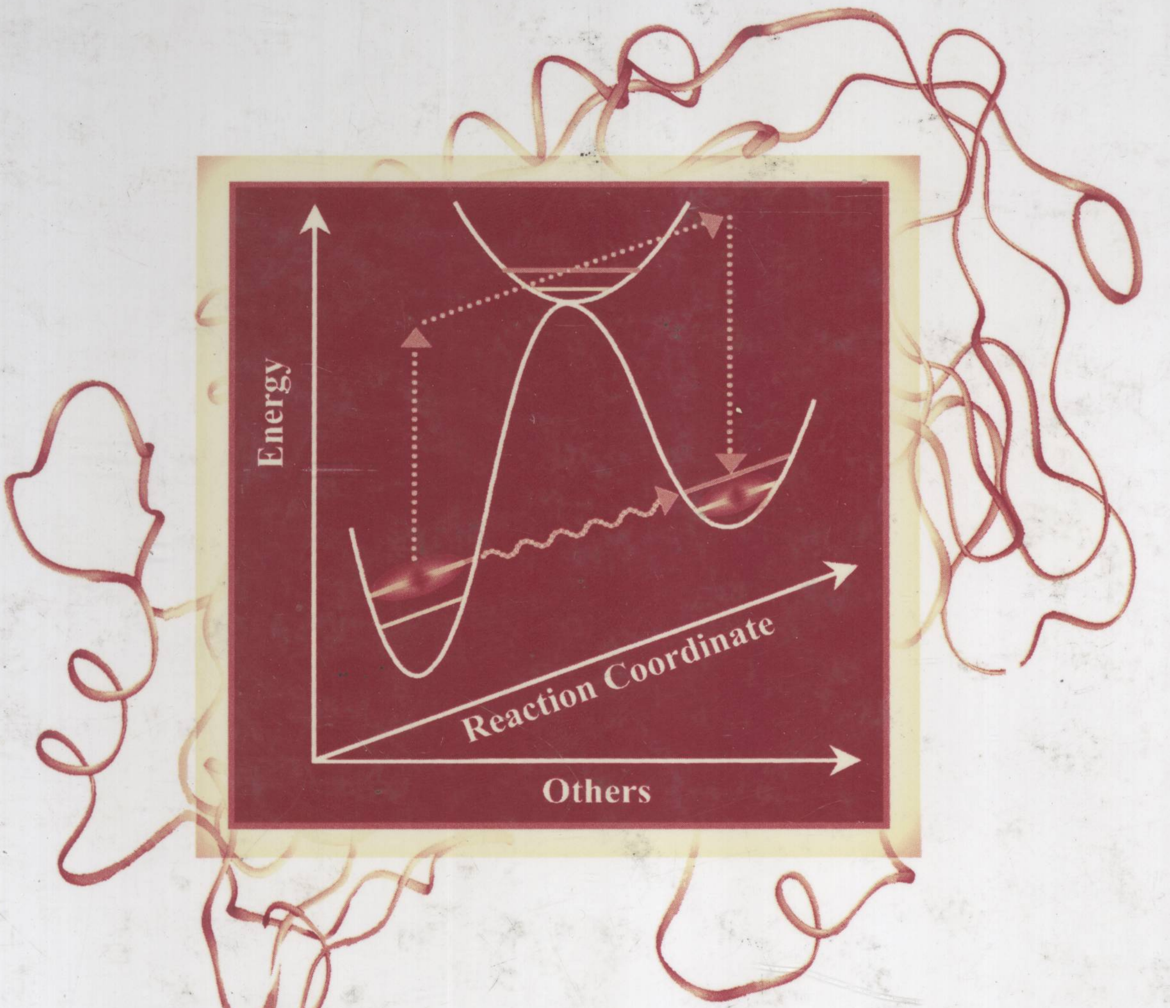
Isotope Effects in Chemistry and Biology



