

Journal of Organometallic Chemistry, 234 (1982) 355–365
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE ANALYSIS OF THE NEAR IR OF SOME ORGANIC AND ORGANO-METALLIC COMPOUNDS BY PHOTOACOUSTIC SPECTROSCOPY

LARRY N. LEWIS **

*Monsanto Research Corporation, Mound **, Miamisburg, Ohio 45342 (U.S.A.)

(Received January 18th, 1982; in revised form March 19th, 1982)

Summary

The photoacoustic spectrum (PAS) was measured in the near IR region (1000 to 2600 nm) for organic compounds (C_6H_6 , C_6D_6 , C_7H_8 , and C_6H_{12}) and organometallic compounds (Cp_2Fe , $Cp_2Fe_2(CO)_4$, $Cp_4Fe_4(CO)_4$, $Cp_4Fe_4S_4$, $C_6H_6Cr(CO)_3$, $CpCo(C_4Ph_4)$ and $CpCo(CO)_2$). Band assignments were made by comparison to the infrared spectra. The bands were assigned as the C–H overtone stretch and combinations of C–H and other IR fundamentals. These bands provide fingerprint spectra for these compounds.

Introduction

Photoacoustic spectroscopy (PAS) is finding increasing use in many phases of analysis [1]. Traditionally, it has been used in the UV/visible region. Lately, coupled with FTIR, PAS is finding wide use in the infrared region [2]. Recent work has shown that the often ignored near IR region contains valuable information, mostly in the form of overtones and combinations of strong IR fundamentals [3,4]. It is possible to assign the near IR peaks by examining a series of related organic and organometallic compounds.

This report deals with the assignment of peaks for aromatic hydrocarbons, namely benzenes and cyclopentadienyl. These assignments are made on the basis of comparison to similar compounds and examination of the infrared spectra.

* Mound is operated by Monsanto Research Corporation for the U.S. Department of Energy under Contract No. DE-AC04-76-DP00053.

** Current address: Larry Lewis, General Electric Research and Development Center, Schenectady, New York 12301.

Experimental

PAS were taken with a PAR Model 6001 photoacoustic spectrometer. The sample holder was a fused quartz cavity of dimensions: $1 \times 0.5 \times 0.2$ cm. The instrument [5] uses a high pressure Xenon arc lamp and incorporates gratings and filters which permit spectra to be recorded from 250 to 2600 nm. The light source was modulated at 40 Hz. The scan rate was 200 nm/min (from 250 to 800 nm) and 800 nm/min from 800 to 2600 nm. Thus a single scan from 1000 to 2600 nm took about 2 min. The signal to noise ratio could be improved by signal averaging from three to five scans. A sample sensitivity of 50 or 100 was employed. Infrared spectra were recorded on a Perkin-Elmer Model 1330 spectrometer as neat liquids or KBr pellets. Organic solvents were reagent grade and used without purification. C_6D_6 was obtained from Aldrich (99.5% D) and showed no C-H overtone in the PAS. The organometallic compounds were either purchased and used without further purification or synthesized. $CpCoC_4Ph_4$ was synthesized according to the method of Rausch and Gennetti [6], $Cp_4Fe_4(CO)_4$ was made according to the procedure of King [7] and $Cp_4Fe_4S_4$ was prepared via the method of Schunn et al. [8]. The term PAS will be used throughout to refer to those photoacoustic spectra run in the near IR from 1000 to 2600 nm.

Results and discussion

The region of study in this paper is from 1000 to 2600 nm. At higher energy (below 1000 nm) electronic transitions obscure the overtones and combinations. The lamp stability defines the lower limit (2600 nm) of observation. Due to the range of wavelengths investigated all peaks are derived from either overtones of the C-H stretch ($3100-2900\text{ cm}^{-1}$)* or combinations of C-H with other IR fundamentals. Table 1 summarizes the PAS peaks observed and their important infrared peaks.

As previously reported [4], the PAS of benzene contains three major peaks (Fig. 1). The high energy peak at 6025 cm^{-1} (1660 nm) has been assigned to the first overtone of the C-H stretch. This is confirmed by comparison of the spectrum to C_6D_6 (Fig. 2). The C-D stretch in the IR occurs at 2260 cm^{-1} . This peak occurs at slightly higher energy than it would if the molecule behaved as a perfect harmonic oscillator. The observation of a single sharp peak in Fig. 2 helps to confirm the assignment of the other two benzene peaks in Fig. 1. The bands at 4675 (2140 nm) and 4100 cm^{-1} (2440 nm) are assigned as combination bands of $\nu(C-H)$ with two benzene IR peaks located at 1470 and 1030 cm^{-1} , respectively. The former IR band is the C-C stretch which mixes strongly with the C-H in plane bend. The later peak is due to the HCC bending motion [9]. The combination of $\nu(C-D)$ with these fundamentals would be outside the region of observation (below 2600 nm).

