

DENSITY DEPENDENCE OF SPECTRAL DETAIL IN PRESSURIZED AND SUPERCRITICAL CARBON DIOXIDE ELECTRONIC ABSORPTION SPECTRA

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The density dependence of pressurized and supercritical carbon dioxide (CO₂) electronic absorption spectra was explored by vacuum ultraviolet (VUV) spectroscopy over the wavelength range 1455-2000 Å. The peak energy position of the lowest absorption band of gaseous CO₂ does not change upon pressurizing up to and beyond the thermodynamic critical point (137 bar, 308 K). Upon increase of density, the known diffuse vibrational structure inherent to the VUV absorption spectrum of gaseous CO₂ gradually diminishes in magnitude and nearly disappears upon reaching a density of 0.767 g cm⁻³. This loss of spectral detail cannot be explained solely by collisional broadening and/or dimerization. We suggest that perturbation of the monomer potential energy surfaces belonging to multiple upper electronic states leads to increased coupling between binding and dissociative states. This perturbation is caused by the near proximity of CO₂ molecules at high densities and a variety of orientations without the need for equilibrated dimers, and in turn gives rise to the observed spectral changes. Based on a high-quality CO₂ dimer potential energy surface, we estimate a critical radius of 4.1 +/- 0.2 Å between molecules necessary to cause such perturbations.