Aeronomy of the Middle Atmosphere

ATMOSPHERIC AND OCEANOGRAPHIC SCIENCES LIBRARY

VOLUME 32

Editors

Lawrence A. Mysak, *Department of Atmospheric and Oceanographic Sciences, McGill University, Montreal, Canada*
Kevin Hamilton, *International Pacific Research Center, University of Hawaii, Honolulu, HI, U.S.A.*

Editorial Advisory Board

L. Bengtsson	Max-Planck-Institut für Meteorologie, Hamburg, Germany
A. Berger	Université Catholique, Louvain, Belgium
P.J. Crutzen	Max-Planck-Institut für Chemie, Mainz, Germany
J.R. Garratt	CSIRO, Aspendale, Victoria, Australia
G. Geernaert	DMU-FOLU, Roskilde, Denmark
M. Hantel	Universität Wien, Austria
A. Hollingsworth	European Centre for Medium Range Weather Forecasts, Reading, UK
H. Kelder	KNMI (Royal Netherlands Meteorological Institute), De Bilt, The Netherlands
T.N. Krishnamurti	The Florida State University, Tallahassee, FL, U.S.A.
P. Lemke	Alfred-Wegener-Institute for Polar and Marine Research, Bremerhaven, Germany
P. Malanotte-Rizzoli	MIT, Cambridge, MA, U.S.A.
S.G.H. Philander	Princeton University, NJ, U.S.A.
D. Randall	Colorado State University, Fort Collins, CO, U.S.A.
J.-L. Redelsperger	METEO-FRANCE, Centre National de Recherches Météorologiques, Toulouse, France
R.D. Rosen	AER, Inc., Lexington, MA, U.S.A.
S.H. Schneider	Stanford University, CA, U.S.A.
F. Schott	Universität Kiel, Kiel, Germany
G.E. Swaters	University of Alberta, Edmonton, Canada
J.C. Wyngaard	Pennsylvania State University, University Park, PA, U.S.A.

The titles published in this series are listed at the end of this volume.

Aeronomy of the Middle Atmosphere

Chemistry and Physics of the Stratosphere and Mesosphere

Third revised and enlarged edition

Guy P. Brasseur

Max Planck Institute for Meteorology,
Hamburg, Germany
and
National Center for Atmoshpheric Research,
Boulder, CO, U.S.A.

and

Susan Solomon

NOAA Aeronomy Laboratory,
Boulder, CO, U.S.A.

Springer

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN-10 1-4020-3284-6 (HB)
ISBN-13 978-1-4020-3284-4 (HB)
ISBN-10 1-4020-3824-0 (e-book)
ISBN-13 978-1-4020-3824-1 (e-book)

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

www.springeronline.com

Printed on acid-free paper

All Rights Reserved
© 2005 Springer
No part of this work may be reproduced, stored in a retrieval system, or transmitted
in any form or by any means, electronic, mechanical, photocopying, microfilming, recording
or otherwise, without written permission from the Publisher, with the exception
of any material supplied specifically for the purpose of being entered
and executed on a computer system, for exclusive use by the purchaser of the work.

Printed in the Netherlands.

Contents

Preface

Since the industrial revolution, the chemical composition of the atmosphere has changed at a rate unprecedented in recent history. The concentration of carbon dioxide has increased by about 25% during the 20^{th} century as a result of fossil fuel combustion, and is expected to further increase substantially over the next several decades. The level of methane is more than a factor 2 higher than a century ago, due in large part to agricultural practices. The aerosol load of the atmosphere has been perturbed by such practices as the intensive use of coal as a primary energy source. The release of nitrogen oxides, carbon monoxide and hydrocarbons, as a result of fossil fuel and biomass burning has led to enhanced abundances of ozone and other oxidants in the troposphere. Organic halogenated compounds including the industrially manufactured chlorofluorocarbons have become a dominant source of ozone-depleting chlorine and bromine in the stratosphere. The science of the ozone layer and its interactions with halogenated chemicals are the focus of this book.

These human-induced changes have led to significant perturbations in the Earth's global environment, and will further affect it in the decades ahead. Among these perturbations are the degradation of air quality with associated health effects, the acidification of precipitation with potential consequences for ecosystems, changes in the oxidizing power of the atmosphere and hence on the ability of the atmosphere to eliminate pollutants, changes in the Earth's climate in response to modified absorption and emission of radiation by atmospheric trace constituents, and stratospheric ozone depletion leading to enhanced levels of harmful solar ultraviolet radiation at the Earth's surface.

Ozone plays a central role in the Earth's environment. By absorbing DNA damaging ultraviolet light originating from the Sun, it protects living organisms including humans from lethal effects. It also strongly affects the thermal structure of the atmosphere, and maintains a dynamically stable layer, –the stratosphere–, between approximately 10 and 50 km altitude. Ozone, a greenhouse gas and a powerful oxidant, also influences the Earth's climate and plays a key role in the ability of the atmosphere to destroy several chemical compounds, including many primary or secondary pollutants.

The depletion of the stratospheric ozone layer captured the attention of scientists, policy makers, and the public, particularly in the 1970s, 1980s, and 1990s. Active research quickly provided an improved understanding of the mechanisms involved in the formation and fate of stratospheric ozone. Ozone depletion emerged as one of the most important environmental issues of the 20th century as the evidence grew for substantial human influences on the ozone abundances over much of the globe. An international environmental agreement (The Montreal Protocol and its amendments and adjustments) now governs the global use of ozone-depleting halocarbons. In the 21st century, interest remains strong in the science, the history, and the future of the stratospheric ozone layer.

The purpose of this volume is to provide to graduate students and research scientists a comprehensive view of the chemical, dynamical and radiative processes that affect ozone and other chemical compounds in the middle atmosphere. The title of this volume –Aeronomy of the Middle Atmosphere– has been chosen to highlight the topics covered in this book. The word “Aeronomy” is defined as the science dealing with planetary atmospheres with reference to their chemical composition, physical properties, relative motions and reactions to radiation from outer space (Chambers Dictionary). The field of aeronomy is therefore highly interdisciplinary, drawing on the fields of chemistry, physics, fluid dynamics, meteorology, statistics, mathematics, engineering, etc. The middle atmosphere is defined as the region extending from the tropopause (approximately 12 km) to the homopause (about 100 km altitude).

