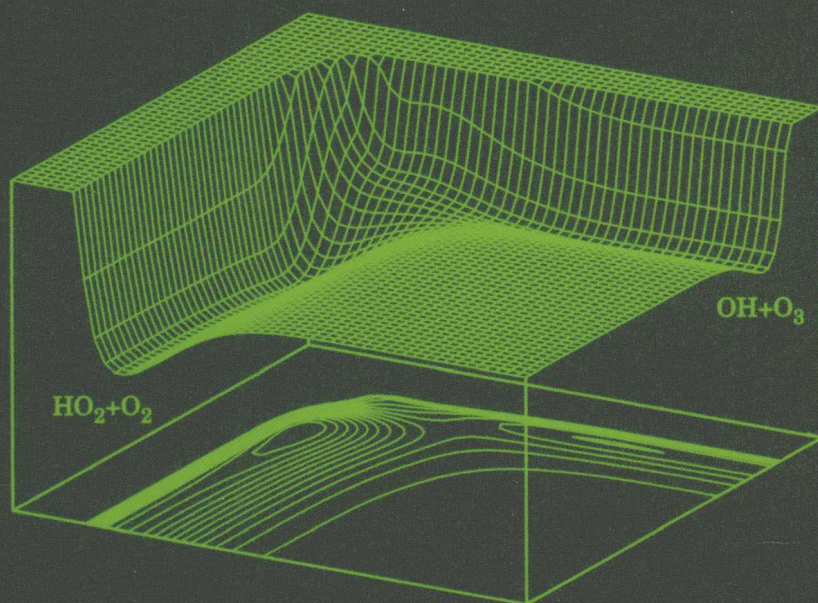


THEORETICAL AND APPLIED RESEARCH FOR POLYATOMIC COMPLEX SYSTEM REACTION DYNAMICS

Lei Zhang
Pingya Luo



Sichuan University Press

国家自然科学基金 (20873104)

四川省国际科技合作与交流研究计划项目基金 (2009HH0031)

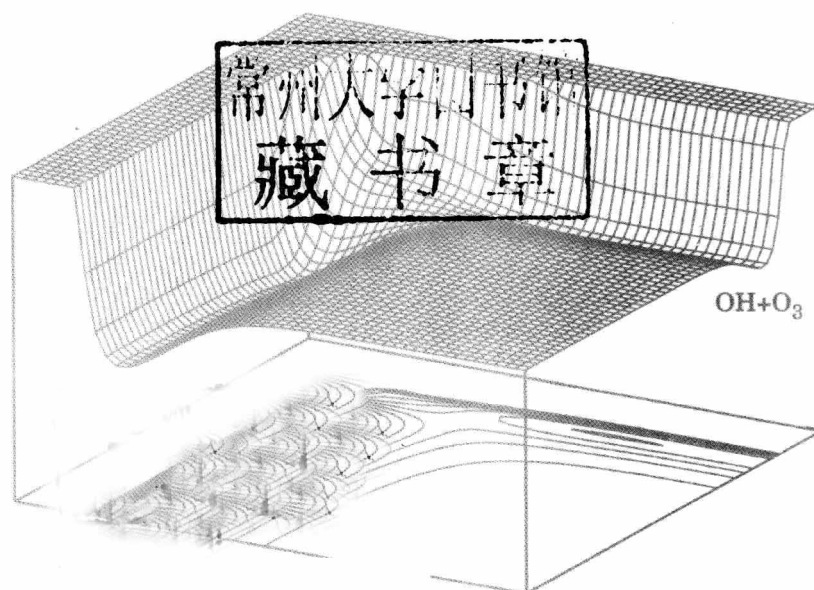
四川省青年科技基金

“油气藏地质及开发工程”国家重点实验室基金

国家人社部留学人员科技活动项目择优资助基金

THEORETICAL AND APPLIED RESEARCH FOR POLYATOMIC COMPLEX SYSTEM REACTION DYNAMICS

Lei Zhang
Pingya Luo



Sichuan University Press

特邀编辑:唐 飞
责任编辑:毕 潜
责任校对:夏 宇
封面设计:墨创文化
责任印制:李 平

图书在版编目(CIP)数据

多原子复杂体系反应动力学的理论与应用研究 =
Theoretical and Applied Research For Polyatomic
Complex System Reaction Dynamics ; 英文 / 张雷, 罗
平亚著. —成都: 四川大学出版社, 2012. 4
ISBN 978-7-5614-5770-2

