Laboratory Investigations into the Temperature Dependence of the Collisional Removal of Oxygen in the Herzberg States

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Emission from the O_2 Herzberg states ($A^3\Sigma_u^+$, $A'^3\Delta_u$, $c^1\Sigma_u^-$) is an important component of the ultraviolet nightglow on earth and Venus. Collisional processes involving these excited electronic states affect the altitude distribution, intensity, and temporal evolution of the nightglow. The oxygen emission comes from an atmospheric layer near 95 km where the temperature varies between 150 and 250 K. Unfortunately, most laboratory collisional energy transfer studies are performed at room temperature.[1,2] At SRI, we are in the midst of a laboratory program to measure collisional removal rate constants for the important atmospheric colliders at the temperature of the emitting O_2 layer.

We use a two-laser state-specific multiphoton ionization method to study these states. The first laser pulse excites O_2 to a specific level in one of the states and the second time-delayed laser pulse ionizes from either the excited level or a neighboring level. Thus far, we have measured the temperature dependence of the collisional removal of O_2 in the $v = 9$ level of the $A^3\Sigma_u^+$ state[3] and in the $v = 9$ and 10 levels of the $c^1\Sigma_u^-$ state. For the $A^3\Sigma_u^+$ state, the removal rate constant with O_2 collider is independent of temperature between room temperature and 200 K and increases by 50% going from 200 K to 150 K.[3] For the colliders N_2 and CO_2 the rate constant is independent of temperature between room temperature and 150 and 225 K, respectively. Unlike the trend for $O_2(A^3\Sigma_u^+, v = 9)$, the rate constants for the $v = 9$ level of the $c^1\Sigma_u^-$ state decrease as temperature decreases by a factor of five and three at 125 K when compared to the values at room temperature for the colliders O_2 and N_2, respectively. Preliminary results for the $v = 10$ level indicate that the removal rate constant with O_2 is five times faster than that for the $v = 9$ level and that about 80% of the removal collisions result in vibrational cascade to the $v = 9$ level of the $c^1\Sigma_u^-$ state. This significant difference in the temperature dependence of the collisional removal between the $A^3\Sigma_u^+$ state and $c^1\Sigma_u^-$ results shows the importance of examining each state for all atmospherically relevant colliders.

References:

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