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PROTON-PHONON INTERACTION AND POLARON MASS IN ABO_3 PEROVSKITES

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ABSTRACT

The motivation of the present paper lies in some recent experimental and first-principles studies of the phonon-aided long-range proton transfer in solid oxides. We extend the results of our previous papers in order to provide theoretical underpinnings for these evidences. A model for the underlying mechanism of the phonon-assisted proton hopping is considered. A new concept of the Euclidean time relevant to proton conductors is introduced. The model is able to explain how the hopping rate depends on the resonant infrared light that selectively excites the O-H stretch mode and would affect both the activation energy barrier and effective mass for proton polarons. Those Holstein type polarons, which are fundamental objects of condensed matter physics, are also found interesting from the perspective of new designs of energy devices like fuel cells, called here phonon-assisted fuel cells.

KEYWORDS: Protonic ceramic fuel cell; Operating temperature; Proton polaron; Laser-enhanced proton conduction

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1. INTRODUCTION

Conception of proton polaron (PP) phenomena offers an interesting option for the development of such devices as fuel cells based on proton conducting oxides [1-4]. On the one hand, energy devices using such a new transfer type could provide opportunities to tackle relatively low operating temperature (T), ranging from room T to, say, 400 ºC, not feasible with classical solid oxide conduction methods with a demanding condition of extremely high T (higher than 800 ºC), see, e.g., [1, 2]. On the other hand, the devices with the phonon-assisted transfer mechanism might bypass some technical problems, such as the additional heat production, low energy conversion efficiency and use of expensive interconnectors. The point is that the generally accepted viewpoint on polaron transfer in perovskite oxides exists only for electrons, and a satisfactory theory that provides the foundation for the protonic counterpart is only to be expected. The PP scenario in perovskites has been yet experimentally realized only by several groups, with an external stimulation of the polaron formation (as by resonant infrared illumination or high pressure) [2, 4-6]. The development of such a new area of research on proton-conducting materials that would perform rapid polaron-like transfers of protons (and perhaps implement the desired lowering of the operating T) that are needed for efficient generation of energy in fuel cells is presently attracting a great attention.

In Refs. [1-10] one interpreted these evidences in terms of the formation of Holstein type polarons or even postulating the existence of a small proton polaron as a universal charge-carrier-transport characteristic of condensed-matter systems, not restricted to electrons. In so doing, the needed vibrational properties of proton-conducting solids can be described by the phonon density of states, accessible through various experimental methods [10]. While the PP hopping is also relevant to a number of physical phenomena outside the scope of this article (for example, for the charge migration through DNA it is a routine matter), PP effects with the details of the bath-system interaction in solid proton conducting oxides only begin to be investigated with high precision. For a definitive survey and an inclusive set of references see the recent article by Li et al. [5], in which the PP state in ceramics uniquely suitable to applications in fuel cell technology can be read via a selective excitation technique.

In general, the PP properties and the details of its migration mechanism in ABO_3 are not very well understood. An answer to these important questions can be found only by starting from the model of PP which has hitherto been approved by experiment. Phonon-assisted proton jumps, including those in external fields, have been studied theoretically and experimentally in single crystals and acceptor-doped ceramics in a very broad range of T, from tens to thousand K. The most important conclusion to be drawn from the existing experimental evidence on this question is perhaps that the interest at present is in studying different assist phonons (APs), coupled to protons, that are separated from the rest of the bath. Phonon coupling on the ultrashort time scale of the proton motion will lead to changes in the reaction rate ω^{-1} [see Fig. 1 in Ref. 1] or PP effective mass (EM) m^*, with lattice vibrations that propel the proton motion interpreted through coupled modes such as wagging or bending modes [7,10], and should be observable in pump-probe measurements like those of Ref. [2]. Moreover, low-frequency (ω) APs should be distinguishable in their influence from bulk phonon modes directly in the time domain providing a detailed perspective on proton-polaron transport in proton-conducting solids and films near room T.

Many aspects of hydrogen behavior in perovskite-type oxides are not fully captured by routine conductivity measurements, the reason being that vibrational properties, including vibrationally excited states, must be also taken into account. Various lines of evidence indicate that the pre-exponential factor D_0 of the diffusion coefficient

$$D = D_0 \exp\left(\frac{-E_a}{kT}\right) \quad (1)$$

in protonic perovskites (here E_a is the classical activation energy, T is the temperature and k the Boltzmann constant) may absorb the phonon dynamics. For example, the behavior of the proton diffusion in the presence of phonons in $BaZrO_3$ type materials at T near 300 K may reflect dynamics that are unusual, in that sometimes the tunneling and over-the-barrier jumping processes are hardly distinguished [11,12]. In general, one may also say that the polarization of the oxide lattice and crystal structure distortions, which are bound to occur in perovskites due to the proton charge, must lead to a relatively strong proton-bath coupling u and are likely to remain a challenging problem for the determination of the PP effect. What is the impact of proton-phonon interactions and, in particular, of the frequency w of the AP needed to form the initiating PP, onto the process of proton hopping? At present, it does not appear possible to arrive at definite conclusion on this subject because we do not have a very good understanding of how this PP arises. What function the phonon reservoir plays for proton transport in perovskite-type oxides is not fully evident. Answers to these questions still require a direct way of modeling the phonon-aided transfer using the thermal phonon number $<n(\omega,T)>$ (the Bose-Einstein function), i.e., a theory beyond the classical Brownian motion and classical fluctuation-dissipation theorem (FDT) used in the standard stochastic theory [13] of superionic conduction.

