We thank the reviewer for her/his time and comments, which are reproduced in *black italic font* below. Our responses are shown in regular font. Revised text (as it appears in the manuscript) is shown in blue font. Line numbers are those of the revised manuscript with changes accepted.

Anonymous Referee #2 Received and published: 12 June 2020

The authors present an optimized HONO calibration source that is based on the design of Febo et al., 1995, where HCl vapor is passed over solid NaNO2. They used a permeation tube to achieve lower (< 4 ppmv) HCl mixing ratios which is key to achieve higher purity as ClNO formation is slowed down. They quantified the impurities by using FTIR spectroscopy and TD-CRDS and found the optimized design of the source to be of > 97 % purity. With the optimized design (lower HCl supply) they were able to generate HONO concentrations in the low ppm range and by further dilution in the lower ppb range. The stabilization time of 1.5 h was short compared to other source designs.

Furthermore, the source is portable and after stabilization, HONO mixing ratios are readily tunable. Due to its instability, there are no permeation tubes or standard gases for HONO available and it must be produced in situ. Therefore, to calibrate gas phase mixing of HONO such a compact and easy deployable source is of interest for the atmospheric chemistry community. The study is well performed and the manuscript well written. Therefore, I support publication after considering the minor comments given below.

Response: We appreciate the reviewer's supportive comments.

General comments:
As surfaces are unavoidable in laboratory setups, the role of surface reactions should be discussed. Although I guess that HONO formation from NO2 impurities is not of importance, there are also heterogeneous decomposition reactions for HONO that form NO (and NO2) and might therefore important to keep impurities low. See esp. (Finlayson-Pitts et al., 2003).

Response: We agree with the reviewer that surface chemistry is an important consideration. Finlayson-Pitts et al. (2003) discussed the mechanism of heterogeneous conversion of NO_2 (to HONO and HNO_3) on Pyrex which involves formation and wall-adsorption of NO_2 dimer (i.e., N_2O_4) as the initial steps. Another paper by the same group (Syomin and Finlayson-Pitts, 2003) discusses HONO decomposition on glass surfaces, which was linked to wall-adsorbed HONO reacting with wall-adsorbed HNO_3.

We believe this chemistry is limited in our setup as we have taken several steps to avoid it becoming factor. First of all, the chemistry described by Finlayson-Pitts et al. (2003) and Syomin and Finlayson-Pitts (2003) was observed in a static system on a time scale of hours or required cell conditioning with HNO_3; in our system, the 50 mL reaction vessel was continuously flushed (at a flow of ~150 mL min^{-1} from the zero air generator when in use and continuously with ~20 mL min^{-1} from the O_2 cylinder), such that there was little time for this chemistry to create much of an effect. In addition, formation of N_2O_4 scales with the square of the NO_2 concentration, which was low in our experiments. More importantly, the Pyrex reaction vessel was heated, which promotes partitioning of wall-adsorbed species to the gas-phase and reduces the extent of surface chemistry. Furthermore, the equilibrium constant for the reaction $2NO_2 \rightleftharpoons N_2O_4$ is temperature-dependent favoring N_2O_4 dissociation at higher temperature. The NASA-JPL compilation recommends an equilibrium constant of 5.9×10^{-29} cm^3 $molecule^{-1}$ $e^{(6643/T)}$ (Burkholder et al., 2015). When the temperature is increased from room temperature to 50 °C, the equilibrium constant decreases by a factor of ~6.

The following was added to the manuscript on line 97:

"In the second source ("source 2"), the $NaNO_2$ was placed in a two-neck, 50 mL Pyrex round bottom flask which was covered in aluminium foil to prevent photolysis of nitrite and nitrous acid and was externally heated to a temperature of 50 °C using a water bath and mechanically agitated using a magnetic stir bar as described by Febo et al. (1995). Heating this vessel promotes dissociation of molecular clusters such as N_2O_4 and partitioning of wall-adsorbed molecules to the gas-phase, which, if present, can drive HONO decomposition on borosilicate glass surfaces (Syomin and Finlayson-Pitts, 2003)."

Another consideration is surface chemistry in the connecting tubing. We constructed all our connecting tubing out of inert Teflon material and kept it under continuous flow (with an inert gas such as N_2 or O_2) when not in use (a detail we added to the manuscript - see our response to the question on L88 below).

Regarding the FTIR measurements: Can the authors provide more details about the reference spectrum used for HONO (spectrum of cis or trans isomer or total spectrum? taken at which temperature?). The spectral features will change with temperature as the amounts of cis and trans isomers of HONO change with temperature (e.g. Barney et al., 2000). Furthermore, please provide temperature and humidity values of the gas stream if possible.

