Giant Enhancement of Hydrogen Transport in Rutile TiO₂ at Low Temperatures

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Measurements of the O-H and O-D vibrational lifetimes show that the room-temperature hydrogen diffusion rate in rutile TiO₂ can be enhanced by 9 orders of magnitude when stimulated by resonant infrared light. We find that the local oscillatory motion of the proton quickly couples to a wag-mode-assisted classical transfer process along the c channel with a jump rate of greater than 1 THz and a barrier height of 0.2 eV. This increase in proton transport rate at moderate temperatures provides new insight into hydrogen transport in solids, which could play a role in applications ranging from fuel cells to hydrogen production.

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Proton (H) conduction in solids is a fundamental process that has attracted considerable attention based on important developments and applications in hydrogen energy research. Particularly in the case of solid oxides, this phenomenon is usually observed at high temperatures in the range of 700–1000 °C. The thermal energy is required to break the O-H bond so that the proton can move between oxygen (O) atoms by the well-characterized Grotthuss mechanism [1,2]. This requirement limits the practical application of devices. For example, in solid oxide fuel cells high temperatures cause slow startup times, reduce operational lifetimes due to thermal stress, and require the use of expensive catalytic electrodes [3]. Therefore, it is of great interest to develop mechanisms that can promote a high conductivity without the drawbacks associated with high-temperature operation [4]. Indeed, in the early 1980s, Chen and co-workers found that electron radiation could induce the diffusion of protons and deuterons (D) in titanium dioxide (TiO₂)—even at room temperature [5]. More recently, photon-stimulated H tunneling has been observed in the proton conductor potassium tantalate (KTaO₃), which led to an increase in the H transfer rate of 7 orders of magnitude compared to tunneling from the ground state [6]. From a theoretical standpoint, infrared photon (IR) stimulated H transport has been suggested in zinc oxide (ZnO) [7]; however, direct experimental observation and characterization of this phenomenon in oxides are lacking.

Rutile TiO₂ is a particularly well-suited material to investigate IR-stimulated proton transport because the diffusion is highly efficient with low energy barriers along the large open c channels. Polarized IR absorption studies have shown that, in equilibrium, the O-H dipole is oriented perpendicular to the c axis [8] with a bond length of 1.09 Å [9]. Long-range migration consists of proton jumps between near-neighbor oxygen atoms in a helical path along the c-axis direction and is indicated in Fig. 1(a) [10].

The potential energy surface for hydrogen in solids is often successfully modeled with a simple Morse-type double-well potential. Figure 1(b) illustrates such an energy surface of a cross section of the c channel where the three oxygen sites shown represent the proton host (I), the adjacent near-neighbor site (II), and the site directly across the c channel (III). It is evident that the barrier is much higher along the O-H stretching direction than in the direction of an adjacent oxygen neighbor; thus, the preferred diffusion path involves a conformational transfer step consistent with a helical progression in the c direction. The horizontal lines in the left side well represent the ground and first vibrational states of the O-H stretch-mode which play a key role in dictating how the proton
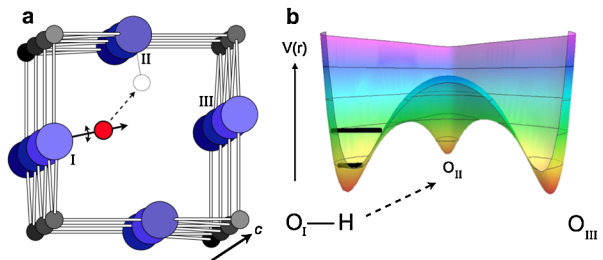

FIG. 1 (color online). (a) The rutile TiO₂ structure is shown here to emphasize the characteristic open c channel. The black circles represent titanium atoms while the large or blue circles are the oxygen atoms to which the hydrogen bonds (small red circle). Solid arrows indicate the vibration of the stretch and wag modes while the dashed arrow indicates the reaction pathway for proton migration. (b) A schematic representation of the potential surface for the proton in the c channel. The proton occupies a double Morse-type potential with barrier heights dependent on the O-O direction. The dashed arrow indicates the preferred reaction coordinate for proton migration to a near-neighbor oxide ion. The horizontal lines depict vibrational levels for the O-H stretch-mode.

traverses this energy surface. Therefore, a clear identification of the O-H decay process is needed for a complete understanding of proton transport in oxides.

