

## ***Interactive comment on “Impacts of electronically photo-excited NO<sub>2</sub> on air pollution control strategies in the South Coast Air Basin of California” by J. J. Ensberg et al.***

**Anonymous Referee #2**

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General Comments:

The authors consider the effect of adding photo-excited nitrogen dioxide (NO<sub>2</sub><sup>\*</sup>) chemistry to a photochemical air quality model that treats the formation of ozone and secondary particulate matter (ammonium nitrate). The model is applied to an old and often-studied air pollution episode from summer 1987 in southern California. There are uncertainties in the rate of NO<sub>2</sub><sup>\*</sup> plus water vapor reaction (labeled R7 in the discussion paper), and this reaction appears to be significant only if the highest published value is adopted for the rate coefficient.

Specific Comments:

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1. Chemical mechanism issues. The authors need to identify clearly the base chemical mechanism they are using in this study. The cited references suggest that an obsolete (LCC) chemical mechanism is still being used; such an outdated description is not appropriate now for publication in ACP. Table 1 provides information on rate coefficients for reaction R7, whereas information for rates of R6 and R8 is not provided. The text following R6-R8 on page 18987 implies that photon energy affects the rates of formation of NO<sub>2</sub><sup>\*</sup> versus NO<sub>2</sub> photolysis, but the numerical values (nm) were omitted from the discussion paper. More details of how the rate of R6 is calculated and how it compares to the NO<sub>2</sub> photolysis rate as a function of solar zenith angle are needed. Likewise information is needed for how the rate of R8 is defined. Electronically excited NO<sub>2</sub><sup>\*</sup> can also be formed by the reaction of O<sub>3</sub>+NO (this is the basis for chemiluminescence detection, NO<sub>2</sub><sup>\*</sup> emits light as it returns to ground state). Is such chemistry relevant here? There must be some upper as well as lower limit on the wavelength of photons capable of forming NO<sub>2</sub><sup>\*</sup>?

2. Emission inventory issues. The authors emphasize that adding reactions R6-R8 can have policy-relevant effects on air pollution control strategies. But this is illustrated using historical conditions from summer 1987, which is a long time ago now. While the meteorological conditions of the specific episode considered may remain relevant, the emission situation has changed dramatically since 1987, and a discussion of control strategies for that timeframe is no longer of much interest or practical significance.

It is unconventional to report emissions for individual grid cells (top of p. 18997), as ozone formation is a regional-scale process that involves emissions at upwind locations as well. It is not normal practice to consider only local emissions in one model grid cell to define chemical regimes determining VOC vs. NO<sub>x</sub> limitations, the upwind context of the air mass must also be considered as part of the analysis.

3. Air quality model issues. The spatial extent of the model domain used here is limited, and the analysis is also limited to a single 2-day summertime air pollution episode. Given that the authors are considering effects on particulate nitrate, consideration of

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other seasons/meteorological conditions would improve the generality of the analysis.

I agree with the other reviewer that model performance statistics have little bearing on which choice of rate for R7 is the most realistic. There are too many possible compensating errors (including emissions and other chemical mechanism issues) for the performance statistics to be informative about correct choice of rate for R7 in the way the authors want them to be. Also there is no evaluation of the predictions for PM nitrate against observations.

Technical Corrections:

Page 18987, line 21: wavelengths in nm are missing from the text

Page 18996, lines 21-22: higher ozone concentrations of ozone?

Page 18997, line 5-9: excessive precision in most of the numbers stated in this paragraph

Page 19002, line 27: should be Winner, D. A.

Page 19003, Table 1: units should be molec not mol

Page 19004, Table 2: peak prediction accuracy statistics are typically reported for ozone, but not NO and NO<sub>2</sub>. All the performance statistics in this table should be rounded to the nearest whole percentage point, excessive precision currently.

Page 19005, Figure 1: Why is Irvine shown in the Figure if no observations/analysis are presented for that location?

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 18985, 2009.