

HOT BANDS IN JET-COOLED AND AMBIENT TEMPERATURE SPECTRA OF CHLOROMETHYLENE

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Rotationally resolved spectra of several bands lying to the red of the origin of the $\tilde{A}^1A'' - \tilde{X}^1A'$ band system of chloromethylene, HCCI, were recorded by laser absorption spectroscopy in ambient temperature and jet-cooled samples. The radical was made by excimer laser photolysis of dibromochloromethane, diluted in inert gas, at 193nm. The jet-cooled sample showed efficient rotational, but less vibrational cooling. Analysis showed the observed bands originate in the $(v_1, v_2, v_3) = (010)$, (001) and (011) vibrational levels of the ground electronic state of the radical, while the upper state levels involved were (000) , (010) , (001) , and (011) . Vibrational energies and rotational constants describing the rotational levels in the lower state vibrational levels were determined by fitting to combination differences. The analysis also resulted in a re-evaluation of the C–Cl stretching frequency in the excited state and we find $E'_{001} = 13206.57 \text{ cm}^{-1}$ or 926.17 cm^{-1} above the $\tilde{A}^1A''(000)$ rotationless level for HC^{35}Cl . Scaled ab initio potential energy surfaces for the \tilde{A} and \tilde{X} states were used to compute the transition moment surface and thereby the relative intensities of different vibronic transitions, providing additional support for the assignments and permitting the prediction of the shorter wavelength spectrum. All observed upper state levels showed some degree of perturbation in their rotational energy levels, particularly in $K_a = 1$, presumably due to coupling with near-resonant vibrationally excited levels of the ground electronic state. Transitions originating in the low-lying \tilde{a}^3A'' were also predicted occur in the same wavelength region, but could not be identified in the spectra.

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