IMPOSING A MECHANICAL MODEL ON AN IRREGULAR ELECTRONIC STATE: THE $A\,^1\Sigma^+$ STATE OF AgH

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Almost since its first observation in 1925, it has been clear that the $A\,^1\Sigma^+$ state of AgH is irregular, in that its level energy patterns and isotope effects resisted conventional systematic description.[a] A proposal by Gerö and Schmid[b] that this irregular behaviour was due to perturbation by the nearby $B\,^1\Sigma^+$ state was disputed by Learner,[c] who argued that the problem was due to an avoided crossing which gives rise to a "shelf" on the outer part of the potential well. Recent *ab initio* studies by Witek *et al.*[d,e] suggest that the irregular behaviour is actually due to two avoided crossings, and that the resulting effective potential has what we call "anti-shelf" behaviour which is qualitatively different than that described by Learner.[c] The present paper describes our efforts to determine an accurate effective potential function and delineate the degree and nature of residual non-mechanical behaviour for this state from a combined-isotopologue analysis of all available experimental data.

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[d] H.A. Witek, T. Nakijima and K. Hirao, *J. Chem. Phys.* **113**, 8015 (2000).
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