STIMULATED EMISSION PUMPING SPECTROSCOPY OF HCP NEAR THE ISOMERIZATION BARRIER

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We have been carrying out spectroscopic investigations of HCP $\longleftrightarrow$ CPH isomerization of HCP molecule. Our experimental and many theoretical studies succeeded in interpretation of the generation of "isomerization" states in the vibrational energy region of 12000 – 20000 cm^{-1} above the potential minimum [b]. Several years ago, we have reported the SEP spectroscopy of HCP near the isomerization barrier [c]. In the previous study, it was shown that some of vibrational levels observed have very large B-values which are about 10-18% larger than that of the vibrational ground level. It was claimed that the amplitude of the bending vibration must be very large in these levels.

In the present study, we have extended the energy region sampled by SEP spectra up to 26800 cm^{-1} from the vibrational ground level. This value is very close to the height of the isomerization barrier (27400 cm^{-1}) predicted by the theoretical study. It was found that several vibrational levels exhibit complicated perturbation patterns. These perturbations should be related to Coriolis type interaction which is predicted based on the spherical pendulum model by Jacobson and Child [d]. It is one of the spectroscopic indications of the change in the vibrational character at the isomerization barrier. The vibrational dynamics in the energy region near the isomerization barrier will be discussed based on our experimental observation and the spherical pendulum model.

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