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Investigating the sensitivity of nitric oxide infrared emissions to electron impact

L Campbell[1], M J Brunger[1] and M. Allan[2]

[1] ARC Centre for Antimatter-Matter Studies, SoCPES, Flinders University, GPO Box 2100, Adelaide, SA 5001, Australia

[2] Department of Chemistry, University of Fribourg, chemin du Musée 9, 1700 Fribourg, Switzerland

E-mail: laurence.campbell@flinders.edu.au

Abstract. Integral cross sections for low energy electron excitation of the 0→1, 0→2 and 0→3 vibrational modes in nitric oxide have quite recently become available [Trevisan *et al.* PRA **71**, 052714 (2005)]. In this study we adapt our recent work [Campbell and Brunger GRL, in press (2007)], to look at the effect of these new cross sections on the production of nitric oxide infrared radiation. Predictions from our model are compared with measurements from Espy *et al.* [Planet. Space Sci. **36**, 543 (1988)], with the inclusion of the new cross sections improving the agreement of the shape of the spectrum with the measurements.

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1. Introduction

Nitric oxide is a minor constituent of the upper atmosphere. However, it is important because infrared radiation from nitric oxide is a significant cooling mechanism in this region. Thus computational models of the energy transfer processes in the atmosphere need to predict both the density of NO and the rate of infrared emission from it. We recently described an investigation of the contribution of electron impact to both the production of NO and its infrared emissions [1], particularly for pathways that have been neglected in other studies.

Electron impact produces NO indirectly by a number of mechanisms. The principal one is that photoelectrons (produced by sunlight) and auroral electrons dissociate N_2 into atoms that then take part in a chemiluminescent reaction with O_2. In this reaction most of the NO is produced in a vibrationally excited state and either radiatively decays, producing infrared emission, or is quenched in collisions. It is generally assumed that this chemiluminescent reaction, along with collisional excitation, accounts for all of the infrared emission from NO.

We have shown previously that other mechanisms due to electron impact may be important. The reactions of excited N_2 with O atoms are predicted to make a significant contribution to the NO density in both daytime and auroral conditions [2]. In our earlier work [1, 3] we employed low-energy electron impact cross sections for vibrational excitation of NO from [4, 5] that led for instance to predictions that electron impact makes a significant contribution to the $1 \rightarrow 0$ emission from NO. Here we reprise that earlier work by employing relatively recent vibrational (0→1, 0→2 and 0→3) integral cross sections [6] for electron impact excitation of NO. Those new cross sections include both theoretical complex-Kohn results, as well as experimental values derived by Trevisan *et al.* [6] from the excitation function measurements of Allan [7].

In this paper we compare our predictions to rocket measurements [8], in which all the electron-driven mechanisms need to be considered. The measurements are of infrared emissions produced in an aurora. As they depend on the NO density, this density is also calculated [1] for the conditions of the experiment. Based on this density the infrared emissions are predicted and then compared with the measurements. The sensitivity of the calculated results to various available integral cross sections [3, 6] is considered.

2. Sources of NO and emissions

NO in the upper atmosphere is produced principally by the reactions of ground and excited state nitrogen atoms, $N(^4S)$ and $N(^2D)$, with O_2 [9] :

$$N(^4S) + O_2 \rightarrow NO + O \quad \text{(R1)}$$

$$\text{and } N(^2D) + O_2 \rightarrow NO + O\ . \quad \text{(R2)}$$

In sunlight nitrogen atoms are produced by photodissociation of N_2 and reactions of ions produced by photoionisation. The latter creates photoelectrons which produce nitrogen atoms by dissociation and indirectly by further ion production. Nitrogen atoms and NO are similarly produced by electron impact by secondary electrons in aurora. These reactions, among others in a photochemical model, were used by Barth [9] to calculate densities of NO in the upper atmosphere.

Nighttime infrared emissions from vibrationally excited nitric oxide (NO^*) have been identified as due [8] to collisional excitation by O atoms (called nightglow),

$$NO(\nu' = 0) + O \rightarrow NO^*(\nu' = 1) + O \quad \text{(R3)}$$

and the chemiluminescent reaction:

$$N(^2D) + O_2 \rightarrow NO^*(\nu' = 1 - 12) + O\ . \quad \text{(R2}'\text{)}$$

The similar reaction

$$N(^4S) + O_2 \rightarrow NO^*(\nu' = 1 - 9) + O\ . \quad \text{(R1}'\text{)}$$

has been omitted in some cases due to its much lower reaction rate [10] , but is included in the calculations below.

The measurements [4, 5] of integral cross sections for low-energy electron-impact vibrational excitation of NO

$$NO(\nu'' = 0) + e^- \rightarrow NO^*(\nu' = 1 - 3) + e^-$$

made it possible to consider this as a source of NO^*. Those measurements were combined into the "current" set of cross sections [3] that were used in a detailed simulation of NO infrared measurements [1].

