Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE INFRARED AND RAMAN SPECTRA OF CYCLOPENTADIENYLVANADIUM TETRACARBONYL DERIVATIVES: EVALUATION OF THE CARBON-OXYGEN FORCE CONSTANTS

J. R. DURIG, A. L. MARSTON*,
Department of Chemistry, University of South Carolina, Columbia, South Carolina (U.S.A.)
R. B. KING** AND L. W. HOUK***
Department of Chemistry, University of Georgia, Athens, Georgia (U.S.A.)
(Received November 15th, 1968)

SUMMARY

Infrared (250–4000 cm^{-1}) and laser Raman spectra (75–3300 cm^{-1}) were obtained on $C_5H_5V(CO)_4$ and $CH_3COC_5H_4V(CO)_4$. A vibrational assignment is proposed which is based upon the concept of "local symmetry". The cyclopentadienyl ring breathing frequency was found to be associated with the strong sharp Raman line at 1117 cm^{-1}. Force constants calculated for the carbonyl stretching vibrations were comparable to those of similar π-bonded metal carbonyls.

INTRODUCTION

Recent work has demonstrated a high correlation between the proton NMR chemical shift of the π-C_5H_5 ring and the k(CO) stretching force constants for 78 cyclopentadienyl metal carbonyl derivatives of the first row (3*d*) transition metals[1]. This made of interest an investigation of a similar correlation for derivatives of the second row (4*d*) transition metals. However, the greatest variety of available cyclopentadienyl metal carbonyl derivatives of the 4*d* transition metals are the molybdenum derivatives of the type $C_5H_5Mo(CO)_3R$ (I). Unfortunately, a compound of structure (I) has three ν(CO) frequencies but four force constants involving the carbon–oxygen bonds (the two stretching force constants k_1 and k_2 and the interaction force constants k_{12} and k_{22}). Therefore ν(CO) data on $C_5H_5Mo(CO)_3R$ derivatives are insufficient to determine these force constants. The most reasonable solution to this dilemma is an approach similar to that used by Cotton and Kraihanzel[2] for certain octahedral metal carbonyl derivatives where a relationship between two interaction force constants is assumed giving but one interaction force constant k_i (rather than two) to be determined from the ν(CO) frequency data.

A compound of closely related stereochemistry is cyclopentadienyltetracarbonylvanadium, $C_5H_5V(CO)_4$ (II). This compound has three force constants involving

---

* On special assignment to the University of South Carolina from the Savannah River Laboratory, Aiken, South Carolina.
** Fellow of the Alfred P. Sloan Foundation, 1967–1969.
*** Post-doctoral Fellow at the University of Georgia, 1967–1968.

the carbon–oxygen bonds. One of these force constants is a stretching force constant (k) and the other two are interaction force constants involving interactions between carbonyl groups located across the *side* (k_s) or the diagonal (k_d) of the square with the carbon atoms at the vertices. Since $C_5H_5V(CO)_4$ (II) (C_{4v} local symmetry) has three ν(CO) frequencies (A_1, B_1 and E) it is possible to calculate the three force constants k, k_s, and k_d directly from the ν(CO) data. Such an empirical determination of a relationship between k_d and k_s in $C_5H_5V(CO)_4$ (II) would provide a basis for the assumption of a relationship between the analogous force constants k_{22} and k_{12} in compounds of the type $C_5H_5Mo(CO)_3R$ (I). It was necessary to use Raman rather than IR data to obtain the ν(CO) frequencies of $C_5H_5V(CO)_4$ (II) since all three ν(CO) vibrations (A_1, B_1 and E) are Raman-active but only two of these normal modes (A_1 and E) are IR-active. In order to provide an indication of the effect of structural changes on the relationship between k_d and k_s the ν(CO) frequencies of the acetyl derivative $CH_3COC_5H_4V(CO)_4$ (III) were also measured and the corresponding force constants k, k_s, and k_d calculated.

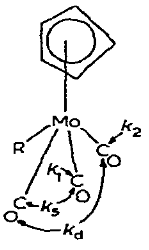
We also were interested in pursuing the concept of "local symmetry" that was proposed by Cotton *et al.*[3] and used by Lippincott *et al.*[4] to simplify the interpretation of the vibrational spectra of $C_5H_5Mn(CO)_3$. According to Adams[5], few complete vibrational studies have been made of metal carbonyls substituted with π-bonded rings. The vibrational spectra of numerous metal carbonyls have been investigated but since these compounds are colored, most workers have contented themselves with IR absorption data. The advent of the helium–neon laser as an excitation source for Raman spectra affords the possibility of obtaining Raman scattering frequencies and polarization data.