The book is intended to provide an overview in a manner understandable to persons familiar with college level chemistry and physics. After a general introduction presented in Chapter 1, Chapter 2 reviews basic concepts from physical chemistry, which are of relevance to atmospheric studies. Chapter 3 presents a highly simplified view of dynamical and transport processes above the tropopause, and Chapter 4 summarizes important aspects of radiative transfer in relation to the energy budget and photolytic processes in the middle atmosphere. Chapter 5 presents an overview of the key chemical processes, which influence the chemical composition of the middle atmosphere, while Chapter 6 discusses human-induced perturbations affecting ozone and other compounds. The chapter also presents a detailed discussion of ozone depletion, particularly the formation of the spectacular Antarctic ozone hole is provided in this chapter. Finally, Chapter 7 provides an overview of ionization processes in the mesosphere and stratosphere. Although the discussion focuses on the atmospheric layers ranging from 10 to 100 km, we have sometimes found it necessary to discuss processes occurring in the troposphere (surface to about 12 km altitude) and thermosphere (region above 100 km) in order to explain the roles of these neighboring regions.

Due to the large number of topics to be addressed in the present volume, we have found it impossible to provide a complete review of the available literature. We anticipate that the interested reader will regard the discussions as a starting point and find additional references by consulting publications cited here. The periodic international assessments of the state of the ozone layer, published by the World Meteorological Organization and the United Nations Environment Program, provide additional information.

When we wrote the first edition of this book in the early 1980's, we did not anticipate that the question of stratospheric ozone would soon receive so much scientific attention. The discovery of the Antarctic ozone hole sparked the rapid development of exciting scientific programs and new research understanding. Since the publication of the early editions of this book, new measurement techniques (including space platforms and instruments), more accurate laboratory methods, and more sophisticated atmospheric models have become available. Our understanding of the middle atmosphere, including the role of chemical transformations on the surfaces of liquid or solid particles and the complexity of the air motions, has improved dramatically. More importantly, the discovery and explanation of the Antarctic ozone hole has shown that human activities can lead to major changes in the chemical composition of the atmosphere not just locally and regionally, but at the global scale. The new edition of the present volume attempts to synthesize some of the most recent findings.

The review of critical portions of the manuscript by colleagues has certainly improved the quality of this volume. Material provided to us has also been of great help. We particularly thank S. Chabrillat, D. Edwards, R. Garcia, M. Giorgetta, H. Graf, C. Granier, M. Hagan, J. Holton, I. Karol, K. Kodera, E. Kopp, S. Madronich, E. Manzini, D. Marsh, M. Mlynczak, J. Orlando, T. Peter, W. Randel, A. Smith, Stan Solomon, X. Tie, G. Tyndall, S. Walters, X. Zhu. We deeply appreciate the assistance of R. Terrell Bailey, Paula Fisher, and Debe Fisher for the preparation of the camera-ready manuscript, of C. Granier for her proofreading of the manuscript, and of the Imaging and Design Center at the National Center for Atmospheric Research (NCAR) for their expert figure drafting. We also acknowledge the Atmospheric Chemistry Division at NCAR for supporting the preparation of this book.

Guy P. Brasseur
Susan Solomon
Boulder, Colorado
March, 2005

Chapter 1

THE MIDDLE ATMOSPHERE AND ITS EVOLUTION

1.1 Introduction

Our atmosphere is the medium for life on the surface of the planet, and the transition zone between Earth and space. Humankind has always been interested in the characteristics, manifestations and perturbations of the atmosphere — in its changing weather patterns, and its brilliant sunsets, rainbows, and aurorae.

The lower part of the atmosphere has been continuously studied over many years through meteorological programs. The development of rocket and satellite technology during the past 40 years has also led to the investigation of the upper atmosphere, establishing a new field of research.

The intermediate region which extends from about 10 to 100 km altitude is sometimes called the *middle atmosphere*. This region is somewhat less accessible to observation and has only been systematically studied for the past 25 to 30 years. The purpose of this volume is to outline some of the factors which control the behavior of this layer of the atmosphere, a region which is particularly vulnerable to external perturbations such as solar variability and volcanic eruptions or the emission of anthropogenic material, either at the surface or at altitude.

One of the most important chemical constituents in the middle atmosphere is *ozone*, because it is the only atmospheric species that effectively absorbs ultraviolet solar radiation from about 250-300 nm, protecting plant and animal life from exposure to harmful radiation. Therefore, the stability of the ozone layer (located near 15 to 25 km) is a central part of the study of the middle atmosphere.

In the study of planetary atmospheres it has been customary to distinguish between thermodynamic and dynamic aspects, which constitute a portion of the field of *meteorology*, and the chemical and photochemical aspects, which are part of the domain of *aeronomy*. However, the interactions between these different disciplines play an important role, particularly in the altitude region which we shall address here, so that an effort to examine the coupled dynamical, chemical, and radiative problem must be made in order to understand the observed variations in atmospheric chemical constituents.

1.2 Evolution of the Earth's Atmosphere

The terrestrial atmosphere has evolved considerably over the course of time. The details of this evolution, however, are not well established, and not all scholars agree on how it occurred. Reviews of our current understanding of the atmospheric evolution are given, for example, by Walker (1977) and Kasting (1993).

The universe was created some 15-20 billion years ago when an enormous explosion of a dense center of matter took place (the *big bang*). The Earth was formed approximately 4.6 billion years ago by accretion of small celestial bodies (planetisimals) that had condensed from the solar nebula during its cooling. The gases present at the early stage of the Earth's formation, which could have formed the primordial atmosphere, rapidly dissipated before they could be retained by a strong gravitational field. Instead, a secondary atmosphere was produced by the gradual release of gases from the Earth's interior (which was extremely warm due to radiative decay of uranium, thorium, and potassium contained in the planetisimals). Support for this idea stems in part from the depletion of inert gases such as He, Ne, Ar, and Kr on Earth, relative to their observed abundance in the solar system. Since there is no known process which could remove these very unreactive species from the atmosphere, their low abundance suggests that they never represented as large a fraction of our atmosphere as they do elsewhere in our solar system (*e.g.*, Moulton, 1905).

It is believed that the secondary atmosphere contained large quantities of carbon dioxide (CO_2), water vapor (H_2O), nitrogen (N_2) and perhaps hydrogen chloride (HCl) and trace amounts of other substances. As the planet cooled, water vapor condensed, initiating a vigorous hydrological cycle and producing large oceans. The sediments of the early Earth were probably produced by weathering of the primordial igneous rock minerals by dissolved carbon, nitrogen, chlorine, and sulfur acidic rain water.

An important question related to the evolution of the Earth's climate is the so-called "faint young sun paradox". Like other stars, the Sun evolves with time, so that the radiative energy it provides was probably 25-30% smaller 4 billion years ago than it is today. In spite of the small energy available, the planet's average temperature was always higher than the water frost point (based on the analysis of geological records). It is probably the presence of high quantities of CO_2 in the atmosphere (on the order of 100 times the present value) and perhaps of other greenhouse gases (*i.e.*, methane, ammonia) at the early stage of the Earth's evolution that prevented the planet from being frozen (a condition required for life to develop).

