PERTURBATION FACILITATED DISPERSED FLUORESCENCE AND STIMULATED EMISSION PUMPING SPECTROSCOPIES OF HCP

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Perturbations among molecular rovibronic levels provide us with mainly two benefits. Perturbations themselves are characteristic features of structure and dynamics of molecules. We have been investigating dynamics of highly excited vibrational levels of HCP in the $\tilde{X}\ ^1\Sigma^+$ state by dispersed fluorescence (DF) and stimulated emission pumping (SEP) spectroscopies of the $\tilde{C}\ ^1A' - \tilde{X}\ ^1\Sigma^+$ transition[a]. In the case of $\tilde{X}\ ^1\Sigma^+$ HCP, its vibrational dynamics is well described by the Fermi resonance between the bend and the CP stretch modes. Based on the analysis of the Fermi resonance, we have succeeded in revealing the change in character of the bending motion in highly excited vibrational levels. In addition, perturbations enable us to explore rovibrational levels into much wider region that cannot be accessed under limits of selection rules.

Jacobson and Child showed that the Coriolis interaction becomes very strong in the highly excited levels near and the above the CPH barrier[b]. For the experimental confirmation of their prediction, the observation of the $v_{\rm CH} \neq 0$ and the $\ell'' \neq 0$ levels are necessary. However, due to the selection rules and the Franck-Condon selectivity, only the $v_{\rm CH} = 0$ and the $\ell'' = 0$ levels had been observed. In the course of our study, we have found a perturbed level in the $\tilde{C}$ state. In general, a very clear even-v_2 progression appears in the DF spectra of HCP. However, in the DF spectra measured by using the perturbed level as the intermediate both the odd- and even-v_2 levels are observed. Moreover, several $v_{\rm CH} = 1$ levels are observed in the spectra. The perturbation-facilitated DF and SEP spectroscopies are very powerful tools to exploring the highly excited vibrational levels of HCP. Details of the perturbation-facilitated DF and SEP spectroscopies are presented in the paper.

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[a] H. Ishikawa, *et al. J. Chem. Phys.* **109**, 492 (1998); H. Ishikawa, *et al. Annu. Rev. Phys. Chem.* **50**, 443 (1999).

[b] M. P. Jacobson and M. S. Child *J. Chem. Phys.* **114**, 262 (2001).