I. ①多… II. ①张…②罗… III. ①多原子分子—
化学动力学—研究—英文 IV. ①0643.1

中国版本图书馆 CIP 数据核字 (2012) 第 066576 号

书名 **THEORETICAL AND APPLIED RESEARCH FOR
POLYATOMIC COMPLEX SYSTEM REACTION DYNAMICS**
多原子复杂体系反应动力学的理论与应用研究

| | |
|------|-------------------------|
| 著 者 | 张 雷 罗平亚 |
| 出 版 | 四川大学出版社 |
| 地 址 | 成都市一环路南一段 24 号 (610065) |
| 发 行 | 四川大学出版社 |
| 书 号 | ISBN 978-7-5614-5770-2 |
| 印 刷 | 郫县犀浦印刷厂 |
| 成品尺寸 | 210 mm×285 mm |
| 印 张 | 17 |
| 字 数 | 330 千字 |
| 版 次 | 2012 年 4 月第 1 版 |
| 印 次 | 2012 年 4 月第 1 次印刷 |
| 定 价 | 52.00 元 |

版权所有◆侵权必究

◆读者邮购本书,请与本社发行科
联系。电 话:85408408/85401670/
85408023 邮 政 编 码:610065
◆本社图书如有印装质量问题,请
寄回出版社调换。
◆网址:<http://www.scup.cn>

国家自然科学基金 (20873104)

四川省国际科技合作与交流研究计划项目基金 (2009HH0031)

