General response:

Reviewers indicated that the work presented in this article is insightful in quantifying the potential effects of NO_2 photoexcitation on pollutant formation. However, they indentified several shortcomings in the original manuscript that questioned the reliability of some conclusions from the present work. Several comments were repeated among reviewers. In consequence, authors believe that one consolidated document is the best means to address in a concise manner all the questions and comments formulated by the reviewers.

The main concern raised by most reviewers was that the 1987 emissions were too old to provide relevant information on the impact of the new reactions on emission control strategies. This has been addressed by analyzing ozone and PM isopleths using 2005 emissions. As indicated in the point-by-point response to reviewers, results do not vary qualitatively, although the magnitude of the impacts of NO_2 photoexcitation using updated emissions is smaller than in the case with 1987 emissions.

A second concern was that the paper somewhat implied the validity of the reaction rate proposed by Li et al. was demonstrated by presenting an improvement in overall model performance. Authors agree that this assertion is unfounded and the discussion and conclusions have been corrected and clarified. Additional discussion on model uncertainty has been included as per reviewers' request.

A third concern was related to the chemical mechanism, the implementation of chemical reactions and the discussion on the mechanisms that drive the observed changes in ozone and particulate matter concentrations. Part of the confusion was caused due to the omission of the chemical mechanism description in the original manuscript. The chemical mechanism is now described and referenced, and the discussion on the reactions and mechanisms that cause pollutant concentration changes is revised based on the reviewers' comments.

These main comments and the rest of specific comments have now been addressed, and as a result, the quality and clarity of the paper has been improved substantially. A point-by-point response is included below. Individual comments by the reviewers are in blue, followed by the response in black.

The authors wish to thank all the comments by the reviewers, which contributed to produce a scientifically sound manuscript that merits the interest of the readership of Atmospheric Chemistry and Physics.

Reviewer #1

(1.0) This paper describes results of model simulations of effects of HONO formation from the reaction of electronically excited NO2 on ozone and PM formation in the California South Coast Air Basin. The gas-phases chemical mechanisms used in urban and regional models for predicting ozone, PM and other measures of air quality have not included this reaction, but recent results from Li et al (2008) suggest that it may occur to a sufficient extent that it may have a non-negligible effect on model predictions. The published literature is ambiguous concerning the rate of this reaction, with previous work of Crowley and Carl (1997) indicating that it may also occur but at a much slower rate than that indicated by Li et al (2008). In this manuscript, calculations of O3, NO, and PM are presented assuming this reaction is negligible (base case), using the Crowley and Carl (1997) rate constant (low reaction rate), and using the Li et al (2008) rate constant (high reaction rate) for the reaction governing this process. A small effect of using the low rate constant is seen but it is minor and probably not significant, and (as expected) a larger effect is seen using the high rate constant, which the authors conclude is significant.

The paper concludes that the reaction could be important enough to affect control strategy conclusions and needs to be included in the model. However, the rate constant governing this process (the reaction of excited NO2 with H2O forming HONO) is highly uncertain and they also conclude that further experimental work on this reaction is needed. If the lower rate constant is correct (which I suspect is more likely to be the case) then the effect on model predictions is minor. This paper is useful, however, in quantifying the magnitude of this effect, at least for an air basin with relatively low VOC/NOx ratios.

Authors agree with the reviewer that the reaction rate reported by Li et al. is highly uncertain and that further studies are necessary to reevaluate that constant. Authors also agree with the reviewer that the present work is useful in quantifying the magnitude of photoexcitation, using the upper bound suggested by Li et al. Authors addressed all the comments listed below in a point-by-point response. Consequently, the authors believe that this article is relevant to the readership of ACP, and should be accepted for publication upon addressing the comments from reviewers.

(1.1) Although this paper is useful, it has several problems that I think need to be addressed prior to acceptance for final publication. No discussion is given concerning the many other uncertainties in the model and the input data that would have far larger effects on O3, PM, and control strategy predictions than the relatively small effect of using even the larger excited NO2 rate constant. Effects of uncertainties in emissions far outweigh effects of uncertainties in this rate constant, and uncertainties in the meteorological and transport model combined with uncertainties in emissions are probably the main factors driving model performance. In addition, other uncertainties in the gas-phase chemical mechanisms may have equal or larger effects on model predictions than uncertainties in the excited NO2 rate constant. Model studies have shown that differences in ozone predictions between the Carbon Bond and SAPRC mechanisms are at least as great as the effects of using the higher excited NO2 rate constant, and uncertainties in the OH + NO2 rate constant may cause effects of comparable or greater magnitude. Because of this, it is absurd to conclude that the slightly improved model performance statistics resulting from the use of the higher rate constant implies that the higher rate constant is more likely to be correct. They do not state this outright, but they are hinting at this in several places in the manuscript, including the conclusions.

The authors agree that it cannot be concluded that the reaction rate proposed by Li et al. is correct because the model accuracy improves with the inclusion of NO_2 photoexcitation. As the reviewer mentions, there are many uncertainties that outweigh the importance of the NO_2 photoexcitation reaction.

Rodriguez et al. 2003 presented the uncertainty analysis for the CACM mechanism in a box model, and suggested uncertainties of up to 44% in ozone concentration due to reaction rate constant uncertainties alone. Uncertainty in photolysis of NO_2 and aldehydes produced the highest model sensitivity. In addition, formation of nitric acid from NO_2 and OH, and the titration of ozone by NO also contribute to model uncertainty at low VOC-to-NO_X ratios. For sensitivity of ozone formation due to model input uncertainties in a three-dimensional model, Rodriguez et al. 2007 suggested that NO_X emissions are the highest contributor to model uncertainty when modeling ozone formation in the SoCAB, followed by VOC boundary conditions. In addition, ozone boundary conditions affect uncertainty in modeled ozone formation in coastal areas and the titration of ozone by NO contributes to ozone uncertainty in locations downwind from Los Angeles, such as Riverside.

Carreras-Sospedra et al. 2006 reported sensitivity of the model to meteorological conditions and suggested a strong sensitivity of peak ozone concentration to temperature changes. Carreras-Sospedra et al. 2006 also reported increases in ozone peak concentrations of more than 100 ppb with respect to simulations with Urban Airshed Model (UAM) using the CBIV chemical mechanism.

This discussion is now included in the manuscript.

