HIGHLY PREDISSOCIATIVE LEVELS OF THE CH_3S $A\ ^2A_1$ STATE DETERMINED WITH DEGENERATE FOUR-WAVE MIXING

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We have determined highly predissociative levels of the $A\ ^2A_1$ state of CH_3S 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 CH_3 stretching mode is identified, and several lines in the range 1290-1410 cm^{-1} above the origin may be assigned to the CH_3 deformation (ν_5) and the first overtone of CH_3 rocking ($2\nu_6$) modes. Observed vibrational wave numbers are consistent with theoretical predictions.