SPECTROSCOPIC INVESTIGATION OF THE GENERATION OF “ISOMERIZATION” STATES OF HCP: EIGENVECTOR ANALYSIS OF THE BEND– CP STRETCH POLYAD

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Highly excited vibrational levels of HCP, in which bend–CP stretch polyads are the most fundamental vibrational structure, have been investigated by dispersed fluorescence and stimulated emission pumping spectroscopies. HCP $\longleftrightarrow$ CPH system is a prototype of the isomerization reaction of triatomic monohydride, HAB, that is the most simplest bond-breaking isomerization. Stimulated by the experimental observation of vibrational levels with rotational constants (B-values) 5-10% larger than other observed levels,[a] Schinke and coworkers noticed that these large-B levels were characterized by atypical nodal structures indicative of large amplitude motion along the minimum energy HCP $\longleftrightarrow$ CPH isomerization path.[b] Vibrational levels having such nodal structures can be referred to as “isomerization” levels. In order to elucidate the generation of the “isomerization” states, a global least squares fit, based on a traditional spectroscopic (algebraic) effective Hamiltonian polyad model, was carried out. An analysis of eigenvectors of the Hamiltonian matrix shows that all of the observed “isomerization” states belong to polyads and that the eigenvectors of this $\mathbf{H}^{\mathrm{eff}}$ model have the qualitatively distinct nodal structure first noticed by Schinke and coworkers. The “isomerization” states are not indicative of a breakdown of the polyad model; rather they are a natural consequence of this traditional spectroscopic model.

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[a] H. Ishikawa *et al.*, J. Chem. Phys. **105**, 7383 (1996).

[b] C. Beck *et al.*, J. Chem. Phys. **107**, 9818 (1997).