

SPECTROSCOPY AND PHOTOCHEMISTRY OF PLANETARY ATMOSPHERES AND IONOSPHERES

The chemical composition of any planetary atmosphere is of fundamental importance in determining its photochemistry and dynamics in addition to its thermal balance, climate, origin, and evolution. Divided into two parts, this book begins with a set of introductory chapters, starting with a concise review of the Solar System and fundamental atmospheric physics. Chapters then describe the basic principles and methods of spectroscopy, the main tool for studying the chemical composition of planetary atmospheres and of photochemical modeling and its use in the theoretical interpretation of observational data on chemical composition. The second part of the book provides a detailed review of the carbon dioxide atmospheres and ionospheres of Mars and Venus and the nitrogen-methane atmospheres of Titan, Triton, and Pluto. Written by an expert author, this comprehensive text will make a valuable reference for graduate students, researchers, and professional scientists specializing in planetary atmospheres.

Now retired, VLADIMIR A. KRASNOPOLSKY was previously a research professor in the Department of Physics at the Catholic University of America, Washington, DC. An expert on spectroscopy and photochemical modeling, he is the author of 3 books, 6 book chapters, and 182 refereed publications. He is one of the most highly cited scientists working on planetary atmosphere research and was awarded the USSR State Prize in 1985 for his studies of Venus. He has worked on many space missions throughout his career and was the principal investigator of the airglow spectrometer on the Mars 5 spacecraft and the Venera 9 and 10 missions to Venus, the three-channel spectrometer on the Vega mission to Venus, and the infrared spectrometer on the Phobos 2 orbiter.



CAMBRIDGE PLANETARY SCIENCE

Series Editors

Fran Bagenal, David Jewitt, Carl Murray, Jim Bell, Ralph Lorenz, Francis Nimmo, Sara Russell

Books in the Series

1. *Jupiter: The Planet, Satellites and Magnetosphere*[†] Edited by Bagenal, Dowling, and McKinnon 978-0-521-03545-3

2. Meteorites: A Petrologic, Chemical and Isotopic Synthesis[†] Hutchison

978-0-521-03539-2

3. The Origin of Chondrules and Chondrites[†]

Sears

978-1-107-40285-0

4. Planetary Rings[†]

Esposito

978-1-107-40247-8

5. The Geology of Mars: Evidence from Earth-Based Analogs[†]

Edited by Chapman 978-0-521-20659-4

6. The Surface of Mars[†]

Carr

978-0-521-87201-0

7. Volcanism on Io: A Comparison with Earth[†]

Davies

978-0-521-85003-2

8. Mars: An Introduction to its Interior, Surface and Atmosphere[†]

Barlow

978-0-521-85226-5

9. The Martian Surface: Composition, Mineralogy and Physical Properties

Edited by Bell

978-0-521-86698-9

10. Planetary Crusts: Their Composition, Origin and Evolution[†]

Taylor and McLennan

978-0-521-14201-4

11. Planetary Tectonics[†]

Edited by Watters and Schultz

978-0-521-74992-3



12. Protoplanetary Dust: Astrophysical and Cosmochemical Perspectives[†] Edited by Apai and Lauretta 978-0-521-51772-0

13. Planetary Surface Processes

Melosh

978-0-521-51418-7

14. *Titan: Interior, Surface, Atmosphere and Space Environment* Edited by Müller-Wodarg, Griffith, Lellouch, and Cravens 978-0-521-19992-6

15. Planetary Rings: A Post-Equinox View (Second edition) Esposito

978-1-107-02882-1

 Planetesimals: Early Differentiation and Consequences for Planets Edited by Elkins-Tanton and Weiss 978-1-107-11848-5

17. Asteroids: Astronomical and Geological

Bodies Burbine

978-1-107-09684-4

18. *The Atmosphere and Climate of Mars*Edited by Haberle, Clancy, Forget, Smith, and Zurek
978-1-107-01618-7

