Force constant calculations for (chloromethyl)mercury(II) chloride and (bromomethyl)mercury(II) bromide

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Abstract

Normal coordinate analyses have been carried out for the $ClCH_2HgCl$ and $BrCH_2HgBr$ molecules by use of the FG-matrix method and a simple valence force field incorporating ten primary and five interaction force constants. Some re-assignments and modifications of the published experimental vibrational assignments are proposed, and other tentative assignments are confirmed by these calculations. A decrease in value of the Hg–C stretching force constant on going from $(CH_3)_2Hg$ to $ClCH_2HgCl$ is observed. A comparison is made of the stretching force constants for the series of molecules $(CH_3)_2Hg$, $ClCH_2HgCl$ and Cl_3CHgCl, and the effect of substitution of the Cl atom in a methyl group of $(CH_3)_2Hg$ is discussed.

Introduction

Force constant calculations on CH_3HgCl [1] and Cl_3CHgCl [2] have been carried out previously. However, the effect of complete substitution of the hydrogen atoms in the methyl group by chlorine atoms resulted in very strong coupling between the carbon–chlorine stretching, mercury–chlorine stretching, and carbon–chlorine deformation modes. The observed vibrational wavenumbers of Cl_3CHgCl could therefore only be described by using large values for the interaction constants; the extensive "mixing" of the carbon–chlorine vibrational modes, for example, is demonstrated by the presence of well-resolved chlorine isotope features in the symmetric CCl_3 deformation in the Raman spectrum of Cl_3CHgCl [3]. Also, there are no reports in the literature of the vibrational spectrum or force constant calculations on the Br_3CHgBr species, so information on the substitution of Br atoms for H atoms in the methyl group of CH_3HgBr is not available.

In this study, we report the results of force constant calculations on the mono-substituted species $ClCH_2HgCl$ and $BrCH_2HgBr$, which have only recently been the subject of vibrational spectroscopic studies [4,5]. Problems due to coupled

vibrations arising from the CX_3 groups, where $X = Cl$, Br, in CX_3HgX which complicate the force-field fitting procedures are now removed. Also, it becomes possible for the first time to compare quantitatively the effect of substitution of a single Cl or Br atom in the methyl group of CH_3HgCl or CH_3HgBr on the mercury–carbon and mercury–halogen bonds.

Experimental: force constant calculations

The molecular structure of the XCH_2HgX species ($X = Cl$, Br), deduced from vibrational spectroscopy [4,5], is shown in Fig. 1 and has been assigned to the molecular point group C_s. The spectroscopic activity is given by

$$\Gamma_{vib} = 8A' + 4A''$$

all of which are active in the infrared and Raman, and the 8A′ modes will be polarized in the Raman spectra. For the published Raman spectra of $ClCH_2HgCl$ and $BrCH_2HgBr$, complete vibrational assignments have been given, but several of these may be open to other interpretation. An important function of the force constant calculations described here will be the confirmation of the vibrational assignments by examination of the potential energy distributions of the assigned molecular vibrations.

Force constant calculations were carried out by use of a modified form of the original program employed by Snyder and Schachtschneider [6] with the changes in formatting data input suggested by Fuhrer et al. [7], and further adapted by ourselves for running on a Cyber 180-830 computer. The calculations used the Wilson FG-Matrix method [8] and a simple valence force field with primary force constants and interaction force constants. Input data consisted of molecular parameters, symmetry elements, the number of atoms in the molecule, molecular stereochemistry and the observed molecular vibrational wavenumbers. The input stages, sub-routines, and mechanism of operation of the program have been described previously [9]. At each stage of the calculations checks were made to verify that the program was running correctly and that the correct information was being processed.

The molecular parameters used in our calculations were taken from the literature [10,11] and are given in Table 1; atomic masses in relative a.m.u. were taken from

Table 1

Molecular parameters for XCH_2HgX species ($X = Cl$, Br)

	X = Cl	X = Br	Ref.
Bond lengths (Å)			
Hg–X	2.282	2.406	10
Hg–C	2.094	2.094	11
C–X	1.781	1.939	10
C–H	1.096	1.096	11
Bond angles (°)			
CHgX	180	assumed	
HCH	109.5	[11]	
HCCl	109.5	assumed	

standard tables, e.g. [12]. In the absence of X-ray structural data for these molecules, the molecular parameters given in Table 1 were adopted.

