

# Revised line-strengths and peak-positions for *cis*-HONO at 1660 $\text{cm}^{-1}$ using a new cw-QC TILDAS



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## Abstract

Nitrous acid, HONO, is a significant source of atmospheric HO, and the production of HONO may be responsible for the recycling of deposited  $\text{NO}_x$  back into the atmosphere in active form. Many current techniques rely on wet-chemical extractive methods, but are potentially prone to interferences and have not always shown good agreement with optical techniques<sup>5</sup>. Spectroscopy offers an alternative method with greater specificity, however, the rotational-vibrational transitions of HONO in the mid-infrared region are not well known. We present results from an experiment using a new tunable continuous-wave quantum cascade laser absorption spectrometer. We measured the *cis*-HONO spectra between 1659 and 1660  $\text{cm}^{-1}$  and the *trans*-HONO spectra near 1275  $\text{cm}^{-1}$  (both at a resolution of about 0.001  $\text{cm}^{-1}$ ). Absolute mixing ratios of total HONO were determined by catalytic conversion to NO followed by calibrated absorption spectroscopy. The effective line-strengths for *cis*-HONO near 1660  $\text{cm}^{-1}$  were about a factor of 2.5 smaller than those listed in the ATMOS database, but line-strengths for *trans*-HONO around 1275  $\text{cm}^{-1}$  agreed well with reported values.

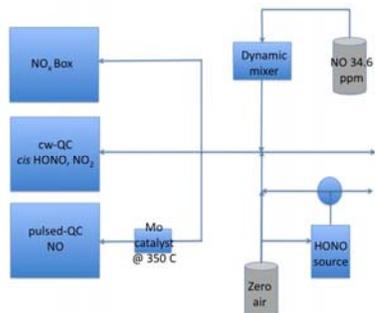
<sup>5</sup> J. Kleffmann, J. C. Lörzer, P. Wiesen, C. Kern, S. Trick, R. Volkamer, M. Rodenas and K. Wirtz, *Atmospheric Environment*, **40**, March 2006.

## Method + Setup

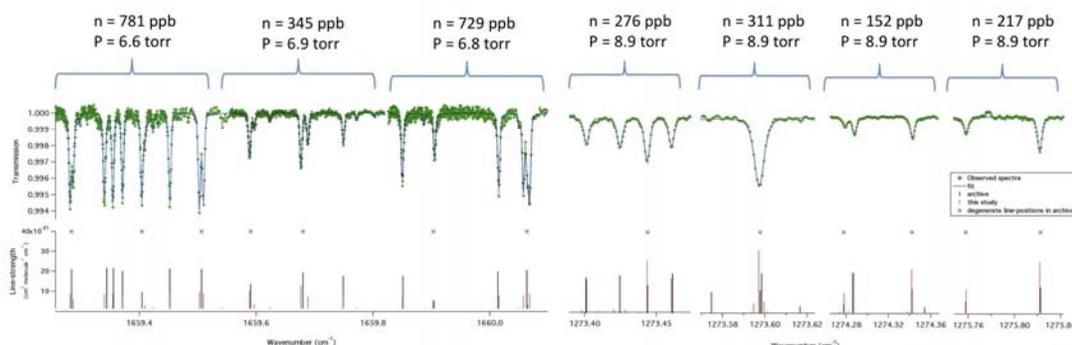
- High purity HONO generated and simultaneously sampled by two spectrometers to determine the effective line-strengths of the ro-vibrational transitions of the *cis* conformer of HONO;

- One spectrometer equipped with two cw QC lasers simultaneously measured HONO absorbance (1659 to 1660  $\text{cm}^{-1}$ ) and  $\text{NO}_2$  (1604  $\text{cm}^{-1}$ ) mixing ratio over a 210 m path-length in a 5 L astigmatic multi-pass sampling cell;

- Second spectrometer (pulsed QC laser) measured NO (1906  $\text{cm}^{-1}$ ) resulting from the complete reduction of HONO to NO by heated Mo converter and was calibrated by a traceable standard.



## Results



• Effective line-strengths (at 303 K) for the ro-vibrational transitions of *cis*-HONO (1659 to 1660  $\text{cm}^{-1}$ ) are low by a factor of  $\sim 2.5$  compared to archive values (based on ATMOS), and consistent with those listed in PNNL database (not shown);

• Line-strengths for *trans*-HONO (1273 to 1276  $\text{cm}^{-1}$ ) within 10% of both archive and PNNL database.

