First detection of meso-thermospheric Nitric Oxide (NO) by ground-based FTIR solar absorption spectroscopy

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Received 7 October 2005; revised 20 December 2005; accepted 3 January 2006; published 9 February 2006.

[1] We report the first detection of mesospheric-lower thermospheric (MLT, 50–130 km) NO from ground-based FTIR solar absorption spectra using Lorentz- and Doppler-broadened solar absorption lines in the stratosphere and in the MLT, respectively. We present the first characterization of vertical sensitivity in the FTIR NO retrieval and show that MLT NO partial columns can be retrieved with ~1 independent piece of information using a climatological NO profile extending up to 130 km. The information content analysis also improves the characterization of stratospheric partial column retrievals and is relevant to NO results obtained at other Network for the Detection of Stratospheric Change (NDSC) FTIR sites. We apply our approach to spectra recorded at Complementary NDSC site Toronto (43.66°N, 79.40°W) during the solar storms of Oct–Nov 2003 and at Primary NDSC site Eureka (80.05°N, 86.42°W) during Feb–Mar 2004. MLT NO enhancements are found at Eureka, while possible enhancements at Toronto cannot be attributed to a particular altitude. **Citation:** Wiacek, A., N. B. Jones, K. Strong, J. R. Taylor, R. L. Mittermeier, and H. Fast (2006), First detection of meso-thermospheric Nitric Oxide (NO) by ground-based FTIR solar absorption spectroscopy, *Geophys. Res. Lett.*, *33*, L03811, doi:10.1029/2005GL024897.

1. Introduction

[2] NO is an important atmospheric trace constituent. In the troposphere it is a precursor of ozone (O_3) formation, whereas in the stratosphere it participates in its catalytic destruction. Increased MLT NO serves as a proxy for increased solar activity, with mesospheric NO produced by Solar Proton Events (SPE) and thermospheric NO produced by, for example, energetic electrons or increased X-ray activity [e.g., *Semeniuk et al.*, 2005]; X-ray sources of NO need not be confined to the magnetic pole. NO produced by any of these mechanisms can be transported into the stratosphere during polar night by downwelling meridional circulation where it can later cause significant O_3 destruction [*Callis et al.*, 1996; *Jackman et al.*, 2005; *Rozanov et al.*, 2005]. *Rinsland et al.* [2005] recently showed the long-lasting effects on NO_x(= NO + NO_2) of the powerful Oct–Nov 2003 SPEs [*Woods et al.*, 2004] and subsequent production.

[3] In this study we outline a retrieval approach used with the well-characterized optimal estimation-based [*Rodgers*, 2000] retrieval algorithm SFIT-2 (v.3.91) [e.g., *Hase et al.*, 2004; *Rinsland et al.*, 1998], which enables the detection of MLT NO. The proper treatment of the MLT NO spectral signature in the inversion process also leads to an improved characterization of stratospheric partial column NO retrievals. We characterize the retrieval performed on a discrete 41 layer grid in terms of vertical resolution and information content from 0–130 km, and finally, apply our approach to spectra recorded at Toronto (54°N geomagnetic latitude) during the period of enhanced solar activity in Oct–Nov 2003 and at Eureka during the previously-described chemical enhancements of Feb–Mar 2004 [*Natarajan et al.*, 2004; *Orsolini et al.*, 2005; *Randall et al.*, 2005; *Rinsland et al.*, 2005; *Seppälä et al.*, 2004].