TABLE 1

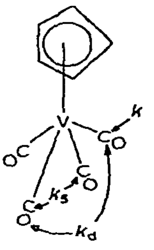
PREVIOUS VIBRATIONAL DATA ON π-CYCLOPENTADIENYLVANADIUM TETRACARBONYL COMPOUNDS (cm^{-1})

π-$C_5H_5V(CO)_4$		π-$CH_3COC_5H_4V(CO)_4$	
Piper, Cotton and Wilkinson[7]	Fritz[9]	Fischer and Plesske[8]	Fritz[9]
Solution	*Solid?*	*Solid*	*Solid?*
3110 m	3096		3165
	?		3145
2019 vs	2016	2045 s φ	2045
1951 vs		1972 (sh)	
solid only			
1919 vs	1916	1941 s	1949?
		1683 acetyl	
1430 m	1427		1427
1370 w			
		1285 acetyl	
1120 vw	1122		1120
1060 w			
1010 m	1012	No absorption at 1000	?
840 s	839		846
	?		?
	353		374

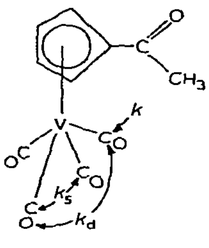
The first complete vibrational analysis of a π-cyclopentadienyl metal carbonyl [$C_5H_5Mn(CO)_3$] was reported by Lippincott *et al.*[4] who first used Raman data. Their recent paper provided a model for our similar analysis of $C_5H_5V(CO)_4$ and $CH_3COC_5H_4V(CO)_4$. The rather meagre previous vibrational data for these compounds are shown in Table 1.



(I)



(II)



(III)

EXPERIMENTAL

The samples of $C_5H_5V(CO)_4$ and $CH_3COC_5H_4V(CO)_4$ were prepared by published procedures[6-8]. The samples used were purified by vacuum sublimation at 100°/0.1 mm. This type of compound undergoes photodecomposition and is air-sensitive. Halogenated hydrocarbons in particular cause decomposition of samples dissolved in them. These complexes are much more sensitive to oxygen when in solution. All traces of oxygen, therefore, must be removed from solvents. The best technique is to sublime the sample into the cell and then add solvent by distillation. Our attempts to get Raman spectra in benzene solution were unsuccessful although Lippincott *et al.* were able to obtain Raman spectra of benzene solutions of $C_5H_5Mn(CO)_3$[4]. Fischer and Plesske[8] who first prepared $CH_3COC_5H_4V(CO)_4$ reported the red monoclinic-crystals to be air stable but the solutions to decompose rapidly upon air exposure. We found this to be the case; in fact, the solutions decomposed so rapidly in the laser beam to yield turbid solutions and gas bubbles that we could not even observe the strongest Raman lines of the solvents used in the investigation.

IR spectra were recorded with Perkin–Elmer 521 and 621 spectrophotometers from 4000 to 250 cm^{-1}. Atmospheric water vapor was removed from the spectrophotometer housing by flushing with dry nitrogen. In the high frequency region the instruments were calibrated in the usual manner[10] whereas the lower frequency region was calibrated by using atmospheric water vapor and the assignments of Randall *et al.*[11]. All reported frequencies are expected to be accurate to $\pm 2\,cm^{-1}$. Solid spectra were recorded of Nujol mulls and KBr disks. Solution spectra were obtained in CS_2, CCl_4, and cyclohexane solutions in path lengths ranging from 0.1 mm to 0.5 mm. The spectra of the pure solvents also were reported under identical conditions.

Raman spectra were obtained with a Cary Model 81 spectrometer which had a Spectra–Physics helium–neon laser for excitation. Spectra were taken in the solid state and in cyclohexane solution. The laser beam decomposed solutions of $CH_3COC_5H_4V(CO)_4$ so rapidly that it was impossible to obtain reliable data for this compound in solution. The solid itself gave evidence of decomposition in the laser beam. Therefore frequent sample changes were needed to record the entire spectra from 75–3300 cm^{-1}.

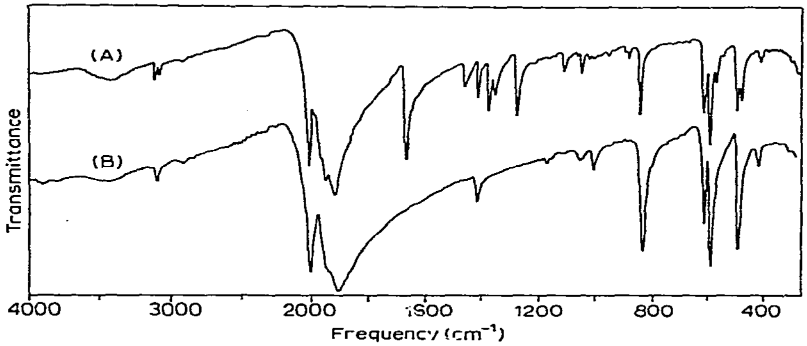


Fig. 1. Infrared spectra of solid $C_5H_5V(CO)_4$ (B) and $CH_3COC_5H_4V(CO)_4$ (A) (KBr pellets).