* Note that the PAS is linear in nm. IR peaks will be reported in cm^{-1} . PAS peaks will be given in cm^{-1} with nm in parentheses. The PAS spectra in the figures are in the nm scale.

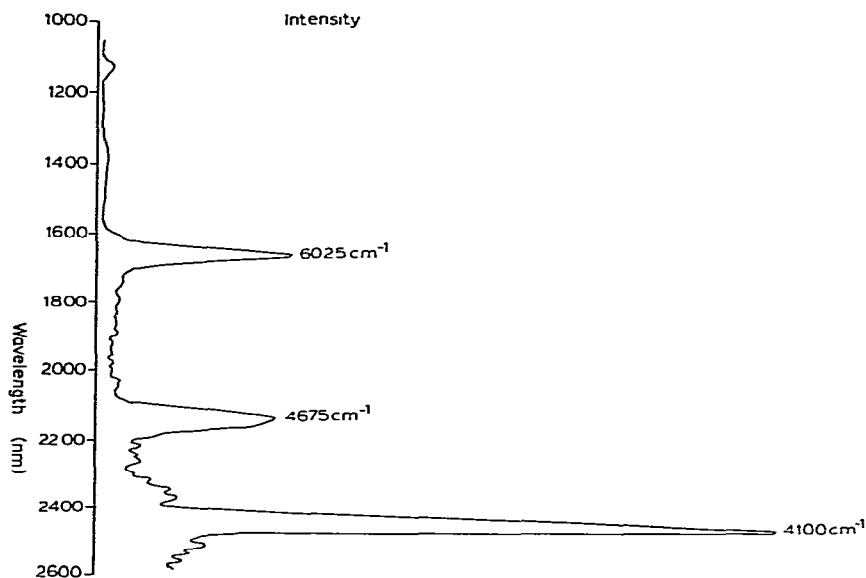


Fig. 1. The near-infrared PAS of benzene.

The PAS of toluene (Fig. 3) was examined in order to see the effect of adding an aliphatic group to benzene. The main effect is due to the presence of two types of $\nu(\text{C-H})$ in the infrared (aromatic, 3120 and aliphatic, 2910 cm^{-1}). In addition the ring bending and stretching modes are more complicated due to the presence of CH_3 and the reduction of symmetry. The C-H overtone band at

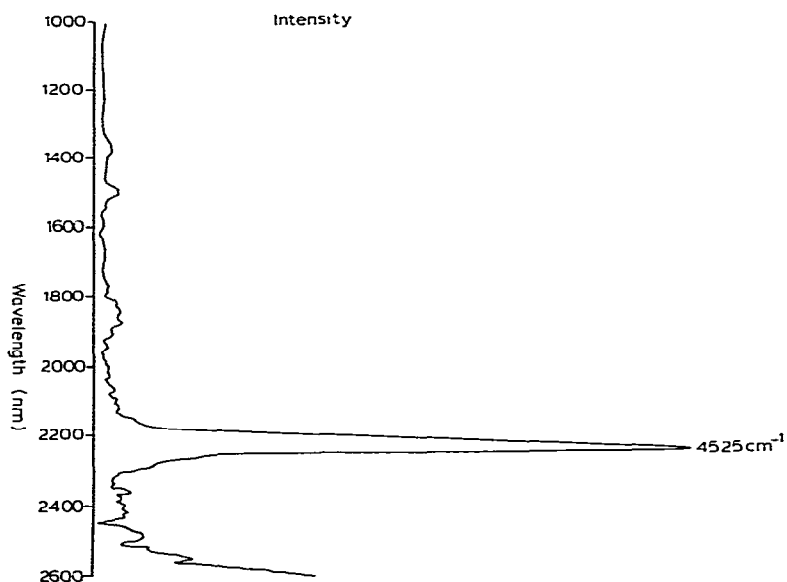


Fig. 2. The near-infrared spectrum of C₆D₆ (Aldrich 99.5% D).

