General valence force fields of the free and the coordinated cyclopentadienyl anion

T. Polzer, W. Kiefer *

Institut für Physikalische Chemie der Universität Würzburg, Marcusstraße 9-11, D-97070 Würzburg, Germany

Abstract

The modified general valence force field (GVFF) of the free cyclopentadienyl (Cp) anion was developed with internal coordinates to perform the normal coordinate analysis (NCA). Further it is shown that it is possible to transfer the GVFF of the free ring to the coordinated form. The NCA and the GVFF of (Cp)Tl with inclusion of the ring ligand is presented for the first time. Good agreement between observed and calculated wavenumbers has been achieved for both model calculations, the (Cp)K and the (Cp)Tl. The force fields together with force constants and potential energy distribution are given.

1. Introduction

Recently, we have studied the vibrational spectra of ferriosilanes of the type $(Cp)(OC)_2Fe(SiR_3)(Cp = C_5H_5$; $SiR_3 = SiH_3$, $SiMe_3$, $Si(Cl)Me_2$, $Si(Cl)_2Me$ or $SiCl_3)$ [1,2]. These molecules are photochemically active and therefore are of general interest for model studies of hydrosilylation. In these papers we focused our interest on the determination of the metal–ligand vibrations. In a first step towards the development of the valence force field of a complete ferriosilane molecule we carried out the normal coordinate analysis (NCA) of the trihydridosilane of the type $(Cp)(OC)_2$-$Fe(SiH_3)$ where the ring ligand was treated as a point mass [3]. For inclusion of the complete ring ligand into the force field instead of the point mass approximation it is necessary to develop first the NCA of the free ring ligand, the cyclopentadienyl (Cp) anion.

In this paper we present the general valence force field (GVFF) of the Cp anion. The NCA was performed with the use of internal coordinates instead of possible symmetry-adapted coordinates for better transferability of the force field to the ferriosilanes which have lower symmetry. This principle was successfully used in our investigations concerning the development of the NCA

of a complete osmium(II) half-sandwich molecule [4–6]. We have proven the validity of the force field performed for the free Cp for the coordinated state of the ring by application of the force field on the simpliest form of a η^5-coordinated Cp, the molecule (Cp)Tl. Therefore we have also developed the general valence force field for (Cp)Tl. For both the free and the Tl-coordinated Cp anion, we used the vibrational data given in the literature.

2. Group symmetry considerations

The cyclopentadienyl anion has D_{5h} symmetry, and the 24 vibrational degrees of freedom are distributed amongst the symmetry species as

$$2A'_1(\text{Ra}) + A'_2(\text{n.a.}) + A''_2(\text{IR}) + 3E_1(\text{IR})$$

$$+ E''_1(\text{Ra}) + 4E'_2(\text{Ra}) + 2E''_2(\text{n.a.})$$

Therefore the ring has 14 bands with four of A-type symmetry and ten of E-type symmetry. Three bands are inactive and their band positions have to be calculated without available experimental data.

In the case of η^5 coordination on the thallium atom the symmetry of the molecule is lowered to C_{5v}. The former inactive modes of type E''_2 now transform as E_2 and are Raman active. The group-theoretical treatment

---

* Corresponding author.

yields 27 normal modes which are distributed as follows:

$$4A_1(\text{Ra, IR}) + A_2(\text{n.a.}) + 5E_1(\text{Ra, IR}) + 6E_2(\text{Ra})$$

There are three additional normal modes compared with the free ring. One is the symmetric ring–metal stretch vibration of symmetry type A_1 and two are degenerated with symmetry type E_1 and form the corresponding antisymmetric ring–metal stretch vibration. The symmetric C–H out-of-plane deformation mode $\delta_s(\text{C–H})_{oop}$ of symmetry type A''_2 now has A_1 symmetry, whereas the two inactive out-of-plane deformations of E''_2-type symmetry are now of E_2 symmetry and Raman active.

3. Normal coordinate analysis

3.1. Structure parameters

Regular pentagons for the rings were assumed. The bond lengths were taken from the literature [7,8] as follows: C–C bond, 1.417 Å; C–H bond, 1.110 Å; Tl–C bond, 2.680 Å; C–C–C angle, 108°; C–Tl–C angle, 55°.

