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Force constant calculations for tetrakis(tribromophosphine)nickel(0), $Ni(PBr_3)_4$

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Abstract

Force constant calculations have been carried out for $Ni(PBr_3)_4$ using a simple valence force field with interaction constants. The force constant values are compared for the coordinated and free ligand and also with *k*(Ni–P) stretching in the series of molecules $Ni(PX_3)_4$ where X = F, Cl, Me. The *k*(Ni–P) stretching force constant in $Ni(PBr_3)_4$ is much lower than its corresponding values for other members of the series. This is discussed in relation to the observed experimental instability of the compound and the electronegativities of the substituents X in PX_3.

Introduction

Tetrakis(tribromophosphine)nickel(0), $Ni(PBr_3)_4$, was first prepared some years ago [1] but the vibrational spectrum has only been reported recently [2]. The compound is rather unstable, especially in solution, where decomposition to the parent phosphine occurs, and polarisation data could not be obtained from the Raman spectrum. Despite this, thirteen of the fourteen active vibrational frequencies were assigned although some of these assignments were necessarily rather tentative. Force constant calculations [3] for $Ni(PX_3)_4$ molecules, where X is F, Cl, Br and Me, based only on the three vibrational frequencies of the A_1 species, resulted in large discrepancies between observed and calculated wavenumbers except for the case of $Ni(PF_3)_4$. For example, the r.m.s. deviation between observed and calculated wavenumbers for the $Ni(PBr_3)_4$ species was 11%. It has since been demonstrated [4–6] that molecules of the type $M(PF_3)_4$, are better described using more complicated force fields with interaction constants which utilise all the available vibrational spectroscopic information. In the case of $Ni(PCl_3)_4$, six primary and five interaction force constants were used [5] to fit fourteen observed wavenumbers with a r.m.s. deviation between the observed and calculated wavenumbers of 2.7%. It was realised [5] that, as the mass of the substituent X in the phosphorus ligand PX_3 increased, then the importance of the stretch–stretch or stretch–bend type interactions also increased.

To complete our studies on the $Ni(PX_3)_4$ species and to examine the quantitative effect of the electronegativity of X on the metal–phosphorus stretching force constant, we report here the results of force constant calculations on $Ni(PBr_3)_4$, using all the available vibrational spectroscopic data and a simple valence force field (SVFF) with interaction constants.

Experimental: force constant calculations

The vibrational spectrum of $Ni(PBr_3)_4$ has been assigned [2] on the basis of T_d molecular symmetry. The vibrational activity is given by

$$\Gamma_{vib} = 3A_1 + 1A_2 + 4E + 4F_1 + 7F_2$$

for which $3A_1 + 4E + 7F_2$ will be Raman active, $7F_2$ will be IR active and $1A_1 + 4F_1$ will be inactive in both the Raman and the IR. For comparison purposes, force constant calculations were made on the free ligand PBr_3, which has a molecular point group C_{3v} and

$$\Gamma_{vib} = 2A_1 + 2E$$

all of which are active in both the Raman and the IR.

Description of the setting-up and running of the programmes have already been given in the literature and will not be discussed further here [4, 5]. The molecular parameters which were used in the calculations (Table 1) were taken from the literature [7] for PBr_3 and, in the absence of similar structural data for $Ni(PBr_3)_4$, were transferred without alteration to this molecule.

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TABLE 1. Bond lengths and angles used in the calculations for PBr_3 and $Ni(PBr_3)_4$

Parameter	Length (Å)	Angle (°)
PBr_3		
P–Br	2.18 [7]	
Br–P–Br		101.5 [7]
$Ni(PBr_3)_4$[a]		
Ni–P	2.12 [8]	
P–Br	2.18 [7]	
Br–P–Br		101.5 [7]
P–Ni–P		109.5 [8]
P–Ni–Br		117.7 [8]

[a] Bond lengths and angles of NiP_4 skeleton assumed the same as for $Ni(PF_3)_4$ [8] and coordinated PBr_3 to be the same as the free ligand.

An estimate of the nickel–phosphorus bond distance in $Ni(PBr_3)_4$ was made on the basis of a summation of the covalent radii which was refined by comparison with the observed [8] r(Ni–P) distance in $Ni(PF_3)_4$.