For the CH_2XHgX species 14 internal coordinates were necessary for the generation of the full set of 12 normal vibrations in the A' and A'' symmetry classes. The internal coordinates used are shown in Fig. 1. In the initial stages of SVFF force-field refinement ten primary force constants were used for each species, namely:

k_r HgX stretching
k_R HgC stretching
k_d CX stretching
k_D CH stretching
k_α XCHg deformation
k_β HCHg deformation
k_γ HCCl deformation
k_δ CH_2 deformation
k_θ CHgX in-plane deformation
k_ϕ CHgX out-of-plane deformation

Further refinement necessitated the incorporation of interaction constants into the force-field. However, since there are only twelve observed vibrational wavenumbers for each species, such refinements would normally only permit a maximum of two interaction force constants to be included in the force-field. The importance of the interaction constants and the use of all the available vibrational information for the force-field refinement has been demonstrated for organometallic species containing ligands coordinated through carbon or phosphorus [9,13,14]. Achievement of the necessary refinement to the observed wavenumbers with a realistic force-field, therefore, required that several primary force constants, such as k_θ and k_ϕ, be held constant while other interaction constants were added and refined with the varying primary force constants. Hence, the presence or otherwise of the interaction force constants and their relative importance could be assessed by allowing them to vary individually. In common with force-field analyses of similar molecules [14], it was found that some interaction constants, such as $k_{\gamma\gamma}$, were important for the force-field stability even though their values were rather small.

Results and discussion

The values of the force constants obtained from the best-fit refinements for $ClCH_2HgCl$ and $BrCH_2HgBr$ are shown in Tables 2 and 3; in both cases the rms error in fitting the observed and calculated wavenumbers is less than 0.1%.
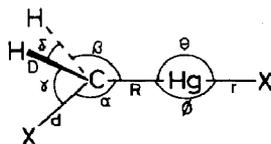

Fig. 1. Molecular structure and internal coordinates for XCH_2HgX species (X = Cl, Br)

Table 2

Potential energy distributions, vibrational wavenumbers and force constants for $ClCH_2HgCl$

ν	Symmetry class	Vibrational wavenumber (cm^{-1})		Force constants														
		Obs.	Calc.	k_r	k_r	k_D	k_d	k_θ	k_ϕ	k_δ	k_γ	k_β	k_α	$k_{\beta\gamma}$	$k_{\alpha\gamma}$	$k_{d\alpha}$	$k_{\gamma\gamma}$	k_{dD}
				Value [a] 2.01	1.51	4.86	1.63	0.19	0.04	0.16	0.27	0.24	0.26	-0.01	-0.02	0.21	0.02	0.10
ν_1	A'	2940	2940	0	0	100.0	0	0	0	0	0	0	0.1	0	0	0	0	-0.1
ν_2		1237	1237	0	3.2	0	2.4	0.1	0	0.1	42.5	46.8	0.1	1.5	1.7	0.2	1.5	0
ν_3		971	971	0	0.3	0	0.8	0.1	0	60.6	22.4	17.8	0.5	-0.7	-2.5	-0.2	0.08	0
ν_4		547	547	0	5.9	0.1	84.1	6.0	0.6	0	2.0	0.1	6.4	0	2.7	-7.7	0.1	-0.2
ν_5		486	486	0.9	60.6	0.1	1.4	2.5	0.2	0.9	1.4	8.5	30.2	0.1	-4.7	-2.1	0	0
ν_6		336	336	98.1	0.1	0	0.1	0.1	0	0.1	0	0.2	1.3	0	-0.2	0.1	0	0
ν_7		185	185	0.8	23.8	0	13.3	25.4	2.5	2.5	0.2	1.4	25.5	0	-1.5	6.2	0	-0.1
ν_8		-	114	0.1	6.1	0	0.8	56.7	5.7	2.9	0.3	1.9	29.4	0	-2.3	-1.6	0	0
ν_9	A''	3020	3020	0	0	99.8	0	0	0	0	0.1	0.1	0	0	0	0	0	0
ν_{10}		1045	1045	0	0	0	0	0	0	0	48.7	54.7	0	-1.7	0	0	-1.7	0
ν_{11}		721	721	0	0	0.2	0	0	0.4	0	54.5	45.0	0	1.7	0	0	-1.9	0
ν_{12}		100	100	0	0	0	0	0	99.5	0	0.2	0.2	0	0	0	0	0	0

[a] Stretching and stretch–stretch interaction force constants in units of mdyn $Å^{-1}$; angle deformation and angle–angle deformation interaction force constants in mdyn $Å^{-1}$ rad^{-2}.