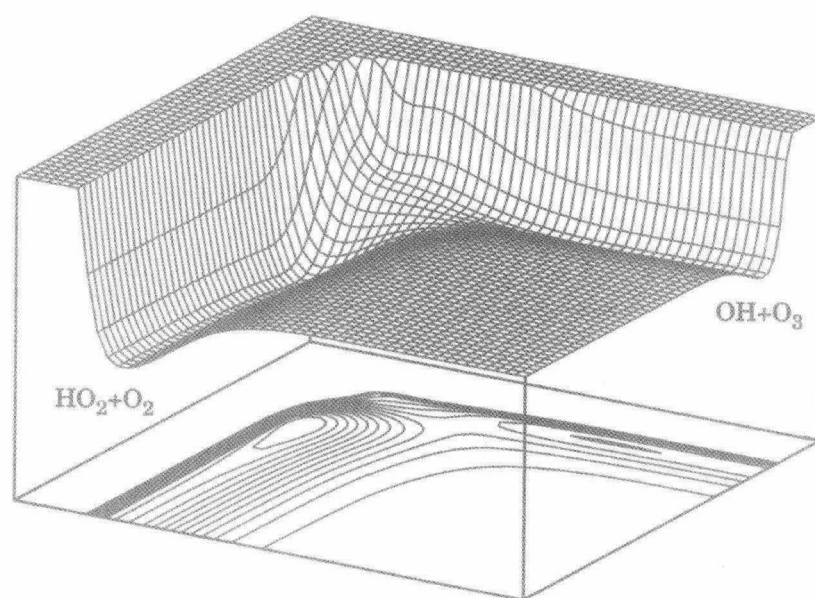
四川省青年科技基金

“油气藏地质及开发工程”国家重点实验室基金

国家人社部留学人员科技活动项目择优资助基金

多原子复杂体系 反应动力学的理论与应用研究

张 雷 罗平亚 著



四川大学出版社

前 言

近年来,随着反应动力学的理论方法和实验技术的日臻完善,多原子反应动力学的研究正处于一个蓬勃发展阶段,成为欧美发达国家高技术研究中的一个热点。过去的研究工作大都局限于原子与双原子分子或双原子与双原子分子的碰撞反应。目前该项研究方向已扩展到至少一个反应物/产物是三原子或更大的分子。这些多原子碰撞过程在环境化学、燃烧化学、天体化学、激光化学等诸多领域中起着至关重要的作用。深入研究该方向所涉及的理论与实际问题不仅在学术上具有十分重要的意义,同时还具有广阔的应用前景。

作为地球大气层的重要组成部分,臭氧(O_3)分子对地球上的生态环境有非常重要的保护作用。系统地了解其特性,进而建立大气中臭氧的反应机理及动力学模型是世界各国重点关注的问题之一(在国家重点基础研究发展计划中,已将研究大气平流层动力-物理-化学过程与变化趋势及臭氧层变化与平流层环境预测列为2009年度重要支持方向)。该动力学模型的建立涉及大气中大量的多原子碰撞反应。其中两个代表性的反应系列就是大气平流层中臭氧消耗的 HO_x 催化循环及大气中臭氧消耗的 SO_x 反应。与其他含氮、氯的反应系列相比, HO_x 反应循环不需要氧原子的参与。因此,在含自由态氧原子浓度较低的平流层中下部, HO_x 催化循环系列至关重要(在国家自然科学基金委重大项目中,将研究大气 HO_x 自由基化学的特征列为“十二五”期间重要支持方向);另一方面, SO_x 反应系列所涉及的硫及硫氧化物均为大气中的重要污染物。在研究含硫天然气开采中所涉及的大气污染问题,制订相应控制对策时, SO_x 反应系列具有重要意义。鉴于大气层中还含有大量处于振动激发态的反应物分子,本书将在深入研究 HO_x 催化循环系列及 SO_x 反应系列的基础上,系统阐述反应物内能对该反应/逆反应系列的影响以及在碰撞过程中振动能量传递及分配等问题,这对准确评价臭氧反应的机理及模型的建立有重要的理论意义和实用价值。特别需要指出,本书所涉及的内容是一项综合性的、多种学科交叉、渗透的前沿工作,使大气中臭氧动力学模型的建立及大气污染

控制对策的制订与现代理论计算化学的研究成果更为紧密结合,同时可为现代分子动态学及分子设计理论在油气田开发工程中的应用探索方法和途径。

全书分为两个部分:第一部分为多原子复杂体系反应动力学所涉及的理论基础及研究前沿;第二部分为作者在 *Phys. Chem. Chem. Phys.*, *J. Phys. Chem. A.*, *Chem. Phys. Lett.* 等欧美知名学术期刊上发表 SCI 收录论文代表作,主要涉及大气平流层中臭氧消耗的 HO_x 催化循环反应的基础理论研究以及大气中臭氧消耗的 SO_x 反应的前期理论研究。

作者非常感谢葡萄牙科学院院士、著名国际理论化学家、葡萄牙科英布拉大学化学系 A. J. C. Varandas 教授对本书编写给予的关心和支持。

作者对国家自然科学基金(20873104)、四川省国际科技合作与交流研究计划项目基金(2009HH0031)、四川省青年科技基金、“油气藏地质及开发工程”国家重点实验室基金以及国家人社部留学人员科技活动项目择优资助基金的大力资助致以最诚挚的谢意。对四川大学出版社对本书的编辑和出版所给予的支持表示衷心的感谢。

四川大学张光澄教授、侯泽华副教授、成都理工大学郭科教授、西南交通大学曾蓉博士和西南石油大学硕士研究生陶玉林、张婉荞、陈一鸣、梁红、许国超、马远荣、郝吉鹏、陈虞亮、李智、胡丽春、彭琳等帮助整理本书初稿做了大量细致的工作,作者在此一并表示谢意。

