Electron- or Hole-Assisted Reactions of H Defects in Hydrogen-Bonded KDP

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We present an *ab initio* study of the stability and defect reactions of neutral and charged H interstitial (H_i) and H vacancy (H_v) in KH_2PO_4 (KDP). We find that while there is no interaction between the neutral H_i and the host, the addition of an electron leads to the ejection of a H host atom and the subsequent formation of an interstitial H_2 molecule and a H_v. In sharp contrast, the addition of a hole results in the formation of a hydroxyl bond. Thus, H_i in both charged states severs the H-bonded network. For the H_v, the addition of a hole leads to the formation of a peroxyl bridge. The neutral H_i and the positively charged H_v induce states in the gap. The results elucidate the underlying atomic mechanism for the defect reactions suggested by experiment.

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Hydrogen bonded (HB) ferroelectrics have attracted wide and sustained interest for several decades (for a review see [1]), because of the continuing controversy over the nature of the phase transition, their technological importance, and their use as convenient systems in which to study hydrogen bonding. Potassium dihydrogen phosphate, KH_2PO_4 (KDP), the prototype of this family of HB ferroelectrics [2–4], is an important nonlinear optical material with many applications in laser physics, such as the various high-power large-aperture laser systems located at the National Ignition Facility. A key feature of the crystal structure of KDP is covalently bonded molecular PO_4 units linked by a network of hydrogen O-H-O bonds. It is known that each proton is equally likely to be in either of two positions in the hydrogen bond above the ferroelectric phase transition at $T_c = 122$ K, where the structure is tetragonal, and is nearly entirely in one site below T_c, where the structure is orthorhombic [5–9]. Recent neutron Compton scattering experiments [4] have shown that the proton is coherent over both sites in the high temperature phase, a result that invalidates the commonly accepted order-disorder picture [2] of the transition.

A major concern in the practical applications of KDP at room temperature is the appearance of unwanted optical-absorption bands in the 300–650 nm spectral region, when KDP crystals are exposed to intense ultraviolet or x-ray irradiation [10–13]. The laser-induced optical absorption, which limits the device performance, was attributed to point defects created during crystal growth or generated by irradiation. Davis *et al.* hypothesized [10] that *proton transport* (the radiation-induced displacement of a proton from its normal site) is a major component of the mechanism responsible for the transient optical absorption. The formation of the absorbing defect centers proceeds through the following proposed scenario: Two-photon interband absorption of high-intensity laser radiation generates electron-hole pairs, a portion of which may eventually evolve into electronic defect states that often lie within the band gap. A H^+ ion occupying a normal lattice site traps an electron to become a neutral H atom, which in turn becomes ejected from its original site. The oxygen atom closest to the H vacancy thus formed, traps the hole and forms the $[HPO_4]^-$ radical. Subsequent electron paramagnetic resonance [14] and resonance Raman scattering [12] experiments provided direct spectroscopic evidence of the $[HPO_4]^-$ hole center and of the hydrogen interstitial H^0 electron center, in support of the proton-transport mechanism. Thus, overall the experimental results suggest that hydrogen point defects play a major role in both the ferroelectric transition and the optical-absorption properties of KDP.

Understanding point defects in solids has been a subject of great interest and importance in improving device performance and materials quality. Recently, theoretical efforts have predominantly focused on understanding the role of hydrogen defects in Si [15], GaAs [16], and SiO_2 [17,18], and of oxygen defects in SiO_2 [19] in their various charge states. On the other hand, despite extensive experimental studies of HB molecular crystals, little is known theoretically of the defect physics in these systems.

