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<b>Reference number:</b>	944
Dates of Visit:	1 <sup>st</sup> April 2006 - 31 <sup>st</sup> July 2006
The title of project:	Electron induced reactions in pre-biotic planetary atmospheres

## **Purpose of Visit**

Ozone is believed to be one of the most important bio markers [1, 2, 3, 4, 5] for detection of extrasolar Earth-like planets. Its detection together with reducing gases (e.g. CH<sub>4</sub>) is suggested to be strong evidence and signposting for biological processes and hence for life being present on the planet [6, 7]. In contrast abiotic processes (electron or photon induced) are considered to be less likely but may be responsible for the initial formation of an ozone layer and thence protection of planetary surface from UV radiation allowing life to develop.

The main aim of visit was to develop a link between applied (atmospheric) research and the study of fundamental electron interactions as developed under the EIPAM research programme. An experimental study of ozone production has been carried in  $CO_2$ ,  $H_2O$ ,  $O_2$  mixtures to quantify the electron driven processes and scale them for processes in planetary atmospheres. These measurements will be used to extend the systematic studies on this topic previously carried out by group of Prof. J. D. Skalný at Comenius University, Bratislava.

#### Description of the work carried out during the visit

In our study, we have focused on pre-biotic atmospheres of Earth and Mars to understand chemical patterns of ozone creation for different initial conditions present on Earth and Mars related to abiotic processes. Two methods have been used for experimental approach - direct (negative and positive) current corona discharge and photochemical trial with a UV lamp.

Since it is believed that the early Earth's atmosphere [8] was composed of  $CO_2$  with traces of  $N_2$  and  $H_2O$ , in experiment the atmospheres of Mars and Earth were represented by dry and/or humidified  $CO_2$ ,  $CO_2+O_2$  in range 50-500 ppm respectively. A new mixing chamber was built to prepare more complex gas mixtures containing trace amounts as low as 10 ppm. The addition of  $CH_4$  and/or  $N_2$  is planned in future mixtures (however some additional upgrades to the apparatus will be needed). The experiments were conducted over a pressure range between 300-700 Torr in a 'flowing regime'. The lowest pressure was limited both by the UV spectrometer's sensitivity and because this was the pressure at which the discharge changed from a corona to a glow discharge, the latter being unstable. The flow rate at 700 Torr was 5 sccm and was scaled for the lower pressures to keep the residence time of the gas mixture in the reactor constant. Every experimental was repeated (at least 3 times) to achieve maximum reliability of measured data.

#### Description of the main results obtained

- Discharge properties: The properties of a direct current corona discharge at low pressures has been studied in mixtures of CO<sub>2</sub>+H<sub>2</sub>O, CO<sub>2</sub>+O<sub>2</sub> and CO<sub>2</sub>+O<sub>2</sub>+H<sub>2</sub>O. At low pressure the corona discharge loses its uniformity and the discharge appears as discrete points (tufts) along the wire. This effect is common in negative corona discharges but positive corona are uniform at atmospheric pressure. When higher voltages were applied and lower pressures used the central electrode wire was observed to vibrate and the volt-amp characteristics of corona discharge modified.
- Ozone production: Ozone production was monitored in CO<sub>2</sub>+H<sub>2</sub>O, CO<sub>2</sub>+O<sub>2</sub> and CO<sub>2</sub>+O<sub>2</sub>+H<sub>2</sub>O gas mixtures for pressures between 300 and 700 Torr. We observed:
  - That the presence of water in CO<sub>2</sub> inhibits ozone production. By contrast the presence of molecular oxygen enhances the ozone yield in mixture (Fig.1).
  - Relative ozone concentratios R<sub>c</sub>(CO<sub>2</sub>+H<sub>2</sub>O) and R<sub>c</sub>(CO<sub>2</sub>+O<sub>2</sub>) (relative ozone concentration R<sub>c</sub>(gas mixture) is a ratio of ozone produced in gas mixture against ozone created in pure CO<sub>2</sub> at the same Becker parameter) in a DC corona discharge were similar for positive and negative polarities and were independent independent of pressure. The Ozone concentration increases linearly with added O<sub>2</sub> concentrations (Fig.2a) but decreases exponentially with increasing H<sub>2</sub>O concentration (Fig.2b).
  - A strong pressure dependence has been observed with results using a 300 Torr gas pressure being considerably different from results at 700 Torr. At 700 Torr there is only a small (10%) change in the nascent ozone yield over a wie range of water/oxygen rations. However at 300 Torr as the water to oxygen ration is increased the ozone yield falls rapidly.

