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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The observation of chemiluminescent NiO* emissions in the laboratory and in the night airglow" *by* W. F. J. Evans et al.

Anonymous Referee #2

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Article: The observation of chemiluminescent NiO* emissions in the laboratory and in the night airglow. Authors: W.F.J. Evans, R.L. Gatiinger, A.L. Broadfoot, and E.J. Llewellyn

Referee Comment: This is a well written article which reports on the observations of chemiluminescent NiO* emissions observed in the night airglow using the GLO-1 and Osiris spectrographs. These are space-born limb-viewing instruments purported to enhance the spectra by a factor of 50 due to a reduction of the atmospheric background.

The method involved is to take the averaged spectrograph data, subtract from it a simulated night airglow spectrum matching several known features and arrive at a difference

spectrum which will contain the NiO* emission. The result is shown in panel C of figure 2 in the article. A somewhat broad and tenuous feature is seen in the blue spectral region with an emission onset around 440nm and extending to the red. Also indicated in panel C of the figure is a chemiluminescent spectrum of NO + O $\rightarrow$ NO* which is somewhat similar to the NiO* emission — the shape looks very similar but the onset is nearer 400nm. A spectrum of the FeO* emission is also given which looks like it may be responsible for a feature in the 590-600nm region.

The authors have developed a model spectrum for the NiO* emission based on known spectroscopic constants from laboratory data and by adapting the laboratory spectrum to conditions in the lower pressure mesopause. The authors state that the details of the model will be reported elsewhere as it is currently "preliminary". However the preliminary model is used in figure 3 to make comparisons to the GLO-1 difference spectrum from panel C of figure 2. Clearly the authors are using this to indicate that the emission observed is NiO*. This is troubling as without the details, either of the spectroscopic constants used, which vibrational levels are populated in the mesopause vs the laboratory, temperature, etc., no one else would be able to reproduce the model spectrum.

The same technique was also applied to the Osiris spectrograph data. The results are shown in figure 5 with panel C again giving the difference spectrum. A model spectrum of FeO* is again given in panel C for comparison. To my eye it seems that the FeO* emission accounts for the features in the difference spectrum and very little if any NiO* emission is present. Indeed the authors indicate that there is a huge variability in the observed NiO* to FeO* ratio in the night airglow. The authors indicate that the ratio is 3:1 in the GLO-1 data and approximately 1:3 in the Osiris data. This brings up another point which is also troubling and has been mentioned by referee #1 — the NO2 spectrum was not shown in the Osiris plot. If there is some variability in the NO2 emission, particularly if the emission were weaker, then the onset of the NO2 emission would be in the noise at the blue end but the stronger broad hump to the red would still show up. This would have the effect of appearing to have an onset of emission more to the red of 400nm — near 450nm for instance — while the broad peak in through the 500-600nm region would explain the emission that is present in the GLO-1 difference spectrum. This is speculation but is certainly worth some discussion.

I think it reasonable to expect that both of the points raised above must be clarified before this paper could be accepted for publication.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 11839, 2011.