



Cite this: DOI: 10.1039/d6el00027d

# Hydrogen migration, surface accumulation, and nonradiative recombination in perovskite solar cells

 Yong Huang,<sup>†a</sup> Xiqi Yang,<sup>†a</sup> Xiaoqing Chen,<sup>\*a</sup> Rongkun Zhou,<sup>a</sup> He Huang,<sup>a</sup> Di Lu,<sup>a</sup> Yongcai He,<sup>a</sup> Wencai Zhou,<sup>\*b</sup> Hui Yan<sup>a</sup> and Zilong Zheng<sup>id</sup><sup>\*a</sup>

Perovskite solar cells (PSCs) have achieved efficiencies exceeding 27%, yet their performance remains limited by defect-induced nonradiative recombination. Although hydrogen interstitials ( $H_i$ ) are conventionally considered as bulk defects, this study reveals the dynamic instability of  $H_i$  within the bulk lattice of  $FAPbI_3$ , which drives spontaneous migration to surface sites due to thermodynamic stabilization at the interface. By combining all-atom molecular dynamics (AAMD) with nonadiabatic molecular dynamics (NAMD), we elucidate the migration pathway of  $H_i$  and its electronic implications. Surface-trapped  $H_i$  induces significant lattice distortion, resulting in the formation of deep-level defect states and a modified potential energy landscape. This reorganization reduces the electron capture barrier ( $\Delta E_n$  decreasing from 0.09 eV to 0.03 eV) and the hole capture barrier ( $\Delta E_p$  dropping from 0.24 eV to 0.17 eV), and increases carrier capture coefficients by an order of magnitude (from  $10^{-8} \text{ cm}^3 \text{ s}^{-1}$  to  $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ ). Strengthened vibronic interactions and enhanced nonadiabatic couplings shorten the carrier lifetime from 0.8 ns (bulk  $H_i$ ) to 0.1 ns (surface  $H_i$ ), indicating surface-accumulated  $H_i$  is the dominant nonradiative recombination source rather than bulk  $H_i$ . These findings emphasize that interfacial hydrogen management, rather than conventional bulk passivation, is critical for designing suppression strategies to overcome performance limitations in PSCs.

 Received 12th February 2026  
Accepted 11th April 2026

DOI: 10.1039/d6el00027d

rsc.li/EESolar

## Broader context

Perovskite solar cells (PSCs) face fundamental efficiency limits from defect-induced recombination. While hydrogen interstitial ( $H_i$ ) defects are recognized as detrimental, their dynamic behavior and spatial redistribution have been significantly overlooked. This work establishes that  $H_i$  in  $FAPbI_3$  are intrinsically unstable in the bulk lattice and migrate spontaneously to surface sites, where they achieve thermodynamic stabilization. This surface accumulation induces severe lattice distortion and deep-level trapping state that enhance carrier capture coefficients and reduce carrier lifetimes by nearly an order of magnitude compared to bulk-located defects. Our findings shift the focus of defect management by demonstrating that interfacial hydrogen, rather than its bulk form, dominates recombination losses. This new understanding resolves a critical limitation of conventional bulk passivation, which proves inadequate for managing high-mobile defects. This conclusion is supported by recent advances in passivation strategies, for instance multifunctional molecules that simultaneously engage with surface defects and co-modification approaches that reconstruct the perovskite surface to suppress defect activity. By connecting hydrogen migration dynamics with interfacial recombination kinetics, this study provides an understanding of mobile defects in soft lattice materials. These insights are essential for overcoming efficiency limitations in PSCs and provide strategic guidance for defect engineering in related semiconductor technologies.

## Introduction

Metal-halide perovskites have emerged as one of the most promising photovoltaic materials, due to their outstanding

optoelectronic properties, facile solution processability, and rapid efficiency improvements.<sup>1,2</sup> Perovskite solar cells (PSCs) have achieved certified power conversion efficiencies (PCE) exceeding 27%,<sup>3</sup> positioning them as competitive contenders against established photovoltaic technologies. However, this remarkable progress remains constrained by the Shockley–Queisser (SQ) limit of 33%,<sup>4</sup> as defect-induced nonradiative recombination constitutes the dominant energy loss mechanism that limits device performance. The minimization of trap-assisted nonradiative recombination (or Shockley–Read–Hall, SRH) process has therefore become a critical direction for performance enhancement in PSCs.<sup>5–7</sup>

Extensive investigation over the past decade has explored the defect physics in metal halide perovskites through combined

<sup>a</sup>State Key Laboratory of Materials Low-Carbon Recycling, Beijing Key Lab of Microstructure and Properties of Advanced Materials, College of Materials Science and Engineering, School of Information Science and Technology Key Laboratory Optoelectronics Technology of Ministry of Education, Beijing University of Technology, Beijing 100124, China. E-mail: zilong.zheng@bjut.edu.cn; chenxiaoping@bjut.edu.cn

<sup>b</sup>Hubei Key Lab of Photoelectric Materials and Devices, School of Materials Science and Engineering, Hubei Normal University, Huangshi, Hubei 435002, China. E-mail: zwc@hbnu.edu.cn

<sup>†</sup> Yong Huang, Xiqi Yang contributed equally to this paper.



experimental and theoretical approaches. Early research focused predominantly on B-site (Pb) and X-site (I) defects as principal nonradiative recombination centers, consistent with the orbital characteristics of the band edge states.<sup>8</sup> More studies have revealed the significant role of hydrogen-related defects originating from the A-site (MA and FA) cation deprotonation. For instance, hydrogen vacancies ( $V_{\text{H}}$ )<sup>9</sup> and hydrogen interstitials ( $\text{H}_i$ ),<sup>10</sup> have been identified as major contributors to non-radiative losses in  $\text{MAPbI}_3$  and  $\text{FAPbI}_3$  perovskites.