The IR and Raman spectra of solid $C_5H_5V(CO)_4$ and $CH_3COC_5H_4V(CO)_4$ are shown in Figs. 1 and 2. The discontinuities in the Raman spectra correspond to introduction of fresh sample into the laser beam. Figure 3A shows the Raman spectra of a cyclohexane solution of $C_5H_5V(CO)_4$ and the solid in the carbonyl stretching region, whereas Fig. 3B compares IR and Raman data of the same cyclohexane solutions in the carbonyl stretching region. The series of combination bands reported by Lippincott to lie between 2400–2700 cm^{-1} also were evident in the IR spectra of the vanadium compounds but are omitted from Tables 4 and 5.

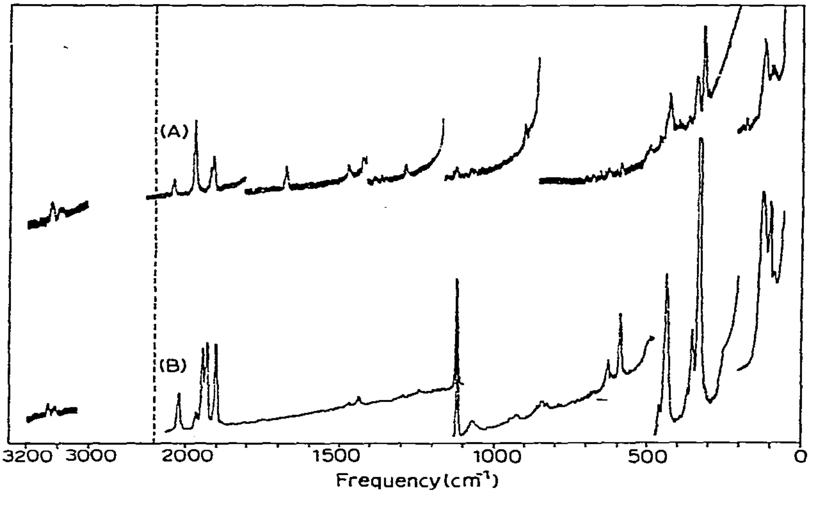


Fig. 2. Raman spectra of solid $C_5H_5V(CO)_4$ (B) and $CH_3COC_5H_4V(CO)_4$ (A) (powder).

DISCUSSION

(*a*). *Vibrational analysis*

We assume that there is little interaction between the ring and the $V(CO)_4$ vibrations so that the method of "local symmetry" is applicable. The ring will behave as though it had C_{5v} symmetry and the $V(CO)_4$ moiety as though it had C_{4v} symmetry. In C_{4v} symmetry the 21 normal modes of the moiety $V(CO)_4$ span the representations

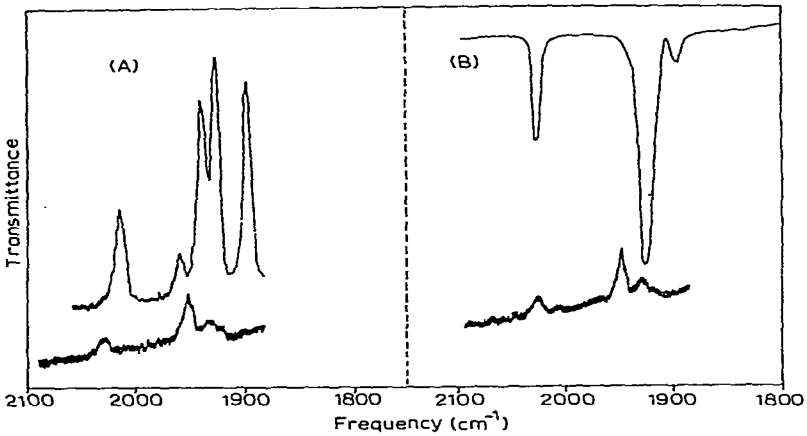


Fig. 3A. Comparison of solution and solid Raman spectra in carbonyl stretch region for $C_5H_5V(CO)_4$.
Fig. 3B. Infrared and Raman spectra of carbonyl stretch region for cyclohexane solutions of $C_5H_5V(CO)_4$.

$4A_1+A_2+4B_1+2B_2+5E$. Of these, A_1 and E are IR-active; A_1, B_1, B_2 and E are Raman-active. The "group" vibrations are divided into symmetry species as shown in Table 3. The ring-to-$V(CO)_4$ skeletal motions are A_1, A_2, and $2E$. For the cyclopentadienyl ring with C_{5v} symmetry the 24 normal modes are distributed as $2A_1+A_2+3E_1+4E_2$ in the plane of the ring and $A_1+E_1+2E_2$ perpendicular to it. Species A_1 and E_1 are IR-active; A_1, E_1 and E_2 are Raman-active. This information is summarized in Table 2.