The modification needed to incorporate the role of PP in a rational way would seem to require some sort of semi-classical framework and even more sophisticated approach, based on the concept of the quantum Brownian motion and the quantum FDT (at least, its Markovian limit in terms of c numbers [14]). Note that this kind of semi-classical description in c numbers, introduced by this concept, is quite different from the genuine classical theory of diffusion that incorporates Einstein fluctuation-dissipation relation defining D_0 as a constant. Indeed, in the case of the phonon-assisted diffusion we do not need Eq. (1) with a constant D_0 and a constant E_a. The use of the quantum FDT with c number has proved itself to be a suitable

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tool [1,8,9] for the derivation of a polaronic analog of E_a in Eq. (1) as a function $E_a(\omega,u,T)$ which is consistent with the spirit of the semi-classical Holstein theory of polaron [15]. Here, we discuss a version of this system-reservoir (Brownian oscillator) model approach in the light of recent studies and reconsider the PP hopping in perovskites in a broader context, including a comparison to the Larsen EM approximation for electron polarons [16]. We show that an analog of Larsen's EM equation can be derived as part of the *c*-number FDT formalism, in analogy to what was done with the derivation of $E_a(\omega,u,T)$.

This paper may be considered to be an additional theoretical foundation to an interesting recent publication [3] concerning a relevant and important problem of PP in proton-conducting oxides used in energy devices. In particular, the present work will elucidate on the subject of PP-type carriers, important for fuel cell development strategy at intermediate T, in terms of a new concept of the Euclidean time relevant to proton-conducting oxides.

2. THEORETICAL FRAMEWORK

The main attention of this paper will be focused on the specific example of the low-T (but classical looking, i.e., over-the barrier) hopping of protons under the laser excitation proposed in [2], since this is a basic method. Much of the current interest in the subject is centered on the details of how AP may be included in the elemental transfer act of the released "hot" protons, as they moved through the lattice after the OH decay under resonant infrared pulse. The real-time study of the microscopic dynamics of excess proton is able to elucidate how it is coupled to a neighboring vibration with a high degree of reliability. In principle, the pump-probe technique with high temporal resolution constitutes one of the best means of determining the low-T proton transfer rate (τ^{-1}_{LT}) on the picosecond time scale. At favorable conditions the time between proton jumps, t_0, can be really like the time with which the hydrogenic local modes decay. Clearly, high T is not the optimal case. In [2], one fits the spectroscopic data on OH lifetime T_1 in terms of the PP model proposed in [7] which permits to sidestep the question of what τ^{-1}_{LT} actually is, i.e., to express τ^{-1}_{LT} via T_1. The main advantage of this technique of the laser excitation of vibrational modes is that it provides a quantitative measure of carrier lifetime distribution that can be used to analyze whole or partial mode decay channels and permits to match the laser pulse duration with the lifetime.

To fix the ideas, we begin by considering a system-reservoir model with the reservoir being a collection of oscillators with eigen frequency w_0. It is well known that the phonon itself may be considered within the quantum system-reservoir framework as an oscillator. The unique oscillator (UO) with a frequency $\Omega \sim \omega_0$ needed to promote the proton over the phonon-modulated barrier $E_a(\omega,u,T)$ may exhibit a wide variety of forms. By its very nature, any scenario of this sort is concerned with real lattice vibrational modes modeled as bath oscillators. For proton conduction of doped ABO_3 such as $BaCeO_3$ and $SrCeO_3$ at high T, the high-frequency O-H stretch and O-B-O bend modes or even vibrations of BO_6 octhaedra as a whole were suggested as candidates for AP [4,7]. A somewhat different behavior is seen at low and room T when the AP is rather to be regarded a wagging mode [2] which has to be isolated from the rest of the reservoir. Such a condition is known to be satisfied for, say, $BaZrO_3$ (strictly speaking, for a higher T), where the frequency of O–H stretch vibration is well-separated from those of other lattice vibrations, and thus its selective excitation would be really used to provide energy to promote proton conduction [5]. For simplicity, here the same situation is suggested for other perovskite structures. As a theoretical speculation, we emphasize that the frequency separation is not specific for the said O-H oscillator, but that the same behavior is also to be expected for the APs which will be present in any small-polaron proton conductor. Specifically, we focus on the role of the critical temperature T_0 [1,8] such that, roughly speaking, separates AP from the rest of the bath:

$$\hbar\Omega \approx 2kT_0 \tag{2}$$

For the proton diffusion with the Ω-dependent coefficient D, the PP picture offers a clear view of how AP determines both the factor D_0 and the activation energy described by a set of couplings of their own (denoted here by A and u, respectively). Consider these quantities in order to lay a foundation for our discussion of the optical stimulation. The ordinary stochastic theory of ion transfer defines E_a as a constant barrier height V^* located at $x=x^*$ with x being the position in space [4]. To interpret τ^{-1}_{LT} in terms of AP, it is reasonable to treat Ω as a phenomenological parameter satisfying the condition (2) that follows [8] directly from an analysis based on a quantum FDT and sets a value of T_0 at which the given AP operates optimally. For the case of stimulation, the barrier is other than V^* and is controlled by three major factors Ω, u and T. Then, the classical expression $D_0=(1/2)v_a d^2$ (here d is the jump distance and $v_a = const$ is the attempt frequency) is abandoned in favor of

$$D_0^{(d)} = (1/2)A\Omega d^2 \tag{3}$$

for the diffusion coefficient recast in terms of a jumping probability w:

$$D_{LT} = d^2 w \tag{4}$$

with A being a coefficient of proportionality. If so, the phonon-assisted room-T analog for the attempt frequency then would be

$$\nu_{aRT} = A\Omega \tag{5}$$

that is, directly proportional to a coupled mode frequency.

