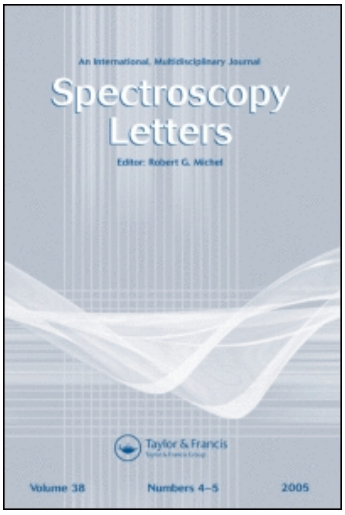

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Normal Coordinates Analysis for The $M(NH_3)^2_4$ Complex Ions in D_{4h} and T_d Symmetries. Simplified Molecular Models

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NORMAL COORDINATES ANALYSIS FOR THE $M(NH_3)_4^{2+}$ COMPLEX IONS IN D_{4h} AND T_d SYMMETRIES. SIMPLIFIED MOLECULAR MODELS

Keywords: Molecular Vibrations, Force Constants, $M(NH_3)_4^{2+}$, D_{4h}, T_d.

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ABSTRACT

A normal coordinates analysis for the $M(NH_3)_4^{2+}$ complex ions in T_d symmetry (M = Zn, Cd, Co) and in D_{4h} symmetry (M = Cu, Pd, Pt) has been undertaken on the basis of a General Valence Force Field (GVFF), using

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simplified molecular models. Throughout the course of the present work, we have relaxed the point mass approximation for the NH_3-ligands in order to investi - gate, on a quantitative basis, some relevant ligand - framework coupling vibrations. The simplest molecular model able to accomplish this purpose is to treat the ammino group, in a linear ligator approximation. We show that these model calculations provide a satisfac - tory set of vibrational frequencies as well as consist- ent sets of force constants.

INTRODUCTION

Several spectroscopic studies based upon the I.R and Raman spectra of the $M(NH_3)_4^{2+}$ complex ions in T_d(M = Zn, Cd, Co) and in D_{4h} (M = Cu, Pd, Pt) symmetries have been carried out by several research groups during the last years[1]. Normal coordinates ana- lysis for these complex ions, using both the 5 and the 17 atoms system models have been worked out on the basis of a GVFF and a UBFF[2-14].

The internal force constants in the literature,are given for the sake of completness in Table I.

From this Table, it can be seen that a systematic study for these complex ions, in both T_d and D_{4h} symmetry have been performed by Schmidt and Muller[12],on the basis of a point mass model (5 atoms system). These authors inform for this serie of complex ions, the metal - Nitrogen stretching force constants.

To provide a more complete set of internal force constants, we decided to undertake a systematic normal coordinates analysis for this kind of complex ions, by utilizing a modified general valence force field (MGVFF).

TABLE I

Internal force constants (in mdyne/Å), reported in the literature for $M(NH_3)_4^{2+}$ complex ions. T_d and D_{4h} symmetries

A.- Stretching M-N

Cu-N	Pd-N	Pt-N		Zn-N	Co-N	Cd-N	
0.840	1.710	1.920	2[a,d]	0.540	-	-	4[a,d]
-	-	2.804	7[a]	-	1.190	-	10[a]
-	-	2.100	8[a]	-	1.310	-	10[b]
-	2.200	-	9[a]	-	1.380	-	10[c]
-	-	2.440	13[b]	1.100	-	-	11[a]
1.420	2.150	2.540	12[b]	1.500	-	-	11[b]
-	-	-	-	1.430	1.440	1.240	12[b]
-	-	-	-	1.800	-	1.200	14[b]

B.- Bending N-M-N

NCuN	NPdN	NPtN	Ref	NZnN	NCoN	NCdN	Ref
0.255 (0.158)	-	-	3[a,d]	-	0.090	-	10[a]
-	0.100	-	9[a]	-	0.120	-	10[b]
-	-	0.190	7[a]	-	0.120	-	10[c]
-	-	0.190	8[b]	0.020	-	-	11[a]
-	0.100	-	9[a]	0.018	-	-	4[a]

C.- Rocking M-N-H

CuNH	PdNH	PtNH	Ref	ZnNH	CoNH	CdNH	Ref
0.107	-	-	3[a]	0.048	-	-	4[a]
0.107	0.150	0.180	2[a]	-	-	-	-

Footnote: [a]UBFF [b]GVFF [c]Fadini's method
[d]Seventeen atoms system
(other cases, a point mass model has been used).

