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The Vibrational Spectrum of (Butadiene) Iron Tricarbonyl

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The vibrational spectrum of $C_4H_6Fe(CO)_3$ has been studied. An assignment of the frequencies on the basis of the local symmetry of the $Fe(CO)_3$ fragment (C_{3v}) explains most of the observations, but the Fe–C and C–O stretching modes of E symmetry are both split. Therefore the effective symmetry must be C_s. The C_4H_6 vibrations are assigned on the basis of C_s symmetry throughout.

Introduction

Much work has been done on the i.r. spectra of (hydrocarbon)$M(CO)_n$ systems, where the hydrocarbon fragment is π-bonded to a transition-metal. Such compounds are, almost without exception, coloured, and therefore their Raman spectra were inaccessible using the conventional mercury arc excitation. The development of Raman excitation sources in the red end of the visible spectrum has enabled the complete vibrational spectrum to be recorded in many cases where yellow or red samples must be used. Several systems have now been examined in this way, *e.g.* (Cyclooctatetraene)$Fe(CO)_3$,[1] (cyclopentadienyl)$Mn(CO)_3$,[2] (cyclopentadienyl)$V(CO)_4$,[3] (mesitylene-$Cr(CO)_3$ and (mesitylene)$Mo(CO)_3$.[4]

All the above complexes involve a cyclic hydrocarbon but very many non-cyclic olefins (conjugated and non-conjugated) can also form π-bonded complexes with transition metal carbonyl systems. Among the simplest of these is 1.3. butadiene; and perhaps the best characterised butadiene π-complex is $C_4H_6Fe(CO)_3$. This was first prepared by Reihlen *et. al.*[5] and described in more detail by Hallam and Pauson.[6] The crystal structure[7] clearly shows that the butadiene fragment is *cis*, planar and situated almost parallel to the plane defined by the three carbonyls. The iron atom is equi-distant from the four butadiene carbon atoms, and all the C–C distances are equal within experimental error. The structure can be represented as shown in Figure 1 (the exact nature of the Fe–C_4H_6 bonding is not specified).

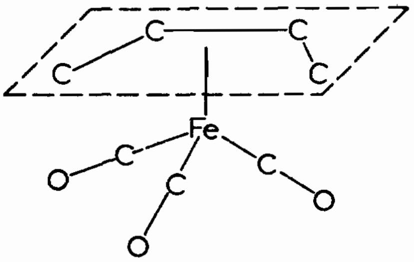

Figure 1. Molecular structure of $C_4H_6Fe(CO)_3$

This compound is particularly suitable for study by Raman spectroscopy as it is a liquid at room temperature (m.pt. 19°) and therefore Raman polarisation data should be readily obtainable. Hallam and Pauson[6] reported C–O stretching frequencies (from the i.r. spectrum) of 2051 cm^{-1} and 1978 cm^{-1}, and a band (assigned as a C=C stretch) at 1464 cm^{-1} (all these frequencies refer to the neat liquid). Reckziegel and Bigorgne,[8] on the other hand, resolved three C–O stretches for $C_4H_6Fe(CO)_3$ in an alkane solvent (2055, 1989 and 1979 cm^{-1}), indicating an effective symmetry of C_s for the $Fe(CO)_3$ fragment. Recently, a more detailed investigation of the i.r. spectrum has been carried out,[9] but assignments were proposed for the C_4H_6 vibrations only.

I.r. and Raman data are available for a closely analogous system, (cyclooctatetraene)$Fe(CO)_3$, in which the cyclic polyene is acting as a conjugated (1.3.)-diene towards the $Fe(CO)_3$.[1] However, the complexity of the spectrum due to the C_8H_8 made detailed assignments of the observed frequencies difficult. In view of the discussions concerning the bonding in $C_4H_6Fe(CO)_3$,[10] a study of its complete vibrational spectrum, with a view to obtaining as complete an assignment as possible, appeared to be a worthwhile exercise.

Experimental Section

The (Butadiene)iron tricarbonyl used in this work was a commercial sample, obtained from Alfa Inorganics Inc., purified by distillation *in vacuo*.