著 者

2011. 10

于西南石油大学

“油气藏地质及开发工程”

国家重点实验室

Contents

| | |
|---------------------------|-------|
| Introduction | (1) |
| Bibliography | (1) |

Part I Theoretical Framework

| | |
|---|--------|
| Chapter 1 Potential Energy Surfaces | (10) |
| 1.1 Born-Oppenheimer approximation | (12) |
| 1.1.1 The total Hamiltonian | (12) |
| 1.1.2 Adiabatic representation | (12) |
| 1.1.3 Diabatic representation | (14) |
| 1.1.4 Diabatic-to-Adiabatic transformation | (16) |
| 1.1.5 Two-State model | (17) |
| 1.2 The solution of the electronic problem | (18) |
| 1.3 <i>Ab initio</i> potential energy surfaces | (21) |
| 1.3.1 Correlation energy partitioning | (23) |
| 1.3.2 Semiempirical correction of <i>ab initio</i> energies | (24) |
| 1.4 Semiempirical global potential energy surfaces | (26) |
| 1.4.1 Diatomics-in-molecules theory | (26) |
| 1.4.2 The double many-body expansion method | (28) |
| 1.4.3 Energy-switching scheme for spectroscopically accurate functions | (31) |
| Bibliography | (32) |

| | |
|---|--------|
| Chapter 2 Reaction Dynamics | (37) |
| 2.1 Classical scattering | (42) |
| 2.1.1 Molecule collision theory | (42) |
| 2.1.2 Statistical averaging | (46) |
| 2.2 The quasiclassical trajectory method | (47) |
| 2.2.1 Classical Hamiltonian mechanics | (47) |
| 2.2.2 Coordinate systems and transformations | (50) |
| 2.2.3 Selection of initial states | (52) |
| 2.2.4 Integration of the equations of motion | (58) |
| 2.2.5 Analysis of final states | (59) |
| 2.2.6 Treatment of the zero-point energy problem | (60) |
| 2.3 Quantum reaction dynamics; a synopsis | (62) |
| 2.3.1 The interaction picture | (63) |
| 2.3.2 Time-dependent approaches | (64) |
| 2.3.3 Time-independent approaches | (66) |
| 2.3.4 Reduced dimensionality approaches | (69) |
| Bibliography | (71) |

Part II Case Studies

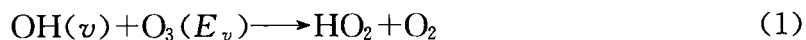
| | |
|--|---------|
| Chapter 3 Dynamics of the $\text{OH}(v) + \text{O}_3(E_v)$ Atmospheric Reaction | (80) |
| Test Studies on the Potential Energy Surface and Rate Constant for the $\text{OH} + \text{O}_3$ Atmospheric Reaction | (81) |
| Dynamics of the $\text{OH}(v=1, 2, 4) + \text{O}_3$ Atmospheric Reaction | (96) |
| $\text{OH}(v) + \text{O}_3$: Does Chemical Reaction Dominate over Non-reactive Quenching? | (116) |
| Dynamics Study of the $\text{OH} + \text{O}_3$ Atmospheric Reaction with Both Reactants Vibrationally Excited | (131) |
| Vibrational Relaxation of Highly Vibrationally Excited O_3 in Collisions with OH | (149) |
| Dynamics Study of the Atmospheric Reaction Involving Vibrationally Excited O_3 with OH | (165) |

| | | |
|------------------|--|-------------|
| Chapter 4 | Dynamics of the $\text{O}_2(v) + \text{HO}_2(E_v)$, and $\text{HO}_2 + \text{O}_3$ Atmospheric Reaction | (187) |
| | Dynamics Study of the $\text{O}_2(v) + \text{HO}_2$ Atmospheric Reaction | (188) |
| | Dynamics of the $\text{O}_2 + \text{HO}_2$ Atmospheric Reaction with Both Reactants Vibrationally Excited | (212) |
| | Vibrational Relaxation of Highly Excited HO_2 in Collisions with O_2 | (229) |
| | Dynamics of $\text{HO}_2 + \text{O}_3$ Reaction Using a Test DMBE Potential Energy Surface: Does It Occur via Oxygen or Hydrogen Atom Abstraction | (246) |

