Proton transfer in barium zirconate: Lattice reorganization, Landau-Zener curve-crossing approach

Grégory Geneste

CEA, DAM, DIF, Arpajon F-91297, France

ABSTRACT

The reorganization of the environment of a self-trapped proton in a polarizable medium is a necessary step making proton transfer possible, in addition to the decreasing distance between the donor and the acceptor. We focus here on the mechanisms of proton transfer (PT) in the cubic perovskite oxide $BaZrO_3$. From density-functional theory (DFT) calculations, we show that the self-trapping distortion, as well as the reorganization motion in this compound mostly originate from a rotation/deformation of the four oxygen octahedra surrounding the proton. This identification allows to extend the Landau-Zener curve-crossing approach describing PT in solutions with polar solvents [D. Borgis, J. T. Hynes, J. Phys. Chem. **100**, 1118 (1996)] to this system. Following the idea that PT is quantum by nature, the process is described as resulting from thermal fluctuations of (classical) lattice coordinates, among which oxygen octahedral rotations/deformations play the same role as the solvent reorganization in a solution: this reorganization allows the system to reach *coincidence* configurations, in which the protonic ground levels in the initial and final wells are equalized, resulting in a possible transfer, with a probability given by the Landau-Zener formula. The PT rate is expressed as a sum of contributions over all possible coincidence configurations, treating on equal footing ground-state non-adiabatic tunneling transfers, adiabatic transfers in which the proton zero-point energy lies above the energy barrier in the proton coordinate, and all other intermediate situations. A simplified model is proposed, in which the energy of the system depends on two relevant lattice distortions, (i) the amplitude S of the reorganization motion (which appears as the natural reaction coordinate for PT), and (ii) the distance Q between the two oxygens involved in the transfer. DFT calculations are used to feed the model, and calculate the contribution of each coincidence configuration to the transfer rate. Within this model, the slow dynamics of the reorganization (typical vibration frequency $\sim$ 3–5 THz), combined with the soft profile of the coincidence energy as a function of Q, make adiabatic transfers (and tunneling with large transfer probability) dominate down to low temperature (via almost "barrierless" coincidence configurations with short oxygen-oxygen separation), excluding the possibility of a non-adiabatic tunneling regime.

1. Introduction

Proton-conducting oxides are promising systems, with strong potentialities for clean energy applications. Indeed, they can be used in many electrochemical devices [1], such as electrolytes in Protonic Ceramic Fuel Cells (PCFCs) or Electrolyzer Cells (PCECs). Most of them have the perovskite structure ABO_3 (or derived), and may be obtained by (aliovalent) substitution of a fraction of B-site ions by lower-valence elements, yielding the appearance of charged oxygen vacancies. In humid atmosphere, the system undergoes hydration. This is an exothermic reaction during which water molecules dissociate in the vacancies, producing protonic defects: $H_2O + V_O^{\bullet\bullet} + O_O^X > \rightarrow 2(OH)_O^{\bullet}$. Very good proton-conducting oxides can be found among acceptor-doped alkaline-earth cerates, e.g. $BaCeO_3$, zirconates, e.g. $BaZrO_3$

(BZO), or stannates, e.g. $BaSnO_3$ (BSO).

It is commonly admitted that protons diffuse in those systems by the succession of two elementary mechanisms: (i) *transfer*, during which the covalent OH bond is broken, with H^+ jumping along an hydrogen-bond, leaving a (donor) oxygen to bind onto a nearest (acceptor) oxygen; (ii) *reorientation*, during which the OH group is turning by $\sim$ 90°, involving breaking/forming of the hydrogen-bond. In perovskite oxides, the succession of both mechanisms is necessary to allow for long-range diffusion of the protons. Moreover, it is commonly admitted that in many perovskites, transfer is the rate-limiting step [2]. In addition, the protonic diffusivity may be affected by the presence of point defects (e.g. negatively charged dopants [3-10], or cationic vacancies [11, 12]), of other protons [13] and of surfaces [14, 15]. Among the two mechanisms, proton transfer (PT) is the one which is mostly

impacted by the strong quantum effects related to the light mass of the hydrogen nucleus, because it mainly involves the stretching vibration of the OH bond, for which the energy quantum is as large as $\hbar\omega \sim 0.4$ eV ($\hbar\omega/k_B \sim$ 4600 K).

