SPECTROSCOPIC SIGNATURES OF BOND BREAKING INTERNAL ROTATION IN HCP

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Changes in the eigenvalue structure in the vicinty of a saddle-point on the potential energy suface 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 resonace polyads, and the breakdown of the polyad model as the bending frequency tunes out of 2:1 resonance with the CP stretch[a].
(b) The observation of 'quantum mondromy' 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[b].
(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[c].

[a] M. P. Jacbson and M. S. Child, J. Chem. Phys., **114,** 250 (2001)
[b] M. P. Jacobson and M. S. Child, J. Chem. Phys., **114**, 262 (2001).
[c] M. S. Child, M. P. Jacobson and C. D. Cooper, J. Phys. Chem., **105**, 8446 (2001).