Here, we demonstrate resonant IR-stimulated proton migration in TiO_2 at low temperatures (10–270 K). Measurements of the vibrational lifetime of the O-H (3287 cm^{-1}) and O-D (2445 cm^{-1}) stretch modes reveal a fast reorientation-transfer step with a jump rate greater than 1 THz at room temperature, which is 9 orders of magnitude higher than the thermally activated hopping rate [11]. We find this transfer process to have an energy barrier of 0.2 eV and to be aided by the O-H wag motion.

For this investigation, rutile (001) TiO_2 single crystals were grown by the flame fusion method. They contained a high "as-grown" concentration of hydrogen and needed no further treatment. Deuterated samples were prepared by first annealing at 1050 °C under vacuum for 24 h and then in D_2O vapor for up to 72 h. The vibrational lifetimes were investigated using a picosecond transient bleaching technique [12] combined with high-resolution (0.2 cm^{-1}) IR absorption spectroscopy. The transient bleaching signal S_b for the O-D stretch mode is shown in Fig. 2(a) revealing a lifetime of $T_1 = 5.41$ ps at 60 K. This is in excellent agreement with the measured IR linewidth $\Gamma = 0.97 \text{ cm}^{-1}$ [$T_1 = 1/(2\pi c\Gamma) = 5.47$ ps at 10 K] shown in the inset. The O-H lifetime was found to be $T_1 \sim 1.5$ ps, close to our laser pulse width [Fig. 2(b)], and consistent with the linewidth of $\Gamma = 3.03 \text{ cm}^{-1}$ ($T_1 \sim 1.75$ ps). The agreement between the measured lifetimes and linewidths indicates that inhomogeneous broadening mechanisms do not play a significant role in TiO_2.

The temperature dependence of the vibrational lifetime provides valuable information about the proton dynamics. Figure 3 shows T_1 as a function of temperature for the O-H and O-D stretch modes. The latter was measured directly by the transient bleaching technique, and the former was

obtained from the homogeneous linewidth (Γ) where

$$\Gamma = \frac{1}{2\pi c T_1} + \frac{1}{\pi c T_2^*} \tag{1}$$

using the dephasing time T_2^* determined from the linewidth of the O-D mode [13].

According to the frequency-gap law, which relates H local mode phonon decay order to vibrational lifetime, the observed lifetime of ~ 2 ps for O-H and ~ 5 ps for O-D would correspond to a one or two phonon decay channel [14]. The highest phonon frequencies in TiO_2 are around 850 cm^{-1} [15], which would require at least four phonons for the proton decay. Additionally, the inclusion of a high frequency wag mode ($1000–1400 \text{ cm}^{-1}$ for O-H) would still constitute a three-phonon decay process [16]. Moreover, the shape of the O-H and O-D lifetime temperature dependence in Fig. 3 is not characteristic of multiphonon decay [6]. Therefore, this cannot be the dominant relaxation channel for the O-H and O-D stretch modes in TiO_2.

Other than multiphonon decay, vibrational relaxation can also occur via a proton rotation or transfer step—either by a classical "over the barrier" motion or by quantum mechanical tunneling from the excited state. The latter is unlikely because the observed isotope effect is too small. Tunneling would predict an isotope ratio of at least several hundreds based on a simple WKB estimate of tunnel probabilities in a double-well potential. Thus, the most likely decay channel is a classical transport process.

As indicated in Fig. 1(a), the reaction pathway involves a certain degree of coupling to the wagging motion of the O-H bond. We obtain excellent fits of the lifetime temperature dependence to a model for a vibration-assisted proton hopping process where the time between jumps is given by
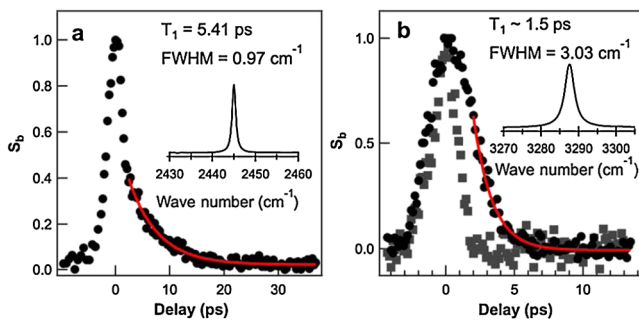