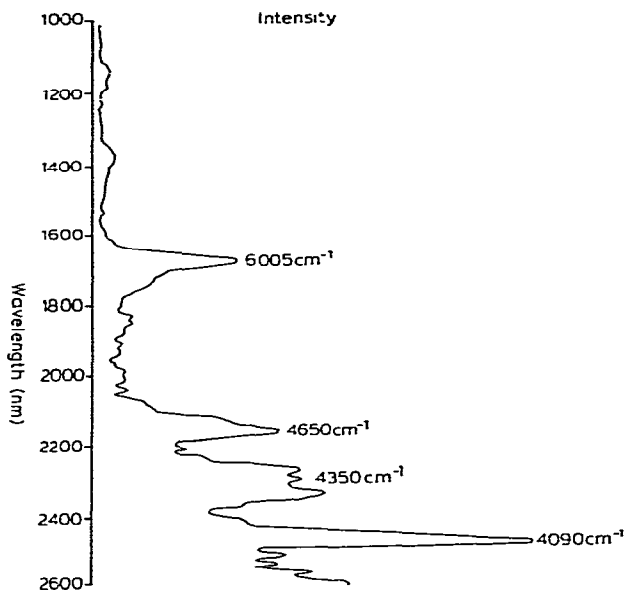


Fig. 3. The near-infrared spectrum of toluene, C_7H_8 .

6005 cm^{-1} (1665 nm) is seen to be broader than its benzene counterpart. The toluene peak is 20 nm wider at half height than the analogous benzene peak. The two combination bands of benzene are present in the PAS of toluene. Notable is the appearance of a new broad band in toluene at $4425\text{--}4310\text{ cm}^{-1}$ ($2260\text{--}2320\text{ nm}$). The assignment of the peak is consistent with it being a combination of the aliphatic C—H with the ring C—C stretching modes which appear from $1490\text{--}1440\text{ cm}^{-1}$.

The PAS of cyclohexane (Fig. 4) was used to confirm some of the toluene assignments. The C—H overtone arising from the pure aliphatic C—H stretch (2910 cm^{-1}) occurs at 5800 cm^{-1} (1725 nm). This would partially explain the broadness of the toluene overtone peak compared to benzene. The toluene overtone peak is wide enough to include contributions from the aromatic and aliphatic C—H stretch. A peak in cyclohexane at 4310 cm^{-1} (2320 nm) compares with the broad aliphatic combination band of toluene. Note the absence in cyclohexane of the peaks at 4675 (2140 nm) and 4100 cm^{-1} (2440 nm) which were assigned as aromatic ring stretching and bending combinations. Cyclohexane has instead a series of three peaks (see Table 1 and Fig. 4) whose assignments are consistent with combinations of $\nu(\text{C—H})$ with three strong infrared ring stretching and bending fundamentals (see IR of C_6H_{12} , Table 1).

The PAS of ferrocene (Fig. 5) consists of four main peaks. The peak at 6105 cm^{-1} (1638 nm) is assigned as the C—H stretch overtone ($\nu(\text{C—H})$ at 3080 cm^{-1}). The infrared of ferrocene has been the subject of numerous investigations [10,11] such that the assignments of infrared peaks are reasonably certain. The PAS peaks are combination bands of $\nu(\text{C—H})$ with the following: The PAS peak at 4495 (2225 nm) is a combination with the IR peak at 1400 cm^{-1} which is

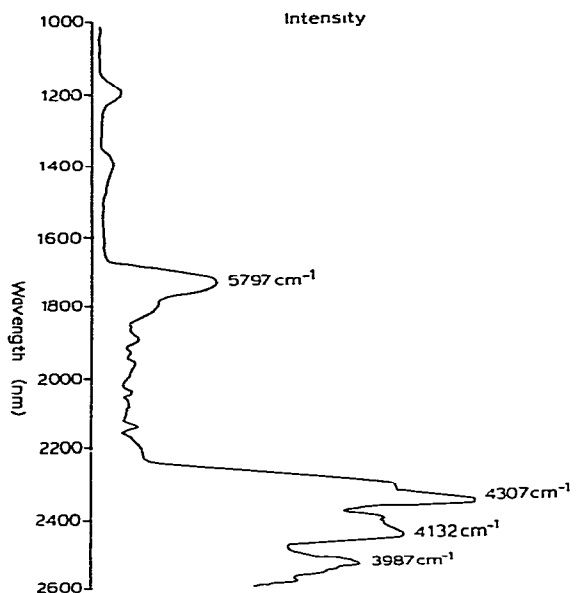


Fig. 4. The near-infrared spectrum of cyclohexane, C_6H_{12} .