Infrared spectra were obtained on a Perkin Elmer 521 (4000-300 cm^{-1}) and on a Beckman IR 11 (600-

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[8] A. Reckziegel and M. Bigorgne, *J. Organometallic Chem.*, *3*, 341 (1965).
[9] M. J. Grogan and K. Nakamoto, *Inorg. Chim Acta*, *1*, 228 (1967).
[10] G. E. Coates, M. L. H. Green and K. Wade, « Organometallic Compounds » (Methuen and Co. Ltd., London 1968) Vol. II p. 70.

Table 1. Infrared and Raman bands for liquid $C_4H_6Fe(CO)_3$ (all frequencies in cm^{-1})

I.R.	Raman	Assignment
102 w, brd.	102 vs, dp.	(C_4H_6)—Fe—$(CO)_3$ def. (E)
	115 sh. pol. (?)	C—Fe—C def. (A_1)
137 w, brd.	133 ms, dp.	C—Fe—C def. (E)
	351 s, pol.	(C_4H_6)—Fe str. (A_1)
362 m	363 m, dp.	(C_4H_6) tilt (E)
378 m	380 vs, pol.	Fe—C str. (A_1)
416 m	417 w, dp. (?)	? C—C=C bend (A″)
452 sh	453 w, pol. (?)	? Fe—C str. (E)
463 ms	465 w, dp.	
492 ms	494 m, pol.	C—C=C bend (A′)
510 s	~516 sh	Fe—C—O def. (E)
567 s		Fe—C—O def. (E)
612 vs	614 w,pol.	Fe—C—O def. (A_1)
643 m, w		
669 ms	670 w	CH wag (A′)
715 vw		
774 m		?
789 ms	792 w, dp. (?)	CH wag (A″)
835 vw,brd.		
896 m		CH_2 wag (A″)
924 m	927 m, pol.	CH_2 rock (A′) and CH_2 wag (A′)
952 m	956 sh,	CH_2 twist (A′)
970 w, brd.	965 w, dp.	CH_2 rock (A′)
1021 w		
1048 m	1049 sh	CH_2 twist (A″)
1057 w	1062 m, pol.	? C—C str. (A′) or CH bend (A′)
1086 w, brd.		
1124 vw		
1151 vw		
1173 ms	1175 w, dp. (?)	CH bend (A″)
1203 s	1206 m, pol.	? CH bend (A′) or C—C str. (A′)
1262 vw brd.		
1304 vvw		
1369 m	1371 mw, dp.	CH_2 scissors (A″)
1407 vw		
1439 m		C=C str. (A″)
	1449 w, pol.	CH_2 scissors (A′)
1479 ms	1477 w, pol.	C=C str. (A′)
1503 vw		
1534 vw		
1555 vw		
1578 vw		
1680 w		
1691 w		
1739 w		
1824 w		
1846 w		
1876 w		
1966 vs (1975 vs; C_6H_{12} soln)	1970 s, dp.	CO str. (E)
1995 sh (1984 vs, C_6H_{12} soln)	1998 sh	
2048 vs (2057 vs, C_6H_{12} soln)	2051 ms, pol.	CO str. (A_1)
2143 w		
2264 vw		
2345 w		
2377 vw		
2438 w		
2465 m		
2516 w		
2542 w		
2585 w		
2621 vw		
2666 w		
2880 vw		
2926 m	2932 vw, brd.	CH str. (A″)
2950 w, sh		? CH_2 str. (A″)
3010 m	3014 w, pol.	CH str. (A″) and CH_2 str. (A′)
3065 m	3069 w, pol.	CH_2 str. (A′) (? + CH_2 str. (A″)
3376 vw		
3461 vw		
3526 vw		
3720 w		
3936 mw		

70 cm^{-1}). Samples were run as liquid films of varying thickness, between CsI or KBr plates (521) or polythene plates (I.R. 11) and in cyclohexane solution (1700-2200 cm^{-1} only).

The spectra in the higher frequency region (>300 cm^{-1}) were calibrated using characteristic bands of CH_4, HBr, CO, NH_3 and H_2O; all measured frequencies should be ± 2 cm^{-1}.

