



The electronically excited and ionic states of sulphur dioxide; an *ab initio* molecular orbital CI study and comparison with spectral data

M. H. Palmer, D. A. Shaw and M. F. Guest

University of Edinburgh, School of Chemistry, Joseph Black Building, West Mains Road, Edinburgh, Scotland EH9 3JJ

The electronically excited singlet and triplet valence, and Rydberg states, in the excitation energy range 1-16eV, have been determined, by configuration interaction methods. Theoretical values for the excitation energies and oscillator strengths for a range of Rydberg states converging on the first six IPs have been calculated. The sequence of ionic states have been redetermined and the results support the recent study by Li et al (2004), that the sequence of IPs should be reordered to $2A1 < 2B2 < 2A2 \ll 2B1 < 2A1 < 2B2 \ll 2A1$. Several adiabatic excited and ionized state equilibrium structures, were determined using CCSD(T) and CI methods. The gap in the published experimental VUV spectrum between 992 and 1078Å has been completed using new data, and by re-evaluation of the Price and Simpson (1938) photographic data. A number of new Rydberg states in both the gap and nearby regions have been identified. The experimental assignment of the electronic spectrum is critically assessed in some detail. Assignment of the lower singlet and triplet manifolds and comparison of the theoretical intensity envelope with the VUV absorption and photoionization spectra has been made.