(1.2) The paper does not need to discuss the many other model uncertainties in great detail, but at least it should mention the most important of them and put the uncertainties related to the excited NO2 reaction in proper perspective. Either that or they cut back significantly on their discussion of "model evaluation" and focus just on the sensitivity studies of the effects of the excited NO2 reactions.

The model evaluation section in the original manuscript included detailed descriptions of well known statistical metrics used by the atmospheric science community. Also, the model used in this paper has been evaluated previously, and hence, it is not crucial to present model evaluation in such deep detail. In contrast, the original manuscript lacked discussion on the overall uncertainty in the chemical mechanism and the full three-dimensional air quality model. Therefore, the model evaluation section has been modified to include the discussion above and allow more space for discussion of model sensitivity to NO_2 photoexcitation.

(1.3) Whether or not to include the formation of HONO from excited NO2 in the model is a chemical mechanism issue, but nowhere does the paper state which chemical mechanism is used in the calculations it presents. The only reference in the "Methodology" section they give for the model they use is Harley et al (1993), who describe a version of the UCI-CIT model using the LCC mechanism. The LCC mechanism is way out of date and no longer widely used, and was not designed for PM modeling. However, more recent papers and reports from this group describe using the CACM mechanism in the UCI-CIT model, and I suspect that this is the mechanism they use, especially since they report PM predictions and CACM is designed for modeling PM. The actual mechanism used needs to be stated explicitly and a reference where one can obtain a mechanism listing needs to be given. If the mechanism uses an OH + NO2 rate constant that is higher than currently accepted or if the mechanism used is known to give lower O3 predictions than other current mechanisms, then these would be other reasons for the generally low O3 bias in the base case model predictions.

The chemical mechanism used in the model is the Caltech Atmospheric Chemistry Mechanism (CACM) mechanism (Griffin et al. 2002), which stems from the SAPRC99 mechanism, but it includes a more comprehensive treatment of VOC oxidation in order to simulate the formation of secondary organic aerosols. It tends to produce higher ozone concentration than SAPRC-99 (Jimenez et al. 2005), although it leads to lower ozone concentrations in the ozone valleys, near high NO_X emissions. The manuscript now clearly states the mechanism used and includes additional references to the model.

(1.4) There are several instances where I either do not agree with or misunderstand the chemical mechanistic reasons given in the manuscript for the sensitivity results. On page 18992 starting at line 20 they seem to imply that the reason that using the high rate constant decreases NO is because there is less NO formed from the photolysis of NO2 because of the increased competition by the excited NO2 reactions. Actually, I don't think the excited NO2 reactions directly affects the rate of NO + O3P formation from NO2 to any significant extent because the latter occurs at much higher rate. The excited NO2 reactions affect NO (and also O3, HNO3 and VOC reacted) because the HONO formed causes more radical initiation than otherwise would be the case, with the higher radicals causing increased rates of NO consumption O3 and HNO3 production, and VOC reaction. Likewise, on Page 18997 starting at line 12 they imply that the reaction of excited NO2 decreases the amount of NO2 available to react with OH and therefore reduces termination. I think the effect of this reduction of available NO2 on termination is minor compared to the effect of the formation of HONO on initiation. Also, the HONO photolysis re-forms NOx in the form of NO, which is rapidly converted back to NO2 under conditions when O3 is present.

The role of NO_2 photoexcitation on NO_2 consumption was overstated, and the role of OH production on pollutant concentrations needs to be discussed further.

The rate of NO_2 photolysis is approximately 3-4 times lower than the rate of photoexcitation. However, the rate of quenching photoexcited NO_2 down to electronic ground state is 1000 times faster than the reaction of NO_2* with water, resulting in an effective rate of NO_2 removal through photoexcitation that is 10^4 times lower than the photolysis of NO_2. Conversely, the formation of OH through NO_2 photoexcitation can be a significant contributor to total OH formation, especially in areas with high NO_X emissions and relatively low ozone concentrations. For typical concentrations of NO_2 and O_3 of 50 ppb and 90 ppb for 1987, photoexcitation contributes to nearly 5% of OH production at noon in the high rate case, and only 0.4% in the low rate case. For typical concentrations of NO_2 and O_3 of 30 ppb and 60 ppb in 2005, the contribution of photoexcitation to OH production is of the same order in relative terms. As the reviewer suggests, changes in NO, NO_2, O_3 and HNO_3 due to NO_2 photoexcitation can be explained by the overall increase in OH production, and the decrease in NO_2 concentration due to photoexcitation is insignificant compared to the loss of NO_2 due to photolysis.

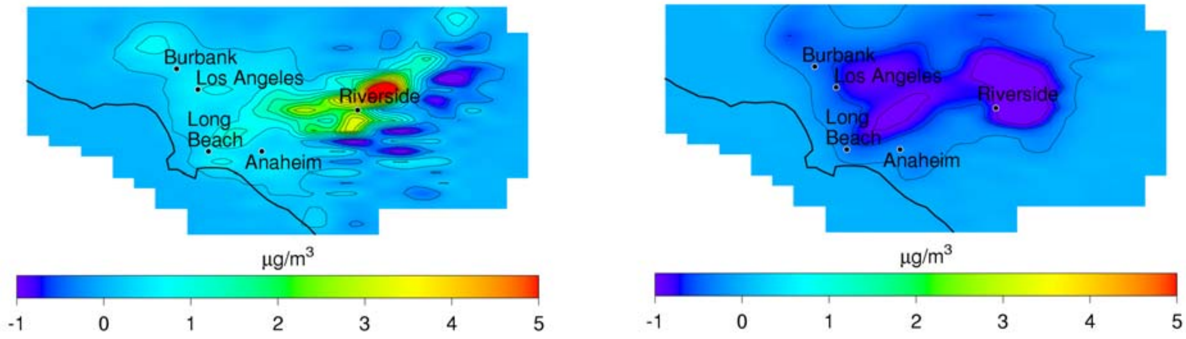
The manuscript now includes this detailed discussion on the OH formation from NO_2 photoexcitation, and its role on pollutant concentrations.

(1.5) The discussion of the reasons for the dependence of O3 on the VOC/NOx ratio on page 18996 is an oversimplification and neglects the importance of radical levels, and radical initiation and termination processes, in affecting this dependence. As indicated above, I suspect that the main reason that the excited NO2 reaction affects this dependence is because it is a radical initiation process. If the authors disagree with this, they need to give more convincing arguments to the contrary.