Fifty-eight internal coordinates were necessary to generate the full set of forty-five normal vibrations. In the construction of the SVFF force field six primary force constants were used, namely: k_r (P–Br stretching), k_R (Ni–P stretching), k_θ (BrPBr angle deformation), k_α (PNiP angle deformation), k_β (NiPBr angle deformation), k_τ (PNiPBr torsion). Starting values for k_r, k_R and k_θ were taken from an earlier calculation in the literature on the A_1 species vibrations only [3]. Since previous values of k_α, k_β and k_τ were not available, reasonable starting values of 0.5 mdyn $Å^{-1}$ rad^{-2} were assumed. When a good fit between the calculated and observed wavenumbers was obtained for the A_1 species vibrations the potential energy matrix was examined and the sensitivity of the other vibrations to the force constants could be evaluated. Interaction constants were now added and refined until the best fit was obtained with the 13 observed vibrational wavenumbers. The final SVFF comprised the six primary force constants defined above and the interaction constants: k_{rr} (P–Br, P–Br stretch–stretch interaction), k_{rR} (Ni–P, P–Br stretch–stretch interaction), k_{RR} (Ni–P, Ni–P stretch–stretch interaction), $k_{\theta\theta}$ (PBr_2, PBr_2 angle–angle deformation interaction), $k_{\alpha\alpha}$ (NiP_2–NiP_2 angle–angle deformation interaction). Starting values of the interaction force constants were 0.4 mdyn $Å^{-1}$ and 0.3 mdyn $Å^{-1}$ rad^{-2} for the stretch–stretch and angle–angle deformation interactions, respectively.

Results

After several iterations the convergence between the observed and calculated wavenumbers was achieved with best-fit r.m.s. deviations of 0 and 3% for the PBr_3 and $Ni(PBr_3)_4$ species, respectively. The calculated and observed wavenumbers, the potential energy distributions and the final force constant values for the best-fit refinement are given in Table 2–4. The r.m.s. deviation of $|\Delta\tilde{\nu}_{obs} - \Delta\tilde{\nu}_{calc}|$ in the best-fit calculation is ± 7 cm^{-1}.

The fit between the observed and calculated wavenumbers in Tables 2 and 3 for the PBr_3 ligand and $Ni(PBr_3)_4$ is very good. Examination of the potential energy distributions in Table 4 for $Ni(PBr_3)_4$ indicates that extensive mixing occurs between the Ni–P stretching, NiPBr deformation and PBr_3 deformation modes. It is clear that the vibrational modes of the PBr_3 ligands coordinated to Ni describe 'breathing' motions in which the P atoms are moving; this is not unexpected in consideration of the relative atomic masses of Ni, P and Br. The descriptions of the vibrational modes ν_1–ν_{19} given in Table 3 for $Ni(PBr_3)_4$ are, thus, idealised versions of a much more complicated situation in which, for example, six force constants play an important role in the potential energy distributions of the ν_{18} mode with greater than 10% contribution of each force constant to the whole. The interaction constants play an important role, e.g. k_{RR}, which describes NiP–NiP stretch–stretch interaction, has important contributions to the ν_{16}, ν_{18} and ν_{19} modes.

In contrast, however, the stretching and bending modes of the PBr_3 as a free ligand are well characterized by their respective steering force constants and by the k_{rr} and $k_{\theta\theta}$ interaction constants, e.g. the PBr_3 symmetric deformation at 162 cm^{-1} is 97% pure.

Since the observed Raman and IR spectra [2] for $Ni(PBr_3)_4$ were assigned on the basis of a comparison with PBr_3 and analogous species such as $Ni(PCl_3)_4$, without the benefit of polarization data from solution, it was expected that some of the assignments were necessarily tentative. Generally, however, the vibrational assignments for this species are essentially correct within the approximate descriptions of the vibrational modes described in Table 3. In addition, the force-constant calculations have given values for the ν_8, ν_9–ν_{12} modes for the first time which were not obtainable from the observed spectra.

With regard to the mixing of the modes, the $Ni(PBr_3)_4$ species behaves in a similar fashion to other members of the $Ni(PX_3)_4$ series, X = F, Cl, Me, but to a greater extent and this is borne out by a comparison of the results of the present work with the simplified SVFF calculations carried out earlier [3] on the A_1 species modes only. For $Ni(PBr_3)_4$, the earlier calculations using only three primary-force constants revealed that an instability of the force-field set in around 11% r.m.s. deviation, at which the k_R was 1.40 mdyn $Å^{-1}$ and k_θ 0.62 mdyn $Å^{-1}$ rad^{-2}, compared with the results of the present work using eleven force constants which

TABLE 2. Potential energy distributions, wavenumbers and force constant values for the vibrations of PBr_3

ν	Symmetry class	Vibrational wavenumbers (cm^{-1})		Force constants			
		Obs.	Calc.	k_r	k_θ	k_{rr}	$k_{\theta\theta}$
ν_1	A_1	380	380	86.6	20.6	30.7	−37.9
ν_2		162	162	0.1	96.9	0.0	2.9
ν_3	E	400	400	122.3	11.8	−21.7	−12.4
ν_4		116	116	38.8	120.7	−6.9	−52.6
Force constant value[a]				2.31	0.24	−0.41	−0.15

[a] Stretching and stretch–stretch interaction force constants have units of mdyn $Å^{-1}$, angle deformation and angle–angle deformation interaction force constants have units of mdyn $Å^{-1}$ rad^{-2}. 1 mdyn $Å^{-1} \equiv 10^2$ N m^{-1}.

