{-1}$  as the third overtone of the olefinic C-H stretch.

Comparing the third overtone transition wavenumber of cyclopentadiene to the lowest transition for the metallocenes, we believe that these four peaks arise from the third overtone of the olefinic stretch and are split by coordination to the metal. The spectrum does not depend on the metal since the frequencies are very similar for the iron, ruthenium and titanium compounds.

The internal rotation moves in a potential described according to Flygare's development<sup>2</sup> by the following equation

$$V = V_{10}/2 [1 - \cos 5\phi - A_{s-e} \cos (5\phi + 36^\circ)]$$

where  $\phi$  represents the angle of rotation in degrees,  $V_{10}$  is the magnitude of the staggered to eclipsed barrier, and  $A_{s-e}$  is the relative depth of the staggered and eclipsed conformers. The potential possesses 5-fold symmetry with two different alternating well depths. In the case of ferrocene the  $V_{10}$  is about 1 kcal/mole and  $A_{s-e}$  is 2/3 to approximate the energy difference between the staggered and eclipsed forms. By substituting one ring for a trichloride structure the internal rotation potential is altered; it still has the 5-fold symmetry but the well depths must be different than in ferrocene. In spite of this change the spectrum remains unchanged. Placing a functional group on one cyclopentadiene ring should further alter the rotational potential, however the spectrum remains similar to that of ferrocene.

According to our preliminary work on benzenechromiumtricarbonyl, the spectrum is dramatically different for the  $\eta_5$  and  $\eta_6$  coordination compounds. The benzene derivative has five possibly six vibrational transitions, the lowest of which corresponds to the gaseous benzene third overtone transition<sup>3</sup>. Work continues on the assignment of these spectra. The final interpretation will reveal features of the ligand bonding in these sandwich compounds.

### References

1. Blackburn, F.R.; Snavely, D.L.; Oref, I. *Chem. Phys. Lett.* **1991**, 178, 538.
2. "Molecular Structure and Dynamics", W.H. Flygare @ 1978 by Prentice-Hall, Inc.
3. Reddy, K.V.; Heller, D.F.; Berry, M.J. *J. Chem Phys.* **1982**, 76(6), 2814.

### Figure Captions

Figure 1 Overtone spectrum of gaseous ferrocene.

Figure 2 Overtone spectrum of gaseous ruthenocene.

Figure 3 Overtone spectrum of acetylferrocene.

Figure 4 Overtone spectrum of cyclopentadienyltitaniumtrichloride.

Figure 1 Overtone spectrum of gaseous ferrocene.