As time evolved and the energy provided by the sun increased, the gradual removal of carbon dioxide from the atmosphere became critical to avoid a "runaway greenhouse effect" (with extremely high surface temperatures) as observed on Venus. This removal of CO_2 was accomplished by weathering of calcium silicate ($CaSiO_3$) minerals by acidic CO_2-rich rainwater, leading to the formation of limestone ($CaCO_3$).

The evolution of atmospheric CO_2 on geological time scales became regulated by the storage of limestone (and of dead organic carbon which appeared later as life developed) in the interior of the Earth's crust (as a result of plate tectonic motions) and the volcanic ejection of CO_2 produced by metamorphism in the Earth's sediments (chemical activation of limestone and dead organic carbon in high pressure and high temperature environments).

The first atmospheric molecules of oxygen (O_2) were probably formed as a result of water vapor photolysis. This source, however, is insufficient to account for the large percentage of oxygen found in the present atmosphere. The evolution of oxygen was rather closely tied to the evolution of life. Several hypotheses have been presented to describe the emergence of life on the planet some 3.5-4.0 billion years ago. One of them, supported by the historical laboratory experiment of Miller (1953) and Miller and Urey (1959), suggests that organic molecules such as amino acids and sugar (which may be the precursors of living matter) could have been formed by spark discharges (*i.e.*, lightning flashes) in a mixture of gases containing methane, ammonia, hydrogen, and water molecules. Organic molecules could also have been injected from space by bombardment of micro-meteorites which include molecules containing carbon, hydrogen, oxygen, and nitrogen. A more plausible hypothesis is that life began in specialized regions of the ocean (*e.g.*, in volcanic vents) where high concentrations of sulfide may have favored the formation of organic molecules. Some of the first living creatures survived by fermentation. These were followed by chemoautotrophs which obtained energy from chemical reactions, and finally photosynthetic organisms began to produce oxygen in much larger amounts, eventually increasing the oxygen content to contemporary levels. The evolution from an oxygen-free, reducing atmosphere to an oxidizing atmosphere (one that can sustain life for higher organisms) has been a special characteristic of the Earth. Today, the most abundant gases in the atmosphere of our neighboring planets, Mars and Venus, are not nitrogen (N_2) and oxygen (O_2) as on Earth, but carbon dioxide (CO_2).

Present photosynthetic life is protected from harmful solar radiation by oxygen and ozone. Thus we must ask how these original creatures survived and evolved to the present state even as they formed the protective shield which their descendants would enjoy. It is possible that they were a form of algae, protected by liquid water from the sun's rays. It has also been suggested that primitive microbes could have been protected by layers of purine and pyrimidine bases, which absorb in the ultraviolet range (Sagan, 1973).

In conclusion, it is clear that the evolution of the Earth's atmosphere depended on many factors, including its albedo, the biosphere (plant and animal life), the oceans, the sun, and the composition of the solid Earth. Physical processes such as volcanic eruptions together with biological activity at the surface have contributed to the evolution of the composition of the terrestrial atmosphere and of the Earth's climate over geological time. Lovelock and Margulis (1974), for example, have argued that the Earth's environment is controlled primarily by the biota in a way that is favorable to life. Thus, the stability of our atmosphere is a complex function of both organic and inorganic processes. Today, many of these processes are disrupted by the human species. In the rest of this chapter and throughout this volume, we discuss the natural processes which control the present atmosphere, and assess the possible impact which human activities may have upon it.

1.3 Anthropogenic Perturbations

The possible modification of the chemical composition of the atmosphere, and the attendant climatic effects, is a problem which attracts the attention of the international scientific community, decision makers, and the public. Some of the processes which may produce these modifications will be briefly identified in this section. A more detailed analysis will be presented in Chapter 6.

We first consider the effects of the agricultural revolution and ask whether the modification of the Earth's ecosystems may influence the atmosphere. In tropical regions, for example (Brazil, Central Africa, Southeast Asia), large regions of forest and savannah are burned for agricultural reasons. It has been estimated that 160000 km^2 of wooded land are destroyed each year (*e.g.*, Kandel, 1980). The combustion produces numerous chemical species, such as CO_2, CO, CH_4 (and many other organic compounds), H_2, N_2, N_2O, NO, NO_2, COS, CH_3Cl, CH_3Br, CH_3I, HCN, CH_3CN, as well as aerosol particles (*e.g.*, black carbon; see Crutzen *et al.*, 1979; Andreae and Merlet, 2001). Some of these compounds eventually reach the middle atmosphere, where they can influence the budgets of several minor species, particularly ozone. Further, the introduction of modern agricultural techniques, especially the intensive use of nitrogen fertilizers, has altered the natural nitrogen cycle by increasing the fixation of this element in the form of ammonia, amino acids, and nitrates. During nitrification and denitrification, part of the nitrogen is emitted to the atmosphere in the form of N_2O rather than N_2. N_2O provides the principal source of NO in the middle atmosphere and accelerates the destruction of ozone in the stratosphere (see Chapter 5).

The rate of nitrogen fixation on the Earth's surface is not known with great accuracy. The contributions of natural biological fixation, as well as the effects of lightning and combustion must be considered. It is estimated, however (Vitousek, 1994), that the annual amount of nitrogen fixed naturally by the biosphere is between 50 to 200 Tg N/yr, while fixation by combustion represents about 20 to 40 Tg/yr. The contribution from nitrogen fertilizers probably exceeds 80 Tg N/yr, and the fixation by legume crops is of the order of 30-50 Tg N/yr. An additional 2-20 Tg N/yr are fixed by lightning in thunderstorms and 20 Tg N/yr in internal combustion engines. Since human-induced nitrogen fixation has increased with time, the effect of this artificial source on the ozone layer (pointed out by Crutzen, 1974, and McElroy *et al.*, 1976) could become significant in the future.

The possible effects of nitrogen oxides on the middle atmosphere have been very actively studied since Crutzen (1970) and Johnston (1971) indicated that the injection of large quantities of these species in aircraft exhaust might alter the protective ozone layer. Later, calculations showed that the effect introduced by such aircraft depends directly on the flight altitude: An injection of nitrogen oxide could contribute to ozone production at altitudes below about 15 km (Brasseur *et al.*, 1998; IPCC, 1999), but to ozone destruction if the craft flew at higher altitudes. It is estimated that current commercial aircraft release approximately 0.5 Tg N/yr (a third of which is being released in the stratosphere) and that the fleet of 500 high-speed civil transport aircraft projected in the early 1970s would have injected 0.1 Tg N/yr (mostly as NO) near 15-22 km altitude. Another source of nitrogen oxides which perturbed the atmosphere in the 1950s and 1960s is the explosion of powerful atomic bombs. Approximately 0.15 to 0.55 Tg N were injected into the stratosphere during the Soviet tests in the fall of 1962. This figure is a significant fraction of the 1 Tg N produced naturally from N_2O oxidation.