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3. PROTON-POLARON JUMP TIME IN PEROVSKITES

For protons in the presence of an external field we will need to generalize this latter definition somewhat. In terms of Eqs. (2) - (5), the characteristic time $t_0 \sim w^{-1}$ appears in the form of Eq. (1) as

$$\tau_0 \approx (A\Omega)^{-1}\exp\left(\frac{E_a^{(d)}}{kT}\right) \quad (6)$$

which explains well the experimentally determined quantity T_1 vs T when the corresponding data sets (in fact, T_1 to be fitted is extracted from the vibrational linewidth) were fitted [2] to our model [7] of lattice-assisted proton hopping. For illustration, in Fig. 1 in Ref. [1] we have presented a characteristic T-dependence of the jump time for a set of parameters, which provides a clearer insight into the origin of the high enhancement in hopping rate (which appears to be just the inverse of t_0).

On the other hand, we would like to see the same time at levels of practical utility, to provide a jump-rate control mechanism of potential interest in device design. Such devices with polaronic proton conduction will be capable of achieving the jump rate of greater than 1 THz. The model proposed here makes this rate estimate easy to understand. All real crystals will have a certain number of OH oscillators. If the proton conduction in stimulated ABO_3 lattices is driven by a laser field, then t_0 must be connected both to laser properties and to the basic mode decay channel. For our purposes, in terms of laser spectroscopy the full width at half maximum (FWHM) is [2]

$$\Gamma = \frac{1}{2\pi c T_1} \quad (7)$$

In terms of ABO_3, T_1 is just the induced O-H decay time. In terms of a jump, T_1 is nothing but $w^{-1} \approx t_0$. If the PP hopping is a dominant relaxation channel, the maximum velocity with which the excess protons are propelled from the OH stretch is suggested to be dependent strongly on the resonant frequency of the radiation. Then the incident laser flux really does utilize a photon quantum $\hbar\omega_{phot}$ to free each proton from an O-H group and give it some energy to couple with a wagging oscillator, and thus to promote hopping according to Eq. (6). Of the various methods which nowadays are at hand, the laser probe system constitutes perhaps one of the most striking examples and of the best means of determining the value of t_0. The efficiency of the PP mechanism is now characterized by specifying the set of possible quantum numbers relevant to the laser-excited O-H oscillator involved in the process [1,2,6]. It is quite obvious that it is desirable to use the maximum possible oscillator frequency (higher oscillator levels) to obtain the most efficient PP transport process (see later discussion of OH overtones). It is further interesting and very important to note that the same rule must work when one applies the method of selective excitation to any other potential PP-type conductors like protonic ceramics investigated in [4]. In terms of FWHM, the phonon-assisted proton hopping rate is [2] $\tau^{-1}_{LT} \approx 2\pi c\Gamma$.

Our calculations show that it is in this self-consistent manner (this excludes that the OH decays much faster than t_0) that the current must reach its maximum limiting density. A further increase of the laser intensity will, however, not increase the produced current level. Exact calculations with this model have shown that for real PP parameters in rutile the average proton jump time near room T is in the *ps*-range. So, for potential devices based on excitation of modes such as OH networks, to work effectively the PP characteristic times are here chosen to be of order 1-7 ps for a broad range of T from 100 to 500 K. The value of t_0 corresponding to the height of the barrier ($\sim \hbar\omega_{phot}$) 0.2 eV still continues to be of order 1 ps from 150 to 250 K, although beyond this point increase of T produces no further change in t_0 up to 400 K. The experimental evidence is [2] that the shape of $T_1(T)$ in TiO_2 after irradiation is not characteristic of a multi-phonon decay or tunneling, but is just the one predicted by the lattice-assisted hopping model, with a neighboring bending motion being the most likely AP. The excitation of core modes may dominate if the photon energy E_{phot} exceeds the OH excitation energy, producing a highly energetic proton and a vibrating environment. So, a physical mechanism of synchronization between laser action and OH dissociation is to be implicitly invoked by us. This is a key viewpoint in our fuel-cell's strategy. This yields excess protons, which cause further excitation with small temporal oscillations, producing proton-mode couplings, which in turn deposit energy near the initial site of the outlet channel across the lattice. However, it should be also stressed that each released proton remains, as the pump-probe studies suggest [6], primarily localized on the initial (OH) potential well which in its turn deposits some energy before the excess proton begins to migrate in the outlet channel. An interesting and practically important unsolved problem in laser-stimulated proton conduction enhancement is how these loss-energy states could be an additional useful property of the general mechanism of synchronization.

Now we have to introduce a physical coordinate q which serves instead of x for the experimental detection of the PP, i.e., a real lattice coordinate needed to define an effective low-T lattice potential $V(q)$ governing the proton current i within our system-reservoir framework. Here this is done without any formal modification of the Gurevich-Kharkats method [13] of deriving a stochastic form of D from a classical FDT approximation, except that their Boltzmann distribution (the x-dependent Boltzmann PDF) has to be replaced by a similar Wigner function $W(q)$ taken with respect to the harmonic oscillator that is in contact with the thermostat at a finite T. Omitting the technical details all of which can be found in our earlier papers [8,9], we note only the essence of our substitution procedure. The resulting form of the macroscopic low-T current i_{LT} can be obtained by simply recasting the well-known Boltzmann type probability current [13] in terms of $W(q)$ as

$$i_{LT} = -eD_q W_0 \frac{d}{dq}\left(\frac{W}{W_0}\right) \quad (8)$$

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where e is the charge, D_q is the analog of D and the index q refers to the proton diffusion along the q-axis. Then we integrate it between the neighboring points q_1 and q_2 (each way from the point q^* of the barrier top $V(q^*)=V^*_q$) to express the net flow of protons in terms of the values of W and W_0 at q_1 and q_2 with the assumption that $W=W_0$ at one well (say q_1) and $W(q_2)=0$, as is standard for the stochastic method. It is easy to find that, by expanding a typical "system-reservoir" parabolic potential $V(q)$ (entering into $W(q)$ [8,9]) around q^* and integrating (8), the macroscopic exchange current i_{0LT} defining the diffusion coefficient (4) becomes

