PARTIAL PHOTODISSOCIATION CROSS SECTIONS FOR O₂ IN THE 1205 Å REGION

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Measurements of the photoabsorption cross section of O₂ and the partial photodissociation cross section yielding O(¹D) have been made over the wavelength region of the Tanaka second band, (1,0) $E^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$. Photodissociation in this wavelength region predominantly results in the atomic species O(¹D) + O(²P), from predissociation via the $B^3\Sigma_u^-$ electronic state. 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 line widths of the $np\pi_u^3\Sigma_g^-$ Rydberg states. The CSE calculations give results consistent with the measured branching ratio into the O(¹D) and O(²P) dissociation channels. The residual cross section is identified as arising from the $(4,0) 3p\pi_u^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ band. This band is known to interfere strongly with the second band.

We conclude that, whereas the $np\pi_u^3\Sigma_g^-$ Rydberg states dissociate entirely into O(¹D) + O(²P) 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 $3\Sigma_g^-$ states, resulting in only O(²P) products. Indirect predissociation arises from a spin-orbit interaction between the $3p\pi_u$ Rydberg $3\Sigma_u^+$ and $3\Sigma_g^+$ states, yielding O(¹D). This interaction also provides the intensity of the $(4,0)D^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ band.

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*The mixed Rydberg-valence E electronic state is also labelled $B'$ by some authors.*


*The D electronic state also labelled $\beta$ by some authors.*