Nonequilibrium calculations of the role of electron impact in the production of NO and its emissions

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Electron impact (photoelectron and auroral) in the Earth's upper atmosphere plays a major part in the production of nitric oxide and in infrared emissions from this species. The main production mechanism is electron impact ionisation and dissociation of atmospheric species, which produces $N(^2D)$ (excited N) that then reacts with O_2 to produce NO. A minor source is electron impact excitation of $N_2[A^3\Sigma_u^+]$, which reacts with O atoms to produce NO and $N(^2D)$. This $N(^2D)$ reacts with further O_2 to produce even more NO, enhancing the effect of this excitation source. The NO produced by $N(^2D) + O_2$ is vibrationally excited, leading to chemiluminescent infrared emissions. Recently direct electron impact excitation has also been shown to contribute to infrared emission by NO.

In order to investigate the importance of the $N_2[A^3\Sigma_u^+]$ source of NO, a model which predicts NO density in the atmosphere was developed. Above 130 km the NO density reaches a chemical equilibrium value that varies with solar insolation and auroral input. NO is transported downwards by molecular diffusion at altitudes above about 110 km and by eddy diffusion below this height. Vertical winds produced by auroral heating may also redistribute NO vertically. As a result of these transport processes the NO density does not reach a chemical equilibrium value at altitudes below 130 km, so a nonequilibrium calculation is required to predict the NO density in the region of its peak at around 110 km.

The model has been applied to predict the NO density profile in the upper atmosphere at the equator, and at 65° N with moderate auroral input. It was run with and without the $N_2[A^3\Sigma_u^+] + O$ reaction and in both the equatorial and high-latitude cases it was found that the contribution of this reaction is significant, and that the predicted densities are closer to the observed values when the $N_2[A^3\Sigma_u^+]$ contribution is included.

The model was then used to calculate the background NO density as part of an investigation of infrared emissions from NO. Auroral electron impact produces such emissions principally by chemiluminescent emission from NO* (vibrationally excited NO) that is produced by the $N + O_2$ reaction. However, measurements [1,2] of electron impact excitation of the first three vibrational levels of NO made possible calculations of the contribution of electron impact to the infrared emissions. It was found that the contribution is significant relative to chemiluminescence for the $v'=1$ level, while the smaller contribution for the other levels may nevertheless alter the spectrum from that of chemiluminescence in a way that could be exploited in remote sensing [3].

The nonequilibrium model to calculate NO density allowed a detailed calculation of these electron-driven infrared emissions for the particular conditions of a rocket measurement. It allowed both a calculation of the background NO density for the time and place, and of the increase in the density due to the auroral input. While there was a discrepancy between the absolute value of the predicted emissions and the experiment, it was found that the shape of the predicted spectrum of NO fundamental emissions matched the measurements better when direct electron excitation was included.

This simulation of the rocket measurements was recently repeated with new measurements [4] and theoretical calculations [5] of electron impact vibrational excitation of NO. In both cases the agreement with the measurements is improved for the $v'=1$ level [6], particularly using the new theoretical cross sections. However, the new values lead to an overestimation for $v'=2$.

In the three cases above, the reactions involved have a very wide range of reaction rates. Some of them (such as the excitation rates and radiative transition probabilities involved in calculating the production of $N_2[A^3\Sigma_u^+]$) have high rates so that equilibrium is reached in a small time. Others, such as those that produce and destroy NO, are sufficiently slow that the NO density does not reach chemical equilibrium in the time scale set by solar insolation and auroral variations. We use statistical equilibrium calculations for the fast reactions and time-step simulation for the slow reactions, so these two approaches need to be combined. For $N_2[A^3\Sigma_u^+]$ this is straight forward. The population densities of the excited states are calculated using statistical equilibrium and then imported into the time-step calculation. However, there are sets of related reactions, such as those involving $O^+(^4S)$, $O^+(^2D)$ and $O^+(^2P)$, where some of the reactions are too fast to be included in the time-step calculation. Our approach so far to these has been to identify the fast reactions and put an equilibrium calculation for each into the time-step code. We are currently looking at both conceptual and coding improvements to the methods of merging the equilibrium and nonequilibrium calculations.

[1] L. Josić, T. Wróblewski, Z. Lj. Petrović, J. Mechlińska-Drewko and G. P. Karwasz, *Chem. Phys. Lett.* **350** 318–324 (2001)

[2] M. Jelisavcic, R. Panajotovic and S. J. Buckman, *Phys. Rev. Lett.* **90** 203201-1–4 (2003)

[3] L. Campbell, M. J. Brunger, Z. Lj. Petrovic, M. Jelisavcic, R. Panajotovic and S. J. Buckman *Geophys. Res. Lett.* **31** L10103-1–4 (2004)

[4] M. Allan *J. Phys. B: At. Mol. Opt. Phys.* **38** 603–14 (2005)

[5] C. S. Trevisan, K. Houfek, Z. Zhang, A. E. Orel. C. W. McCurdy and T. N. Rescigno *Phys. Rev.* A **71** 052714-1–12 (2005)

[6] L. Campbell, M. J. Brunger and M. Allan *J. Phys. Conf. Ser.* in press (2008)