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A compact, high-purity source of HONO validated by Fourier transform infrared and thermal-dissociation cavity ring-down spectroscopy

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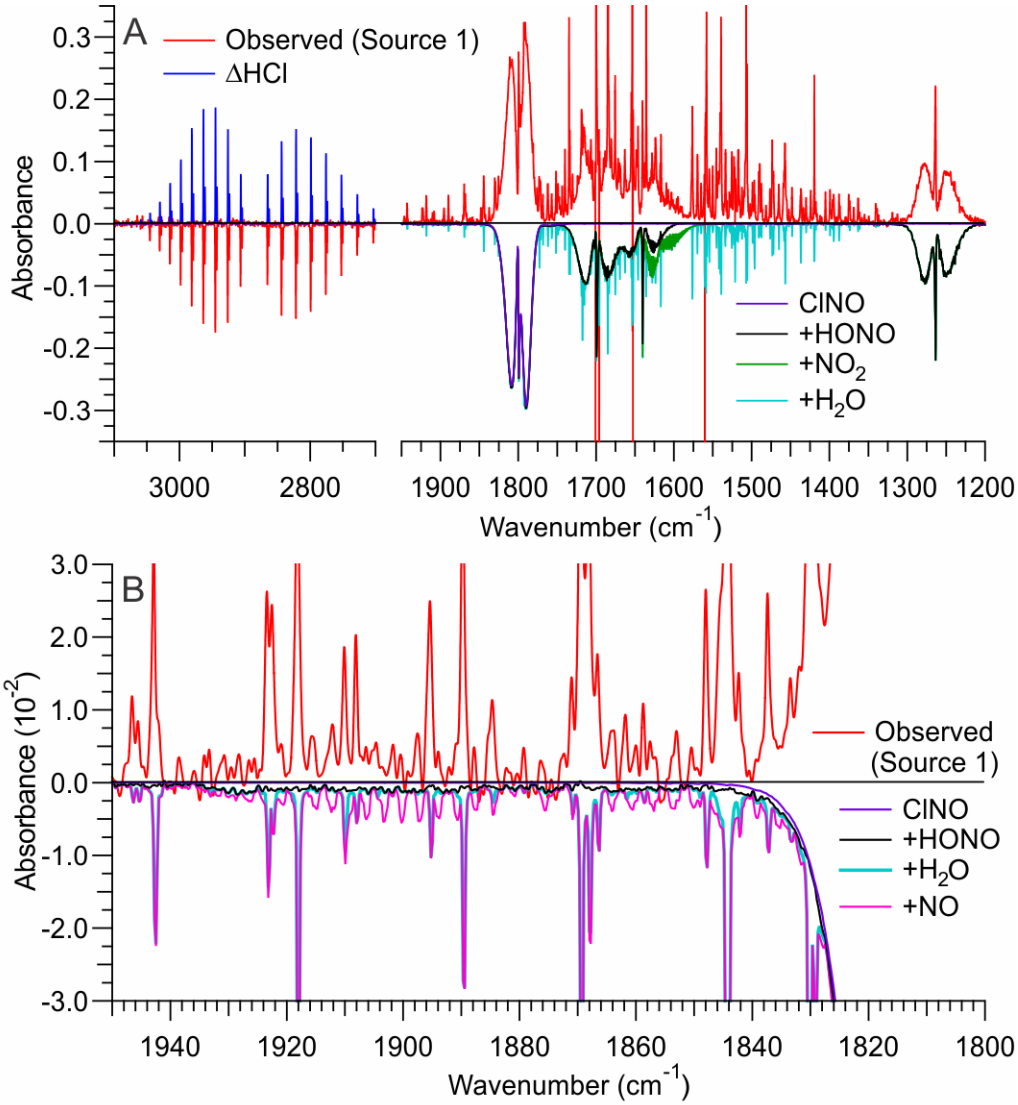