In contrast to  $V_{\text{H}}$ , which exhibit self-healing behavior through coordination with lattice ions thereby suppressing their carrier capture coefficients,<sup>11–13</sup>  $\text{H}_i$  present a more severe challenge to device stability and performance.  $\text{H}_i$  form persistent deep-level traps that induce significant nonradiative recombination within the bulk lattice.<sup>10</sup> More critically,  $\text{H}_i$  exhibit high mobility with low migration potential barrier (0.17 eV) and strong thermodynamic driving force for redistribution.<sup>14–16</sup> This unfavorable combination may promote the dynamic accumulation of  $\text{H}_i$  at charge sensitive regions such as surfaces.<sup>17</sup> The  $\text{H}_i$  migration behavior has been experimentally confirmed and further accelerated under illumination and humidity,<sup>18,19</sup> providing a mechanistic explanation for observed device instabilities, including current–voltage hysteresis, surface recombination, and environmental degradation.

Conventional bulk passivation strategies, for instance halogen mixing and alkali-metal incorporation, have demonstrated restricted effectiveness in mitigating  $\text{H}_i$  defects due to their inherent high mobility.<sup>20–23</sup> This limitation becomes particularly significant when considering the distinct physical and chemical environment present in perovskite, where differences exist between bulk and surface regions that can fundamentally modify defect energetics and dynamics.<sup>24</sup> The variation in local coordination and chemical potential suggests that surface-accumulated  $\text{H}_i$  may exhibit different recombination characteristics compared to bulk-located  $\text{H}_i$ . This critical divergence between surface and bulk  $\text{H}_i$  behavior highlights a fundamental knowledge gap in understanding the microscopic mechanisms and recombination impact of surface-accumulated  $\text{H}_i$  defects.

To address this challenge, we employed a multiscale computational framework integrating density-functional theory (DFT), all-atom molecular dynamics (AAMD), and nonadiabatic molecular dynamics (NAMD) to investigate the  $\text{H}_i$  migration and carrier capture kinetics from bulk to surface in  $\text{FAPbI}_3$ . This approach combines the strengths of AAMD in capturing defect migration dynamics over nanosecond scales, the accuracy of DFT in determining electronic structures and defect energetics, and the capability of NAMD in simulating nonradiative carrier recombination processes. We find that  $\text{H}_i$  are intrinsically unstable in the bulk lattice, spontaneously migrating to surface sites within sub-nanosecond timescales due to a strong thermodynamic driving force, where they become energetically stabilized. This surface accumulation leads to a pronounced alteration in the defect electronic activity. The charge carrier capture barriers are significantly reduced, which in turn elevates the nonradiative carrier capture coefficient by an order of magnitude. Consequently, the carrier lifetime is drastically

shortened from 0.8 ns for bulk-located  $\text{H}_i$  to 0.1 ns for surface-accumulated  $\text{H}_i$ , indicating surface-rich  $\text{H}_i$  as a severe recombination center that limits the performance of PSCs.

This work delivers fundamental insights into the surface-dominated  $\text{H}_i$  recombination. By connecting hydrogen migration dynamics with surface stabilization mechanisms and carrier capture kinetics, our findings highlight interfacial hydrogen management as an essential strategy for advancing high-performance PSCs.

## Results and discussion

### Migration dynamics and surface stabilization of $\text{H}_i$

In order to investigate the migration and stabilization behavior of  $\text{H}_i$  in  $\text{FAPbI}_3$ , we performed large-scale all-atom molecular dynamics (AAMD) simulations. This approach effectively addresses the constraints of both length and time scales in *ab initio* molecular dynamics (AIMD), enabling the tracking of  $\text{H}_i$  dynamics across microsecond-scale trajectories and over system sizes spanning hundreds of nanometers. The extended simulation capability allows for exploring  $\text{H}_i$  pathways and configurational relaxation toward thermodynamic minima.

The migration trajectory of  $\text{H}_i$  at 300 K is depicted in Fig. 1a. When initially positioned in the bulk region approximately 6 nm below the surface (Fig. 1b),  $\text{H}_i$  exhibits continuous directional drift toward the surface along with random thermal fluctuations, indicating a thermodynamic preference for surface accumulation. At the beginning (0–0.6 ns),  $\text{H}_i$  exhibited high mobility through rapid localized motion within neighboring unit cells. Subsequent migration to the surface (0.6–0.9 ns) is followed by lateral confinement and two-dimensional diffusion (0.9–1.2 ns), confirming surface stabilization.

The thermodynamic driving force for this behavior is clarified by the potential energy profile along the direction perpendicular to the surface, as shown in Fig. 1c. A pronounced energy minimum obtained at the surface region provides a quantitative explanation for the spontaneous accumulation of  $\text{H}_i$ , confirming that the surface possesses a lower energy state compared to the bulk. This potential energy gradient drives both directional migration and subsequent stabilization of  $\text{H}_i$  at the surface under room-temperature conditions.

### Surface-induced modifications in $\text{H}_i$ electronic structure

Based on the surface accumulation tendency of  $\text{H}_i$  in  $\text{FAPbI}_3$ , we further investigated how surface environments influence their local atomic arrangements and electronic properties. Comparative studies between bulk and surface configurations show that surface accumulation affects both  $\text{H}_i$  stability and electronic characteristics. In bulk regions, positive  $\text{H}_i^+$  forms an H–I bond (1.75 Å), while neutral  $\text{H}_i^0$  preferentially occupy the interstitial site between adjacent Pb–I bonds, forming a Pb–H–I bridging configuration. Additional electron capture generated  $\text{H}_i^-$ , resulting in noticeable  $\text{PbI}_6$  octahedral distortion and stretching the opposing Pb–I bond to 4.22 Å (Fig. 2c). Surface environments introduce changes to these configurations, particularly for  $\text{H}_i^-$  which shows enhanced distortion that