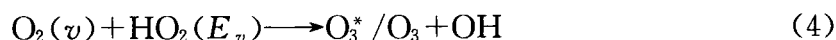
Introduction

In the last decades, interest in detailed studies of polyatomic reaction dynamics has blossomed. Improved experimental techniques, more powerful quasiclassical dynamical methods, and accurate electronic structure capabilities have all combined to focus attention on detailed dynamical questions for larger and larger systems. Many of these questions have previously been tackled primarily for atom-diatom or diatom-diatom collisions or isolated triatomics. Thus the “polyatomic” will be operationally defined to refer to a collision in which at least one collision partner or product is a triatomic or larger or to a unimolecular process involving four or more atoms. Clearly, such collisional processes play a very important role in many fields such as atmospheric chemistry, combustion chemistry, laser processes, and so on. In fact, a detailed knowledge of the properties of such collisional processes is a key element both for modelling the chemical components arising in environmental problems and for the interpretation of work with lasers. This study is therefore an intriguing topic since it offers an understandable bridge between reaction mechanisms and many complicated phenomena which have practical and even social implications.

As far as atmospheric chemistry is concerned, the processes addressed in this book refer to the hydrogen-oxygen system of reactions in the chemistry of ozone, namely



and the reverse of reaction (1)





where the star indicates that the ozone formed has an internal energy above the dissociation limit.

The hydroxyl radical OH, in both the ground and vibrationally excited states, is of particular interest because of its importance as a chain carrier in a number of systems. In addition, it plays a preeminent role in the chemistry of both the lower and upper atmosphere. Indeed, atmospheric OH in the ground state has been measured and vibrationally excited OH has been identified in the upper atmosphere and auroras. Though reaction and relaxation dynamics of OH are reasonably well understood in the troposphere and stratosphere, complete characterization in higher atmospheric layers has remained elusive. Since hydroxyl radicals are produced vibrationally excited, $\text{OH}(v \leq 9)$, in the upper stratosphere and mesosphere by the reaction of hydrogen atoms with ozone, they are also important in the study of infrared emission from the earth's upper atmosphere. In fact, spectral and temporal information from such emissions is commonly used in monitoring atmospheric phenomena and in creating models of atmospheric chemistry and kinetics.

Once produced, hydroxyl radicals either uoresce, react, or undergo deactivation in collisions with the ambient species such as O, O_2 , O_3 , N_2 , CO_2 , and so on. Over the past decade, significant progress has been made in measuring the vibrational level dependence of the total removal rate constants for collisional processes in the laboratory. However, essentially absent from the list of collision/reaction partners is O_3 , which is a major constituent of the atmosphere. Yet, the reaction $\text{OH} + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2$ influences the steady state concentration of many traces gases which are important in stratospheric chemistry, and is part of the HO_x catalytic cycle for ozone depletion in the natural stratosphere.

On the other hand, as it has been well established, ozone plays a crucial role in the stratospheric and mesospheric chemistry. Vibrationally excited $\text{O}_2(^3 \sum_g^-)$, generated in the ultraviolet photolysis of ozone, has been proposed to explain the limitations of atmospheric ozone models.^[1, 2] Indeed, there has been a long-standing problem with ozone models for the upper stratosphere and mesosphere, where the models underpredict the measured ozone concentrations, and this unexpected ozone source was viewed as a possible explanation for the discrepancy. The "ozone deficit"

problem has prompted much effort to identify new sources of ozone.^[3-8] Spectroscopic detection of highly vibrationally excited O_2 produced from photodissociation of O_3 at^[9] 248 and^[10] 226 nm has shown that states as high as $v=27$ are formed with significant efficiency. The reaction of highly vibrationally excited O_2 upon collision with a variety of species has been studied extensively. However, remarkably absent from the list of species is HO_2 , which is a vital natural component of the atmosphere. In addition, the HO_2 radical is also an important intermediate for many chemical reactions such as those involved in atmospheric chemistry, stratospheric formation and destruction of ozone, and photochemical air pollution. Clearly, investigation of the collisional properties of highly vibrationally excited O_2 with the HO_2 radical is of great interest.