More recently Allan [7] measured the cross sections for these transitions at 135°. These excitation functions were scaled by 4π for comparison with new theoretical values of Trevisan *et al.* [6]. While such a scaling is probably not physical, even at these low energies, due to the anisotropy of scattering from NO, it was illustrative nonetheless. The three sets of cross sections are compared in figure 1, where the differences between them are manifest.

3. Prediction of NO Infrared Emissions

Measurements by Espy *et al.* [8] of the NO(1→0) emission during an aurora are shown in figure 2, as brightness (apparently at zenith, although this is not explicitly stated) as a function of height. The large scatter in the measurements is ascribed by Espy *et al.* to an instrumental problem. They present a fit to the data, using the measurement error as a guide to the weighting given to each data point, but they note that "the fitted curve probably underestimates the intensity at the higher altitudes".

Using the methods described by Campbell and Brunger [1], predictions of these emissions are made for a 3-minute aurora with a 557.7-nm brightness [11] of 40 kR, added on to a background NO density estimated for the solar and auroral conditions for the time of the measurement.

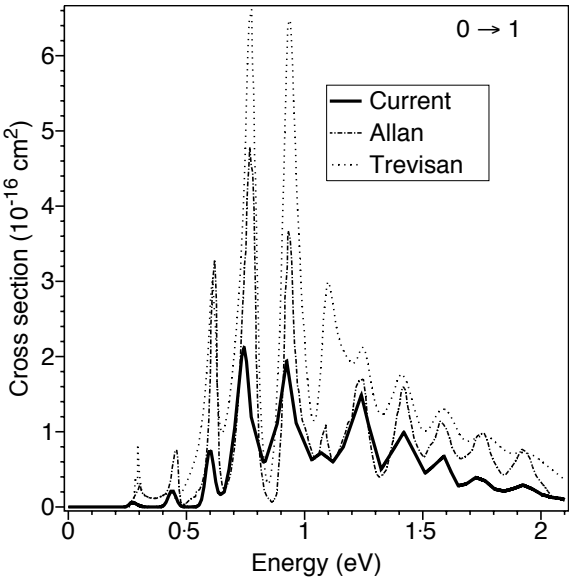

Figure 1. Integral cross sections for electron impact vibrational excitation (0→1) of NO from measurements [3] (———) and theory [6] (- - -), and the 4π-scaled measurements of Allan [6] (– · –).

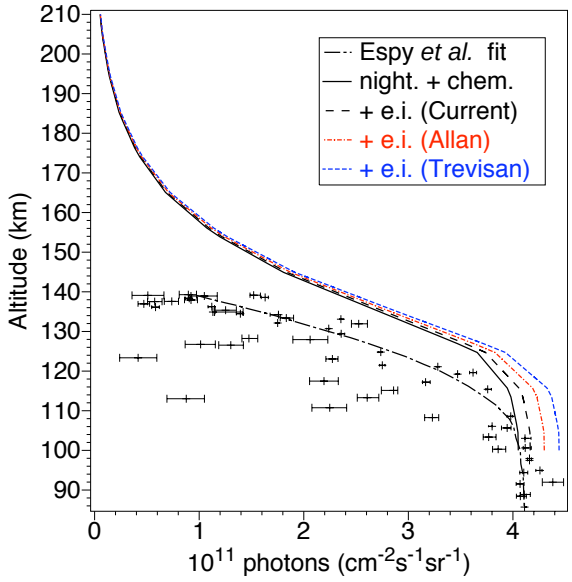

Figure 2. Measurements (|—|—|) of the brightness (looking upwards at the height on the vertical axis) of NO(1→0) emission and a fit (——— –) to them [8]. Predictions for nightglow plus chemiluminescent reactions only (———) and nightglow plus chemiluminescence plus electron impact for the "current" cross sections [3] (– – – –), the 4π-scaled values of Allan [6] (– · –) and the theoretical calculations of Trevisan *et al.* [6] (- - -) are shown.

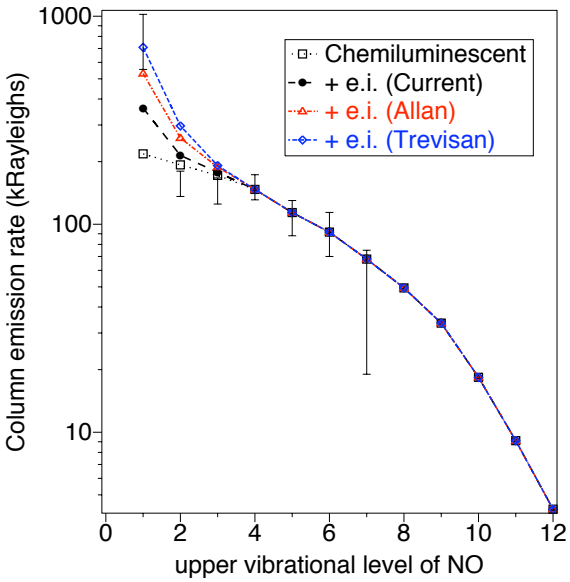

Figure 3. Measured [8] NO fundamental infrared emissions (I) as a function of the vibrational level of NO. Also shown are our predictions for chemiluminescent reactions only (··□··), and for chemiluminescent reactions plus electron impact calculated for the current cross sections (● – – ●), the 4π-scaled values of Allan (△–·–△) and the theoretical calculations of Trevisan *et al.* (◇ - - - ◇).

