HIGHLY EXCITED VIBRATIONAL STATES IN HCP: TRANSITION FROM NORMAL-MODE BENDING TO ISOMERIZATION MOTION

R. SCHINKE, H.-M. KELLER, and C. BECK, *MPI für Strömungsforschung, D-37073 Göttingen, Germany*;
S. C. FARANTOS, *Department of Chemistry, University of Crete, Iraklion 711 10, Crete, Greece*.

We present the results of extensive bound-state calculations for HCP in its electronic ground state. The potential energy surface (PES) has been constructed with *ab initio* electronic structure calculations (MRCI) and the bound-state calculations have been performed using a contraction-truncation scheme. The dimension of the final Hamilton matrix is about 9000. All eigenvalues and -functions up to the 700th level have been carefully examined and assigned if possible. Due to a strong 1:2 anharmonic resonance between the CP stretching (ν_3) and the HCP bending (ν_2) mode the spectrum consists of polyads $(0, P, 0)$, $(0, P-2, 1)$, $\ldots (0, 0, P/2)$. This polyad structure is astonishingly intact until $P = 26$, when some new features suddenly appear in the spectrum. While all bending wave functions below $P = 26$ are restricted in the angular coordinate, with $P = 26$ new states appear, which clearly follow the isomerization path from H–CP to CP–H. Periodic classical trajectories successfully predict the general behaviour of the quantum mechanical wave functions and provide qualitative explanations. The two different types of states excited in the angular coordinate have significantly different B rotational constants. At the conference we will discuss in detail the 'evolution' of vibrational states from the bottom of the potential well all the way to isomerization. Possible relations to other theories as well as new experimental data of Field, Ishikawa and coworkers will be discussed.