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## Impacts of electronically photo-excited NO<sub>2</sub> on air pollution in the South Coast Air Basin of California

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**Abstract.** A new path for hydroxyl radical formation via photo-excitation of nitrogen dioxide (NO<sub>2</sub>) and the reaction of photo-excited NO<sub>2</sub> with water is evaluated using the UCI-CIT model for the South Coast Air Basin of California (SoCAB). Two separate studies predict different reaction rates, which differ by nearly an order of magnitude, for the reaction of photo-excited NO<sub>2</sub> with water. Impacts of this new chemical mechanism on ozone and particulate matter formation, while utilizing both reaction rates, are quantified by simulating two summer episodes. First, sensitivity simulations are conducted to evaluate the uncertainty in the rate of reaction of photo-excited NO<sub>2</sub> with water reported in the literature. Results indicate that the addition of photo-excited NO<sub>2</sub> chemistry increases peak 8-h average ozone and particulate matter concentrations.

The importance of this new chemistry is then evaluated in the context of pollution control strategies. A series of simulations are conducted to generate isopleths for ozone and particulate matter concentrations, varying baseline nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds (VOC) emissions. Isopleths are obtained using 1987 emissions, to represent past conditions, and 2005, to represent current conditions in the SoCAB. Results show that the sensitivity of modeled pollutant control strategies due to photoexcitation decreases with the decrease in baseline emissions from 1987 to 2005. Results show that including NO<sub>2</sub> photo-excitation, increases the sensitivity of ozone concentration with respect to changes in NO<sub>x</sub> emissions for both years. In particular, decreasing NO<sub>x</sub> emissions in 2005 when NO<sub>2</sub> photo-excitation is included, while utilizing the higher reaction rate, leads to ozone relative reduction factors that are 15% lower than in a case without photo-excited NO<sub>2</sub>. This implies that photoexcitation increases the effectiveness in reducing ozone through NO<sub>x</sub> emissions reductions alone, which has implications for the assessment of future emission control strategies. However, there is still disagreement with respect to the reaction rate constant for the formation of OH. Therefore, further studies are required to reduce the uncertainty in the reaction rate constant before this new mechanism is fully implemented in regulatory applications.

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