

Interactive comment on “Oxidative capacity of the Mexico City atmosphere – Part 1: A radical source perspective” by R. Volkamer et al.

R. Volkamer et al.

Received and published: 8 January 2010

The comment attributes the faster-than expected HONO photolysis exclusively to the UV spectral portion of the spectrum. This is not correct, as technically also OH overtone pumping at visible and infrared wavelengths (Donaldson et al., 1997) does lead to photolysis of HONO from the electronic ground-state. This process is as such independent from the UV absorption cross section. In practice, these processes are probably small, but they do play a role at higher altitudes (Witonsky et al., 2001), and might play a role at the elevated altitudes in Mexico City.

Further, our observation that model predicted HONO decreases slower than HONO observations is quite independent from the findings by Wall et al., (2006). We have reworded the language in the new section 3.4.1. to make this clear. The accuracy or lack thereof of the results from Wall et al., 2006 is not the subject of this paper, and we

S10051

limit our response to comments that relate to our own data.

We further argue that it is not clear that the absolute value of the HONO absorption cross-section is indeed known to 10% accuracy, as the author claims. This accuracy certainly applies to our knowledge of the differential cross-section, for which the determination is independent of changes in the stability of the lamp output. However, the absolute cross-section does suffer from lamp drifts, and is less certain. (Stutz et al. 2000) actually argue that lamp drifts are responsible for at least 13% uncertainty in HONO photolysis. They set $\sigma(405\text{nm})$ to zero to account for the lamp drifts that they observed, and ased on this assumption they find negative cross-section values at wavelengths shorter than 310nm. The 13% error in $J(\text{HONO})$ is estimated exclusively based on the negative numbers that result from this assumption, and does not account for any error in the assumption itself, and possible other errors that could relate to the merging of separately measured spectral ranges into a single spectrum that are difficult to quantify (Stutz et al., 2000). Based on this lower limit uncertainty, they conclude that an additional cross-section of $7.5 \cdot 10^{-21} \text{ cm}^2$ is needed; this offset leads on average to a ~13% faster HONO photolysis rate (~10% in the MCMA during mid morning), and is within error compatible with the ~20% faster photolysis rate based on the cross-section by (Bongartz et al., 1991). Notably, the differential cross sections between both studies agree within <5% (Stutz et al., 2000), highlighting that uncertainties in estimates of HONO photolysis rates are primarily related to the absolute cross-section value.

We do not claim to have the accuracy from our field data/ model analysis to quantify the offset in the HONO cross-section with the necessary level of accuracy that the issue of HONO photolysis deserves. But Figure 4 adds to existing evidence that $J(\text{HONO})$ is uncertain. We note that the factor of 1.43 is marginally compatible with ~20% uncertainty in the HONO photolysis due to uncertain offsets in the UV spectrum. Given the considerable attention that has been paid to HONO photolysis as a radical source, lowering the uncertainty in the absolute HONO absorption cross section remains desirable.

S10052

In response to the comment by Birger Bohn on the faster-than-expected HONO photolysis Section 3.4.1. was added in the revised paper. Therein it is also explained how the factor 1.43 was derived, and how uncertain it is.

Bongartz, A., J.Kames, F.Welter, and U.Schurath. Near-Uv Absorption Cross-Sections and Trans Cis Equilibrium of Nitrous-Acid. *Journal of Physical Chemistry* 95:1076-1082, 1991.

Donaldson, D.J., G.J.Frost, K.H.Rosenlof, A.F.Tuck, and V.Vaida. Atmospheric radical production by excitation of vibrational overtones via absorption of visible light. *Geophysical Research Letters* 24:2651-2654, 1997.

Stutz, J., E.S.Kim, U.Platt, P.Bruno, C.Perrino, and A.Febo. UV-visible absorption cross sections of nitrous acid. *Journal of Geophysical Research-Atmospheres* 105:14585-14592, 2000.

Wall, K. J., C. L. Schiller, and G. W. Harris, Measurements of the HONO photodissociation constant, *Journal of Atmospheric Chemistry*, 55, 31-54, 2006.

Witonsky, S.K., M.R.Canagaratna, S.L.Coy, J.I.Steinfeld, R.W.Field, and A.A.Kachanov. The 3 $\nu(1)$ overtone band of trans-nitrous acid: Rotational and perturbation analysis and absolute intensity. *Journal of Chemical Physics* 115:3134-3143, 2001.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 7, 5365, 2007.