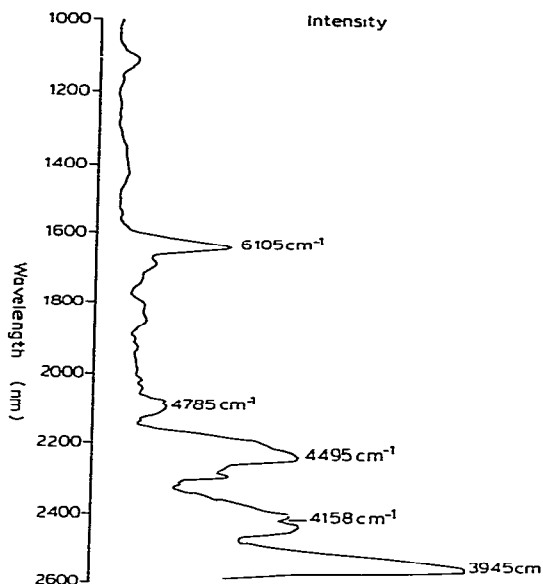


Fig. 5. The near-infrared spectrum of ferrocene, $FeCp_2$.

the C—C stretch; the doublet PAS peak centered at 4167 (2400 nm) is a combination band with the IR peaks at 1100 and 1000 cm^{-1} which are due respectively to the antisymmetric and symmetric ring breathing modes; the PAS peak at 3945 (2535 nm) is a combination of $\nu(C-H)$ with the IR peak at 810 cm^{-1} assigned to the C—H bend. Two lesser peaks are observed in the PAS of ferrocene whose assignments are less certain. These two, a broad peak from 4830–4773 cm^{-1} (2070–2095 nm) and the peak at 4367 cm^{-1} (2290 nm) may arise from combinations of $\nu(C-H)$ with two IR inactive bands: 1560 (C—C stretch) and 1257 cm^{-1} (C—H bend), respectively [10] (see below).

The PAS of $Cp_2Fe_2(CO)_4$ and $Cp_4Fe_4(CO)_4$ (Fig. 6 and 7) demonstrate that the salient features of the Fe—Cp unit are reproducible. In addition combinations with the carbonyls can be observed. The subtle differences that arise between the Fe—Cp units in these compounds and ferrocene are detected by PAS. Thus this technique demonstrates its ability to plot a fingerprint spectrum for a molecule. In both cases the $\nu(C-H)$ overtone appears in nearly the same manner as it does in ferrocene. The new feature in these two compounds is the combination band of $\nu(C-H)$ with the carbonyl fundamentals. The IR of $Cp_2Fe_2(CO)_4$ has two carbonyl bands at 1920 and 1745 cm^{-1} for the terminal and bridging carbonyls respectively. The tetrahedral molecule, $Cp_4Fe_4(CO)_4$, has a single band for the triply bridging carbonyls at 1610 cm^{-1} .

The PAS of $Cp_2Fe_2(CO)_4$ has two bands at 5115 (1955 nm) and 4920 cm^{-1} (2033 nm) which are assigned as combinations of $\nu(C-H)$ with the terminal and bridging carbonyls respectively. $Cp_4Fe_4(CO)_4$ has a PAS peak at 4785 cm^{-1} (2090 nm) which is assigned as the combination of $\nu(C-H) + \nu(C-O)$. The

TABLE 1
RELEVANT IR AND PAS PEAKS

vs = very strong, s = strong, m = medium, w = weak, vw = very weak, "/" represents peaks in a doublet or triplet

Compound	IR (cm ⁻¹)		PAS (cm ⁻¹ (nm))
I C ₆ H ₆	3070vs/3025vs 1030s	1470s	6025(1660), 4675(2140), 4100(2440)
II C ₆ D ₆	2260vs		4525(2210)
III C ₇ H ₈	3120vs/2910vs 1080s/1025s	1490vs/1450vs	6005(1665), 4717(2120)/4650(2150), 4425(2260)—4310(2320), 4090(2445)
IV C ₆ H ₁₂	2010vs 1250s 1035s/1010m	1440s	5797(1725), 4376(2285), 4307(2322), 4200(2380)/4132(2420), 3987(2508)
V C _{p2} Fe	3080w 1100s/1000s	1400m 810s	6105(1638), 4830(2070)—4773(2095), 4495(2225), 4367(2290), 4181(2392)/4132(2420), 3945(2535)
VI C _{p2} Fe ₂ (CO) ₄	3100vw 1110w/1050w/1010w/995w	1410w 825s	6154(1625), 5115(1955), 4920(2033), 4505(2220), 4425(2260)—4386(2780), 4167(2400)—4132(2420) 3968(2520), 3906(2560)
VII C _{p4} Fe ₄ (CO) ₄	3080vw 1115w/1060m/1008m	1420m 860m/830s/820s	6143(1628), 4785(2090), 4505(2220), 4153(2408), 3968(2520)
VIII C _{p4} Fe ₄ S ₄	3050w 1350w 1110w/1050m/1000m	1420m 830m/810s	6116(1635), 4484(2230), 4132(2420), 3945(2535)
IX C ₆ H ₆ Cr(CO) ₃	3090w 1150m, 1010m, 975w/960w, 900m	1440m 780s	6090(1642), 5025(1990), 4630(2160), 4464(2240) 4264(2345), 4115(2430), 3953(2530)
X CpCo(C ₄ Ph ₄)	3040—20w 1170w, 1105w, 1060w, 1020m, 1000w	1585m/1490s/1435m 910w, 805s, 780s, 740s	6017(1662), 4673(2140), 4505(2220), 4386(2280), 4090(2445), 3960(2525)
XI CpCo(CO) ₂	2920m [15] 1350m 1015w, 980w, 935w	1440m 810s	6154(1625), 4504(2220)/4454(2245) 4062(2462)/3976(2515)/3906(2560)

