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Force Constant Calculations for the In-Plane Vibrations of Complexes *cis*-$[MX_2(CO)_2]^{n-}$ (for n = 0, MX = PtCl or PtBr; for n = 1, MX = RhCl, RhBr or IrCl)

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Force constants for planar complexes cis-$[MX_2(CO)_2]^{0\ or\ -}$ *(MX = RhCl, RhBr, IrCl, PtCl and PtBr) have been calculated using a modified valence force field, with constrained off-diagonal force constants based on* $[MX_4]^{2-}$ *and* $[MX_3(CO)]^-$ *(M = Pt or Pd) studies.*

The MC stretching force constants are proportionately more sensitive than those for CO, but for members of the same transition series the trends are in fair agreement with the proportionate changes in bond orders. For the platinum complexes, incorporation of PtC n.m.r. coupling data improves the agreement.

As between $[PtCl_3(CO)]^-$ *and* $[PdCl_3(CO)]^-$*, the lowering of the metal–carbon stretching force constant between* $[IrCl_2(CO)_2]^-$ *and* $[RhCl_2(CO)_2]$ *is much greater than for metal–chlorine and it is suggested that the lower availability of 4d orbitals than 5d strongly affects the Rh–CO σ-bonding as well as the π-bonding.*

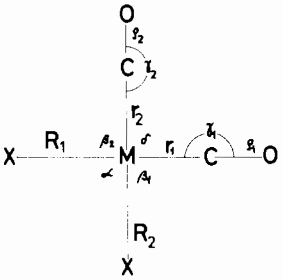

Fig. 1. Internal Coordinates for planar $[MX_2(CO)_2]^{n-}$ Structures (n = 0.1).

Introduction

We have made extensive studies of vibrational spectra and force fields of simple square-planar complexes. These include $[MX_4]^{2-}$ (MX = PdCl, PdBr, PtCl, PtBr or PtI) [1], $[AuX_4]^-$ (X = Cl or Br) [1], $[M_2X_6]^{2-}$ (M = Pd or Pt; X = Cl, Br or I) [2] and $[MX_3(CO)]^-$ (MX = PdCl, PdBr, PtCl, PtBr or PtI)

TABLE I. Internal Valence Symmetry Coordinates for the In-Plane Vibrations of *cis*-$[MX_2(CO)_2]$ Species.

$$A_1\ S_1 = \frac{1}{\sqrt{2}}(\Delta\rho_1 + \Delta\rho_2)$$

$$S_2 = \frac{1}{\sqrt{2}}(\Delta\gamma_1 + \Delta\gamma_2)$$

$$S_3 = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2)$$

$$S_4 = \frac{1}{\sqrt{2}}(\Delta R_1 + \Delta R_2)$$

$$S_5 = \frac{1}{\sqrt{2}}(\Delta\alpha - \Delta\delta)$$

$$S_6 = \frac{1}{2}(\Delta\alpha - \Delta\beta_1 - \Delta\beta_2 + \Delta\delta)$$

$$B_1\ S_7 = \frac{1}{\sqrt{2}}(\Delta\rho_1 - \Delta\rho_2)$$

$$S_8 = \frac{1}{\sqrt{2}}(\Delta\gamma_1 - \Delta\gamma_2)$$

$$S_9 = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2)$$

$$S_{10} = \frac{1}{\sqrt{2}}(\Delta R_1 - \Delta R_2)$$

$$S_{11} = \frac{1}{\sqrt{2}}(\Delta\beta_1 - \Delta\beta_2)$$

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TABLE II. Relationships between Force Constants in Symmetry Coordinate Representation and Those in Internal Coordinate Representation for *cis*-[$MX_2(CO)_2$] Species.