The authors agree with the reviewer in that formation of radicals, initiated by the formation of OH from NO_2 photoexcitation is the main cause for pollutant concentration changes. The discussion has been updated to include additional discussion concerning the increase of OH production due to photoexcitation of NO_2, as described in point (1.4).

(1.6) More information is needed concerning their model predictions of PM in order for the reader to properly understand why the excited NO2 reaction increased predicted PM formation. Is most of the PM formed in this model coming from HNO3 via Reaction (R11) or is secondary organic aerosol (SOA) and other PM sources also important in this model? If it is mainly R11 it would because of the increased HNO3 formed because of the increased OH, and if it is SOA it would be because the higher radical levels cause more VOC reactions.

PM formation in the South Coast Air Basin of California is heavily influenced by nitrate dynamics. Peak fine PM concentrations have been measured consistently near the Riverside area. Peaks are mostly composed of nitrate and ammonium. Nguyen and Dabdub confirm such dynamics. Namely, high emissions of NO_X oxidize to produce nitric acid that reacts with ammonia to produce ammonium nitrate. Because NO_2 photoexcitation leads to an increase in nitric acid production, concentration of nitrate in the aerosol tends to increase with the addition of this new reaction (Figure 1a). In contrast, the addition of photoexcitation leads to a slight decrease in the formation of secondary organic aerosol (Figure 1b).



(a) (b)

Figure 1: Differences in aerosol concentrations due to the high reaction rate case on PM_{10} species (high reaction rate case minus base case): (a) differences in Nitrate PM_{10}, (b) differences in secondary organic PM_{10}

(1.7) I do not understand what is meant by "nm" in Line 21 on page 18987.

The values of the wavelength ranges were omitted during typesetting. The values are included in the revised manuscript.

Reviewer #2

(2.0) General Comments:

The authors consider the effect of adding photo-excited nitrogen dioxide (NO2*) 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 NO2* 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.

As the reviewer indicates, the original manuscript focused on an episode in the year 1987 to evaluate the impacts of NO_2 photoexcitation. The reason behind using the 1987 episode was to analyze the effect of NO_2 photoexcitation with a well-studied episode that has been vetted and evaluated by numerous studies. That particular episode includes a well-grounded emissions inventory, widely accepted by the atmospheric scientist community. However, authors agree that that episode does not provide a good representation of current atmospheric conditions. In particular, it does not represent current emission levels, which limit the impacts of photoexcitation on secondary pollutant formation.

Upon comments of all the reviewers, now the paper includes additional results using emissions for 2005. These new simulations provide a more up-to-date representation of the potential impacts of NO_2 photoexcitation in present conditions than the results for the 1987 episode.

A point-by-point response to the reviewer's comments is included below.

(2.1) Specific Comments:

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 NO2* versus NO2 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 NO2 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 NO2* can also be formed by the reaction of O3+NO (this is the basis for chemiluminescence detection, NO2* 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 NO2*?

The chemical mechanism used in the present study is the CACM. A short discussion of the chemical mechanism and its corresponding references has been added in the manuscript. Additional information on the rate of reactions R6 and R8 is also provided in the manuscript.

The photoexcitation reaction rate is derived from the absorption spectrum of NO_2 (Finlayson-Pitts and Pitts). For the NO_2 photolysis, the quantum yield of the reaction ($\phi_{photolysis}$) is one from 290 nm to 400 nm and decreases rapidly to zero from 400 nm to 420 nm. It is assumed that all NO_2 radiated by sunlight is photoexcited, and from the wavelength range of 290 nm to 400 nm, NO_2^* is completely dissociated into NO and O^3P. Then, the effective quantum yield for NO_2^* formation is 1-$\phi_{photolysis}$, and hence, formation of NO_2^* occurs at wavelengths longer than 400 nm (see Figure 2).

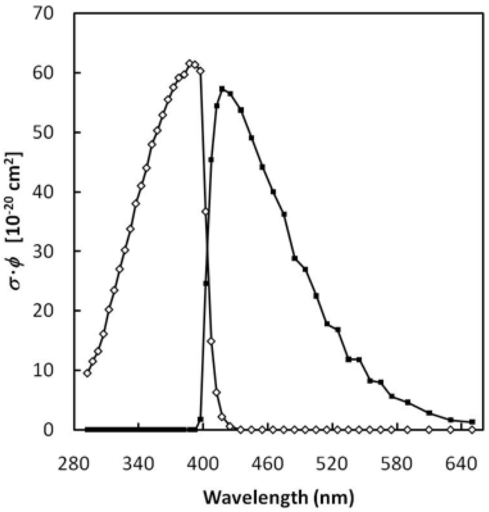


Figure 2: Absorption spectrum (σ) of NO_2 times the quantum yield (ϕ) of NO_2 photolysis (hollow diamonds) and NO_2 photoexcitation (solid squares).

As all photolytical rates, NO_2 photolysis and photoexcitation depend on the solar zenith angle that depends on the latitude, the time of the year, and the time of the day. For Los Angeles, on August 27, the variation of the photolysis and photoexcitation rates during the day is shown in Figure 3. The rate of photoexcitation is 3-4 times higher than the photolysis of NO_2, which is consistent with values presented by Crowley and Carl (1997).

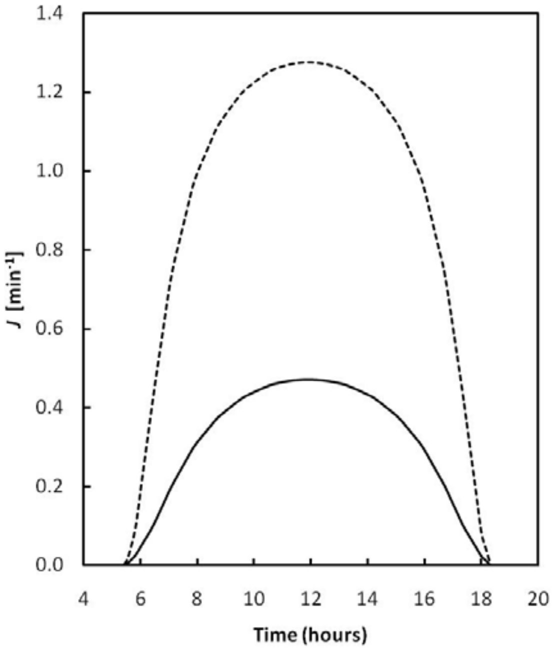


Figure 3: Rate of photolysis (solid line) and photoexcitation (dotted line) as a function of hour of the day, for August 28, 1987, in Los Angeles.