3.2. Vibrational data

The first step of performing a NCA is the determination of the vibrational wavenumbers of the chosen compound. In contrast with benzene and its derivatives the Cp anion exists only as a salt with a counter-ion. The compound with predominently ionic character of the metal–ring bond is (Cp)K whose vibrational data we will use as those of a "free" Cp anion in this paper. There are several studies concerning the vibrational spectra of alkali metal cyclopentadienides [9–12]. However, some of the band positions of the normal modes of (Cp)K are still uncertain. The bands with A''_2- and E''_2-type symmetry are not IR active and not Raman active. Whereas a band at about 1260 cm^{-1} was derived from solid state studies for the $\delta_s(\text{C–H})_{ip}$ vibration, there exist only calculated wavenumbers for the E''_2-type symmetry bands [13]. For one of these, the $\delta_{as}(\text{C–C})_{oop}$ band, a wavenumber of about 600 cm^{-1} has been calculated. This value seems to be too large because the comparable normal mode of benzene is at about 400 cm^{-1}. The antisymmetric C–H stretch vibration of E'_2-type symmetry has been assumed in Refs. [12,13] to be at about 3060 cm^{-1}. Since in all other cyclopentadienides the wavenumber value of this band was determined to be about 5–15 cm^{-1} below the corresponding antisymmetric C–H stretch vibration of E'_1-type symmetry, we estimated a value of 3050 cm^{-1} in our calculations. Observed and calculated wavenumbers for the Cp anion in (Cp)K are compiled in Table 1 together with the assignments and the potential energy distribution (PED).

For the NCA of the η^5-coordinated Cp anion on

Table 1
Observed and calculated wavenumbers of the Cp anion in (Cp)K with assignments and potential energy distributions

Symmetry (D_{5h})	Assignment	Observed wavenumber [a] (cm^{-1})	Calculated wavenumber (cm^{-1})	PED [b] (%)
A'_1	$\nu_s(\text{C–H})$	3088	3088	$99s_2$
	$\nu_s(\text{C–C})$	1119	1119	$98s_1$
A'_2	$\delta_s(\text{C–H})_{ip}$	— [c]	1260	100β
A''_2	$\delta_s(\text{C–H})_{oop}$	700	700	100κ
E'_1	$\nu_{as}(\text{C–H})$	3061	3061	$99s_2$
	$\nu_{as}(\text{C–C})$	1440	1440	$46\beta + 44s_1 + 9\alpha$
	$\delta_{as}(\text{C–H})_{ip}$	1008	1008	$64\beta + 30s_1 + 6\alpha$
E''_1	$\delta_{as}(\text{C–H})_{oop}$	719	719	$55\tau + 44\kappa$
E'_2	$\nu_{as}(\text{C–H})$	($\approx$ 3050) [d]	3050	$99s_2$
	$\delta_{as}(\text{C–C})_{ip}$	1346	1346	$56s_1 + 23\alpha + 21\beta$
	$\delta_{as}(\text{C–H})_{ip}$	1070	1070	$86\beta + 6s_1 + 6\alpha$
	$\delta_{as}(\text{C–C})_{ip}$	854	854	$54s_1 + 39s_2 + 6\beta$
E''_2	$\delta_{as}(\text{C–H})_{oop}$	— [c]	841	$63\tau + 37\kappa$
	$\delta_{as}(\text{C–C})_{oop}$	— [c]	334	$64\tau + 36\kappa$

[a] [9–11].
[b] PED values below 3% are omitted.
[c] Not Raman active nor IR active.
[d] Estimated value (see text).

Table 2

Observed and calculated wavenumbers of the η^5-coordinated Cp anion (Cp)Tl with assignments and potential energy distributions

Symmetry (C_{5v})	Assignment [a]	Observed wavenumber [b] (cm^{-1})	Calculated wavenumber (cm^{-1})	PED [c] $(\%)$
A_1	$\nu_s(C-H)$	3096	3096	$99 s_2$
	$\nu_s(C-C)$	1120	1120	$96 s_1$
	$\delta_s(C-H)_{oop}$	727	727	98κ
	$\nu_s(Tl-Cp)$	160	160	$100 s_3$
A_2	$\delta_s(C-H)_{ip}$	1255	1255	100β
E_1	$\nu_{as}(C-H)$	3070	3070	$99 s_2$
	$\nu_{as}(C-C)$	1425	1425	$49\beta + 44 s_1 + 6\alpha$
	$\delta_{as}(C-H)_{ip}$	1008	1008	$66\beta + 29 s_1 + 4\alpha$
	$\delta_{as}(C-H)_{oop}$	754	754	$67\kappa + 31\tau$
	$\nu_{as}(Tl-Cp)$	290	290	$94 s_3 + 4\kappa$
E_2	$\nu_{as}(C-H)$	3065	3065	$99 s_2$
	$\delta_{as}(C-C)_{ip}$	1350	1350	$59 s_1 + 22\beta + 18\alpha$
	$\delta_{as}(C-H)_{ip}$	1060	1060	$93\beta + 6\alpha$
	$\delta_{as}(C-C)_{ip}$	843	843	$73 s_1 + 18\alpha + 7\beta$
	$\delta_{as}(C-H)_{oop}$	804	804	$69\kappa + 27\tau + 4 s_3$
	$\delta_{as}(C-C)_{oop}$	— [d]	361	$40 s_3 + 33\tau + 26\kappa$