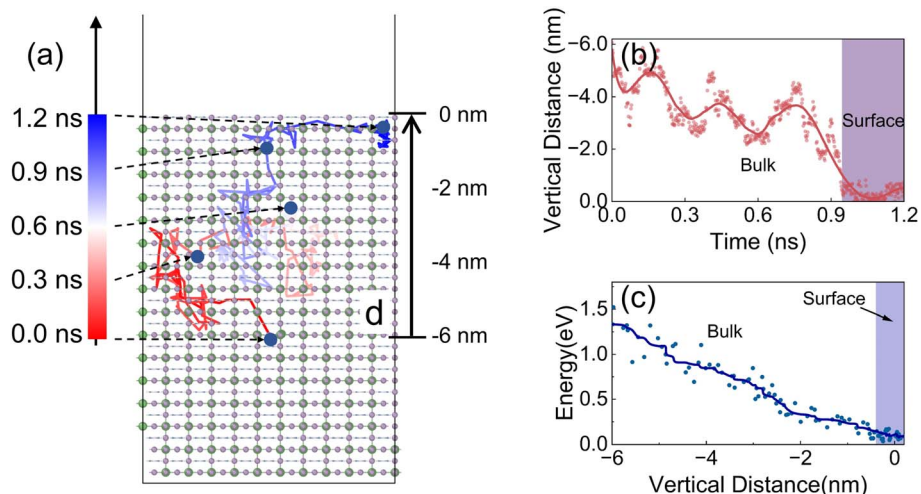


Fig. 1 (a) Migration trajectory showed  $H_i$  spontaneously moving from an initial depth of 6 nm in the bulk region to the surface within 0.9 ns, followed by trapping and lateral diffusion at the interface (0.9–1.2 ns). (b) Time evolution of  $H_i$  vertical distance from the surface, illustrating its rapid approach and subsequent stabilization at the interface. (c) Potential energy profile perpendicular to the surface, showing a distinct minimum at the interface that explains the thermodynamic preference for surface accumulation at 300 K.

breaks the Pb–I bond and extends it to 4.80 Å (Fig. 2d), indicating stronger electron-phonon interactions at the surface.

$H_i$  formation energies and charge-state transition levels show modifications in surface environments, see Fig. 3.  $H_i$  introduces three distinct charge-state transition levels within the bandgap,  $\epsilon(\pm)$ ,  $\epsilon(0/-)$  and  $\epsilon(+/0)$ . The  $\epsilon(\pm)$  transition involves a two-electrons capture process, which is less probable and therefore contributes weakly to nonradiative recombination. Consequently, the overall recombination kinetics are predominantly governed by the single-carrier capture transitions  $\epsilon(0/-)$  and  $\epsilon(+/0)$ .<sup>25</sup> In the bulk, the  $\epsilon(0/-)$  level sits 0.41 eV above the valence band maximum (VBM), while  $\epsilon(+/0)$  lies 0.32 eV below the conduction band minimum (CBM), indicating the role of  $H_i$  as

a recombination center. Surface accumulation shifts these levels to 0.53 eV above VBM and 0.38 eV below CBM, with  $\epsilon(0/-)$  moving 0.12 eV closer to the conduction band, consistent with the enhanced lattice relaxation seen in surface-stabilized  $H_i$  in Fig. 2.

### Enhanced carrier capture kinetics at surface sites

While Shockley-Read-Hall theory indicates carrier capture rates decline exponentially with the deeper transition levels, this relationship requires examination through potential energy surface (PES) calculations. We employed a one-dimensional quantum model to map PES for charge-state transitions along the configuration coordinate ( $Q$ ),<sup>26</sup> defined through mass-weighted atomic displacements between initial and final configurations. This approach provides quantitative energies of carrier capture barrier.

$$\Delta Q^2 = \sum_{\alpha} m_{\alpha} (R_{\alpha,t} - R_{\alpha,i})^2$$

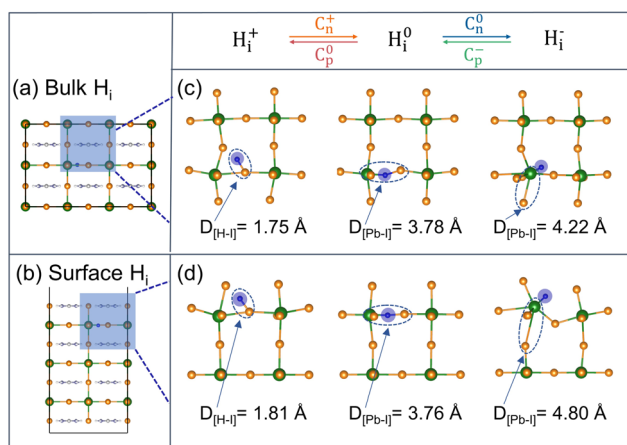


Fig. 2 (a and b) Computational models for  $H_i$  in bulk and surface slab. (c and d) Equilibrium configuration of  $H_i$  in charge states +, 0 and – in bulk and at surface, respectively. In the bulk,  $H_i^+$  forms H–I bond,  $H_i^0$  adopts a bond-center configuration, and  $H_i^-$  forms distorted H–Pb coordination with octahedral deformation. Electron capture transitions ( $C_n^+$  and  $C_n^0$ ) and hole capture transitions ( $C_p^-$  and  $C_p^0$ ) corresponding to charge-state changes were indicated.

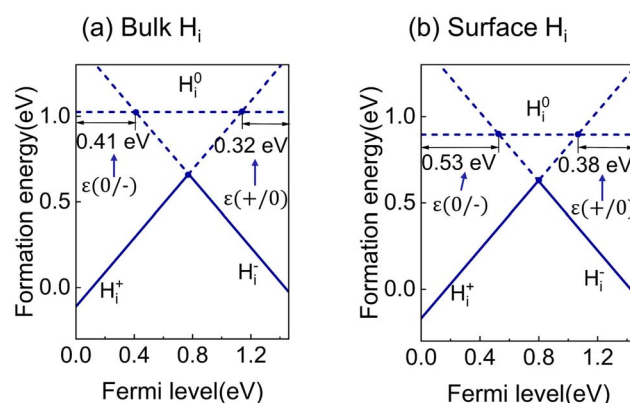


Fig. 3 Formation energies of  $H_i$  as a function of Fermi level under H-rich conditions for (a) bulk and (b) surface configurations, respectively.



where  $\Delta Q$  is the displacement of  $Q$  coordinate;  $m_\alpha$  is the mass of atom  $\alpha$  in the configurations of defects;  $R_{\alpha f}$  and  $R_{\alpha i}$  are the Cartesian coordinates of atom  $\alpha$  in the final and initial defect configurations.