A Cary 81 spectrophotometer was used to record the Raman spectra. A Spectra-Physics 125 He--Ne laser was used as excitation source (output approx. 60 mw. at 632.8 nm). Liquid samples were used, in capillary cells (approx. 1 mm i.d.); the samples were made up in air, and no decomposition was noticed over several hours, but as a precaution no sample was kept for more than 24 hours. Depolarisation ratios were determined by observing the spectrum with the plane of the polarised incident light parallel and perpendicular, respectively, to the axis of the polaroid analyser. True values were not given directly, but the sample cell was calibrated using accurately known standards.

The experimental results are listed in Table I, and the Raman spectrum is illustrated in Figure 2. The i.r. spectrum is essentially identical to that illustrated by Grogan and Nakamoto.[9]

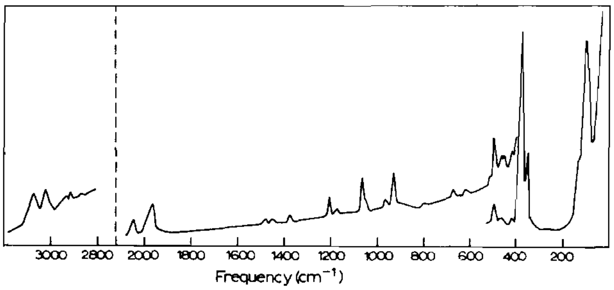

Figure 2. Raman spectrum of $C_4H_6Fe(CO)_3$ (liquid)

Discussion

i) *Vibrational analysis.* The overall symmetry of the molecule will be C_s, and if we can use the method of « local symmetry » the symmetry of the $Fe(CO)_3$ fragment will be C_{3v} while that of the C_4H_6 will still only be C_s. The vibrations of C_4H_6 can be classified into the approximate normal modes which are listed in Table II (the classification for the free molecule (C_{2v}) is included).

The remaining vibrations of the complex can be divided into those of the $Fe(CO)_3$ portion and those involving the (C_4H_6)–$Fe(CO)_3$ system as a whole. The expected numbers and symmetry species of these vibrations are presented in Table III.

The observed frequencies can now be assigned to these normal modes (almost all of which are approximations, as extensive mixing of modes will doubtless occur). The assignment will be attempted in two distinct parts (a) the vibrations of the C_4H_6 itself; (b) the $Fe(CO)_3$ and (C_4H_6)–Fe–$(CO)_3$ vibrations.

Table II. Classification of normal modes for cis. 1.3 butadiene

	C_{2v}	C_s
CH_2 stretch	$2A_1+2B_2$	$2A'+2A''$
CH stretch	A_1+B_2	$A'+A''$
C=C stretch	A_1+B_2	$A'+A''$
CH_2 scissors (i.p.)	A_1+B_2	$A'+A''$
CH bend (i.p.)	A_1+B_2	$A'+A''$
C—C stretch	A_1	A'
CH_2 twist (o.o.p.)	A_2+B_1	$A'+A''$
CH_2 rock (i.p.)	A_1+B_2	$A'+A''$
CH_2 wag (o.o.p.)	A_2+B_1	$A'+A''$
CH wag (o.o.p.)	A_2+B_1	$A'+A''$
C—C=C bend	A_1+B_2	$A'+A''$
C_4 torsion	A_2	A''

(Activities: C_{2v}: A_1, R(p), IR; B_1 and B_2, R(dp), IR; A_2, R(dp) only. C_s: A′, R(p), IR; A″, R(dp), IR).

Table III. Classification of normal modes for —$Fe(CO)_3$ and (C_4H_6)—Fe—$(CO)_3$

	C_{3v}	C_s
C—O stretch	A_1+E	$2A'+A''$
Fe—C—O def.	A_1+A_2+2E	$3A'+3A''$
Fe—C stretch	A_1+E	$2A'+A''$
(C_4H_6) tilt	E	$A'+A''$
(C_4H_6)—Fe stretch	A_1	A'
(C_4H_6) twist	A_2	A''
C—Fe—C def.	A_1+E	$2A'+A''$
(C_4H_6)Fe—$(CO)_3$ def.	E	$A'+A''$

(Activities: C_{3v}: A_1, R(p), IR; A_2 inactive; E, R(dp), IR: C_s: A′, R(p), IR; A″, R(dp), IR).

