

ULTRAVIOLET SPECTROSCOPY OF SUBCRITICAL AND SUPERCRITICAL METHANOL

IRENEUSZ JANIK, *Radiation Laboratory, University of Notre Dame, Notre Dame, IN, USA*; TIMOTHY W MARIN, *Physical Science, Benedictine University, Lisle, IL, USA*.

Measuring far UV light transmission through thin fluid films, methanol's absorption spectra were recorded between 150 and 220 nm (8.27-5.63 eV). Spectral changes were monitored in the function of temperature (from ambient to supercritical conditions) and pressure (at 250°C i.e., above the supercritical point). The room temperature spectrum peak is shifted red by 4.5 nm from the previously reported position obtained by the same technique, yet agrees well with the position recorded by the attenuated total reflection (ATR) method. Unlike in water, the neat methanol spectrum shows no apparent red tail, which contradicts previous findings based on ATR studies. Upon an increase in temperature, the edge of the spectrum progressively shifts red. Still, unlike in water, this is not a symmetrical shift of the band as the lower part of the band shifts almost twice as much as the upper one, and the apparent peak position progressively shifts blue by an overall 0.13 eV upon reaching 250°C. At this temperature, a gradual decrease of pressure from 150 to 85 bar results in continuous narrowing and red shifting of the apparent band to 7.8eV, accompanied by a steady growth of an additional broad continuum band at 6.7eV. Further decrease of pressure to 14.5 bar leads to the full emergence of the low-density spectrum of supercritical MeOH. This spectrum resembles the methanol monomer, with characteristic 1st weak absorption band at 6.7eV due to the promotion on oxygen from 2p_z (HOMO) to 3s Rydberg orbital (acquiring antibonding character along the OH vibrational coordinate) and 2nd structured band at 7.84eV due to transition between a'' and the 3p Rydberg orbitals. An increase in density depresses the intensity of the first band. It has a dramatic effect on the second absorption band, in which the sharp vibrational structure gradually diminishes in magnitude and disappears above 0.1 g cm⁻³. This loss of detail cannot be explained solely by collisional broadening and/or dimerization. Still, it may suggest a gradual shift of the character of a transition from Rydberg to exciton.