TABLE 2

SPECTRAL EXPECTATIONS FOR π-CYCLOPENTADIENYL RING VIBRATIONS WITH C_{5v} SYMMETRY

C_5	C_5H_5	C_5	C–H	Activity
A_1	3	1 (ω)	2 (ν, γ)	p, M_z
A_2	1		1 (δ)	fb, ia
E_1	4	1 (ω)	3 (ν, δ, γ)	dp, M_x, M_y
E_2	6	3 (ω, Δ, γ)	3 (ν, δ, γ)	dp, ia

For the acetyl-substituted compound the point group symmetry of the ring is

TABLE 3

SPECTRAL EXPECTATIONS FOR SKELETAL AND RING-TO-SKELETON VIBRATIONS OF $C_5H_5V(CO)_4$ WITH C_{4v} SYMMETRY

C_{4v}	$C_5H_5V(CO)_4$	VC_4	C≡O	Ring-to-skeleton	Activity
A_1	5	2 (ν, δ)	2 (ν, δ)	1 (str.)	p, M_z
A_2	2		1 (δ)	1 (twist)	fb, ia
B_1	4	2 (ν, δ)	2 (ν, δ)		dp, ia
B_2	2	1 (δ)	1 (δ)		dp, ia
E	7	2 (ν, δ)	3 (ν, δ, δ)	2 (tilt, bend)	dp, M_x, M_y

either C_s or C_1. All ring vibrations will be IR and Raman active. In the absence of polarization data, there is little benefit to be gained from the group theoretical treatment of these comparatively low symmetries. Presumably, the symmetry of the V(CO)$_4$ moiety remains C_{4v}, although the π-bonded ring and V(CO)$_4$ skeletal modes may exhibit greater interaction with consequent relaxation of the C_{4v} selection rules.

Schematic representations of likely normal modes of the M(CO)$_3$ moiety are depicted in ref. 12; those of V(CO)$_4$ should be more numerous, but similar. The vibrational forms of the cyclopentadienyl anion are given in Fritz's review[9].

In the absence of extensive Raman data on solutions where the selection rules should hold, only a crude assignment of the internal modes can be made from the solid spectral data. The problem is further compounded by the low site symmetry in the solid. The crystal structure is reported to be *Pnma* with four molecules in the unit cell[13]; the cyclopentadienyl rings are disordered and have two possible orientations with respect to the V(CO)$_4$ moiety. As similarly noted by Lippincott with π-C_5H_5Mn(CO)$_3$, the "local symmetries" of ring and M(CO)$_4$ moiety cannot be sub-groups of this D_{2h}^{16} space group; hence, one should also consider the lower site group (C_i or C_s) symmetry. This leads to the expectation that all vibrations may be infrared and/or Raman active and degenerate vibrations of C_{5v} and C_{4v} "local symmetry" may be split in the solid as a result of either site group or factor group splitting. As Tables 4 and 5 show, the number of precise coincidences between the IR mull spectra and the powder Raman spectra is comparatively small, an observation from which we are led to conclude that different components of degenerate modes are being observed in the two cases and that the selection rules are frequently violated for a C_{4v} model of the V(CO)$_4$ moiety.

The following generalizations* aided in assignment of vibrational modes especially for the metal–carbonyl portion of the molecule:

(1) Totally symmetric vibrations always occur in Raman spectra, are sharp, and usually have high intensity.
(2) Degenerate modes usually give broad bands that often are split in solid phase spectra.
(3) External modes shift as a function of temperature.
(4) In ring–metal–ligand "sandwich" compounds only vibrations that have vector components along the molecular axes can couple through the central metal atoms.
(5) The A_1 carbonyl stretch frequency varies with metal and number of CO groups bonded to the metal.
(6) CMC angle deformations are always near 100 cm^{-1}.
(7) MC stretching vibrations are rarely above 500 cm^{-1} in neutral species.
(8) MCO angle deformations are sensitive to environment and can be anywhere between 735 and 235 cm^{-1}.
(9) All M–C stretching frequencies have higher intensity and fall at lower frequencies than the MCO deformations.

The assignments will be discussed in two parts:

(a) the cyclopentadienyl ring
(b) the V(CO)$_4$ moiety and the six motions of the ring with respect to the V(CO)$_4$ moiety.

---

* These stem from the cumulative experience of the authors and Adams[14].

TABLE 4

OBSERVED INFRARED AND RAMAN BANDS AND THEIR ASSIGNMENT FOR $C_5H_5V(CO)_4$ (cm^{-1})