The effects of industrial activities, especially the emission of gaseous effluents and their possible effects on climate, have also attracted considerable attention. The most well known problem is certainly that of CO_2, but the cycling of this gas between the atmosphere, biosphere, hydrosphere (clouds and oceans), and the lithosphere (solid Earth) remains insufficiently well quantified. The emission of CO_2 as a result of combustion of fossil fuels (coal, oil) appears to be responsible for the increase in the CO_2 concentration which has been observed in the atmosphere. Between 1960 and 1990 the total amount of CO_2 in the atmosphere increased from 2.53 to 2.81×10^{12} tons. Such an increase influences the thermal budget of the atmosphere, both by cooling of the upper layers due to an increase in the emission of infrared radiation to space, and through heating in the lower layers due to absorption of the infrared emission from the Earth's surface and lower atmosphere (the so-called greenhouse effect). Global models indicate that the globally averaged surface temperature of the Earth should increase by 1.4 to 5.8°C over the period 1990-2100, depending on the adopted scenario for future emissions (IPCC, 2001). Such changes would greatly influence the polar ice caps and global precipitation processes. The exact magnitude of the effect of increased greenhouse gas emissions is difficult to establish because of the complicated feedbacks that exist between the atmosphere, oceans, and biosphere. Observations indicate that a systematic increase in the Earth's mean surface temperature has occurred in the twentieth century. Since the secular temperature variation is also dependent on the aerosols released by combustion processes and perhaps on solar variability, this trend cannot be unambiguously attributed entirely to CO_2 and other greenhouse gases.

Changes in the atmospheric temperature alter the rates of many photochemical processes and therefore the concentrations of minor species. For example, the increase in CO_2 between 30 and 50 km should lead to a small increase in the ozone content, according to current models. Thermal perturbations can also influence atmospheric dynamics (see Chapter 3).

The emission of chlorine and bromine compounds also is a matter of interest, because stratospheric ozone is easily destroyed by these halogen species (Stolarski and Cicerone, 1974; Molina and Rowland, 1974; Wofsy *et al.*, 1975). Chlorine and bromine atoms are present in a variety of industrial products dispersed in the atmosphere, but many of these are rapidly destroyed at low altitudes and therefore do not reach the middle atmosphere where the bulk of the atmospheric ozone layer resides. Some industrial compounds do, however, have sufficiently long lifetimes to represent a potential perturbation. This is the case, for example, for halogenated hydrocarbons such as the chlorofluorocarbons (CFCs), and specifically for trichlorofluoromethane ($CFCl_3$ or CFC-11), dichlorodifluoromethane (CF_2Cl_2 or CFC-12), carbon tetrachloride (CCl_4), and methylchloroform (also called trichloroethane or CH_3CCl_3). CFCs are very stable compounds and, hence, have been used as refrigerants, solvents, foam-blowing agents and, until the late 1970s, as aerosol spray propellants. Methyl chloride (CH_3Cl) is the major natural chlorocarbon of relevance for the stratosphere; it is produced in seawater and released by biomass burning. As these long-lived organic molecules penetrate into the stratosphere, they are photodecomposed and release ozone-destroying agents. It is estimated that in the early 1990s when the emissions of industrially produced CFCs represented approximately 1 Tg/yr, about 85% of the stratospheric chlorine was of anthropogenic origin. There is strong evidence today that the ozone depletion observed in the 1980s and 1990s, and specifically the formation of a large "ozone hole" in Antarctica each spring since about the early 1980s, has been caused by the rapid increase in the chlorine load of the stratosphere. The CFCs are also believed to be responsible for the ozone depletion recorded in the Arctic during many winters since the early 1990s.

International agreements (Montreal Protocol in 1987 and subsequent amendments), as well as national regulations, have strongly limited the production and the use of the CFCs. These chemical compounds have been gradually replaced by partially halogenated hydrocarbons, and specifically by hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). These alternative products are relatively easily destroyed in the troposphere and hence their lifetimes are substantially shorter than those of the CFCs (typically 1-10 yrs as opposed to 10-100 yrs). The ozone depletion potential of the HCFCs is about an order of magnitude smaller than that of the fully halogenated halocarbons. HFCs are not a threat to ozone because they do not contain any chlorine or bromine atoms.

Bromine, whose potential to destroy ozone (per atom) is about 50 times higher than that of chlorine, is released in the stratosphere by photodecomposition of methyl bromide and other brominated organic compounds, including the so-called halons (*e.g.*, CF_2ClBr or Halon-1211, and CF_3Br or Halon-1301). CH_3Br is produced by biological activity in the ocean, biomass burning, automobile exhaust, and agricultural usage (*i.e.*, as a pre-planting and post-harvesting fumigant). The anthropogenic source of CH_3Br represents about 40% of the total emission. Halons, whose lifetime is several decades, are used in fire extinguishers. Their production is now banned owing to their harmful effects on stratospheric ozone.

Numerical models have been used to predict the potential ozone depletion in response to the emission of halocarbons, based on different plausible scenarios. All of these models indicate that the time required for the middle atmosphere to respond to surface emissions of these halocarbons is very long (several decades). In particular, even with the measures taken to reduce or phase-out the emissions of the CFCs and other halocarbons, it is expected that the Antarctic ozone hole will be observed each spring (September-October) at least until the year 2040. It should also be noted that the halocarbons are active in the infrared, and contribute to the greenhouse effect.

The analysis of perturbations to the middle atmosphere must also include natural processes, such as the effects of volcanic eruptions, which produce large quantities of fine particles as well as water vapor and SO_2, which eventually produces H_2SO_4 and sulfate aerosols. The amount of gas injected, the composition and the maximum altitude of injection vary with the intensity of the eruption. Such events can alter the budgets of some atmospheric constituents and are clearly reflected in the middle atmospheric aerosol content. Particles also provide sites for surface reactions to occur. Such heterogeneous reactions may activate chlorine and enhance the depletion of ozone by industrially manufactured halocarbons.

We have also noted the important role of the sun in establishing the thermal and photochemical conditions in the Earth's environment. Variations in the solar output are caused by its 27-day rotation period, the 11-year solar cycle, and by solar flares. Each of these processes may account for part of the natural variability of the atmosphere.