19. Planetary Ring Systems

Edited by Tiscareno and Murray

978-1-107-11382-4

20. Saturn in the 21st Century

Edited by Baines, Flasar, Krupp, and Stallard 978-1-107-10677-2

21. Mercury: The View after Messenger

Edited by Solomon, Nittler, and Anderson

978-1-107-15445-2

22. Chondrules: Records of Protoplanetary Disk Processes

Edited by Russell, Connolly, and Krot

978-1-108-41801-0

23. Spectroscopy and Photochemistry of Planetary Atmospheres and Ionospheres Krasnopolsky

978-1-107-14526-9

[†]Reissued as a paperback





SPECTROSCOPY AND PHOTOCHEMISTRY OF PLANETARY ATMOSPHERES AND IONOSPHERES

Mars, Venus, Titan, Triton, and Pluto

VLADIMIR A. KRASNOPOLSKY

Catholic University of America, Washington, DC





CAMBRIDGEUNIVERSITY PRESS

University Printing House, Cambridge CB2 8BS, United Kingdom
One Liberty Plaza, 20th Floor, New York, NY 10006, USA
477 Williamstown Road, Port Melbourne, VIC 3207, Australia
314–321, 3rd Floor, Plot 3, Splendor Forum, Jasola District Centre, New Delhi 110025, India
79 Anson Road, #06–04/06, Singapore 079906

Cambridge University Press is part of the University of Cambridge.

It furthers the University's mission by disseminating knowledge in the pursuit of education, learning, and research at the highest international levels of excellence.

www.cambridge.org
Information on this title: www.cambridge.org/9781107145269
DOI: 10.1017/9781316535561

© Vladimir A. Krasnopolsky 2019

This publication is in copyright. Subject to statutory exception and to the provisions of relevant collective licensing agreements, no reproduction of any part may take place without the written permission of Cambridge University Press.

First published 2019

Printed in the United Kingdom by TJ International Ltd. Padstow Cornwall

A catalogue record for this publication is available from the British Library.

Library of Congress Cataloging-in-Publication Data
Names: Krasnopol'skiĭ, V. A. (Vladimir Anatol'evich), 1938– author.

Title: Spectroscopy and photochemistry of planetary atmospheres and ionospheres: Mars, Venus,
Titan, Triton and Pluto / Vladimir Krasnopolsky (Catholic University of America).

Description: Cambridge, United Kingdom; New York, NY: Cambridge University Press, 2019. |
Series: Cambridge planetary science; 23 | Includes bibliographical references and index.

Identifiers: LCCN 2018040321 | ISBN 9781107145269 (hardback: alk. paper)

Subjects: LCSH: Planets—Atmospheres. | Spectrum analysis.

Classification: LCC QB603.A85 K75 2019 | DDC 551.5099/2–dc23

LC record available at https://lccn.loc.gov/2018040321

ISBN 978-1-107-14526-9 Hardback

Cambridge University Press has no responsibility for the persistence or accuracy of URLs for external or third-party internet websites referred to in this publication and does not guarantee that any content on such websites is, or will remain, accurate or appropriate.



Contents

	Preface	page xiii
	1 About the Book	xiii
	2 About Me	xiii
1	The Solar System	1
	1.1 Objects and Sciences	1
	1.2 Planetary Atmospheres	4
	1.3 Outer Planets	5
	1.4 Asteroids, Transneptunian Objects, and Comets	6
	1.5 Formation of the Solar System	8
2	Atmospheric Structure	11
	2.1 Barometric Formula and Its Versions	11
	2.2 Vertical Transport	14
	2.3 Thermal Balance	18
	2.4 Upper Atmosphere	22
	2.5 Escape Processes	26
3	Spectroscopy	30
	3.1 Quantum Mechanics and Schroedinger Equation	30
	3.2 Hydrogen-like Atoms: Energy Levels and Quantum Numbers	31
	3.3 Radiation Types and Transition Probabilities	33
	3.4 Spectra of Hydrogen-like Atoms	34
	3.5 Multielectron Atoms	36
	3.6 Energy Levels and Selection Rules	37
	3.7 Spectra of Multielectron Atoms	38
	3.8 Rotational and Vibrational Levels of Diatomic Molecules	41
	3.9 Rotational and Rovibrational Spectra	43
	3.10 Electronic States of Diatomic Molecules	46
	3.11 Electronic Spectra of Diatomic Molecules	47
	3.12 Polyatomic Molecules	51

