Hydrogen Transfer: Experiment and Theory

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This overview paper provides a short introduction into the topics discussed at the International Autumn Bunsen Discussion meeting 1997 on "Hydrogen Transfer: Theory and Experiment" which took place in Berlin during 10–13 September 1997 under the auspices of the Deutsche Bunsengesellschaft für Physikalische Chemie and the Freie Universität Berlin.

Introduction

There is no other element at the interface between physics, chemistry, biology and technology like hydrogen. It forms covalent bonds and hydrogen bonds in inorganic, organic and biochemical systems, exists as free or solvated proton, hydrogen atom or hydride anion, quantum-mechanical material wave and has four isotopes, i.e. myonium (Mu), ^{1}H (H), ^{2}H (D), ^{3}H (T), exhibiting the mass ratios 1/9:1:2:3, leading to large isotope effects. Thus, Hydrogen Transfer has been a hot topic for experiments and theory for decades [1–11], and the interest in this element is not surprising in times of the rapid development of novel experimental and theoretical methods. The International Autumn Bunsen Discussion meeting 1997 on "Hydrogen Transfer: Theory and Experiment" which took place during 10–13 September 1997 under the auspices of the Deutsche Bunsengesellschaft für Physikalische Chemie and the Freie Universität Berlin in the Harnack-House of the Max-Planck-Gesellschaft reflects this development. In 52 talks and 62 posters international scientists presented their new results and discussed their – sometimes different and complementary views of the – progress in this field. The present special issue represents a partial account of this discussion.

A. Coherent vs. Incoherent Hydrogen Dynamics Across or Through a Barrier

In the first part of the conference the problem of coherent vs. incoherent hydrogen dynamics across or through a barrier taking place in polyatomic molecules in the gas-phase and condensed matter was addressed. The simplest coherent hydrogen transfer process involving a symmetric double well potential is the inversion of ammonia in the gas phase. The description of this phenomenon was first proposed by Hund [12]. It leads to split vibrational states delocalized in both potential wells. The splitting of states corresponds in the time domain to the frequency of coherent tunneling observed for ammonia in the gas phase by microwave spectroscopy.

On the other hand, in polyatomic molecules proton transfer corresponds, generally, to a rate process involving kinetic H/D isotope effects. Initially, an incoherent tunneling process had been invoked by Bell [13] to explain these effects. This picture is based on the description of Gamov [14] for the description of the emission of α-particles by radioactive nuclei. When a material wave hits a barrier, there is a certain probability that the wave tunnels through the barrier even if its energy is not large enough to overcome the barrier. This phenomenon should occur more frequently for hydrogen than for any other atom, due to its light mass. Using the tunneling explanation, Bell could explain the kinetic H/D isotope effects on the electrolysis of water. A new theory of kinetic isotope effects was proposed by Bigeleisen [15] by the combination of his theory of equilibrium isotope effects with Eyring's transition state theory [16]. Here, the effects are described mainly in terms of zero-point energy changes between the reactant and transition states. In later years, Bell combined Bigeleisen's theory with his tunneling model, today known as the "Bell"-model, which treats tunneling in terms of a one-dimensional incoherent process with a continuous distribution of states on both sides of the barrier. Naturally, this model is oversimplified, and different theoretical approaches based on quantum-mechanical description are needed on the way towards an "ab initio" description of molecular rate processes. For an experimentalist, it is still a big task to develop criteria to separate tunneling and over-barrier contributions to rate constants and kinetic isotope effects.

The problem of the transition between coherent and incoherent proton transfer came into attention already several decades ago [17]. A special type of tunneling where this transition can be observed directly is the case of dihydrogen bound to transition metals. Therefore, these compounds are interesting models for the study of this transition. In addition, these systems are important since the mobility of hydrogen in transition metal compounds is a central problem of chemical energy storage using the hydrogen technology.

B. Proton Localization in Hydrogen Bonds

The barrier for proton transfer is strongly reduced when the proton donors are able to form strong hydrogen bonds with the bases to which the proton is going to be transferred. Various experimental techniques are applied to this problem, such as IR, Raman, Inelastic neutron scattering,

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NMR and Crystallography, which provide often different views. Here, the problems of proton transfer, hydrogen bond geometry and hydrogen bond dynamics merge [18]. Hydrogen appears as a divalent element able to be engaged in two covalent bonds with two heavy atoms, characterized by a bond order of about 1/2 and a quantal proton motion. H/D isotope effects appear related to structural changes and zero-point energy changes after deuteration, arising from a proton motion in very anharmonic potentials. These phenomena are strongly dependent on the environment in which the hydrogen bonds are embedded. Thus, the question arises whether a polar solvent changes the hydrogen bond symmetry and the potential for the proton motion. This problem appears when acid-base properties in aprotic environments such as organic liquids, solids, surfaces, etc. become important.

C. Excited State Proton Transfer

All of the problems encountered in the ground-state proton transfer cases are now combined, and even extended. On one hand, the excited state constitutes a complication due to the presence of additional and competing processes such as internal conversion, intersystem crossing, and the difficulty to evaluate ab initio potential energy surfaces and wavepacket dynamics with adequate accuracy. On the other hand, it provides a simplification as the propagation of selective states can be followed in the gas phase or molecular beams. In the liquid state, ultrafast proton transfers in the excited state may proceed more rapidly than competing relaxation phenomena induced by the environment, i.e. the proton transfers are often confined to single molecules or molecular complexes. Solid state measurements allow one to tailor the geometric structure of the reactants. The time scale of those processes is typically in the domain of femtoseconds to picoseconds, calling for adequate methods of femtosecond chemistry [11].

D. Proton Transfer in Complex Systems, Liquids and Biological Systems

As far as proton transfer is concerned, liquid and solid water represent extremely complicated systems as they exhibit a large number of coupled hydrogen bonds which break and form, reorientate in space, react to the electric field of ions complicating the description of the multiple proton transfers. Although these processes have been studied experimentally by Eigen et al. [19] years ago, the theoretical description of the proton motion in water is still a disputed subject [20]. Proton transfer plays an important role in environmental chemistry, e.g. during ozone degradation on stratospheric ice surfaces, in organic liquids, solid state proton conductors and enzymes, where they often represent the key steps. It is refreshing to observe that both experimental and theoretical methods do not fear to attack the most complex systems like enzymes.

Conclusions

As conclusion we hope that the present special issue may be considered as stimulating interim report, representing important progress which has been made recently and, simultaneously, pointing to enormous challenges for the forthcoming years. Continuous fascination about the advances which have been made recently, and encouragement for research towards many additional discoveries, was conveyed adequately by Professor R. R. Ernst in his closing “Dahlem”-lecture “Interdisciplinary Research. Nuclear Magnetic Resonance, a Show Piece par Excellence”.

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E 9794