

This paper addresses the severe underprediction of nitrous acid (HONO) concentrations by the Community Multi-scale Air Quality model (CMAQ). However, this underprediction is not very surprising because the model omits gas-phase and many heterogeneous reactions that produce HONO. This paper is a welcome addition to the literature on this important topic although much experimental work to better determine these reactions is needed.

The authors provide a summary of the HONO reactions that they include in their version of the gas-phase Carbon Bond mechanism, CB6r3, in Table 1. Although I am doubtful that much, if any, HONO is produced through gas-phase reaction,  $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HONO}$  ( $k_f$ ), the authors should check to see if rate coefficients for this reaction and its reverse,  $\text{HONO} + \text{HONO} \rightarrow \text{NO} + \text{NO}_2 (+ \text{H}_2\text{O})$  ( $k_r$ ) are consistent with the HONO equilibrium constant. The equilibrium constant for this pair of reactions is:  $\text{Keq} = ([\text{HONO}] [\text{HONO}])/([\text{NO}][\text{NO}_2][\text{H}_2\text{O}])$  and  $\text{Keq} = k_f/k_r$ ; this expression is correct regardless, if the system is in equilibrium or not.

The value of Keq of 5E-20 derived from Table 1 seems very small considering the value given by Chan et al., (*Environ. Sci. Technol.*, 10, 1976, 674 – 682). [The Chan et al. Keq for HONO was used by Stockwell and Calvert to estimate experimental absorption cross-sections of gas-phase HONO (*J. Photochem.*, 8, 193 - 203, 1978) from equilibrium mixtures. The fact that these HONO absorption cross-sections remain consistent today with those produced by more direct methods (see: Burkholder, et al., "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 19," JPL Publication 19-5, Jet Propulsion Laboratory, Pasadena, 2019 <http://jpldataeval.jpl.nasa.gov>) support the validity of the Chan et al. Keq for HONO.]

The authors make a surprising statement about HONO chemistry at Lines 69 – 70. They state that the reaction,  $\text{HO} + \text{NO} \rightarrow \text{HONO}$ , was added to WRF-Chem. But this reaction is included in several of the standard chemical mechanisms in the WRF-Chem model. For example, it is included in the Regional Atmospheric Chemistry Mechanism, version 2 (RACM2).

Lines 148 – 154: The authors correctly state that several heterogeneous HONO producing reactions have been proposed. The possible significance of heterogeneous chemistry for the production of HONO was proposed several decades ago and it would be good if the authors provides some acknowledgement of that fact. For example, Finlayson-Pitts, B. J., and J. N. Pitts Jr. 2000, "Chemistry of the upper and lower atmosphere: Theory, experiments and applications" New York: Academic Press cite a number of investigations of heterogeneous HONO producing reactions. While I acknowledge that the authors' paper is not a historical review, it would be good if they could provide a clear picture of long search by many international researchers for these heterogeneous reactions.

In discussing both gas-phase and aqueous-phase photolysis (Lines 120 – 122; 177 – 184; elsewhere?) The authors make a common mistake in terminology. A photolysis rate is the product of a photolysis frequency (or "photolysis rate coefficient" or "J-value") and the concentration of the substance being photolyzed. An example of a photolysis rate is  $J [\text{HONO}]$ . Absorption cross-section and quantum yield data are used for calculating J but it is not a photolysis rate by itself.

The presented measurements and modeling following Line 266 in the Results and Discussions Section are well performed and very interesting. As expected the authors' modeling found that gas-phase chemistry alone can't explain the observed concentrations. It is striking that the HONO day/night behavior and nighttime concentrations in present-day Beijing are

similar to that observed by Platt et al. in Los Angeles during 1980 (Platt et al., Observations of nitrous acid in an urban atmosphere by differential optical absorption, *Nature*, 285, 312-314, 1980).

In summary, the authors have examined the relative importance of the various HONO producing reactions and shown that HONO can have a dominate effect on the HO budget. These results are potentially relevant to the development of policies to improve air quality in large urban regions. I strongly suggest that the authors address the gas-phase mechanism points as presented in their paper although I doubt modifications of the rate coefficients for the  $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HONO}$  and  $\text{HONO} + \text{HONO} \rightarrow \text{NO} + \text{NO}_2 (+ \text{H}_2\text{O})$  reactions will change their modeling conclusions. Please use either “photolysis frequency” or “photolysis rate coefficient” to describe a J-value to avoid furthering the use of misleading terminology in atmospheric chemistry literature.