[a] The assignments of the ring vibrations are those of the free ring for better comprehension.
[b] [12–14].
[c] PED values below 3% are omitted.
[d] Band position uncertain (see text).

thallium we used the vibrational data reported in the literature. The wavenumbers of the ring vibrations were derived from solid state Raman and IR spectroscopy [14,15], whereas the metal–ring stretch vibrations were detected by microwave spectroscopy [16]. Table 2 summarizes the observed and calculated values similar to those of Table 1. As can be recognized, most of the vibrations of the ring in (Cp)Tl have only slightly changed band positions of up to 35 cm^{-1} when compared with the free ring vibrations.

3.3. Vibrational force fields

The internal coordinates are defined in Figs. 1 and 2 for (Cp)K and for (Cp)Tl respectively; s denotes the stretch coordinates, α and β denote the in-plane deformation coordinates, and κ and τ denote the out-of-plane coordinates.

The free Cp anion can be described by a force field with 35 diagonal elements including ten stretch, 15 in-plane bend, five out-of-plane bend and five torsion coordinates. In the case of the (Cp)Tl the internal coordinates are the same as used for the free ring with addition of the metal–ring stretch coordinates. To perform the NCA of (Cp)Tl, the optimized GVFF of the free Cp anion was expanded with the Tl–C stretch coordinates and necessary interaction force constants. The force field was then refined by use of the assignments and band positions of (Cp)Tl as stated above.

The normal coordinate calculations were performed by use of the FG matrix method of Wilson et al. [17] and of a modified version of QCMP-067 [18] and VIA [19]. The calculations were carried out on a SPARC/2 workstation and on a personal computer.
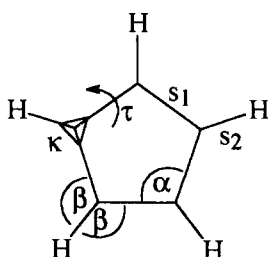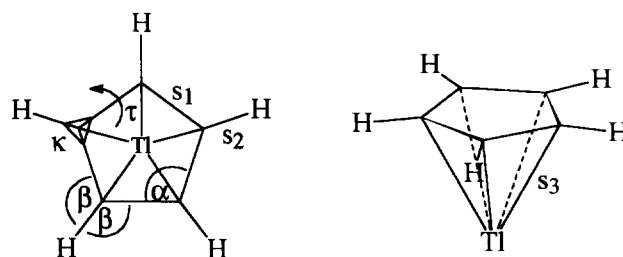

Fig. 1. Defined internal coordinates for the free cyclopentadienyl anion: s_1, C–C stretch; s_2, C–H stretch; α, C–C–C bend in plane; β, C–C–H bend in plane; κ, C–H bend out of plane; τ, C–C torsion.

Fig. 2. Defined internal coordinates for the η^5-coordinated cyclopentadienyl anion: s_1, C–C stretch; s_2, C–H stretch; s_3, Tl–C stretch; α, C–C–C bend in plane; β, C–C–H in plane; κ, C–H bend out of plane; τ, C–C torsion.

4. Results and discussion

As already mentioned above, the wavenumbers calculated for (Cp)K and (Cp)Tl are compiled in Tables 1 and 2 respectively and compared with their observed values. The corresponding potential energy distribution of each normal mode is also given. The resulting force constants and their definitions are compiled in Table 3.

Good agreement between the calculated and observed wavenumbers for both the free and the coordinated Cp anion was obtained. The wavenumbers of the 24 normal modes of (Cp)K and of the 27 normal modes of (Cp)Tl were calculated with deviations smaller than 1 cm^{-1} in all cases. For the (Cp)K we used a force field

with 35 diagonal elements and 150 off-diagonal elements represented by 26 different force constants. The force field of (Cp)Tl was performed by means of 40 diagonal and 195 off-diagonal elements and the number of different force constants is increased to 35.