The predictions are made for the three cross-section sets *i.e.* the "current" case [3], the 4π-scaled values of Allan [6] and the theoretical values [6]. At 100 km the predicted brightness

is consistent with the measurements for all three cross-section sets. As the 1→0 emission is dominated by the nightglow, which is proportional to the NO density and therefore has an uncertainty of $\sim 10\%$ [2], no particular significance can be attached to the fact that one set gives better agreement than another. At higher altitudes the predicted values are larger than the measurements, but this is consistent with the likely "underestimation" referred to by Espy *et al.*

In figure 3 the predictions using the three cross-section sets are compared with values of the column emission rate (*i.e.* brightness looking towards zenith) for the fundamental ($\nu' \rightarrow \nu' - 1$) auroral emissions from NO calculated by Espy *et al.* from their measurements. The 557.7-nm brightness of 40 kR used in the calculations is much higher than the 5 kR specified by Espy *et al.* for the time of the measurements, but is chosen to match the predicted emission due to chemiluminescent reactions to the observations for $\nu' > 3$.

Espy *et al.* ascribed the peak in the auroral component for $\nu' = 1$ to the difficulty of separating it from the nightglow. However, as shown earlier [1], the inclusion of electron impact, based on the "current" cross sections [3] accounts for part of that peak for $\nu' = 1$. The predicted peak at $\nu' = 1$ is larger when the 4π-scaled values of Allan [6] are used. For the recent theoretical cross sections [6] the electron impact contribution is larger again and brings the prediction into good agreement with the measurements. However, the enhancement of the 2→1 emissions using the recent cross sections increases the discrepancy with the measured values. A possible explanation is that the new electron impact cross sections for 0→2 excitation are too large and that the "current" values are better. Another possibility is that the separation of the different emissions by Espy *et al.* was based on the assumption of a rotational temperature of 300 K for the chemiluminescent emissions, whereas the rotational temperature is likely to be different for electron impact.

4. Conclusions

A previous study involving predictions of auroral infrared emissions from nitric oxide has been repeated for more recent experimental and theoretical electron impact integral cross sections for vibrational excitation of NO. The more recent cross sections, particularly the theoretical, lead to predictions of a larger contribution due to electron impact. For the $1 \rightarrow 0$ emission the more recent experimental cross sections account for most of the previously unexplained spectral peak for this line, while the theoretical cross sections bring the predictions for $1 \rightarrow 0$ into agreement with the measurements. However, the discrepancy for the $2 \rightarrow 1$ emission is increased when using the more recent cross sections. Thus it would be advantageous to resolve the differences between different theoretical and experimental determinations of the electron impact vibrational cross sections in order to perform more accurate modeling of NO infrared emissions in the upper atmosphere.

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References

[1] Campbell L and Brunger M J 2007 *Geophys. Res. Lett.* **34** L22102, doi:10.1029/2007GL031743
[2] Campbell L, Brunger M J and Cartwright D C 2007 *J. Geophys. Res.* **112** A08303, doi:10.1029/2007JA012337
[3] Campbell L, Brunger M J, Petrovic Z Lj, Jelisavcic M, Panajotovic R and Buckman S J 2004 *Geo. Res. Lett.* **31** L10103, doi:10.1029/2003GL01915
[4] Josić L, Wróblewski T, Petrović Z Lj, Mechlińska-Drewko J and Karwasz G P 2001 *Chem. Phys. Lett.* **350** 31824
[5] Jelisavcic M, Panajotovic R and Buckman S J 2003 *Phys. Rev. Lett.* **90** 203201–4

[6] Trevisan C S, Houfek K, Zhang Z, Orel A E, McCurdy C W and Rescigno T N 2005 *Phys. Rev.* A **71**, 052714, doi: 10.1103/PhysRevA.71.052714
[7] Allan M 2005 *J. Phys. B: At. Mol. Opt. Phys.* **38** 603-14
[8] Espy P J, Harris C R, Steed A J, Ulwick J C, Haycock H and Straka R 1988 *Planet. Space Sci.* **36** 543–51
[9] Barth C A 1992 *Planet. Space Sci.* **40** 315–36
[10] Caledonia G E and Kennealy J P 1982 *Planet. Space Sci.* **30** 1043–56
[11] Campbell L, Cartwright D C, Brunger M J and Teubner P J O 2006 *J. Geophys. Res.* **111** A09317, doi:10.1029/2005JA011292