MILLIMETER WAVE SPECTRA OF THE INTERNAL ROTATION EXCITED STATES OF (o)H₂-H₂O AND (o)H₂-D₂O

K. HARADA, Y. IWASAKI, T. GIESEN, and K. TANAKA, Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka, 812-8581 JAPAN.

H₂-H₂O is a weakly bound complex and it has a various states according to the internal rotation for both H₂ and H₂O moieties. In our previous study, we have reported the pure rotational transitions of the (o)H₂ complex in the ground H₂O rotational state, 0_{00}(Σ), for both H₂-H₂O and H₂-D₂O, where (o)H₂ (j_{H₂}=1) is rotating perpendicular to the intermolecular axis to give the projection of j_{H₂} to the axis k_{H₂} to be zero (i.e. Σ state).

In the present study, we have observed the rotational transitions for the 0_{00} (Π) states in the millimeter-wave region up to 220 GHz, where the (o)H₂ is rotating around the intermolecular axis to give the projection k_{H₂} to be one (i.e. Π state). The center of mass bond lengths derived from the observed rotational constants for 0_{00}(Π) are longer by 5 % than those for 0_{00}(Σ), while force constants for the intermolecular stretching for 0_{00}(Π) derived from centrifugal distortion constants are smaller by 23 % than those for 0_{00}(Σ), suggesting the Π and Σ substates have quite different structures.

The recent theoretical calculation indicates that for 0_{00}(Σ), (o)H₂ is bound to the oxygen site of H₂O, while for the 0_{00}(Π) state, (o)H₂ to the hydrogen site of H₂O, and the 0_{00}(Σ) state is by 14 cm⁻¹ more stable than the 0_{00}(Π) state. Observed molecular constants for 0_{00}(Σ) and (Π) are consistent with the structures given by the theoretical calculation.

We also observed the rotational spectrum in the 1_{01}(Σ) and (Π) states, where Σ and Π correspond to the rotation of H₂O perpendicular and parallel to the intermolecular axis and (o)H₂ is calculated to be bound to the oxygen site of H₂O. The energy difference between the 1_{01}(Σ) and (Π) states will be discussed due to the Criolis interaction between these substates.