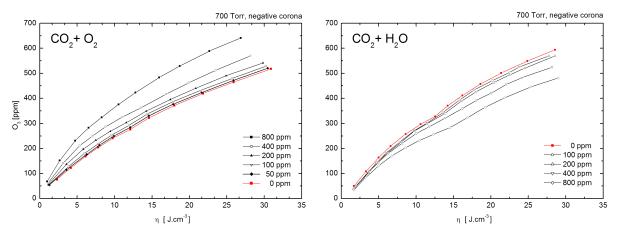


Fig.1: Dependence of produced  $O_3$  concentration in negative corona discharge in  $CO_2$  after adding trace amounts of  $O_2$  and  $H_2O$  respectively into the mixture (to enhance visibility error bars are not shown).

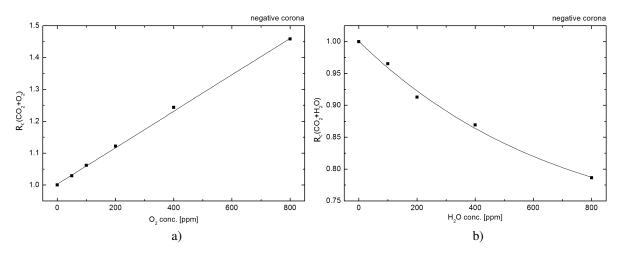


Fig.2: Relative ozone concentrations for  $CO_2+O_2$  and  $CO_2+H_2O$  mixtures respectively.

• Applied for planetary atmospheres: These experiments show that the presence of water is a critical factor in regulating the amount of ozone produced in CO<sub>2</sub>+O<sub>2</sub>+H<sub>2</sub>O mixtures. In a low pressure atmosphere it is necessary to have high concentrations of molecular oxygen (10 O<sub>2</sub> : 1 H<sub>2</sub>) to maintain ozone concentrations found in a pure CO<sub>2</sub> atmosphere (Fig.3). We can explain this as being due the two-body reaction O<sub>3</sub>+OH (ozone breakup) dominating the three-body association O+O<sub>2</sub>+M (leading to O<sub>3</sub> formation). Hence in any early planetary atmosphere rich in CO<sub>2</sub> it will be hard to form an ozone layer if any water is present until molecular oxygen is introduced into the atmosphere by biological processes. Thus it would be hard to form an ozone layer by pure abiotic processes suggesting that the assumption that an ozone layer (observed with water) in any exoplanetary atmosphere is a good biomarker!

## Future collaboration with host institution

This visit has initiated linkage between applied (atmospheric) research and the fundamental electron interactions in gas discharges and has demonstrated the possibilities and strength of laboratory experiments in modelling planetary atmospheres. The experimental apparatus built during visit has the potential to be used in further studies with other gas mixtures to cover other phenomena of pre-biotic atmospheres. Deeper examination of photochemistry is also necessary for reliable scaling and proving a direct link to real planetary atmospheres.

## Projected publications/articles resulting or to result from the grant

The data obtained during visit at Open University will be analyzed and published in the near future.

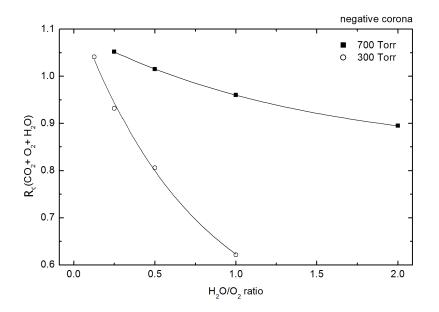


Fig.3: Relative ozone concentrations for CO<sub>2</sub>+O<sub>2</sub>+H<sub>2</sub>O mixtures are strongly pressure dependent.

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