curious observation is that the carbonyl combination bands occur some 100 cm^{-1} higher in energy than would be predicted from simple addition of $\nu(\text{C-H})$ and $\nu(\text{C-O})$. For example, from the combination band for $\text{Cp}_4\text{Fe}_4(\text{CO})_4$ at 4785

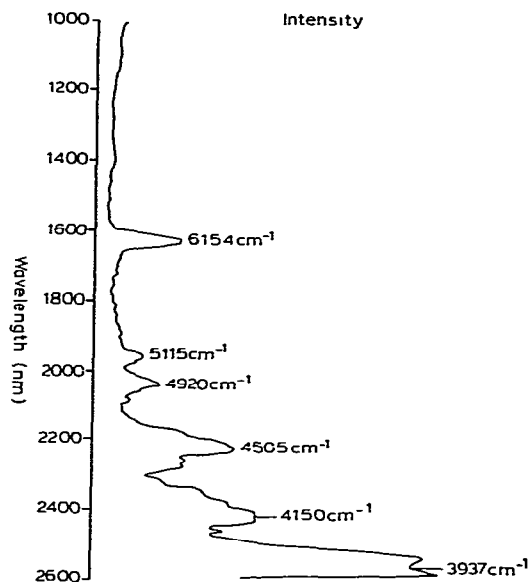


Fig. 6. The near-infrared spectrum of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$.

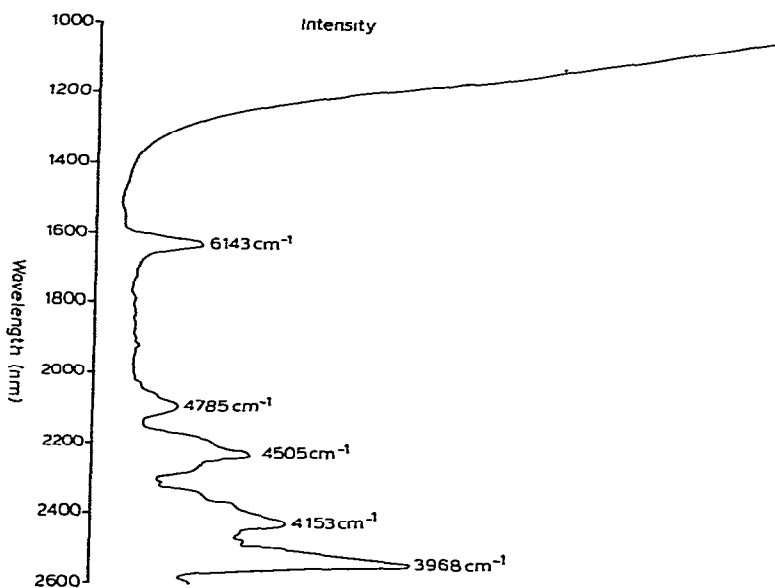


Fig. 7. The near-infrared spectrum of $\text{Cp}_4\text{Fe}_4(\text{CO})_4$. The "tail-off" from 1000–1400 nm is the low energy side of an electronic absorption.

one would expect $\nu(\text{C—O})$ to appear at 1705 cm^{-1} (and not the observed 1610 cm^{-1}). A possible explanation for this is that the combination bands arise from $\nu(\text{C—H})$ and all the carbonyl bands, both IR active and inactive, i.e., $\text{Cp}_4\text{Fe}_4(\text{CO})_4$, should have, in addition to the IR active T_2 band, Raman active T_2 and A_1 bands. Thus $\nu(\text{C—H})$ may combine with coupled carbonyl bands, not all of which are observed from IR alone.