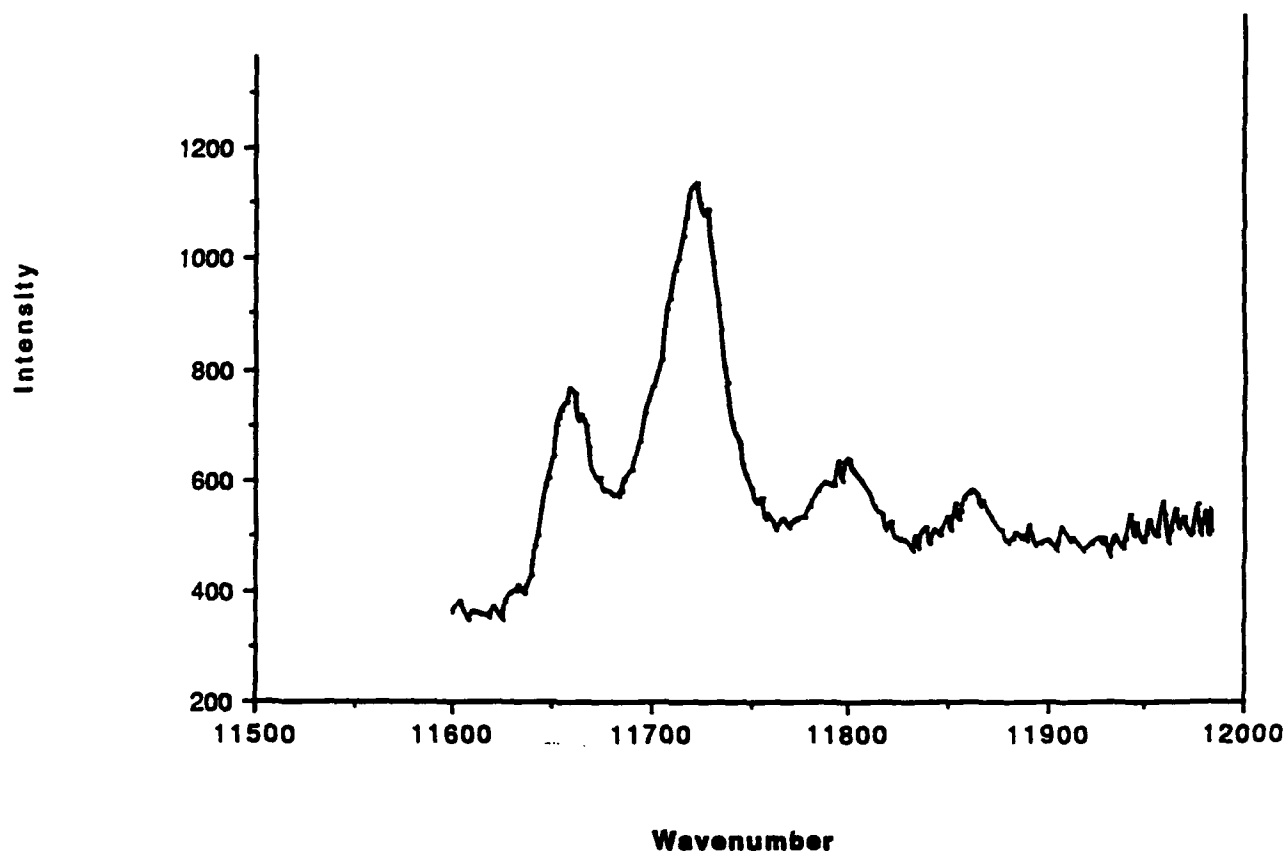


Figure 2 Overtone spectrum of gaseous ruthenocene.