$$i_{0LT} \sim \exp\left(-\frac{V_q^*}{kT_\omega}\right) \tag{9}$$

where kT_ω is the energy of oscillator mode with the frequency $\omega \sim \omega_0$, which is here suggested to be equal to the energy known in the statistical physics as the average lattice mode energy, and is the low-T analog of kT for our quantum oscillators in the quantum FDT framework. As already mentioned above, the key idea of our approach is to introduce the T-dependent proton-phonon coupling generated by a hop of a PP composed of the excess proton and the AP of an effective frequency Ω_{eff}. Comparing the expression for $kT_{\omega 0}$ and (9), it is reasonable to take the naturally arising ratio between the effective energy barrier and the vibrational energy quantum $\hbar\Omega \sim \hbar\Omega_{\text{eff}}$ in i_{0LT} as the definition of the PP coupling

$$u^2 = \frac{V_q^*}{\hbar\omega} \tag{10}$$

governing both the polaronic E_a and m^*. It is just this basic quantity of the PP theory that was recently derived from first principles for Y-doped $BaCeO_3$ [3], which is in beautiful agreement with our theory. Fortunately, in practice, for estimating optimal value of u giving the best results for τ^{-1} and m^* (to assess the efficacy of fuel cells and long-term effectiveness of laser-generated proton transport), we do not need to actually calculate the quantity V^*_q connected with a given AP, because it has to be taken from experiment. In the case under study, it can be matched with a certain laser energy [2]. While q is a formally real coordinate, the change of the reaction coordinate connected with the excitation of the lattice is, in fact, an implicit procedure which need not be written out explicitly for the proton transitions we are considering. Note, however, that q-direction and OH stretch are recognized from general considerations - at least implicitly - mutually orthogonal. So, in the conceptual framework in which the low-to-intermediate T proton transfer is treated as phonon-assisted, (10) may be predicted by a simple system-reservoir approach presented above.

4. EUCLIDEAN TIME AS A MEASURE OF THE TEMPERATURE FOR LATTICE VIBRATION MODES INVOLVED

As a very interesting and useful example of our theory, in this section we will show that the notion of an Euclidean time may serve as a measure of the inverse temperature for lattice oscillators involved in the carrier lifetime distribution and transport. In experiments with IR lasers under study it is possible both to create an excess proton in the oxide lattice and to control its energy, using the same picosecond pump-probe technique. The above approach provides a definite answer to the question of how the proton motion couples to AP coordinate. If we admit that there is a proportionality between V^*_q and the average energy loss of the proton δ to environmental bath vibrations, introduced commonly in the Kramers escape problem (for a related discussion of the Kramers problem, see [17,18]), $V^*_q \sim \delta$, we are able to extract a substantial amount of information from a close inspection of δ. In his book [18], Prof. Krieger from the University of Southern California explains why our solution [17] of the latter problem with arbitrary δ can be written formally as a solution of the Ising model. We mention this mathematical fact in order to notice that the Ising model lies in the route of our understanding of the phonon-assisted diffusion in the perovskite-type lattices. A fundamental result of the study of perovskite proton conductors in terms of the Kramers problem [11,17] is that at barrier the magnitude of δ has an intermediate value of order kT or somewhat higher, implying that at room T we have $\delta \sim \hbar\omega_0$ with ω_0 being a characteristic vibrational frequency. The latter relationship is physically reasonable because the elemental energy transfer in our case is assigned to phonons, as, say, in the desorption processes with surface phonons [19]. In terms of Eqs. (2) and (10), this relationship immediately implies for $T \sim T_0$ of the range up to 300 K that

$$E_a^{(d)} \approx u^2\hbar\omega \tag{11}$$

with $\omega=\Omega/2$, which furnishes a means for justifying the phonon modulation of the barrier in the experiment under discussion. As known, in general there is a correction for $\omega=k_0\Omega$ (k_0 =1 or 1/2) which is needed to Einstein's one-phonon oscillator model of solids at sufficiently low T [20].

Within our approach, the Bose-Einstein distribution [14]

$$\langle n_\omega \rangle = \left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1\right]^{-1} \tag{12}$$

with ω being a phonon frequency can be explicitly incorporated to obtain a more accurate result. Using the known relation $<n(\omega)> +1/2 =(1/2)\coth(\hbar\omega/2kT)$, we can see that it is the mean mode energy

$$kT_{\omega 0} = \left(\frac{\hbar\omega_0}{2}\right)\coth\left(\frac{\hbar\omega_0}{2kT}\right) \tag{13}$$

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with an eigen frequency ω_0 which reflects the role of the thermal phonon number (12) in the phonon-modulated barrier which does enter implicitly the relation (9). By rewriting (9) in form of Eq. (1) with kT in the denominator, the net result appears automatically as

$$E_a^{(d)} = 2kTu^2 \tanh\left(\frac{\hbar\Omega}{4kT}\right) \tag{14}$$

To be more precise, in terms of ω [Eq. (11)] we obtain $2kT$ instead of $4kT$ in the denominator of Eq. (14) corresponding to $\omega=\Omega$. Perhaps for the case of room T, Eq. (11) would suffice to give an accurate value of ω. However, Eq. (14) is more similar to Holstein's electron polaron.