Edited by
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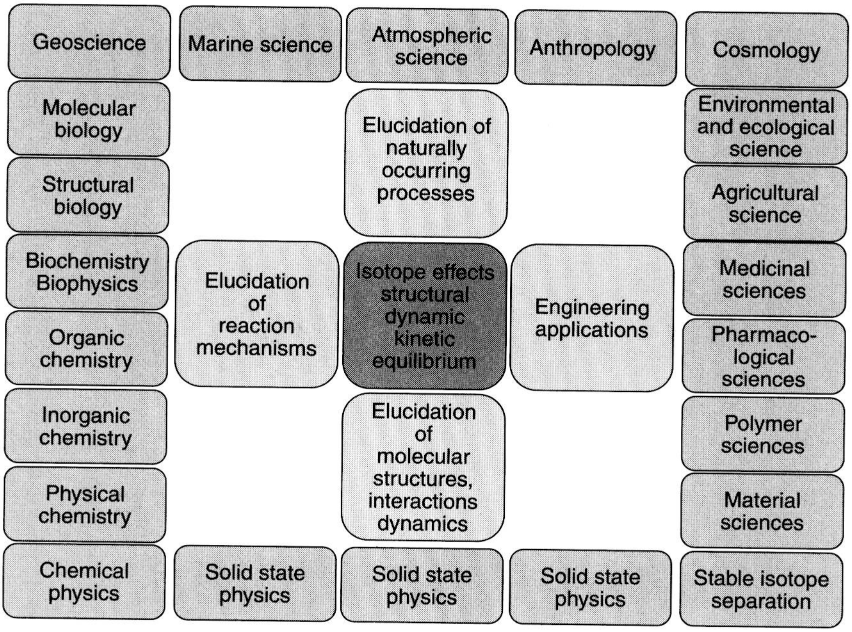
Preface

The unifying theme of this book is the application of isotopic methods to make significant advances in chemistry and biology. Isotopes are atoms with identical nucleic electrical charges and identical electronic properties. Isotopes contain the same number of protons but a different number of neutrons, hence they exhibit different masses and different nuclear spins. Isotope effects can be classified into three categories, i.e., kinetic isotope effects (KIEs), equilibrium isotope effects (EIEs), and anharmonic isotope effects (AIEs). KIEs are the ratio of reaction rates involving reactants that only differ by their isotopic composition. These are one of the only measures that directly probe the nature of the reaction's transition state, and thus are very useful tools in studies of reactions' mechanisms. EIEs are the ratio of two isotopes that are distributed between stable populations in thermodynamic equilibrium. These are a unique measure of the difference in the chemical potential of these two populations. AIEs lead to geometric changes of molecules and molecular systems via the anharmonicity of zero-point vibrations. Isotope effects are of substantial importance and utility in many fields of science and technology. The use of isotope effects is prevalent in a wide variety of disciplines. Scheme 1 below summarizes many of the areas that utilize isotope effects.

The book's nine parts and 42 chapters provide a comprehensive review of developments in isotope effects studies to date. The chapters were written by internationally recognized leading researchers in their fields. Authors from 13 countries contributed to the book: Canada, Denmark, France, Germany, Israel, Japan, Poland, Russia, Spain, Sweden, Switzerland, UK, and USA (by alphabetical order).



Scheme 1. The many applications and implications of isotope effects and their relationship to many fields of science and technology. This Scheme was drawn by Takanobu Ishida and modified by Hans Limbach.