Confirmation for the fact that the band at 4785 cm^{-1} (Fig. 7) is the combination band of $\nu(\text{C—H}) + \nu(\text{C—O})$ in $\text{Cp}_4\text{Fe}_4(\text{CO})_4$ comes from examination of the spectrum of $\text{Cp}_4\text{Fe}_4\text{S}_4$ (Fig. 8). $\text{Cp}_4\text{Fe}_4\text{S}_4$ is isostructural with $\text{Cp}_4\text{Fe}_4(\text{CO})_4$, where triply bridging sulfurs replace the triply bridging carbonyls. The IR spectra for these compounds are very similar except that the infrared for $\text{Cp}_4\text{Fe}_4\text{S}_4$ lacks the carbonyl stretch. As expected the PAS in Fig. 8 closely matches that for $\text{Cp}_4\text{Fe}_4(\text{CO})_4$. Note that the peak assigned to the $\nu(\text{C—H}) + \nu(\text{C—O})$ combination at 4785 cm^{-1} is absent in Fig. 8. The rest of the PAS for $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ and $\text{Cp}_4\text{Fe}_4(\text{CO})_4$ are essentially the same as the corresponding regions in ferrocene. Minor differences arise from the minor differences in the IR which exist between these compounds and ferrocene.

A number of other compounds were examined which display the metal-Cp "fingerprint region". These include Cp_2Ru , Cp_2TiCl_2 and a number of substituted ferrocenes.

The PAS of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (Fig. 9) reinforced a number of the principles described above for an organometallic with a ring other than cyclopentadiene. The $\nu(\text{C—H})$ overtone occurs at 6090 cm^{-1} (1642 nm). The combination band

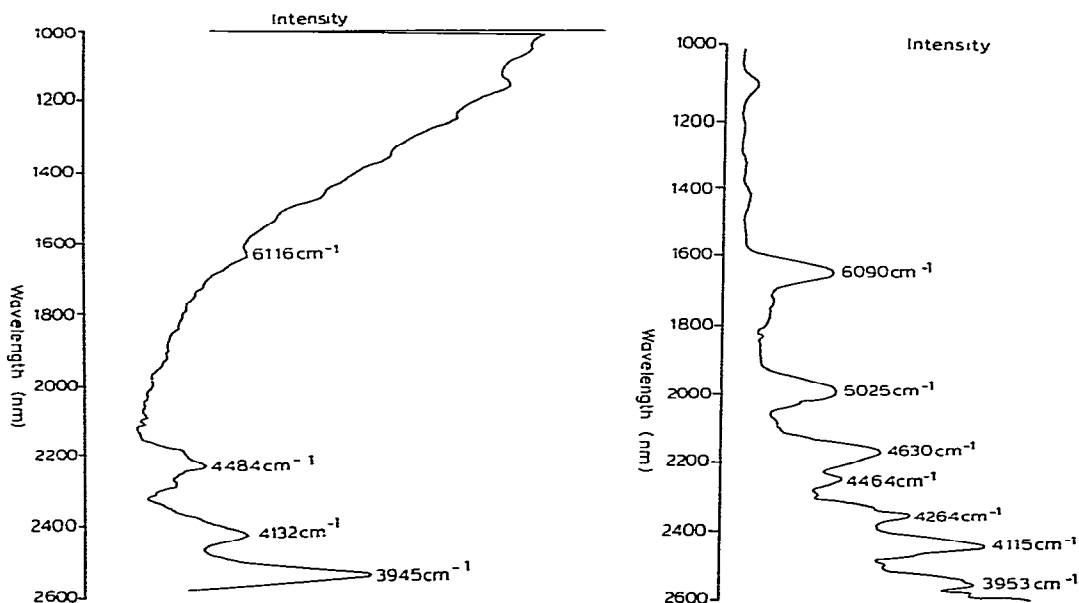


Fig. 8. The near-infrared spectrum of $\text{Cp}_4\text{Fe}_4\text{S}_4$. An electronic absorption extends from the visible to midway through the near IR (ca. 1800 nm).

Fig. 9. The near-infrared spectrum of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$.

of $\nu(\text{C-H})$ with carbonyl is a single broad band at 5025 cm^{-1} (1990 nm) (width at half height 70 nm). The infrared spectrum has two carbonyl bands at 1950 and 1840 cm^{-1} . Unlike the iron examples above, this molecule possesses C_{3v} symmetry and should have the same two IR and Raman bands. The observed PAS peak is taken to be the combination of $\nu(\text{C-H})$ and the two coupled carbonyl peaks.