With (14), the time between protonic jumps will be assumed to be of the form

$$\tau_0 = (A\Omega)^{-1} \exp\left(2u^2 \tanh\left(\frac{\Omega\tau_1}{4}\right)\right) \tag{15}$$

where the Euclidean time $\tau_1 = \hbar/kT$ is introduced. As known, this "classical" Euclidean time is a measure of the inverse temperature ($\beta = 1/kT$) in condensed media [21]. By analogy, we now introduce a similar measure for low-T lattice oscillators with eigen frequency ω_0 as

$$\tau_{1LT} = \frac{\hbar}{kT_{\omega 0}} \tag{16}$$

To the best of our knowledge, this definition of the low-T Euclidean time has not been explored so far for the description of lattice oscillators by other authors. The notion τ_{1LT} can be useful if one is willing to redefine, in what we feel is a physically meaningful way, what one wishes to mean by the dynamic activation energy function described by an equation like Eq. (11). From Eqs. (13) and (16) we have

$$\tau_{1LT} = \left(\frac{2}{\omega 0}\right) \tanh\left(\frac{\hbar\omega_0}{2kT}\right) \tag{17}$$

For the lattice phonon with $\omega \sim \omega_0$, we arrive at

$$E_a^{(d)} = u^2 \hbar\omega \left(\frac{\tau_{1LT}}{\tau_1}\right) \tag{18}$$

So, two forms of activation-energy equations have been discussed above: (11) and (14). Some related equations recast in terms of the Euclidean time are just interesting for their special properties. Say, if $\tau_{1LT} \sim \tau_1$, we reobtain Eq. (11) from (18). What does all this signify? We can say that the form (11) of $E_a^{(d)}$ for PP is justified when the measure β is the same for both the quantum oscillator and for its environment. This transfer mechanism is such that the transferring proton "sees" a suitable local mode (different in local T from the bulk) in so far as this AP, when coupled with the proton in a most easy way, is also able to choose the easiest path to conduct. We believe that it is just this isolation mode instance which was used in the experiment [5] with resonant laser, but from a different perspective. We see that Eq. (11) fits well the PP jump time in the range approximately from 200 to 400 ºC. We then conclude that the optimal operating T for devices with small-polaron conduction must lie in this interval. This conclusion agrees with the analysis performed in the works on Ba-based ceramics [3,5] by analyzing how vibrational effects influence the proton-transfer properties of these materials.

5. THE USE OF OVERTONES AS A MEANS TO FURTHER ENHANCE THE PROTON HOPPING

Another example we consider in this paper is the role of OH/OD/OT overtones, following pioneering work [2]; here OD (OT) refers to the deuterium (tritium) stretch mode. The interest to such a complete characterization of excited protonic states in the time domain is due to a possibility to further enhance the transition probability depending on the light energy. According to Eq. (9), in photon field

$$u^2 \approx \frac{E_{phot}^{(th)}}{\hbar\omega} \tag{19}$$

where a photon threshold energy $E^{(th)}_{phot} = \hbar\omega^{(th)}_{phot}$ and ω is the polaron frequency which determines the characteristic proton-transport properties of the perovskite as it interacts with light at given T. Since in rutile u is expected to be close to unity at room T, the relation $\omega \sim \omega_{phot}$ has to be fulfilled in order for the highly efficient PP hopping migration to take place even at not too high T.

We can move along this route and introduce the photon-energy dependent proton rates. This route allows for an additional channel of laser stimulation using higher quantum numbers of the O-H oscillator, which may be of importance for practical applications. The linewidths of the O-H mode become broader with increasing energy, indicating the possibility of a very short upper-state lifetime at the higher levels [2]. According to Eqs. (6) - (8), a very large enhancement of the transfer rate is expected in this case [1,2], in the sense that there is a Debye ω^2-dependence of the lifetime function.

In the case of the excited levels $(OT)_{01}$, $(OD)_{01}$, $(OH)_{comb}$ and $(OH)_{02}$ suggested for rutile (here subscripts indicate the vibrational quantum numbers of the stretch oscillator, and the notation "comb" refers to a combined mode), the above FDT

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formalism is well suited. In particular, experimental time-resolved data on a broadening of Γ are well fitted within our model [1] by an analytic expression

$$\tau_{LT}{}^{-1} = k_r\left(E_{phot} - E_{phot}^{(th)}\right)^2 \quad (20)$$

where the laser energy is taken from experiment. Clearly, it defines at the same time the real migration barrier. According to our calculations, for rutile TiO_2 the constant in Eq. (20) is k_r = 28.163 THz/eV and the barrier-defining value of the laser energy is [2] $E^{(th)}_{phot}$ = 0.217 eV. The splitting level distance is clearly seen as a *photon* ω^2_{phot}-dependence (see Fig. 2 in Ref. [1]). This direct analogy to the Debye model, inherent to *phonon* density of states in the understanding of a two-level system (TLS), is of great interest. The spontaneous and quite unexpected appearance of the Debye-type phonon-density curve (recall that the latter is a fundamental building block of quantum theory of the absorption of radiation, say for the analysis of optical and vibrational dephasing experiments [22]) in equations of photon-driven proton motion, such as hopping rate τ^{-1}_{LT}, can hardly be considered as mere accidents. In our view, this is a manifestation of the above-discussed synchronization mechanism, when absorption of *ps* laser pulses in the inlet channel results in the energy relaxation through the combined effect of lattice vibration and proton coupling in the outlet channel (what we just defined to be a PP) on the analogous *ps* interval. As a conclusion to these ideas, we stress that the discussed low-T phonon-assisted proton transition may be classified by itself as a new example of TLS.

An overtone of combined character may come into play due to a large free distance between $(OH)_{01}$ and $(OH)_{02}$ levels implying that a possible AP may not be a single wag mode, but might represent a phonon mixture. In (16) we tacitly assume that the operating energy value of the $(OH)_{comb}$ state must be near the fit curve describing other quantum states. This is in agreement with our earlier assumption [8] that a mixing phonon can come into play as a complex-structured AP appropriate for perovskites. The experimental verification of these predictions is of interest.