There have been very few experimental reports on the $OH(v) + O_3$ reaction, with the work of Coltharp *et al.*^[11] being the only study carried out to investigate the influence of vibrational quanta of OH on the $OH + O_3$ interaction. Unfortunately, these results are now suspect because of faulty kinetic analysis of the raw data.^[12-16] Time-dependent measurements of absolute rate constants were initiated by Greenblatt and Wiesenfeld.^[12] They measured the relaxation of $OH(v=9)$ by O_3 , and found that O_3 is efficient at removing such vibrationally excited hydroxyl radicals. Thus, we may distinguish three distinct sets of v states: $v=0$ for which the rate of reaction with O_3 is well established;^[17] $v=9$ which has been the subject of a reliable absolute rate constant measurement for $OH(v)$ removal; $1 \leq v \leq 8$ and $v \geq 10$ states where there is essentially no experimental data.

Until recently, no single theoretical study of the $OH(v) + O_3(E_v)$ reaction and its reverse reaction has been reported in the literature. Such a lack of theoretical work can only be attributed to difficulties in calculating a reliable $HO_4(^2A)$ potential energy surface by correlated *ab initio* methods. Although largely due to the number of electrons involved, such computational difficulties get compounded by the fact that it is a five-atom system spanning a nine-dimensional (9D) configuration space. In fact, although there has been an increasing number of studies on four-atom reactions, very few have so far been carried out on five-atom ones using global potential energy surfaces that cover all possible reaction channels. To our knowledge, the only available studies refer to five-atom^[18,19] and six-atom^[18] hydrogenic systems (H_n), and hence benefit from the small number of electrons and high permutational symmetry of the molecular system. Based on previous

work,^[20-25] we have developed the required realistic surface by using the double many-body expansion^[26,27] (DMBE) method as implemented for single-valued functions. Moreover, we have used this novel HO₄ surface to study the OH(*v*) + O₃ reaction.^[28-30] In particular, for the state *v*=0, good agreement has been found with the data recommended by the IUPAC Subcommittee on Gas Kinetics Data Evaluation for Atmospheric Chemistry;^[17] for 1 ≤ *v* ≤ 4 states, since there is essentially no experimental data, a comparison with available results on the OH(*v*) quenching based on nonreactive collisions has been presented. The results indicate that vibrational excitation strongly enhances reactivity, with the removal of vibrationally excited OH occurring predominantly through chemical reaction.

It should be noted at this stage that available experiments for *v* = 9 did not monitor the products of reaction, and hence the possibility exists that such results might not be due to reactive quenching. This issue has been raised by Teitelbaum *et al.*^[15] who were the first to suggest that OH(*v*=9) removal was dominated by vibrational relaxation and not by chemical reaction. However, it is well established that OH in *v*=0 does react with O₃. Although this rate constant has a relatively small value,^[14] $6.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, there is no reason in principle why reactivity could not be maintained or even enhanced for vibrationally excited OH radicals. Furthermore, new chemical channels accessible at these higher energies can provide a simple rationale for large vibrational enhancement effects. For example, bond breaking to form O₂ + O₂ + H or O₂ + OH + O becomes energetically open for OH(*v* ≥ 3). According to the Polanyi rules they might be sensitive to OH vibrational excitation. One might argue that the increased OH(*v* = 9) quenching cross-section with O₃ is the result of chemical reaction occurring in parallel with vibrational relaxation. In fact, theoretical work^[30] for the states *v* = 6 and 9 using the HO₄ DMBE potential energy surface produced total (reactive plus nonreactive) removal rate constants in good agreement with both the measurements of Greenblatt *et al.*^[12] and the latest experimental report of Nizkorodov^[31] while supporting the view that reactive scattering cannot be discarded, and even be dominant over non-reactive scattering.