At low temperature, H^+ is frozen in its vibrational ground state (GS), and thus transport is not possible by thermal agitation of the proton itself. Instead, it is made possible, "assisted", by thermal agitation of the (more classical) heavier lattice atoms, especially the oxygens [16]. In its most stable state far from defects, H^+ is *self-trapped*, i.e. it is trapped by the distortion created by itself all around, but occasionally, thermal fluctuations of lattice atoms produce "coincidence" configurations [17, 18], in which the potential seen by H^+ (denoted hereafter as "potential in the proton coordinate" or "proton potential") is a symmetric double well, and the energy levels of H^+ in the two wells are in coincidence. These coincidence configurations are favorable to resonant tunneling between protonic ground states through the remaining barrier in the H^+ coordinate – if the proton Zero-Point Energy (ZPE) is smaller than this barrier – or to an adiabatic behavior ("quantum over-barrier" [18]) if the proton ZPE exceeds this barrier.

At higher temperature, H^+ jumps have been described as involving proton excited states, evolving to a semi-classical over-barrier motion [17]. The temperature at which such transition takes place is, however, dependent on the type of jump. Reorientation, for instance, should transit to the semi-classical regime at temperatures much lower than transfer. This regime has been described, in BZO [17], using the quantum-mechanically modified version of harmonic Transition State Theory [19] (QTST). From path-integral simulations, Zhang et al. interpreted PT in BZO between 300 and 600 K as a semi-classical over-barrier motion [20]. In BSO, we have suggested that this high-temperature PT regime [21] (typically above 300–450 K) consists in the occurrence of coincidence configurations with short oxygen-oxygen separation, in which a rapid oscillation of the proton between the donor and the acceptor oxygens takes place: this oscillating motion should involve, at least, the ground and 1st excited proton states in the double well potential in the proton coordinate of this transition state configuration. This is in line with the picture described by Kreuer et al. in the case of a "soft array of oxygens" [16]. In this regime, the quantization of H^+ energy levels (along the transfer direction) remains visible, in experimental measurements of the H/D isotope effect on the conductivity in many oxides: a typical difference of 0.03–0.06 eV on the activation energy [22] is observed between D and H, which is usually well explained by the ZPE correction, larger for H than for D [22-24], and rather well reproduced by QTST in several oxides [17, 18, 25]. In metals (e.g. Nb, Ta), the high-temperature regime for H diffusion has been described by the contribution of jumps between excited states in coincidence configurations [26-28], suggesting that thermal fluctuations of the lattice play an important role in the diffusion properties of H, even at high temperature.

Proton transport in perovskite oxides is therefore probably strongly "assisted" by thermal vibrations of the lattice atoms [29, 30], even at the high temperatures characteristic of the working regime of PCFCs [16, 31, 32]. PT in those systems has been investigated by Kreuer and coworkers [16, 31-33], who pointed out that H^+ transfer may be facilitated by the "softness" of the oxygen array, i.e. by the possibility for the oxygen lattice to deform without a too large energy cost, following some specific mode (typically the O-B-O bending mode), and create configurations in which the donor and the acceptor oxygens are close to each other. Several numerical works support this picture: following the work of Cherry et al. [34, 35], who simulated such a configuration with short oxygen-oxygen separation, Sundell et al. have computed in BZO two PT coincidence configurations with oxygen-oxygen distance of 2.59 and 2.42 Å (hereafter denoted as C1 and C2), and found the same energy for the two (0.19 eV). Similarly, Merinov and Goddard III have shown that, in BZO, reducing the oxygen-oxygen separation strongly reduces the PT barrier without producing a too large energy cost [36]. In BSO, the two similar configurations as the ones calculated by Sundell

et al. have also close energies (0.17 and 0.21/0.18 eV after inclusion of proton ZPE corrections) [18].