The neutral  $H_i^0$  introduces deep-level defect states within the bandgap, in contrast to the shallow states associated with  $H_i^+$  and  $H_i^-$  defects, as discussed later. The configuration coordinate diagram shows carrier capture processes. For the  $H_i^+ \leftrightarrow H_i^0$  transition, following photoexcitation, the system progresses through three distinct stages. Initially,  $H_i^+$  remains inactive toward carrier capture, denoted as  $H_i^+ \cdots e^- \cdots h^+$ ; subsequently, electron capture transitions the defect to  $H_i^0$ , denoted as  $(H_i^+ + e^-) \cdots h^+$ ; finally, hole capture returns the system to  $H_i^+$ , denoted as  $(H_i^+ + e^- + h^+)$ , see Fig. 4a. The capture potential barriers were obtained from the saddle point on the PES. The electron capture barrier ( $\Delta E_n^+$ ) corresponds to the energy at saddle point between  $H_i^+ \cdots e^- \cdots h^+$  and  $(H_i^+ + e^-) \cdots h^+$  transition; while hole capture barrier ( $\Delta E_p^0$ ) is derived from saddle point between  $(H_i^+ + e^-) \cdots h^+$  and  $(H_i^+ + e^- + h^+)$  transition.

For the  $(+0)$  transition of bulk  $H_i$ , the associated configuration-coordinate displacement is  $\Delta Q = 14.4 \text{ \AA amu}^{1/2}$ . The corresponding electron capture process falls within the Marcus inverted region, characterized with a relative small configuration coordinate  $Q = 2.6 \text{ \AA amu}^{1/2}$  ( $0 < Q < \Delta Q$ ). In this

regime, the  $\Delta E_n^+$  decreases as the  $(0/+)$  level shifts deeper below the CBM. In contrast, hole capture occurs in the Marcus normal region with  $Q = 16.4 \text{ \AA amu}^{1/2}$  ( $Q > \Delta Q$ ), resulting in an increased  $\Delta E_p^0$  with rising transition energy relative to the VBM. With the  $(+0)$  level located at 0.32 eV below the CBM, the resulting energy barriers are  $\Delta E_n^+ = 0.13 \text{ eV}$  for electron capture and small  $\Delta E_p^0 = 0.08 \text{ eV}$  for hole capture. These values yield carrier capture coefficients of  $2.0 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  for electrons ( $C_n^+$ ) and  $2.8 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  for holes ( $C_p^0$ ) at room temperature, see Fig. 4c. The modest barriers and efficient capture processes confirm  $H_i$  as an effective nonradiative recombination center in bulk regions.

The  $(0/-)$  transition of bulk  $H_i$ , exhibits distinct characteristics due to large lattice relaxation ( $\Delta Q = 31.9 \text{ \AA amu}^{1/2}$ ), with both electron and hole capture processes occurring in the Marcus inverted regions ( $0 < Q < \Delta Q$ ). The  $(0/-)$  transition level are positioned at 0.41 eV above the VBM. The smaller electron capture barrier ( $\Delta E_n^0 = 0.09 \text{ eV}$ ) compared to hole capture barrier ( $\Delta E_p^- = 0.24 \text{ eV}$ ) results in a significantly disparity in capture coefficients. The electron capture coefficient ( $C_n^0$ ) reached  $1.2 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ , whereas the hole capture coefficient ( $C_p^-$ ) is limited to  $1.9 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ . Therefore, the overall capture coefficient ( $C_{\text{tot}}$ ) is governed by the slower hole capture process, with the value of  $1.9 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ , derived from following equations under steady-state conditions.<sup>27</sup>