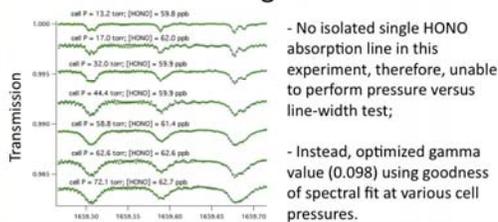
Archive: line-positions and relative line-strengths derived from high-resolution FTIR spectra [M. Herman], and scaled using values listed in the ATMOS database to obtain absolute strengths. The *trans*  $\nu_3$  (1200  $\text{cm}^{-1}$ ) band was scaled using absolute values provided in ATMOS for the *trans*  $\nu_2$  (1700  $\text{cm}^{-1}$ ) band.

### Experimental results

| Peak position ( $\text{cm}^{-1}$ ) | Line strength ( $\text{cm}^{-1}$ ) |
|------------------------------------|------------------------------------|
| 1659.2117                          | 0.001                              |
| 1659.2991                          | 0.001                              |
| 1659.3495                          | 0.001                              |
| 1659.3999                          | 0.001                              |
| 1659.4503                          | 0.001                              |
| 1659.5007                          | 0.001                              |
| 1659.5511                          | 0.001                              |
| 1659.6015                          | 0.001                              |
| 1659.6519                          | 0.001                              |
| 1659.7023                          | 0.001                              |
| 1659.7527                          | 0.001                              |
| 1659.8031                          | 0.001                              |
| 1659.8535                          | 0.001                              |
| 1659.9039                          | 0.001                              |
| 1659.9543                          | 0.001                              |
| 1660.0047                          | 0.001                              |
| 1660.0551                          | 0.001                              |
| 1660.1055                          | 0.001                              |
| 1660.1559                          | 0.001                              |
| 1660.2063                          | 0.001                              |
| 1660.2567                          | 0.001                              |
| 1660.3071                          | 0.001                              |
| 1660.3575                          | 0.001                              |
| 1660.4079                          | 0.001                              |
| 1660.4583                          | 0.001                              |
| 1660.5087                          | 0.001                              |
| 1660.5591                          | 0.001                              |
| 1660.6095                          | 0.001                              |
| 1660.6599                          | 0.001                              |
| 1660.7103                          | 0.001                              |
| 1660.7607                          | 0.001                              |
| 1660.8111                          | 0.001                              |
| 1660.8615                          | 0.001                              |
| 1660.9119                          | 0.001                              |
| 1660.9623                          | 0.001                              |
| 1661.0127                          | 0.001                              |
| 1661.0631                          | 0.001                              |
| 1661.1135                          | 0.001                              |
| 1661.1639                          | 0.001                              |
| 1661.2143                          | 0.001                              |
| 1661.2647                          | 0.001                              |
| 1661.3151                          | 0.001                              |
| 1661.3655                          | 0.001                              |
| 1661.4159                          | 0.001                              |
| 1661.4663                          | 0.001                              |
| 1661.5167                          | 0.001                              |
| 1661.5671                          | 0.001                              |
| 1661.6175                          | 0.001                              |
| 1661.6679                          | 0.001                              |
| 1661.7183                          | 0.001                              |
| 1661.7687                          | 0.001                              |
| 1661.8191                          | 0.001                              |
| 1661.8695                          | 0.001                              |
| 1661.9199                          | 0.001                              |
| 1661.9703                          | 0.001                              |
| 1662.0207                          | 0.001                              |
| 1662.0711                          | 0.001                              |
| 1662.1215                          | 0.001                              |
| 1662.1719                          | 0.001                              |
| 1662.2223                          | 0.001                              |
| 1662.2727                          | 0.001                              |
| 1662.3231                          | 0.001                              |
| 1662.3735                          | 0.001                              |
| 1662.4239                          | 0.001                              |
| 1662.4743                          | 0.001                              |
| 1662.5247                          | 0.001                              |
| 1662.5751                          | 0.001                              |
| 1662.6255                          | 0.001                              |
| 1662.6759                          | 0.001                              |
| 1662.7263                          | 0.001                              |
| 1662.7767                          | 0.001                              |
| 1662.8271                          | 0.001                              |
| 1662.8775                          | 0.001                              |
| 1662.9279                          | 0.001                              |
| 1662.9783                          | 0.001                              |
| 1663.0287                          | 0.001                              |
| 1663.0791                          | 0.001                              |
| 1663.1295                          | 0.001                              |
| 1663.1799                          | 0.001                              |
| 1663.2303                          | 0.001                              |
| 1663.2807                          | 0.001                              |
| 1663.3311                          | 0.001                              |
| 1663.3815                          | 0.001                              |
