Indian J. Phys. **54B**, 520–522 (1980)

Pseudo-exact force constants for $[Mg\ (NH_3)_6]^{2+}$

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Received 11 July 1978

Abstract: The normal coordinate analysis has been performed for the complex $[Mg(NH_3)_6]^{2+}$ having an octahedral framework structure. Recently reported isotopic shifts have been used to determine the pseudo-exact force constants and mean amplitudes of vibration with the help of point mass model (PMM). Pseudo-exact force constants due to $^{24}Mg/^{26}Mg$ isotopic shifts are also employed to determine the mean amplitudes of vibration at room temperature.

1. Introduction

Recently, Plus (1976) has studied the infrared and Raman spectra of many substituted magnesium chloride hexa-ammines, and measured the frequency shifts for all active vibrational bands He has also reported the vibrational frequencies and isotopic shifts for MgL_6^{2+} ($L = NH_3, ND_3$) Therefore it was considered worthwhile to compute the pseudo-exact force constants for this complex using point mass model in conjunction with isotopic shifts data

Pseudo-exact force constants thus obtained have been used to calculate the mean amplitudes of vibration at room temperature Using L matrix method mean amplitudes of vibration are also reported at $T = 0$, 298·15 and 500 K

2. Theoretical consideration

The octahedral XY_6 type system belongs to symmetry group, O_h, and the six vibrational modes are classified according to symmetry type as follows :

$$\Gamma_{vib.} = A_{1g}+E_g+2F_{1u}+F_{2g}+F_{2u},$$

where g and u represent gerade and ungerade modes that are Raman and infrared active respectively But the mode F_{2u} is inactive in both and is determined with the help of Wilson's relation $\nu_5 = \sqrt{2}\nu_6$, if the binary combination is not permitted.

Force constant parameters are evaluated, assuming (NH_3) group as a point mass and taking into account the isotopic shifts, using the secular determinants (Wilson *et al* 1955) $|GF-\lambda E| = 0$. These symmetrized force constants have

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been used to evaluate the elements of matrix using the Cyvin's (1968) secular determinants $|\Sigma G^{-1}-\Delta E| = 0$ alongwith $|\Sigma F-\lambda\Delta E| = 0$ in their usual notations.

3. Results and Discussion

We have employed heavy atom substitution ($^{24}Mg/^{26}Mg$ and $^{14}N/^{15}N$) and H/D substitution techniques for the determination of pseudo-exact force constants (Table 1). Force constants obtained by heavy atom substitution technique are in excellent agreement with each other but H/D substitution technique yields values slightly higher than those due to heavy atom substitution technique. However, it is reported in literature (Duncan and Mills 1964, Thakur 1971, McDowell and Goldblatt 1971, McDowell *et al* 1972: Mohan and Müller 1972) that heavy atom substitution technique yields better results owing to the small frequency shifts compared to H/D substitution technique We have, therefore, used pseudo-exact force constants obtained on using $^{24}Mg/^{26}Mg$ isotopic shifts in the determination of mean amplitudes of vibration at room temperature ($l_{Mg\cdot N} = 0{\cdot}0959$ Å, $l_{N\cdots N} = 0{\cdot}1408$ Å for linear, and $l_{N\cdots N} = 0{\cdot}1151$ Å for non-

Table 1. Force constants (mdyn/Å) for the frameworks of $[Mg(NH_3)_6]^{2+}$.

Force Constant	Isotopic shift		
	$^{24}Mg/^{26}Mg$	$^{14}N/^{15}N$	H/D
A. Symmetry force constants			
$F_{11}(A_{1g})$	1·126	1 126	1·149
$F_{22}(E_g)$	0·592	0 597	0·608
$F_{33}(F_{1u})$	0·902 ± 0·023	0·866 ± 0·045	0 934 ± 0·017
$F_{34}(F_{1u})$	− 0·251 ± 0·032	−0·219 ± 0·199	−0·302 ± 0·068
$F_{44}(F_{1u})$	0 124 ± 0·016	0 112 ± 0·113	0·152 ± 0·044
$F_{55}(F_{2g})$	0·089	0 089	0·091
$F_{66}(F_{2u})$	0·089	0·089	0·091
B. Internal force constants			
f_r	0·836	0·819	0·861
f_{rr}	0·088	0·088	0·090
f'_{rr}	− 0·066	−0 046	−0·072
$f'_{r\alpha}-f''_{r\alpha}$	− 0 125	−0·109	−0·151
$f_\alpha-f''_{\alpha}{}'_{\alpha}$	0·106	0·101	0·122
$f_{\alpha\beta}-f''_{\alpha\alpha}$	0·009	0·006	0·015
$f'_{\alpha\alpha}-f_{\alpha}{}''_{\alpha}{}'$	0·009	0·006	0·015

linear) The mean amplitudes of vibration at T = 0, 298·15 and 500 K evaluated using L approximation method (Table 2) fairly agree with these values and therefore point mass model can be successfully employed in the case of such complexes.

Table 2. Selected mean amplitudes (Å) for $[^{24}Mg(^{14}NH_3)_6]^{2+}$

Distance	T = OK	298·15K	500 K
Mg-N	0·0718	0·0894(0·0959)	0·1096
N N (Linear)	0·0972	0·1479 (0·1409)	0 1871
N .N (non-linear)	0·0860	0·1151(0 1151)	0 1434

Values in ( ) are calculated using pseudo-exact force constants for $^{24}Mg/^{26}Mg$ shifts

Acknowledgment

Two of the authors (ANP and VK) are thankful to UGC New Delhi for financial assistance. UPV is thankful to CSIR, New Delhi for awarding senior fellowship

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