As the reviewer suggests, there is another path of formation of NO_2^* from the titration of NO with O_3, which has not been included in this study. NO_2^* formed from O_3 + NO is electronically excited ranging from 590 to 2800 nm. Assuming that all NO_2^* photoexcited at that wavelength range can react with water to form OH, the instantaneous rate of production of NO_2^* can be expressed as:

$NO_2 + h\nu \rightarrow NO_2^*$ $R_{NO2+hv} = j_{NO2^*} [NO_2]$ (R6)

$NO + O_3 \rightarrow NO_2^* + O_2$ $R_{NO+O3} = k_{NO+O3} [NO][O_3]$ (R12)

$R_{total\ NO2^*} = R_{NO2+hv} + R_{NO+O3}$

The peak formation of NO_2^* due to photoexcitation occurs at noon, when the solar intensity is the highest. Formation of NO_2^* due to ozone titration by NO peaks between the morning rush hours and noon, when ozone concentration starts to pick up due to higher solar intensity and concentrations of NO are still relatively high after the morning commute. In areas such as Los Angeles, with typical noon concentrations of NO, NO_2

and O_3 of 10, 30 and 40 ppb, respectively, the contribution of R12 to total NO_2* production is approximately 23%. Crowley and Carl (1997) suggested that titration of ozone could contribute to 10% of the total NO_2* formation in remote atmospheres. This mechanism of NO_2* production is not included in the analysis however. Therefore, the effects of reaction R7 (NO_2^* + H2O → OH + HONO) on ozone concentrations could be larger than the suggested by this study.

This discussion is now included in the manuscript.

(2.2) 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.

Authors agree that the use of 1987 emissions is not appropriate to discuss effects of future pollutant control strategies. The paper has been restructured so that the 1987 emissions case is presented for sensitivity purposes. Additional runs have been conducted with emissions for summer of 2005. The emissions were obtained from the South Coast Air Quality Management District of California, and correspond to an episode of July 14-15, 2005, which is part of a set of emissions used in the 2007 Air Quality Management Plan (SCAQMD, 2007). Figure 4 shows new isopleths generated using 2005 emissions. The decrease in ozone concentrations from the 1987 case to the 2005 case is significant. As suggested by the isopleths for 1987, the effect of photoexcitation is milder in the case of 2005 compared to the case of 1987, due to the significant decrease in NO_X emissions. For the case of 2005, increases in peak 8-hour average ozone concentration due to the high case of photoexcitation are up to 8 ppb, which are comparable to the impacts suggested by Sarwar et al. (2009), for an episode in 2002.

Figure 5:

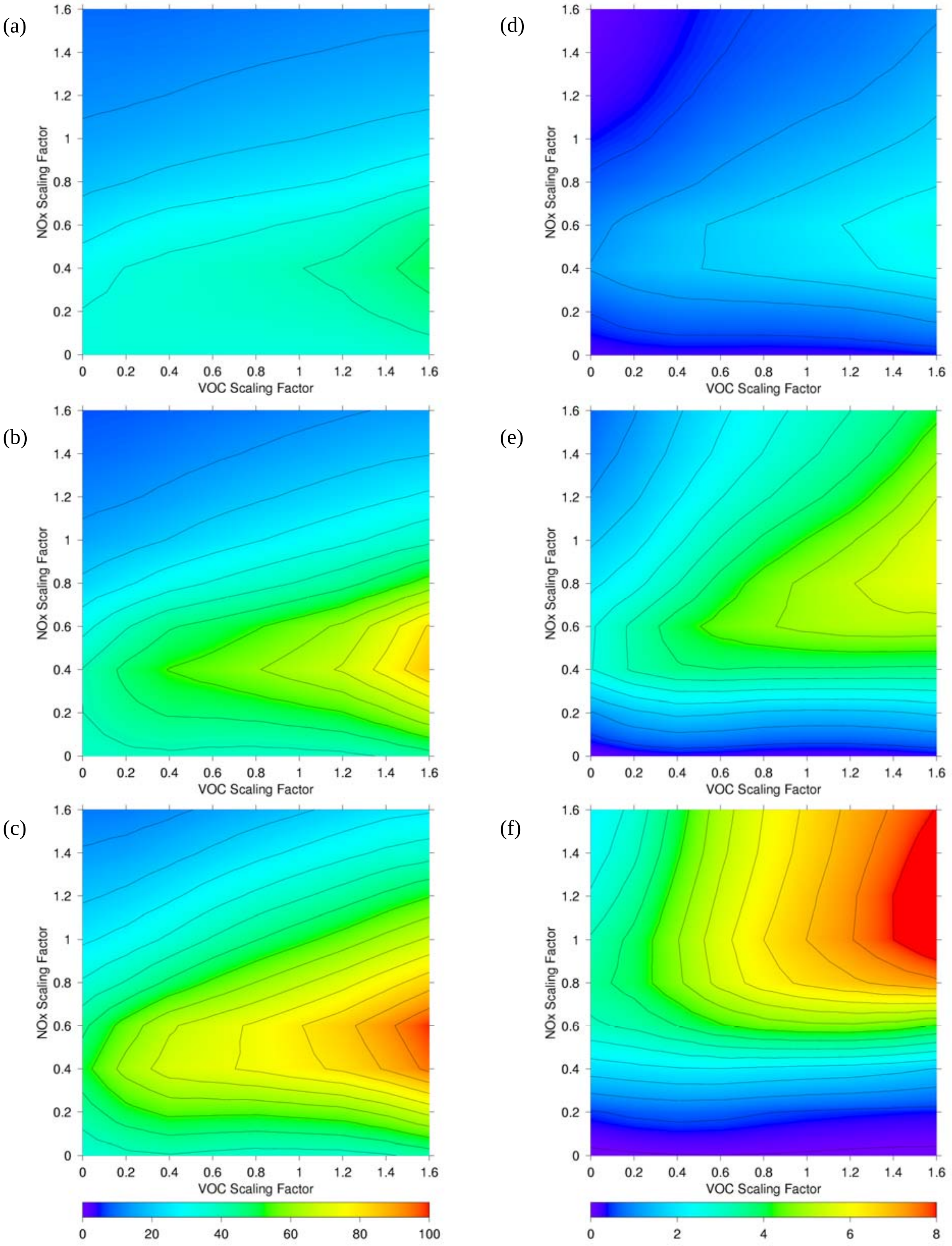

(a)
(b)
(c)
(d)
(e)
(f)
NOx Scaling Factor
VOC Scaling Factor
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
20
40
60
80
100
0
2
4
6
8