2. Retrieval Approach

[4] The NO fundamental band absorption feature near 1900 cm^{-1} used in ground-based (g-b) solar absorption Fourier Transform InfraRed (FTIR) spectroscopy is known for its relatively low and highly variable Signal-to-Noise Ratio (SNR) primarily due to broad absorption features by water (H_2O). *Notholt et al.* [1995] have reported g-b vertical column densities of NO retrieved from this interval using a non-linear least squares spectral fitting algorithm. The approximate volume mixing ratio (vmr) a priori profile used by *Notholt et al.* is shown in Figure 1, together with the revised and vertically extended NO vmr a priori profile used in our study, which is based on 123 HALOE sunset profiles between 1991 and 2004 within ±5° N-S and E-W of Toronto. Within each HALOE profile only measurements with random errors less than 50% of the retrieved value were used to calculate seasonal means, which were then averaged to give an annual mean. At altitudes below 20 km the MIPAS reference profile for NO was used (www.atm.ox.ac.uk/group/mipas/species/no.html); however, the retrieval is not sensitive to the high densities found near the surface since their spectral signatures are highly pressure broadened and well below the detection limits dictated by the SNR. Figure 1 also shows satellite measurements of NO_x enhancements highlighted by, for example, *Semeniuk et al.* [2005], some nearly two orders of magnitude larger than normal.

[5] We have extended the retrieval grid lid from 100 to 130 km since approximately 74% of the thermospheric column (90–130 km) and 11% of the total column (0–130 km) are found between 100–130 km during undisturbed conditions (Table 1). This upper limit captures the thermospheric peak of NO and NO variability [*Barth et al.*, 2003]. Assuming a 10-fold vmr enhancement between 90–

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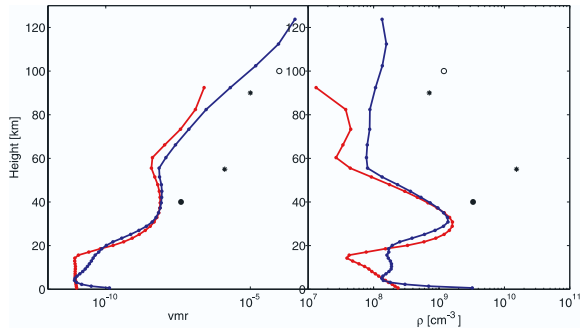

Figure 1. The NO a priori profile used in this study (blue; see text for details). NO a priori profile after *Notholt et al.* [1995] (red) and satellite measurements of NO enhancements are shown for reference (open circle = HALOE 75S Nov 2003; solid circle = HALOE 71N Apr 2004; asterisk = ACE-FTS 80N Feb 2004).

130 km typical of enhanced solar activity or wintertime auroral activity, as much as 53% of the total column of NO can be found between 100–130 km (64% between 90–130 km), which will lead to errors in the retrieved vertical distribution of NO when the retrieval lid is only at 100 km. The effect of setting the NO vmr to 1e-11 between 50–130 km (a depletion relative to the vmr profile in Figure 1) on the forward modelled spectrum is shown in Figure 2. Neglecting NO in the MLT in this manner results in ≈6% higher transmission levels for Solar Zenith Angle (SZA) of 85°. Conversely, the effect of a 10-fold enhancement in the MLT NO vmr profile results in ≈40% lower transmission levels (Figure 2). When transmissions are modelled at SZA = 45° (not shown), the peak differences are still well within the detection limits of the g-b FTIR technique at ≈2% and 17%, respectively. Thus, the impact of extending the retrieval grid above 130 km is non-negligible during conditions of strong enhancement.

[6] Our retrieval approach consists of simultaneously fitting the high resolution (0.004 cm^{-1}) solar absorption spectrum of NO in the microwindows listed in Table 2. NO absorption features were identified using the line-finding program of *Notholt et al.* [2006]. Using the spectroscopic parameters of HITRAN 2004 [*Rothman et al.*, 2005] and pressure and temperature profile information from daily sonde launches (available only for Eureka) and NCEP (obtained from the Goddard Automailer, science@

Table 1. Fraction (×10^{14} molec/cm^2) and Percent (in Brackets) of Total NO Column Formed in Each Region of the Atmosphere for the *a priori* vmr Profile Used in This Study and (A) 0–100 km Retrieval Grid, (B) 0–130 km Retrieval Grid, (C) 10-fold vmr Enhancement Between 90–130 km, (D) 10-fold vmr Enhancement Between 50–90 km (Both Enhancements are Consistent With Satellite Measurements in Figure 1)