In addition, based on such a reliable potential energy surface for HO₄ (²A), we have also reported the theoretical study of the O₂ (*v*) + HO₂ (*E_v*) multichannel reaction,^[32,33] which gives the first information for HO₂ as a collision partner. The results indicate that it can be a potential source of ozone in the upper atmosphere.

Furthermore, theoretical investigations of vibrational relaxation of highly vibrationally excited HO_2/O_3 in collisions with O_2/OH have also been presented.^[35,37] Finally, we investigated the dynamics of $\text{HO}_2 + \text{O}_3$ reaction using a global DMBE potential energy surface for $\text{HO}_5(^2A)$ developed by us.^[34]

Ten of the atmospheric reactions in the present review of this book have great relevance to stratospheric ozone chemistry. Although they are only a subset of the reactions necessary for modelling the chemistry of stratospheric ozone, such reactions are the most influential since only natural species which have a high abundance in the atmosphere are involved. Thus, they may be used to provide a model prediction from first principles of the hydrogen-oxygen atmosphere in which contamination by other chemicals is absent. Hopefully, this account of the present status of $\text{OH}(v) + \text{O}_3(E_v)$ and its reverse reaction dynamics will stimulate more experimental and theoretical interest in these important species which relate rather intimately in one way or another to our daily life. Finally, it would be interesting to see the extent to which the methodology discussed in this account is working its way to address other five-atom and larger polyatomic reactions which are currently at the forefront of reaction dynamics.

This book is organized in two parts. The first part gives theoretical introduction, while the second part presents detailed case studies. In particular, the first chapter of the second part presents a single-valued potential energy surface for $\text{HO}_4(^2A)$ from the double many-body expansion method and dynamics studies of $\text{OH}(v) + \text{O}_3(E_v)$ atmospheric reaction.^[28-30,36-38] The second chapter provides detailed investigation of $\text{O}_2(v) + \text{HO}_2(E_v)$ reaction,^[32, 33,35] and $\text{HO}_2 + \text{O}_3$ reaction.^[34]

The system of units adopted throughout the book is not uniform since we have used, depending on the context, the units which best suit the particular subject or which make comparisons with other studies easier.

Bibliography

- [1] M. A. J. Eluszkiewicz and M. Allen, J. Geophys. Res. 98, 1069 (1993).
- [2] D. E. Siskind, B. J. Connor, R. S. E. E. E. Remsberg, J. J. Tsou, and A. Parrish, J. Geophys. Res. 100, 11191 (1995).
- [3] J. M. Price, J. A. Mack, C. A. Rogaski, and A. M. Wodtke, Chem. Phys. 175, 83 (1993).