Figure 4: Impact of excited nitrogen dioxide chemical reactions on ozone in the South Coast Air Basin of California for an episode using 2005 summer emissions: (a) Peak 8-h average ozone concentrations for base case in Los Angeles, (b) Peak 8-h average ozone concentrations for base case in Pomona, (c) Peak 8-h average ozone concentrations for base case in Riverside, (d) Peak 8-h average ozone concentrations for high reaction rate case minus those from base case in Los Angeles, (e) Peak 8-h average ozone concentrations for high reaction rate case minus those from base case in Pomona, (f) Peak 8-h average ozone concentrations for high reaction rate case minus those from base case in Riverside

(2.3) 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. NOx limitations, the upwind context of the air mass must also be considered as part of the analysis.

The point of presenting emissions in single cells is to show in a quantitative way the ranges in emissions from areas such as Los Angeles, with high NO_X emissions, and downwind locations such as Pomona and Riverside, where emissions of NO_X are much lower. Showing these values does not imply that transport of pollutant from upwind is not accounted for. Nevertheless, the section has been rewritten substantially to clarify the discussion.

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

The model domain represents the South Coast Air Basin of California, which typically experiences the worst air quality of the United States. Hence, although it is a small area, it is of great interest, and has been studied in numerous efforts. The typically high emissions of NO_X in this area constitute an important factor for the study of NO_2 photoexcitation. Nevertheless, the authors agree that the spatial extent of the basin limits the generalization of the results. However, the high NO_X emissions and intense insolation experienced in the area could be considered as parameters for an upper bound for the effects of NO_2 photoexcitation on O_3.

The episode selected for this study represents typical meteorological conditions that lead to high ozone formation. The episode has been studied extensively, and provides a good benchmark for model evaluation. The meteorological conditions of the episode are expected to facilitate the extent of the photoexcitation reaction, and hence, provide meteorological conditions for the upper bound for NO_2 photoexcitation.

(2.5) 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.

The text has been reworded to eliminate any suggestion that photoexcitation should be included because it increases model accuracy.

Nguyen and Dabdub (2002) reported measured nitrate $PM_{2.5}$, which is compared to simulated concentrations in Figure 5. Griffin et al. (2002) evaluated the UCI-CIT model using a different meteorological episode (September 8-9, 1993), and they showed good agreement in selected locations in terms of total PM mass and species distribution in the aerosol.

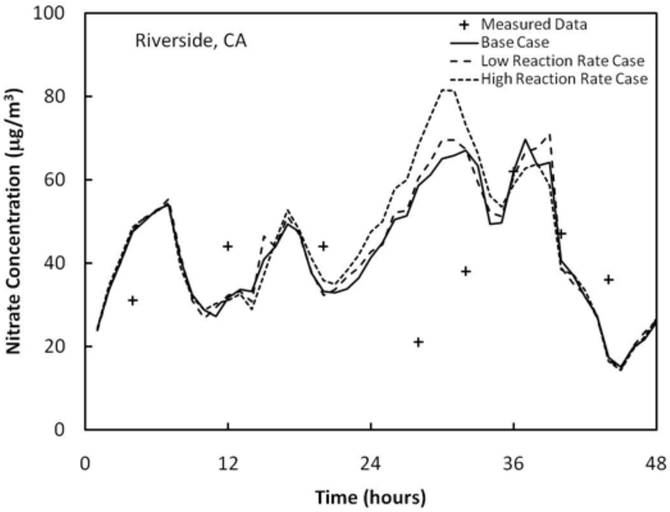


Figure 5: Simulated and measured nitrate $PM_{2.5}$ in Riverside, California, for Aug. 27-28, 1987. The figure depicts four cases which include 1-h average Nitrate $PM_{2.5}$ concentrations for the UCI-CIT base case, 1-h average Nitrate $PM_{2.5}$ concentrations for a case with NO_2 photo-excitation chemistry utilizing the low reaction rate, [Crowley and Carl, 1997], 1-h average Nitrate $PM_{2.5}$ concentrations for a case with NO_2 photo-excitation chemistry utilizing the high reaction rate [Li et al., 2008], and measured concentrations reported by Nguyen and Dabdub (2002). The numerical values of the high and low reaction rates are shown in Table 1 of the manuscript.

Additional discussion has been included to provide information on model evaluation of PM and the effects of NO_2 photoexcitation on different constituents of the aerosol phase. See reply to comment 1.6 for discussion on the effect of NO_2 photoexcitation on nitrate PM.

(2.6) Technical Corrections:

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

Wavelength values are now included in the manuscript.

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

This has been corrected.

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

This discussion has been revised extensively in the updated manuscript.

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

This has been corrected.

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

This has been corrected.

Page 19004, Table 2: peak prediction accuracy statistics are typically reported for ozone, but not NO and NO2. All the performance statistics in this table should be rounded to the nearest whole percentage point, excessive precision currently.

Peak prediction accuracy for NO and NO2 has been removed, and values have been rounded up to the nearest whole percentage point.

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

Irvine has been removed from Figure 1.

Reviewer #3

(3.0) GENERAL COMMENTS:

This paper examines the extent to which a new pathway for formation of HONO and OH involving photo-excited NO2 may be important for ozone and particulate matter (PM) control strategies in southern California. The authors incorporate the new pathway into a photochemical air quality model and simulate the impacts on ozone and PM for a two day episode. The topic addressed by this paper is an important one, since there is currently much uncertainty regarding the rate of this process and its potential importance for control strategies has not been fully

> characterized. The authors consider the range of reaction rates reported by two conflicting papers that examined these reactions. However, inadequate and inaccurate photochemical modeling and a questionable method for incorporating the new mechanism undermine the ability of this paper to provide reliable or meaningful results. The authors are encouraged to resubmit this work with a more robust modeling episode and more careful incorporation of the new reactions.

The reviewer indicates that the topic addressed in the paper is important, and encourages authors to resubmit the article after addressing some parts of the work that are questioned by the reviewer. All comments raised by the reviewer are addressed in the point-by-point response included below.

