1.27 μm O_2 CONTINUUM ABSORPTION IN O_2/CO_2 MIXTURES

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The collision-induced, near-infrared O_2 continuum band overlapping the weak $a^1\Delta_g - X^3\Sigma_g^-$, v = 0 - 0, 1.27 μm discrete band of O_2 has been investigated in O_2/CO_2 mixtures at room temperature (T = 296 K) for total densities from 1.8 to 9.3 times that of an ideal gas under standard conditions (T = 273.15 K and P = 101.325 kPa), i.e., from 1.8 to 9.3 amagats. Absorption spectra were recorded at 0.5 cm^{-1} resolution using a Fourier-transform spectrometer and an 84-m pathlength. A least-squares analysis of the integrated band strength, $S_{total} = S_{O2}\rho_{O2} + S_{O2-O2}{\rho_{O2}}^2 + S_{O2-CO2}\rho_{O2}\rho_{CO2}$, as a function of the carbon dioxide density, ρ_{CO_2}, and the oxygen density, ρ_{O_2}, yields $S_{O_2-CO_2} = 2.95(40) \times 10^{-43}$ cm^{-2}(molecule/cm^3)$^{-2}$ [i.e., $2.13(29) \times 10^{-4}$ cm^{-2} amagat^{-2}]. The S_{O2-CO2} coefficient is approximately three times greater than the corresponding S_{O2-N2} coefficient determined from studies of O_2/N_2 mixtures, illustrating the efficiency of large electric multipolar moments in inducing continuum absorption in the 1.27 μm band of O_2. A similar large enhancement of the O_2 continuum absorption by CO_2 is observed for the v = 1 - 0, O_2 vibrational fundamental. The results support the calculations by Brown and Tipping, which demonstrate the importance of water, with its large electric dipole moment, in enhancing the collision-induced absorption bands of O_2 and N_2 in the atmosphere. We suggest that the apparent inability of radiative-transfer models to accurately account for the increased atmospheric absorption present when water-vapor levels increase may be due in part to the neglect of the intensity enhancement of a number of continuum bands and of the far wings of discrete bands by water-vapor collisions.