There are two effects on the benzene ring upon metal coordination; redistribution of electron density and lowering of local symmetry. The consequence of the former effect is to shift in energy the ring fundamental bands while the consequence of the latter effect is the appearance of new bands in the infrared [12,13]. Further examination of Fig. 9 demonstrates these points further (by comparison to benzene in Fig. 1). Two bands in Fig. 9 closely match the two combination bands of benzene. For $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ they occur at 4630 (2160 nm) and 4115 cm^{-1} (2430 nm) and correspond to the combination of $\nu(\text{C-H})$ with the C-C stretch/ring bend and the HCC bending mode respectively. Note (from Table 1) that the former peak is shifted 45 cm^{-1} higher in energy while the latter peak is shifted 15 cm^{-1} lower in energy. The consequence of reduced local symmetry is the observation of new (compared to free benzene) bands in the IR. These are observed in the PAS at 4464 (2240 nm), 4264 (2345 nm) and 3953 cm^{-1} (2530 nm). The latter two peaks are consistent with combinations of $\nu(\text{C-H})$ with ring IR peaks at ca. 1150 and ca. 900 cm^{-1} , respectively. Assignment of the PAS peak at 4464 is less certain. The difficulty in assigning these bands may be related to the fact that combination bands can arise from infrared inactive bands.

A final compound was examined which contained a ring other than Cp. Fig. 10 shows the PAS of $\text{CpCo}(\text{C}_4\text{Ph}_4)$. The C-H overtone at 6017 cm^{-1} (1662 nm)

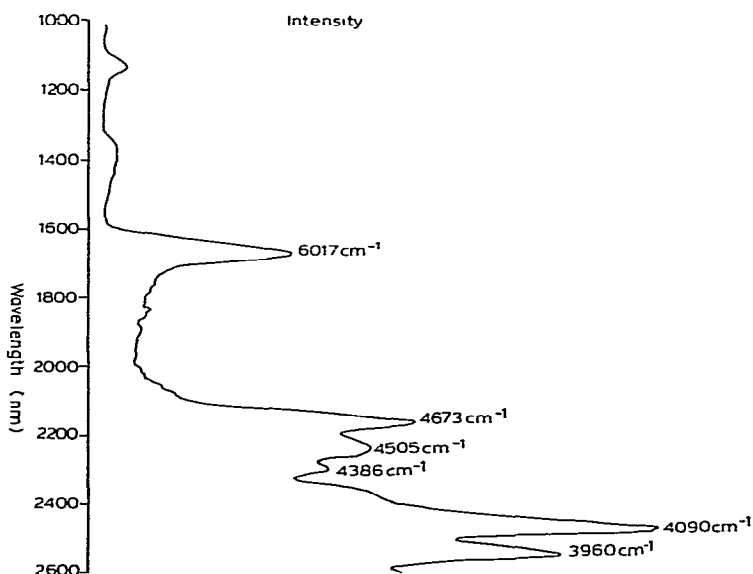


Fig. 10. The near-infrared spectrum of $\text{CpCo}(\text{C}_4\text{Ph}_4)$.

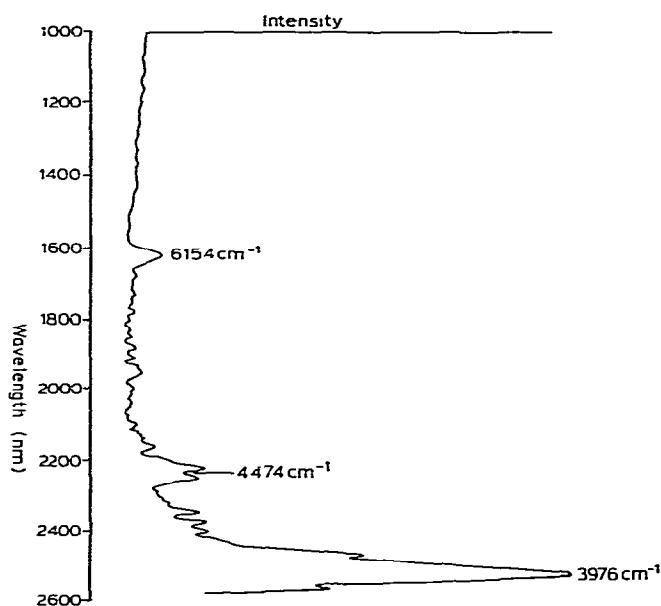


Fig. 11. The near-infrared spectrum of $\text{CpCo}(\text{CO})_2$.