(ii) *Assignment of frequencies.* (a) *C_4H_6 vibrations.* The vibrational spectrum of 1.3 butadiene has been extensively studied (*e.g.*[11-16]), and this work, together with other physical measurements, shows that the molecule exists almost exclusively in the *trans*-form. As the butadiene is complexed to $Fe(CO)_3$ in the *cis*-configuration, data from the free (*trans*) molecule may not be directly comparable. A calculation of the expected frequencies for the *cis* isomer has been made by Sverdlov and Tarasova,[12], however, which may be of considerable help in the assignment. The only investigation of the C_4H_6 vibrations in this molecule has been carried out by Grogan and Nakamoto.[9] A complete assignment of these frequencies was proposed by these authors on the basis of the i.r. spectrum alone, but no discussion or justification was given. As the Raman data reported here are new, it seems worthwhile to discuss the assignment of the butadiene frequencies.

Bands due to CH_2 and CH stretching modes occur in free butadiene from 3000-3100 cm^{-1}, and the same range is predicted for the *cis* isomer. It has been found in $C_6H_6Cr(CO)_3$, however, that some of the CH stretching frequencies can be reduced by up to 100

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(11) C. M. Richards and J. R. Nielsen, *J. Opt. Soc. Am.* *40*, 438 (1950).

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(16) E. M. Popov and G. A. Kogan, *Opt and Spectroscopy*, *17*, 362, (1964).

cm^{-1},[17] and so we might expect to find such bands down to about 2900 cm^{-1} in $C_4H_6Fe(CO)_3$. Bands which could be assigned as fundamentals are in fact found at 3067, 3012 and 2929 cm^{-1}. The first two are polarised in the Raman spectrum, but the polarisation of the last (weak, broad) band could not be determined. They are assigned as follows: 3067: CH_2 stretches (A′+A″); 3012: CH stretch (A′) and CH_2 stretch (A′); 2929: CH stretch (A″). This leaves one more A″ class CH_2 stretch (2985 cm^{-1} in free butadiene) which might be assigned tentatively to a weak band (i.r. only) at 2950 cm^{-1}

The C=C stretches are found in free butadiene at 1638 cm^{-1} and 1599 cm^{-1}. These frequencies would be expected to be decreased by complex formation. A band at 1471 cm^{-1} has been attributed to the C=C stretch of C_4H_6 in $K_2[C_4H_6(PtCl_3)_2]$[9] and the same authors assign a frequency of 1479 cm^{-1} to the same mode in $C_4H_6Fe(CO)_3$. The present work indicates that the A′ C=C stretch corresponds to a polarised Raman band at 1477 cm^{-1}, with a corresponding i.r. absorption. The A″ mode is assigned to a medium intensity i.r. band at 1439 cm^{-1} (no Raman counterpart).

The (in-plane) CH_2 scissors deformations occur at 1439 cm^{-1} and 1385 cm^{-1} in free butadiene. The predicted values for *cis*-butadiene are close to these, and they are not expected to be very different in the complex. Therefore a polarised Raman band at 1449 cm^{-1} is assigned as the A′ scissors, and a depolarised feature at 1371 cm^{-1} (i.r. at 1369) is assigned as the A″ mode. These assignments agree with those of Grogan and Nakamoto.[9]

The assignment of the (in-plane) CH bending modes (A′+A″) and the C–C stretch (A′) presents more of a problem. All three are between 1200 and 1300 cm^{-1} in free (*trans*) butadiene, but Sverdlov and Tarasova[12] predict a much lower value (approx. 1000 cm^{-1}) for the C–C stretch in *cis* butadiene. Raman bands are found at 1206 cm^{-1} (pol.), 1175 cm^{-1} (probably depol.) and 1062 cm^{-1} (pol.) each one having an i.r. counterpart. The A″ CH bending mode can be assigned quite easily to the 1175 cm^{-1} band, but this leaves the two A′ modes to be assigned as 1206 cm^{-1} or 1062 cm^{-1}. Sverdlov and Tarasova's predications suggest that the former is the CH bending mode, the latter the C–C stretch. The « C–C » bond in C_4H_6 will be considerably modified on complex formation, however, and the crystal structure shows[7] that the « C–C » and « C=C » bond lengths are equal (1.45 Å). It is suggested, therefore, that the A′ C–C stretch should be assigned to the Raman band at 1206 cm^{-1} with the 1062 cm^{-1} band as the A′ CH bend, although this must be regarded as tentative.

