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Guest editorial

The effects of the sun's rays on living organisms and inanimate materials were recognised in antiquity, but the systematic study of photochemical reactions can probably be dated back to the 17th century, when Angelo Sala reported in 1614 on the blackening of silver nitrate exposed to the sun (although it was not until 1725 that Johann Schulze showed that light, rather than heat, was responsible). Until the late 1940s, research was hampered by poor temporal resolution that permitted the investigation only of slow elementary reactions or of the final products in complex reaction systems. The breakthrough of the development in 1949 of flash photolysis by Norrish and Porter, for which they awarded the Nobel prize in 1967, was a milestone of great significance for the development of our understanding of photochemical processes, and, in particular, of our ability to probe the elementary steps of significance in atmospheric chemistry.

Techniques for the study of photophysical, photochemical and chemical processes have continued to be developed at a great pace. Coupled with the subsequent development of the discharge-flow approach for kinetic studies, the arrival of flash photolysis in the laboratory, and the development and exploitation of a variety of sensitive detection techniques based on spectroscopy, initiated and heralded a new era of experimental research on photochemical processes. Pump-and-probe laser-flash photolysis and molecular-beam investigations can now be made on a time scale faster than that at which any gas-phase reaction occurs, thus even enabling information to be gained about the transition states in selected chemical systems.

The earth's atmosphere is significantly different in composition from the atmospheres of its planetary neighbours: it is not in chemical equilibrium but rather in a biogeochemical stationary state. The generation and maintenance of the stratospheric ozone layer, which protects the earth's surface from biologically damaging radiation, depends on photochemical and chemical reactions. Chemical emissions from the earth's surface, as a result of natural biological and geophysical processes, and in modern times as a result of pollution, interact with sunlight. The chemistry of the atmosphere that follows is primarily a photo-oxidation process, which 'cleanses' the atmosphere of these emissions. As a result, free radials and ions are generated, whose reactions, during their transport within the atmosphere, determine the composition of both the bulk and trace constituents. The chemistry of the homosphere, comprising the troposphere, stratosphere and mesosphere, is largely dominated by free-radical reactions, whereas in the heterosphere ion–molecule reactions are dominant.

In the last 30 years, it has become recognised that the results of anthropogenic activity can influence the behaviour of the atmosphere on scales from the local to the global. This influence has become a matter of scientific controversy and public concern, with the anthropogenically induced phenomena such as the ozone hole, summer smog, and global warming gaining notoriety and being thought of as synonymous with the lack of care by mankind for our environment in our striving for an 'improved' standard of living.

In order to assess accurately the impact of anthropogenic activity on the behaviour of the atmosphere and to predict precisely the extent of climate change, a detailed understanding of the elementary processes that determine the physical and chemical response of the atmosphere is required. The need for accurate physico-chemical information about the earth–atmosphere system has resulted in the study of atmospheric processes changing from its primarily being an academic study to providing in addition input for the development of international environmental policy.

This special issue of the *Journal of Photochemistry and Photobiology*: *A Chemistry* reflects the current interest and importance of atmospheric photophysics, photochemistry and chemistry. It provides a showcase for some of the more important topics of current research. Studies of previously unknown photolytic processes, investigations of the absorption cross sections of important atmospheric species in the ultra violet and visible spectral regions, and quantum yields for atmospheric processes following the absorption are all presented. Similarly, the infrared absorptions of a variety of trace species having a potential greenhouse effect have been studied. New results are reported for the rate coefficients of the reactions of the tropospheric photo-oxidants, the hydroxyl (OH) and nitrate (NO_3) free radicals, with a variety of important atmospheric molecules, and radical reactions of stratospheric significance are also discussed. Reactions in both gas and aqueous

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phases are described, and studies of multi-phase reactions presented.

The objective of this special issue is to provide a representative sample of the type of atmospheric research being pursued at present in laboratories around the world. Most of the areas of photochemical research currently of scientific interest to atmospheric research are included here. The Guest Editors would like to thank all the authors and the *Journal of Photochemistry and Biology* for providing this opportunity at the beginning of the new millennium to report and record the results of this important research.

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