vii



viii Contents

4	Aerosol Extinction and Scattering	52
	4.1 Spherical Particles: Mie Formulas	52
	4.2 Some Approximations and Nonspherical Particles	54
	4.3 Particle Size Distributions: Photometry, Polarimetry, and Nephelometry	
	of Aerosol Media	55
	4.4 On the Radiative Transfer	57
	4.5 Aerosol Altitude Distribution	61
5	Quantitative Spectroscopy	65
	5.1 Line Broadening	65
	5.2 Line Equivalent Widths and Curves of Growth	67
	5.3 Ground-Based Spatially Resolved High-Resolution Spectroscopic	0,
	Observations	69
	5.4 Equivalent Widths in the Observation of HF on Venus	70
	5.5 Fitting of Observed Spectra by Synthetic Spectra	73
6	Spectrographs	78
	6.1 CVF and AOTF Spectrometers	78
	6.2 Grating Spectrographs	78
	6.3 Echelle Spectrographs	80
	6.4 Fourier Transform Spectrometers	82
	6.5 Tunable Laser and Cavity Ring-Down Spectroscopy	83
	6.6 Infrared Heterodyne Spectrometers	84
7	Spectroscopic Methods to Study Planetary Atmospheres	86
	7.1 Spacecraft, Earth-Orbiting, and Ground-Based Observations	86
	7.2 Nadir Observations to Measure Species Abundances	87
	7.3 Vertical Profiles of Temperature from Nadir Observations of the CO ₂	
	Bands at 15 and 4.3 µm	87
	7.4 Vertical Profiles of Temperature and CO Mixing Ratio from CO Line	
	Shapes in the Submillimeter Range	90
	7.5 Vertical Profiles of Terrestrial Ozone from Nadir UV Spectra	90
	7.6 Measurements of Rotational Temperatures and Isotope Ratios	94
	7.7 Inversion of Limb Observations	96
	7.8 Solar and Stellar Occultations	98
	7.9 Some Other Applications of Spectroscopy	100
	7.10 Mass Spectrometry and Gas Chromatography	100
8	Solar Radiation, Its Absorption in the Atmospheres, and Airglow	103
	8.1 Structure of the Solar Atmosphere	103
	8.2 Solar Spectrum	105
	8.3 Airglow	108
	8.4 Photodissociation and Photoionization of CO ₂ and Related	
	Dayglow	109



More Information

	Contents	1X
	8.5 Resonance Scattering and Fluorescence	112
	8.6 Photoelectrons and Energetic Electrons	115
	8.7 Chemiluminescent Reactions	118
9	Chemical Kinetics	120
	9.1 Double and Triple Collisions of Molecules	120
	9.2 Thermochemical Equilibrium	121
	9.3 Bimolecular Reactions	122
	9.4 Unimolecular Reactions	132
	9.5 Termolecular Association	136
	9.6 Heterogeneous Reactions	137
	9.7 Literature on Reaction Rate Coefficients, Absorption Cross Sections,	
	and Yields	138
10	Photochemical Modeling	140
	10.1 Continuity Equation and Its Finite Difference Analog	141
	10.2 Solution of the Problem and Boundary Conditions	142
	10.3 Example: Modeling of Global-Mean Photochemistry in the Martian	
	Lower and Middle Atmospheres	144
	10.4 Time-Dependent Models	148
	10.5 Isotope Fractionation	149
11	Mars	155
	11.1 History of Studies, General Properties, Topography, and Polar Caps	155
	11.2 CO ₂ , Aerosol, and Temperature	158
	11.3 Water Vapor, HDO, and Ice	167
	11.4 Carbon Monoxide and Molecular Oxygen	173
	11.5 Mass Spectrometric Measurements in the Lower Atmosphere	
	and Martian Meteorites: Variability of Argon	178
	11.6 Photochemical Tracers: Ozone, O ₂ Dayglow at 1.27 μm,	
	and Hydrogen Peroxide H ₂ O ₂	180
	11.7 Methane	187
	11.8 Some Upper Limits	194
	11.9 Photochemistry of the Lower and Middle Atmosphere	197
	11.10 Variations of Mars Photochemistry	201
	11.11 Dayglow	204
	11.12 Nightglow, Polar Nightglow, and Aurora	213
	11.13 Upper Atmosphere and Ionosphere	219
	11.14 Some Aspects of Evolution	232
12	Venus	238
	12.1 General Properties and History of Studies	238
	12.2 CO ₂ , N ₂ , Model Atmosphere below 100 km, Atmospheric Dynamics,	
	and Superrotation	242