Infrared				Raman		Assignment
Solution		Solid		Solution	Solid	
CS_2	CCl_4	KBr	Mull	C_6H_{12}		
3940 w						
3860 w						
3840 w						
					3128	A_1 CH str.
3115 w, m	3110 w	3100 m	3100 m		3108	E_1, E_2 CH str.
		2915 w	N			
2080 w						
2030 s	2030 s	2015 s	2020 s	2031 w	2015 m	A_1 CO str.
					1960 w	^{13}CO
		1940 (sh)	1950 w	1954 m	1940 s	B_1 CO str.
1920 vs (br)	1930 s (br)	1910 vs (br)	1920 s	1933 w	1927 s	E CO str.
			1890 w		1897 s	
CS_2			N		1462 w (br)	E_2 C=C str.
		1420 m			1434 w (br)	E_1 C=C str.
1290 w			1300 w			
1225 vw					1237 vw	A_2 ip CH def.
1178 w, m		1175 w	1175 w (br)			E_2 ip CH def.
1120 w		1115 w			1117 s	A_1 ring breath.
1060 m		1055 w (br)	1055 w (br)		1065 w (br)	E_2 op CH def.
1002 s		1005 w	1005 m			E_1 ip CH def.
950 w		950 vw	950 vw			
		910 vw			917 w (br)	E_2 ip ring def.
835 m		835 s (br)	835 s		838 w (br)	A_1 op CH def.
822 s					822 w (br)	E_1 op CH def.
					623 w	A VCO def.
		615 s	615 s		610 vw	E VCO def.
595 vs		590 s	590 s			E VCO def.
					584 m	B_1,B_2 VCO def.
495 vs		495 s	495 s			E VC str.
490 (sh)					487 w (br)	E_2 op ring def.
					456 w	B_1 VC str.
CS_2		425 m	425 m		432 s	A_1 VC str.
					362 w	
					349 m	E ring tilt
		325 w	325 (sh)		329 vs	A_1 ring–V str.
					240 w	A_2 ring twist
					122 m (br)	A_1, E CVC def.
					99 m	E ring–V–$(CO)_4$ bend
					84 w	B_1 CVC def.

In his review, Abel[15] emphasized both the need to compare frequencies of IR spectra obtained in the same solvent and the superiority of solution spectra to those obtained on mulls or halide disks. The same admonitions would apply to the comparison of IR with Raman spectral data; hence, in the absence of complete spectral data for solution and related Raman polarization measurements, our assignments lean heavily on those of Lippincott *et al.*[4] for $C_5H_5Mn(CO)_3$.

The five CH stretching modes obviously lie in the region 3125–2840 cm^{-1}. However, the low sensitivity of the detector for the laser spectrometer in this spectral

TABLE 5

OBSERVED INFRARED AND RAMAN BANDS AND THEIR ASSIGNMENT FOR $CH_3COC_5H_4V(CO)_4$ (cm^{-1})

Infrared				Raman	Assignment
Solution		Solid		Solid	
CS_2	CCl_4	KBr	Mull		
		3120 m	3120	3125	A_1 CH str.
3110 m	3110 w	3095 m	3095	3090	E_1, E_2 CH str.
		2930 w	N		CH_3 str.
2035 m	2035 s	2030 s	2035 s	2030 m	A_1 CO str.
	1960 m	1970 (sh)	1960 m	1963 s	B_1 CO str.
		1950 m			
1935 s (br)	1930 s (br)	1922 vs	1935 s	1910 w (sh)	
				1905 s	E CO str.
1680 vs		1670 s	1670 s	1672 m	Acetyl CO
CS_2		1465 m	N	1470 m	Acetyl and E_2 C=C str.
		1420 m	1420 m	1420 m	Acetyl and E_1 C=C str.
		1380 m	N	1380 w	Acetyl
1360 m		1360 m	N	1350 w	Acetyl
1280 vs		1282 s	1280 s	1282 w	Acetyl
1220 w		1225 vw	1225 vw		A_2 ip CH def.
1170 w		1175 vw	1175 vw		E_2 ip CH def.
1120 s		1118 w	1118 m	1120 w	A_1 ring breathing
1060 w		1070 w	1070 w	1070 w	E_2 op CH def.
1045 m		1055 w	1055 m		E_1 ip CH def.
1025 w		1030 w	1030 w		
1015 vw		1015 w	1015 w		
1000 vw					
960 w		960 w	960 w		
		940 (sh)	940		
895 w		900 (sh)	900 w	895 w	E_2 ip ring def.
			890 m		E_1 op CH def.
CS_2		845 (sh)	845 s (sh)		A_1 op CH def.
		840 s			
				675 w	A_2 VCO def.
620 s		620 s	620 s	625 w	A_1 VCO def.
595 vs		600 vs	600 vs	600 vw	E VCO def. and acetyl
		580 w	580 s	582 m	B VCO def.
		555 vw (sh)	555 w		
495 s		500 m	500 s		E VC str.
485 (sh)		490 m	490 s	490 m (br)	E_2 op ring def.
				450 w	B_1 VC str.
CS_2		422 w	425 w	425 s	A_1 VC str.
		395 vw	390 vw	392 w	Acetyl?
				336 m	E ring tilt
		315 vw		315 s	A_1 ring–V str.
265 m				265 w	
				180 w	A_2 twist ring–V–$(CO)_4$
				120 s	A, E CVC def.
				90 m	E ring–V–$(CO)_4$ def. and B_1 CVC def.

range makes difficult their observation and assignment. The band at 3128 cm^{-1} is assigned to A_1 and the solid IR band at 3115 cm^{-1} to the E_1 mode. A solid IR band at 3090 cm^{-1} may be the E_2 mode. The two C=C stretching modes. E_1 and E_2, are observed at 1434 and 1462 cm^{-1} in the solid Raman and the E_1 at 1420 cm^{-1} in IR spectra of the solution.