| 1663.4319                          | 0.001                              |
| 1663.4823                          | 0.001                              |
| 1663.5327                          | 0.001                              |
| 1663.5831                          | 0.001                              |
| 1663.6335                          | 0.001                              |
| 1663.6839                          | 0.001                              |
| 1663.7343                          | 0.001                              |
| 1663.7847                          | 0.001                              |
| 1663.8351                          | 0.001                              |
| 1663.8855                          | 0.001                              |
| 1663.9359                          | 0.001                              |
| 1663.9863                          | 0.001                              |
| 1664.0367                          | 0.001                              |
| 1664.0871                          | 0.001                              |
| 1664.1375                          | 0.001                              |
| 1664.1879                          | 0.001                              |
| 1664.2383                          | 0.001                              |
| 1664.2887                          | 0.001                              |
| 1664.3391                          | 0.001                              |
| 1664.3895                          | 0.001                              |
| 1664.4399                          | 0.001                              |
| 1664.4903                          | 0.001                              |
| 1664.5407                          | 0.001                              |
| 1664.5911                          | 0.001                              |
| 1664.6415                          | 0.001                              |
| 1664.6919                          | 0.001                              |
| 1664.7423                          | 0.001                              |
| 1664.7927                          | 0.001                              |
| 1664.8431                          | 0.001                              |
| 1664.8935                          | 0.001                              |
| 1664.9439                          | 0.001                              |
| 1664.9943                          | 0.001                              |
| 1665.0447                          | 0.001                              |
| 1665.0951                          | 0.001                              |
| 1665.1455                          | 0.001                              |
| 1665.1959                          | 0.001                              |
| 1665.2463                          | 0.001                              |
| 1665.2967                          | 0.001                              |
| 1665.3471                          | 0.001                              |
| 1665.3975                          | 0.001                              |
| 1665.4479                          | 0.001                              |
| 1665.4983                          | 0.001                              |
| 1665.5487                          | 0.001                              |
| 1665.5991                          | 0.001                              |
| 1665.6495                          | 0.001                              |
| 1665.6999                          | 0.001                              |
| 1665.7503                          | 0.001                              |
| 1665.8007                          | 0.001                              |
| 1665.8511                          | 0.001                              |
| 1665.9015                          | 0.001                              |
| 1665.9519                          | 0.001                              |
| 1666.0023                          | 0.001                              |
| 1666.0527                          | 0.001                              |
| 1666.1031                          | 0.001                              |
| 1666.1535                          | 0.001                              |
| 1666.2039                          | 0.001                              |
| 1666.2543                          | 0.001                              |
| 1666.3047                          | 0.001                              |
| 1666.3551                          | 0.001                              |
| 1666.4055                          | 0.001                              |
| 1666.4559                          | 0.001                              |
| 1666.5063                          | 0.001                              |
| 1666.5567                          | 0.001                              |
| 1666.6071                          | 0.001                              |
| 1666.6575                          | 0.001                              |
| 1666.7079                          | 0.001                              |
| 1666.7583                          | 0.001                              |
| 1666.8087                          | 0.001                              |
| 1666.8591                          | 0.001                              |
| 1666.9095                          | 0.001                              |
| 1666.9599                          | 0.001                              |
| 1667.0103                          | 0.001                              |
| 1667.0607                          | 0.001                              |
| 1667.1111                          | 0.001                              |
| 1667.1615                          | 0.001                              |
| 1667.2119                          | 0.001                              |
| 1667.2623                          | 0.001                              |
| 1667.3127                          | 0.001                              |
| 1667.3631                          | 0.001                              |
| 1667.4135                          | 0.001                              |
| 1667.4639                          | 0.001                              |
| 1667.5143                          | 0.001                              |
| 1667.5647                          | 0.001                              |
| 1667.6151                          | 0.001                              |
| 1667.6655                          | 0.001                              |
| 1667.7159                          | 0.001                              |
| 1667.7663                          | 0.001                              |
| 1667.8167                          | 0.001                              |
| 1667.8671                          | 0.001                              |
| 1667.9175                          | 0.001                              |
| 1667.9679                          | 0.001                              |
