

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.

J. Kelly

jkelly@arb.ca.gov

Received and published: 30 October 2009

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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.

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(1) The study is based on simulations with outdated emissions from a two-day episode in 1987.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.

(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.

(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

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

future-year emissions-reduction and base-year emissions scenarios is 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 NO_2^* chemistry can influence absolute ozone concentrations is not sufficient for concluding that the reactions would impact air pollution control strategies.

(4) Two experimental studies (Crowley and Carl, 1997; Carr et al., 2009) indicate that the rate of the $\text{NO}_2^* + \text{H}_2\text{O}$ reaction reported by Li et al. (2008) is too high. These studies suggest that the impact of NO_2^* 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.

James Kelly, Chenxia Cai, Jeremy Avise, and Ajith Kaduwela

References:

Carr, S., Heard, D. E., and Blitz, M. A.: Comment on "Atmospheric Hydroxyl Radical Production from Electronically Excited NO_2 and H_2O ," *Science*. 324(5925), doi: 10.1126/science.1166669, 2009.

Crowley, J. N. and Carl, S.A.: OH formation in the photoexcitation of NO₂ beyond the dissociation threshold in the presence of water vapor, *J. Phys. Chem. A*, 101(23), 4178-4184, 1997.

Hogrefe, C., Civerolo, K. L., Hao, W., Ku, J. Y., Zalewsky, E. E., and Sistla, G.: Rethinking the assessment of photochemical modeling systems in air quality planning applications, *J. Air Waste Manage.. Assoc.*, 58(8), 1086-1099, 2008.

Li, S. P., Matthews, J., and Sinha, A.: Atmospheric hydroxyl radical production from electronically excited NO₂ and H₂O, *Science*, 319(5870),1657-1660, 2008.

Sarwar, G., Pinder, R. W., Appel, K. W., Mathur, R., and Carlton, A. G.: Examination of the impact of photoexcited NO₂ chemistry on regional air quality, *Atmos. Environ.*, doi:10.1016/j.atmosenv.2009.09.012, 2009.

[Interactive comment on Atmos. Chem. Phys. Discuss.](#), 9, 18985, 2009.

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)