The small deviations of the band positions between free and coordinated ring lead also to small changes in the PEDs. Most of the force constants also differ only by small amounts. Larger changes were observed only for the diagonal force constant of the torsion coordinate τ which decreases from 0.595 mdyn Å^{-1} for (Cp)K to 0.153 mdyn Å^{-1} for (Cp)Tl. This is caused through the coupling with the Tl–C stretch coordinate because the displacements of both coordinates coincide. Likewise

Table 3
Internal coordinates and calculated force constants of the free and the η^5-coordinated Cp anion (for definitions see Figs. 1 and 2)

Internal coordinate	Definition	[(Cp)$^-$] (D_{5h}) value [a]	[(Cp)Tl](C_{5v}) value [a]
Diagonal			
C–C stretch	s_1	5.311	5.136
C–H stretch	s_2	5.047	5.080
Tl–C stretch	s_3	—	0.690
C–C–C bend in plane	α	1.583	1.013
C–C–H bend in plane	β	0.460	0.466
C–H bend out of plane	κ	0.245	0.213
C–C torsion	τ	0.595	0.153
Stretch–stretch interaction			
C–C stretch–C–C stretch (adjacent)	$s_1 s_1'$	0.859	0.949
C–C stretch–C–C stretch (1 adjacent)	$s_1 s_1''$	−0.002	−0.009
C–C stretch–C–H stretch	$s_1 s_2$	0.007	0.009
C–C stretch–Tl–C stretch (adjacent)	$s_1 s_3'$	—	0.015
C–C stretch–Tl–C stretch (1 adjacent)	$s_1 s_3''$	—	−0.021
C–H stretch–C–H stretch (adjacent)	$s_2 s_2'$	0.030	0.027
C–H stretch–C–H stretch (1 adjacent)	$s_2 s_2''$	0.007	0.009
C–H stretch–Tl–C stretch	$s_2 s_3$	—	0.013
Tl–C stretch–Tl–C stretch (adjacent)	$s_3 s_3'$	—	−0.108
Tl–C stretch–Tl–C stretch (1 adjacent)	$s_3 s_3''$	—	−0.143
Stretch–Bend interaction			
C–C stretch–C–C–C bend in plane	$s_1 \alpha$	−0.032	−0.116
C–C stretch–C–C–C bend in plane (adjacent)	$s_1 \alpha'$	−0.110	−0.150
C–C stretch–C–C–H bend in plane	$s_1 \beta$	0.098	0.172
C–C stretch–C–C–H bend in plane (adjacent)	$s_1 \beta'$	−0.062	0.062
C–H stretch–C–C–H bend in plane	$s_2 \beta$	0.018	0.001
Tl–C stretch–C–C–C bend in plane (adjacent)	$s_3 \alpha'$	—	−0.014
Tl–C stretch–C–C–C bend in plane (1 adjacent)	$s_3 \alpha''$	—	−0.005
Tl–C stretch–C–C–H bend in plane	$s_3 \beta$	—	0.001
Bend–bend interaction			
C–C–C bend in plane–C–C–C bend in plane (adjacent)	$\alpha \alpha'$	−0.124	−0.568
C–C–C bend in plane–C–C–C bend in plane (1 adjacent)	$\alpha \alpha''$	0.090	0.086
C–C–C bend in plane–C–C–H bend in plane	$\alpha \beta$	0.032	0.002
C–C–C bend in plane–C–C–H bend in plane (adjacent)	$\alpha \beta'$	0.057	0.022
C–C–H bend in plane–C–C–H bend in plane	$\beta \beta$	0.039	0.053
C–C–H bend in plane–C–C–H bend in plane (adjacent)	$\beta \beta'$	0.051	0.086
C–C–H bend in plane–C–C–H bend in plane (1 adjacent)	$\beta \beta''$	0.028	0.052
C–H bend out of plane–C–H bend out of plane	$\kappa \kappa$	0.036	0.064
C–H bend out of plane–C–C torsion	$\kappa \tau$	0.166	0.212
C–C torsion–C–C torsion	$\tau \tau$	0.206	0.001

[a] Values for stretches and their interactions are in millidynes per ångström, for bendings, waggings and torsions and all interactions thereoff in millidyne ångströms per square radian and for interactions of stretches with bendings, waggings and torsions in millidynes per radian.

the interaction force constant $\tau\tau$ is lowered from 0.206 to 0.001 mdyn Å rad^{-2}.

The antisymmetric C–C deformation modes δ_{as}(C–C)$_{ip}$ of E_2 symmetry were found at 1346 cm^{-1} and 854 cm^{-1} in (Cp)K. Owing to coordination, the first is raised to 1350 cm^{-1} and the other is lowered to 843 cm^{-1}. These small changes in the band positions cause a decrease in the interaction force constant $\alpha\alpha'$ in the force field which is lowered from -0.124 to -0.568 mdyn Å rad^{-2}.