In this Letter, we present an *ab initio* study of two types of hydrogen point defects (interstitial and vacancy) in KDP. The calculations elucidate the underlying atomic mechanism of the effect of charge state on the relevant atomic configurations, stability, and defect reactions suggested by experiment. We find that the atomic structure of the H interstitial and the H vacancy and the defect states induced in the band gap strongly depend on their charge states: The H neutral interstitial remains intact and does not interact with the host in sharp contrast with the charged states. In the positively charged state, the H interstitial forms an extra O-H bond, while in the negatively charged state, the H interstitial forms a H_2 molecule with

the simultaneous creation of a H vacancy. Thus, H interstitial in both charged states catalyzes the severing of the HB network. For the H vacancy, the most remarkable result is that the addition of a hole leads to a dramatic decrease of the O-O bond length between the oxygen atoms close to the vacancy and the formation of a peroxyl bridge.

The *ab initio* calculations we performed are based on density-functional theory (DFT) with the CASTEP implementation [20] and ultrasoft pseudopotentials [21]. The Perdew-Burke-Ernzerhof gradient-corrected functional [22] was used for the exchange-correlation potential. An isolated defect is simulated in periodic boundary conditions via a repeated supercell which consists of eight KH_2PO_4 formula units and contains 64 ± 1 atoms. The kinetic energy cutoff for the plane-wave basis was set to be 680 eV, yielding a convergence for the total energy better than 1 meV/atom [8]. Integrations over the Brillouin zone were done using the Monkhorst-Pack scheme [23] with six k points in the relevant irreducible wedge. Results have been obtained for the fully relaxed geometries including all atoms and the lattice constants of the supercell with the use of the conjugate gradient techniques. For the studies of the charged defects, an electron is added or removed from the neutral system and a uniform background with opposite polarity is adopted automatically to keep the neutrality of the whole system; this in turn prevents the divergence in the total energy [24].

Figure 1 shows the change of the relaxed atomic structure induced by an interstitial hydrogen (H_i) atom with the two nearest-neighbor PO_4 tetrahedral units for the neutral [Fig. 1(a)], negative [Fig. 1(b)], and positive [Fig. 1(c)] charge states. Values of the bond length and overlap population for the H_i-O_h and H_i-H_h bonds between the H interstitial and its nearest-neighbor O host (O_h) or H host (H_h) atoms are listed in Table I. In the neutral state, the hydrogen defect remains intact in the interstitial position and does not form any bonds with the host atoms. We will refer to this configuration as the "isolated H_i." The addition of an electron yields a dramatic change in the defect configuration. A host H atom is attracted to the interstitial H_i and gets displaced from its normal lattice site. This results in the formation of an interstitial H_2 molecule leaving behind a hydrogen vacancy, which will be referred to as the "$H_2 + H_v$" configuration. The H_h-H_i bond length is 0.76 Å, close to the values of 0.77 Å for the free H_2 and of 0.74 Å for molecular hydrogen in silica [17]. The formation of the vacancy leads to an increase of the O-O separation to

