MILLIMETER WAVE SPECTRA OF THE INTERNAL ROTATION EXCITED STATES OF (o)H_2-H_2O AND (o)H_2-D_2O

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H_2-H_2O is a weakly bound complex and it has a various states according to the internal rotation for both H_2 and H_2O moieties. In our previous study,[a] we have reported the pure rotational transitions of the (o)H_2 complex in the ground H_2O rotational state, $0_{00}(\Sigma)$, for both H_2-H_2O and H_2-D_2O, where (o)H_2 (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)H_2 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 $0_{00}(\Pi)$ are longer by 5 % than those for $0_{00}(\Sigma)$, while force constants for the intermolecular stretching for $0_{00}(\Pi)$ derived from centrifugal distortion constants are smaller by 23 % than those for $0_{00}(\Sigma)$, suggesting the Π and Σ substates have quite different structures.

The recent theoretical calculation[b] indicates that for $0_{00}(\Sigma)$, (o)H_2 is bound to the oxygen site of H_2O, while for the $0_{00}(\Pi)$ state, (o)H_2 to the hydrogen site of H_2O, and the $0_{00}(\Sigma)$ state is by 14 cm^{-1} more stable than the $0_{00}(\Pi)$ state. Observed molecular constants for $0_{00}(\Sigma)$ and (Π) are consistent with the structures given by the theoretical calculation.

We also observed the rotational spectrum in the $1_{01}(\Sigma)$ and (Π) states, where Σ and Π correspond to the rotation of H_2O perpendicular and parallel to the intermolecular axis and (o)H_2 is calculated to be bound to the oxygen site of H_2O. The energy difference between the $1_{01}(\Sigma)$ and (Π) states will be discussed due to the Criolis interaction between these substates.

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[a] C. J. Whitham, K. Tanaka, and K. Harada, *The 56th OSU Symposium*, **RD08** (2001).

[b] Ad. van der Avoid and D. J. Nesbit, *J. Chem. Phys.* **134**, 044314 (2011).