(3.1) SPECIFIC COMMENTS:

> The photochemical modeling applied here is inadequate for addressing the questions at hand. Among the most serious flaws in the modeling approach:
>
> (1) Only 2 days are simulated, which is inadequate to fully characterize summertime ozone formation and wholly unsuited to characterizing nitrate formation that occurs year-round,

The episode used in the present study corresponds to a representative meteorological episode for ozone formation. Assuming that the meteorological conditions leading to high ozone formation also lead to high photoexcitation, this episode is selected to showcase an upper bound for the potential effects of NO_2 photoexcitation. We concur with the reviewer in that the effects presented here must be contextualized and cannot be widely generalized. However, the results still provide insights on the inclusion of this new mechanism. Recently, Sarwar et al. presented a similar study for the entire United States, using a 12-km resolution. Results presented here on ozone concentration are in line with the impacts of NO_2 photoexcitation reported by Sarwar et al. for the Los Angeles area. Authors do not intend to suggest that results for $PM_{2.5}$ are representative of the entire year. Maximum PM concentrations in the SoCAB occur generally in late fall months, but the impact of NO_2 photoexcitation during that time of the year is limited by the lower insolation with respect to summer months. As a result, authors believe that the impacts on PM under summer conditions presented in the present article represent an upper bound for the effects of NO_2 photoexcitation on secondary PM.

This observation is now included in the manuscript.

(3.2) (2) The underlying chemical mechanism is not described and may be outdated given the age of the model,

The chemical mechanism used in the current version of the model is the Caltech Atmospheric Chemical Mechanism (CACM, Griffin et al. 2002) which stems from the SAPRC-99 chemical mechanism (Carter, 2000), and contains detailed treatment of VOC oxidation to characterize secondary organic aerosol formation. The outdated LCC mechanism mentioned by reviewers was part of an older version of the CIT model not used in this study.

A brief description and references to the chemical mechanism is now included in the manuscript.

(3.3) (3) An unconventional and likely inadequate approach is applied to initialize the model, using the episode days themselves rather than previous spin-up days for initialization,

The first set of two days is used to spin-up the effect of emissions and the photoexcitation reactions. Carreras-Sospedra et al. showed that it takes 2 days to minimize the effect of initial conditions in the South Coast Air Basin of California, under these meteorological conditions. The second set of two days is then used for analysis. Even though this approach does not represent a real episode, it serves the purpose to assess the impacts that the new mechanism has on baseline concentrations and emission controls during a high ozone forming conditions. As other reviewers indicate, authors believe that results still provide a useful quantification of the effects of NO_2 photoexcitation under typical summer conditions, when the impacts of this new reaction are expected to be the highest.

This caveat is included in the manuscript.

(3.4) (4) A very old (1987) episode is considered, which is unrepresentative of current South Coast conditions as emission and pollutant levels have fallen dramatically. The first three flaws are in part reflected in the unacceptably high levels of error for ozone reported in Table 2, which far exceed error ranges typically allowed in regulatory modeling; model performance for PM is not reported. The outdated episode likely leads to severe overestimates of the importance of photo-excited NO2 to current or future South Coast control strategies, since the results (Figure 3) show that impacts of this pathway diminish as emissions are reduced.

Authors agree that the use of 1987 emissions is not appropriate to discuss effects of future pollutant control strategies. Additional runs have been conducted with emissions for summer of 2005. See response to comment 2.2 for a more detailed discussion.

(3.5) The method for incorporating Reactions 6-8 in the model is suspect. Page 18997 refers to these reactions causing a “deactivation” of NO2 that would slow other reactions involving NO2. Similarly, p. 18992 reports decreases in NO because some of the NO2 is not in its ground state to enable photolysis. However, in fact, the rate constants for NO2 photolysis and (NO2+OH) were probably computed in laboratory studies that ignored the state of NO2, so it is dubious to assume that some of the NO2 is unavailable for those reactions. The way R6-R8 were incorporated could significantly bias the results.

The discussion regarding NO_2 deactivation due to photoexcitation was included based on the comparison of NO_2 photolysis and NO_2 photoexcitation reaction rates. Since photoexcitation is 3-4 times faster than photolysis, it could appear that photoexcitation could compete with photolysis for the consumption of NO_2. Namely, photoexcitation would consume a large portion of NO_2, and hence deactivate NO_2 for photolysis. However, this is not the case as the reviewer correctly points out. Further analysis reveals that reaction of photoexcited NO_2 with a third body recycles NO_2 very rapidly, and the effective reaction rate for consumption of NO_2 through photoexcitation is only 10^{-4} times the reaction rate for photolysis. See reply to comment 1.4 for more details.

