Perpendicular Amplitude Correction Coefficients of Free and Complexed Benzene and the Cyclopentadienide Anion

J. BRUNVOLL,[a] S. J. CYVIN[a] and LOTHAR SCHÄFER[b]

[a] Institute of Theoretical Chemistry, Technical University of Norway, N-7034 Trondheim NTH, Norway and [b]Deparment of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA

Previous total vibrational analyses of metalorganic sandwich compounds have revealed the similarity of the mean vibrational amplitudes of free and complexed ligands (free and complexed benzene;[1,2] free (ionic) and complexed (covalent) cyclopentadienide[3]). In view of the differences of the vibrational spectra of both molecules in the free and complexed states, the observed similarity of the vibrational amplitudes is at first sight astonishing. The calculated quantities, however, are root-mean-square parallel amplitudes[4] and refer to the planes of the ligands, while the most characteristic changes should be expected in the direction of the main symmetry axis, perpendicular to the ring planes. In fact, the most significant frequency shifts are observed for the non-planar ligand vibrations which also show an interesting kinematic coupling to some framework normal modes.[1,3,5,6]

Looking for similar quantities which may describe the different natures of the free and complexed states of molecules of the mentioned type, we have calculated the perpendicular mean-square amplitudes[4] for C_6H_6, $Cr(C_6H_6)_2$, C_6D_6, $Cr(C_6D_6)_2$, $C_5H_5^-$, $Fe(C_5H_5)_2$, $C_5D_5^-$, and $Fe(C_5D_5)_2$, using the previously described[1,3] harmonic force fields. These quantities are used to con-

Table 1. Perpendicular amplitude correction coefficients of free and complexed cyclopentadienide anion (in Å).

Distance	C_5H_5		$Fe(C_5H_5)_2$	
	0 K	298 K	0 K	298 K
$C_1 - H_1$	.0184	.0194	.0169	.0183
$C_1 - C_2$	.0019	.0020	.0029	.0048
$C_1 \cdots C_3$	.0008	.0008	.0027	.0056
$C_1 \cdots C_1'$	—	—	.0012	.0021
$C_1 \cdots H_2$	.0087	.0092	.0089	.0109
$C_1 \cdots H_3$	.0053	.0056	.0067	.0094
$Fe - H$	—	—	.0058	.0070
$Fe - C$	—	—	.0012	.0019

Table 2. Perpendicular amplitude correction coefficients for the perdeuterated cyclopentadienide anion and ferrocene.

Distance	C_5D_5		$Fe(C_5D_5)_2$	
	0 K	298 K	0 K	298 K
$C_1 - D_1$	.0130	.0148	.0123	.0143
$C_1 - C_2$	.0020	.0022	.0029	.0048
$C_1 \cdots C_3$	.0010	.0011	.0026	.0056
$C_1 \cdots C_1'$	—	—	.0012	.0021
$C_1 \cdots D_2$	.0061	.0070	.0066	.0089
$C_1 \cdots D_3$	.0035	.0040	.0050	.0079
$Fe - D$	—	—	.0042	.0056
$Fe - C$	—	—	.0013	.0019

Table 3. Perpendicular amplitude correction coefficients for benzene and dibenzenechromium.

Distance	C_6H_6		$Cr(C_6H_6)_2$	
	0 K	298 K	0 K	298 K
C_1-H_1	.0164	.0170	.0169	.0182
C_1-C_2	.0024	.0028	.0031	.0045
$C_1\cdots C_3$	.0011	.0013	.0024	.0045
$C_1\cdots C_4$	.0006	.0007	.0021	.0043
$C_1\cdots C_1'$	—	—	.0012	.0020
$C_1\cdots H_2$	.0086	.0094	.0096	.0118
$C_1\cdots H_3$	.0053	.0058	.0069	.0098
$C_1\cdots H_4$	.0043	.0044	.0062	.0091
$Cr\cdots H$	—	—	.0060	.0074
$Cr-C$	—	—	.0013	.0019

Table 4. Perpendicular amplitude correction coefficients for perdeuterated benzene and dibenzene-chromium.

Distance	C_6D_6		$Cr(C_6D_6)_2$	
	0 K	298 K	0 K	298 K
C_1-D_1	.0117	.0128	.0123	.0142
C_1-C_2	.0024	.0028	.0030	.0045
$C_1\cdots C_3$	.0012	.0015	.0023	.0045
$C_1\cdots C_4$	.0008	.0008	.0020	.0043
$C_1\cdots C_1'$	—	—	.0011	.0020
$C_1\cdots D_2$	.0063	.0074	.0072	.0098
$C_1\cdots D_3$	.0037	.0044	.0053	.0084
$C_1\cdots D_4$	.0029	.0032	.0047	.0079
$Cr\cdots D$	—	—	.0043	.0060
$Cr-C$	—	—	.0013	.0019

struct the perpendicular amplitude correction coefficients (K-values),[4] which are also of importance in electron diffraction studies and are given in Tables 1 – 4.

A comparison of the values shows that the K values for the complexed ligands are usually greater than those of the free molecules except for values larger than 0.01 Å. This may indicate a certain loosening of the molecular frameworks of the complexed species. On the other hand excessive deformation out of the ring plane may be sterically hindered by the presence of the central atom and the other ring. Motions with large perpendicular amplitudes, therefore, are somewhat restricted in the complex and the corresponding values may be larger in the free molecule.

1. Brunvoll, J., Cyvin, S. J. and Schäfer, L. *J. Chem. Phys.* **54** (1971) 1517.
2. Schäfer, L., Southern, J. F., Cyvin, S. J. and Brunvoll, J. *J. Organometal. Chem.* **24** (1970) C13.
3. Brunvoll, J., Cyvin, S. J. and Schäfer, L. *J. Organometal. Chem.* **27** (1971) 107.
4. Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*, Universitetsforlaget, Oslo, and Elsevier, Amsterdam 1968.
5. Cyvin, S. J., Cyvin, B. N., Brunvoll, J. and Schäfer, L. *Acta Chem. Scand.* **24** (1970) 3420.
6. Brunvoll, J., Cyvin, S. J. and Schäfer, L. *Acta Chem. Scand.* **24** (1970) 3427.