TABLE 3. Observed and calculated wavenumbers (cm^{-1}) and assignments [2] for $Ni(PBr_3)_4$

Symmetry class	ν	Approximate description of mode	$Ni(PBr_3)_4$	
			Obs.	Calc.
A_1	ν_1	PBr symmetric stretch	361	362
	ν_2	PBr_3 symmetric deformation	149	162
	ν_3	NiP symmetric stretch	78	88
A_2	ν_4	PBr_3 torsion	–[a]	–
E	ν_5	PBr asymmetric stretch	419	417
	ν_6	PBr_3 asymmetric deformation	228	242
	ν_7	PBr_3 rock	126	125
	ν_8	NiP_4 deformation	n.o.[b]	73
F_1	ν_9	PBr asymmetric stretch	–	400
	ν_{10}	PBr_3 asymmetric deformation	–	237
	ν_{11}	PBr_3 rock	–	73
	ν_{12}	PBr_3 torsion	–	56
F_2	ν_{13}	PBr symmetric stretch	419	421
	ν_{14}	PBr asymmetric stretch	392	393
	ν_{15}	PBr_3 symmetric deformation	247	259
	ν_{16}	PBr_3 asymmetric deformation	193	189
	ν_{17}	PBr_3 rock	168	172
	ν_{18}	NiP asymmetric stretch	126	125
	ν_{19}	NiP_4 deformation	48	48

[a] Inactive in vibrational spectrum. [b] n.o. = not observed.

included six primary and five interaction force constants, giving values of 1.27 mdyn $Å^{-1}$ and 0.62 mdyn $Å^{-1}$ rad^{-2}, respectively. A comparison of the k_R values for the $Ni(PBr_3)_4$ series is given in Table 5, when the low value of the Ni–P stretching force constant in $Ni(PBr_3)_4$ concurs with the observed experimental instability of the compound relative to other members of the series, especially $Ni(PF_3)_4$, which has a k_R some 300% larger.

From the results of the present work it is possible to make the following points.

(i) There is an observed decrease in the k_R (P–Br) stretching force constant of 33% from the free PBr_3 ligand to its coordination with Ni in $Ni(PBr_3)_4$. This is consistent with a similar decrease noted for k_r from PCl_3 to $Ni(PCl_3)_4$ [5] and is at variance with the observed results for the fluoro- and methyl-phosphine analogues, $Ni(PF_3)_4$ [4] and $Ni(PMe_3)_4$ [6] in which an increase of 1% and a decrease of 2%, respectively, from free to coordinated ligand k_rs were observed. The similar behaviour of the bromo- and chloro-phosphine analogues is in accord with the comparable electronegativities of Cl and Br in contrast to F and Me.

(ii) The k_R (Ni–P) stretching force constant is significantly reduced in the series $Ni(PF_3)_4$, $Ni(PCl_3)_4$ and $Ni(PBr_3)_4$, Table 5, and in $Ni(PBr_3)_4$ is only 30% of the k_R value in $Ni(PF_3)_4$. This observation may be correlated with the ready decomposition of $Ni(PBr_3)_4$ and the instability noted in the literature [1, 2]. The observed decrease in the k_r (P–Br) stretching force constant in $Ni(PBr_3)_4$ from free PBr_3 correlates with

TABLE 4. Potential energy distributions, vibrational modes and force constants of Ni(PBr$_3$)$_4$

