Experimental and theoretical study of the quenching of electronically-excited oxygen with the rare gases

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At moderate collision energies, collisions between electronically-excited oxygen atoms in their lowest-lying metastable O(^{1}D) state and rare gas (Rg) atoms can lead to O(^{3}P) formation via three intersections of adiabatic surfaces: the RgO($^1\Sigma^+$, $^1\Pi$) surfaces have been shown to intersect the two RgO ($^3\Sigma^-$ and $^3\Pi$) surfaces, which adiabatically correlate to O(^{3}P) + Rg(^{1}S), at three points, namely ($^1\Sigma^+/^3\Sigma^-$), ($^1\Sigma^+/^3\Pi$), and ($^1\Pi/^3\Sigma^-$).

From O(^{1}D) + Rg(^{1}S) the first two crossing points are accessed without an adiabatic barrier on the attractive RgO($^1\Sigma^{+-}$) surface, whereas the third, lying energetically above the O(^{1}D) + Rg(^{1}S) asymptote, is accessed along the repulsive ($^1\Pi$) surface and is expected to contribute a positive *T*-dependence to the overall O(^{1}D) quenching rate constant. [1]

From a theoretical perspective, Rg – O(^{1}D) provides a *relatively* simple series to study the character of molecular adiabatic states in the presence of various degrees of spin-orbit coupling due to the progression in reduced mass, and relative energy and extent of overlap of the above surface intersections. From a practical perspective, Rg-O(^{1}D) to Rg-O(^{3}P) quenching rate constants with rare gases are required for modeling oxygen-based or oxygen-seeded plasmas, and certain planetary atmospheres in order to establish the O(^{1}D) quasi-steady-state concentrations. The opposite process – triplet-to-singlet crossing – has been applied to rationalize very long distance migration (> 100 Angstrom) of O atoms in cold Xe and Kr matrices. [2]

We have performed a series of experiments to very accurately determine the magnitude and temperature dependence of rate constants, *k*, of Xe, Kr, Ar, Ne + O(^{1}D) over an extended moderate temperature range and provide and a new upper limit for the rate constant of O(^{1}D) + He below 900 K. Notably, *k* (Xe + O(^{1}D)) is the only one of the series to exhibit significant positive temperature dependence over the temperature range covered.

The rate constants determinations were carried out in a specially-designed temperature-graded reaction cell with parallel simultaneous detection of O(^{1}D) at different sections (temperatures) of the reaction chamber using a series of photomultiplier tubes. The O(^{1}D) decays were monitored in real-time using the novel chemiluminescence method employing the reaction O(^{1}D) + $C_2F_4 \rightarrow CF_2(^3B_1)$ + products.

The results are compared to our theorectical *k* predictions based on quantum statistical analysis combined with spin-orbit coupling calculations.

References

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