Subjects range from the physical and theoretical origin of isotope effects to modern uses of these effects in chemical, biological, geological, and other applications. The following Table of Contents clearly emphasizes the multidisciplinary nature of this book. The book starts with the problem of isotope effects on molecular geometries arising from anharmonic vibrations and the consequences for isotope-dependent non-covalent interactions. Chemical bond breaking and formation dynamics are then addressed using the examples of simple molecules in the gas phase, also including the motif of hydrogen transfer. Novel mass independent isotope effects are discussed. The problem of hydrogen transfer, tunneling, and exchange is picked up for condensed matter, ranging from polyatomic molecules to enzymes. When the barrier for hydrogen or proton transfer becomes small, the area of low-barrier hydrogen bonds is reached and explored experimentally and theoretically. A unique application is provided in a chapter devoted to water isotope effects under pressure. Isotope effect studies in organic and organometallic reactions are needed for the understanding of the sessions that follow on isotope effects in more complex enzyme reactions.

The book brings together a wide scope of different points of view and practical applications based on our current knowledge at the beginning of the new millennium. Some chapters summarize the perspective of a well-established subject while others review recent findings and ongoing research. It may appear that some of these later items are not consistent with each other. This reflects contemporary conclusions and controversies in the field. We chose to present such studies only in cases where clear scientific arguments and discussion are presented by all relevant authors. This approach demonstrates the way research progresses, and we hope it will enhance the reader's curiosity and interest.

Editors

Amnon Kohen was born in a kibbutz in northern Israel. He received his B.Sc. degree in chemistry in 1989 from the Hebrew University in Jerusalem and his D.Sc. in 1994 from the Technion-Israel Institute of Technology. After that he was a postdoctoral scholar with Judith Klinman at the University of California at Berkeley. In 1999, he moved to the University of Iowa and is currently (2005) an associate professor in the Department of Chemistry. His main interest is bioorganic chemistry, and he enjoys studying the mechanisms by which enzymes activate C–H bonds and N2 triple bonds. His research focuses on the relationship between enzyme structure, dynamics, and catalytic activity. Isotope effects were one of the main tools used by his group in recent years.

Hans-Heinrich Limbach was born in Bruehl near Cologne, Germany. He studied chemistry at the Universities of Bonn and Freiburg. He did his doctoral research (Dr. rer. nat.) under the direction of Herbert W. Zimmermann at the University of Freiburg. After his Habilitation he was a visiting scientist with C.S. Yannoni at the IBM Research Laboratory, San Jose and with C.B. Moore at U.C. Berkeley. He is currently a professor of physical chemistry at the Freie Universität Berlin. His research interests include the chemistry of hydrogen and its isotopes in liquids, organic solids, and mesoporous systems up to enzymes, which he is studying by liquid and solid state nuclear magnetic resonance.

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1 Theoretical Basis of Isotope Effects from an Autobiographical Perspective

Jacob Bigeleisen

CONTENTS

I. FROM SODDY–FAJANS THROUGH UREY–GREIFF

Isotopes were discovered in radiochemical investigations of the decay of the heavy elements. Products were found with different nuclear properties, which could not be separated chemically, but stood in the same place in the Periodic Table; e.g. Radium, ^{226}Ra, an α emitter with a half life of 1600 years, Mesothorium 1, ^{228}Ra, a β emitter with a half life of 5.7 years and Actinium X, ^{223}Ra, an α emitter with a half life 11.7 days. They were named isotopes by Soddy[1] from the Greek words ισοσ τοποσ, the same place. Isotopes had the same nuclear charge, but different atomic masses. This was firmly established by the determination of the atomic weights of the lead isotopes which were the end products of the three radioactive series. Lead from the thorium series was found to have an atomic weight of 207.77; lead from the uranium–radium series had an atomic weight of 206.08. Fajans,[2] a major figure in radiochemistry, concluded that isotopes had similar, but not identical, chemical properties. Since isotopes have different atomic masses, molecules substituted with sister isotopes (isotopomers) would have different vibrational frequencies. Consequently they would have different heat capacities, entropies, and free energies. After WWI, Lindemann[3,4] subsequently known as Lord Cherwell, derived the equations for the differences in vapor pressures of isotopes. For a monatomic solid with a Debye frequency distribution, Lindemann found