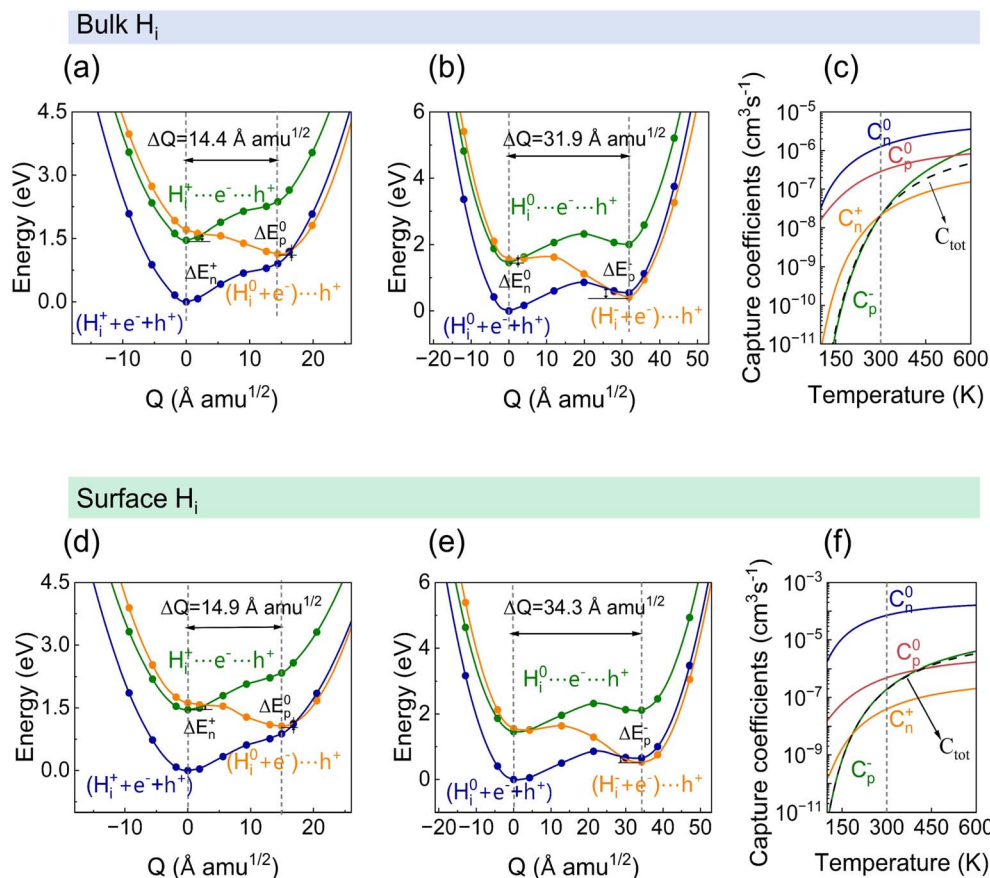


Fig. 4 (a and b) Configuration coordinate diagrams of  $(+0)$  and  $(0/-)$  charge state transitions of bulk  $H_i$  in  $\text{FAPbI}_3$ . (c) Carrier capture coefficients as a function of temperature for bulk  $H_i$ . (d and e) Configuration coordinate diagrams of  $(+0)$  and  $(0/-)$  charge state transitions of surface  $H_i$ . (f) Carrier capture coefficients as a function of temperature for surface  $H_i$ .



$$C_{\text{tot}} = \frac{C_n^0 + C_p^0}{1 + \frac{C_n^0}{C_p^-} + \frac{C_p^0}{C_n^+}}$$

$H_i$  surface-trapping substantially modifies these capture kinetics. Surface  $H_i$  exhibit larger lattice relaxation  $\Delta Q = 34.3 \text{ \AA amu}^{1/2}$  (see Fig. 4d and e), yielding softer PESs and lower capture barriers for both electrons and holes. For the (0/−) transition level, the electron capture barrier ( $\Delta E_n^0$ ) decreases from 0.09 eV (bulk  $H_i$ ) to 0.03 eV (surface  $H_i$ ), while the hole capture barrier ( $\Delta E_p^-$ ) drops from 0.24 eV (bulk  $H_i$ ) to 0.17 eV (surface  $H_i$ ). These reduced energy barriers lead to a rise in both  $C_n^0$  (up to  $7.0 \times 10^{-5} \text{ cm}^3 \text{ s}^{-1}$ ) and  $C_p^-$  (up to  $1.8 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ ) by over one order of magnitude, see Fig. 4f. The overall  $C_{\text{tot}}$  remained limited by the slower hole capture process of  $H_i^-$ , yielding  $C_{\text{tot}} = 1.8 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  at 300 K, approximately an order of magnitude higher than that in bulk ( $1.9 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ ).

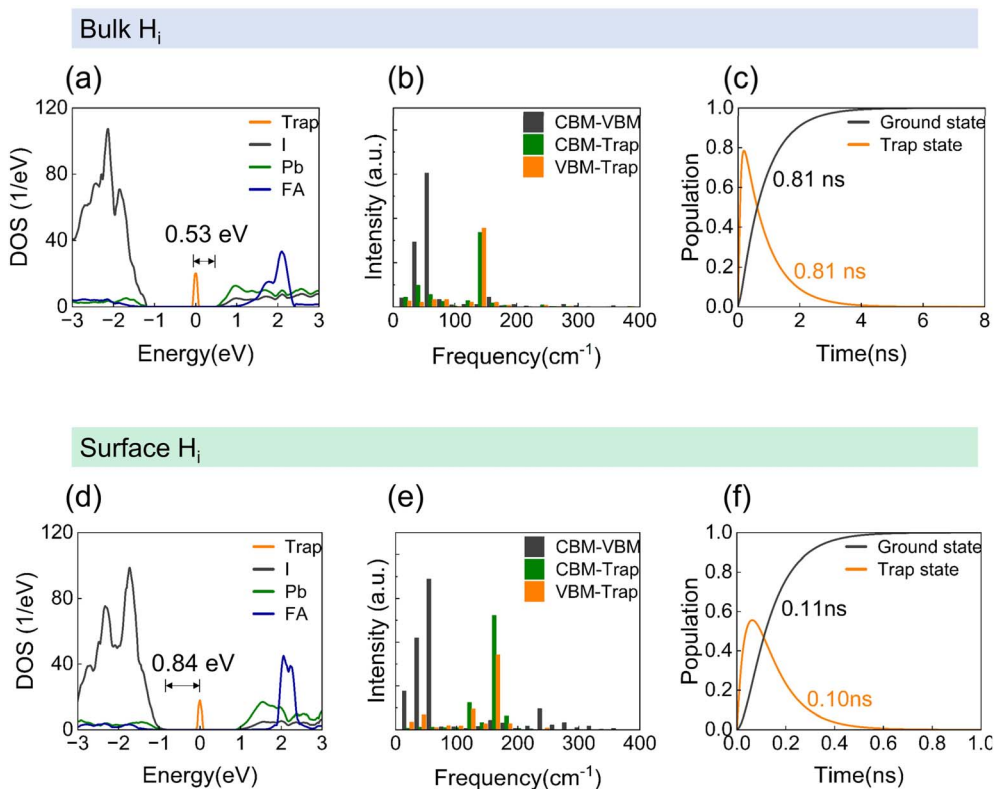
### Nonadiabatic dynamics of $H_i$ recombination

To elucidate the real-time carrier recombination dynamics mediated by  $H_i$ , we performed nonadiabatic molecular dynamics (NAMD) simulations. This approach couples electronic transitions with atomic motions, capturing the ultrafast timescales and mechanisms of defect-assisted nonradiative

recombination that extend beyond static multi-phonon emission models.<sup>28,29</sup>

Our electronic structure results revealed that among three charged states of  $H_i$  ( $H_i^+$ ,  $H_i^0$ ,  $H_i^-$ ), only the neutral  $H_i^0$  introduces a persistent deep-level defect state within the bandgap. While  $H_i^+$  has a negligible influence on the band edges, and  $H_i^-$  forms only shallow defect states level 0.16 eV away from the band edge (Fig. S1 and S2 in SI),  $H_i^0$  creates a localized state that acts as a recombination center. Notably, this defect level deepens from being 0.53 eV away from the band edge in the bulk to 0.84 eV at the surface. Therefore,  $H_i^0$  was considered as the dominant recombination active species and all subsequent NAMD analysis focused on its behavior. The charge densities of the defect states for both bulk  $H_i$  and surface  $H_i$  were provided in Fig. S3 of SI.

