

OBSERVATION OF THE  $5^1\Sigma_u^+$  and  $5^1\Pi_u$  STATES OF  $\text{Rb}_2$  BY POLARISATION LABELLING SPECTROSCOPY <sup>a</sup>

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Two-colour polarization labeling experiments have been used to explore the excitation spectrum of the rubidium dimer in the region 25500 - 27000  $\text{cm}^{-1}$ , aiming to establish the symmetry of excited states observed by Han and Heaven<sup>b</sup> in earlier work. The spectra we recorded in fact probe quite different electronic states; we identify them from *ab initio* calculations as the  $5^1\Sigma_u^+$  and  $5^1\Pi_u$  states, dissociating to  $\text{Rb } 5s + \text{Rb } 5d$  atoms. The home-made pulsed laser used to label levels in the electronic ground state, with nominal linewidth of 0.3  $\text{cm}^{-1}$ , is not sufficiently selective for this heavy-alkali species. The spectra are a tangled confusion of short and rather irregular progressions of P,R doublets and/or Q lines. We have had to use cross-correlation techniques to identify transitions seen in different spectra that share a common ground state level, to establish assignments. Analysis confirms unusual vibrational patterns in the lowest vibrational levels, from avoided crossings with ion pair states.

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<sup>b</sup>J. Han, M. Heaven, *J. Mol. Spectrosc.* 268 37-41 (2011)