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Force Field Calculations In Octahedral Water Complexes

by

V. Ananthanarayanan

Introduction

The vibrational spectrum of the octahedral water complexes in crystals had been studied by the author in considerable detail (1). In one of the more recent publications a critical study of the Raman and Infrared Spectra of the $\text{Co}(\text{H}_2\text{O})_6$ ion in $\text{K}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystal has been published by the author and Danti (2). A detailed theoretical analysis of the whole range of the low frequency spectrum of this crystal has enabled definite assignments of frequencies due to lattice, hydrogen bond and $\text{Co}(\text{H}_2\text{O})_6$ modes.

The absence of such data has prevented any rigorous force field analysis of this ion impossible till now. In view of the changed circumstances, force field calculations of $\text{Co}(\text{H}_2\text{O})_6$ ion vibrations have been done by the author and the results are presented.

Symmetry, Selection Rules and Spectral Data For $\text{Co}(\text{H}_2\text{O})_6$ Ion

The spectrum of $\text{Co}(\text{H}_2\text{O})_6$ ion was analysed by treating it as belonging to the octahedral O_h (group xy_6 type: $X = \text{C}_0$ and $Y = \text{H}_2\text{O}$) and by taking the water molecule as a single unit of mass 18.

The free O_h group has six normal vibrations designated as follows:

— triply

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tive.

The $\text{K}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystallizes in the monoclinic class space group C_{2h}^3 with two molecules in the unit cell. The $\text{Co}(\text{H}_2\text{O})_6$ groups have only a site symmetry C_1 inside the monoclinic unit cell. But experimental studies have definitely shown that both the site group and factor group splittings of the $\text{Co}(\text{H}_2\text{O})_6$ frequencies are too small to be detected.

The following wavenumbers (2) have been experimentally observed for the $\text{Co}(\text{H}_2\text{O})_6$ ion:

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The free O_h group has six normal vibrations designated as follows: \mathcal{V}_1 (A_{1g} - totally symmetric), \mathcal{V}_2 (E_g - doubly degenerate), $\mathcal{V}_3, \mathcal{V}_4$ (F_{1u} - triply degenerate), \mathcal{V}_5 (F_{2g} - triply degenerate) and \mathcal{V}_6 (F_{2u} - triply degenerate). Of these $\mathcal{V}_1, \mathcal{V}_2$ and \mathcal{V}_5 are Raman active and the rest infrared active.

The $\text{K}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystallizes in the monoclinic class space group C_{2v}^{21} with two molecules in the unit cell. The $\text{Co}(\text{H}_2\text{O})_6$ groups have only a site symmetry C_1 inside the monoclinic unit cell. But experimental studies have definitely shown that both the site group and factor group splittings of the $\text{Co}(\text{H}_2\text{O})_6$ frequencies are too small to be detected.

The following wavenumbers (2) have been experimentally observed for the $\text{Co}(\text{H}_2\text{O})_6$ ion: (all in cm^{-1} units). \mathcal{V}_1 (397), \mathcal{V}_2 (212), \mathcal{V}_3 (410), \mathcal{V}_4 (257), \mathcal{V}_5 (271) and \mathcal{V}_6 (146).

Theoretical Considerations

The most widely applied method for obtaining the normal frequencies of molecules is the one utilizing the Wilson's F — G matrix method, where the elements of a matrix F (related to the potential energy) and the elements of a matrix G (related to the kinetic energy) are obtained. From these matrices, equations relating the vibrational frequencies to the force constants of the molecule are constructed (3) as follows:

For A_{1g} type:

$$\lambda_1 = F_{11} G_{11} = (f_d + 4f_{dd} + f_{dd}') \mu_y$$

For E_g type:

$$\lambda_2 = F_{11} G_{11} = (f_d - 2f_{dd} + f_{dd}') \mu_y$$

For F_{1u} type:

$$\lambda^2 - \lambda [F_{11} G_{11} + 2F_{12} G_{12} + F_{22} G_{22}] + \begin{vmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{vmatrix} \cdot \begin{vmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{vmatrix} = 0$$

Where the roots are λ_3 and λ_4 .

