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Force Constant For Be–O Stretching in Behoite and in Chrysoberyl

DALE A. HUCKABY, TERRY L. WRIGHT[1]

Chemistry Department,

AND ARTHUR J. EHLMANN

Geology Department,
Texas Christian University, Fort Worth, Texas 76129

Abstract

An absorption band near 780 cm^{-1} in the infrared spectra of behoite [β-$Be(OH)_2$] and of chrysoberyl [Al_2BeO_4] was assigned to the vibration of a beryllium atom moving in a tetrahedral cage of four fixed oxygen atoms. Using this simple model, a force constant of 2.4 mdyne/Å was calculated for Be–O stretching in behoite and chrysoberyl.

Introduction

The infrared spectrum of behoite [β-$Be(OH)_2$] was given by Ehlmann and Mitchell (1970), and the infrared spectrum of β-$Be(OH)_2$ has been studied by Funck (1964) and by Bear, Lukaszewski, and Turnbull (1965). The β-$Be(OH)_2$ crystal is composed of tetrahedral $Be(OH)_4$ groups (Seitz, Rösler, and Schubert, 1950).

The IR spectrum of chrysoberyl [Al_2BeO_4] has been studied by Henning and Volke (1966), Povarennykh and Gevorkyan (1971), Povarennykh and Nefedov (1971), and Plyusnina (1963). Chrysoberyl contains tetrahedral BeO_4 groups and octahedral AlO_6 groups (Farrell, Fang, and Newnham, 1963).

For crystals having a small number of degrees of freedom in the unit cell, an analysis using lattice dynamics is feasible. Nusimovici (1969) has performed a lattice dynamical calculation for beryllium oxide, a crystal which contains tetrahedral BeO_4 groups. Using the Raman spectrum, he obtained a value of 2.3 mdyne/Å for the Be–O stretching force constant.

For crystals containing the BeO_4 group but having a large number of degrees of freedom in the unit cell, the infrared spectrum is often interpreted as arising principally from the vibrations of the tetrahedral BeO_4 group. A tetrahedral unit exhibits a nondegenerate vibration of frequency ν_1, a doubly degenerate vibration of frequency ν_2, and two triply degenerate vibrations at ν_3 and ν_4 (Wilson, Decius, and Cross, 1955). Generally, only ν_3 and ν_4 are infrared active, but distortions of the tetrahedral symmetry and couplings with other parts of the crystal can result in ν_1 and ν_2 appearing in the infrared and can break the degeneracy of the modes ν_2, ν_3, and ν_4.

Funck (1964) has looked at ν_3 for several BeO_4-containing molecules from the standpoint of a light central atom surrounded by heavy ligands. Using $\tilde{\nu} \approx 800$ cm^{-1} for the BeO_4 group, he obtained a metal-ligand force constant for Be–O of 1.79 mdyne/Å.

Model for the 780 cm^{-1} Band

A simple model is proposed to account for the band near 780 cm^{-1} which occurs in the infrared spectra of several BeO_4-containing minerals. This band is interpreted as arising from the vibration of a beryllium atom moving in a tetrahedron of fixed oxygen atoms. The frequency, ν_{Be}, of this vibration would be triply degenerate for a perfect tetrahedron, the degeneracy being broken by slight distortions of the tetrahedron.

The same procedure that would be used to evaluate the Einstein frequency of a crystal (Rice, 1967) is

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[1] Robert A. Welch Foundation Undergraduate Scholar.

employed to express ν_{Be} in terms of the Be–O stretching force constant K. A situation is considered in which a beryllium atom experiences a displacement from equilibrium in the amount $\vec{r}_{\mathrm{Be}} = \vec{r}_i - \vec{r}_i^*$, where $\vec{r}_i$ is the instantaneous displacement of the beryllium atom from the i^th^ neighboring oxygen atom, and $\vec{r}_i^*$ is the corresponding equilibrium displacement. Neglecting all but central force interactions, the potential due to the displacement $\vec{r}_{\mathrm{Be}}$ is given by this model as

$$V = \frac{1}{2} K \sum_{i=1}^{4} (r_i - r_i^*)^2,$$

where the sum extends over the four fixed oxygen atoms.

Upon expanding $r_i = |\vec{r}_i^* + \vec{r}_{\mathrm{Be}}|$ to first order in $\vec{r}_{\mathrm{Be}}$ and writing the $\vec{r}_i^*$ in any convenient coordinate system, the simple expression

$$V = \frac{1}{2}\left(\frac{4K}{3}\right) r_{\mathrm{Be}}^2$$

is obtained. Hence the beryllium atom behaves as a simple harmonic oscillator vibrating with a frequency

$$\nu_{\mathrm{Be}} = \frac{1}{2\pi}\left[\frac{4K}{3}\right]^{1/2},$$

where m is the mass of a beryllium atom. This expression is similar in form to that of Funck (1964), except that ν_{Be} above shows no dependence on the mass of the outer oxygen atoms. A value for K is obtained upon assignment of an infrared band to ν_{Be}.

Using the infrared spectrum of behoite reported by Ehlmann and Mitchell (1970), a band composed of peaks at 875, 780, 750, and 720 cm^{-1} was assigned to the vibration of the Be in a tetrahedron of fixed OH groups. The average frequency, 781 cm^{-1}, was taken as $\tilde{\nu}_{\mathrm{Be}}$. These frequencies are similar to the assignments of $\tilde{\nu}_3$ = 875, 775, and 700 cm^{-1} given by Funck (1964) and close (somewhat similar) to the assignments of $\tilde{\nu}_3$ = 880, 875, 825, and 780 cm^{-1} made by Bear *et al* (1965).

A band in the infrared spectrum of chrysoberyl with peaks at 750, 775, and 820 cm^{-1} was tentatively assigned to $\tilde{\nu}_3$ by Henning and Volke (1966). The average of these peaks, 782 cm^{-1}, is close to the assignment of 780 cm^{-1} made for $\tilde{\nu}_3$ by Povarennykh and Nefedov (1971), and is not inconsistent with the assignment of $\tilde{\nu}_3$ = 1000, 860 and 780 cm^{-1} given by Povarennykh and Gevorkyan (1971). A quite different assignment was given by Plyusnina (1963) who tentatively assigned to $\tilde{\nu}_3$ a band having peaks ranging from 963 to 1161 cm^{-1}.

Using the frequency 780 cm^{-1} for $\tilde{\nu}_{\mathrm{Be}}$ in both behoite and chrysoberyl, a Be–O stretching constant of K = 2.4 mdyne/Å is obtained, in good agreement with the Be–O stretching constant of 2.3 mdyne/Å obtained by Nusimovici (1969) for beryllium oxide.

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