The effects of human activities on the composition of the atmosphere have been clearly detected on local, regional, and global scales. Agricultural development and industrial activities are likely to influence terrestrial ecosystems as well as the climate system. It is therefore important to understand the behavior of the atmosphere, which is so vulnerable to external perturbations and so essential to the climatic and photochemical environment on Earth.

References

Andreae, M.O., and P. Merlet, Emission of trace gases and aerosols from biomass burning. *Glob Biogeochem Cycles: 15*, 955, 2001.

Brasseur, G.P., R.A. Cox, D. Hauglustaine, I. Isaksen, J. Lelieveld, D.H. Lister, R. Sausen, U. Schumann, A. Wahner, and P. Wiesen, European scientific assessment of the atmospheric effects of aircraft emissions. *Atmos Env: 32*, 2327, 1998.

Crutzen, P.J., The influence of nitrogen oxide on the atmospheric ozone content. *Quart J Roy Met Soc: 96*, 320, 1970.

Crutzen, P.J., Estimates of possible variations in total ozone due to natural causes and human activity. *Ambio: 3*, 201, 1974.

Crutzen, P.J., L.E. Heidt, J.P. Krasnec, W.H. Pollock, and W. Seiler, Biomass burning as a source of the atmospheric gases CO, H_2, N_2O, NO, CH_3Cl, and COS. *Nature: 282*, 253, 1979.

IPCC (Intergovernmental Panel on Climate Change), *Aviation and the Global Atmosphere.* J. Penner *et al.* (eds.), Cambridge University Press, 1999.

IPCC (Intergovernmental Panel on Climate Change), *Climatic Change 2001: The scientific basis.* J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. Van de Linden, X. Da, K. Maskell, and C.A. Johnson (eds.), Cambridge University Press, 2001.

Johnston, H.S., Reduction of stratospheric ozone by nitrogen oxide catalysts from supersonic transport exhaust. *Science: 173*, 517, 1971.

Kandel, R.S., *Earth and Cosmos.* Pergamon Press, 1980.

Kasting, J.F., Earth's early atmosphere. *Science: 259*, 920, 1993.

Lovelock, J.E., and L. Margulis, Atmospheric homeostatis by and for the atmosphere: The gaia hypothesis. *Tellus: 26*, 2, 1974.

McElroy, M.B., J.W. Elkins, S.C. Wofsy, and Y.L. Yung, Sources and sinks for atmospheric N_2O. *Rev Geophys Space Phys: 14*, 143, 1976.

Miller, S.L., A production of amino acids under possible primitive earth conditions. *Science: 117*, 528, 1953.

Miller, S.L., and H.C. Urey, Organic compound synthesis on the primitive earth. *Science: 130*, 245, 1959.

Molina, M.J., and F.S. Rowland, Stratospheric sink for chlorofluoromethanes: Chlorine atom catalyzed destruction of ozone. *Nature: 249*, 810, 1974.

Moulton, F.R., On the evolution of the solar system. *Astrophys J: 22*, 165, 1905.

Sagan, C., Ultraviolet selection pressure on the earliest organisms. *J Theo Bio: 39*, 195, 1973.

Stolarski, R.S., and R.J. Cicerone, Stratospheric chlorine: A possible sink for ozone. *Can J Chem: 52*, 1610, 1974.

Vitousek, P.M., Beyond global warming: Ecology and global change. *Ecology: 75*, 1861, 1994.

Walker, J.C.G., *Evolution of the Atmosphere.* McMillan Pub., 1977.

Wofsy, S.C., M.B. McElroy, and Y.L. Yung, The chemistry of atmospheric bromine. *Geophys Res Lett: 2*, 215, 1975.

Chapter 2

CHEMICAL CONCEPTS IN THE ATMOSPHERE

2.1 Introduction

Almost all of the constituents that are present in the middle atmosphere undergo chemical and photochemical processes, which greatly affect their spatial and temporal distributions. Chemical reactions can occur in the gas phase, in the condensed phase, or at the interface between these phases. The energy provided by the Sun can break the chemical bonds of many species, producing reactive fragments which interact with other compounds. Most of these fragments are *free radicals* (particles containing one or more unpaired electrons). Gas phase reactions typically involve at least one "free radical" species, while condensed phase reactions can include molecules only. Reactions occurring in the middle atmosphere are discussed in detail in Chapter 5. Rate constants for chemical reactions are measured in the laboratory. Quantitative values of these rate constants are regularly compiled by the Jet Propulsion Laboratory (see *e.g.*, JPL, 2002). The absorption of solar energy also plays an important role in the thermal budget and dynamical properties of the middle atmosphere. To understand the aeronomy of the middle atmosphere, we must first understand some of the basic principles of spectroscopy, photochemistry, kinetics and thermodynamics. In this chapter, we attempt to outline how these enter into the chemistry of the middle atmosphere, and present examples of their use. The discussion presented here will be very elementary; the reader may wish to examine the bibliography for detailed treatments. See, for example, the comprehensive textbook by Finlayson-Pitts and Pitts (1999). Some useful definitions are provided in Box 2.1.

2.2 Energy Levels of Molecules

The motions of molecules can be decomposed into translational, rotational and vibrational motions. Radiation, once absorbed by a molecule, affects only its rotational and vibrational states. Therefore, translation motions will not be further considered here, even though we should note that once absorbed, the incoming energy can be converted into translational energy (kinetic energy) and hence transformed into heat through collisions with the medium. The absorption of radiation can also lead to changes in the electron distribution and hence in the electronic state of the molecules. Transitions between rotational, vibrational and electronic states are quantified, and obey certain selection rules, which can be derived from quantum mechanics principles (*e.g.*, Steinfeld, 1978). These selection rules describe the ease with which transitions occur. It is common to refer to transitions as “forbidden” or “allowed”. In practice, even highly “forbidden” transitions occur under certain circumstances, although much more slowly than “allowed” transitions. Therefore, we will refer to transitions here as “unfavorable” or “allowed”.

The energy associated with transitions between electronic states is relatively large, of the order of electron-volts (eV), and the photons capable of inducing such transitions are generally in the ultraviolet and the visible. The energy associated with vibrational transitions is significantly smaller, and corresponds to the near-infrared (wavelengths of typically 10 μm). In the case of rotational transitions, the energy involved is even smaller, and corresponds to the far-infrared and microwave regions (wavelengths of the order of 10 mm).

Box 2.1 Some Useful Definitions

(Adapted from Ebbing, 1990)

Photon	Quantum of electromagnetic radiation with energy proportional to the observed frequency ν of the light: $E = h\nu$ (where h is Planck’s constant).
Atom	An extremely small particle of matter that retains its identity during chemical reactions.
Nucleus	Central core of an atom containing one or more positive charges.
Proton	A particle found in the nucleus of an atom. Its electric charge is equal in magnitude, but opposite in sign, to that of an electron and its mass is 1836 times that of the electron.
Neutron	A particle found in the nucleus of an atom. Its mass is almost identical to that of a proton. It has no electric charge.

