

A calculation of vibrational frequencies of H₂O in beryl channel by FG matrix method

Junichi Fukuda[1]; # Keiji Shinoda[2]

[1] Dept. Earth & Space Sci., Osaka Univ.; [2] Geosciences, Osaka City Univ.

Two orientations of water molecules, type I and type II have previously been recognized in beryl channels. Type I water molecules are not coupled with other extra-frame work cations present in beryl channels, and have H-H vectors oriented parallel to the crystallographic c-axis. Type II water coordinates to a cation in the channel and its H-H vector is perpendicular to the c-axis. Subtle variations of frequencies in infrared (IR) absorption spectrum have been predicted based on the coordination of water molecules. In this study, polarized IR spectra of hydrated synthetic beryl and natural beryl were measured to clarify the relations between the frequencies of absorption bands and the coordinating states of type II water. Four bands due to type II were confirmed in the hydrated synthetic beryl at 3602cm⁻¹ and 3589cm⁻¹ for n₁ mode and at 1631cm⁻¹ and 1619cm⁻¹ for n₂ mode. Na⁺ is assumed to be the predominant cation to cause type II water in the channel by chemical analyses. Measurements of absorbance of the four bands at various points of the crystal revealed that absorbance of 3602cm⁻¹ and 1619cm⁻¹ show a clear quantitative linear relation, as do 3589cm⁻¹ and 1631cm⁻¹ bands. This indicates that 3602cm⁻¹ and 1619cm⁻¹ are n₁ and n₂ modes of type II coupled with Na⁺, and that 3589cm⁻¹ and 1631cm⁻¹ are due to another type II which must be modified from the former. Based on some experimental and theoretical studies, we assigned the 3602cm⁻¹ and 1619cm⁻¹ bands to n₁ and n₂ modes of doubly coordinated type II, and 3589cm⁻¹ and 1631cm⁻¹ bands to singly coordinated type II in the channel. These assignments are supported by IR measurements of annealed natural beryl. Intense absorption bands at 3700, 3600 1625cm⁻¹ were observed in a raw natural beryl. After annealing the natural beryl at 850C, the band at 3700cm⁻¹ did not change its frequency and disappeared rapidly, the band at 3600cm⁻¹ decreased gradually and shifted to 3589cm⁻¹, and the band at 1625cm⁻¹ also decreased gradually and shifted to 1631cm⁻¹. These band shifts during dehydration indicate that doubly coordinated type II is dominant in beryl with high H₂O concentration, and that singly coordinated type II becomes dominant with reduced H₂O concentration, supporting our assignment of IR modes in beryl. Based on these experimental frequencies of H₂O in beryl channel, we carry out basic theoretical calculations of frequencies of three IR active modes of H₂O by FG matrix method assuming Urey-Bradley force constants. Because simple and basic parameters were used for the calculations, precise frequencies were not calculated out. However, tendencies of peak shifts of three modes were clearly observed. In general, peak shifts of stretching and bending motions of H₂O are due to deviation of force constants of OH stretching and HOH bending motions by hydrogen bonding. In this study, calculation by fixing the force constants of OH stretching and HOH bending motions, and varying a force constant of HH repulsion revealed that frequencies of symmetric stretching motion and bending motion reversely shift and asymmetric stretching motion is fairly constant. This suggests that frequencies of H₂O can be varied without hydrogen bonding. This calculation is consistent with the results of polarized IR spectra of hydrated beryl.