A_1 Species	B_1 Species
$F_{1\,1} = f_\rho + f_{\rho\rho}$	$F_{7\,7} = f_\rho - f_{\rho\rho}$
$F_{2\,2} = \rho r(f_\gamma + f_{\gamma\gamma})$	$F_{8\,8} = \rho r(f_\gamma - f_{\gamma\gamma})$
$F_{2\,3} = 2rf_{r\gamma}$	$F_{9\,9} = f_r - f_{rr}$
$F_{3\,3} = f_r + f_{rr}$	$F_{9\,10} = f_{rR'} - f_{rR}$
$F_{3\,4} = f_{rR'} + f_{rR}$	$F_{9\,11} = rf_{r\beta}$
$F_{3\,6} = -\frac{1}{\sqrt{2}}\, rf_{r\beta}$	$F_{10\,10} = f_R - f_{RR}$
$F_{4\,4} = f_R + f_{RR}$	$F_{10\,11} = -Rf_{R\alpha}$
$F_{4\,5} = Rf_{R\alpha}$	$F_{11\,11} = rRf_\beta$
$F_{5\,5} = \frac{1}{2}(R^2f_\alpha + r^2f_\delta)$	
$F_{5\,6} = \frac{1}{\sqrt{2}}\,[\frac{1}{2}(R^2f_\alpha - r^2f_\delta) - R^2f_{\alpha\beta} + r^2f_{\beta\delta}]$	
$F_{6\,6} = \frac{1}{4}R^2f_\alpha + \frac{1}{2}rRf_\beta + \frac{1}{4}r^2f_\delta - R^2f_{\alpha\beta} - r^2f_{\beta\delta}$	

[3]. Recently, we reported spectra of the *cis* complexes [4] [$PtX_2(CO)_2$], [$RhX_2(CO)_2$]$^-$ and [$IrCl_2(CO)_2$]$^-$ and now present details of force field studies for these systems.

As far as possible, vibrational wavenumbers measured for solutions have been used in calculations, but in a few cases features were only determined for solids. Throughout this series of investigations we have made similar assumptions in order that comparison between force constant of different complexes should be valid, even though they are not absolute in so far as they are force field dependent.

Normal Co-ordinate Calculations

The in-plane internal co-ordinates used are shown in Figure 1. The non-redundant valence symmetry co-ordinates are listed in Table I, and the relationship between force constants in symmetry co-ordinate representation and those in internal co-ordinate terms is shown in Table II. The G matrix calculation and force constant refinement procedures have been outlined previously [5, 6]. As in our previous paper we have assumed a CO bond length of 114 pm, a Metal–Carbon bond length of 176 pm, Metal–Chlorine bond length of 232 pm, PtBr as 241 pm, and RhBr as 242 pm.

With eleven in-plane vibrations, $6A_1 + 5B_1$, we can in principle refine eleven force constants and have chosen the three stretching, four bending, three stretch–stretch interactions between like bonds, and the MCO, MCO bend–bend interaction force constants. All other force constants must be constrained.

For [$PtCl_2(CO)_2$] assignments have been proposed for all modes except the skeletal deformations [4]. Features have been observed in the appropriate region for the latter and we suggest that the two strong Raman bands of the solid at 158 and 114 cm^{-1} are A_1 modes, with one of the additional infrared features (135 cm^{-1}) the B_1 mode. Thus all eleven in-plane vibrations may be accounted for. As with [$PtCl_3(CO)$]$^-$ we have adopted the *trans* and *cis* stretch–stretch interaction constants [1] from [$PtCl_4$]$^{2-}$ for the *trans* and *cis* PtC, PtX interactions, $f_{rR'}$ and f_{rR}, respectively. The stretch–bend interactions $f_{R\alpha}$ and $f_{r\beta}$ have both been given the value of ($f_{r\alpha} - f_{r\alpha'}$) from [$PtCl_4$]$^{2-}$, while for the bend–bend interaction $f_{\alpha\beta}$ we have used the value 0.05 calculated for [$PtCl_3(CO)$]$^-$.† Small arbitrary values of $f_{\beta\delta}$ and $f_{r\gamma}$ (taking $f_{r_1\gamma_1} = f_{r_1\gamma_2} = f_{r_2\gamma_1} = f_{r_2\gamma_2}$) have been included, the latter to enable calculated wavenumbers of the PtC stretching and PtCO bending modes of the same symmetry to approach each other more closely. Without appropriate isotopic data we are unable to determine the PtC, CO stretch–stretch interaction constant and have omitted this and any other off-diagonal terms involving the CO group from the calculation and Table II.