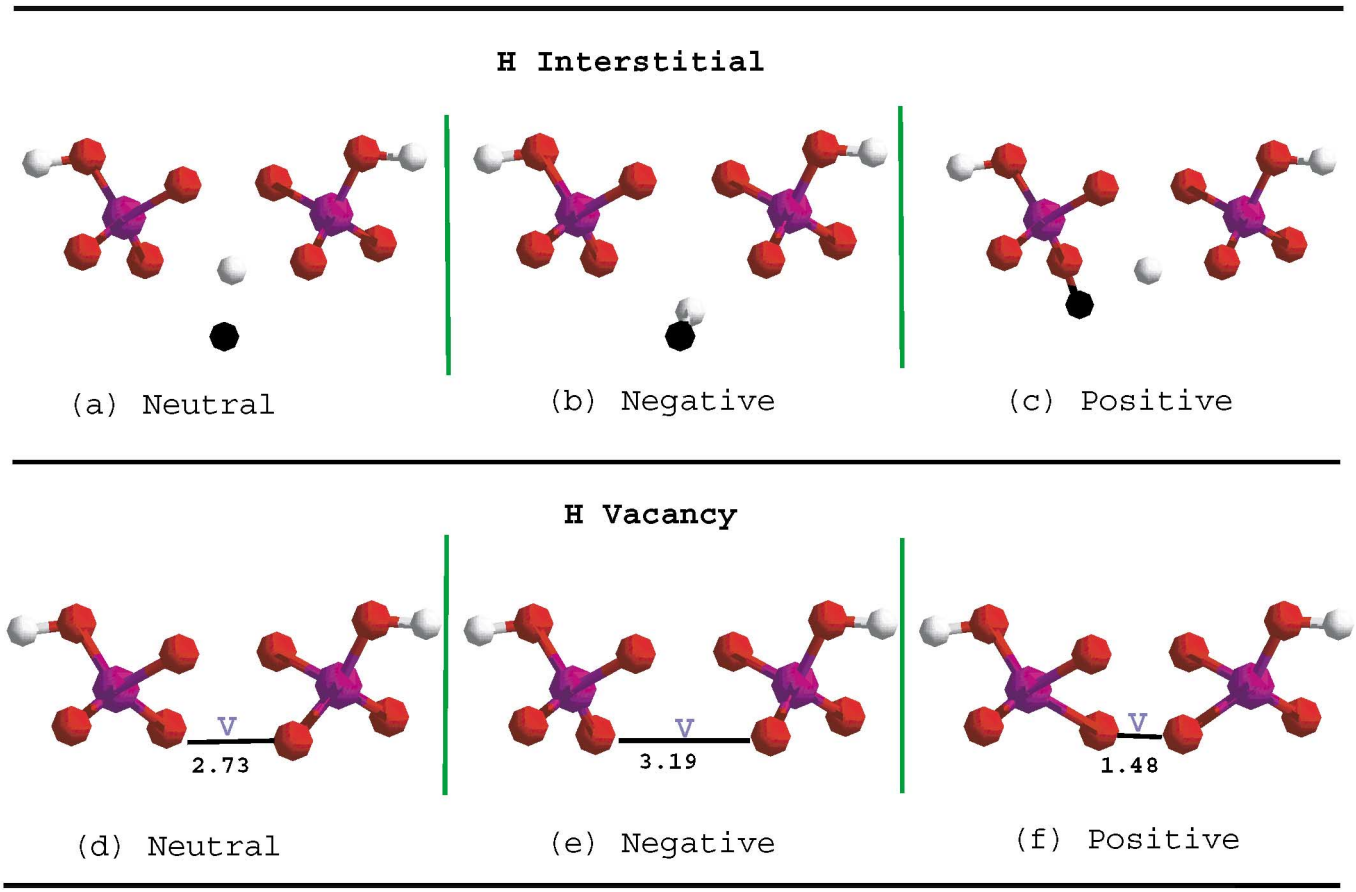

FIG. 1 (color). Relaxed atomic configurations and reactions for interstitial H for the neutral (a), negative (b), and positive (c) charged states. Also we show the relaxed atomic configurations for the H vacancy in the neutral (d), negative (e), and positive (f) charged states. The black, white, red, and purple circles denote H interstitial, H host, O, and P atoms, respectively.

TABLE I. O_h-H_i and H_h-H_i distance (Å) and overlap population ($|e|$) for the interstitial hydrogen in the neutral, negative, and positive charge states. O_h and H_h denote the nearest O and H host atoms to the H interstitial H_i.

	O_h-H_i (distance/population)	H_h-H_i (distance/population)
Neutral state	1.90/ − 0.02	1.89/ − 0.02
Negative state	2.41/ − 0.02	0.76/1.30
Positive state	0.98/0.66	2.07/ − 0.03

3.36 Å from the corresponding value of 2.48 Å in pure KDP. In sharp contrast, in the positively charged state, the hydrogen interstitial bonds with its nearest-neighbor O atom creating an extra O-H bond (0.98 Å), which in turn greatly weakens the neighboring O-H bond of the host atoms. This configuration will be referred to as the "hydroxyl" configuration. Thus, H interstitial in both charged states catalyzes the scission of the HB network.