	Tropo 0–15	Strato 15–50	Meso 50–90	Thermo 90–130[a]	Total 0–130[a]
(A)	0.55 (17)	2.24 (69)	0.34 (10)	0.15 (05)	3.27 (100)
(B)	0.55 (15)	2.24 (61)	0.34 (09)	0.57 (15)	3.70 (100)
(C)	0.55 (06)	2.24 (26)	0.35 (04)	5.60 (64)	8.74 (100)
(D)	0.55 (09)	2.24 (35)	3.06 (47)	0.59 (09)	6.45 (100)

[a]Except in (A) where only 90–100 km and 0–100 km.

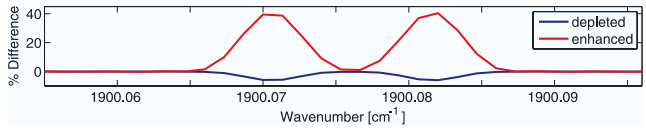

Figure 2. Modelled transmission differences (SZA = 85°) for an a priori profile that is depleted or enhanced in NO between 50–130 km (see text for details).

hyperion.gsfc.nasa.gov), NO was fitted as a profile while the a priori profiles of H_2O and O_3 were scaled by a single factor in the retrieval. In each microwindow we also retrieved a single wave number shift, a broad slope and a curvature parameter; interfering solar CO absorption features were also modelled and retrieved.

[7] The measurement covariance matrix (S_e) for Eureka retrievals was set to be diagonal and to correspond to a SNR of 500, which is on average appropriate for all microwindows and spectra. Toronto retrievals (only performed over microwindows with sufficiently high SNRs) used a variable S_e to account for the varying SNR in the spectra due to strong absorption by H_2O. Finally, the NO a priori covariance matrix (S_a) was set to be diagonal and 100% on all levels for both sites.

3. Retrieval Characterization

[8] When the NO a priori vmr profile is increased to agree with the HALOE climatology (which is much lower than the observed enhancements) and the retrieval grid is extended to 130 km then sensitivity to the MLT region increases in the NO retrieval. The weighting function matrix (Figure 3) shows two distinct regions of vertical sensitivity: in the stratosphere (mixed Lorentz and Doppler broadening) and in the MLT (Doppler broadening). While each partial column region is characterized by more than one independent piece of information (degrees of freedom for signal (d_s) > 1), the partial column averaging kernels are not ideally separated in altitude (Figure 3); therefore, the retrieved partial columns are not completely uncorrelated. This is expected since the spectral signatures of mixed Lorentz and Doppler broadening and pure Doppler broadening shown in Figure 3 are of comparable width.

[9] It is instructive to contrast these findings with strato-mesospheric retrievals of CO reported by *Kasai et al.* [2005]. Since CO is mainly a tropospheric species, there is a sharp contrast between the broad tropospheric Lorentz lineshapes and the narrow Doppler lineshapes of higher altitudes. Accordingly, the averaging kernels for that retrieval are better separated in altitude. In the case of NO, whose peak density is normally found in the stratosphere, the Lorentz broadening is already narrow and comparable to

Table 2. Retrieval Intervals (cm^{-1}), Interfering Species and SNR for Toronto (T) and Eureka (E)

	(E)	SNR (E)	(T)	SNR (T)
1875.795–1875.830	NO	500	–	–
1900.055–1900.100	NO	500	NO	320
1900.500–1900.540	NO	500	NO	250
1903.050–1903.200	NO	500	NO, H_2O	150
1906.120–1906.175	NO	500	–	–
1975.283–1975.408	H_2O, O_3	500	–	–