For both [$PtBr_2(CO)_2$] and [$IrCl_2(CO)_2$]$^-$ constrained force constants are based on [$PtBr_4$]$^{2-}$ and [$PtBr_3(CO)$]$^-$, while for [$RhCl_2(CO)_2$]$^-$ they are taken from [$PdCl_4$]$^{2-}$ and [$PdCl_3(CO)$]$^-$. For [$RhBr_2(CO)_2$]$^-$ spectra below 200 cm^{-1} have not been recorded and we have used estimates for bending force constants based on PdBr systems whilst only refining eight force constants in relation to eight frequencies; we showed in our studies on [$PtCl_3(CO)$]$^-$ that the other force constants were

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†This is erroneously quoted as 0.00 in Table VI of ref. 3.

TABLE III. In-Plane Force Constants of *cis*-$[MX_2(CO)_2]$ in Symmetry Coordinate Representation.

	$[PtCl_2(CO)_2]$	$[PtBr_2(CO)_2]$	$[RhCl_2(CO)_2]^-$	$[RhBr_2(CO)_2]^-$	$[IrCl_2(CO)_2]^-$	
A_1 $F_{1\,1}$	17.88	17.66	16.04	16.03	15.49	a
$F_{2\,2}$	0.41	0.44	0.46	0.59	0.61	b
$F_{2\,3}$	−0.04	−0.06	−0.06	−0.06	−0.05	a^+
$F_{3\,3}$	3.28	3.16	3.51	3.36	4.53	a
$F_{3\,4}$	0.36	0.28	0.28	0.28	0.28	a^+
$F_{3\,6}$	−0.08	−0.17	−0.11	−0.12	−0.11	c^+
$F_{4\,4}$	2.55	2.27	1.71	1.60	1.99	a
$F_{4\,5}$	0.14	0.22	0.22	0.23	0.22	c^+
$F_{5\,5}$	0.91	0.66	0.66	0.65^+	0.86	b
$F_{5\,6}$	0.13	0.42	0.18	0.22^+	0.19	b
$F_{6\,6}$	0.62	0.74	0.75	0.41^+	0.60	b
B_1 $F_{7\,7}$	17.39	17.20	14.82	15.06	14.13	a
$F_{8\,8}$	0.45	0.40	0.57	0.56	0.61	b
$F_{9\,9}$	2.84	2.71	2.90	2.78	4.50	a
$F_{9\,10}$	0.21	0.16	0.08	0.08	0.16	a^+
$F_{9\,11}$	0.11	0.16	0.15	0.17	0.16	c^+
$F_{10\,10}$	2.23	1.97	1.45	1.32	1.65	a
$F_{10\,11}$	−0.14	−0.22	−0.22	−0.23	−0.22	c^+
$F_{11\,11}$	0.97	1.21	0.65	0.50^+	0.74	b

Units a = 10^2 N m^{-1}; b = 10^{-18} N m rad^{-2}; c = 10^{-8} N rad^{-1}

$^+$Constrained values, see text.

TABLE IV. Assignments Used and Wavenumbers Calculated for In-Plane Vibrations of *cis*-$[MX_2(CO)_2]$ Species.

Assignment and approximate description of mode		$[PtCl_2(CO)_2]$		$[PtBr_2(CO)_2]$		$[RhCl_2(CO)_2]^-$		$[RhBr_2(CO)_2]^-$		$[IrCl_2(CO)_2]^-$	
		Obs.	Calc.	Obs.[a]	Calc.	Obs.[b]	Calc.	Obs.[c]	Calc.	Obs.[b]	Calc.
A_1 ν_1	CO stretching	2175	2168.8	2163	2154.4	2069.5	2061.4	2068	2065	2056	2056.3
ν_1*		2148	2156	2130	2142.6	2035	2043.3	2044	2047.3	–	–
ν_2	MCO bending	472	482	460	457.3	510	508.6	514	515.2	528	524.6
ν_3	MC stretching	459.5	455	454	448.3	492	482.2	487[d]	481	547.5	547.1
ν_4	MX stretching	374	374	252	252.2	315.5	315.8	227	227.8	329	328.9
ν_5	XMX deformation	158	157.8	105	124.4	146	165.2	–	120.1	156[e]	160.5
ν_6	CMC deformation	115	114.3	80	80	107	107.4	–	83.3	122[e]	113.1
B_1 ν_7	CO stretching	2134	2132.2	2121.5	2121.6	1992	1982	1993	1990.8	1973	1973
ν_7*		2093	2093.1	2086	2081.7	1940	1950.6	1957[d]	1959.1	–	–
ν_8	MCO bending	462	461.8	450	450.5	492	495	486	485.8	513	511
ν_9	MC stretching	430	429.3	421[e]	419.1	455	456.1	447	445.7	526	527.8
ν_{10}	MX stretching	352	351.8	235	235.2	288	288.1	203	203.5	299	299
ν_{11}	XMX deformation	135	134.5	125[e]	124.7	120	120.1	–	122.3	122[e]	122