x Contents

	12.3	Noble Gases and Isotopes	248
	12.4	Carbon Monoxide, Oxygen, and Ozone	251
	12.5	Sulfur Species	257
	12.6	Hydrogen-Bearing Species: H ₂ O, HCl, HF, HBr, NH ₃ ,	
		and Their D/H Ratios	266
	12.7	Nitric Oxide and Lightning	275
	12.8	Thermosphere	279
	12.9	Ionosphere	290
	12.10	Night Airglow	298
	12.11	Day Airglow	310
	12.12	Escape of H, O, and He and Evolution of Water	325
		Clouds and Haze	330
	12.14	Chemical Kinetic Model for Lower Atmosphere	
		(0–47 km)	342
	12.15	Photochemistry of the Middle Atmosphere (47–112 km)	350
		Nightglow and Nighttime Chemistry at 80–130 km	362
		Some Unsolved Problems	365
13	Titan		367
13	13.1	General Properties and Pre-Voyager Studies	367
		Voyager 1 Observations	370
	13.3	Ground-Based and Earth-Orbiting Observations	376
	13.4	Observations from the Huygens Landing Probe	382
	13.5	Cassini Orbiter Observations below 500 km	387
	13.6	Cassini/UVIS Occultations and Airglow Observations	396
		Ion/Neutral Mass Spectrometer Measurements	403
		Ionosphere	409
		Isotope Ratios	420
		Photochemical Modeling of Titan's Atmosphere	
		and Ionosphere	424
	13.11	Unsolved Problems	441
14	Triton		443
17		General Properties and Pre-Voyager Studies	443
		Interior and Surface	444
		Atmosphere	449
		Photochemistry	456
		Friton's Atmosphere after the Voyager Encounter	460
15		and Charon	467
13		Discovery and General Properties	467
		Interior and Surface	468
	13.3	Atmosphere before New Horizons and ALMA Observations	473



Contents	xi
15.4 Atmosphere: New Horizons and ALMA Observations	478
15.5 Haze	485
15.6 Photochemistry	489
References	497
Index	536

Color plate section to be found between pages 304 and 305





Preface

1 About the Book

This book is based on the author's experience in the field and is intended for senior and graduate students and research scientists specializing in planetary atmospheres. The book comprises two parts, the first of which includes 10 chapters: three chapters (Chapters 1, 2, and 8) present some basic science on the Solar System, atmospheric physics, and effects of solar radiation in atmospheres; five chapters (Chapters 3, 4, 5, 6, and 7) are related to spectroscopy and spectroscopic tools to study atmospheres; and two chapters (Chapters 9 and 10) describe photochemical modeling.

Some chapters are sufficient for practical work in our science, while the others are brief introductions or reviews. For example, the review of different types of spectrographs in Chapter 6 may help in making a choice for a given task but is not supportive for detailed instrument design.

Five chapters of the second part of the book include present data on the structure and composition of the atmospheres and ionospheres of Mars, Venus, Titan, Triton, and Pluto, respectively. There are hundreds of research articles on the subject; my goal was to describe concisely the basic facts with indications of how they were obtained. Therefore only some papers are cited, and many are missing. However, I hope that these chapters on specific atmospheres are complete and will help the reader gain time in studying an atmosphere of interest. This book is not a substitute for the current research literature on specific problems that a researcher may study.

2 About Me

I was born in 1938 in Moscow, Russia (which was part of the Soviet Union at that time). In June 1941, Germany, which controlled most of continental Europe, attacked Russia, approaching the Moscow suburbs in November of that year. My father was an engineer in the aviation industry. The loss of Moscow seemed imminent, and so his institution, with all its employees and their families, moved east to Saratov, a city on the Volga River. However, during the following autumn in 1942, the Germans reached Volgograd

xiii



xiv Preface

(Stalingrad), where the most critical battle of World War II was to take place. It was to the south of Saratov, and the German bombers appeared from time to time over our city. We returned to Moscow in 1943.

A hundred boys graduated from my school in 1955, and four of us were awarded gold medals and four silver medals. (The schools were separate for boys and girls. My gold medal was number one.) The school program covered the basic sciences and was rather broad, and our classrooms for physics and chemistry were well equipped.