Table 3

Potential energy distributions, vibrational wavenumbers and force constants for $BrCH_2HgBr$

ν	Symmetry class	Vibrational wavenumber (cm^{-1})		Force constants														
		Obs.	Calc.	k_r	k_R	k_D	k_d	k_θ	k_ϕ	k_δ	k_γ	k_β	k_α	$k_{\beta\gamma}$	$k_{\alpha\gamma}$	k_{Rd}	$k_{\gamma\gamma}$	k_{dD}
				Value [a] 1.81	1.69	4.86	1.47	0.21	0.07	0.16	0.26	0.25	0.24	0.01	0.02	0.16	0.02	−0.10
ν_1	A'	2948	2948	0	0	99.5	0.1	0	0	0.1	0	0	0.1	0	0	0	0	0.2
ν_2		1221	1221	0	2.3	0	3.0	0.3	0.1	0.3	52.5	45.3	0	−8.2	0.5	−0.5	4.5	0
ν_3		1044	1044	0	1.2	0.1	0.4	0.2	0	54.3	11.6	25.7	0.9	2.9	1.6	0.1	1.0	0
ν_4		510	509	0.2	23.4	0.5	30.1	8.2	1.4	0.3	7.1	0.9	28.9	0.4	−7.0	5.5	0.6	−0.4
ν_5		486	486	0.3	58.7	0.1	43.3	2.5	0.4	0	1.7	3.1	0.4	−0.4	0.4	−10.5	0.1	−0.2
ν_6		232	232	96.8	0	0	0.8	0.2	0	0	0.2	0	2.3	0	−0.3	0	0	0
ν_7		–	138	2.0	7.8	0.1	23.4	39.7	6.9	0.3	1.9	0.1	17.9	0.1	−2.9	2.8	0.2	−0.1
ν_8		90	80	0.8	7.8	0	0.4	34.1	6.0	0.8	5.1	0.3	51.9	0.2	−8.0	0.3	0.4	0
ν_9	A''	3020	3020	0	0	99.8	0	0	0	0	0.1	0.1	0	0	0	0	0	0
ν_{10}		1122	1123	0	0	0	0	0	0	0	43.6	52.1	0	8.0	0	0	−3.7	0
ν_{11}		691	691	0	0	0.2	0	0	1.0	0	65.9	48.0	0	−9.4	0	0	−5.6	0
ν_{12}		130	131	0	0	0	0	0	99.0	0	0.6	0.5	0	−0.1	0	0	−0.1	0

[a] Stretching and stretch–stretch interaction force constants in units of mdyn Å^{-1}; angle deformation force constants and angle–angle deformation interaction force constants in units of mdyn Å^{-1} rad^{-2}.

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However, the full refinements and force-field stability to change in individual force constants could only be achieved by the incorporation of several reassignments to the observed spectral wavenumbers. Original vibrational spectroscopic assignments are often quite subjective and force constant calculations can indicate the correctness or otherwise of the assumptions. For example, in the vibrational spectra of the $ClCH_2HgCl$ and $BrCH_2HgBr$ species, three bands were observed [4,5] in the region of $\Delta\tilde{\nu} = 450-600$ cm^{-1}. According to our force-constant calculations and during the setting-up of the FPERT program [9], it became clear that only two fundamentals should occur in this region with the correct symmetries. On a re-examination of the observed spectral assignments it was realised that a mis-assignment had been made; the band at $\Delta\tilde{\nu} = 677$ cm^{-1} (A') for $ClCH_2HgCl$ described as a CH_2Cl rock was clearly in error. Calculations indicated that this band could be the first overtone (A' symmetry) of the HgCl stretching fundamental at 336 cm^{-1} or a combination of the fundamentals at 185 cm^{-1} (A') and 486 cm^{-1}, which would itself also be of A' symmetry. Support for the latter assignment is provided by the spectroscopic data reported by Beattie and Gilson [15], who noted the presence of a similar feature in the same region of the Raman spectrum of Hg_2Cl_2, a molecule with similar skeletal features.

Likewise, the band at 633 cm^{-1} assigned in the original spectroscopic work on $BrCH_2HgBr$ to a CH_2Br rock fundamental was here reassigned to a combination of the fundamentals at 130 and 486 cm^{-1}.