Figure S1. (A) Infrared spectrum (shown in red colour) of a gas stream generated by reaction of $HCl_{(g)}$ with $NaNO_{2(s)}$ using source 1. The reference spectrum was collected when $NaNO_2$ was bypassed, i.e., contained HCl. The transmission spectrum (not shown) was void of HCl lines, indicating quantitative conversion of HCl. Literature spectra (Sharpe et al., 2004) were multiplied by the optical path length of 6.4 m and mixing ratios of the identified trace gases to reproduce the observed spectrum; the expected spectra were multiplied by -1 (i.e., inverted) prior to presentation. In this example, source 1 emitted ~38 ppmv of HONO, ~15.5 ppmv of ClNO, ~4.0 ppmv of NO_2 and ~100 ppmv of H_2O and consumed > ~38 ppmv of HCl. (B) Expanded view of the 1950 to 1800 cm^{-1} spectral region. The spectrum expected for ~4.0 ppmv of NO is superimposed.

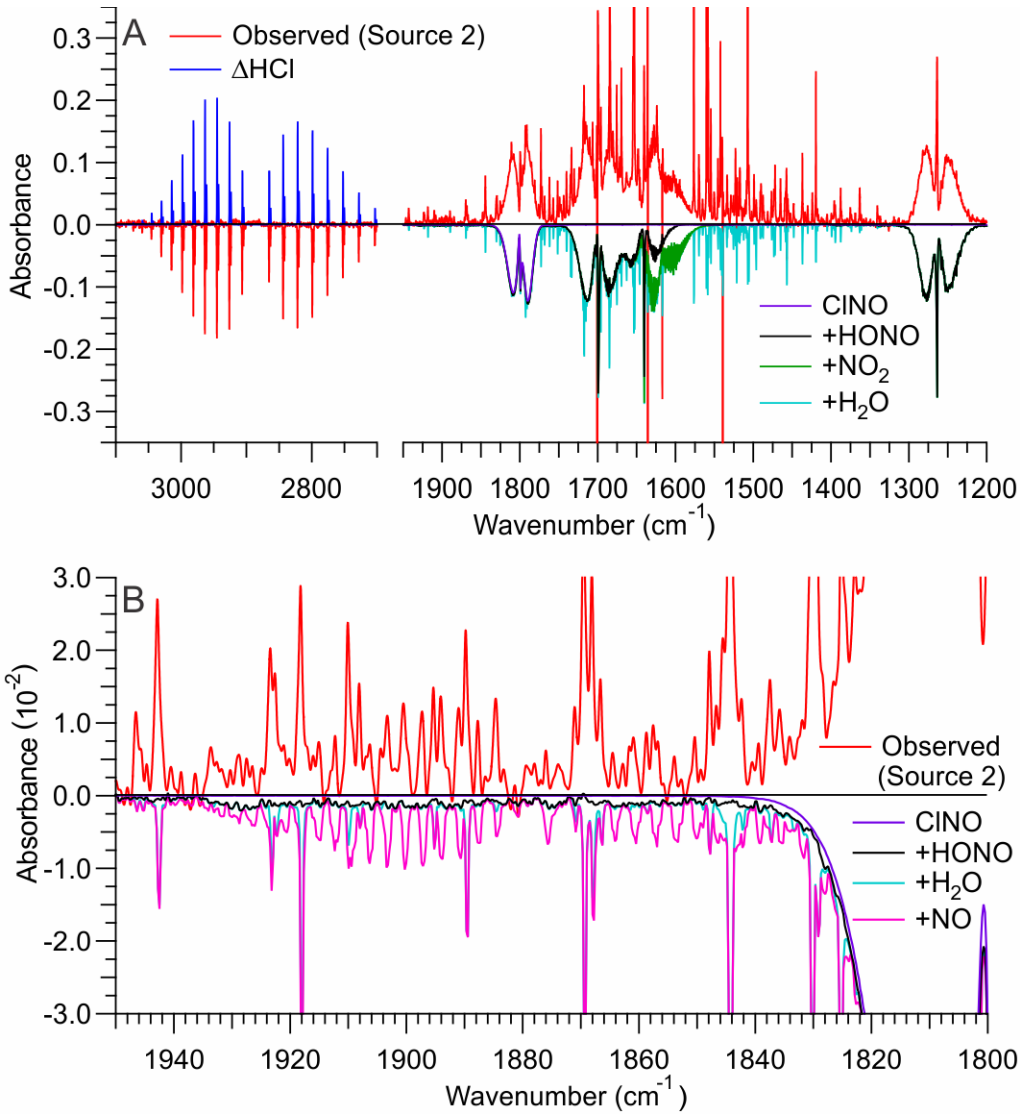

Figure S2. Infrared spectrum (shown in red colour) of a gas stream generated by reaction of $HCl_{(g)}$ with $NaNO_{2(s)}$ using source 2. In this example, source 2 emitted ~48 ppmv of HONO, ~6.5 ppmv of ClNO, ~8.0 ppmv of NO_2 and ~80 ppmv of H_2O and consumed >41.5 ppmv of HCl. (B) An expanded view of the 1950 to 1800 cm^{-1} spectral region. The spectrum expected for ~8.0 ppmv of NO is superimposed.

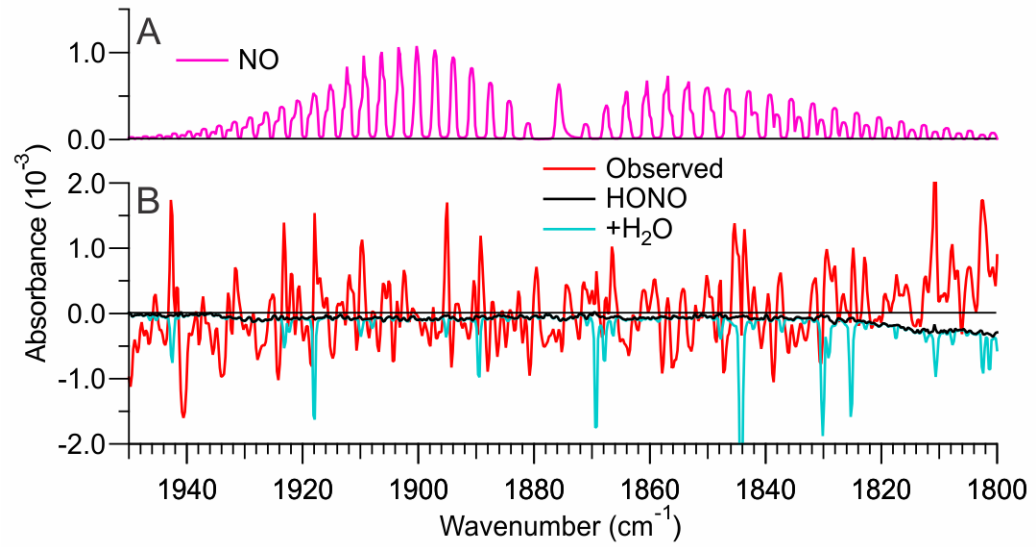

Figure S3. (A) Expected spectrum (Sharpe et al., 2004) for ~1.0 ppmv of NO. (B) Infrared spectrum (shown in red colour) of the optimized source demonstrating the absence of NO.