To explore the phonon-driven recombination mechanism, we calculated the spectral density *via* Fourier transform of the fluctuations in the energy gaps between relevant states, including CBM-VBM, CBM-Trap, VBM-Trap (see Fig. 5b and e). Each peak in the spectral density characterizes the strength of electron-phonon coupling for a specific phonon mode. The results indicated that the CBM-VBM energy gap coupling is dominated by low-frequency phonon modes (below  $100 \text{ cm}^{-1}$ ), which are associated with Pb-I lattice bending and stretching.<sup>30,31</sup> In contrast, the energy gaps involving the  $H_i^0$  trap state (CBM-Trap and VBM-Trap) are significantly modulated by



**Fig. 5** (a) Projected density of states (PDOS) of bulk  $H_i$ . (b) Spectra density for bulk  $H_i$ , obtained from Fourier transform of the auto-correlation functions for the CBM-VBM, CBM-trap, and VBM-trap transitions. (c) Nonradiative electron-hole recombination dynamics for bulk  $H_i$ . (d) PDOS of surface  $H_i$ . (e) Spectra density for surface  $H_i$ , obtained from Fourier transform of the auto-correlation functions for CBM-VBM, CBM-trap, VBM-trap transitions. (f) Nonradiative electron-hole recombination dynamics for surface  $H_i$ .



higher-frequency modes (100–300  $\text{cm}^{-1}$ ) originating from the vibrations and torsions of organic FA molecules.<sup>30</sup> This suggests that organic cation dynamics play an indirect but crucial role in the nonradiative recombination process mediated by  $\text{H}_i^0$ .

Although  $\text{H}_i^0$  defect couples to similar phonon modes in both bulk and surface environments, the coupling intensity is stronger at the surface. This enhancement arises from under-coordinated surface iodide ions and increased rotational freedom of FA cations near the surface. These stronger vibronic interactions also accelerated electronic decoherence, as confirmed by the dephasing functions obtained from the second-order cumulant expansion of the energy gaps correlation functions (see Fig. S4 in SI).<sup>32,33</sup> Our calculated decoherence times for the bulk are 9.9 fs (CBM-VBM), 3.5 fs (CBM-Trap), and 3.8 fs (VBM-Trap), consistent with previous reports.<sup>34–36</sup> Surface  $\text{H}_i^0$  exhibited even shorter decoherence times of 4.7 fs (CBM-VBM), 2.3 fs (CBM-Trap), and 2.4 fs (VBM-Trap), reflecting the stronger dynamic disorder at the surface. Although faster decoherence can, in principle, slow down the recombination rates, our findings indicated recombination is significantly accelerated at the surface. This implies that decoherence is not the rate-limiting factor here, prompting the following investigation into the non-adiabatic couplings (NAC).

We therefore quantified the NAC strength,  $\langle \varphi_i | \nabla_{\mathbf{R}} | \varphi_f \rangle$ , which governs the probability of electronic transitions and is correlated with the wavefunction overlap between initial ( $\varphi_i$ ) and final ( $\varphi_f$ ) states. The results were summarized in Table 1 and S1. In the bulk, the CBM-to-VBM NAC was negligible (0.3 meV), leading to a very slow band-to-band recombination rate (0.008  $\text{ns}^{-1}$ ). In contrast, NAC value between the  $\text{H}_i^0$  trap state and the band edges was substantially larger (2.5 meV for CBM-Trap and 0.8 meV for VBM-Trap), resulting in much faster defect-assisted trapping rates of 15.8  $\text{ns}^{-1}$  (electron capture) and 1.2  $\text{ns}^{-1}$  (hole capture).

Critically, at the surface, the defect-mediated NACs increased to 1.9 meV (CBM-trap) and 2.9 meV (VBM-trap), while CBM-VBM coupling remained weak (0.2 meV). This enhancement, driven by the increased lattice distortion and wavefunction localization at the surface, resulted in electron and hole capture rates of 9.4  $\text{ns}^{-1}$  and 25.4  $\text{ns}^{-1}$ , respectively. Since the slower carrier capture process dictates the overall recombination rate, the surface recombination rate (9.4  $\text{ns}^{-1}$ ) is nearly an order of magnitude faster than that (1.2  $\text{ns}^{-1}$ ) in the bulk. These results indicated that  $\text{H}_i$ -induced severe nonradiative recombination at the surface is dominated by enhanced non-adiabatic coupling rather than quantum decoherence effects.

Finally, by integrating the effects of lattice vibration, quantum decoherence, and non-adiabatic coupling effects, we performed

NAMD simulations to track the recombination kinetics, see Fig. 5c and f. For bulk  $\text{H}_i$ , approximately 80% of electrons in the CBM were captured by the trap state within tens of picoseconds, followed by recombination with holes in the VBM yielding an overall carrier lifetime of 0.8 ns. In contrast, for surface-accumulated  $\text{H}_i$ , an ultrafast hole capture process was followed by rapid recombination with CBM electrons, drastically shortening the carrier lifetime to 0.1 ns. This order-of-magnitude acceleration in recombination at the surface confirms that surface  $\text{H}_i$  acts as a detrimental nonradiative recombination center.

## Conclusion

In summary, this work reveals that hydrogen interstitials ( $\text{H}_i$ ) in FAPbI<sub>3</sub> perovskite solar cells (PSCs) exhibit intrinsic dynamic instability within the bulk lattice, driving spontaneous migration to surface sites, where they achieve thermodynamic stabilization. The surface-accumulated  $\text{H}_i$  undergoes significant lattice reorganization, forming deep-level defect states that substantially enhance nonradiative recombination. Compared to bulk-positioned  $\text{H}_i$ , surface-accumulated  $\text{H}_i$  exhibits reduced electron capture barrier ( $\Delta E_n$  from 0.09 eV to 0.03 eV) and hole capture barrier ( $\Delta E_p$  from 0.24 eV to 0.17 eV), alongside an order of magnitude increase in carrier capture coefficients (from  $10^{-8} \text{ cm}^3 \text{ s}^{-1}$  to  $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ ). This leads to a drastic reduction in carrier lifetime from 0.8 ns to 0.1 ns. The accelerated recombination kinetics at the surface are primarily driven by strengthened vibronic interactions and strong nonadiabatic couplings. These findings establish surface-accumulated  $\text{H}_i$ , rather than conventional bulk  $\text{H}_i$ , as the dominant nonradiative recombination center in PSCs. This work underscores the importance of interfacial hydrogen management for suppressing nonradiative losses and provides a fundamental basis for designing advanced passivation strategies to overcome efficiency limitations in PSCs.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: detailed computational methods, figures, kinetic equations, and table. See DOI: <https://doi.org/10.1039/d6el00027d>.

