OBSERVATION OF THE "ISOMERIZATION" STATES OF HCP: "ISOMERIZATION" STATE VS. "NORMAL-MODE-TYPE" STATE

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Among various kinds of bond-breaking isomerization reactions, the isomerization of a triatomic monohydride, HAB, is the simplest one: HAB $\longleftrightarrow$ ABH. This system is most fundamental for both experimental and theoretical studies. On the basis of a time-*independent* picture, the isomerization process can be characterized by analysis of rotation-vibration eigenstates in the high energy region. In this study, highly excited vibrational states of HCP $\widetilde{X}\ ^1\Sigma^+$ were investigated by dispersed fluorescence and stimulated emission pumping spectroscopies. As a result, two distinct families of vibrational states were observed in the $13400 - 17500$ cm^{-1} energy region.[a] One of them is well characterized by polyads involving the bending (ν_2) and CP stretching (ν_3) vibrations. This 1:2 polyad structure is very robust and valid in the lower energy region. This family can be referred to as "normal-mode-type" states. On the other hand, vibrational levels of the other family appear suddenly at 13400 cm^{-1}. The rotational constants of these levels are much larger than those of the "normal-mode-type" states. Moreover, these levels exhibit strong anharmonicity. We have assigned this family of vibrational levels as delocalized "isomerization" states whose existence was predicted by a recent theoretical study.[b] This assignment is based on the good agreement between the present spectroscopic observations and the theoretical predictions. Thus, "isomerization" states have been identified *experimentally* for the first time.

[a] H. Ishikawa *et al.*, J. Chem. Phys. **106**, 2980 (1997).
[b] S. C. Farantos *et al.*, J. Chem. Phys. **104**, 10055 (1996).