FIG. 2 (color online). The O-D vibrational lifetime is measured to be 5.41 ps at 60 K. The vibrational linewidth (inset) is in excellent agreement with the measured lifetime using Eq. (1). (b) The black circles indicate the pump-probe signal from the O-H stretch mode. Fitting to an exponential decay yields a lifetime estimate of 1.5 ps—also consistent with the linewidth (inset). The gray squares indicate an off-resonant measurement representative of the laser pulse.
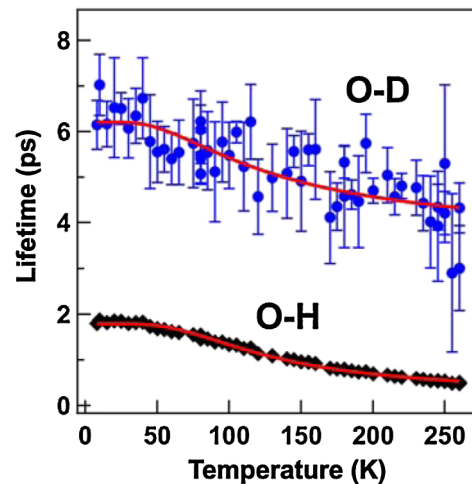

FIG. 3 (color online). Temperature dependence of the measured O-D lifetime (blue circles) along with the O-H lifetime extracted from the vibrational linewidth (black diamonds). Both data sets are fitted to a model for a lattice-assisted proton transfer process [Eq. (2)].

$$\tau \approx A\Omega e^{2u^2 \tanh(\hbar\Omega/4k_bT)}, \qquad (2)$$

where Ω is the frequency of the assist phonon and A and u are constants related to the coupling strength [17]. Fits to our data, shown in Fig. 3, give assist phonon frequencies of $\Omega = 372 \pm 8.6$ cm^{-1} for the O-H lifetime and $\Omega = 278 \pm 60.5$ cm^{-1} for the O-D data. The other fit parameters for the O-H data are $A = 4.87 \times 10^{-4} \pm 4.17 \times 10^{-5}$ cm/ps and $u = 1.07 \pm 0.015$, and for the O-D data, we find $A = 0.13 \pm 3.8 \times 10^{-3}$ cm/ps and $u = 0.534 \pm 0.041$. Both assist phonon frequencies are within the bulk phonon bands, but it is unlikely that both isotopes transfer via different assist phonons. The ratio of the assist phonon frequencies is 1.34 and is in excellent agreement with the ratio of the O-H and O-D stretch modes, therefore indicating the wag motion is the most likely assist mode responsible for promoting the proton over the potential barrier. Additionally, it is possible that the low frequencies obtained here explain the lack of experimental observation of the wag modes in TiO$_2$. This assignment is consistent with the transverse direction of the diffusion path shown in Fig. 1, which requires the hydrogen atom to move at an angle almost perpendicular to the c axis.