Box 2.1 (Continued)

Electron	A light particle (mass = 9.1096×10^{-31}kg) that carries a unit negative charge (1.6022×10^{-19}C) and exists in the region around the positively-charged nucleus.
Element	A substance that cannot be decomposed by any chemical reaction into simpler substances. A type of matter composed of one kind of atom.
Molecule	A group of atoms that are tightly connected by attractive forces (that are chemically bonded together).
Isomers	Compounds of the same molecular formula but with different arrangements of atoms.
Covalent Bond	A chemical bond formed by the sharing of a pair of electrons between atoms in a molecule.
Free Radical	Highly reactive species (*e.g.*, H, OH, NO, NO_3, Cl) with one or more unpaired electrons
Mole	The quantity of a given substance that contains as many molecules as the number of atom in exactly 12g of carbon –12. The amount of substance containing 6.0222137×10^{23} molecules.
Compound	A substance composed of two or more elements chemically combined in fixed proportions.
Ion	An electrically-charged particle obtained from an atom or a chemically-bonded group of atoms by adding or removing one or more electrons.
Plasma	An electrically neutral gas made up of ions and electrons.
Gas	The form of matter that is an easily compressible fluid.
Vapor	The gaseous state of matter.
Liquid	The form of matter that is a relatively incompressible fluid; it has a fixed volume, but no fixed shape.
Solid	The form of matter that is characterized by rigidity; it is relatively incompressible and has a fixed shape and volume.
Condensation	The changing of a gas to either the liquid or the solid state.
Vaporization	The changing of a solid or a liquid to the vapor state.
Sublimation	The changing of a solid to the vapor state.
Fusion	The changing of a solid to the liquid state.
Aerosols	Liquid droplets or solid particles dispersed throughout a gas.
Nucleation	The formation of particles in a supersaturated vapor (or in the air).
Coagulation	A process in which particles grow by collisions.
Diffusion	A process whereby a gas spreads out through another gas to occupy the space with uniform partial pressure.
Chemical Reaction	A change in which one or more kinds of matter are transformed into a new kind of matter or several new kinds of matter. It consists of the rearrangement of atoms present in the reacting substances to give new chemical combinations characterizing the substances formed by the reaction.

Box 2.1 (Continued)

Chemical Equilibrium	The state reached by a reaction mixture when the rate of forward reaction becomes equal to the rate of reverse reaction.
Exothermic Process	A chemical reaction or physical change in which heat is released.
Endothermic Process	A chemical reaction or physical change in which heat is absorbed.
Internal Energy (U)	The sum of the kinetic and the potential energies of the particles making up a system.
Enthalpy (H)	An extensive property of a substance that can be used to obtain the heat absorbed or released by a chemical reaction or physical change at constant pressure. It is defined as the sum of the internal energy (U) and the product of the pressure and the volume of the system (PV) $H = U + PV$.
Entropy (S)	A thermodynamic quantity that is a measure of the randomness or disorder of a system.
Free Energy (G)	A thermodynamic quantity defined by $G = H - TS$ where H is the enthalpy, S the entropy, and T the absolute temperature.
Oxidation	A chemical reaction in which a compound or a radical loses electrons.
Reduction	A chemical reaction in which a compound or a radical gains electrons.
Catalyst	A substance that increases the rate of reaction without being consumed in the overall reaction.

Figure 2.1.a presents a typical potential energy diagram for a hypothetical diatomic molecule XY. The bond between the two atoms X and Y can be viewed as an oscillating spring, in which the internuclear distance varies with a frequency that is determined by the strength of the bond and the masses of the atoms. In the idealized case of a harmonic oscillator, the restoring force acting on the atoms is proportional to the displacement from the equilibrium position located at the minimum of the potential energy curve, which is represented by a parabola. Quantum mechanics (Schrödinger's equation solved for the harmonic oscillator) shows that, in this case, the vibrational energy is quantized with energy levels equally spaced. The corresponding quantum numbers v are equal to 0 (fundamental state), 1, 2, 3, etc. Transitions can only modify the energy level by one quantum at the time. The selection rule for the harmonic oscillator is therefore $\Delta v = \pm 1$. For a non-idealized oscillator, the curve representing the potential energy becomes asymmetric and is

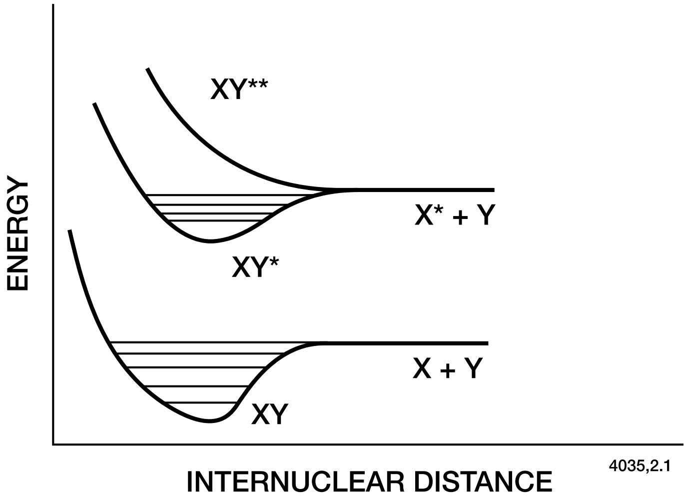

Figure 2.1.a. Typical potential energy diagram for a hypothetical diatomic molecule XY. The lower curve corresponds to an anharmonic oscillator, showing a strong repulsive branch for small internuclear distances and an attractive branch allowing, however, the dissociation of the molecule, when the molecular bond is stretched beyond a given internuclear distance. Electronic states corresponding to XY and XY* exhibit maximum stability at the minimum of the potential energy curve, so that this state represents a stable bound configuration of the molecule. In these bound states, vibrational levels (v=0, 1, 2, etc.) are represented by horizontal lines. Rotational levels are not shown. The electronically excited XY** state, represented by the uppermost curve, is repulsive for all values of the internuclear distance, and is thus unstable.

often called the Morse curve (see Figure 2.1.a). The potential energy increases sharply towards smaller internuclear distances, as charge repulsion becomes more intense. For large internuclear distances, the molecular bond is stretched and can break; in this case, the molecule dissociates. In the non-idealized case, weak overtone transitions with $\Delta\mathrm{v} = \pm 2, \pm 3$, etc. are possible and the vibrational energy levels are not equidistant anymore, but are more closely spaced with increasing quantum number v. Note, in addition, that vibrational transitions occur only if the electric field of the radiation can interact with an oscillating electric field produced by the dipole moment of the vibrating molecule. Only heteronuclear diatomic molecules such as NO or CO produce such an oscillating dipole moment, while homonuclear species like O_2 and N_2 do not undergo vibrational transitions. Since the energy corresponding to a vibrational transition is relatively large compared to the thermal energy, most molecules present in the atmosphere are found to be in their lowest vibrational state (v = 0). Vibrationally excited species can be produced by photon absorption, collision with an atom or a molecule, or as a result of a chemical reaction (see *e.g.*, reaction 2.95). De-excitation can result from a collision or from spontaneous radiative emission from level u to level ℓ. The probability of this latter process is provided by the Einstein coefficient $A_{u,\ell}$, whose value is determined in the laboratory. Vibrational energy transitions play a particularly important role in the thermal balance of the middle atmosphere, because they are the fundamental processes responsible for most of the infrared cooling occurring there (see Chapter 4).