Response: The reference spectrum was obtained from the Pacific Northwest National Laboratory digital library (Sharpe et al., 2004). According to their meta data file, they acquired this spectrum at 25 °C and atmospheric pressure and with dry nitrogen as diluent gas and generated HONO in situ from the reaction of $NaNO_2$ with HCl. We would hence expect the same distribution of HONO isomers as we would have generated in our experiments, which were conducted at room temperature.

We added more detail to section 2.2 ("Analysis of HONO source output by FTIR") on line 115 as requested by the reviewer:

"Room-temperature spectra were acquired continuously at a time resolution of 30 s. .... Mixing ratios of trace gases were determined from fits (by least squares error minimization over a selected wavelength range) of room-temperature reference spectra from the Pacific Northwest National Laboratory (Sharpe et al., 2004), ... the pressure inside the multi-pass cell (which was equal to that of the room) was monitored using a pressure transducer (Omegadyne PX419–015A5V)."

Because the bulk of the diluent gas was generated by passing room air through a scrubber, the relative humidity of the gas was approximately the same as the room (~30%; accounting for dilution with dry oxygen and neglecting H_2O co-emitted by the HCl perm tube, RH is estimated at ~25% for the data shown in Figure 2). Since the background spectrum was acquired with this H_2O background, the FTIR only shows drifts in H_2O. The following was added on line 187:

"A sample FTIR spectrum of this source's output is shown in Figure 2. With a freshly prepared HCl permeation tube and an estimated relative humidity in the round bottom flask of ~25%, > ~2.5 ppmv HCl were consumed and ~3.0 ppmv of HONO were produced. "

Specific comment:
L88: Why diluting with 20 mL min-1 flow of oxygen?

Response: The additional flow is probably not essential, but we found it practical to keep part of the setup under flow of a clean gas - our laboratory air contains surprisingly high levels of NO_x delivered from the building's air intake, plus the continued flow would remove any impurities that might build up. The use of a second mass flow controller was also advantageous as it allowed the residence time and HCl concentration to be changed on the fly without disturbing the permeation tube setup (which can take quite a long time to return to a stable output when flows are changed).

We modified the text as follows:

"The permeation tube was placed inside a glass chamber (VICI Dynacalibrator Model 120) whose temperature was controlled at 25.0 °C and which was continuously flushed at a flow rate of ~0.15 L min^{-1} with room air scrubbed using activated charcoal for a period of several days into a fume hood. The use of scrubbed air ensured that the gas stream contained water to maintain efficient HONO production (Schiller et al., 2001). The HCl output was diluted in a gas stream of O_2 (~20 mL min^{-1}); this gas stream also served to continuously flush the connecting tubing when not in use."

References:

Barney, W. S., Wingen, L. M., Lakin, M. J., Brauers, T., Stutz, J. and Finlayson-Pitts, B. J.: Infrared Absorption Cross-Section Measurements for Nitrous Acid (HONO) at Room Temperature, J. Phys. Chem. A, 104, 1692–1699, 2000.

Febo, A., Perrino, C. and Sparapani, M. Gherardi. R.: Evaluation of a High-Purity and High-Stability Continuous Generation System for Nitrous Acid, Environ. Sci. Technol, 29, 2390–2395, 1995.

Finlayson-Pitts, B. J., Wingen, L. M., Sumner, A. L., Syomin, D. and Ramazan, K. A.: The heterogeneous hydrolysis of NO2 in laboratory systems and in outdoor and indoor atmospheres: An integrated mechanism, Phys. Chem. Chem. Phys., 5, 223-242, 2003.

Burkholder, J. B., Sander, S. P., Abbatt, J. P. D., Barker, J. R., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 18, National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 2015.

Schiller, C. L., Locquiao, S., Johnson, T. J., and Harris, G. W.: Atmospheric measurements of HONO by tunable diode laser absorption spectroscopy, J. Atmos. Chem., 40, 275-293, 10.1023/A:1012264601306, 2001.

Sharpe, S. W., Johnson, T. J., Sams, R. L., Chu, P. M., Rhoderick, G. C., and Johnson, P. A.: Gas-phase databases for quantitative infrared spectroscopy, Appl. Spectrosc., 58, 1452-1461, 2004.

Syomin, D. A., and Finlayson-Pitts, B. J.: HONO decomposition on borosilicate glass surfaces: implications for environmental chamber studies and field experiments, Phys. Chem. Chem. Phys., 5, 5236-5242, 10.1039/b309851f, 2003.