The assignment of the C_5H_5 ring breathing frequency has been a subject of considerable debate. According to Fritz[9], Stammreich found the lines at 1408 and 1104 cm^{-1} in ferrocene to both be polarized and thus be totally symmetric. Since only two totally symmetric modes were expected in this region for ferrocene, the ring breathing mode and an out-of-plane C–H deformation (out-of-phase between the 2 rings), they were accordingly assigned. One argument for assigning the breathing mode to the higher frequency was the observation that the 1100 cm^{-1} band is weak or absent from IR spectra of ionic metal cyclopentadienides but it would be forbidden if these compounds actually had D_{5h} symmetry. Lippincott argues that the breathing frequency should be very intense in the Raman and should fall near the frequency for the breathing mode in benzene, ~1000 cm^{-1}. He thus assigned the 1104 cm^{-1} band in $C_5H_5Mn(CO)_3$ to the breathing mode. There is little doubt that the strong sharp Raman band at 1117 cm^{-1} is the A_1 ring breathing mode. In the acetyl-substituted compound this band is considerable weaker as expected.

The remaining assignments of the in-plane and out-of-plane hydrogen deformations for the π-cyclopentadienyl ring modes very closely parallel those of Lippincott. The assignments of the acetyl group frequencies are predicated upon IR data of Thompson and Torkington[16] and Bellamy for aryl ketones such as acetophenone. The A_2 and E_2 ring modes in $C_5H_5V(CO)_4$ are weak in the IR as expected from the selection rules. All assignments are summarized in Table 6. In the absence of polarization or deuterium substitution data, it is unreasonable to discuss the ring assignments further.

The assignment of the $V(CO)_4$ vibrations is facilitated by assuming the C_{4v} selection rules hold reasonably well for solid $C_5H_5V(CO)_4$ and are considerably relaxed for solid $CH_3COC_5H_4V(CO)_4$. This means that the B modes will appear in the Raman, but not in the IR spectra of $C_5H_5V(CO)_4$; however, the bands due to B modes probably will be evident in the IR spectra of $CH_3COC_5H_4V(CO)_4$. Because of their importance in the force constant calculations, the assignments of the carbonyl stretching modes will be discussed first.

To compare band frequencies and intensities, IR and Raman scans of the carbonyl stretching region were made on freshly prepared solutions of $C_5H_5V(CO)_4$ in cyclohexane (see Fig. 3B). The A_1 mode appeared with medium intensity in both spectra; the E mode appeared strong in the IR and medium in the Raman at 1930 cm^{-1}; and the B_1 mode appeared strong in the Raman at 1950 cm^{-1} and was absent from the IR.

In IR spectra of CCl_4 solutions of $CH_3COC_5H_4V(CO)_4$ the symmetry-forbidden B_1 mode appeared as a weak band at 1960 cm^{-1}. With this apparent relaxation of the selection rules, presumably due to interactions between the acetyl-substituted ring and the $V(CO)_4$ moiety, an effort was made to resolve the E mode at 1930 cm^{-1}. This band is markedly broader in the acetyl than the unsubstituted molecule. No splitting could be effected in CCl_4 solutions with narrow slits and high amplifier gain but spectra in CS_2 revealed a distinct shoulder at 1938 cm^{-1}. As noted by Brown

TABLE 6

COMPARISON OF ASSIGNMENT FOR π-CYCLOPENTADIENYL METAL CARBONYLS[a]

Ring modes Description	Sym. for C_{5v}	$C_5H_5Mn(CO)_3$	$C_5H_5V(CO)_4$	$CH_3COC_5H_4V(CO)_4$
CH str.	A_1	3120	3128	3125
CH str.	E_1	3098	3115	3110
CH str.	E_2	3098	3100	3090
C=C str.	E_1	1428	1434	1420
C=C str.	E_2	1520	1462	1470
Ring breath.	A_1	1120	1120	1120
ip Ring def.	E_2	920	917	895
op Ring def.	E_2	487	487	490
ip CH def.	A_2	1267	1237	1220
ip CH def.	E_1	1010	1002	1045
ip CH def.	E_2	1152	1178	1170
op CH def.	A_1	848	835	845
op CH def.	E_1	834	822	890
op CH def.	E_2	~1056	1060	1060
C=O str.				1680

Non-ring modes Description	Sym. for C_{3v}	$C_5H_5Mn(CO)_3$	Sym. for C_{4v}	$C_5H_5V(CO)_4$	$CH_3COC_5H_4V(CO)_4$
ν(R–M)	A_1	350	A_1	329	315
Tw[R–M–$(CO)_n$]	A_2	160	A_2	240	180
R tilt	E	375	E	349	336
δ[R–M–$(CO)_n$]	E	100 or 120	E	99	90
ν(MC)	A_1	500	A_1	432	425
ν(MC)	E	480	B_1	456	450
ν(MC)		[b]	E	495	495
δ(C–M–C)	A_1	140	A_1	122	120
δ(C–M–C)	E	120 or 100	B_1	84	90
δ(C–M–C)		[b]	B_2		
δ(C–M–C)		[b]	E	122	120
ν(CO)	A_1	2025	A_1	2030	2035
ν(CO)	E	1940	B_1	1940	1960
ν(CO)		[b]	E	1920	1930
δ(M–C–O)	A_1	540	A_1	623	620
δ(M–C–O)	A_2	610	A_2		675
δ(M–C–O)	E	635	B_1	584	582
δ(M–C–O)	E	670, 665	B_2	584	582
δ(M–C–O)		[b]	E	595	595
δ(M–C–O)		[b]	E	610	595

[a] Solution data shown where available, otherwise solid frequencies cited (cm^{-1}). [b] No other skeletal modes of this description in $C_5H_5Mn(CO)_3$.

and Sloan[17] the solvent was greater for the E than the A mode.