In Fig. 1 we also show the local atomic structural changes induced by a hydrogen vacancy with its two nearest-neighbor PO_4 tetrahedral units for the neutral [Fig. 1(d)], negative [Fig. 1(e)], and positive [Fig. 1(f)] charge states. The most remarkable feature in this case is that the addition of a hole gives rise to the formation of a peroxyl bridge between the two oxygen atoms close to the vacancy. Namely, the hole leads to a dramatic decrease of this O-O bond length from 2.73 Å in the neutral case to 1.48 Å, compared to the values of 1.19 Å in the free molecular oxygen and of 1.49 Å for the peroxyl bridge in vitreous silica [25].

In order to explore the energetics of the reactions of the interstitial, we have calculated the energy of a series of intermediate configurations in which all the degrees of freedom but the H_i-H_h or the H_i-O_h distance are relaxed. Figure 2 shows the relative total energy versus the H_i-H_h distance for the neutral [Fig. 2(a)] and the negative charged states [Fig. 2(b)], and versus the H_i-O_h distance for the positive charged state [Fig. 2(c)], respectively. In the neutral state [Fig. 2(a)], we find two energy minima at 1.9 and 0.75 Å corresponding to the isolated H_i configuration and to the $H_2 + H_v$ configuration, respectively. We find that the first configuration has the lowest energy and that an energy barrier of 1.2 eV needs to be overcome to move from the isolated H_i to the $H_2 + H_v$ configuration. In contrast, the addition of an electron [Fig. 2(b)] removes the energy barrier and yields a single stable structure at 0.75 Å corresponding to the $H_2 + H_v$ configuration. Thus, the additional electron greatly assists the formation of an interstitial H_2 molecule. In the positively charged state [Fig. 2(c)], we find that an energy barrier of 1.4 eV needs to be overcome to move from the isolated H_i to the stable O-H hydroxyl configuration.

In Fig. 3 we show the total density of states of a few representative cases, namely, the pure KDP (a), the neutral H_i (b), and the H_v in the positive charged state (c). In the neutral state, the H_i induces occupied H-*s* derived

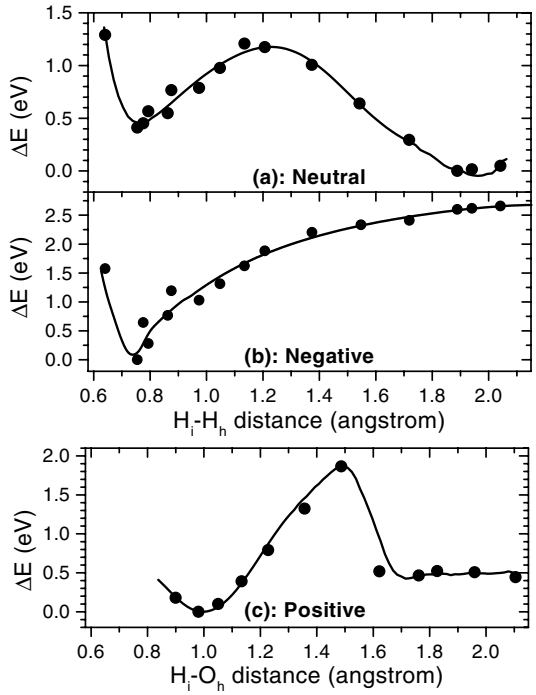

FIG. 2. Relative total energy for the H interstitial as a function of the H_i-H_h distance for the neutral state (a) and the negatively charged state (b), and as a function of H_i-O_h distance for the positively charged state (c), respectively. The minima at 1.9 Å in (a) and at 0.75 Å in (a) and (b) correspond to the "isolated H_i" configuration and to the "$H_2 + H_v$" configuration, respectively. The lines are guides to the eyes.