An examination of the potential energy distributions from the best-fit refinements of the force constant calculations shows some interesting features. Several fundamentals are mixed, some strongly mixed. For example, although the HgCl and HgBr stretching fundamentals (ν_6) may be considered as nearly pure modes, with little evidence of mixing, the so-called CHgCl and CHgBr deformations (ν_7) are strongly mixed and involve substantial contributions from the HgC stretching, CX stretching (X = Cl, Br), CHgX in-plane deformation and XCHg deformation modes. The ν_7 modes may, therefore, be more correctly described as "breathing" motions of the CH_2X group attached to the CHgX skeleton. In Table 4, the new assignments of vibrational wavenumbers are given with the proposals for re-definition of the mode descriptions for both $ClCH_2HgCl$ and $BrCH_2HgBr$. Similar patterns of mixing were reported for the previous force-constant calculations for Cl_3CHgCl and $(Cl_3C)_2Hg$ [2], but the mode mixing would be even more serious in these cases because of the complete substitution of the methyl group by Cl atoms.

Force constant values for the $ClCH_2HgCl$ and $BrCH_2HgBr$ molecules are compared with related molecules in Table 5, from which several points of comparison can be made.

The force constant of HgX stretching, k_r (HgCl or HgBr stretching) for $BrCH_2HgBr$ is 90% of its value for the chloro-substituted compound $ClCH_2HgCl$; this is in accord with the k_r values for CH_3HgCl and CH_3HgBr [1] and also with those for the unsubstituted halides $HgCl_2$ and $HgBr_2$, for which the k_r values [16] are 2.64 and 2.32 mdyn Å^{-1}, respectively. This indicates that the substitution of a methyl group for a halogen atom in the $HgCl_2$ or $HgBr_2$ species, and further substitution of Cl or Br for H within the methyl group itself, does not affect the Hg–Cl or Hg–Br bonds.

A different picture emerges when the force constant k_R (HgC stretching) is considered; substitution of the Cl or Br atom in the methyl group of CH_3HgCl or

Table 4

Vibrational assignments for XCH_2HgX species (X = Cl, Br)

Symmetry class	ν	$ClCH_2HgCl$ wavenumber (cm^{-1})	$BrCH_2HgBr$ wavenumber (cm^{-1})	Approximate description of vibrational mode
A′	ν_1	2940	2948	CH_2 symmetric stretch
	ν_2	1237	1221	CH_2 rock; CHX deformation
	ν_3	971	1044	CH_2 symmetric deformation
	ν_4	547	510	CX stretch; CHg stretch
	ν_5	486	486	HgC stretch
	ν_6	336	232	HgX stretch
	ν_7	185	[138] [a]	XCHg breathing
	ν_8	[114] [a]	90	XCHg deformation; CHgX in-plane deformation
A″	ν_9	3020	3020	CH_2 asymmetric stretch
	ν_{10}	1045	1122	CH_2 rock; CHX deformation
	ν_{11}	721	691	CH_2 rock; CHX deformation
	ν_{12}	100	130	CHgX out-of-plane deformation

[a] Predicted wavenumbers from force constant calculations.

CH_3HgBr has reduced the value of k_R to 60% and 69% of its previous value, respectively. This may be attributed to the effect of the electronegativities of the halogen substituents on the Hg–C bond, the chlorine atom having a larger effect because of its greater electron-withdrawing power. However, comparisons of the k_R values with those of the $(CH_3)_2Hg$ [11] and Cl_3CHgCl species [2] are more difficult to explain. Substitution of three chlorine atoms in the methyl group of CH_3HgCl results in the reduction of the k_R value to only 93% of its previous value; the substitution of all the H atoms in $(CH_3)_2Hg$ for Cl atoms to produce $(Cl_3C)_2Hg$ results in a reduction of the HgC stretching force constant of only 8%, to 2.17 mdyn $Å^{-1}$ [2] in the latter compound. We feel that these decreases in k_R value are rather

Table 5

Force constants [a] for $ClCH_2HgCl$, $BrCH_2HgBr$ and related molecules; treated as $XCH_2Hg\ X'$ type species (X = H, Cl, Br; X′ = CH_3, Cl, Br)