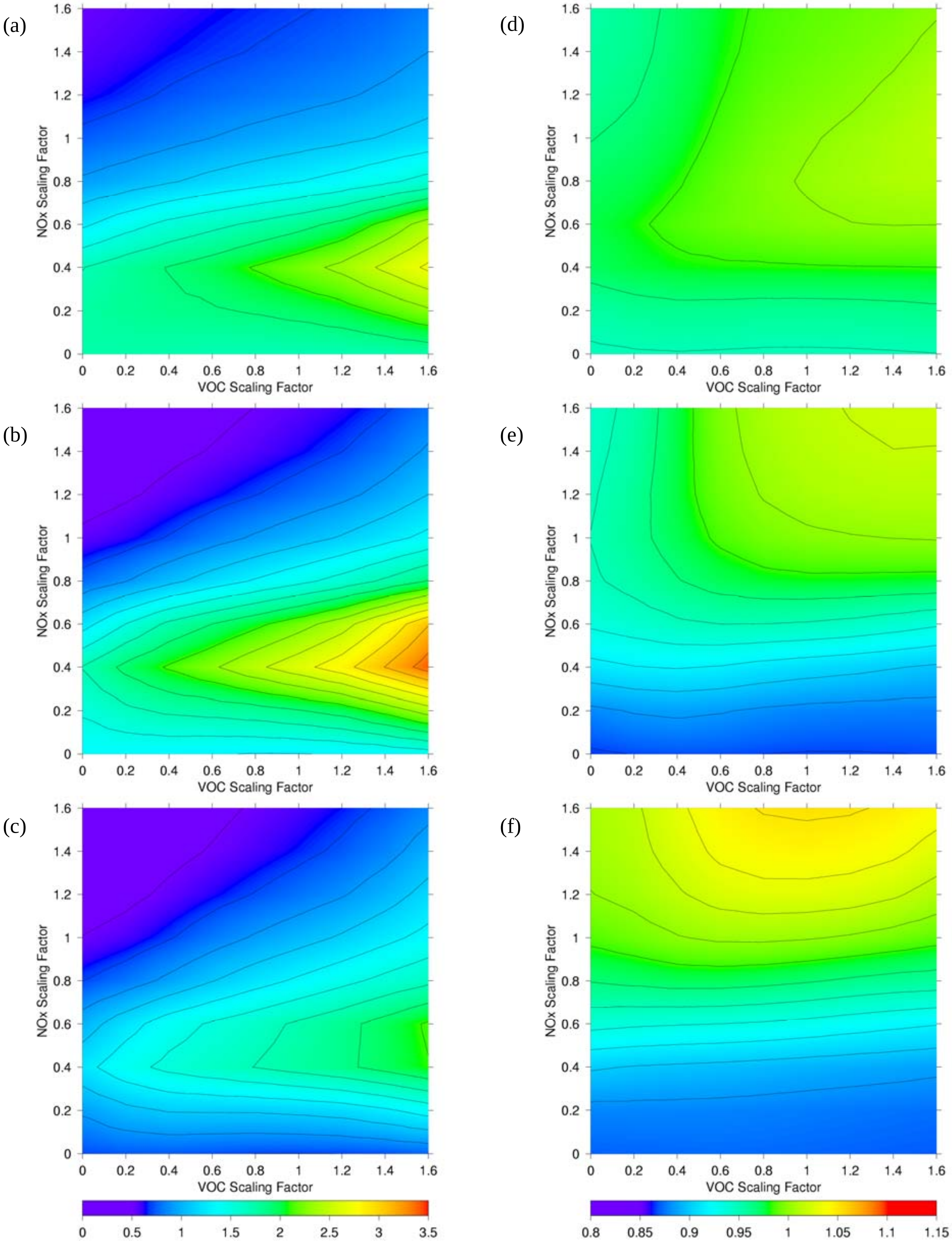
For modeling purposes, NO_2 is assumed to be in its ground state to undergo photolysis and reaction with OH. Even if NO_2* could undergo reactions with OH, O_3 and organic radicals, the rate of those reactions are typically orders of magnitude lower than the reaction with water to form OH and HONO. Hence, assuming that all NO_2 is in ground state for those reactions is a good approximation.

Updated discussion is included in the manuscript.

(3.6) It would be helpful for the authors to describe the extent to which the new mechanism causes any shifts between NOx-limited and VOC-limited chemistry, or the per-ton effectiveness of NOx and VOC controls. It is difficult to deduce this information from Figure 3.

Results show that the SoCAB is VOC limited, with and without the addition of NO_2 photoexcitation. Namely, a moderate decrease in NO_X from baseline emissions increases ozone concentrations. In general, the addition of NO_2 photoexcitation increases ozone concentrations at increasing NO_X levels with respect to the case without the new reactions. Then, a reduction of NO_X emissions in the photoexcitation case produces a lesser increase in ozone with respect to the case without NO_2 photoexcitation. This trend is easier to observe in isopleths constructed using the ratio between relative reduction factors obtained with and without the new reactions. The RRF obtained with NO_2 photoexcitation are smaller than RRF obtained without the new reactions. Consequently, NO_X emission controls with NO_2 photoexcitation tend to produce more effective results than NO_X emission controls without it.

Figure 6:



(a)
(b)
(c)
(d)
(e)
(f)
NOx Scaling Factor
VOC Scaling Factor
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
0.5
1
1.5
2
2.5
3
3.5
0.8
0.85
0.9
0.95
1
1.05
1.1
1.15

Figure 6: Impact of excited nitrogen dioxide chemical reactions on ozone in the South Coast Air Basin of California for an episode using 2005 summer emissions: (a) Peak 8-hour average relative reduction factors (RRF) for base case in Los Angeles, (b) RRF for base case in Pomona, (c) RRF for base case in Riverside, (d) ratio of RRF for high reaction rate case divided by RRF from base case in Los Angeles, (e) ratio of RRF for high reaction rate case divided by RRF from base case in Pomona, (f) ratio of RRF for high reaction rate case divided by RRF from base case in Riverside

This discussion and additional isopleths constructed using the RRF are now included in the manuscript.

(3.7) The authors present no data to assess the PM model performance, or the speciation of the PM. Without this information, it is impossible to know whether the percentage changes in total PM are meaningful, since presumably this mechanism would be more significant for some components (i.e., nitrate) than others. Discussion of PM results should be omitted unless the performance of the PM modeling can be demonstrated.

Additional discussion has been included to provide information on model evaluation of PM and the effects of NO_2 photoexcitation on different constituents of the aerosol phase. See reply to comment 1.6 and to comment 2.5.

(3.8) TECHNICAL COMMENTS:

p. 18987: There are also other sources of OH, such as acetone.

The introduction is not intended to provide an exhaustive list of OH sources. Authors acknowledge that there are other sources of OH not listed in the paper.

p. 18987: Typo in sentence “For nm, . . .”

The lambda values in the manuscript were omitted during type setting. The values will be included in the revised manuscript.

p. 18988, line 18: The term “negative” is ambiguous.

This has been reworded. Instead of “decreasing NO_X emissions may even have negative effects on peak ozone concentrations”, the now paper states: decreasing NO_X emissions may increase peak ozone concentrations”.

p. 18990: Was the 60 ppb threshold applied for bias, or only for error?

Yes. The threshold was applied for both bias and error. This is clarified in the text.

> p. 18995, line 9: It is not true that the Los Angeles and Riverside results were functions “only of whether or not R6-R8 are included”.

This paragraph is now rephrased to improve the clarity of the discussion.

> p. 18996, line 7: Authors claim “reactions between NOx and OH dominate.” Do you mean reaction of NO2 and OH? And are you sure this is true, given that OH+CO is important to HOx cycling.

While cycling of HO_X due to CO is important, CO is not the main contributor to ozone formation destruction. In contrast, cycling of NO_X and termination of ozone production due to NO_2 + OH are major factors in ozone production.

> p. 18996, line 10: Reaction 9 always results in termination. The threshold ratio just indicates the relative importance of this reaction among HOx termination processes.

Authors agree. Text has been revised:

There is a specific VOC to NO_2 ratio above which there is a net destruction of ozone due to termination reaction (Reaction R9).