By analogy with free butadiene, and the calculations for the *cis*-isomer, the region 900-1100 cm^{-1} should contain the following modes: CH_2 (in-plane) rock (A′+A″); CH_2 (out-of-plane) twist (A′+A″) and CH_2 (out-of-plane) wag (A′+A″). From the limited amount of polarisation data available, the most likely assignment to the observed bands is as follows: 1048 cm^{-1}, A″ CH_2 twist; 968 cm^{-1} (depol.), A″ CH_2 rock; 954 cm^{-1}, A′ CH_2 twist; 926 cm^{-1} (pol.) A′ CH_2 rock and, probably, CH_2 wag also; 896 cm^{-1} (i.r. only), A″ CH_2 wag.

The remaining modes are two CH wagging modes, two C–C=C deformations and the C_4 torsion. The last (A″) is not detected (unless it is coincident with one of the low frequency $Fe(CO)_3$ deformations, see below). Bands appear which are assignable to the others, although matters are complicated by the occurrence of $Fe(CO)_3$ vibrations in the same regions. The assignment of the latter can be put upon a firmer basis than for the C_4H_6 vibrations, and so the bands left after assigning the $Fe(CO)_3$ vibrations (*vid. inf.*) are allotted to the four C_4H_6 vibrations, thus: CH wag, 791 cm^{-1} (A″) and 669 cm^{-1} (A′) C–C=C deformations, 493 cm^{-1} (A′) and 417 cm^{-1} (A″).

None of these values are unreasonable when compared with the values for free butadiene, although the A″ CH wag is rather high in frequency at 791 cm^{-1}. Some of the assignments differ from those of Grogan and Nakamoto,[9] but the present set is more consistent with the Raman results, and with the assignment of skeletal frequencies. A summary of the proposed assignment is given in Table IV, using a symmetry of C_s as a basis.

Table IV. Assignment of C_4H_6 vibrations in $C_4H_6Fe(CO)_3$ (all frequencies in cm^{-1})

	A′	A″
CH_2 stretch	3067	3067
CH_2 stretch	3012	2950
CH stretch	3012	2929
C=C stretch	1477	1439
CH_2 scissors	1449	1370
C–C stretch	1205	—
CH bend	1060	1174
CH_2 twist	954	1048
CH_2 rock	926	968
CH_2 wag	926	896
CH wag	669	791
C–C=C bend	493	417
C_4 torsion	—	not observed

(b) *$Fe(CO)_3$ and (C_4H_6)–Fe–$(CO)_3$ vibrations.* The CO stretching region for pure liquid $C_4H_6Fe(CO)_3$ appears to show two bands in both the i.r. and the Raman spectra, in agreement with predictions for C_{3v} symmetry (A_1+E). The lower-frequency feature is noticeably asymmetric, however, with a shoulder on the high-frequency side. In solution in cyclohexane this band is split into two, giving sharp bands at 1975 cm^{-1} and 1984 cm^{-1} in addition to that at 2057 cm^{-1}. Thus effective C_s symmetry must be assumed for the $Fe(CO)_3$ group, although as we shall see, most of the E modes (C_{3v}) are not noticeably split (into A′+A″) in the pure liquid. The splittings are not so obvious because of line-broadening, due to intermolecular forces, in the pure liquid compared with the (dilute) cyclohexane solution. To return to the CO stretches the highest frequency band is strongly polarised in the Raman spectrum,

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[17] H. P. Fritz and J. Manchot, *Spectrochim. Acta*, *18*, 171 (1962).

which makes the assignment to the $A_1(A')$ mode completely certain. The lower frequency band is obviously E ($A'+A''$ for C_s).

The remaining frequencies for the skeletal modes are all expected to lie below 700 cm^{-1}. A considerable amount of accumulated evidence for other carbonyl systems, especially those of the general type (hydrocarbon)M(CO)$_n$ can be used to assist the assignment.[1-3,17-19] A symmetry of C_{3v} for $Fe(CO)_3$ will be assumed initially as a first approximation.