As a molecular model we have chosen a 9-atoms system model, that is we regard the NH_3-ligands as a linear ligator, thus the calculation is undertaken for a system like $M(NX)_4$, where X represents an effective mass, corresponding to three times the mass of a hydrogen atom projected on the M-N axis at a distance of 0.30 Å beyond the Nitrogen nucleus. The N-H bond distance is equated to 1 Å[15].

MOLECULAR MODELS AND VIBRATIONAL ANALYSIS

The twenty one normal modes of vibration associated with a $M(NX)_4$ molecular system are distributed among the irreducible representations of both; the T_d and the D_{4h} point molecular groups, as given below:

$$\Gamma_{vib}(T_d) = 2\alpha_1(R) + 2\varepsilon(R) + \tau_1(-) + 4\tau_2(R, IR)$$

and

$$\Gamma_{vib}(D_{4h}) = 2\alpha_{1g}(R) + 2\beta_{1g}(R) + 2\beta_{2g}(R) + 4\varepsilon_u(IR) + \\ + \alpha_{2g}(-) + \varepsilon_g(R) + 2\alpha_{2u}(IR) + 2\beta_{2u}(-)$$

The internal coordinates needed to perform the normal coordinates analysis are shown in Fig. 1.

Furthermore, the analytic expressions for the matrix elements of the G-matrix, in T_d and in D_{4h} symmetries can be found in Refs. 16 and 17, respectively.

For the sake of completness, we list the elements of the F matrices, in Tables II and III.

To build up an initial F-matrix, we have used the following procedure: The metal - Nitrogen force constants have been taken from Ref. (12), while those

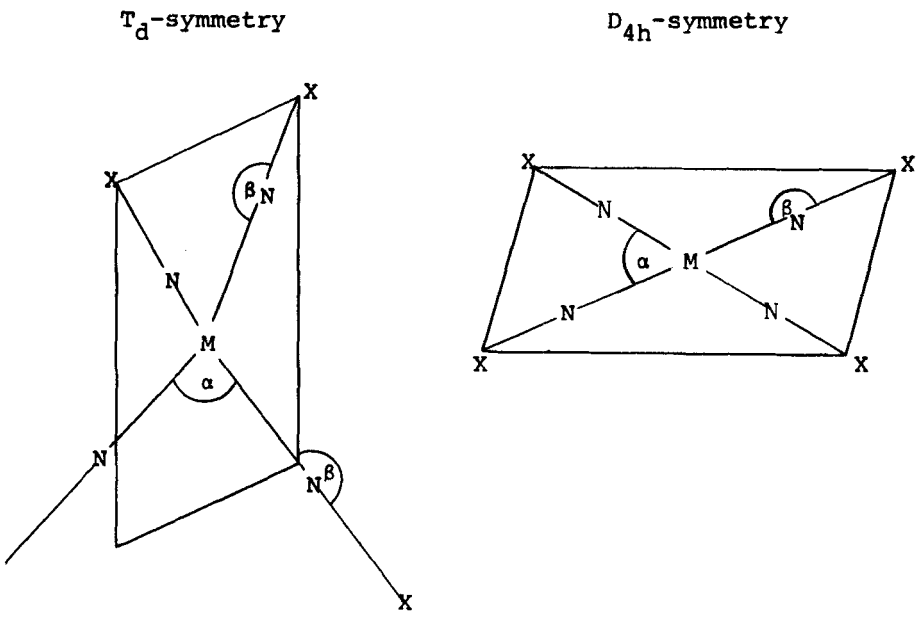

Figure 1

Footnote: In D_{4h}-symmetry, the angles perpendicular to α(say θ) and β(say φ) should also be considered. The M-N bond distances have been taken from Ref(1).

corresponding to the rocking vibrations M-N-H and the bending vibrations N-M-N have been transfered from those given for the hexamminochromium (III) ion[15] (0.14 and 0.25 mdyne/Å, respectively). Also the N-H stretching force constants have been taken from the value reported by Cyvin et al[6] for the NH_3 in gas phase (6.46 mdyne/Å).