I was a student of the Department of Physics, Lomonosov Moscow State University, in 1955–61. Besides attending lectures and seminars, we spent one day weekly in a physics practicum. For example, Millikan's experiment to measure electron charge was assigned to a student, and he or she was given a booklet with a description of the experimental idea and the equipment to study at home. Then the student had six hours to study the installation directly, make measurements, analyze them, and report the results to a tutor. That was during the first 3 years; later students chose their fields in physics and participated in research at proper university labs or at research centers in Moscow. I took some courses in theoretical physics from the famous theorist Lev Landau. His lectures made the exciting suggestion that physics could be created using only logic and math.

In 1961, I joined a lab headed by Professor Aleksandr Lebedinsky at the Nuclear Research Institute of Moscow State University. Lebedinsky was excited by perspectives of space studies of the Solar System, and our work was not related to nuclear physics. I was a radio amateur during my student years and had some experience in designing and adjusting electronic devices, which proved to be advantageous in developing scientific instruments for space missions. In June 1961 Lebedinsky told me that a mission to Venus with a landing on the planet had been planned for a launch in August 1962 – science fiction at that time. Lebedinsky visited M. V. Keldysh, president of the Academy of Sciences, and proposed a simple instrument to distinguish landing on the solid surface from landing on water. The instrument was based on a mercury level with platinum contacts. The circuit was on if the probe was horizontal within $\pm 3^{\circ}$ (water) and off on a solid surface with a mean deviation of $\approx 15^{\circ}$.

Keldysh approved the proposal, and Lebedinsky asked me to be technically responsible for the instrument. I was happy and proud to do that work. Finally, the instrument could also measure the period and amplitude of waves on water and gamma radiation of the surface rocks if the surface was solid. Its mass of 550 g looks reasonable even now. However, the fourth stage of the rocket failed, and the mission was lost. The Mariner 2 flyby of Venus in December 1962 indicated that the intense radio emission of Venus originates in the lower atmosphere, not in the ionosphere, and the hot lower atmosphere rules out liquid water on Venus.

Attempts to reach Venus and Mars continued in Russia, and Lebedinsky was principal investigator (PI) of a UV spectrometer (170–340 nm) onboard the Venera 2 (flyby) and of a photometer on Venera 3 (descent probe) missions. I was technically responsible for both instruments. (Here I exclude other of Lebedinsky's experiments that did not include my participation.) Both missions were launched in November 1965 and were lost before they



Preface xv

approached Venus. A mission to Mars was planned to be launched in 1965 as well; however, the launch window was lost because of some delays, and the spacecraft was directed to the Moon as the Zond 3 mission. We had the UV spectrometer at Zond 3 and gathered UV spectra of the Moon's rocks. The UV spectrometer was also installed onboard two Cosmos orbiters that were launched in 1965 and 1966 and gave the first satellite data on the global ozone distribution. In June 1967, I defended my PhD thesis; two months later, Lebedinsky had a heart attack while swimming in the Black Sea and passed away.

Our team prepared a UV spectrometer for the unsuccessful Mars 1969 mission and a dayglow multiband photometer for one of the Cosmos orbiters. In 1971, I transferred to the Space Research Institute, to its planetary department headed by Professor Vasiliy I. Moroz. I proposed and became PI of the visible nightglow spectrometers for the Mars 5 and Venera 9 and 10 orbiters that reached Mars in February 1974 and Venus in October 1975, respectively. Mars' nightglow was not detected with some sensitive upper limits, while the observations of Venus revealed the nightglow spectra, their morphology, and some data on lightning and haze. Analysis and interpretation of the observations and photochemical modeling of the atmospheres of Mars and Venus (with V. A. Parshev), including two books (*Photochemistry of the Atmospheres of Mars and Venus*, Moscow: Nauka, 1982; Berlin: Springer, 1986; *Physics of the Planetary and Cometary Airglow*, Moscow: Nauka, 1987), took up most of my time through the mid-1980s. In June 1977, I defended my thesis for the degree doctor of physics and math, and in 1985, I was awarded the USSR State Prize (for studies of Venus).