6. PROTON EFFECTIVE MASS

As was said above, the PP properties and its migration mechanism in ABO_3 are not well elucidated. Further generalizations of Eq. (9) for cases that are not considered in [2] might be possible. For example, it might be interesting to consider the case of a T-dependent m^*, arising due to the explicit account of the Bose function (12) in analogy to how we deal with $E_a^{(d)}$ instead of E_a in Eq. (1) based on our framework.

While for rutile and doped barium cerates indirect and direct experimental evidences of PP have been reported in the literature, no direct EM measurements have yet been made. In contrast to a true Holstein polaron, here the dynamical structure of the polaron involves "phonon dressing" of the proton in the form of nearest low- or high-w vibrations that promote the polaron translational hop in oxides. After the laser-induced decay of the O-H bond, the excess proton moves to quickly couple to AP that would be accompanied by a consequent lattice distortion (by distortion phonons). This is the cause of the T-dependence in m^*. There is a converse conjecture: if u appears to be fitted by a recognizable function of w for a given T, if such function exists (it does not need generally to exist, because there is a definite phonon distribution in the thermal bath), then there should exist as yet hypothetical AP (or an assist mixture of phonons) which defines both t^{-1} and m^*. The problem is that no such function, used in the experiments in the usual sense of fitting function, is reported in the literature. The frequently used constant coupling u_0 must be understood as a limiting case of such function simulated without taking into account the thermal phonon number.

In this paper we attempt to clarify this situation somewhat by restricting ourselves to the class of EM equations of Holstein-Larsen type [16]. Unlike the relatively simple search for stationary coupling u_0 in order to determine t^{-1}, the evaluation of the T-dependent m^* in terms of operating AP frequencies via explicit treatment of proton-phonon interaction is anything but trivial. The vibrational relaxation is a form of energy transfer in which the energy of an excited vibration is redistributed over lower-energy degrees of freedom, eventually leading to a full thermalization of the energy [22]. In our case, the distribution of the vibrational energy to AP can be accounted for on theoretical grounds by measuring the lifetime spectra of the originally stable O-H oscillators under laser field, making identification of the phonon assistance more consistent. Starting with the O-H decay, the PP hopping then manifests as a thermalization. So, it is a two-step mechanism: the first step is a fast coupling of the decaying O-H oscillator to a vibrating environment and the second is the subsequent hopping of the “hot” proton along a T-dependent phonon mode. Therefore, the excess protons in the systems under study are to be in an effective T-dependent phonon field with an effective coupling function that we define as

$$u(\omega, T) = u_0 f(\omega, T) \quad (21)$$

where $f(\omega,T)$ is a function introduced to account for T-dependent phonon spectra. Though m^* and E_a are dissimilar in many respects, they do share common elements when viewed from a general structural point of view. To find the common features, we must have some insight into the effects of phonon dressing in the polaron theory from an abstract point of view, at which we arrive by ignoring the technical details of the Holstein theory. Since $<n(\omega,T)>$ yields the phonon contribution to the transition rate at all T accessible to experiments as the thermal Bose-Einstein distribution, one must have some displaced-phonon effect in the dynamic EM behavior of necessity. In essence, the result given by (21) is a phonon-modulated coupling per oscillator, being conceptually the same as for phonon-modulated dynamic barrier expressed above as $E_a(\omega,T)$ in terms of Eq. (12) for the thermal phonon number $<n(\omega,T)>$. In a simplified scenario, suggested here as a preliminary estimative

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example, we simply take $f(\omega,T) = 1 / \langle n(\omega,T)\rangle$. The corresponding protonic EM equation will then appear as the simplest of possible modifications of the low-order Larsen EM equation [16]

$$\frac{m^*}{m} - 1 = \frac{\alpha}{6} \tag{22}$$

with m being the band mass and α the electron-phonon coupling. So, our corrections to the T-independent m and the T-independent coupling u_0 are taken into account in terms of Eqs. (12) and (17) by changing α with $u(\omega,T)$ to yield the PP mass as

$$m^* = m\left(1 + \frac{u_0}{6\langle n(\omega,T)\rangle}\right) \tag{23}$$

Such assumptions are relevant for PP at an intermediate coupling ~ 1 - 5, which is just the case of the above experiments [2,4], but a much different behavior might be observed at very strong coupling or very small coupling, which is beyond the scope of this paper. Equations (21) and (23) state that, from the viewpoint of the lattice phonons, multiplying the average coupling $u(\omega_0,T)$ of a single oscillator with an average frequency ω_0 by the thermal phonon number to obtain the average coupling u_0 for the collection of oscillators at frequency $\omega \sim \omega_0$, we have the suggestive formula for m^*. For the wag-mode-aided proton transfer with $u_0 \approx 1{,}07$ at room T [2], this gives $m^* \approx 2\ m$. So, especially this phonon-assisted regime is functionally different from the transfer of free carriers. Our general theoretical framework predicts that at much lower temperatures compared to room T the EM enhancement in various oxides due to the phonon dressing might be, in principle, essentially larger with a reasonable u_0, but only under condition if an appropriate AP from the lattice frequency spectrum exists (see Fig. 1 below). At very high T the mass enhancement is not so remarkable implying that the PP may be not a principal carrier in oxides like rutile (the transport is rather related to free protons). This latter conclusion is in agreement with first-principle simulation of perovskites performed in [3].

