REMPI AND IMAGING STUDIES OF SINGLET O_2 FOLLOWING SPIN-FORBIDDEN PHOTODISSOCIATION OF OZONE

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Ozone photodissociation in the Hartley (200-300 nm) and Huggins (310-370 nm) bands has been the focus of numerous studies due to its critical role in atmospheric chemistry. While Hartley band dissociation occurs primarily through two spin-allowed dissociation channels, three additional spin-forbidden channels have previously been observed following dissociation in the Huggins band. We report 1-D and 2-D REMPI spectra and velocity-mapped ion images of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ fragments following spin-forbidden dissociation in the Huggins band. We have previously observed a preference for the formation of even rotational states of $O_2(a^1\Delta_g)$ arising from Hartley band dissociation due to a Λ-doublet propensity. In the Huggins band, however, odd rotational states are enhanced in the REMPI spectrum, which we attribute to greater coupling between the initial excited state of O_3 and $^3A''$ states producing odd rotational states of $O_2(a^1\Delta_g)$, than between the initial excited state and $^3A'$ states producing even rotational states. Ion image angular distributions of the $O_2(a^1\Delta_g)$ fragment in odd and even rotational states showed significant differences following Hartley band dissociation, supporting the Λ-doublet propensity model, but are indistinguishable following Huggins band dissociations. This supports a preference for the A$'$ Λ-doublet and even rotational states following O_3 transitions from the B state to $^3A'$ states and a preference for the A'' Λ-doublet and odd rotational states following O_3 transitions from the B state to the $^3A''$ states, but indicates that in the Huggins band, the A$''$ Λ-doublet does not originate from a warmer distribution of parent molecules as seen in the Hartley band. 2D-REMPI allows simultaneous measurements of the rotational distributions for v=0-2 of the $b^1\Sigma_g^+$ state as well as v=0 of the $a^1\Delta_g$ state. The relative signal in v=0-2 of the $b^1\Sigma_g^+$ can provide information about the vibrational distribution, and rotational state distributions of each vibrational state can be fit individually. Spectra indicate a broad rotational distribution of the $O_2(a^1\Delta_g)$ fragment and a narrow distribution of the $O_2(b^1\Sigma_g^+)$ fragment. While determination of the $O_2(a^1\Delta_g)$ rotational distribution is limited due to the highly perturbed resonant state accessed in the REMPI scheme, a broad distribution is additionally supported by the multimodality of the radial distributions in the ion images.