Finally, we have employed for the force constant corresponding to the interaction between two M-N stretching, the value 0.12 mdyne/Å. This later value was reported by Muller et al[11] for the $Zn(NH_3)_4^{2+}$ ion.

TABLE II

Symmetrized F matrix elements. The Tetrahedral $M(NX)_4$ model.

α_1-symmetry

$F_{11} = f_{MN} + 3f_{MN/MN}$

$F_{12} = 0$

$F_{22} = f_{NH}$

τ_1-symmetry

$F_{11} = f_{\beta} - f'_{\beta\beta}$

ε-symmetry

$F_{11} = f_{\alpha} - 2f'_{\alpha\alpha} + f''_{\alpha\alpha}$

$F_{12} = \sqrt{3}(f'_{\beta\alpha} + f'''_{\beta\alpha})$

$F_{22} = f_{\beta} + f'_{\beta\beta}$

τ_2-symmetry

$F_{11} = f_{MN} - f_{MN\,/\,MN}$

$F_{12} = 0$

$F_{13} = \sqrt{2}(f'_{MN,\,\alpha} - f''_{MN,\,\alpha})$

$F_{14} = 4(f'_{MN,\,\beta} - f''_{MN,\,\beta})$

$F_{22} = f_{NH}$

$F_{23} = 0$

$F_{24} = 0$

$F_{33} = f_{\alpha} - f''_{\alpha\alpha}$

$F_{34} = \sqrt{2}(f'_{\beta\alpha} - f'''_{\beta\alpha})$

$F_{44} = f_{\beta} + f'_{\beta\beta}$

Interaction force constants between internal coordinates

f_{α} : NMN bending f_{β} = MNH rocking

$f'_{\alpha\alpha}$: NMN with one MN bond, in common

$f''_{\alpha\alpha}$: NMN with one atom, in common

$f'_{\beta\alpha}$: With one MN bond in common

$f'''_{\beta\alpha}$: With one atom, in common

$f'_{MN}\{^{\alpha}_{\beta}$: With one MN bond, in common

$f''_{MN}\{^{\alpha}_{\beta}$: With one atom, in common

TABLE III

Symmetrized F matrix elements. The Planar $M(NX)_4$ model

α_{1g}-symmetry

$F_{11} = f_{NH}$

$F_{12} = 0$

$F_{22} = f_{MN} + 2f^{c}_{MN/MN} + f^{t}_{MN/MN}$

α_{2g}-symmetry

$F_{11} = f_{\beta} + f''_{\beta\beta}$

ε_g-symmetry

$F_{11} = f_{\phi} - f''_{\phi\phi}$

β_{1g}-symmetry

$F_{11} = f_{NH}$

$F_{12} = 0$

$F_{22} = f_{MN} - 2f^{c}_{MN/MN} + f^{t}_{MN/MN}$

β_{2g}-symmetry

$F_{11} = f_{\beta} + f''_{\beta\beta}$

$F_{12} = 0$

$F_{22} = f_{\alpha} + f''_{\alpha\alpha}$

α_{2u}-symmetry

$F_{11} = f_{\phi} + f''_{\phi\phi}$

$F_{12} = \sqrt{2} f_{\theta\phi}$

$F_{22} = f_{\theta}$

β_{2u}-symmetry

$F_{11} = f_{\phi} - f''_{\phi\phi}$

$F_{12} = 0$

$F_{22} = f_{\theta}$

ε_u-symmetry

$F_{11} = f_{NH}$

$F_{12} = F_{13} = F_{14} = F_{34} = 0$

$F_{22} = f_{MN} - f^{t}_{MN/MN}$

$F_{23} = 2f_{MN/\beta}$

$F_{24} = \sqrt{2}(f_{MN/\alpha} - f''_{MN/\alpha})$

$F_{33} = f_{\beta} - f''_{\beta\beta}$

$F_{44} = f_{\alpha} - f''_{\alpha\alpha}$

Interactions force constants, between internal coordinates:

$f_{MN/MN}$: between two MN-bonds: c = cis and t = trans

f_{ϕ} : MNH rocking (ϕ and β are perpendicular to each other)

f_{θ} : MNH rocking (θ and α are perpendicular to each other)

$f''_{\beta\beta}$: between two MNH angles (opposite)

These initial force constants, were firstly modified by a trial and error method, on the basis of the data reported in Ref. (1), and then refined by the so called "simplex method" put forward by Nectoux et al[18].