The symmetric Fe–C stretch is assigned to a very strong, polarised Raman band at 380 cm^{-1} (i.r. absorption at 378 cm^{-1}). Another such band is found at 351 cm^{-1}, which is assigned as the (symmetric) Fe–(C_4H_6) stretch. In all previous cases where analogous molecules have been studied, the relative positions of these two bands has been as suggested here.[1-4] In this case, their frequencies are unusually close, and there will doubtless be very extensive mixing of the modes.

For C_{3v} symmetry there should be one more Fe–C stretch (E), which varies in frequency from approx 300 to 500 cm^{-1} in a variety of complexes of this type.[1-4,17] The most likely assignment here is to a doublet (i.e. $A'+A''$) at 453 cm^{-1} (probably depol.) and 465 cm^{-1} (pol.); each component possesses an i.r. counterpart. As with the C–O stretches, the assumption of C_{3v} symmetry is inadequate.

M–C–O deformations (A_1+A_2+2E for C_{3v}) are found at a higher frequency than M–C stretches, are more intense than the latter in the i.r. spectrum, but less intense in the Raman spectrum.[3,18] For C_4H_6 $Fe(CO)_3$ three well-defined and strong bands are found in the i.r. at 510, 567 and 612 cm^{-1}. From their position and intensity the assignment of these as Fe–C–O deformations seems quite reasonable. A weak, polarised Raman band at 614 cm^{-1} suggests that $A_1(A')$ deformation can be assigned to this frequency, leaving the other two as the E modes (no splitting of these was observed).

The only remaining vibrations associated with the $Fe(CO)_3$ unit alone are C–Fe–C deformations (A_1+E for C_{3v}). These have been assigned to features between 100 and 150 cm^{-1}.[1-4,18-19] A medium strong, depolarised Raman band at 133 cm^{-1} is believed to represent the E mode (i.r. at 137 cm^{-1}), while a low-frequency shoulder (at 115 cm^{-1}) is almost certainly polarised, and is assigned as the A_1 mode. Grogan and Nakamoto assign an i.r. band at 135 cm^{-1} as the C_4 torsion of the C_4H_6 fragment.[9] Such modes rarely give strong Raman bands, and an assignment of this frequency as a C–Fe–C deformation seems more likely, although it is possible that the torsion may be accidentally degenerate.

The last modes are concerned with vibrations of the whole (C_4H_6)–Fe–$(CO)_3$ unit. The Fe–(C_4H_6) stretch was discussed above, leaving the (C_4H_6) tilt (E for C_{3v}) and the (C_4H_6)–Fe–$(CO)_3$ deformation (also of E symmetry). The tilt frequency is usually higher than that of the M–(Ring) stretch in (Ring)M-(CO)$_n$ systems,[1,4] and here the tilt is assigned to the Raman band (depol.) at 363 cm^{-1}. The (C_4H_6)–Fe–$(CO)_3$ deformation will occur at about 100 cm^{-1},[2-4] and it is assigned to the very strong Raman band (depol.) at 102 cm^{-1} (i.r. 102 cm^{-1} also).

The proposed assignments are summarised in Table V.

Table V. Assignment of $Fe(CO)_3$ and (C_4H_6)–Fe–$(CO)_3$ vibrations (all frequencies in cm^{-1})

A_1	C–O stretch	2057
	Fe–C–O def.	613
	Fe–C stretch	379
	(C_4H_6)–Fe stretch	351
	C–Fe–C def.	115
A_2	Fe–C–O def.	—
	(C_4H_6) twist	—
E	C–O stretch	1984 1975
	Fe–C–O def.	567
	Fe–C–O def.	512
	Fe–C stretch	464 453
	(C_4H_6) tilt	363
	C–Fe–C def.	135
	(C_4H_6)–Fe–$(CO)_3$ def.	102

Conclusion

In order to obtain a satisfactory assignment of the vibrational modes of $C_4H_6Fe(CO)_3$ an effective overall symmetry of C_s must be assumed. For the $Fe(CO)_3$ portion a « local symmetry » of C_{3v} suffices to explain *most* of the observations, but the Fe–C and C–O stretches each give rise to 3 frequencies (2 predicted by C_{3v}). For the C_4H_6 portion C_s symmetry is assumed throughout, and the resulting assignment is almost complete, although some of the proposals must be regarded as only tentative.

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