> p. 18997: The discussion from lines 4-10 could be deleted.

The discussion has been revised significantly.

> p. 19000: Authors claim that this study is first to incorporate excited NO2 pathway in 3-D model. However, these results have already been reported by Wennberg and Dabdub (Science 2008, 319, 1624-1625).

This is now included in the text.

> p. 19000: Authors claim that “model predictions . . . improve” by including new mechanism. But given the similar and unacceptably high levels of error in all cases (Table 2), this conclusion is not justified. Similarly, the claim of “increased accuracy” (p. 18995, line 12) is not justified.

References to model accuracy have been revised. Additional information on model uncertainties has been included in the manuscript (See response to comment 1.1).

> p. 19001: Is it R6 or R7 reaction rate that is uncertain, or both?

The discussion is on the uncertainty suggested by the experimental work of Li et al. and Crowley and Carl on Reaction (R7).

> Table 1: How was Reaction rate R6 (J NO2-> NO2*) determined?

Description of how the rate of reaction R6 is calculated is described in the manuscript now. See response to comment 2.1.

Reviewer #4 – James Kelly (ARB)

(4.0) General Comments:

Ensberg et al. have conducted a valuable study of the impact of incorporating electronically photo-excited NO2 (NO2*) chemistry into a 3-D chemistry transport model. While uncertainty in the rate of the NO2*+H2O reaction makes any conclusions on the atmospheric significance of the reactions tentative, the manuscript makes a useful contribution by examining the potential of this chemistry to impact predicted ozone concentrations and highlighting the need for additional clarifying experiments. However, their discussion of the impact of the reactions on air pollution control strategies is misleading, and their conclusion that the reactions should be incorporated into 3- D air quality models for contemporary control-strategy applications is unreliable (see Specific Comments). Before acceptance in ACP, we strongly recommend that the discussion on air-pollution control strategies be revised significantly or removed, and the title should be changed to move the focus away from control strategies to the impact of NO2* chemistry on ozone concentrations in polluted environments.

Reviewer indicates that the work presented in the manuscript is valuable and that results contribute to the understanding of the potential impacts caused by NO_2 photoexcitation. The main concern raised by the reviewer is on the discussion of control strategies using 1987 emissions. In general, authors agree that 1987 emissions are not representative of current conditions, and that old emissions have little relevance for future control strategies. All comments have been addressed as indicated in the point-by-point response included below.

(4.1) Specific Comments:

Conclusions about the importance of NO2* chemistry for contemporary air pollution control strategies are unreliable for the following reasons:

(1) The study is based on simulations with outdated emissions from a two-day episode in 1987. In a recent study, Sarwar et al. (2009) demonstrate with box-model and 3- D simulations that increases in ozone concentration associated with NO2* chemistry are significantly smaller for contemporary conditions than for the 1987 conditions that are the focus of this manuscript. They conclude that the impact of NO2* chemistry on ozone concentration in the U.S. is small for current atmospheric conditions. Considering Sarwar et al.'s findings, Ensberg et al.'s conclusions based on results of their 1987 simulation do not appear relevant to the development of air pollution control strategies for contemporary conditions in the South Coast Air Basin of California.

Authors agree that the use of 1987 emissions is not appropriate to discuss effects of future pollutant control strategies. The paper has been restructured so that the 1987 emissions case is presented for sensitivity purposes. Additional runs have been conducted with emissions for summer of 2005. The impacts obtained with 2005 emissions are of the same magnitude as the ones presented by Sarwar et al. See reply to comment 2.2 for detailed isopleths using 2005 emissions.

(4.2) (2) The study focuses on peak 1-hour average ozone concentration, whereas the latest National Ambient Air Quality Standard (NAAQS) for ozone regulates daily maximum 8- hour average ozone concentration. When compared on the basis of the 8-hour average concentration specified by the NAAQS, differences in ozone predictions for cases with and without NO2* chemistry are likely to be smaller and less significant than when compared on the basis of peak 1-hour average predictions as reported by Ensberg et al.

The manuscript has been updated with the discussion based on 8-hour average. Qualitatively, results show the same trends, but the magnitude of impacts is slightly lower, as the reviewer suggests. See response to comment 2.2 for more detailed explanation.

(4.3) (3) The study focuses entirely on predictions of absolute pollutant concentration, whereas model predictions are now used in a relative sense in developing air pollution control strategies. In regulatory applications, the ratio of concentrations associated with future-year emissions-reduction and base-year emissions scenarios are used to scale the base-year ambient ozone design value to determine compliance with NAAQS. Different models can have significantly different absolute ozone concentration predictions, but they will not lead to different future-year design values or air pollution control strategies if their relative response to emission reductions is the same. Hogrefe et al. (2008) demonstrate this point in a recent study, where they find marked model-to-model differences in ozone concentrations of up to 20 ppb, but only minor differences in the relative response of ozone concentrations to emission reductions. These minor differences in relative response for the models resulted in differences of a few ppb or less in estimated future-year design values for ozone. Therefore, Ensberg et al.'s finding that NO2* chemistry can influence absolute ozone concentrations is not sufficient for concluding that the reactions would impact air pollution control strategies.

While authors agree that from a regulatory perspective reporting results based on relative reduction factors would be very valuable, authors believe that presenting absolute concentrations provide a scientific value to the study. Hence, authors base the analysis of photoexcitation on absolute values, and complement with additional discussion on how the changes in absolute values affect relative reduction factors.

Additional discussion and isopleths have been included to introduce the values for relative reduction factors (RRF). See response to comment 3.6 for more detailed discussion.

(4.4) (4) Two experimental studies (Crowley and Carl, 1997; Carr et al., 2009) indicate that the rate of the NO2*+H2O reaction reported by Li et al. (2008) is too high. These studies suggest that the impact of NO2* chemistry on ozone concentrations is minor. Considering the balance of evidence toward a

> significantly lower reaction rate than that of Li et al. (2008), further experimental studies should be conducted before this OH production pathway is incorporated into models for regulatory applications. Ensberg et al.'s conclusions should strongly advocate the need for additional studies rather than on including this chemistry in regulatory models.

With newer studies suggesting that the rate of reaction suggested by Li et al. (2008) could be overestimated, authors agree that there is the need for a more conclusive work on the reaction rate for $NO_2^* + H_2O$ before this reaction is included in model for regulatory applications. This conclusion is emphasized in the manuscript.

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