## Acknowledgements

This work was financially supported by Beijing Natural Science Foundation (BNSF, Grants JQ23020), and Natural Science Foundation of China (NSFC, Grants 62034001, 62474013, and 22033006).

## References

- H. Wang, Y. Ge, W. Shao, X. Xiong, G. Li, N. Li, X. Hu, G. Chen, K. Dong, W. Ai, Z. Yu, Z. Zheng, C. Wang, F. Yao,

**Table 1** Non-adiabatic (NA) couplings, dephasing times, and trapping rates for bulk  $\text{H}_i$  and surface  $\text{H}_i$

		NA coupling (meV)	Dephasing (fs)	Rate ( $\text{ns}^{-1}$ )
Bulk $\text{H}_i$	CBM-trap	2.5	3.5	15.8
	VBM-trap	0.8	3.8	1.2
Surface $\text{H}_i$	CBM-trap	1.9	2.3	9.4
	VBM-trap	2.9	2.4	25.4



- X. Cao, S. Li, J. Zhao, W. Ke, C. Tao, Y. Hou, A. Petrozza and G. Fang, Yttrium oxide engineered substrate enables improved durability for perovskite solar cells, *Nat. Commun.*, 2025, **16**, 9508.
- 2 Y. Liang, G. Chen, Y. Wang, Y. Zou, M. Feng, Y. Wang, B. Li, Y. Cho, Y. Chang, T. Liu, T. Zhang, Y. Lou, R. Xu, L. Lu, N. Zhang, K. Meng, C. Zhu, C. Ouyang, Y. Miao, Y. Guo, Y. Chen and Y. Zhao, A matrix-confined molecular layer for perovskite photovoltaic modules, *Nature*, 2025, **648**, 91–96.
- 3 Y. Yang, H. Chen, C. Liu, J. Xu, C. Huang, C. D. Malliakas, H. Wan, A. S. R. Bati, Z. Wang, R. P. Reynolds, I. W. Gilley, S. Kitade, T. E. Wiggins, S. Zeiske, S. Suragtkhuu, M. Batmunkh, L. X. Chen, B. Chen, M. G. Kanatzidis and E. H. Sargent, Amidination of ligands for chemical and field-effect passivation stabilizes perovskite solar cells, *Science*, 2024, **386**, 898–902.
- 4 W. Shockley and H. J. Queisser, Detailed balance limit of efficiency of p–n junction solar cells, *J. Appl. Phys.*, 1961, **32**, 510–519.
- 5 W.-J. Yin, T. Shi and Y. Yan, Unusual defect physics in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite solar cell absorber, *Appl. Phys. Lett.*, 2014, 104.
- 6 D. J. Keeble, J. Wiktor, S. K. Pathak, L. J. Phillips, M. Dickmann, K. Durose, H. J. Snaith and W. Egger, Identification of lead vacancy defects in lead halide perovskites, *Nat. Commun.*, 2021, **12**, 5566.
- 7 W. Jia, R. Sun, J. Qiao, G. Shi, Q. Zhao, Z. Gong, S. Zheng, R. Xu, J. Shang, L. Song, K. Wang, W. Huang, R. Chen, Y. Fang, H. Wang and Z.-Q. Rong, Molecular design-driven interface engineering enabling simultaneous defect passivation and enhanced hole extraction in perovskite solar cells, *Angew. Chem., Int. Ed.*, 2025, **137**, e202513869.
- 8 N. Xu, X. Qi, Z. Shen, L. Hu, J. Lv, Y. Zhong, B. Wang and Z. Zou, Point defects in metal halide perovskites, *Nat. Rev. Phys.*, 2025, **7**, 554–564.
- 9 X. Zhang, J.-X. Shen, M. E. Turiansky and C. G. Van de Walle, Minimizing hydrogen vacancies to enable highly efficient hybrid perovskites, *Nat. Mater.*, 2021, **20**, 971–976.
- 10 Y. Liang, X. Cui, F. Li, C. Stampfl, S. P. Ringer, J. Huang and R. Zheng, Minimizing and controlling hydrogen for highly efficient formamidinium lead triiodide solar cells, *J. Am. Chem. Soc.*, 2022, **144**, 6770–6778.
- 11 W. Zhou, R. Zhou, X. Chen, Z. Zhou, Y. He, C. Qian, H. Yan, Z. Zheng, Y. Zhang and H. Yan, Synergy between dynamic behavior of hydrogen defects and non-radiative recombination in metal-halide perovskites, *Small*, 2024, **20**, 2405201.
- 12 W. Zhou, X. Yang, R. Zhou, H. Huang, Y. He, X. Chen, C. Qian, Z. Zheng and H. Yan, Impact of hydrogen vacancies on non-radiative recombination in metal-halide perovskites, *Angew. Chem.*, 2025, **137**, e202503394.
- 13 X. Tian, A. S. Vasenko, E. V. Chulkov and R. Long, Anharmonic motion-induced self-passivation of hydrogen defects in hybrid organic–inorganic perovskites: Ab initio quantum dynamics, *J. Phys. Chem. Lett.*, 2025, **16**, 10466–10472.
- 14 D. A. Egger, L. Kronik and A. M. Rappe, Theory of hydrogen migration in organic-inorganic halide perovskites, *Angew. Chem., Int. Ed.*, 2015, **54**, 12437–12441.
- 15 Y.-F. Chen, Y.-T. Tsai, L. Hirsch and D. M. Bassani, Kinetic isotope effects provide experimental evidence for proton tunneling in methylammonium lead triiodide perovskites, *J. Am. Chem. Soc.*, 2017, **139**, 16359–16364.
- 16 Y. Feng, Y. Zhao, W.-K. Zhou, Q. Li, W. A. Saidi, Q. Zhao and X.-Z. Li, Proton migration in hybrid lead iodide perovskites: From classical hopping to deep quantum tunneling, *J. Phys. Chem. Lett.*, 2018, **9**, 6536–6543.
- 17 M. Li, D.-G. Xie, E. Ma, J. Li, X.-X. Zhang and Z.-W. Shan, Effect of hydrogen on the integrity of aluminium-oxide interface at elevated temperatures, *Nat. Commun.*, 2017, **8**, 14564.
- 18 D. R. Ceratti, A. Zohar, R. Kozlov, H. Dong, G. Uraltsev, O. Girshevitz, I. Pinkas, L. Avram, G. Hodes and D. Cahen, Eppur si muove: Proton diffusion in halide perovskite single crystals, *Adv. Mater.*, 2020, **32**, 2002467.
- 19 S. Sadhu, T. Buffeteau, S. Sandrez, L. Hirsch and D. M. Bassani, Observing the migration of hydrogen species in hybrid perovskite materials through d/h isotope exchange, *J. Am. Chem. Soc.*, 2020, **142**, 10431–10437.
- 20 Y. Liang, X. Cui, F. Li, C. Stampfl, J. Huang, S. P. Ringer and R. Zheng, Hydrogen-anion-induced carrier recombination in  $\text{MAPbI}_3$  perovskite solar cells, *J. Phys. Chem. Lett.*, 2021, **12**, 10677–10683.
- 21 X. Ma, Z. Liu, W.-H. Fang, R. Long and O. V. Prezhdo, Passivation of hydrogen interstitials in metal halide perovskites: A time-domain ab initio study, *J. Am. Chem. Soc.*, 2025, **147**, 25960–25968.
- 22 W. Cai, Y. Wang, W. Shang, J. Liu, M. Wang, Q. Dong, Y. Han, W. Li, H. Ma and P. Wang, Lewis base governing superficial proton behavior of hybrid perovskite: Basicity dependent passivation strategy, *Chem. Eng. J.*, 2022, **446**, 137033.
- 23 P. Zhang, E. Stippell, Y. Chen, X. Du, Z. Hou, O. V. Prezhdo and W. Li, Atomistic mechanism of defect self-passivation in metal halide perovskites, *Nano Lett.*, 2025, **25**, 14140–14146.
- 24 J. Wang and W.-J. Yin, Revisiting the iodine vacancy surface defects to rationalize passivation strategies in perovskite solar cells, *J. Phys. Chem. Lett.*, 2022, **13**, 6694–6700.
- 25 N. T. Bagraev and V. A. Mashkov, A mechanism for two-electron capture at deep level defects in semiconductors, *Solid State Commun.*, 1988, **65**, 1111–1117.
- 26 A. Alkauskas, Q. Yan and C. G. Van de Walle, First-principles theory of nonradiative carrier capture via multiphonon emission, *Phys. Rev. B Condens. Matter*, 2014, **90**, 075202.
- 27 A. Alkauskas, C. E. Dreyer, J. L. Lyons and C. G. Van de Walle, Role of excited states in shockley-read-hall recombination in wide-band-gap semiconductors, *Phys. Rev. B*, 2016, **93**, 201304.
- 28 M. E. Turiansky, A. Alkauskas, M. Engel, G. Kresse, D. Wickramaratne, J.-X. Shen, C. E. Dreyer and C. G. Van de Walle, Nonrad: Computing nonradiative capture coefficients from first principles, *Comput. Phys. Commun.*, 2021, **267**, 108056.



