HIGHLY PREDISSOCIATIVE LEVELS OF THE CH3S A 2A_1 STATE DETERMINED WITH DEGENERATE FOURWAVE MIXING

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We have determined highly predissociative levels of the A^2A_1 state of CH₃S in a supersonic jet with degenerate four-wave mixing (DFWM) technique. The highest level observed lies 4265 cm⁻¹ above the zero-point-energy level, much greater than corresponding values of 2979 cm⁻¹ observed by fluorescence depletion spectroscopy and 1490 cm⁻¹ by laser-induced fluorescence. Unlike in fluorescence spectra, relative intensities of lines in DFWM spectra closely reflect their Franck-Condon factors; vibronic assignments are thus more straightforward. A new progression involving excitation of the CH₃ stretching mode is identified, and several lines in the range 1290-1410 cm⁻¹ above the origin may be assigned to the CH₃ deformation (ν_5) and the first overtone of CH₃ rocking ($2\nu_6$) modes. Observed vibrational wave numbers are consistent with theoretical predictions.