In the IR spectra of solid $C_5H_5V(CO)_4$, Piper, Cotton and Wilkinson[7] observed the forbidden B mode as a very strong band but did not split the E mode. We see only a weak B mode. Lippincott *et al.*[4] did not observe a splitting of the E mode in the IR spectra of solid $C_5H_5Mn(CO)_3$ either. This is interesting since Fritz[9] reports that degeneracy of the E mode is often removed in the solid state. The shape of the

1930 cm^{-1} band in IR spectra of solid varied considerably with sample preparation but some spectra revealed a doublet structure. In the Raman spectra of the solid $C_5H_5V(CO)_4$ the *E* mode is split into two components that match the B_1 mode in intensity. As hoped, the latter appears only weakly in the IR spectra of $C_5H_5V(CO)_4$ but with medium intensity in the acetyl-substituted compound. R. D. Fischer's[18] data for $C_5H_5Mn(CO)_3$ showed the CO stretch vibrations to shift to higher frequencies in going from KBr disks to cyclohexane solutions; Lippincott's data showed a less pronounced shift. Acetyl substitution on $C_5H_5Mn(CO)_3$ shifted ν(CO) *ca.* 10–15 cm^{-1} to higher values; we observed similar shifts between $C_5H_5V(CO)_4$ and CH_3-$COC_5H_4V(CO)_4$. The isotopic shift for ^{12}CO to ^{13}CO was calculated to be 55 cm^{-1} at 2030 cm^{-1} and 43 cm^{-1} at 1930 cm^{-1}. Only in the Raman spectra of $C_5H_5V(CO)_4$ did the ^{13}CO A_1 stretch appear as a weak band at 1960 cm^{-1}.

The vanadium–carbon valence stretches are expected near 500 cm^{-1} and to be fairly intense. The strong Raman band at 432 cm^{-1} is assigned to the A_1 mode; the corresponding IR band of medium intensity is at 425 cm^{-1}. The *E* mode is assigned to the very strong IR band at 495 cm^{-1} and was too weak to appear in the Raman. The B_1 mode appears as a weak Raman band at 456 cm^{-1} and is missing from the IR as expected. The 495 cm^{-1} IR band is split in the acetyl compound. Fritz and Paulus[19] assigned IR bands at 500 and 597 cm^{-1} to the A_1 and *E* vanadium–carbon valence vibrations in $C_5H_5V(CO)_4$. As predicted by Brown and Carroll[20], the electron withdrawing power of the substituent group in the acetyl compound lowered the metal–carbon valence stretch while it raised the carbonyl stretch.

The eight V–C–O deformations are expected to fall in the range 550–700 cm^{-1} by analogy to Lippincott's work. Unlike $C_5H_5Mn(CO)_3$, which had strong bands at 668, 664 and 633 cm^{-1}, no IR bands were observed between 820 and 620 cm^{-1} in either $C_5H_5V(CO)_4$ or its acetyl derivative, and only one weak Raman band was found in this frequency range for the acetyl compound. Since only the *B* mode of the VCO deformations should be IR inactive, the A_1 and *E* VCO bending modes either are outside of this frequency region or are very weak. We observe strong IR bands at 615 and 595 cm^{-1} and Raman bands at 623 and 584 cm^{-1}. Again, the acetyl derivative shows additional IR bands at 580 and 555 cm^{-1}.

In considering the Lippincott *et al.* assignments we conclude that the A_1 MnCO bending vibration should be assigned to 609 cm^{-1} and was not observed by Lippincott in the Raman owing a nearby benzene solvent band. The 543 cm^{-1} IR and Raman band then may be assigned to the *E* MnC stretch which obviates the need to attribute accidental degeneracy to the comparatively weak out-of-plane cyclopentadienyl ring deformations. The C–V–C deformations were observed only in the Raman since no far-IR data were obtained. The broad moderately intense band at 122 cm^{-1} is believed to encompass these modes. The medium intensity band at 99 cm^{-1} is attributed to the ring–V–$(CO)_4$ degenerate bending mode. Similar frequencies were observed in the acetyl derivative. The A_1 ring–V–$(CO)_4$ appears as a very strong sharp band in the Raman at 329 cm^{-1} in $C_5H_5V(CO)_4$ and at 315 cm^{-1} in the acetyl complex; this is the strongest band in either spectrum as expected.