ν	Calculated wavenumber (cm^{-1})	Symmetry class	Force constants									
			k_r (PBr)	k_R (NiP)	k_θ (BrPBr)	k_α (PNiP)	k_β (NiPBr)	k_γ (PNiPBr)	k_{rr} (PBr–PBr)	k_{rR} (NiP–PBr)	k_{RR} (NiP–NiP)	$k_{\theta\theta}$ (BrPBr–BrPBr)	$k_{\alpha\alpha}$ (PNiP–PNiP)
ν_1	362	A$_1$	80.8	12.1	2.9	0.1	6.4	0.0	−9.6	11.0	4.2	−8.0	−0.2
ν_2	162	A$_1$	31.2	22.3	34.6	1.4	33.2	0.0	−4.5	−18.4	−3.3	−7.8	1.2
ν_3	88	A$_1$	11.0	34.5	25.1	1.9	40.9	0.0	−5.2	−11.7	−0.9	3.3	1.1
ν_5	417	E	81.1	1.1	12.2	3.4	−7.8	0.0	8.6	0.0	0.0	1.6	−6.3
ν_6	242	E	9.0	2.0	2.2	8.3	70.3	1.3	1.1	0.0	0.0	2.7	3.1
ν_7	125	E	2.1	1.1	59.0	1.4	7.7	0.9	0.2	0.1	0.1	22.1	5.3
ν_8	73	E	0.9	0.0	5.4	55.6	11.3	1.1	0.0	0.0	0.0	2.8	23.0
ν_{13}	421	F$_2$	84.2	0.3	0.8	1.7	4.5	0.1	3.3	0.2	0.1	0.1	4.7
ν_{14}	393	F$_2$	81.4	11.3	3.1	1.3	5.3	0.0	0.5	0.2	−1.2	−2.0	0.2
ν_{15}	259	F$_2$	7.5	9.4	5.3	17.2	63.4	1.4	0.8	0.7	−5.4	−6.8	6.6
ν_{16}	189	F$_2$	19.4	48.1	38.1	5.8	60.2	1.1	−4.1	−18.3	−21.0	−30.1	0.9
ν_{17}	172	F$_2$	2.2	0.1	62.3	1.9	14.3	3.1	0.3	0.1	0.0	14.1	1.7
ν_{18}	125	F$_2$	22.1	72.0	19.0	2.1	11.7	0.2	−2.2	−15.4	−11.4	0.9	1.1
ν_{19}	48	F$_2$	19.7	77.8	15.8	80.3	20.3	6.8	−4.6	−17.9	−33.1	−34.7	−30.5
Force constant values[a]			1.61	1.27	0.62	0.26	0.71	0.02	−0.63	−0.32	0.15	−0.20	−0.10

[a] Force constant values defined in Table 2.

TABLE 5. Metal–phosphorus stretching force constants, k_R (mdyn Å^{-1})[a], for Ni(PX$_3$)$_4$ species where X = F, Cl, Br, Me

Compound	k_R
Ni(PF$_3$)$_4$	3.45
Ni(PCl$_3$)$_4$	1.67
Ni(PMe$_3$)$_4$	1.62
Ni(PBr$_3$)$_4$	1.27

[a] 1 mdyn Å^{-1} ≡ 10^2 N m^{-1}.

a reduced dΠ–pΠ backbonding from the nickel atom, and this could also explain the lower value of k_R in this compound.

(iii) The PBr$_3$ deformation force constant, k_θ, is increased significantly on coordination in Ni(PBr$_3$)$_4$, unlike the situation in the analogous compounds Ni(PCl$_3$)$_4$ and Ni(PF$_3$)$_4$ where the k_θ values remain unchanged on coordination. We ascribe this phenomenon to the increased contributions of nickel–phosphorus stretching to the phosphorus–bromine deformation modes (Table 4), e.g. a 22% k_R contribution to the potential energy distribution of the ν_2 symmetric deformation mode (A$_1$ class), compared with a 35% contribution from k_θ, the primary force constant for this mode. Changes in k_θ on coordination of a phosphine to the metal have been related to a change in umbrella-angle of the PX$_3$ group [9].

The order of magnitude of the k_R (Ni–P) stretching force constant for the compounds

Ni(PF$_3$)$_4$ > Ni(PCl$_3$)$_4$ > Ni(PMe$_3$)$_4$ > Ni(PBr$_3$)$_4$

reflects the stability of these compounds, and the ratio of 3× between the k_Rs of Ni(PF$_3$)$_4$ and Ni(PBr$_3$)$_4$ is seen in Table 5. This ratio is somewhat smaller than that of 7.7× which was first proposed in a preliminary study [2] involving the A$_1$ class modes (ν_1, ν_2 and ν_3) only and an SVFF approximation with no interaction constants. The importance of the interaction constants in these calculations is well demonstrated in their contributions to the potential energy distributions for Ni(PBr$_3$)$_4$ in Table 4, and these contributions increase with the size of X in the PX$_3$ ligands. For example, k_{rr} (PX–PX) stretch–stretch interaction is only 14% of the k_r (PX) stretching force constant for Ni(PF$_3$)$_4$ but is 40% for Ni(PBr$_3$)$_4$.

Although the preparation of Ni(PI$_3$)$_4$ has been reported [10], its spectroscopic study has been strictly limited by colour and instability. However, from the results of the present work we would predict that the k_R (Ni–P) stretching force constant would be even smaller for Ni(PI$_3$)$_4$ than for Ni(PBr$_3$)$_4$ and that the interaction constants would be even more important and larger in value because of the increased steric hindrance and mass of the heavy I atoms in the Ni(PI$_3$)$_4$ system.

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