Force constant and description	$ClCH_2HgCl$ This work	$BrCH_2HgBr$ This work	CCl_3HgCl [2]	CH_3HgCl [1]	CH_3HgBr [1]	$(CH_3)_2Hg$ [11]
k_r HgX′ stretching	2.01	1.81	2.04	2.01	1.79	2.38
k_R HgC stretching	1.51	1.69	2.21	2.55	2.48	2.38
k_D CH stretching	4.86	4.86	–	4.82	4.81	4.80
k_d CX stretching	1.63	1.47	2.76	4.82	4.81	4.80
k_θ CHgX′ in-plane bending	0.19	0.21	0.14	0.10	0.09	0.38
k_δ CH_2 bending	0.16	0.16	–	0.49	0.49	0.43
k_β HC Hg bending	0.24	0.25	–	0.47	0.47	0.34
k_α XC Hg bending	0.26	0.24	0.43	0.47	0.47	0.34

[a] Stretching force constants in units of mdyn $Å^{-1}$; angle deformation force constants in units of mdyn $Å^{-1}\ rad^{-2}$.

small for the substitutions involved, and suggest that the presence of a large amount of mode mixing and interactions, especially in the Cl_3C and $(Cl_3C)_2$ species, is responsible. Even without the refinements of the present calculations, a simplified force constant analysis [4] earlier gave a k_R value of 1.8 mdyn $Å^{-1}$ for $ClCH_2HgCl$, and this is quite close to the final refined force constant value in Table 5.

The effect of the introduction of one Cl atom into the methyl group of CH_3HgONO_2 on the dissociation into nitrate ions in aqueous solution has already been evaluated [17]; quantitative Raman spectroscopic measurements of the dissociation of $ClCH_2HgONO_2$ in aqueous solution have demonstrated that the dissociation constant K_c is reduced by 100 × from 30 mol dm^{-3} for CH_3HgONO_2 [18] to 0.3 mol dm^{-3} for $ClCH_2HgONO_2$ [17]. The large effect of the substitution of a single Cl atom into the CH_3Hg entity for nitrate dissociation must surely produce a substantial change in the Hg–C bond force constant, as indicated in our calculations.

The k_D (CH stretching) force constant does not change significantly with substitution in the series, $ClCH_2HgCl$, $BrCH_2HgBr$, CH_3HgCl, CH_3HgBr and $(CH_3)_2Hg$. This is expected from an examination of the potential energy distributions of the CH vibrations in Tables 2 and 3, e.g. ν_1, ν_2, ν_3, ν_9, ν_{10}, ν_{11}, which are subject mainly to CH mode contributions and are little affected by the C–Hg, Hg–X or C–X modes. On the other hand, the CCl stretching force constant, k_d, is considerably different from the reported value for the CCl_3HgCl species [2]; unfortunately, no comparison can be made for the CBr stretching force constant in $BrCH_2HgBr$ and bromo analogues of Cl_3CHgCl as there are no reports of these in the literature. The wavenumber assigned to $\nu(CCl)$ stretching in $ClCH_2HgCl$ at 547 cm^{-1} and to $\nu(CBr)$ stretching in $BrCH_2HgBr$ at 510 cm^{-1} are both much lower than their counterparts in CH_3Cl and CH_3Br at 732 and 611 cm^{-1}, respectively [16]. Examination of the potential energy distributions in Tables 2 and 3 show that although the ν_4 mode for the chloro-species is 84% CCl stretching, there is only 30% CBr stretching in the ν_4 mode of the bromo compound, other important contributions coming from k_R and $k_{\alpha'}$ the HgC stretch and BrCHg deformation. Internal consistency in this work seems to be good, however, since the ratio of the k_d values for bromo- and chloro-CH_2XHgX species here is 90%, exactly the same as the ratio of the k_r values. Mink and Goggin [2] have presented evidence for extensive mode mixing in the CCl_3Hg-species studied in their work using six fundamental primary force constants and two interaction force constants; this could suggest that the neglect of important interaction force constants in those calculations would have serious consequences for the k_d values relating to the Cl_3C groups.

Comparisons of the interaction constants used here demonstrates how important these are in force field refinements for halo-substituted organometallic compounds; in earlier studies [2,3,11] the number of interaction force constants was severely curtailed owing to the limitations of vibrational spectroscopic information available consequent from the higher symmetry point groups of the molecules concerned, e.g. Cl_3CHgCl.

In conclusion, we maintain that the effect of chlorine or bromine substitution in the methyl group of CH_3HgCl or CH_3HgBr has a large effect on the mercury–carbon bond but very little effect on the mercury–halogen bond. The effect of halogen substitution in the methyl group on the mercury–carbon bond in $ClCH_2HgCl$ is greater than that suggested by the results of earlier force constant calculations on

Cl_3CHgCl and $(Cl_3C)_2Hg$ by some 40%, compared to the 8% suggested previously [2].

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