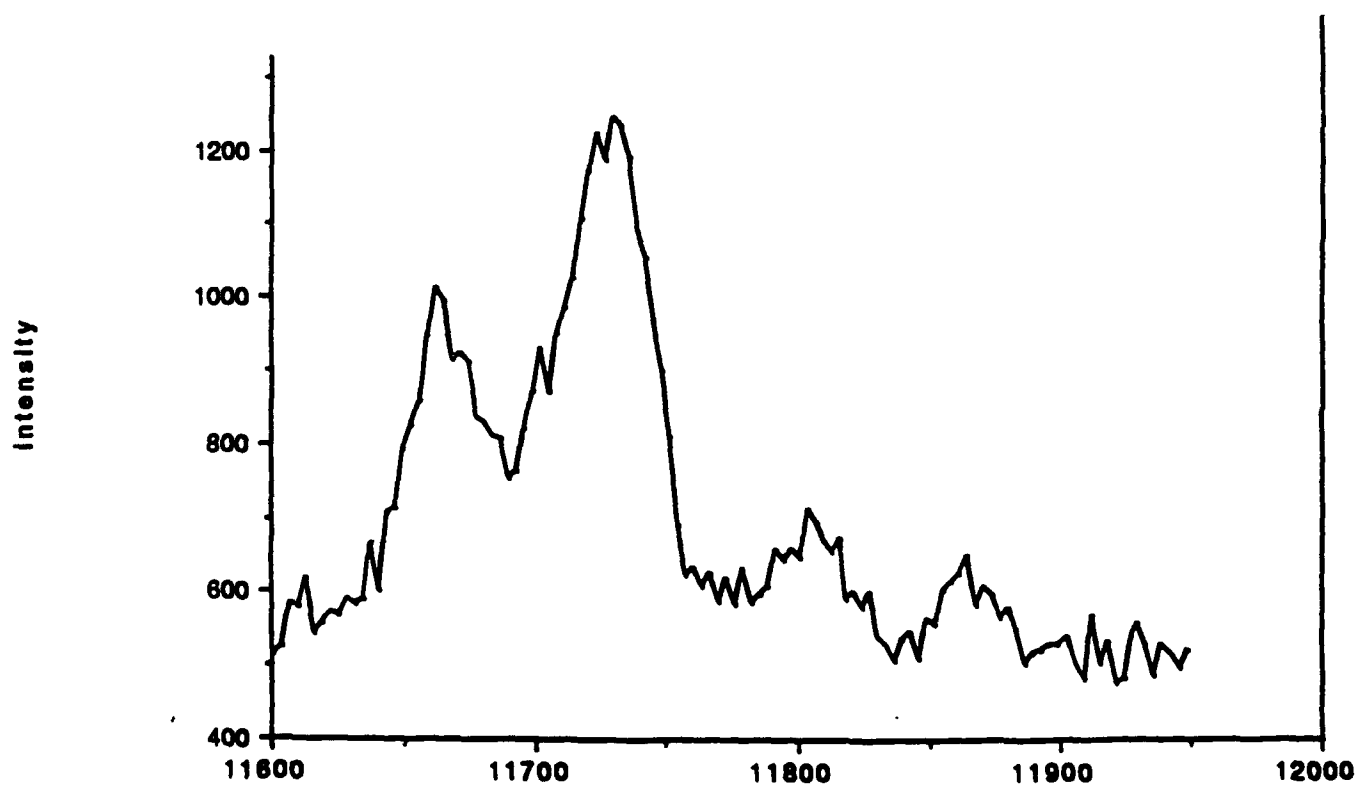


Figure 3 Overtone spectrum of acetylferrocene.