ν_1* and ν_7* belong to the $[MX_2(^{12}CO)(^{13}CO)]$ isotopic species of C_s symmetry.

[a] Mean values of benzene solution i.r. and Raman spectra. [b] Mean values of CH_2Cl_2 solution i.r. and Raman spectra. [c] From i.r. spectra of $CDCl_3$ solution. [d] From i.r. spectra of mull. [e] From Raman spectra of solid.

remarkably insensitive to the skeletal deformation assignments and changes in skeletal deformation force constants.

To start the refinement procedure, initial force constants were taken from $[PtX_4]^{2-}$ and $[PtX_3(CO)]^-$ for $[PtX_2(CO)_2]$, from $[PdX_4]^{2-}$ and $[PdX_3(CO)]^-$ for $[RhX_2(CO)_2]^-$, and from $[PtBr_2(CO)_2]$ for $[IrCl_2(CO)_2]^-$. After completing the refinement for the $[MX_2(^{12}CO)_2]$ systems a further cycle of calculations was undertaken for $[MX_2(^{12}CO)(^{13}CO)]$ systems; using the appropriate G matrix for this C_s symmetry species and refining only f_ρ and $f_{\rho\rho}$.

The force constants obtained in symmetry coordinate terms are given in Table III, and the agreement between experimental and calculated wave-

TABLE V. In-Plane Force Constants (10^2 N m^{-1}) of *cis*-[$MX_2(CO)_2$] Species in Internal Coordinate Representation.

	Coordinates involved	[$PtCl_2(CO)_2$]	[$PtBr_2(CO)_2$]	[$RhCl_2(CO)_2$]$^-$	[$RhBr_2(CO)_2$]$^-$	[$IrCl_2(CO)_2$]$^-$
f_ρ	CO	17.63	17.43	15.43	15.54	14.81
f_r	MC	3.06	2.93	3.21	3.07	4.51
f_R	MX	2.39	2.12	1.57	1.46	1.82
$f_{\rho\rho}$	CO, CO	0.24	0.23	0.61	0.49	0.68
f_{rr}	MC, MC	0.22	0.23	0.30	0.29	0.02
f_{RR}	MX, MX	0.16	0.15	0.13	0.14	0.17
f_γ	MCO	0.21	0.21	0.24	0.29	0.30
$f_{\gamma\gamma}$	MCO, MCO	−0.01	0.01	−0.01	0.01	−0.01
f_β	XMC	0.24	0.29	0.16	(0.12)^a	0.18
f_δ	CMC	0.16	0.05	0.10	(0.12)^a	0.22
f_α	XMX	0.25	0.20	0.19	(0.16)^a	0.20
		Constrained Values				
f_{rR}'	MC, MX (*trans*)	0.28	0.22	0.17	0.15	0.22
f_{rR}	MC, MX (*cis*)	0.08	0.06	0.09	0.07	0.06
$f_{r\gamma}$	MC, MCO	−0.01	−0.02	−0.02	−0.02	−0.01
$f_{R\alpha}$	MX, XMX	0.06	0.09	0.09	0.10	0.09
$f_{r\beta}$	MC, XMC	0.06	0.09	0.09	0.10	0.09
$f_{\alpha\beta}$	XMX, XMC	0.05	0.01	0.02	0.01	0.01
$f_{\beta\delta}$	XMC, CMC	0.02	0.04	−0.01	0.03	0.04

[a] Additional constrained values for [$RhBr_2(CO)_2$]$^-$.