Diatomic molecules with a permanent dipole moment (*i.e.*, heteronuclear molecules) produce an oscillating electric field during their rotation, resulting in light absorption and rotational transitions. These transitions occur between quantified energy levels (with the corresponding quantum numbers J equal to 0, 1, 2, 3, etc.). In the case of an idealized rigid rotor, the selection rule for such transitions is given by $\Delta J = \pm 1$. Since the energy corresponding to rotational transitions is small compared to that of vibrational transitions, and to the thermal energy of the molecules, the population of the rotational energy is not confined to the fundamental state, but is generally significant for levels above $J = 0$.

Since molecules vibrate and rotate simultaneously, combined vibration-rotation transitions (and spectra) need to be considered. In the idealized harmonic oscillator, rigid rotor case, the only significant processes to be considered are the transitions between vibrational level $v = 0$ and level $v = 1$, together with a number of rotational transitions. An example of such system is shown in Figure 2.1.b. The intensity of the corresponding lines observed in the absorption spectra reflects the relative population of the rotational energy levels. The transitions associated with the selection rule $\Delta J = +1$ (*i.e.*, found on the high energy side of the spectrum) produce the so-called R branch, while the transitions associated with $\Delta J = -1$ (low energy side of the spectrum) lead to the so-called P branch.

In the case of polyatomic molecules, such as CO_2, H_2O, O_3, etc., the principles discussed above still apply, but the spectra become more complex. Polyatomic molecules do not rotate only about one single axis, but about three mutually perpendicular axes. In addition, the number of vibrational degrees of freedom is also increased.

Vibrational quanta are distributed among the available vibrational modes of the molecule, which correspond physically to stretching and bending the chemical bonds of the molecule. These are conventionally referred to as ν_1, ν_2, etc.

Figure 2.2 presents a schematic diagram of the possible vibrational modes for diatomic, linear triatomic, and bent triatomic molecules. The vibrational term symbol provides an ordered list of quantum numbers

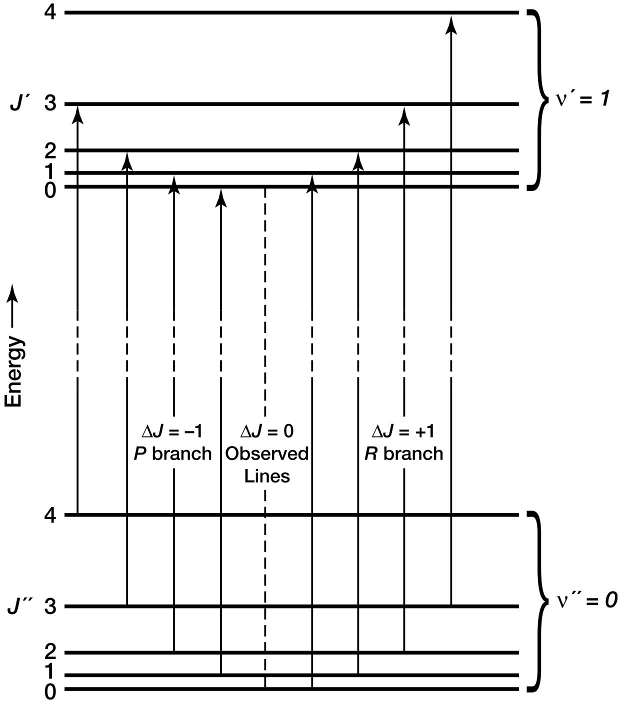

Figure 2.1.b. Schematic diagram of the energy levels and vibration-rotation transitions (after Herzberg, 1950). The lower lines ($v'' = 0$) correspond to the fundamental vibrational state with different rotational states ($J'' = 0, 1, 2, 3, 4$). The first vibrationally excited state ($v' = 1$) with related rotational states ($J' = 0$ to 4) are shown by the upper lines. The transitions corresponding to the P and R branches are indicated. Transition $\Delta J = 0$ is not allowed in the case of the idealized rigid rotor, harmonic oscillator for a linear molecule, but can be observed (Q-branch) in other cases. The notations are from Herzberg (1950).

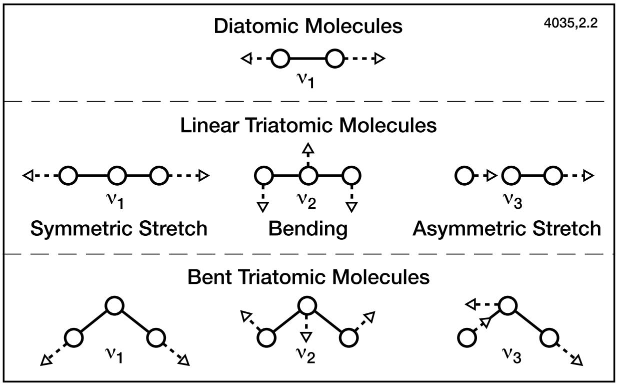

Figure 2.2. Vibrational modes of diatomic and triatomic molecules.

for each mode. For example, (010) means that the quantum number is zero for ν_1, one for ν_2 and zero for ν_3. As we shall see in Chapter 4, the 15μm ν_2 band of CO_2 plays a dominant role in cooling throughout the middle atmosphere.

The absorption of visible and ultraviolet radiation can lead to electronic transitions. The curves labelled XY^* and XY^{**} in Figure 2.1.a correspond to electronically excited states of the hypothetical molecule XY considered earlier. Electronically excited states may be repulsive at any internuclear distance (as in the case of XY^{**}), or may have a stable bound configuration (XY^*) like the ground state, with associated vibrational and rotational levels. If an electronic transition occurs along with simultaneous vibrational and rotational transitions, the selection rules are not as restricted as those described above. Transitions from the fundamental vibrational level $\mathrm{v} = 0$ to high levels ($\mathrm{v} > 1$) becomes possible. Rotational transitions with unchanged quantum number J ($\Delta J = 0$) are observed and produce a Q-branch in the corresponding spectrum.