In these possible transition state configurations with small oxygen-oxygen separation (typically ~ 2.40–2.45 Å in BZO [17] and BSO [18]), the PT energy barrier is expected to be very small [33], so small that H^+ might cross it very rapidly: the extreme case where the proton ZPE exceeds the PT barrier in such configurations [18], certainly results in a very efficient proton transfer. In these (almost) barrierless transition configurations, H^+ may be seen as adiabatically adjusting to its ground state (at low temperature), or rapidly (and incoherently) oscillating (at higher temperature), producing in both cases an efficient transfer [16]. The situation, in which the proton ZPE is larger than the energy barrier in the proton coordinate in the transition configuration,[1] has been referred to, in the case of PT in solutions, as the *PT adiabatic limit* [37]. Kreuer pointed out that "adiabatic proton transfers", involving (almost) barrierless configurations with short O-O distance, are probably common to very good proton conductors [33]. In solid proton conductors, the lattice motions assisting the transfer should therefore be soft enough to allow occurrence of such peculiar atomic arrangements. Moreover, in such low-barrier transition state configurations, the ZPE of the proton should be considerably lower than in its stable state, because H^+ has here the possibility to extend over two sites [21], resulting in a reduction of quantum confinement. This effect, as well as the strengthening of the hydrogen-bond as the oxygen-oxygen distance decreases, certainly contributes to the softness of the oxygen displacements that produce these (almost) barrierless transition state configurations. It follows that this softness probably only exists in the vicinity of the proton.

On the other hand, extensions of the non-adiabatic tunneling model of Flynn-Stoneham (FS) [38], usually applicable to metals at low temperature (e.g. in Nb below 200 K), have been proposed in oxides [39]. The possibility of such non-adiabatic tunneling regime at low temperature in proton-conducting oxides remains an open question, although recent DFT studies in BZO [17], and in BSO [18], seem to indicate that PTs are rather adiabatic even at low temperature, mainly because the coincidence configurations in which ground-state transfers are mostly adiabatic (short O-O distance) have an energy very close to those in which ground-state transfers are mostly non-adiabatic tunneling (larger O-O distance), in relation with the "softness" of the oxygen distortion previously mentioned. This suggests that a non-adiabatic tunneling regime for PT in proton-conducting oxides, if any, is probably confined to extremely low temperatures [40, 41], maybe below the onset of the thermally-assisted quantum regime.[2] We note that tunneling effects associated with H^+ have been reported in $BaCeO_3$ at low temperature [43, 44], however not in transport processes. Moreover, experimental measurements of protonic conductivity in several oxides show that the isotope (H/D) effect on the prefactor of the conductivity is rather small at high temperature, and for some of them, down to room temperature [16, 22], or below (~ 250 K in $Y:SrZrO_3$ in Ref. [16]). This absence of large isotope effect on the prefactor clearly excludes the possibility of a non-adiabatic tunneling regime in the temperature ranges, and for the oxides experimentally investigated.

In metals (Nb, Ta), there exists a unified theory [26, 27] describing, on equal footing, the different contributions to H transport, i.e. ground-state non-adiabatic tunneling jumps (which dominate at low temperature), and excited-state jumps, that induce a transition to an adiabatic regime at high temperature [28]. Similar theory has also been

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[1] The ground-state wave function of a quantum particle confined in a symmetric double-well potential has, in the case where the ZPE exceeds the barrier, a single broad maximum at the barrier top. This is typically the situation of a proton in a coincidence configuration with very short distance between the donor and the acceptor oxygens.

[2] Typically, the thermally-assisted quantum regime corresponds to the lattice atoms behaving classically (many phonons of the lattice excited), while the proton behavior remains quantum (GS contributions mostly). It is commonly admitted that it starts at ~ $T_D/2$, where T_D is the Debye temperature of the lattice [42].