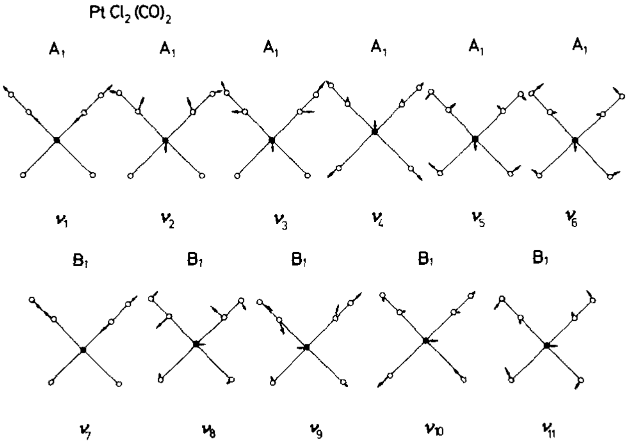

Fig. 2. Mass-weighted Cartesian displacements for the in-plane modes of *cis*-[$PtCl_2(CO)_2$].

numbers in Table IV. Table V gives the force constants expressed in terms of internal co-ordinates. They are quoted to two places of decimals although a greater number of figures was used in the calculation. The values given for f_ρ and $f_{\rho\rho}$ are the mean of those obtained for the two isotopic variants. Some of the force constants have been referred to in our previous paper, but those given here differ marginally from them because we had not incorporated the ^{13}C isotopic data adequately.

Discussion

Mass weighted Cartesian displacements for the in-plane modes of *cis*-[$PtCl_2(CO)_2$] are shown in Figure 2. It can be seen that metal displacement is significant in all the modes except CO stretching. There is considerable mixing of the A_1 PtCO bending and PtC stretching co-ordinates, and the potential energy distribution shows it to be much greater than for the corresponding B_1 modes:

P.E. Distribution A_1	S_2	S_3	B_1	S_8	S_9
ν_2	0.57	0.12	ν_8	0.76	0.02
ν_3	0.16	0.79	ν_9	0.03	0.91

There is very little mixing between these modes and the PtCl co-ordinates. It is fortunate that there are only small contributions to $\nu_1 - \nu_4$ and $\nu_7 - \nu_{10}$ from the skeletal deformations, since it is for the last that assignments are less definitely established and to which most of the constrained interaction constants are applied.

The CO stretching modes have no significant coupling to other motions of the molecule, and the CO stretching force constant is approximately reproduced by $f_{CO} \approx \frac{1}{2}B(\nu_1^2 + \nu_7^2)$ N m^{-1}, if B is taken as 3.8×10^{-4} (*i.e.* lower than the value of 4.04×10^{-4} derived for the CO molecule) [7].

As we found with [$MX_3(CO)$]$^-$ systems [2], the CO and MC stretching force constants of *cis*-[$MX_2(CO)_2$]$^{0 \text{ or } -1}$ systems show relatively little depen-

TABLE VI. Bond orders and Force Constants of $[MX_3(CO)]^-$, *cis*-$[MX_2(CO)_2]^{0\ \mathrm{or}\ -1}$ and $[AuCl(CO)]$.

	Estimated Bond Order		f_{MC} Estimated from Bond Order and f_{MC} of $[PtCl_3(CO)]^-$ or $\{[PdCl_3(CO)]^-\}$	f_{MC} from Calculations
	CO	MC		
$[PtCl_3(CO)]^-$	2.67	1.33		3.90[b]
$[PtBr_3(CO)]^-$	2.66	1.34	3.93 (or 3.86[a])	3.90[b]
$[PtI_3(CO)]^-$	2.62	1.38	4.05 (or 3.83[a])	3.83[b]
cis-$[PtCl_2(CO)_2]$	2.86	1.14	3.34 (or 3.04[a])	3.06
cis-$[PtBr_2(CO)_2]$	2.83	1.17	3.43 (or 3.10[a])	2.93
cis-$[IrCl_2(CO)_2]^-$	2.42	1.58	4.63	4.53
$[AuCl(CO)]$	2.92	1.08	3.17	2.55[c]
$[PdCl_3(CO)]^-$	2.85	1.15		2.36[b]
$[PdBr_3(CO)]^-$	2.82	1.18	{2.42}	2.37[b]
cis-$[RhCl_2(CO)_2]^-$	2.52	1.48	{3.04}	3.21
cis-$[RhBr_2(CO)_2]^-$	2.54	1.46	{3.00}	3.07

[a] With additional scaling according to $^1J(^{195}Pt^{13}C)$ values: $[PtX_3(CO)]^-$ X = Cl, 1732; X = Br, 1701; X = I, 1636 Hz. $[PtX_2(CO)_2]$ X = Cl, 1576; X = Br, 1566. Hz. [b] Ref. 2. [c] J. G. Smith, *Ph.D. Thesis*, Bristol University, 1967.

dence on the halide for a particular metal. They are however, very sensitive to the metal which implies significant differences in the nature of the bonding to CO, as has long been recognised.

