ROTATIONAL ASSIGNMENT OF THE FRACTIONATED C=O STRETCHING FUNDAMENTAL OF CH_3CHO

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In spite of the fact that the C=O stretch is one of only 15 fundamentals in the relatively light acetaldehyde molecule (CH_3CHO), its high-resolution spectrum has completely resisted two previous attempts at assignment (one in the 1980's involving a room-temperature Fourier transform spectrum, the other in the 1990's involving a supersonic-jet-cooled laser spectrum). After the second attempt, the cause of the difficulty was attributed to the fact that the bright C=O stretch was heavily mixed with dark internal-rotation bath states, so that the intensity of each rotational line was distributed (fractionated) among a random small number of randomly displaced lines. (Such mixings had been postulated earlier, of course, by investigators who studied the strong enhancement effect of methyl rotors on the rate of internal vibrational energy redistribution.) The two new features of the present study are: (i) a jet-cooled Fourier transform spectrum (no spectral coverage gaps to hinder the search for combination differences), and (ii) the use of the RITZ program suite for assigning spectra and determining upper state energy levels based on systematic searches for a previously catalogued set of ground-state combination differences. Preliminary results available at the time of abstract preparation suggest that the RITZ procedure was successful in locating A and E rotational energy levels up to about $J = 13$ in the C=O fundamental. Each bright rotational level seems to be fractionated into small clusters (with from 2 to 8 components) of close-lying levels. Work at the present stage is focused on trying to develop empirical validation algorithms and associated visual displays for the levels found, since the possibility of accidental combination difference matches (equivalent to noise in the search procedure) is always present, and since the usual method of testing assignments by fitting them to eigenvalues of a Hamiltonian matrix is not available for these heavily mixed states.