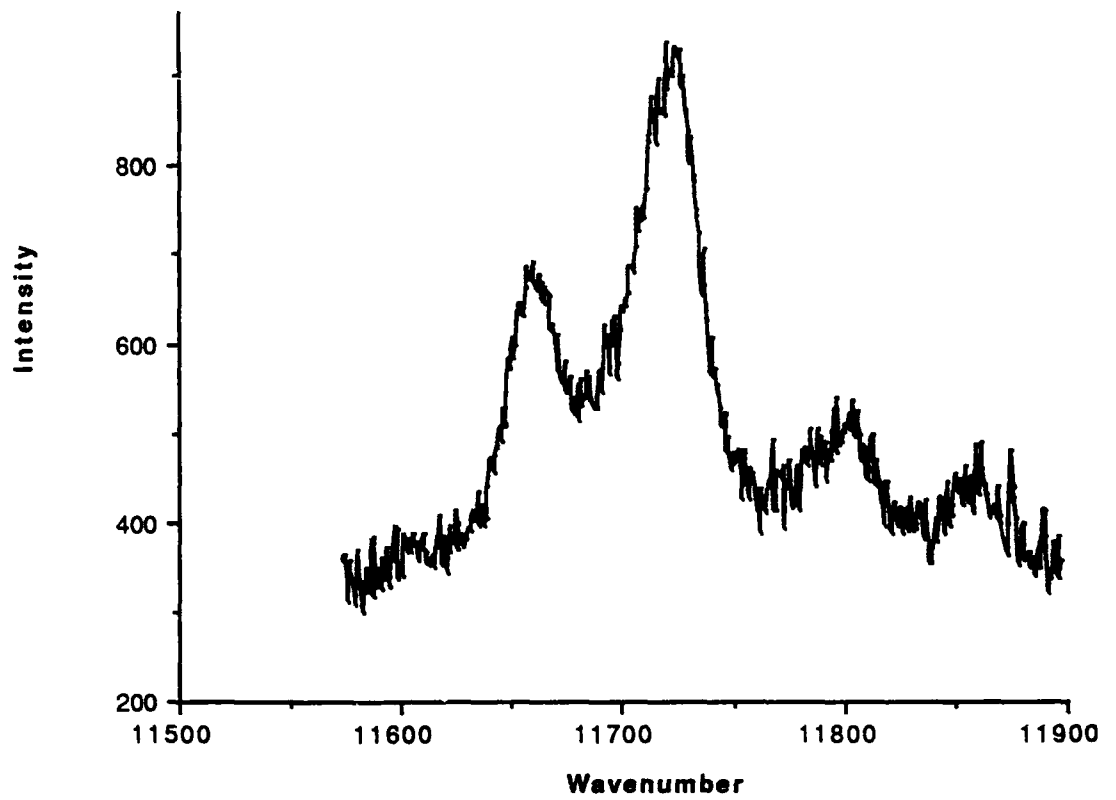
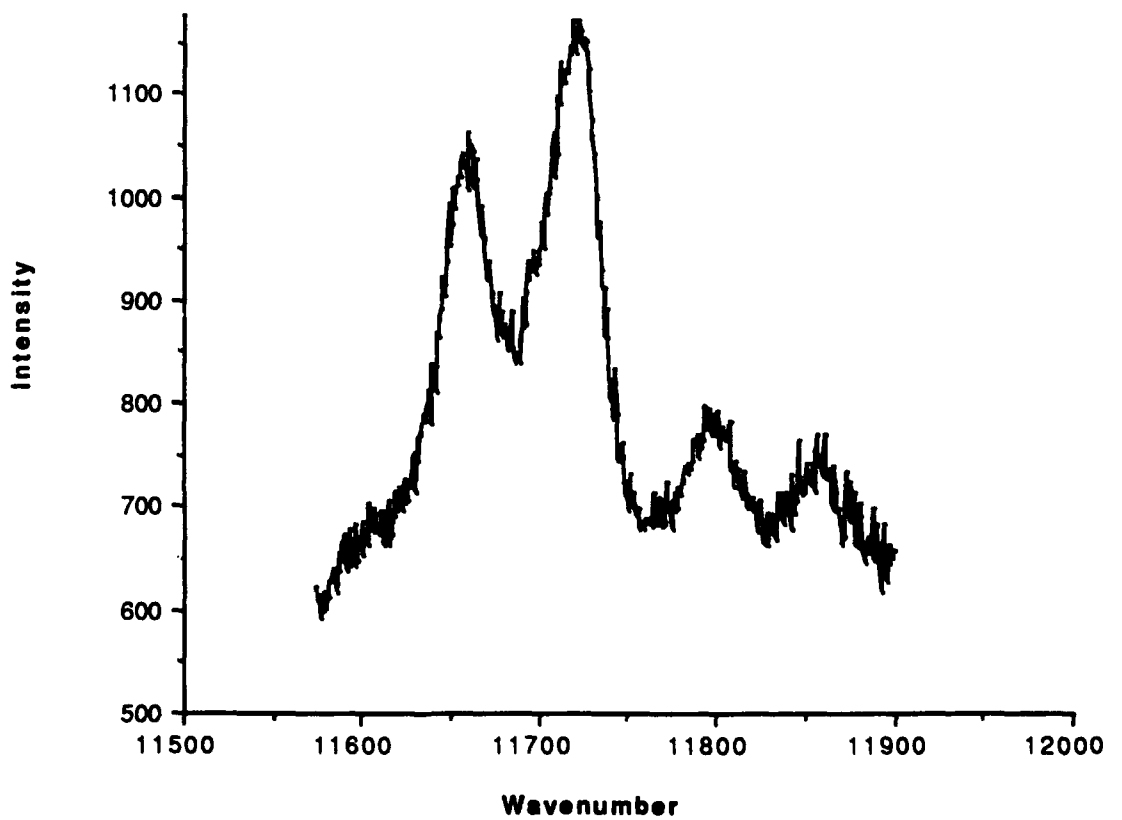


Figure 4 Overtone spectrum of cyclopentadienyltitaniumtrichloride.



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