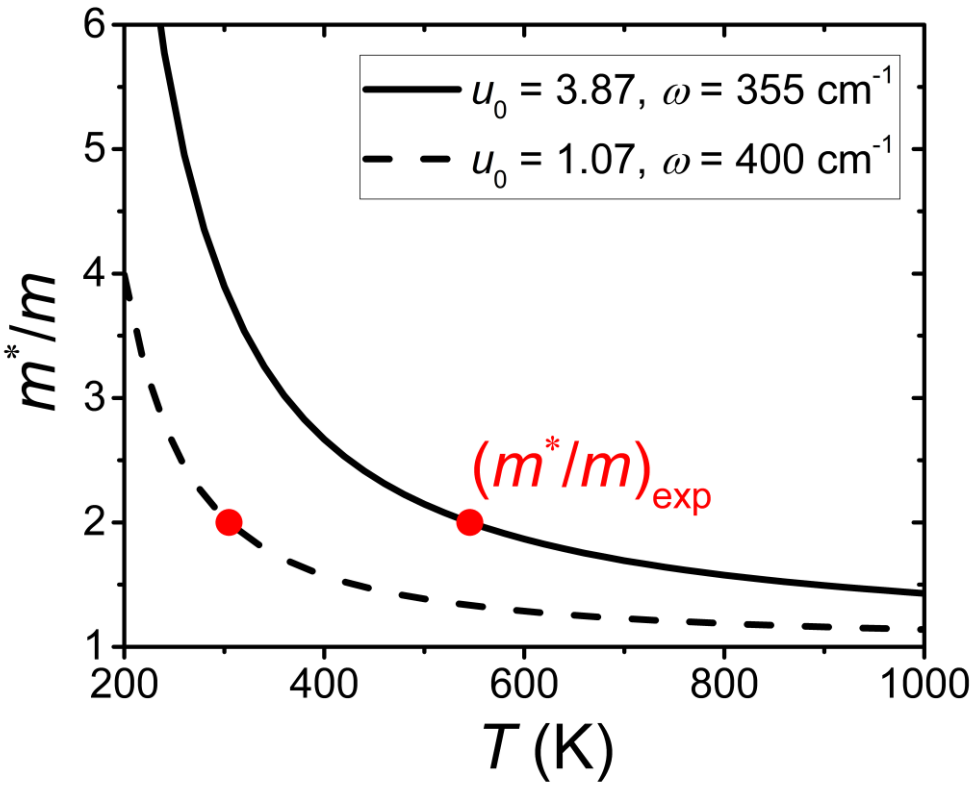


Figure 1: The T-dependence of the proton mass ratio m^*/m for different proton-phonon couplings

7. DISCUSSION

Proton polaronic effects are an emerging topic in the field of solid-state electrolytes, and a more sophisticated understanding is certainly necessary. The question upon PP does not seem to have yet been resolved in the context of proper measurement studies, and we attempt to answer it partially here as well. The study of proton phonon-assisted hopping in ABO_3 perovskite systems is very important because this has practical implications, in particular for strategic design of fuel cells.

In fact, the theoretical framework which here assumes the simplified form of the actual PP, guarantees only that the high-frequency O-H stretch is the decaying mode, and the released proton tends to couple with the (presently unknown) AP governing PP mobility. In oxide perovskites under study and in the T-range of interest, this latter AP is rather a low-frequency vibration mode like the well-known wag-mode in rutile or the Ce-O mode in Ba-based ceramics. However, it is clear that

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other modes, including different bending modes or even the O-H oscillations themselves, may act as APs in more complicated models (such scenarios lie beyond the scope of the present paper). So, in the present model the O-H stretch is not suggested as the dominant AP (in a sense, it is only a source of energetic protons). Furthermore, the proton hopping rate (see Eq. (7)) tends to be zero at photon threshold energies. This signifies that laser pulses would become "glued" to the device as crucial to determining the activation energy for proton hopping. This implies a possibility to further enhance the transition probability depending on the light energy (see Sec. 5).

A fair understanding of the PP evidence in perovskite structures was claimed only in recent times due to some accurate experiments. Despite successes in achieving quantitative analyses of PP in these materials subject under external fields, both theoretical and observational, there remain a number of conceptual and technical problems about this notion. A gap remains in our understanding of various aspects of the decay of OH into proton-phonon excitations, say, of the so-called overtones suggested in [2]. Even the case of proton transitions from the first excited state, in which direct Holstein type interpretations (see Eqs. (4) and (14) above) would be an appropriate way to a fitting of vibrational relaxation effects, is not yet fully understood. Until these rather abstract problems are solved, we cannot expect to arrive at a complete understanding of externally stimulated proton transport regimes such as those of laser-resonance-assisted hopping at room or moderate T, that are of interest and of importance for potential applications in energy devices.

The proton jump time (t_0) in the PP hopping regime is expected to be of order 1 *ps*. The above formalism indicates that the laser-oxide interaction may work as a diode (as was noted earlier in [6]). This is due to the proton charge coupling with promoting modes, which tends to damp the energy available to assist the rate by which the proton leaves the *n*th level of the oscillator after selective decay. Due to this synchronization, the long-range proton transport is of Arrhenius behavior, see Eq. (20). However, to our knowledge, no direct measurements of the latter relation concerning different quantum states have been made and no means for directly measuring such transfer rate have been proposed for proton-conducting ceramics.

