Coexisting superconductivity and charge-density wave in hydrogen-doped titanium diselenide via ionic liquid gating-induced protonation

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The doping of correlated materials with various atomic and molecular species is a staple in the tuning and understanding of their electronic ground states and in the engineering of exotic quantum phenomena. In particular, the recent discovery of near-to-room temperature superconductivity in hydrides under pressure has highlighted the potential of hydrogen as a dopant and to tune the electronic and the phononic spectra of a material. Here, we demonstrate the non-volatile control of the electronic ground state of octahedral titanium diselenide (1T-TiSe2) by means of electric field-driven hydrogen intercalation via the ionic liquid gating method. We show that in HxTiSe2 charge-density waves and superconductivity coexist through most of the phase diagram, with nearly doping-independent transition temperatures. The superconducting phase of HxTiSe2 is gapless-like and possibly multi-band in nature, setting it apart from what observed in TiSe2 via electrostatic gating and copper- or lithium- intercalation. The uniqueness of hydrogen doping is supported by ab initio calculations showing that its impact is not limited to a rigid electron doping of pristine TiSe2, but it can attain a full reconstruction of the band structure. These findings open a new route towards high-temperature superconductivity in hydrogen-rich layered compounds at ambient pressure.

The recent observation of near-to-room-temperature superconductivity in hydrides under high pressure [1, 2] has demonstrated that a superconducting (SC) state with remarkably high critical temperature not necessarily requires an unconventional electron-electron coupling mechanism. The key requirements here are high phonon frequencies, such as those associated to the hydrogen (H) vibration modes, a strong coupling of these modes to the electronic states at the Fermi level, and a non-conventional structural environment (in the specific case, stabilized by pressure) that favours such a coupling. These same ingredients can be used to design new superconducting materials at ambient pressure, with properties of interest for applications even though at lower temperatures.

One of the routes to create H-rich materials is ionic liquid gating-induced protonation. As this technique makes it possible to insert H atoms in crystallographic positions unattainable by a conventional synthesis approach, it has found notable applications in oxides [3–8], demonstrating a great potential in layered materials as well [9, 10].

Among the layered materials, transition metal dichalcogenides (TMDs) are particularly interesting because, despite structural simplicity, they exhibit a variety of quantum phases [11, 12] – charge-density wave (CDW), ferromagnetism, Mott insulating state, etc. – that may be tuned by protonation. In some cases, TMDs display a topological order, hence, once made superconducting, they may host Majorana fermions [13, 14]. TMDs are also easy to handle and can be used to fabricate electronic devices [15–17], even printed ones [18, 19]. Hence, by tailoring their physical properties, one can realize good and affordable prototypes for various quantum-technology applications, superconducting electronics, or quantum computing [20]. In this context, the archetypal TMD semimetallic titanium diselenide (1T-TiSe2) is an ideal candidate to benchmark the ionic-gating-induced protonation technique, since it exhibits strong electron-electron correlations and a variety of intriguing quantum phases [15], akin to those found in other layered materials such as iron-based compounds [21, 22], cuprates [23], and heavy-fermion systems [24]. Furthermore, the electronic ground state of 1T-TiSe2 is readily tunable by a variety of different methods, including chemical intercalation [25–27], applied pressure [28], and electrostatic gating [29, 30].

In this work, we establish ionic liquid gating-induced protonation as a powerful and unique doping technique to control the electronic ground state of layered TMDs by demonstrating a robust and non-volatile control over CDW and SC in 1T-TiSe2. These two quantum phases dominate the phase diagram of 1T-TiSe2 and are found to coexist across all the investigated H doping levels. Fully protonated HxTiSe2 samples exhibit an impressive doping level (x ≈ 2), with negligible structural alterations, vestigial CDW signatures, and robust bulk superconductivity with multi-band and gapless features revealed by different experimental techniques. Our calculations indicate that these peculiarities of protonated
TiSe₂ are caused by the unique capability of H atoms to act not only as pure electron donors since, at sufficiently large H concentrations, they fill the TM-d bands and allow the band structure of 1T-TiSe₂ to mimic that of other archetypal TMD compounds, such as the superconducting 2H-NbSe₂ or the semiconducting 2H-MoS₂. Our results establish a new route for the search of high-temperature superconductivity in layered compounds at ambient pressure.

**RESULTS**

**Electric field-driven hydrogen intercalation.** We control the H loading in our 1T-TiSe₂ samples via the ionic liquid protonation-induced gating method [3, 5, 9, 31], as depicted in Fig. 1a. When the gate voltage V₉ is swept in ambient conditions above a threshold voltage, the intense electric field at the TiSe₂/electrolyte interface splits the water molecules absorbed in the ionic liquid and drives the H⁺ ions into the van der Waal gap of the TiSe₂ crystal. H incorporation in the TiSe₂ lattice is confirmed by nuclear magnetic resonance (NMR) and muon spin rotation (µSR) measurements as discussed later, whereas significant intercalation by the organic ions of the ionic liquid is ruled out via X-ray photoelectron spectroscopy (XPS; see Supplementary Section II). In-situ monitoring of the room-temperature TiSe₂ resistivity during gating (Methods) shows that ρ(300K) remains unaffected by the applied V₉ below the threshold for H intercalation, then rapidly decreases and reaches a minimum (Fig. 1b). Maintaining V₉ = 3 V beyond this point leads to ρ(300K) gradually increasing again over time, eventually reaching a plateau for gating times in excess of ~45 min and up to several days.