for $\text{CpCo}(\text{C}_4\text{Ph}_4)$ reflects the lower C—H stretch for this compound ($3020\text{--}40\text{ cm}^{-1}$) as compared to ferrocene (Fig. 5). This spectrum is complicated by the fact that in addition to the C_5H_5 ring, peaks arise due to the four membered ring alone and the phenyl groups attached to it. One can identify those peaks due to Cp by comparing Fig. 10 to the PAS of ferrocene (Fig. 5) and to the PAS of $\text{CpCo}(\text{CO})_2$ (Fig. 11). Two bands for $\text{CpCo}(\text{C}_4\text{Ph}_4)$ at 4505 (2220 nm) and 3960 cm^{-1} (2525 nm) match the two bands in Fig. 11 for $\text{CpCo}(\text{CO})_2$. In addition these bands match the two bands in ferrocene which were assigned as combinations of $\nu(\text{C—H})$ with $\nu(\text{C—C})$ and the C—H bend. Three additional bands for $\text{CpCo}(\text{C}_4\text{Ph}_4)$ at 4673 (2140 nm), 4386 (2280 nm) and 4090 cm^{-1} (2445 nm) arise from combination bands of $\nu(\text{C—H})$ with IR bands which are due to either Ph or the C_4 ring (no certain distinction is possible).

Conclusion

PAS is finding increasing use in many fields of analysis. Use of the near IR region can be as useful as infrared in terms of measuring a fingerprint spectrum for a compound. It has been demonstrated that aromatic compounds can be distinguished from aliphatic compounds. The different combination bands that arise as a consequence of combinations of the C—H stretch with various fundamentals make possible the distinction between benzene and cyclohexane and between benzene and toluene. The fundamentals which arise from the cyclopentadienyl ring are reproducible among a number of iron organometallics. The combination of $\nu(\text{C—H})$ with $\nu(\text{C—O})$ was observed for the carbonyl compounds. The near IR of two organometallics with rings other than Cp was measured by

PAS. Consistent with the fact that different ring systems give rise to different IR fundamentals, the different ring systems gave rise to bands unique to these systems. In conclusion, PAS enables one to measure fingerprint spectra of materials which cannot be measured via conventional spectroscopy, i.e., opaque materials. Thus, application of this technique toward insoluble polymeric compounds, surface coatings and the like, is expected.

Acknowledgements

Funding was provided by DOE Office of Material Sciences. Drs. Charles Wiedenheft and Aaron Burke are thanked for their helpful discussions. Michael Natale is acknowledged for his technical assistance.

References

- 1 G.F. Kirkbright and S.L. Castleden, *Chem. Brit.*, 16 (1980) 661.
- 2 (a) D.W. Vidrine, *App. Spec.*, 34 (1980) 314; (b) M.G. Rockley, *App. Spec.*, 134 (1980) 405; (c) J.B. Kinney, R.H. Staley, C.L. Reichel and M.S. Wrighton, *J. Amer. Chem. Soc.*, 103 (1981) 4273.
- 3 S.L. Castleden, G.F. Kirkbright and K.R. Menon, *Analyst*, 105 (1980) 1076.
- 4 M.J. Adams, B.C. Beadle and G.F. Kirkbright, *Anal. Chem.*, 50 (1978) 1371.
- 5 For a detailed description of the instrument the reader is referred to J.W-p. Lin and L.P. Dudek, *Anal. Chem.*, 51 (1979) 1627.
- 6 M.D. Rausch and R.A. Gennetti, *J. Org. Chem.*, 35 (1970) 3388.
- 7 R.B. King, *Inorg. Chem.*, 5 (1966) 2227.
- 8 R.A. Schunn, C.J. Fritchie and C.T. Prewitt, *Inorg. Chem.*, 5 (1966) 892.
- 9 N.B. Colthrup, L.H. Daly, S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, (Acad. Press, NY 1975).
- 10 The 1560 cm^{-1} is weakly observed in the Raman spectrum whereas the band calculated at 1257 cm^{-1} is both IR and Raman inactive.
E.R. Lippincott and R.D. Nelson, *Spectrochim. Acta*, 10 (1958) 307.
- 11 H.P. Fritz, *Adv. Organomet.*, 1 (1964) 239.
- 12 R.E. Humphrey, *Spectrochim. Acta*, 17 (1961) 93.
- 13 H.P. Fritz and J. Manhot, *Spectrochim. Acta*, 18 (1962) 171.
- 14 As in the iron carbonyl compounds, it is possible for a combination band to arise from IR inactive bands, if the direct product of the character of each vibration gives a character which is IR active [9].
- 15 It is not clear why the C-H stretch in $\text{CpCo}(\text{CO})_2$ occurs as low as it does. Note that all the other aromatic C-H stretches occur above 3000 cm^{-1} .