

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,^a we have reported the pure rotational transitions of the (*o*)H₂ complex in the ground H₂O rotational state, 0₀₀(Σ), for both H₂-H₂O and H₂-D₂O, where (*o*)H₂ ($j_{\text{H}_2}=1$) is rotating perpendicular to the intermolecular axis to give the projection of j_{H_2} to the axis k_{H_2} to be zero (*i.e.* Σ state).

In the present study, we have observed the rotational transitions for the 0₀₀(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_{H_2} to be one (*i.e.* Π state). The center of mass bond lengths derived from the observed rotational constants for 0₀₀(Π) are longer by 5 % than those for 0₀₀(Σ), while force constants for the intermolecular stretching for 0₀₀(Π) derived from centrifugal distortion constants are smaller by 23 % than those for 0₀₀(Σ), suggesting the Π and Σ substates have quite different structures.

The recent theoretical calculation^b indicates that for 0₀₀(Σ), (*o*)H₂ is bound to the oxygen site of H₂O, while for the 0₀₀(Π) state, (*o*)H₂ to the hydrogen site of H₂O, and the 0₀₀(Σ) state is by 14 cm⁻¹ more stable than the 0₀₀(Π) state. Observed molecular constants for 0₀₀(Σ) and (Π) are consistent with the structures given by the theoretical calculation.

We also observed the rotational spectrum in the 1₀₁(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 1₀₁(Σ) and (Π) states will be discussed due to the Coriolis interaction between these substates.

^aC. J. Whitham, K. Tanaka, and K. Harada, *The 56th OSU Symposium*, **RD08** (2001).

^bAd. van der Avoird and D. J. Nesbit, *J. Chem. Phys.* **134**, 044314 (2011).