This gate-induced change in the electric transport properties is non-volatile. Indeed, as shown in Fig. 1c, ex-situ measurements on samples gated for a fixed amount of time and then removed from the electrochemical cell give values of ρ(300K) that closely follow those determined in situ. Notably, the saturation of ρ(300K) for large gating times suggests that most of the H dopants are driven into the sample in the first few tens of minutes, and further increasing the gating time does not alter the stoichiometry appreciably. This picture is confirmed by assessing the changes to the structural and electronic properties of the protonated samples.

Low-temperature Hall effect measurements (Methods) show an increase in the Hall density nH at T = 4.2 K by more than an order of magnitude, going from ~4·10¹⁹ cm⁻³⁻¹ in pristine TiSe₂ to ~5·10²⁰ cm⁻³⁻¹ in H₂TiSe₂ (Fig. 1d), indicating that H loading introduces a strong electron doping in the protonated TiSe₂ samples. At the same time, a room-temperature X-ray diffraction (XRD) analysis (Fig. 1e) shows that the H loading does not alter the 1T lattice structure of the pristine material, and simply expands the unit cell by up to ~0.9%. Interestingly, the lattice expansion is comparable to that driven by incorporation of Cu atoms in SC Cu₃TiSe₂ (~0.6%) [25] and much smaller than the one reported upon lithiation in SC Li₄TiSe₂ (~12%) [32]. The pronounced broadening of the XRD peaks however indicates that the protonation introduces a large degree of structural disorder in the samples, which may be partially responsible for the reentrant behaviour of ρ(300K) upon gating times in excess of those associated to the local minimum shown in Fig. 1b,c.

Again, both the structural and the electronic modifications to the TiSe₂ crystals occur within the first ~45 min of gating time, confirming the behaviour showcased by the room-temperature resistivity.

The dramatic effect of the protonation on the electric transport properties of TiSe₂ is even more evident when these are measured as a function of temperature. Fig. 1f shows the temperature dependence of the normalized resistivity ρ(T)/ρ(300K) of TiSe₂ crystals gated for different amounts of time (Methods). Pristine crystals exhibit a strongly non-monotonic ρ(T) dependence with a broad peak around ~160 K and no sign of a SC transition. This peak is typical of 1T-TiSe₂ and is caused by the reconstruction of the electronic bandstructure upon the onset of CDW order, which shifts the Fermi level and partially gaps the Fermi surface [25, 26, 29, 33, 34]. A small gating time of ~5 min strongly suppresses the intensity of this CDW peak and leads to the appearance of SC with an onset transition temperature T_c on ≃ 3.3 K. Larger gating times up to ~45 min lead to a further reduction in the intensity of the CDW peak and simultaneously slightly increase T_c on to ~3.7 K (with no clear dependence, see inset to Fig. 1f). Also here, gating times in excess of ~45 min lead to a clusterization of the ρ(T) curves around a common behaviour, characterized by a complete SC transition with T_c on ≃ 3.7 K and a faint trace of CDW order in the form of a slope change below ~200 K.

The number of intercalated protons in HₓTiSe₂ samples pertaining to this state of clustered ρ(T), nₓ and cell volume is quantified by means of ¹H-NMR (Methods and Supplementary Section II). In particular, the decay of the spin-echo amplitude is measured both in a collection of fully-doped TiSe₂ crystals and in a reference sample of hexamethylbenzene (C₁₂H₁₈). A comparison between the signal amplitudes for the two samples allows to estimate that the intercalated TiSe₂ crystals contain an average number x = 2.0 ± 0.3 of protons per TiSe₂ formula unit.

H loading also affects the vibrational properties of TiSe₂, as demonstrated by room-temperature Raman spectroscopy on freshly-cleaved surfaces (Fig. 1g; see Methods). Spectra acquired on pristine TiSe₂ exhibit the two main Raman modes of 1T-TiSe₂, the E₂ mode at ~138 cm⁻¹ and the A₁g mode at ~202 cm⁻¹, consistent with the literature [35–39], and no additional peaks. In spectra acquired on HₓTiSe₂, the same E₂ and the A₁g peaks are redshifted to ~136 cm⁻¹ and ~199 cm⁻¹ respectively. Two additional, broader peaks emerge in HₓTiSe₂ at ~156 cm⁻¹ and ~260 cm⁻¹, which could be ascribed to intercalant-activated two-phonon processes at the L and/or M points [36–38, 40]. Indeed, the appearance of these peaks can be justified on the basis of first-principles calculations (see Supplementary Section VI) by the removal of symmetry of the 1T-TiSe₂ system resulting from the incorporation of H atoms.