Thus we get from the equation above,

$$\lambda_3 + \lambda_4 = (2\mu_x + \mu_y)(f_d - f_{dd}') - 16\mu_x (f_{dd} - f_{dd}'') \\ + (8\mu_x + 2\mu_y)(f_d + 2f_{dd}'' - 2f_{dd}''' - f_{dd}''')$$

$$\text{and } \lambda_3 \lambda_4 = [(f_d - f_{dd}') (f_d + 2f_{dd}'' - 2f_{dd}''' - f_{dd}''') \\ - 4 (f_{dd}'' - f_{dd}''')^2] \times$$

$$[(2\mu_x + \mu_y)(8\mu_x + 2\mu_y) - 16\mu_x^2]$$

For F_{2g} type:

$$\lambda_5 = 4(f_d - 2f_{dd} + f_{dd}''') \mu_y$$

and for F_{2u} type:

$$\lambda_6 = 2(f_d - 2f_{dd} + 2f_{dd}'' - f_{dd}''') \mu_y$$

The definitions of various terms used are given below:

$$\lambda_i = 4\pi^2 c^2 \nu_i^2 \quad (i = 1, 2, 3, 4, 5, \text{ or } 6)$$

c = velocity of light

f_d = force between X and Y atoms

f_{dd}^f = interaction constant between stretching and stretching when there is an angle of 90° between the two stretching bonds

f_{dd}^i = interaction between stretching and stretching when the two bonds are opposite

$f_{d\alpha}$ = interaction between stretching and bending when the stretching bond is also one of the bending bonds

$f_{d\alpha}^i$ = interaction between stretching and bending when the stretching bond is perpendicular to both bending bonds

f_{dd}'' = interaction between stretching and bending when the stretching bond is perpendicular to one and opposite to the other bending bond

f_{α} = force associated with bending

$f_{d\alpha}$ = interaction between bending and bending when one bond is common to both bending pairs and the two others are perpendicular

$f_{d\alpha}^i$ = interaction between bending and bending when one bond is common to both bending pairs and the two others are opposite

$f_{d\alpha}''$ = interaction between bending and bending when one bond of one pair is opposite to a bond of the other pair, while the other bonds are perpendicular to each other

$f_{d\alpha}'''$ = interaction between bending and bending when the two bending angles are opposite each other

μ_x = reciprocal mass of the X atom, i.e. cobalt

μ_y = reciprocal mass of the Y atom, i.e. water molecule

Results

The following numerical values of the force constants (in 10^5 dynes . cum⁻¹ units) were obtained by substituting the proper values of the wave numbers in the equations above, with appropriate approximations.

$$\begin{aligned} (f_{dd} + f_{dd}^i) &= 0.868; & f_{dd} &= 0.198; \\ (f_{d\alpha} - f_{d\alpha}''') &= 0.369 & \text{or} & -0.129; \\ (f_{\alpha} - f_{\alpha}''') &= 0.379 & \text{or} & 0.106; \\ (f_{d\alpha} - f_{d\alpha}''') &= 0.133 & \text{or} & -0.004 & \text{and} \\ (f_{d\alpha}^i - f_{d\alpha}''') &= -0.030 & \text{or} & -0.099. \end{aligned}$$

If we neglect f_{dd}' we could make an estimate of Co -O distance from the value of f_d using Badger's rule (4). Such a procedure leads to a value of 2.17 \AA . This agrees favorably with the bond lengths determined by x-ray structure studies, which report values near 2.1 \AA in few hydrated cobalt sulfates.

REFERENCES

- (1) V. Ananthanarayanan, Z. Phys. Chemie (Leipzig), 222, 102-110, 1963.
- (2) V. Ananthanarayanan and A. Danti, J. Mol. Spect., Vol. 20, 88, 1966.
- (3) E. B. Wilson, Jr., J. Chem. Phys., 7, 1047 (1939); 9, 76 (1941).
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If we neglect σ we could make an estimate of Co-O distance from the value of σ using Badger's rule (4). Such a procedure leads to a value of σ . This agrees favorably with the bond lengths determined by x-ray structure studies, which report values near 2.1 Å in few hydrated cobalt sulfates.

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- (1) V. Ananthanarayanan, Z. Phys. Chemie (Leipzig), 222, 102-110, 1963.
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