The three inactive modes of the Cp anion with A_2'- and E_2''-type symmetry were calculated to be at 1260 cm^{-1}, 841 cm^{-1} and 334 cm^{-1} for the δ_s(C–H)$_{ip}$, δ_{as}(C–H)$_{oop}$ and δ_{as}(C–C)$_{oop}$ bands respectively. For the latter a value of 361 cm^{-1} (Cp)/Tl was evaluated. The high value of τ in the PED is lowered to 33% owing to the strong coupling with s_3 which participated with 40%.

The Tl–Cp vibrations which are described by s_3 are almost completely uncoupled with other coordinates. Only the PED of the metal–ring "tilt" vibration ν_{as}(Tl–Cp) contains a small amount of an out-of-plane deformation coordinate. For the Tl–C stretch coordinate s_3 a value of 0.690 mdyn Å^{-1} was evaluated. This shows the strength of the ring–metal bond of a system with η^5-coordinated Cp. If the ring ligand had been treated as a point mass at the center of the ring, the molecule (Cp)Tl could then be reduced to a two-mass oscillator. In this case, a force constant of 2.443 mdyn Å^{-1} is obtained. Related to a single Tl–C bond this would be 0.498 mdyn Å^{-1}, which means a difference of about 30% compared with the result of the complete NCA. Therefore, the results of the NCA performed with point mass approximations in these cases have to be considered as questionable.

Acknowledgments

References

[1] T. Polzer, U. Posset, C. Engert, V. Deckert and W. Kiefer, in H. Werner, A.G. Griesbeck, W. Adam, G. Bringmann and W. Kiefer (eds.), *Selective Reactions of Metal Activated Molecules*, Vieweg, Braunschweig, 1992, p. 225.

[2] T. Polzer, D. Gernet and W. Kiefer, in W. Kiefer, M. Cardona, G. Schaack, F.W. Schneider and H.W. Schrötter (eds.), *Proc. 13th Int. Conf. on Raman Spectroscopy*, Wiley, Chichester, 1992, p. 730.

[3] T. Polzer and W. Kiefer, in preparation.

[4] T. Polzer, A. Ellebracht, W. Kiefer, U. Wecker and H. Werner, *J. Organomet. Chem., 438* (1992) 319.

[5] T. Polzer and W. Kiefer, *Asian J. Phys., 4* (1995) 4.

[6] T. Polzer and W. Kiefer, *J. Organomet. Chem., 472* (1994) 303.

[7] M.J.S. Dewar and R.C. Haddon, *J. Am. Chem. Soc., 95* (1973) 5836.

[8] E. Frasson, F. Menegus and C. Panattoni, *Nature, 199* (1963) 1087.

[9] (a) H.P. Fritz and L. Schäfer, *Chem. Ber., 97* (1964) 1829; (b) H.P. Fritz, *Adv. Organomet. Chem., 1* (1964) 239.

[10] V.T. Aleksanyan and B.V. Lokshin, *J. Organomet. Chem., 131* (1977) 113.

[11] V.T. Aleksanyan, in J.R. Durig (ed.), *Vibrational Spectra and Structure*, Vol. 11, Elsevier, Amsterdam, 1982, p. 115.

[12] I.A. Garbuzova, O.G. Garkusha, B.V. Lokshin, G.K. Borisov and T.S. Morozova, *J. Organomet. Chem., 279* (1985) 327.

[13] O.G. Garkusha, I.A. Garbuzova, B.V. Lokshin and J. Mink, *J. Mol. Struct., 175* (1988) 165.

[14] R.T. Bailey and A.H. Curran, *J. Mol. Struct., 6* (1970) 391.

[15] O.G. Garkusha, B.V. Lokshin, R.B. Materikova, L.M. Golubinskaya, V.I. Bregadze and A.P. Kurbakova, *J. Organomet. Chem., 342* (1992) 281.

[16] C. Roberts, A.P. Cox and M.J. Whittle, *J. Mol. Spectrosc., 35* (1970) 476.

[17] E.B. Wilson, Jr., J.C. Decius and P. Cross, *Molecular Vibrations*, Dover Publications, New York 1980.

[18] D.F. McIntosh and M.R. Peterson, *QCPE 342*, 1991.

[19] H.C. Fleischhauer, *Ph.D. Thesis*, University of Düsseldorf, 1991.