In 1981, Russia initiated a complicated Vega mission that involved delivery of a balloon and a descent probe to Venus, while the remaining spacecraft moved to comet Halley using Venus' gravity. A few European countries and the United States participated in the scientific payload of the mission. I was Russian PI of a three-channel spectrometer to study the spatial distribution of various species in the coma of comet Halley. French and Bulgarian teams with their PIs, G. Moreels and M. Gogoshev, respectively, contributed very significantly to that instrument. Two twin spacecraft were launched in December 1984, reached Venus in June 1985, and flew through the coma at 8000 km from the nucleus of comet Halley in March 1986.

Detection of the H_2O emission band at 1.38 μ m and total production of water by the comet were among our results. (There had been indirect evidence of water in comets, but direct detection had been lacking.) At a conference on comet Halley in 1987, I was deeply impressed by reports by M. J. Mumma, H. P. Larson, and H. A. Weaver, who observed the H_2O band at 2.7 μ m using a high-resolution spectrometer at the Kuiper Airborne Observatory. Except for total production of water, they measured its temperature using the rotational line distribution, gas expansion velocity using the Doppler shift, and temperature of formation using the para-to-ortho hydrogen ratio, offering proof that high spectral resolution can be advantageous even relative to a close distance to the object during missions to planets.

We had an infrared spectrometer for solar occultations at Phobos 2 that orbited Mars for two months in 1989. Vertical profiles of water vapor and dust had been observed. The



xvi Preface

mission was complicated, and its goal to study Phobos at a close distance down to 50 m with laser evaporation and analysis of the surface material was not achieved.

Three Russian scientists, including me, were invited to be co-investigators for the Voyager 2 flyby of the Neptune system in August 1989. I joined the ultraviolet spectrometer (UVS) team, headed by A. L. Broadfoot, and analyzed the UVS solar occultations of Triton's atmosphere and the data on Triton's haze. Later a photochemical model of Triton's atmosphere and ionosphere was made (with D. P. Cruikshank).

Conditions in Russian science degraded significantly in the 1990s, and I transferred to the United States in 1991. There I was impressed by difficult but possible access to high-level Earth-orbiting observatories, from which some observations could give results that otherwise would require a special instrument on a mission to a planet.

We detected helium on Mars using the Extreme Ultraviolet Explorer (EUVE), and the related modeling showed that He on Mars originates from the captured solar wind alpha particles, not from the radioactive decay of uranium and thorium, as was previously supposed. Then we detected atomic deuterium and molecular hydrogen on Mars using the Hubble Space Telescope (HST) and the Far Ultraviolet Spectroscopic Explorer, respectively. A superior-quality spectrum of Mars dayglow was observed at 90–120 nm as well. Those results changed some aspects of the hydrogen photochemistry and hydrogen isotope fractionation that are related to the evolution of water on Mars. The first UV spectrum of Pluto at 180–255 nm was observed using the HST as well.

Our EUVE and CXO (Chandra X-ray Observatory) observations of comets and analyses of other CXO observations resulted in significant progress in understanding the nature of the unexpectedly bright and initially puzzling X-ray and EUV emissions from comets and in abundances of the solar wind heavy ions that originate these emissions.

Ground-based spatially resolved high-resolution spectroscopy is another powerful tool to study the atmospheres of planets. My long-term observations of Mars and Venus were conducted at the NASA Infrared Telescope Facility using CSHELL and TEXES spectrographs and at the Canada–France–Hawaii Telescope using FTS. The observations of Mars involved variations of the O_2 dayglow at 1.27 μ m as a tracer of photochemistry, variations of CO as a tracer of the subpolar dynamics, dayglow of CO at 4.7 μ m, detection of CH₄ as a tracer of possible microbial life, and variations of HDO/H₂O related to the evolution of water. The observations of Venus referred to the cloud tops and included the first detections of NO and OCS at these altitudes and variations of CO, HCl, HF, H₂O, and SO₂; night airglow of O_2 at 1.27 μ m and OH; dayglow of CO at 4.7 μ m; and isotope D/H ratios in H₂O, HCl, and HF.

Significant efforts were made to photochemically model the atmospheres and ionospheres of Mars, Venus, Titan, Triton, and Pluto. Modeling of some other phenomena, e.g., hydrodynamic escape from Pluto, excitation of X-rays in comets by electron capture by the solar wind heavy ions, and excitation of oxygen emissions on the terrestrial planets, has been done as well. Using the British system, with all achievements equally divided among coauthors, my citation index is the best in the field of planetary atmospheres.