NORMAL COORDINATE ANALYSIS FOR THE WHOLE MOLECULE OF DIBENZENECHROMIUM

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(Received August 31st, 1970)

SUMMARY

Normal coordinate analysis of molecular vibrations was performed for $(C_6H_6)_2Cr$ assuming D_{6h} symmetry. Some frequency shifts from free to complexed benzene are explained by kinematic couplings without violation of the force field for ligand vibrations. Calculated mean amplitudes from the final harmonic force field show excellent agreement with electron diffraction data.

INTRODUCTION

The question of the structure of dibenzenechromium, $(C_6H_6)_2Cr$, has attracted the interest of several investigators. Possible structures with the alternatives of trigonal and hexagonal symmetry for the complexed C_6H_6 have been discussed; see ref. 1 and the bibliography therein. A recent investigation[2] of the IR vapour spectrum seems to prove definitely that the ligand has hexagonal symmetry in the gaseous state. Normal coordinate analyses have been performed[3] for complexed benzene in $(C_6H_6)_2Cr$ and other sandwich compounds, by considering the ligands as isolated systems. In those analyses it was necessary to introduce some force constants different from the corresponding ones in free benzene in order to explain the frequency shifts from free to complexed C_6H_6. In the present work a normal coordinate analysis has been performed for $(C_6H_6)_2Cr$ as a twenty-five atomic molecule, and reveals the very interesting feature that some of the most significant frequency shifts may be explained without changing the force field for ligand vibrations from that in free benzene.

RESULTS AND DISCUSSION

Classification of vibrational modes

The present calculations are based on an eclipsed structure of symmetry D_{6h} for $(C_6H_6)_2Cr$ with planar C_6H_6 ligands. This model agrees with the gas electron diffraction investigation of the molecule[4], from which the structural data were adopted, although that study does not prove the structure unambiguously.

In constructing the symmetry coordinates of molecular vibrations we aimed at preserving the identity of the ligands as much as possible. The following types of symmetry coordinates were produced. (i). In-phase ligand vibrations, which have the symmetric structure of free benzene: $2A_{1g}+A_{2g}+2B_{2g}+E_{1g}+4E_{2g}+A_{2u}+2B_{1u}+2B_{2u}+3E_{1u}+2E_{2u}$. (ii). Out-of-phase ligand vibrations belonging to the symmetry species[5] $2A_{2u}+A_{1u}+2B_{1u}+E_{1u}+4E_{2u}+A_{1g}+2B_{2g}+2B_{1g}+3E_{1g}+2E_{2g}$. (iii). Compensated in phase ligand translations belonging to $A_{2u}+E_{1u}$. (iv). Out-of-phase ligand vibrations of $A_{1u}+E_{1u}$. (v). Parallel out-of-phase ligand translation of symmetry A_{1g}. (vi). Deformed out-of-phase ligand translations of E_{1g}.

Approximate harmonic force field

An initial force field was assumed with no interaction terms between different types of coordinates according to the above classification. For all force constants pertaining to internal ligand vibrations, i.e. coordinates of types (i) and (ii), values from free benzene were taken from previous calculations according to the Brodersen–Langseth assignments[6]. Kinematic couplings between some of the different types of coordinates resulted in interesting frequency shifts from free to complexed benzene which qualitatively reflected the major trends in the observed frequencies.

The most pronounced frequency shifts of the type under consideration occur in species A_{1g} and A_{2u}; see Table 1. The drastic frequency shift from 673 cm^{-1} in free

TABLE 1

OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) OF A_{1g} AND A_{2u} IN DIBENZENECHROMIUM
The force field for free benzene was used without modification for ligand vibrations. Free benzene frequencies are included for comparison.

Dibenzenechromium								Free benzene	
		Calcd.	Obs.			Calcd.	Obs.		
A_{1g}	(i)	3073	3053[a]	A_{2u}	(ii)	3073	3053[b]	a_{1g}	3073[c]
	(i)	993	970[a]		(ii)	993	971[b]	a_{1g}	993[c]
	(ii)	880	791[a]		(i)	916	794[b]	a_{2u}	673[c]
	(v)	254	277[a]		(iv)	439	490[b]		

[a] Ref. 3. [b] Ref. 5 and 7. [c] Ref. 6.

TABLE 2

VIBRATIONAL FREQUENCIES (cm^{-1}) FROM THE FINAL HARMONIC FORCE FIELD
See also Table 1. The calculated frequencies are identical to observed values where available. Values in parentheses are frequencies calculated from the approximate force field. B_{1g}, B_{1u} and E_{2u} frequencies were assumed to be identical with those of B_{2u}, B_{2g} and E_{2g}, respectively.

A_{2g}	(1350)					
A_{1u}	(1375)	152[b]				
B_{2u}	1308[a]	1142[a]				
B_{2g}	2855[a]	(1010)	(993)	(709)		
E_{1g}	2904[a]	1430[a]	999[a]	860[a]	335[a]	
E_{1u}	2904[a]	1426[b]	999[b]	860[b]	459[b]	171[b]
E_{2g}	2955[a]	1631[a]	1143[a]	910[a]	604[a]	409[a]

[a] Ref. 3. [b] Ref. 5 and 7.

TABLE 3

CALCULATED AND OBSERVED MEAN AMPLITUDES (Å) IN DIBENZENECHROMIUM

Distance type	Equil. dist. (Å)	Spectroscopic (298°K)		Electr. diff.[a] (180°C)
		Approx.	Final	
C–H	1.090	0.077	0.079	0.084
C–C	1.423	0.046	0.047	0.045
C···C	2.465	0.055	0.056	0.055
C···C	2.846	0.059	0.059	0.063
C···H	2.183	0.100	0.101	0.100
C···H	3.452	0.097	0.098	0.120
C···H	3.936	0.093	0.095	0.120
Cr–H	2.986	0.122	0.124	0.140
Cr–C	2.151	0.074	0.073	0.070
$C_1 \cdots C_1'$	3.226	0.136	0.134	0.140

[a] Ref. 4.

C_6H_6 (ref. 6) to 794 and 791 cm^{-1} for the corresponding modes in $(C_6H_6)_2Cr$ are seen to be reproduced and even exaggerated by the present calculations. Frequency shifts for the CH stretching frequencies[2] were not reproduced by the present approximate force field; which is not surprising in view of the separability of CH stretching modes.

Final harmonic force field

·Refinements of the initial force field were performed to make it exactly consistent with all the observed frequencies[2,7], which are given in Tables 1 and 2.

Mean amplitudes of vibration

The final force field was used to calculate the mean amplitudes of vibration[8] for $(C_6H_6)_2Cr$. Surprisingly good agreement was found with the reported electron diffraction data[4]; see Table 3.

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Note added in proof. Similar calculations giving the same results for dibenzenechromium were recently performed on the basis of different symmetry coordinates; S. J. Cyvin, J. Brunvoll and L. H. Schäfer, *J. Chem. Phys.*, in press.