So, the main consequence of the laser stimulation is that the decaying unstable O-H oscillations in the oxide lattice must be included into elementary steps of the overall transfer process. In order to take the relaxation channel as the classical looking proton hopping even in the low-T regime, the microscopic jumping path of the proton has to be determined. The latter in rutile is such that the proton has to couple to a nearest transverse mode with a much low potential barrier of approximately 0.2 eV. The promoting mode behavior may be studied using a semi-classical description like the quantum oscillator model developed in our preceding papers [8,9]. In line with such treatment, above we have considered a fit of the jump time in terms of the Euclidean times $\tau_1 = \hbar/kT$ and $\tau_{1LT} = \hbar/kT_{\omega 0}$ and the interpretations of mass m^* and momentary coupling factor u, treating them within the system-reservoir model as functions depending on ω_0 and T with ω_0 being a bath oscillator frequency. It is typical for femtochemistry of water-like media that a single H-bounded complex isolated in a solvent is modeled as a vibrator, and then the coupled vibrations are pictured by a classical stochastic function in the frame of the Langevin theory where the random force is supposed to be a Markovian process [23]. In a similar fashion, our analysis has allowed to quantify the magnitude of the phonon-modulated barrier $E_a = E_a(\omega,u_0,T)$ and then describe how we chose to treat the classical looking proton hopping in rutile and ceramics at different T. Using the above dynamic considerations we show that m^* varies non-monotonically with the T-dependent coupling parameter. Note that one of the fascinating effects of the above theoretical approach is the ability to explain and even change the seemingly immutable mass relation $m^*/m = 2$, seen first in ceramics by Braun and Chen [4] using the quasi-elastic neutron scattering (for a deeper discussion of the double-mass proton problem in perovskites, see our recent works [24,25]). It is a very definite reason that the proton transport in perovskites is a cooperative process [10,25].

We showed that at low T the behavior of AP considered in terms of UO fits naturally into the universal paradigm "system-reservoir" with the proton selected for a system. In view of these observations, the question now arises of whether there are significant differences between the high-T hopping regime based on classical FDT and the low-T hopping one based on quantum FDT for the same oxide. The results obtained [Eqs. (11) - (15)] indicate that theoretically the low T process should be strongly connected to specific vibrational properties. The notion of the low-T Euclidean time introduced above links the effective T of promoting modes to thermal energy. As to practical application, there appears to be a requirement for the light source, resulting from Eqs. (6) and (7), to have a highly correlated frequency component in relation to resonant local vibrational frequencies, which agrees with the experimental results of Ref. [2,6]. As an estimate, consider the rate enhancement due to laser-induced phonon-modulation effects at 300 K compared to that predicted by Eq. (1). Using Eqs. (5) - (8), the AP parameters $\Omega = 400$ cm^{-1}, $u = 2.8$, $A = 5.7$ cm/ps and the required parameters for classical diffusion coefficient in TiO_2 from [2], we obtained the enhancement $D_{LT}/D \sim 10^9$ at 300 K, which can theoretically confirm experimental outcomes. A rate enhancement was also observed for doped $BaZrO_3$ in the experiment [5] with a similar optical stimulation but performed at higher T. While the latter enhancement is lesser in magnitude, its origin is of the same nature.

To our knowledge, here we present a TLS interpretation relevant to the optically stimulated PP hopping in perovskites for the first time. The reason is as follows. In standard infrared spectroscopy or vibrational relaxation, one invokes the notion of TLS to describe a molecule by only two vibrational levels with the condition that the vibrational frequencies of the different modes are sufficiently different, and if either T is low enough so that only the ground state is appreciably populated, or if the anharmonicity is great enough so that individual transitions for a single mode are well separated. In optical experiments, this approximation is adequate as long as the optical transition of interest is well separated from other transitions [22]. By analogy, in our case we expect excited OH oscillators with two vibrational levels to appear; moreover, as we have already mentioned in Sec. 2, in $BaZrO_3$ the O–H stretch vibration is well-separated from other lattice vibrations.

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In the previous discussion of t_0 when T is low enough (~ tens K), we were dealing only with the ground state and the first level of the excited O-H oscillator. With overtones, we then exhibit another type of the TLS generating transfer from a well-separated higher vibrational level, because the anharmonicity of the single-mode potential is great enough so that the individual OH (or OD) states are well separated. The emerging confluence of the physics of PP in a perovskite and vibrational relaxation in a molecule is exciting.

In summing, optical stimulation of perovskites may lead to the formation of PP and an enhanced rate of over-the-barrier proton motion even at low temperatures. The formalism discussed here presents an interest for studies at higher temperatures of order 200-800 ^{o}C. In the field of energy devices like fuel cells, the problem of PP is of practical significance from the viewpoint of the operating temperature.

8. CONCLUSION

The present work provides a model of protons transferred through the ABO_3 oxide in interaction with the phonon field. It is not a final and perfect theory, because currently the type of the assist phonons involved has not yet been precisely and unambiguously identified in the perovskites.

Proton polarons are an emerging important topic, and a more sophisticated understanding is certainly necessary for strategic design of energy devices, such as fuel cells or sensors, and also for attempting to engineer new solid-state proton-conducting electrolytes. The most promising situation seems to be the phonon-assisted proton transfer enhancement in perovskite-like oxides by resonant illumination proposed experimentally in [2,6] from the viewpoint of fuel cells' applications. It is for this reason that we take it as a model system. However, it should again be emphasized that our description is constructed in a phenomenological manner, and the constitutive relations (5), (14) and (19) using the quantum FDT have to be regarded as model calculations where a underlying proton–phonon oscillation (of which the proton-phonon coupling factor and the effective mass are typical examples) should be regarded as a property of the phonon-assisted proton transport itself, and eventually becomes similar to its analogue in the Holstein-Larsen theory. A main theoretical prediction, essential for the development of a novel energy device such as a fuel cell with a phonon-assisted proton current (we may call this type the phonon-assisted fuel cell), is that the proton jump time in ABO_3-type compounds involved at low and intermediate T follows the Holstein electron-polaron model, which is now rather confirmed by corresponding recent experimental [4,5,10] and first-principles [3] studies.

As a first step in this direction our work provides theoretical underpinnings for earlier and recent experiments on proton-polaron formation under external perturbations, and could point to the design of new type energy devices. Today the femtosecond laser technique is on the threshold of becoming a tool of fundamental importance in condensed matter studies. This work shows that it might be useful for applications in the field of fuel cells were high-efficiency channels of proton transfer and reduction of operating temperature are key problems to solve.

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CONFLICT OF INTEREST

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ADDITIONAL INFORMATION

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