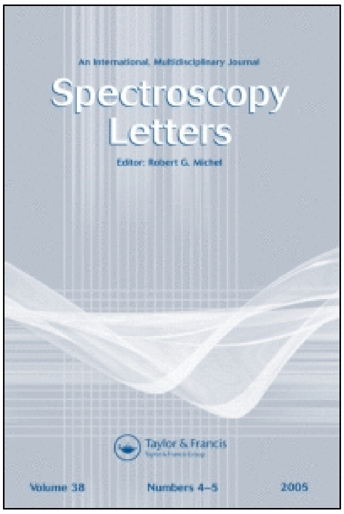

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Normal Coordinates Analysis of the Hexamminochromium (III) Ion. A Simplified $M(NX)_6$ Model

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NORMAL COORDINATES ANALYSIS OF THE HEXAMMINOCHROMIUM (III) ION. A SIMPLIFIED $M(NX)_6$ MODEL

Keywords: Molecular vibrations, Force constants, $Cr(NH_3)_6^{3+}$, O_h.

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ABSTRACT

A normal coordinates analysis for the hexamminochromium (III) ion, in octahedral symmetry has been undertaken. A simplified $M(NX)_6$ model has been adopted, since many of the gerade vibrational frequencies are still unknown. It is found that a very simple and consistent force field is able to reproduce the observed vibrational frequencies as well as gives a reasonable set of force constant for this complex ion. This calculation supports the assignments, made in literature by several workers.

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INTRODUCTION

Several spectroscopic studies on the spectra of Chromium (III) amminecomplexes have been carried out by several workers[1-5].

The most extensive study, in the case of the hexamminochromium (III) ion in cubic lattices, has been undertaken by Flint and Greenough[7].

They recorded the low temperature vibronic spectra associated with the $\Gamma_8(^2\varepsilon_g) \rightarrow \Gamma_8(^4\alpha_{2g})$ phosphorescence and were able to identify and assign many of the odd parity vibrational frequencies, however many of the gerade ones are still unknown.

Nakawa et al[8] performed a normal coordinates analysis for this complex ion, based upon the τ_{14}(7 x 7) block, by utilizing a modified Urey-Bradley force field and including all the ligand atoms. Schmidt et al[9] reported the general valence force field Cr - N stretching force constant, evaluated from Raman and IR data by employing a point mass model and metal isotope.

Here we shall undertake a normal coordinates analysis of the $Cr(NH_3)_6^{3+}$ ion, by adopting a linear ligator approximation for the NH_3 - ligands. A general modified symmetry valence force field (GMSVFF) shall be utilized in this calculation.

A $M(NX)_6$ model for the twenty five atoms system shall be employed, where X represents an effective mass corresponding to three times the mass of a hydrogen atom and located at a distance of 2.38 Å from the central metal atom. The Cr - N bond distance has been taken to be 2.00 Å. The effective mass X has been considered to be linearly connected to Nitrogen.

Next the GF - method of Wilson et al[10] is employed to derive the symmetrical and internal force constants of this complex ion.

MOLECULAR MODEL AND VIBRATIONAL ANALYSIS

The thirty three normal modes of vibration associated with a $M(NX)_6$ molecular system are distributed among the irreducible representations of the octahedral point molecular group as follows:

$$\Gamma_{vib} = 2\ \alpha_{1g}(R) + 2\ \varepsilon_g(R) + \tau_{1g}(R) + 4\ \tau_{1u}(IR) + 2\ \tau_{2g}(R)$$

$$+ 2\ \tau_{24}(R)$$

Jones et al[11] worked out the symmetry coordinates which transform under these representations.

The relationships corresponding to a GMSVFF are given in table I.

Observe that we have taken $F_{ij} = 0$ for $i \neq j$. Next, to build up an initial symmetry adapted F matrix, we have taken $f_R = 1.66$ as reported by Schmidt et al[9]. The other skeletal force constants have been transfered from the calculated ones corresponding to systems of the type $Co(NH_3)_5\ L^{2+}$, where L is a halide anion[12].

The transfered force constants are the following ones:

$f_\beta = 0.18$, $f_\alpha = 0.23$, $f^c_{RR} = 0.07$, $f^t_{RR} = 0.49$, $f_{\beta\beta 1}=0.00$, $f_{\beta\beta 2} = 0.00$ and $f_{\alpha\alpha} = 0.03$, in units of mdyne/Å.

The diagonal F matrix elements $F_{ii}(i = 2, 4, 6)$ involving the N-H stretch coordinate, ie $F_{22}\ (\alpha_{1g})$, $F_{44}\ (\varepsilon_g)$ and $F_{66}\ (\tau_{1u})$ were calculated by means of the relationship:

$$F_{ii} = (\lambda_i/G_{ii}), \text{ where } \lambda_i = 0.5888851\ (\nu_i/1000)^2$$

According to the model employed in this calculation, the actual value corresponding to the N-H stretching force constant f_D, should be 1/3 of the calculated one by using the GF-method of Wilson et al[10].

TABLE I

Internal and symmetry valence force constants for $M(NX)_6$ type of molecules

Internal valence force constants:

Diagonal: f_R; f_D; f_α; f_β

Interaction: f_{DD}, f_{RR} (c = cis, t = trans)

$f_{\beta\beta 1}$ (opposed), $f_{\beta\beta 2}$ (perpendicular)

$f_{\alpha\alpha 1}$ (perpendicular with two atoms in common)

$f_{\alpha\alpha 2}$ (opposed with two atoms in common)

$f_{\alpha\alpha 3}$ (with one atom in common).

