PARTIAL PHOTODISSOCIATION CROSS SECTIONS FOR O_2 IN THE 1205 Å REGION

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Measurements of the photoabsorption cross section of O_2 and the partial photodissociation cross section yielding O(^1D) have been made over the wavelength region of the Tanaka second band, $(1,0)$ $E\,^3\Sigma_u^- - X\,^3\Sigma_g^-$.[a] Photodissociation in this wavelength region predominantly results in the atomic species O(^1D) + O(^3P), from predissociation via the $B\,^3\Sigma_u^-$ electronic state.[b]

We have found a residual component of the cross section which does not yield O(^1D) and therefore arises from a different path to dissociation. The origin of this component is inferred from a coupled-channel Schrödinger equation (CSE) model, involving a manifold of electronic states and interactions previously used to explain experimental predissociation linewidths of the $np\pi_u\,^3\Sigma_u^+$ Rydberg states.[c] The CSE calculations give results consistent with the measured branching ratio into the O(^1D) and O(^3P) dissociation channels. The residual cross section is identified as arising from the $(4,0)$ $3p\pi_u\,D\,^3\Sigma_u^+ - X\,^3\Sigma_g^-$ band.[d] This band is known to interfere strongly with the second band.[e]

We conclude that, whereas the $np\pi_u\,^3\Sigma_u^-$ Rydberg states dissociate entirely into O(^1D) + O(^3P) due to a strong Rydberg-valence interaction, the $3p\pi_u\,^3\Sigma_u^+$ Rydberg state dissociates via two pathways, involving direct and indirect predissociation. The direct predissociation occurs from Rydberg-valence mixing of the $^3\Sigma_u^+$ states, with the electrostatic interaction an order of magnitude smaller than for the $^3\Sigma_u^-$ states, resulting in only O(^3P) products. Indirect predissociation arises from a spin-orbit interaction between the $3p\pi_u$ Rydberg $^3\Sigma_u^+$ and $^3\Sigma_u^-$ states, yielding O(^1D). This interaction also provides the intensity of the $(4,0) D\,^3\Sigma_u^+ - X\,^3\Sigma_g^-$ band.

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[a] The mixed Rydberg-valence E electronic state is also labelled B' by some authors.
[b] L. C. Lee, T. G. Slanger, G. Black, and R. L. Sharpless, J. Chem. Phys. **67**, 5602 (1977).
[c] S. S. Banerjee, Ph.D. Thesis, The Australian National University (1996).
[d] The D electronic state also labelled β by some authors.
[e] B. R. Lewis, S. T. Gibson, M. Emami, and J. H. Carver, J. Quant. Spectrosc. Radiat. Transfer **40**, 469 (1988).