LARGE PARITY SPLITTING AS AN INDICATION OF THE HCP $\longleftrightarrow$ CPH "ISOMERIZATION"

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We have been investigating the HCP $\longleftrightarrow$ CPH "isomerization" of HCP molecule by the stimulated emission pumping (SEP) spectroscopy. In the previous study, we recorded SEP spectra in the energy region up to 26800 cm^{-1} in the $\tilde{X}$ state 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 due to the Coriolis type interaction[a]. Strong Coriolis perturbations in the energy region near the "isomerization" barrier are predicted by Jacobson and Child based on their spherical pendulum model[b]. They also pointed out that the parity splitting in $\ell \neq 0$ levels should be a good spectroscopic indication of the "isomerization" in addition to the rotational constants.

Until now, due to the rotational selection rules, only the $\ell = 0$ levels were observed in the energy region above 20000 cm^{-1}. However, using a perturbed level in the $\tilde{C}$ state as an intermediate, we have succeeded in recording SEP spectra which have sampled $\ell = 1$ levels in the 26250 – 27300 cm^{-1} region in the $\tilde{X}$ state, in the present study. As a result, we have found a good relation between the rotational constants and the parity splittings. Larger-B levels exhibit larger parity splittings. For instance, A vibrational level having a $B_{\mathrm{ave.}}$ of 0.76 cm^{-1} exhibits $\Delta B = 0.13\mathrm{cm}^{-1}$, while another level having a $B_{\mathrm{ave.}}$ of 0.62 cm^{-1} exhibits $\Delta B = 0.03\mathrm{cm}^{-1}$. The ΔB of the former level is about 4 times larger than that of the latter. It is confirmed that the parity splitting is one of the spectroscopic indications of the "isomerization" of the HCP/CPH system as expected.

[a] Y. Muramoto, H. Ishikawa, and N. Mikami, 60th Ohio State University International Symposium on Molecular Spectroscopy, WH03 (2005).
[b] M. P. Jacobson and M. S. Child, *J. Chem. Phys.* **114**, 262 (2001).