The ring tilt is assigned to the band of medium intensity at 349 cm^{-1} and the ring–V–$(CO)_4$ bend to the medium intensity Raman band at 99 cm^{-1}. These assignments are compatible with those of Lippincott as shown in Table 6. The A_2 ring twist mode in the solid is assigned to a weak Raman band at 240 cm^{-1}. This is a most doubtful assignment based on the need to account for this weak band as a fundamental.

(*b*). *Force constant calculations*

For a $C_5H_5M(CO)_4$ molecule of C_{4v} local symmetry the following $\nu(CO)$ frequencies are expected: A_1 (IR and Raman-active), B_1 (Raman-active only), and E (IR and Raman-active). Assignment of the observed three Raman frequencies was unequivocal since the B_1 mode could be assigned to the $\nu(CO)$ frequencies which were observed in the Raman spectra but not in the IR spectra and the E mode could be assigned to one of the $\nu(CO)$ frequencies which was split in the solid state spectra. The force constants were calculated using the following secular equations:

$$\begin{aligned} A_1:&\quad \lambda=\mu\cdot(k+2k_s+k_d)\\ B_1:&\quad \lambda=\mu\cdot(k-2k_s+k_d)\\ E:&\quad \lambda=\mu\cdot(k-k_d) \end{aligned}$$

The force constants (Table 7) obtained by use of these equations and assignments were all reasonable (*i.e.*, positive and of orders of magnitude comparable to similar force constants in other metal carbonyl derivatives).

TABLE 7

$\nu(CO)$ FREQUENCIES AND FORCE CONSTANTS FOR CYCLOPENTADIENYLVANADIUM TETRACARBONYL DERIVATIVES[a]

Compound	Medium	$\nu(CO)$ frequencies			Force constants			
		A_1	B_1	E	k	k_s	k_d	k_d/k_s
$C_5H_5V(CO)_4$	Solution[b]	2031	1954	1933	15.56	0.31	0.48	1.53
$C_5H_5V(CO)_4$	Solid	2015	1940	1912[c]	15.28	0.30	0.52	1.73
$CH_3COC_5H_4V(CO)_4$	Solid	2032	1965	1907	15.41	0.27	0.72	2.68

[a] The frequencies are reported in cm^{-1} and are from the data taken on the laser Raman Spectrometer. The force constants are given in mdynes/Å. [b] Cyclohexane solution. [c] Average of two strong compononts.

Cotton *et al.*[3] calculated a stretching force constant of 14.9×10^5 dynes/cm and an interaction constant of 0.5×10^5 dynes/cm for $C_5H_5V(CO)_4$ on the assumption that the splitting can be treated as the effect of coupled harmonic oscillators.

ACKNOWLEDGEMENT

We are indebted to the National Science Foundation for partial support under Grant GP-8429 of the portion of the work performed at the University of South Carolina and to the Alfred P. Sloan Foundation for partial support of the portion of the work performed at the University of Georgia.

REFERENCES

1 R. B. King, *Inorg. Chim. Acta*, 2 (1968) 454.
2 F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 84 (1962) 4432.
3 F. A. Cotton, A. D. Liehr and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1 (1955) 175.

4 I. J. HYAMS, R. T. BAILEY AND E. R. LIPPINCOTT, *Spectrochim. Acta, Part A*, 23 (1967) 273.
5 D. M. ADAMS, *Metal-Ligand and Related Vibrations*, St. Martins, New York, 1968, p. 96.
6 E. O. FISCHER AND W. HAFNER, *Z. Naturforsch., B*, 9 (1954) 503.
7 T. S. PIPER, F. A. COTTON AND G. WILKINSON, *J. Inorg. Nucl. Chem.*, 1 (1955) 165.
8 E. O. FISCHER AND K. PLESSKE, *Chem. Ber.*, 93 (1960) 1006.
9 H. P. FRITZ, *Advan. Organometal. Chem.*, 1 (1964) 239.
10 *Table of Wavelengths for the Calibration of Infrared Spectrometers*, Butterworths, London, 1961.
11 H. M. RANDALL, D. M. DENNISON, N. GINSBERG AND I. R. WEBER, *Phys. Rev.*, 52 (1937) 160.
12 H. P. FRITZ AND J. MANCHOT, *Spectrochim. Acta*, 18 (1962) 171.
13 J. B. WILFORD, A. WHITLA AND H. M. POWELL, *J. Organometal. Chem.*, 8 (1967) 495.
14 D. M. ADAMS, *J. Chem. Soc.*, (1964) 1771.
15 E. W. ABEL, *Quart. Rev. (London)*, 17 (1963) 133.
16 H. W. THOMPSON AND P. TORKINGTON, *J. Chem. Soc.*, (1945) 640.
17 D. A. BROWN AND H. SLOAN, *J. Chem. Soc.*, (1962) 3849.
18 R. D. FISCHER, *Spectrochim. Acta*, 19 (1963) 842.
19 H. P. FRITZ AND E. F. PAULUS, *Z. Naturforsch. B*, 18 (1963) 435.
20 D. A. BROWN AND D. G. CARROLL, *J. Chem. Soc.*, (1965) 2822.