Symmetry valence force constants:

α_{1g}

$$F_{11} = f_R + 4f^c_{RR} + f^t_{RR}$$

$$F_{22} = f_D + 4f^c_{DD} + f^t_{DD}$$

ε_g

$$F_{33} = f_R - 2f^c_{RR} + f^t_{RR}$$

$$F_{44} = f_D - 2f^c_{DD} + f^t_{DD}$$

τ_{1g}

$$F_{55} = f_\beta + 2f_{\beta\beta 1} + 4f_{\beta\beta 2}$$

τ_{1u}

$$F_{66} = f_D - f^t_{DD}$$

$$F_{77} = f_R - f^t_{RR}$$

$$F_{88} = f_\beta - f_{\beta\beta 1} + 2f_{\beta\beta 2}$$

$$F_{99} = f_\alpha + 2f_{\alpha\alpha 1} + f_{\alpha\alpha 2} - f_{\alpha\alpha 3}$$

τ_{2g}

$$F_{1010} = f_\beta - 2f_{\beta\beta 1} + f_{\beta\beta 2}$$

$$F_{1111} = f_\alpha - 2f_{\alpha\alpha 1} + f_{\alpha\alpha 2}$$

τ_{2u}

$$F_{1212} = f_\beta - f_{\beta\beta 1} - 2f_{\beta\beta 2}$$

$$F_{1313} = f_\alpha - 2f_{\alpha\alpha 1} + 2f_{\alpha\alpha 2} - f_{\alpha\alpha 3}$$

The initial force constants were slightly modified by a trial and error method, see Table 2. The calculated vibrational frequencies derived from this simplified force field are displayed in Table 3. The calculated values agree fairly well with the observed vibrational-frequencies reported by Flint et al[7].

Table 3 also include the calculated PED of these frequencies, supporting the assignments made previously by Flint and coworkers[7].

DISCUSSION

The calculated force constant f_D(N-H stretching force constant)is smaller in the complex ion than in NH_3 system[14]. The weakening of the N-H bond is due to the coordination Cr-N bond.

Regarding the molecular framework, the stretching force constant f_R, does not change with respect to the value given by Schmidt et al[9]. The smaller value of f_R (1.66) compared with the stretching force constant f_{Co-N} (1.72) reported in Ref. 12, shows that the degree of covalency of the M-N bond decreases from Co(III) to Cr(III), as it has been pointed out by Nakagawa et al[8].

TABLE 2

Internal valence force constants for $|Cr(NH_3)_6|^{+3}$ ion (mdyne/Å)

$f_R = 1.660$ $f_{\alpha\alpha 1} = 0.012$ $f^c_{RR} = 0.050$ $f_{\alpha\alpha 2} = 0.010$

$f^t_{RR} = 0.460$ $f_{\alpha\alpha 3} = 0.005$ $f_\beta = 0.145$ $f_D = 5.200$

$f_{\beta\beta 1} = 0.020$ $f^c_{DD} = 0.0$ $f_{\beta\beta 2} = 0.014$ $f^t_{DD} = 0.010$

$f_\alpha = 0.250$

TABLE 3

Calculated vibrational frequencies (cm^{-1}) and potential energy distribution (PED)

Species	Calculated	Experimental[a]	PED[c]
α_{1g}	3267.0	-	$\nu(NH)$ 99%
	509.7	-	$\nu(CrN)$ 99%
ε_{g}	3279.7	-	$\nu(NH)$ 99%
	424.0	425.0	$\nu(CrN)$ 99%
τ_{1g}	956.4	-	$\rho(NH_3)$ 98%
τ_{1u}	3277.7	3270.0	$\nu(NH)$ 99%
	742.5	745.0	$\rho(NH_3)$ 93%
	477.9	473.0	$\nu(CrN)$ 78% + $\delta(NCrN)$18%
	260.7	261.0	$\delta(NCrN)$76% + $\nu(CrN)$ 21%
τ_{2g}	661.5	-	$\rho(NH_3)$ 91%
	281.2	270.0	$\delta(NCrN)$ 91%
τ_{2u}	677.4	670.0	$\rho(NH_3)$ 96%
	207.6	203.0	$\delta(NCrN)$ 95%

[a]From Reference 7. $|100\ F_{ii}L_{ik}^{2}/\lambda_{k}|^{c}$; terms below 15% are omitted.

The constants f_{α} y f^{t}_{RR} are just slightly different from the values given in reference 12, so it may be possible to transfer them to an initial force field to describe similar complex ions.

We also find that the NH_3-rocking force constant f_{β}, decreases approximately a 20% with respect to the corresponding constant in the Co(III)-ammine complex ion[12]. This fact suggests that this force constant could also be considered as a measurement of the degree of covalency for this type of complexes.

Finally, the calculated PED shows that in general there are no coupling among the frequencies, except those concerning the Cr-N stretching (477.9 cm^{-1}) and the NCrN bending (261 cm^{-1}), however this coupling is not important.

CONCLUSION

The consistency of the internal force constants and the agreement between the observed frequencies and the calculated ones, by using a very simple potential field, indicates that the molecular model chosen in this work could be useful to interpret the vibronic spectra of this type of complex ions.

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