The final internal force constants, as well as the calculated frequencies for both the T_d and the D_{4h} symmetries are displayed in Tables IV - VII.

DISCUSSION

The calculated force constants, given in Tables IV and V have reasonable values, and the overall agreement is quite satisfactory. It can be seen, that these sets of force constants reproduce rather nicely the observed vibrational frequencies, see Tables VI and VII. This fact suggests that our simple model calculation is suitable to work out vibrational analysis for this type of ammino complexes, although its simplicity.

With regards to the $Pd(NH_3)_4^{2+}$ ion, our calculation shows that the band which appears at 245 cm^{-1} should be assigned to the NPdN(ε_u) bending mode. Thus, our calculation supports the assignment given in Refs. (9) and (19), and disagree with the assignment proposed (at 295 cm^{-1}) in Ref. (20). Similary, and concerning with the $Pt(NH_3)_4^{2+}$ ion, our calculation supports the assignment made for the band at 236 cm^{-1} by Poulet et al[8], in opposition with the assignment made for this same band at 297 cm^{-1}, in Ref. (20).

According to the model calculation used in the present work, it is obvious that the N-H stretching force constant was obtained as 1/3 of the value obtained by solving the equations of motions for the 9-atoms system.

TABLE IV

Internal force constants (in mdyne/Å)

T_d symmetry

	Zn	Cd	Co
f_{MN}	1.43	1.23	1.45
$f_{MN/MN}$	0.15	0.08	0.057
f_{NH}	5.10	5.20	5.17
f_{α}	0.20	0.22	0.26
$f'_{\alpha\alpha}$	0.005	0.005	0.005
$f''_{\alpha\alpha}$	-0.01	-0.01	-0.01
f_{β}	0.13	0.125	0.135
$f_{\beta\beta}$	-0.04	-0.04	-0.04
$f'_{\beta\alpha}$	0.015	0.006	0.003
$f'''_{\beta\alpha}$	0.015	0.006	0.003
$f'_{MN/\alpha}$	0.010	0.010	0.010
$f''_{MN/\alpha}$	0.045	0.045	0.045
$f'_{MN/\beta}$	0.024	0.024	0.024
$f''_{MN/\beta}$	0.012	0.012	0.012

TABLE V

Internal force constants (in mdyne/Å)

D_{4h} symmetry

	Cu	Pd	Pt
f_{MN}	1.42	2.16	2.55
$f^{c}_{MN/MN}$	0.100	0.100	0.05
$f^{t}_{MN/MN}$	0.20	0.27	0.30
f_{NH}	5.37	5.17	5.06
f_{β}	0.136	0.182	0.188
$f''_{\beta\beta}$	0.004	0.002	0.002
f_{α}	0.24	0.23	0.23
$f''_{\alpha\alpha}$	-0.04	-0.03	-0.03
$f'_{MN/\alpha}$	0.0175	0.0175	0.0175
$f''_{MN/\alpha}$	-0.0175	-0.0175	-0.0175
$f_{MN/\beta}$	-0.035	-0.035	-0.035
f_{ϕ}	0.13	0.16	0.19
f_{θ}	0.20	0.235	0.27
$f_{\phi\phi}$	-0.015	-0.015	-0.010
$f_{\theta\phi}$	-0.035	-0.035	-0.035

TABLE VI

Observed and calculated frequencies (in cm^{-1})

