

CONTENTS

PHOTOPHYSICS OF INTERNAL TWISTING	1
By E. Lippert, W. Rettig, V. Bonačić-Koutecký, F. Heisel, and J. A. Míche	
KINETIC THEORY FOR CHEMICALLY REACTING GASES AND PARTIALLY IONIZED PLASMAS	175
By Yu. L. Klimontovich, D. Kremp, and W. D. Kraeft	
INTERACTION OF CHARGED PARTICLES WITH MOLECULAR MEDIUM AND TRACK EFFECTS IN RADIATION CHEMISTRY	255
By I. G. Kaplan and A. M. Miterev	
AUTHOR INDEX	387
SUBJECT INDEX	399

PHOTOPHYSICS OF INTERNAL TWISTING

E. LIPPERT* AND W. RETTIG

*Iwan N. Stranski-Institut für Physikalische und Theoretische Chemie
Technische Universität Berlin
D-1000 Berlin (West) 12, Strasse des 17. Juni 112*

V. BONAČIĆ-KOUTECKÝ

*Institut für Physikalische und Theoretische Chemie
Freie Universität Berlin
D-1000 Berlin (West) 33, Takustrasse 3*

F. HEISEL AND J.A. MIEHÉ

*Groupe de Photophysique Moléculaire
Centre de Recherches Nucléaires
F-67037 Strasbourg Cedex*

CONTENTS

- I. Introduction
 - A. Adiabatic Photoreactions Involving Charge Transfer
 - B. Electronic and Dynamic Aspects
- II. Dual Fluorescence
 - A. Some Basic Concepts
 - 1. The Notion of TICT States in Aromatic Donor-Acceptor Compounds
 - 2. The Complexity of the Reaction Mechanism
 - 3. Potential Energy Surfaces
 - 4. Kinetic Distinctions
 - B. Steady-State Fluorescence
 - 1. Quantum Yields and Solvatochromism of DMABN
 - 2. The TICT Excited-State Dipole Moment
 - 3. Other Solute Examples

* Adjunct Professor at the Institute for Molecular Science, Okazaki, Japan, from January to July, 1985, where the basic conceptions were developed.

- C. Kinetic Investigations
 - 1. The Conventional Kinetic Model (Time-Independent Rate Constants)
 - 2. Time-Dependent "Rate Constants"
 - 3. Time-Resolved Solvatochromism
- D. Cage Effects
 - 1. Rearrangements in Mixed Solvents
 - 2. Side Reactions: Complex Formation
- III. Electronic Structure of the Bonded π -Donor- π -Acceptor Pairs
 - A. Outline of the Theoretical Treatment
 - B. The Two-Electron, Two-Orbital Model
 - 1. 3×3 Interaction
 - 2. Energies and Wavefunctions of Biradicaloids
 - 3. Heterosymmetric Biradicaloids
 - 4. Homosymmetric Biradicaloids
 - 5. Nonsymmetric Biradicaloids
 - C. Ab Initio CI Models of Simple Double, Charged, and Dative π -Bonds
 - D. Complex Dative π -Bond
 - 1. Free Molecules
 - 2. Environmental Influence
 - E. The Origin of the Dual Fluorescence of 9,9'-Bianthryl
- IV. Stochastic Description of Chemical Reactions
 - A. Introduction
 - B. Markov Processes
 - 1. Definition of Stochastic Processes
 - 2. Continuous and Discrete Markov Processes
 - C. Master Equation
 - D. Birth-Death Processes (or One-Step Processes)
 - 1. General Properties
 - 2. Examples
 - E. Diffusion Processes
 - 1. Definition
 - 2. Kolmogorov's Backward Equation
 - 3. Kolmogorov's Forward Equation
 - 4. Examples
 - F. Kramers-Moyal Expansion
 - G. Langevin Equation
 - 1. Brownian Motion and Langevin Equation
 - 2. Brownian Motion in a Force Field
 - H. Kramers' Approach to Steady-State Rates of Reaction and Its Extension to Non-Markovian Processes
 - 1. Kramers' Approach
 - 2. Non-Markovian Theory of Activated Rate Process
 - I. Unimolecular Reactions in the Absence of a Potential Barrier
 - 1. Time-Dependent Reaction Rate
 - 2. First Passage Time
 - 3. Influence of Initial Conditions
- V. Experimental Results and Interpretation
 - A. Dynamics of DMABN in the Excited State
 - 1. Dynamics of the B^* State Deactivation
 - 2. Temperature Dependence of the B^* State Quantum Yield

3. TICT State Formation

4. Discussion

B. Kinetics of Other Dialkylanilines

C. Some Extended Donor–Acceptor Systems with Anomalous Fluorescence

D. Donor–Acceptor Systems without Anomalous Fluorescence Band

VI. Summary

References

KINETIC THEORY FOR CHEMICALLY REACTING GASES AND PARTIALLY IONIZED PLASMAS

YU. L. KLIMONTOVICH

*Moscow State Lomonossov University
Faculty of Physics, Moscow, 117234, USSR*

D. KREMP

*Wilhelm-Pieck-Universität Rostock
Sektion Physik, Rostock, 2500, DDR*

W. D. KRAEFT

*Ernst-Moritz-Arndt-Universität Greifswald
Sektion Physik/Elektronik, Greifswald, 2200, DDR*