states (indicated by an arrow) in the energy gap of pure KDP. The electronic structure for the neutral H_i corresponds to a superposition of those for the defect-free KDP system and the hydrogen atom; i.e., there is no hybridization between the interstitial H and the KDP host atoms, as is indicated also by the values of the bond length and overlap population in Table I. Interestingly, the addition or removal of an electron removes the H-induced states in the gap. This is due to the fact that H_i in the negatively or positively charged state forms strong bonds with its neighbor host H_h or O_h atoms, respectively. Similar results were found for charged states of interstitial hydrogen in silica [17]. Figure 3(c) shows that the H_v in the positive charged state also induces empty states in the energy gap; these states are derived from the O/p states of the two O atoms next to the hydrogen vacancy, forming a strong O-O bond. The vacancy also induces states in the energy range of 22 to 17 eV below the Fermi energy which are O-*s* derived states. On the other hand, the neutral and negatively charged H_v are not associated with induced states in the gap, due to the large O-O bond length. Despite the well-known intrinsic deficiencies of DFT in yielding too low band gaps compared to experiment, we find that the band gap for the neutral interstitial H and positive charged H vacancy are greatly reduced to 2.6 and 2.5 eV, respectively, compared to the corresponding DFT and experimental

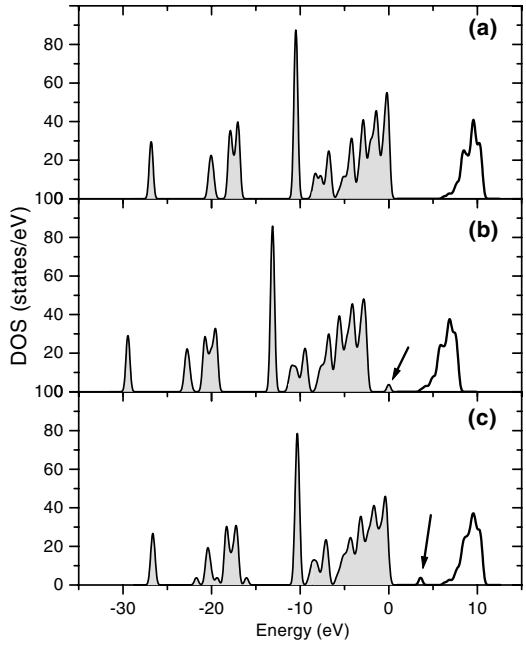

FIG. 3. Total density of states for pure KDP (a), KDP with an interstitial H in the neutral state (b), and KDP with a H vacancy in the positive charged state (c). The arrows in (b) and (c) denote the occupied interstitial H-*s* and the empty O-*p* (O's next to the hydrogen vacancy) derived band gap states, respectively.

[26] values in pure KDP of 5.9 and 7.2 eV, respectively. This suggests that these two types of hydrogen defects may play an important role on the experimentally observed optical absorption in the 355 nm (3.5 eV) spectral region [10–13], and also may be responsible for the lowering of the damage threshold in KDP [27].

In summary, the *ab initio* calculations reveal the underlying atomic mechanism of the effect of the charge state on the stability and reactions of two H point defects in KDP. The addition of an electron or hole alters dramatically the atomic configurations, energetics, reactions and induced gap states of the defects. For the H interstitial, the addition of an electron leads to the ejection of a H host atom and the subsequent formation of an interstitial H_2 molecule and a H vacancy, in sharp contrast to the neutral case. On the other hand, in the positively charged state the hydrogen interstitial forms a hydroxyl bond. For the H vacancy, the addition of a hole leads to the formation of a peroxyl bridge. We have identified that the neutral H interstitial and the positively charged H vacancy may play an important role on the experimentally observed optical absorption. We believe that the conclusions of our calculations should also be applicable to a wider family of H-bonded molecular systems.

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