T_d symmetry. A $M(NX)_4$ model

Species	Description	Zn Cal.	Zn Exp.	Zn Ref.	Cd Cal.	Cd Exp.	Cd Ref.	Co Cal.	Co Exp.	Co Ref.
α_1	ν_1: NH stretch	3233	3234.5	24	3262	3267	1	3258	3260	10
	ν_2: MN stretch	432	431.2	24	385	386	12	405	405	10
ε	ν_3: MNH rock	690	690	24	668	670	1	693	693	10
	ν_4: NMN bend	158	160	24	174	170	12	193	195	10
τ_1	ν_5: MNH rock	712	-	-	675	-	-	637	-	-
τ_2	ν_6: NH stretch	3231	3234.5	24	3267	3267	1	3259	3260	10
	ν_7: MNH rock	688	688	24	667	670	1	693	693	10
	ν_8: MN stretch	410	411.5	24	368	369.5	12	431	430	10
	ν_9: NMN bend	160	160	24	158	160	1	182	195	10

TABLE VII

Observed and calculated frequencies (in cm^{-1})

D_{4h} symmetry

Specie	Description	Cu			Pd			Pt		
		Cal.	Exp.	Ref.	Cal.	Exp.	Ref.	Cal.	Exp.	Ref.
α_{1g}	ν_1: NH stretch	3321	3327	5	3262	3270	25	3231	3236	2
	ν_2: MN stretch	425	420	25	512	512	9	539	538	26
β_{1g}	ν_3: NH stretch	3320	3327	5	3260	3270	25	3230	3236	2
	ν_4: MN stretch	376	375	25	471	468	9	521	526	26
β_{2g}	ν_5: MNH rock	736	735	5	846	849	25	857	842	8
	ν_6: NMN bend	305	300	5	306	305	9	313	270	26
ε_u	ν_7: NH stretch	3320	3327	5	3260	3270	25	3230	3236	2
	ν_8: MNH rock	732	735	5	840	849	25	841	842	8
	ν_9: MN stretch	424	425.5	25	495	495	25	511	510	20
	ν_{10}: NMN bend	255	256	25	242	245	9	232	236	8
ε_g	ν_{11}: MNH rock	747	735	5	821	802	25	878	888	8
α_{2u}	ν_{13}: MNH rock	734	735	5	807	802	25	884	888	8
	ν_{14}: NMN bend	230	226	12	230	237	12	234	235	20

The sequence of the weakening observed in the f_{N-H} stretching force constants for the various molecules correlates with the increasing of the f_{M-N} stretching force constant, along the serie.

It is also shown that the interaction force constants are small. The calculated values may be justified, observing the vecinity of the experimental frequencies.

In passing, let us say that for the complexes in D_{4h} symmetry, our calculation shows that $f_{MN/MN}$ (trans) > $f_{MN/MN}$ (cis). This fact agrees fairly well with previous works on ammino complexes[21-23]. In addition, the values of the MN/MN interaction force constants calculated for the complexes in T_d symmetry may be correlated with those of the $f_{MN/MN}$ (trans) obtained for the complexes in D_{4h} symmetry, considering the smaller angles between the MN bonds in the tetrahedral arrangement of the nucleus in comparision with those angles in trans position in D_{4h} symmetry (resembling the right angle of the cis position for the $M(NH_3)_4^{2+}$ ion, in D_{4h} symmetry).

With regards to the values of the MNH rocking force constants, obtained in the present work for the serie Cu-Pd-Pt, it is seen that they follow the same sequence as given in Ref. (2). This sequence may be correlated to that observed in the M-N stretching force constants. This later fact, may be an evidence of the reality of the calculated rocking force constants for the serie Zn-Cd-Co, where the same trend is observed.

Finally, our calculated potential energy distribution (PED), which is not given here for the sake of brevity, shows that there is a small amount of mixing among vibrational modes of the same symmetry in both T_d and D_{4h} symmetries.

CONCLUSION

The results presented in this work, show that simple model calculations for ammino complexes may be useful to undertake systematic vibrational analysis and in this way to avoid considerable efforts and computing time.

We have shown, that these model calculations are suitable to deal with framework-ligand coupling vibra - tions. Finally, these model calculations can be proved to be useful to undertake explicit calculations on radiative and non radiative transitions in coordination compounds.

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