Further information on the transfer dynamics can be gained from an in-depth analysis of other hydrogen related vibrational modes shown in Fig. 4. A relatively broad line at 4355 cm^{-1} uniquely associated with hydrogen [8] is likely a combination mode as reported by Soffer [18]. This assignment is consistent with stretch + wag combination modes found in other oxides [6,19] as well as values
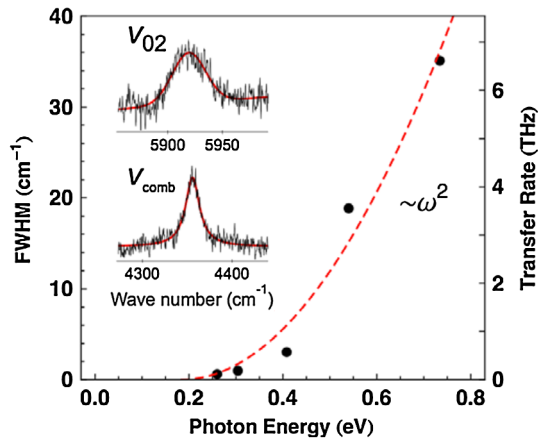
based on first-principles calculations [20]. Additionally, in samples with a large hydrogen concentration we observe a new line at 5920 cm^{-1} at 10 K, as shown in the inset of Fig. 4. This line is interpreted as the first overtone of the O-H stretch mode. Previous studies based on isotope shifts [21] and the calculated stretch-mode potential shape in rutile SnO$_2$ [22] find a large anharmonicity for the O-H stretch. The O-H overtone proposed here requires an even greater anharmonicity and suggests that overtone data can be more sensitive to unusual anharmonic features than have been considered previously for the O-H potential [23]. At lower energy, the tritium (O-T) stretch mode (2070.5 cm^{-1}) has been measured to have a width of 1.2 cm^{-1} at 10 K [21]. By comparison, our O-H and O-D absorbance spectra show linewidth values of a factor of 2 smaller than reported in Ref. [21]. Therefore, a more accurate value for the O-T linewidth is taken to be 0.6 cm^{-1}.

Figure 4 shows that the linewidths of the O-H related vibrational modes become broader with increasing energy. The broad linewidths (Γ) of the higher levels are indicative of a very short upper-state lifetime and, hence, a very high transfer rate ($2\pi c\Gamma$). It is evident from the figure that the transfer rate approaches zero at an excitation energy of ~ 0.2 eV, which therefore corresponds to the barrier height for this transport process. This value is in agreement with the 0.2–0.4 eV barriers calculated by Wardle and co-workers for H reorientation and transfer steps in wurtzite ZnO—which has a slightly (20%) larger O-O separation than in TiO$_2$ [7]. We note that if one interprets the linewidth to be proportional to the density of proton transfer states, then as a rough approximation, the data in Fig. 4 can be fit with a ω^2 dependence consistent with the Debye model for the phonon density of states.

It is worthwhile to compare the IR-stimulated proton transfer rate with standard thermally activated hopping rates obtained in TiO$_2$. The experimental diffusion coefficient along the c channel in TiO$_2$ is given by the Arrhenius expression $D(T) = 1.8 \times 10^{-3} \exp[-0.59 \text{ eV}/k_bT]$ from which a room-temperature hopping rate can be approximated as $D(300 \text{ K})/d^2 \approx 10^3$ s^{-1}, where d is the average jump distance (1.48 Å) [11]. By comparison, the room-temperature IR-stimulated transfer rate (inverse lifetime) is $\sim 10^{12}$ s^{-1}—a giant enhancement representing an increase of 9 orders of magnitude. Such a dramatic enhancement is consistent with optical excitation of the proton to higher vibrational states above the energy barrier for transverse migration.

To summarize, the above analysis indicates that the O-H and O-D stretch modes in rutile TiO$_2$ are relatively unstable oscillations, which quickly couple to a transverse mode with a much lower potential barrier of approximately 0.2 eV. This transverse oscillation then behaves as an assist phonon and promotes the proton to the adjacent oxygen host. The IR-stimulated proton transfer rate is on the order

FIG. 4 (color online). Infrared linewidths (FWHM) for O-H, O-D, and O-T stretch modes in TiO$_2$ measured at 10 K plotted against photon energy. The points shown are for the transitions $\nu(OT)_{01}$, $\nu(OD)_{01}$, $\nu(OH)_{01}$, $\nu(OH)_{comb}$, and $\nu(OH)_{02}$ with increasing photon energy, where subscripts indicate the vibrational quantum number. Absorption lines for the O-H combination and overtone modes are shown in the inset. The transfer rate corresponds to the inverse lifetime determined from the linewidth using Eq. (1), and the zero intercept represents the energy barrier for migration. The dashed line represents a ω^2 fit based on the Debye model for the phonon density of states.

of 1 THz and shows a dramatic enhancement over thermally activated processes. It is reasonable to expect that IR-stimulated migration is possible in similar oxides (e.g., SnO_2, HfO_2, ZnO, among others) in which hydrogen is a highly mobile defect. Ultimately, this new fundamental insight into the microscopic dynamics of protons in TiO_2 establishes an important link between O-H vibrational decay and hydrogen transport in oxides.

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