HIGHLY EXCITED VIBRATIONAL LEVELS OF HCP NEAR THE ISOMERIZATION BARRIER

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We have been carried out spectroscopic investigations of HCP $\longleftrightarrow$ CPH isomerization of HCP molecule. Both 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 [a].

Recently, we have succeeded in recording SEP spectra which sample the vibrational energy region above the isomerization barrier. Until now, eight vibrational levels were observed. It was found that some of them have very large rotatonal constants, B. The largest value of B (0.79 cm-1) is about 18% larger than that of the vibrational ground level, $B_0 = 0.667\mathrm{cm}^{-1}$, whereas other levels have similar B-values to B_0. Such a large difference in the rotational constants should be an indication of distinct vibrational dynamics among these levels.

Very recently, Jacobson and Child have investigated the vibrational dynamics in the highly excited vibrational levels of HCP based on their spherical pendulum model [b]. In their study, it is shown that the changes in the vibrational dependence of molecular constants reflect the change in the vibrational dynamics due to the change in the curvature of the potential energy surface. The vibrational dynamics in the energy region above the isomerization barrier will be discussed based on our experimental observation and also the spherical pendulum model.

[a] H. ISHIKAWA *et al.*, Annu. Rev. Phys. Chem. 50, 443 (1999).
[b] M. P. JACOBSON and M. CHILD, J. Chem. Phys. 114, 262 (2001).