A NEW COLLISION-INDUCED TRANSITION IN THE VACUUM ULTRAVIOLET SPECTRUM OF O_2

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The collision-induced photoabsorption spectrum of O_2, pressurised by He, is presented in the 1180–1340 Å-region. In addition to the collision-broadened wings of the dipole-allowed mixed Rydberg-valence transitions, we have found a series of diffuse peaks whose intensities depend linearly on the foreign-gas pressure. The observed peaks have been assigned as the (1,0)–(5,0) bands of the $\Delta\Lambda = 2$ collision-induced $3p\pi_u\ ^3\Delta_u \leftarrow X\ ^3\Sigma_g^-$ Rydberg transition, partly on the basis of comparisons with the photoabsorption spectrum of metastable $O_2(^1\Delta_g)$.[a] The relative regularity of the spacings between the observed peaks supports the conclusions of Buenker and Peyerimhoff,[b] in an *ab initio* study, that there is little interaction between the $3p\pi_u\ ^3\Delta_u$ Rydberg state and the $A'\ ^3\Delta_u$ valence state, in contrast to the situation for the corresponding states of $^3\Sigma_u^-$ and $^3\Pi_u$ symmetries. Although the complexity of this spectral region and the diffuseness of the bands precludes any detailed line-profile analyses, it is clear that the integrated intensity of the $3p\pi_u\ ^3\Delta_u \leftarrow X\ ^3\Sigma_g^-$ Rydberg system exceeds that of the collision-induced $A'\ ^3\Delta_u \leftarrow X\ ^3\Sigma_g^-$ valence system[c] by at least an order of magnitude. Possible sources for this intensity are discussed.

[a] P. C. Hill, Ph.D. Thesis, Australian National University, (1991).
[b] R. J. Buenker and S. D. Peyerimhoff, Chem. Phys. Lett. **34**, 225 (1975).
[c] V. I. Dianov-Klokov, Opt. Spectrosc. **21**, 233 (1996).