- [4] A. J. C. Varandas and W. Wang, Chem. Phys. 215, 167 (1997).
- [5] A. J. C. Varandas, A. A. C. C. Pais, J. M. C. Marques, and W. Wang, Chem. Phys. Lett. 249, 264 (1996).
- [6] A. J. C. Varandas, Int. Rev. Phys. Chem. 19, 199 (2000).
- [7] A. J. C. Varandas and P. J. S. B. Caridade, Chem. Phys. Lett. 339, 1(2001).
- [8] P. J. S. B. Caridade, L. Zhang, J. D. Garrido, and A. J. C. Varandas, J. Phys. Chem. A 105, 4395 (2001).
- [9] H. Parker and T. G. Slanger, J. Chem. Phys. 100, 287 (1994).
- [10] R. L. Miller, A. G. Suits, P. L. Houston, R. Toumi, J. A. Mack, and A. M. Wodtke, Science. 265, 1831 (1994).
- [11] R. N. Coltharp, S. D. Worley, and A. E. Potter Jr. , Appl. Opt. 10, 1786 (1971).
- [12] G. D. Greenblatt and J. R. Wiesenfeld, J. Geophys. Res. 87, 11145 (1982).
- [13] T. G. Slanger and D. L. Huestis, Int. J. Chem. Kin. 17, 713 (1985).
- [14] J. I. Steinfeld, S. M. Adler-Golden, and J. W. Gallagher, J. Phys. Chem. Ref. Data 16, 911 (1987).
- [15] H. Teitelbaum, P. Aker, and J. J. Sloan, Chem. Phys. 119, 79 (1988).
- [16] T. G. Slanger and R. A. Copeland, Current Problems and Progress in Atmospheric Chemistry (World Scientific, Singapore, 1996).
- [17] R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson Jr. , J. A. Kerr, and J. Troe, J. Phys. Chem. Ref. Data 21, 1125 (1992).
- [18] A. J. C. Varandas and J. N. Murrell, Faraday Discuss. Chem. Soc. 62, 92 (1977).
- [19] A. Aguado, C. Tablero, and M. Paniagua, J. Chem. Phys. 110, 7789 (1999).
- [20] A. J. C. Varandas and J. D. Silva, J. Chem. Soc. Faraday Trans. 88, 941 (1992).
- [21] A. J. C. Varandas and A. I. Voronin, Chem. Phys. 194, 91 (1995).
- [22] M. R. Pastrana, L. A. M. Quintales, J. Brandão, and A. J. C. Varandas, J. Phys. Chem. 94, 8073 (1990).
- [23] A. J. C. Varandas and A. A. C. C. Pais, Mol. Phys. 65, 843 (1988).
- [24] A. J. C. Varandas and H. G. Yu, Mol. Phys. 91, 301 (1997).
- [25] A. J. C. Varandas and A. A. C. C. Pais, in Theoretical and Computational Models for Organic Chemistry, edited by S. Formosinho, I. Czismadia, and L. Arnaut (Kluwer, Dordrecht, 1991), p. 55.
- [26] A. J. C. Varandas, Adv. Chem. Phys. 74, 255 (1988).
- [27] A. J. C. Varandas, in Lecture Notes in Chemistry, edited by A. Lagan_a and A. Riganelli (Springer, Berlin, 2000), vol. 75, p. 33.
- [28] A. J. C. Varandas and L. Zhang, Chem. Phys. Lett. 331, 474 (2000).
- [29] L. Zhang and A. J. C. Varandas, Phys. Chem. Chem. Phys. 3, 1439(2001).
- [30] A. J. C. Varandas and L. Zhang, Chem. Phys. Lett. 340, 62 (2001).

- [31] S. A. Nizkorodov, W. H. Harper, and D. J. Nesbitt, Chem. Phys. Lett. 341, 107 (2001).
- [32] L. Zhang and A. J. C. Varandas, J. Phys. Chem. A 105, 10347 (2001).
- [33] L. Zhang and A. J. C. Varandas, J. Phys. Chem. A 106, 11911 (2002).
- [34] A. J. C. Varandas and L. Zhang, Chem. Phys. Lett. 385, 409 (2004).
- [35] A. J. C. Varandas and L. Zhang, Chem. Phys. Lett. 402, 399 (2005).
- [36] L. Zhang, P. Y. Luo, Z. Y. Huang and A. J. C. Varandas, J. Phys. Chem. A 110, 13836 (2006).
- [37] L. Zhang, P. Y. Luo, Z. Y. Huang, H. Chen and A. J. C. Varandas, J. Phys. Chem. A 112, 7238 (2008).
- [38] L. Zhang, P. Y. Luo, R. Zeng, P. J. S. B. Caridade and A. J. C. Varandas, Phys. Chem. Chem. Phys. 12, 11362 (2010).