CONTENTS

- Introduction
- I. Quantum Statistics of Many-Particle Systems
 - A. The Density Operator
 - B. Equation of Motion for the Density Operator and the Wigner Distribution
- II. Kinetic Equation for Nonideal Gases
 - A. Binary Density Matrix in Two-Particle Collision Approximation—Boltzmann Equation
 - B. Binary Density Operator in Three-Particle Collision Approximation—Boltzmann Equation for Nonideal Gases
 - C. Energy Conservation
- III. Bound States in Kinetic Theory
 - A. Problem of Bound States—Generalization of the Bogolyubov Condition
 - B. Binary Collision Approximation for the Two-Particle Density Operator—Kinetic Equations for Free Particles and Atoms
 - C. Binary Density Operator for Higher Densities—Bound States

- D. Kinetic Equations for Free Particles and for Composite Particles (Atoms)
 - E. Properties of the Kinetic Equations
 - F. Rate Equations for Reactions—Equilibrium Solutions
 - G. The Weak Coupling Approximation
 - IV. Kinetic Equations for Plasmas
 - A. Pair Creation and Annihilation Operators
 - B. The Equations of Motion
 - C. Polarization Approximation for the Atomic Gas—Collision Integral
 - D. Kinetic Equations for Reacting Systems
 - V. Kinetic Theory of Fluctuations in Partially Ionized Plasmas
- References

INTERACTION OF CHARGED PARTICLES WITH MOLECULAR MEDIUM AND TRACK EFFECTS IN RADIATION CHEMISTRY

I. G. KAPLAN AND A. M. MITEREV

*L. Ya. Karpov Institute of Physical Chemistry
ul. Obukha, 10 107120
Moscow B-120, USSR*

CONTENTS

- I. Introduction
- II. Primary Radiolysis Processes (A Qualitative Picture)
 - A. The Time Scale of Elementary Events
 - B. The Stages of Radiolysis
- III. Nature of Highly Excited Molecular States Produced by Ionizing Radiation
 - A. The Evolution of States with a Core Hole
 - B. The Superexcitation States
 - C. The Collective Excitation States of Plasmon Type
- IV. Cross Sections of Interaction of Fast Charged Particles with a Molecular Medium
 - A. General Formulas for the Cross Sections of Scattering of a Charged Particle by a Molecule
 - B. The Born Approximation
 - 1. Differential Cross Sections
 - 2. Properties of Generalized Oscillator Strengths
 - 3. Exchange Effects in Scattering
 - 4. Total Cross Sections of Excitation and Ionization
 - C. The Quasi-Classical Approximation: The Impact Parameter Method
- V. Energy Losses of Charged Particles in a Molecular Medium
 - A. The Molecular Stopping Power
 - 1. Methods of Calculating the Molecular Stopping Power and Its Properties
 - 2. Particular Features of Retardation of Multicharged Ions
 - B. Specific Features of the Interaction of Charged Particles with a Condensed Medium
 - 1. The Ionization Potential in the Condensed Phase
 - 2. The Energy Loss Spectrum in Condensed Media
 - 3. The Influence of the State of Aggregation on the Ionization Losses of Fast Charged Particles

4. The Influence of Dielectric Properties of a Medium on the Distribution of Energy in the Track

VI. Retardation of Slow Electrons

- A. The Subexcitation Electrons
- B. The Main Processes of Slow Electron Interaction with Molecules
- C. The Theory of Retardation of Subexcitation Electrons in Condensed Media
- D. Experimental Studies of Thermalization Path Lengths
 - 1. Radiation-Chemical Methods
 - 2. Photoemission Methods

VII. Delocalization of the Energy of Ionizing Radiation in a Molecular Medium and Its Radiation-Chemical Manifestation

- A. Formulation of the Problem
- B. Delocalization and the Uncertainty Principle
- C. The Delocalization due to Excitation of Collective States
- D. The Radiation-Chemical Manifestation of Delocalization

VIII. Tracks of Charged Particles and Their Structure

- A. Tracks of Fast Electrons
 - 1. Classification of Track Structures
 - 2. Simulation of a Fast Electron Track
- B. The Influence the State of Aggregation of a Medium Has on the Primary Stage of Radiolysis
- C. Vavilov-Cherenkov Radiation and Photoradiation Reactions in Tracks
- D. The Structure of Tracks of Heavy Charged Particles
 - 1. Specific Features of the Way Heavy Charged Particles Transfer Their Energy to a Medium
 - 2. The Track Structure of Ions of Different Nature

IX. Specific Features of Radiation-Chemical Reactions in Tracks of Particles of Different Nature

- A. The Influence of the Spatial Structure of a Track on the Features of Radiation-Chemical Reactions
 - 1. The Influence of the State of Aggregation
 - 2. The Influence of the Track Structure on Track Reactions and the Insufficiency of the LET Conception
- B. The Thermochemical Effect Produced by Charged Particles
- C. On the Problem of Equivalence of the Effects Produced by Different Types of Radiation

References