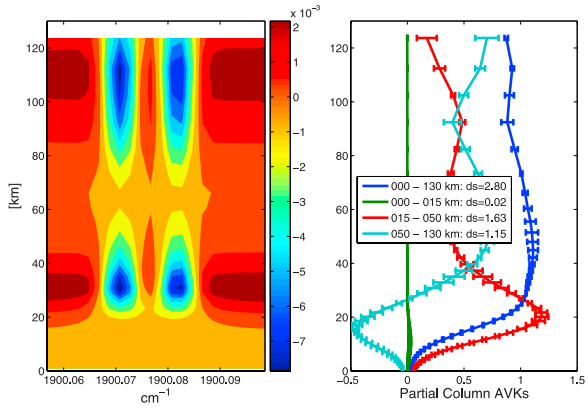

Figure 3. (left) Average (for all Eureka data) NO weighting function matrix in one microwindow. (right) Average Eureka partial column averaging kernels for NO (error bars show std. deviation).

Doppler broadening, leading to potential mis-assignment of altitude in the retrieval. If the a priori profile is unchanged from that used by *Notholt et al.* [1995] then the weighting function matrix will tend to zero in the MLT and any NO enhancements in this region will automatically be assigned to the stratosphere, regardless of the S_e and S_a employed in the retrievals.

[10] The total column averaging kernel for Eureka retrievals (Figure 3) shows good sensitivity from 20–130 km, while in Toronto retrievals (not shown) it drops off above 100 km and reaches ~0.75 at 120 km. This is due to generally smaller SZAs and SNRs in Toronto spectra and is reflected in lower d_s values (0–130 km: 1.67; 0–15 km: 0.03; 15–50 km: 1.06; 50–130 km: 0.58). Furthermore, the average a priori contribution to the retrieved partial columns at Eureka was calculated as 2.3%, 94.1%, −2.7%, and 5.7% between 0–130 km, 0–15 km, 15–50 km, and 50–130 km, respectively. Finally, the average errors in the same partial columns at Eureka due to errors in the temperature profile were calculated as 1.9%, 2.6%, 3.2%, and 6.7%, respectively, assuming a 100 K^2 (25 K^2) temperature variance above (below) 50 km and a 5 km correlation length [see, e.g., *Rodgers*, 2000]. Since larger temperature variations are possible in the MLT region, their effect on retrievals should be investigated further.

4. Observations of NO Enhancements

[11] Temporal sampling of Toronto NO measurements was poor in late 2003 but spectra were recorded on Jun 19, Aug 20, Oct 7, Oct 24, Nov 07, and Nov 10 (Figure 4). The Oct 24 record was well into the period of enhancements but before the super flare of Oct 28; the Nov 7 and Nov 10 records follow the super flare of Nov 5 [*Woods et al.*, 2004]. These fall total columns are as high as those recorded in the summer, possibly indicating a detection of the known MLT NO enhancements; however, in Figure 4, any enhancements in Oct–Nov 2003 are attributed to the stratosphere (stratospheric partial columns are well-correlated with total columns). This is not consistent with the seasonal decrease of stratospheric NO toward the winter at mid-latitudes. In this context, the total column values recorded in Oct–Nov 2003 may indicate MLT enhancements.

[12] Photochemical box model calculations provided by C. A. McLinden (personal communication) indicate that the stratospheric column of NO increases by ≈18% in July and 40% in January from 10AM to 4PM. This is not enough to explain the elevated total column values over Toronto in Oct–Nov 2003, especially given that all 2003 spectra were recorded between 10AM–2PM (2004 Eureka spectra were recorded near 9AM and noon).

[13] Finally, the noontime photochemical lifetime of NO_x in the mesosphere and thermosphere at sunlit midlatitudes is 1–2 days [*Brasseur and Solomon*, 1986; *Jackman et al.*, 2005]. In the lower mesosphere and upper stratosphere the lifetime of NO_x increases to weeks. Thus, given Toronto's geomagnetic latitude and the presence of powerful SPEs and secondary NO sources (X-rays and energetic electrons) that all persisted for about two weeks, it is reasonable to expect that NO would remain enhanced long enough to be measured at Toronto on Oct 24, Nov 07 and Nov 10.