| 1668.0183                          | 0.001                              |
| 1668.0687                          | 0.001                              |
| 1668.1191                          | 0.001                              |
| 1668.1695                          | 0.001                              |
| 1668.2199                          | 0.001                              |
| 1668.2703                          | 0.001                              |
| 1668.3207                          | 0.001                              |
| 1668.3711                          | 0.001                              |
| 1668.4215                          | 0.001                              |
| 1668.4719                          | 0.001                              |
| 1668.5223                          | 0.001                              |
| 1668.5727                          | 0.001                              |
| 1668.6231                          | 0.001                              |
| 1668.6735                          | 0.001                              |
| 1668.7239                          | 0.001                              |
| 1668.7743                          | 0.001                              |
| 1668.8247                          | 0.001                              |
| 1668.8751                          | 0.001                              |
| 1668.9255                          | 0.001                              |
| 1668.9759                          | 0.001                              |
| 1669.0263                          | 0.001                              |
| 1669.0767                          | 0.001                              |
| 1669.1271                          | 0.001                              |
| 1669.1775                          | 0.001                              |
| 1669.2279                          | 0.001                              |
| 1669.2783                          | 0.001                              |
| 1669.3287                          | 0.001                              |
| 1669.3791                          | 0.001                              |
| 1669.4295                          | 0.001                              |
| 1669.4799                          | 0.001                              |
| 1669.5303                          | 0.001                              |
| 1669.5807                          | 0.001                              |
| 1669.6311                          | 0.001                              |
| 1669.6815                          | 0.001                              |
| 1669.7319                          | 0.001                              |
| 1669.7823                          | 0.001                              |
| 1669.8327                          | 0.001                              |
| 1669.8831                          | 0.001                              |
| 1669.9335                          | 0.001                              |
| 1669.9839                          | 0.001                              |
| 1670.0343                          | 0.001                              |
| 1670.0847                          | 0.001                              |
| 1670.1351                          | 0.001                              |
| 1670.1855                          | 0.001                              |
| 1670.2359                          | 0.001                              |
| 1670.2863                          | 0.001                              |
| 1670.3367                          | 0.001                              |
| 1670.3871                          | 0.001                              |
| 1670.4375                          | 0.001                              |
| 1670.4879                          | 0.001                              |
| 1670.5383                          | 0.001                              |
| 1670.5887                          | 0.001                              |
| 1670.6391                          | 0.001                              |
| 1670.6895                          | 0.001                              |
| 1670.7399                          | 0.001                              |
| 1670.7903                          | 0.001                              |
| 1670.8407                          | 0.001                              |
| 1670.8911                          | 0.001                              |
| 1670.9415                          | 0.001                              |
| 1670.9919                          | 0.001                              |
| 1671.0423                          | 0.001                              |
| 1671.0927                          | 0.001                              |
| 1671.1431                          | 0.001                              |
| 1671.1935                          | 0.001                              |
| 1671.2439                          | 0.001                              |
| 1671.2943                          | 0.001                              |
| 1671.3447                          | 0.001                              |
| 1671.3951                          | 0.001                              |
| 1671.4455                          | 0.001                              |
| 1671.4959                          | 0.001                              |
| 1671.5463                          | 0.001                              |
| 1671.5967                          | 0.001                              |
| 1671.6471                          | 0.001                              |
| 1671.6975                          | 0.001                              |
| 1671.7479                          | 0.001                              |
| 1671.7983                          | 0.001                              |
| 1671.8487                          | 0.001                              |
| 1671.8991                          | 0.001                              |
| 1671.9495                          | 0.001                              |
| 1672.0                             | 0.001                              |

$\pm 3\%$  uncertainty in reported line-strengths

## Pressure-broadening coefficient



- No isolated single HONO absorption line in this experiment, therefore, unable to perform pressure versus line-width test;

- Instead, optimized gamma value (0.098) using goodness of spectral fit at various cell pressures.

## Conclusion / future work

- For *cis*-HONO at 1660  $\text{cm}^{-1}$ , ATMOS values high by factor of 2.5, perhaps reported absolute and not effective line-strength;

- Good agreement with ATMOS for *trans*-HONO in the R-branch, but not consistent with findings of Becker et al. [1995], which found values 2 times smaller than those reported by Maki (ATMOS) on the P-branch;

- Comparison to high-resolution FTIR spectra would aid in deciphering the disagreement.