

## SPECTROSCOPIC SIGNATURES OF BOND BREAKING INTERNAL ROTATION IN HCP

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Changes in the eigenvalue structure in the vicinity of a saddle-point on the potential energy surface are illustrated by semi-classical and quantum mechanical studies on model potential energy surfaces for HCP. The following points are addressed:

- (a) The connection between classical periodic orbits and Fermi resonance polyads, and the breakdown of the polyad model as the bending frequency tunes out of 2:1 resonance with the CP stretch<sup>a</sup>.
- (b) The observation of 'quantum monodromy' in the underlying spherical pendulum model, and its influence of the values of the spectroscopic vibration-rotation parameters, as the H atom approaches the P end of the molecule<sup>b</sup>.
- (c) A possible formulation of the spectroscopic theory at the saddle point in terms of spherical pendulum eigenstates, and the nature of the relevant matrix elements<sup>c</sup>.

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<sup>a</sup>M. P. Jacobson and M. S. Child, *J. Chem. Phys.*, **114**, 250 (2001)

<sup>b</sup>M. P. Jacobson and M. S. Child, *J. Chem. Phys.*, **114**, 262 (2001).

<sup>c</sup>M. S. Child, M. P. Jacobson and C. D. Cooper, *J. Phys. Chem.*, **105**, 8446 (2001).