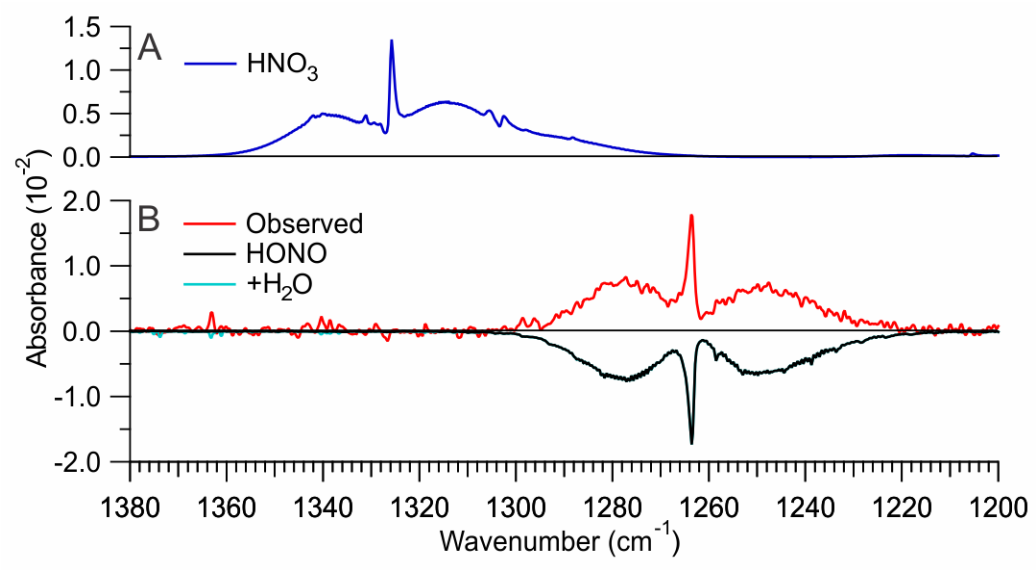

Figure S4. (A) Expected spectrum (Sharpe et al., 2004) for ~1.0 ppmv of HNO_3. (B) Infrared spectrum (shown in red colour) of the optimized source demonstrating the absence of HNO_3.

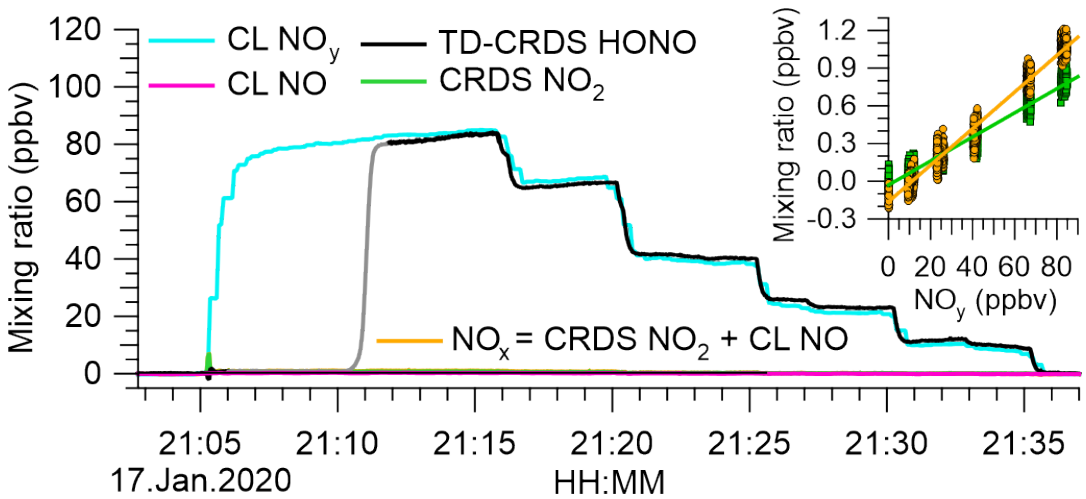

Figure S5. Sample field analysis of the HONO source output. The TD-CRDS and CL instruments sampled scrubbed "zero" air before 21:05 and after 21:36. The HONO source output was added at 21:05:30. Only the CL NO_y responded because the TD-CRDS quartz inlet temperature was 200 °C. At 21:10, the temperature of the quartz inlet was increased from 200 °C to 600 °C to quantify HONO. The absence of an inflection point and prior agreement with the NO_x measurement implies the absence of ClNO. At 21:16 and every ~5 min thereafter, the HONO output concentration was decreased by slightly opening the bypass valve. The insert shows scatter plots of NO_2 and NO_x (calculated by adding CL NO and CRDS NO_2 data) against NO_y. Slopes and offsets were (0.96±0.05)% and -(30±3) pptv for NO_2 (points shown in green) and (1.46±0.08)% and -(164±4) pptv for NO_x (data points shown in orange), respectively.

References

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.