$$\ell n(P'/P) = 9/8(\Theta' - \Theta)_D/T \qquad [\Theta_D = h\nu_D/k > 2\pi] \tag{1.1}$$

$$\ell n(P'/P) = 3/40(\Theta'2 - \Theta^2)_D/T^2 \qquad [\Theta_D = h\nu_D/k < 2\pi] \tag{1.2}$$

where Θ' and Θ are the Debye temperatures for the light and heavy isotopomers, respectively. Equation 1.1 and Equation 1.2 were derived for the case that there was a zero point energy associated with a vibration. He calculated the difference in vapor pressures of ^{206}Pb and ^{208}Pb and predicted the ratio of the vapor pressures of $^{206}Pb/^{208}Pb$ to be 1.0002 at 600 K. A much larger effect of the opposite sign was predicted for the case of no zero point energy. Since no such difference was found, Lindemann correctly concluded that there was a zero point energy. In actual fact, Lindemann's calculation for the zero point energy case is a factor of ten too large; the correct calculation from Equation 1.2 leads to a result of 0.002%; the light isotope, ^{206}Pb, has the higher vapor pressure. Equation 1.2, which had been derived independently by Otto Stern, provided the incentive for Keesom and Van Dijk[5] to achieve a partial separation of the neon isotopes by low temperature fractional distillation.

In planning a search for an isotope of mass 2, Urey[6] decided to carry out an enrichment of hydrogen of natural abundance by a Raleigh distillation. He used Equation 1.1 to estimate the difference in vapor pressures of H_2 and HD. Urey then turned his attention to the question of isotope effects in chemical reactions. He had his student, David Rittenberg, calculate, using quantum statistical mechanics, the equilibrium constant for the exchange reaction

$$H_2 + 2DI = D_2 + 2HI \tag{1.3}$$

as a function of temperature.[7] Their calculations were confirmed by experiment.[8] The method of Urey and Rittenberg was extended to the case of polyatomic molecules by Urey and Greiff.[9] For the isotopic exchange reaction

$$AX + A'Y = A'X + AY \tag{1.4}$$

they expressed the equilibrium constant in terms of partition function ratios.

$$K = (AY/A'Y)/(AX/A'X) = (Q/Q')_{AY}/(Q/Q')_{AX} \tag{1.5}$$

$$Q = \sum_i \exp(-\varepsilon_i/kT) \tag{1.6}$$

For the partition function ratio of molecules of like symmetry, (Q/Q'), and for which the translation and rotation obeyed classical statistical mechanics, they obtained

$$(Q_1/Q_2) = (M_1/M_2)^{3/2}[(ABC)_1/(ABC)_2]^{1/2}\prod_i[(e^{(u_{2i}-u_{1i})/2})(1 - e^{-u_{2i}})/(1 - e^{-u_{1i}})] \tag{1.7}$$

In Equation 1.7 subscripts 1 and 2 refer to the heavy and light isotopes, respectively; M is the molecular weight, A, B, and C are the principal moments of inertia and $u_i = hu_i = h\nu_i/kT$. The terms $e^{(u_{2i}-u_{1i})/2}$ and $(1 - e^{-u_{2i}})/(1 - e^{-u_{1i}})$ are, respectively, the contributions from the zero point energy differences between the light molecule, u_2, and the heavy molecule, u_1, and the Boltzmann excitation factors. Urey and Greiff[9] tabulated values of (Q_1/Q_2) for compounds of the light elements as a function of temperature between 273 and 600 K. The values of (Q_1/Q_2) varied from an order of magnitude for the isotopes of hydrogen to a few percent for isotopes of the elements in the first two rows of the periodic table. The ratios decreased with temperature. The equilibrium constant for an isotopic exchange reaction, which is the quotient of two partition function ratios, is of the order of a few percent excepting those reactions which involve the isotopes of hydrogen. Urey was able to utilize small differences in the chemical properties of the light