Molecular Rydberg Dynamics

Colin Batchelor

Merton College

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Abstract

A simple theory relating the dynamics of electrons to the long-range properties of the molecular ionic core is developed for asymmetric top molecules in general and water in particular. It is combined with the molecular version of multichannel quantum defect theory developed by Fano and Jungen and applied to the resonance-enhanced multiphoton ionization spectra of Child and Glab (M. S. Child and W. G. Glab, *J. Chem. Phys.*, 2001, **112**, 3754–3765), the mass-analysed threshold ionization spectra of Dickinson *et al.* (H. Dickinson, S. R. Mackenzie and T. P. Softley, *Phys. Chem. Chem. Phys.*, 2000, **2**, 4669–4675) and the as-yet unpublished work of Glab on the photoelectron branching ratios of the nd and nf Rydberg lines of the water molecule. The effect of resonances between electronic and rotational motion in Rydberg molecules is investigated using multichannel quantum defect theory with special reference to the time-resolved wave packet experiments of Smith *et al.* (R. A. L. Smith, J. R. R. Verlet, E. D. Boléat, V. G. Stavros and H. H. Fielding, *Faraday Discuss.*, 2000, **115**, 63–70).