THE ASYMPTOTIC REGIONS OF THE POTENTIAL ENERGY SURFACES RELEVANT FOR THE $O(^3P)$ + $O_2(X^3\Sigma_g^-) \rightleftarrows O_3$, $O(^3P)$ + $SO(X^3\Sigma^-) \rightleftarrows SO_2$ REACTIONS

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The photodissociation dynamics and formation of sulfur dioxide and ozone, important trace species in the atmosphere, have been subjected to many studies over the past decades. The long range potential energy functions including spin-orbit couplings for all states correlating with the lowest asymptote of the reactions $O(^3P)$ + X (X stays for $O_2(X^3\Sigma_g^-)$ or $SO(X^3\Sigma^-)$ have been calculated using highly correlated electronic wavefunctions[a].

While the cluster of Σ states lie above the Π states for linear ozone, it is more complicated for linear SO_2. The two orientations SO...O and O...SO lead to different reaction profiles. For SO...O orientation, the potential energy surfaces (PES's) resemble to O...O_2 approach, the Σ states lie above the Π states for large $R_{(SO...O)}$ distances. In the O...SO approach, Π states lie above the Σ states at the asymptote and crossings occur at small distances.

For bent geometries, the Π states split into Renner-Teller components with A' and A" symmetry, respectively. For ozone, the different Π spin multiplets cross for valence angles around 160° and the ^{1}A' component leading to X^1A_1 state becomes the lowest one. The calculations of the matrix elements of the spin-orbit operator show that for valence angles around 160° and close to 90° the mixing among the singlet, triplet and quintet states is strong and the electron spin quantum number is no longer a good quantum number. The potential energy functions of SO_2 are much more complex than previously reported[bc] due to similar couplings. This implies that the reaction dynamics for both reactions can not be treated by using a single adiabatic PES.

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