- 29 A. Alkauskas, Q. Yan and C. G. Van de Walle, First-principles theory of nonradiative carrier capture via multiphonon emission, *Phys. Rev. B*, 2014, **90**, 075202.
- 30 C. Quarti, G. Grancini, E. Mosconi, P. Bruno, J. M. Ball, M. M. Lee, H. J. Snaith, A. Petrozza and F. De Angelis, The raman spectrum of the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  hybrid perovskite: Interplay of theory and experiment, *J. Phys. Chem. Lett.*, 2013, **5**, 279–284.
- 31 A. M. A. Leguy, A. R. Goñi, J. M. Frost, J. Skelton, F. Brivio, X. Rodríguez-Martínez, O. J. Weber, A. Pallipurath, M. I. Alonso and M. Campoy-Quiles, Dynamic disorder, phonon lifetimes, and the assignment of modes to the vibrational spectra of methylammonium lead halide perovskites, *Phys. Chem. Chem. Phys.*, 2016, **18**, 27051–27066.
- 32 S. Mukamel, *Principles of Nonlinear Optical Spectroscopy*, New York: Oxford university press, 1995, **6**, 543.
- 33 J. Liu, S. V. Kilina, S. Tretiak and O. V. Prezhdo, Ligands slow down pure-dephasing in semiconductor quantum dots, *ACS Nano*, 2015, **9**, 9106–9116.
- 34 G. Alkhalifah, B. Wang, O. V. Prezhdo and W.-L. Chan, Suppressing polaronic defect–photocarrier interaction in halide perovskites by pre-distorting its lattice, *J. Am. Chem. Soc.*, 2025, **147**, 2411–2420.
- 35 X. Ma, X. Tian, E. Stippell, O. V. Prezhdo, R. Long and W.-H. Fang, Self-passivation of halide interstitial defects by organic cations in hybrid lead-halide perovskites: Ab initio quantum dynamics, *J. Am. Chem. Soc.*, 2024, **146**, 29255–29265.
- 36 Z. Zhou, Y. Wu, J. He, T. Frauenheim and O. V. Prezhdo, Enhancing extraction and suppressing cooling of hot electrons in lead halide perovskites by dipolar surface passivation, *J. Am. Chem. Soc.*, 2024, **146**, 29905–29912.

