FINGERPRINTS OF SADDLE-NODE BIFURCATION IN SPECTRUM AND DISSOCIATION OF HOCl

S. GREBENSHCHIKOV, J. WEISS, J. HAUSCHILDT, and R. SCHINKE, *MPI für Strömungsforschung Bunsenstraße 10, D-37073 Göttingen, Germany*.

We present a detailed analysis of the bound-state spectrum of HOCl (hypoclorous acid) in the ground electronic state. Exact quantum mechanical calculations (filter diagonalization) are performed employing an *ab initio* potential energy surface. The wave functions of all bound states up to the HO+Cl dissociation threshold are visually inspected in order to assign the spectrum in a rigorous way and to elucidate how the spectrum develops with energy. The dominant features are (1) a 2:1 anharmonic resonance between the bending mode and the OCl stretching mode, which is gradually tuned in as the energy increases, and (2) a saddle-node bifurcation, i.e., the sudden birth of a new family of states, caused by the resonance. We carefuly investigate the bifurcation in terms of the structure of the classical phase space (periodic orbits, continuation/bifurcation diagram). To this end, a two-dimensional adiabatic model is developed, which quantitatively reproduces the exact three-dimensional results. The classical phase space of this dynamical model can be completely mapped using the Poincare surfaces of section. It is shown that the saddle-node bifurcation is associated with splitting of the phase space into a set of zones divided by separatrices. Close correspondence is established between the finest details of the quantum wave functions and the topology of periodic orbits (stable and unstable). Of special interest are the quantum states localized on the classical separatrix. It is also discussed how the spectrum of bound states persists into the continuum and how the various types of quantum mechanical continuum wave functions affect the state-specific dissociation rates.