[14] For spectra recorded at Eureka, the total columns are elevated but not correlated with stratospheric columns as in Toronto data (Figure 5). High values retrieved in the MLT before day 70 also correspond to high Potential Vorticity (PV) values, albeit at lower altitudes (1 mb, Goddard Automailer). After this date the MLT partial columns decrease rapidly over ~5 days, seemingly due to disturbed dynamic conditions. Photochemical destruction is also playing a role in the decreasing MLT concentrations (polar

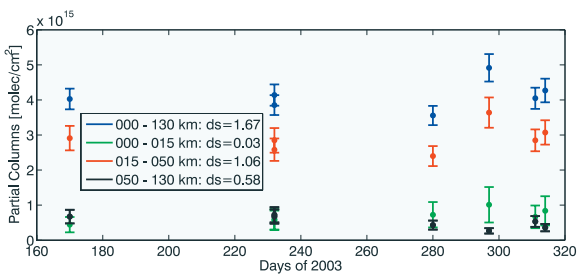

Figure 4. Partial columns of NO retrieved over Toronto (SPEs occurred between day 291–309).

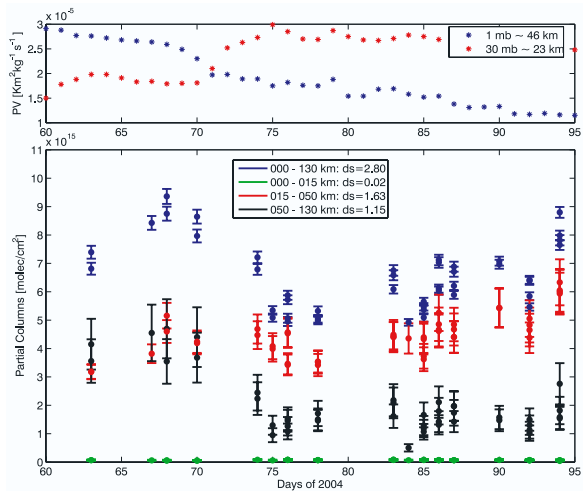

Figure 5. NO partial columns retrieved over Eureka. PV indicates disturbed dynamic conditions near day 70.

sunrise occurs on day 51); however, *Rinsland et al.* [2005] have reported an elevated-NO_x e-folding time of 15 days between day 46–83, thus we still expect to observe elevated MLT concentrations during our measurement interval. After day 70 we observe increasing stratospheric partial columns associated with the release of NO_x from HNO_3 and N_2O_5.

5. Summary and Conclusions

[15] We have demonstrated that the g-b solar absorption FTIR retrieval has a sensitivity to MLT NO partial columns ($d_s \sim 1$) provided that: 1) a reasonable vmr a priori profile is used, 2) the retrieval grid is extended to 130 km, and 3) the spectra are recorded at high SNRs and SZAs. A full averaging kernel and information content analysis reveals that when the above conditions are not met then enhancements in MLT partial columns will be incorrectly assigned to the stratosphere. Further increases to the information content and vertical resolution of NO retrievals are possible given measurements with an increased spectral resolution and a higher signal to noise ratio, as well as through the use of a more detailed forward model of the NO absorption lineshape in the retrieval process.

[16] The g-b FTIR retrieval provides an additional means of constraining satellite measurements of baseline and SPE-enhanced MLT NO concentrations, especially at NDSC sites and during campaigns operated in the vicinity of the magnetic pole, where MLT NO production is high.

[17] **Acknowledgments.** We thank C. A. McLinden for providing photochemical box model calculations. We gratefully acknowledge the Goddard Automailer for providing meteorological data and the HALOE and ACE Teams for making NO data available. TAO received support from NSERC, PREA, CFI, ORDCF, CRESTech and ABB Bomem Inc. A. Wiacek received support from OGS and Zonta International. N. B. Jones received support from ARC grant DP0452910. R. L. Mittermeier and H. Fast thank K. MacQuarrie for recording Eureka spectra.

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