

Roberts.¹ Accordingly, a reinvestigation of the ^{13}C NMR spectrum of (II) was undertaken and in contrast with the earlier reported results all ten possible $^{13}\text{C}-^{19}\text{F}$ couplings were resolved in its proton noise-decoupled ^{13}C -spectrum.⁵ Furthermore, it appears that the magnitudes of the $^{13}\text{C}-^{19}\text{F}$ couplings over more than four bonds in (II) and (III) decrease in an alternating way with increasing number of bonds, leading to the tentative assignment shown in Fig. 2.

Further studies on $^{13}\text{C}-^{19}\text{F}$ couplings which evidently may be of both experimental and theoretical interest, are in progress for other condensed aromatic systems.

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Mean Amplitudes of Vibration of Nickelocene

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We have recently reported the results of total vibrational analyses of several sandwich compounds (dibenzenechromium,¹ ferrocene,² and ruthenocene³). These calculations were initiated mainly

to calculate the mean amplitudes of vibration of these molecules in order to compare the results to the electron diffraction values as far as available.

We now want to continue the series by a study of nickelocene, $\text{Ni}(\text{C}_5\text{H}_5)_2$. An electron diffraction study of this molecule was recently published.⁴ On the basis of a new investigation of its vibrational spectra,⁵ it is now also possible to give an assignment of its vibrational frequencies which is more complete than the one previously published.^{6,7}

The vibrational frequencies for $\text{Ni}(\text{C}_5\text{H}_5)_2$ used in the present calculation are given in Table 1. The IR- and Raman-values of Refs. 5, 6, and 7 were taken for the assignment which was made in analogy to the previously reported investigation of $\text{Fe}(\text{C}_5\text{H}_5)_2$.² This means that in the case of closely neighbored $\text{Ni}(\text{C}_5\text{H}_5)_2$ frequencies the same sequence was followed through the symmetry blocks as in ferrocene. In this fashion a tentative assignment could be given for all frequencies except for the lowest A_2'' mode. For this mode we have used in a very approximate and arbitrary way the unchanged 355 cm^{-1} E_1' $\text{Ni}(\text{C}_5\text{H}_5)_2$ band. Only one band was observed in this spectral range for nickelocene so far.⁶ In ferrocene both the E_1' and the A_2'' modes are closely neighbored (at 490 and 477 cm^{-1} , resp.). Some of the other low frequency modes (the 125 cm^{-1} E_1' and the 186 cm^{-1} A_1'' bands, for example) must also be taken with some reservation.

The force constants used to calculate the mean amplitudes of $\text{Ni}(\text{C}_5\text{H}_5)_2$ were adjusted (starting with the ferrocene force field²) to reproduce exactly the frequencies of Table 1. The result of the amplitude calculations is given in Table 2 (mean amplitudes of vibration) and in Table 3 (perpendicular amplitude correction coefficients). It is usually possible to define many different force fields to reproduce a given set of experimental frequencies. This introduces some uncertainty into the calculated mean amplitudes. It must also be emphasized that the result of the calculations depends very much on the assignment of the experimental frequencies.

For the sake of comparison the available electron diffraction mean amplitudes of vibration⁴ are also given in Table 2. The agreement between observed and calculated values is only fair. It must be left open at this point whether the observed discrepancies are due to imperfec-

Table 1. Observed and calculated vibrational frequencies (cm^{-1}) for $\text{Ni}(\text{C}_6\text{H}_6)_2$.

A_1' (A_{1g})	3108 ^a	1111 ^a	750 ^a	207 ^a		
A_2' (A_{2g})	1218 ^b					
E_1' (E_{1u})	3108 ^c	1423 ^c	1002 ^c	838 ^c	355 ^d	125 ^d
E_2' (E_{2g})	3085 ^a	1331 ^a	1214 ^a	1053 ^a	800 ^a	600 ^a
A_2'' (A_{2u})	3096 ^c	1109 ^c	802 ^c	(355) ^e		
E_1'' (E_{1g})	3102 ^a	1424 ^a	1000 ^a	780 ^a	251 ^a	
E_2'' (E_{2u})	3085 ^b	1335 ^b	1150 ^b	1050 ^b	895 ^b	540 ^b
A_1'' (A_{1u})	1257 ^b	186 ^b				

^a Raman values, Ref. 5.

^b Approximate values for inactive frequencies from weak Raman and IR lines; values chosen in analogy to corresponding ferrocene frequencies; Ref. 2.

^c IR values, Ref. 5.

^d IR-values as proposed in Refs. 6 and 7.

^e See text.

Table 2. Observed and calculated mean amplitudes of vibration (\AA) for nickelocene (numbering of atoms as in Ref. 2).

	0 K ^a	298 K ^a	373 K ^a	373 K ^b
C_1-C_3	0.047	0.047	0.047	0.044
C_1-H_1	0.077	0.077	0.077	0.079
$\text{Ni}-\text{C}$	0.068	0.100	0.110	0.084
$\text{Ni}-\text{H}$	0.123	0.139	0.146	0.147
$\text{C}_1\cdots\text{C}_3$	0.059	0.061	0.064	0.054
$\text{C}_1\cdots\text{H}_2$	0.099	0.099	0.100	(0.090)
$\text{C}_1\cdots\text{H}_3$	0.095	0.096	0.098	(0.100)
$\text{C}_1\cdots\text{C}_6$	0.112	0.192	0.212	
$\text{C}_1\cdots\text{C}_7$	0.099	0.160	0.177	
$\text{C}_1\cdots\text{C}_8$	0.080	0.109	0.119	

^a This study.

^b Electron diffraction values, Ref. 4; the temperature is approximate.

tions of the vibrational analysis (use of a harmonic force field, uncertainties of the vibrational assignment, *etc.*) or to experimental problems of the electron diffraction study (the difficulty to define and determine exactly the temperature of the outflowing gas, overlapping signals, *etc.*).

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Table 3. Perpendicular amplitude correction coefficients (\AA) for $\text{Ni}(\text{C}_6\text{H}_6)_2$ (numbering of atoms as in Ref. 2).

	0 K	298 K	373 K
C_1-C_3	.0033	.0065	.0077
C_1-H_1	.0184	.0209	.0224
$\text{Ni}-\text{C}$.0013	.0022	.0025
$\text{Ni}-\text{H}$.0058	.0071	.0077
$\text{C}_1\cdots\text{C}_3$.0032	.0083	.0101
$\text{C}_1\cdots\text{H}_2$.0097	.0128	.0142
$\text{C}_1\cdots\text{H}_3$.0075	.0114	.0131
$\text{C}_1\cdots\text{C}_6$.0010	.0016	.0018
$\text{C}_1\cdots\text{C}_7$.0009	.0015	.0017
$\text{C}_1\cdots\text{C}_8$.0006	.0009	.0010

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