EVIDENCE OF PERTURBATIONS ON THE S_1 SURFACE OF ACETYLENE FROM PATTERNS IN STIMULATED EMISSION PUMPING SPECTRA

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Stimulated Emission Pumping (SEP) spectra from the 3^4 level of S_1 acetylene to the $N_B = 10$ polyad of S_0 contain evidence of an unexpected interference effect. S_0 intrapolyad intensity distributions are as a rule governed solely by the fractionation of the (single) bright state. However, the intensity distribution in the SEP spectrum observed from 3^4 deviates from the expected pattern. Reduced dimension DVR calculations on the S_1 surface predict a three-state interaction involving one of the S_1 interloper bands. According to the calculation, this cis interloper state engenders an indirect coupling between the $trans$ $2^1 3^1 6^2$ and 3^4 zero order states, causing the eigenstates to lie substantially farther apart than one might expect, and lending intensity to the cis $3^1 6^1$ interloper band that appears between them. These predictions agree quite well with the experimental observations. The intensity distribution in the SEP spectrum observed from 3^4 seems to contain an interfering combination of the bright state patterns seen in the $2^1 3^2$ and the $3^2 B^2$ spectra. This type of indirect effect can yield much information about state mixing, and is particularly interesting in this case since its effects on the level structure cannot reasonably be accounted for by effective Hamiltonian models that rely solely on polyads.