

Interactive comment on “Impacts of electronically photo-excited NO₂ on air pollution control strategies in the South Coast Air Basin of California” by J. J. Ensberg et al.

Anonymous Referee #1

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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

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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/NO_x ratios.

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

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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 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.

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.

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

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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 NO_x in the form of NO, which is rapidly converted back to NO₂ under conditions when O₃ is present.

The discussion of the reasons for the dependence of O₃ on the VOC/NO_x 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.

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 be 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.

I do not understand what is meant by “nm” in Line 21 on page 18987.

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