For the isoelectronic complexes $[PtCl_2(CO)_2]$ and $[IrCl_2(CO)_2]^-$ the CO stretching force constant of the former is substantially the greater, whilst the opposite is the case for MC stretching. If we take 12.1×10^2 N m^{-1} as a typical value for C=O [8] and 18.55 as appropriate for C≡O (*i.e.* using the wavenumber of carbon monoxide stretching uncorrected for anharmonicity) and linearly interpolate, then the CO bond orders would be 2.89 and 2.52 for the platinum and iridium systems respectively. On this basis the respective MC bond orders would be 1.11 and 1.58 and the 48% increase in the MC stretching force constants is in remarkably good agreement with that expectation, especially as the σ-bond force constants can be expected to alter with a change of metal charge. On the same basis, the bond order in $[PtCl_3(CO)]^-$ would be 2.67 for CO and hence 1.33 for PtC. In Table VI we give the MC force constants that a simple linear relationship to bond order would imply for the platinum and iridium compounds, based on the value for $[PtCl_3(CO)]^-$. This approach slightly overestimates the force constants in most cases. For the platinum systems, the n.m.r. coupling constant $J(^{195}Pt^{13}C)$ shows that there are small changes in the nature of the PtC σ-bond; if we scale the notional unit-bond force constant in accordance with the behaviour of J(PtC) lower estimates of f_{PtC} are obtained.

The method does not give agreement with the force constant calculated for $[AuCl(CO)]$, nor does it give a good estimate for rhodium or palladium complexes {*e.g.* it implies f_{RhC} = 4.34 for $[RhCl_2(CO)_2]^-$}. However, using $[PdCl_3(CO)]^-$ as a basis for second transition series compounds reasonable agreement with calculated values is obtained. It is clear from f_{MX} that stretching force constants for the lighter metals are less than for platinum and iridium, but the effect of f_{MC} is even greater than would be predicted from the behaviour of f_{MX} and the reduction in MC bond order. Clearly the 4d orbitals are less available for π-donation to CO in the rhodium and palladium systems than for corresponding iridium and platinum systems, and we suggest it is the

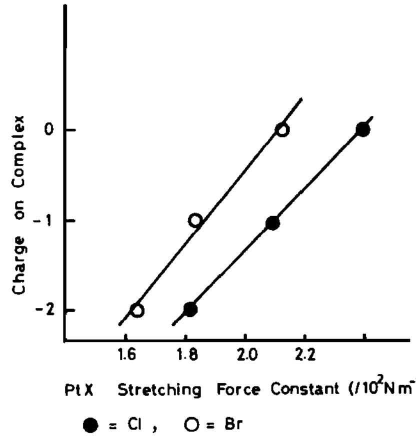

Fig. 3. Relationship between PtX stretching force constant and charge on complex for $[PtX_4]^{2-}$, $[PtX_3(CO)]^-$ and *cis*-$[PtX_2(CO)_2]$.

reduced overlap of the metal $d_{x^2-y^2}$ orbital in the RhC and PdC σ-bonds which is responsible for the extra lowering of their force constants.

In the platinum dicarbonyl complexes the CO, CO stretch–stretch interaction constant is much lower than for the rhodium and iridium anions. This is presumably a consequence of the lower π donation from the metal, and indeed this interaction is approximately proportional to the degree of π bonding and doubtless operates through the delocalised π-system.

We have now calculated the PtCl and PtBr stretching force constants for *cis*-$[PtX_2(CO)_2]$, $[PtX_3(CO)]^-$ and $[PtX_4]^{2-}$. Fig. 3 shows that dependence on overall charge is practically linear; the value shown for $[PtX_3(CO)]^-$ is the weighted mean of the two PtX force constants.

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