The electronic states of molecules and atoms are expressed by quantum numbers, which represent the total orbital angular momentum and the net spin of the electrons. The corresponding symbols and the selection rules for electronic transitions are discussed in Sections 2.2.1 and 2.2.2, respectively. Different electronic configurations of the same particle generally have very different reactive properties; for example, the excited O^1D atom behaves very differently upon collision with a water molecule than does the ground O^3P atom. Photochemical processes involving absorption and emission of photons induce transitions from one state to another, and these occur more readily between certain electronic states than others. The transitions between electronic states, which result from absorption of relatively high energy photons, serve two important purposes in the middle atmosphere. They represent the major source of heating, as will be discussed in Chapter 4, and they initiate photochemical processes (*e.g.*, photodecomposition or *photolysis* and photoionization) which play a major role in establishing the distributions of minor constituents (this is described in detail in Chapters 5 and 7).

2.2.1 Term Symbols

In general, term symbols indicate both spin angular momentum (S for atoms, Σ for diatomic molecules) and orbital angular momentum (L for atoms, Λ for diatomic molecules). The term symbol is written ^{2S+1}L for atoms and $^{2\Sigma+1}\Lambda$ for molecules. We will not concern ourselves here with the derivation of L and Λ. Part of the reason for this is the fact that the selection rules involving orbital angular momentum are often not strictly followed in actual transitions; the restrictions regarding spin are the ones which tend to be most rigidly followed in practice, and we shall concentrate only on these. For increasing L from 0 to 6, the term takes on the values S, P, D, F, G, H. For increasing Λ, the Greek symbols Σ, Π, Δ, and Φ are used. See, for example, Karplus and Porter (1970).

The spin terms can be readily evaluated given knowledge of basic atomic and molecular orbital theory (see Moore, 1962; Karplus and Porter, 1970). The ground state of the oxygen atom is conventionally described as

$$(1\mathrm{s})^2(2\mathrm{s})^2(2\mathrm{p}_1)^2(2\mathrm{p}_2)^1(2\mathrm{p}_3)^1$$

The superscripts denote the number of electrons in each atomic orbital. Electrons must be paired (*i.e.*, of equal and opposite spin) in atomic orbitals containing two electrons. Paired electrons do not contribute to the atomic or molecular spin angular momentum. Hund's rule of maximum multiplicity states that in the lowest energy configuration, the electrons must be spread over as many available orbitals of equal energy as possible, in order to maximize the spin multiplicity. Since three 2p orbitals are available in which 4 electrons must be distributed, the lowest electronic state therefore has two unpaired electrons in each of two 2p orbitals. Each unpaired electron contributes $\frac{1}{2}$ to the spin angular momentum. Thus $2S + 1 = 3$ for the oxygen atom, and the term symbol is ^{3}P.

The oxygen molecule has the ground configuration

$$(\sigma_\mathrm{g}1\mathrm{s})^2(\sigma_\mathrm{u}1\mathrm{s})^2(\sigma_\mathrm{g}2\mathrm{s})^2(\sigma_\mathrm{u}2\mathrm{s})^2(\sigma_\mathrm{g}2\mathrm{p})^2(\pi_\mathrm{u}2\mathrm{p})^4(\pi_\mathrm{g}2\mathrm{p})^2$$

The two π_g2p electrons are unpaired, so that $2\Sigma + 1 = 3$, and the ground state is $\mathrm{X}^3\Sigma_\mathrm{g}^-$. The X is used to denote that this is the ground state of the molecule; first and second excited states are indicated by A, B, or a, b, etc. The subscripts "g" (from the German "gerade" = even) and "u" ("ungerade" = uneven) used for homonuclear diatomic molecules (*e.g.*, O_2) refer to cases where the wavefunction representing the molecular state keeps the same sign or changes sign, respectively, through the center of symmetry of the molecule. The superscripts "+" and "–" apply only to Σ states. Symbol "+" is used when the wavefunction is unaltered by reflection through a plane passing through the 2 nuclei of the molecule. Symbol "–" is used if the wavefunction changes sign. More details regarding the significance of the term symbols can be obtained, for example, in Herzberg (1950).

Polyatomic molecules have different term symbols, but again the spin multiplicity is given by the left-hand superscript. For example, the ground state of the ozone molecule is denoted by the term $^1A_1$. Note that these terms should not be confused with the excited states of diatomic molecules, which can also contain A, B, etc. in their term symbols.

2.2.2 Selection Rules for Electronic Radiative Processes

The importance of the term symbols lies in their use in predicting the ease with which photon absorption

$$\mathrm{A} + \mathrm{h}\nu \rightarrow \mathrm{A}^* \tag{2.1}$$

and radiative decay can occur.

$$\mathrm{A}^* \rightarrow \mathrm{A} + \mathrm{h}\nu \tag{2.2}$$

The selection rules for radiative processes permit us to evaluate the ease or difficulty with which a particular transition can proceed. The basic rules are as follows:

* Spin is unchanged in an allowed transition, for both atoms and molecules. This is generally the most important consideration in establishing the transition probability.

* L or Λ changes of 1 or zero are allowed, except in the case of atoms if $0 \rightarrow 0$ (S → S). Changes of L or Λ of more than one (*i.e.*, D → S) are unfavorable.

* For molecules with g and u subscripts, g → u transitions are allowed, but u → u or g → g transitions are difficult.

* For Σ states, $\Sigma^+ \rightarrow \Sigma^+$ and $\Sigma^- \rightarrow \Sigma^-$ transitions are allowed, while $\Sigma^+ \rightarrow \Sigma^-$ transitions are unfavorable.

Examples of transitions which are of importance in the middle atmosphere are, for example,

$$\mathrm{O_2}\,(^1\Delta_\mathrm{g}) \rightarrow \mathrm{O_2}\,(^3\Sigma_\mathrm{g}^-) + \mathrm{h}\nu \tag{2.3}$$

This process is unfavorable because it involves a change in spin, a change in Λ of two, and a g → g transition. Thus its probability is relatively low, which is reflected in a time constant for radiative decay of almost an hour. Similarly, the cross section for production of $O_2\,(^1\Delta_g)$ by photon absorption from the ground state

$$\mathrm{O_2}\,(^3\Sigma_\mathrm{g}^-) + \mathrm{h}\nu \rightarrow \mathrm{O_2}\,(^1\Delta_\mathrm{g}) \tag{2.4}$$

is small.