**Charge density waves in HₓTiSe₂.** The evolution of the
CDW order with increasing gating time $t$ can be more accurately tracked by considering its onset temperature, $T_{CDW}$, and the intensity of the CDW peak, $I_{CDW}$. The former can be identified with the position of the inflection point in the $\rho(T)$ curves [29, 32, 41], that corresponds to the minimum in $d\rho/dT$. As shown in Fig. 2a, which displays $d\rho/dT$ as a function of $T$ for increasing gating time, the visibility of the local minimum is suppressed by increasing gating time, but its position remains basically unchanged and close to its pristine value $T_{CDW} \approx 198$ K. The intensity can be evaluated as $I_{CDW} = A_{CDW}(t)/A_{CDW}(0)$, where $A_{CDW}(t)$ is the area contained between each normalized $\rho(T)$ curve (shown in Fig. 1f) and a line connecting its two values at 50 and 250 K [32], as exemplified in Fig. 2d. The trends of $T_{CDW}$ and $I_{CDW}$ as a function of gating time are summarized in Fig. 2b (red hexagons and black diamonds, respectively). Clearly, while $T_{CDW}$ is almost constant, $I_{CDW}$ is rapidly suppressed upon increasing gating time, and becomes of the order of 1% of its pristine value in $H_2TiSe_2$ samples. Notably, this behaviour is similar to that reported in $Li_xTiSe_2$ crystals [32], but differs from that of $Cu_xTiSe_2$ [25, 42], $Ti_{1+x}Se_2$ [41], electrostatically ion-gated $TiSe_2$ [29], and $TiSe_2$ under pressure [28], where the suppression of $I_{CDW}$ was accompanied by a decrease of $T_{CDW}$. The insensitivity of $T_{CDW}$ to increasing doping was interpreted, in the case of $Li_xTiSe_2$, as a lack of full in-plane percolation of the dopants, leading to a spatial separation between SC Li-rich regions and CDW-ordered pristine regions [32]. However, such an explanation might be too simplistic, since it is not straightforward that the presence of dopants destroys the CDW order. For example, scanning tunnelling microscopy measurements in $Cu_xTiSe_2$ indicate that CDW order robustly survives even in Cu-rich areas [43, 44].

The temperature dependence of the Hall coefficient $R_H$ (Methods and Supplementary Section III) suggests that also in $H_2TiSe_2$ CDW order could survive in dopant-rich areas, as shown in Fig. 2d,e. In agreement with the established literature [29, 32], pristine $TiSe_2$ exhibits both a strong CDW peak in $\rho(T)$ (black curve in Fig. 2d, $I_{CDW} \approx 0.9$) and a change of sign in $R_H$ around $T \approx 215$ K (black curve in Fig. 2e).
occurs when the onset of CDW order opens a gap at the Fermi level in part of the bandstructure, causing a reconstruction in the Fermi surface [29, 32]. An intermediate H doping (blue curve in Fig. 2d,e) suppresses the CDW peak in $\rho(T)$ ($I_{CDW} \approx 0.13$) and strongly reduces the absolute value of $R_{H}$, but a sign change is still clearly present at $T \approx 225$ K, indicating that the Fermi surface still undergoes a reconstruction. H$_2$TiSe$_2$ alone (red curve in Fig. 2d,e) exhibits no sign change in $R_{H}$ up to $\sim 300$ K, and a CDW peak in $\rho(T)$ reduced to a slope change ($I_{CDW} \approx 0.016$). This could indicate that the CDW gap still opens around $\sim 200$ K in H$_2$TiSe$_2$, but it is shifted below the Fermi level by the increasing electron doping, similar to the case of Cu$_x$TiSe$_2$ [43, 44].

Notably, strong indications of a reconstruction of the Fermi surface around $T \sim 200$ K are also observed in the spin-lattice relaxation rate $T_1^{-1}$ for the $^1$H-NMR of H$_2$TiSe$_2$ samples at $\mu_B H \approx 3.5$ T with $H$ parallel to the $ab$ plane (Methods). The inset to Fig. 2c shows that, for $T \lesssim 170$ K, $T_1^{-1}$ exhibits a linear dependence on $T$ consistent with the so-called Korringa behaviour proper of relaxation processes mediated by itinerant electrons in a metallic matrix [45]. This is in agreement with our $\rho(T)$ measurements and with the results of $^{77}$Se-NMR measurements of $^{77}$Se-enriched TiSe$_2$ and of $^{63}$Cu- and $^{77}$Se-NMR measurements of Cu-intercalated TiSe$_2$ [46, 47]. Higher temperatures $T \gtrsim 170$ K mark a clear departure from the Korringa-like trend. In particular, a plateau of $T_1^{-1}$ between $170$ K and $210$ K is followed by a progressive decrease of the density of states at the Fermi energy and of a crossover to a semimetallic behaviour. The crossover between the two different behaviours is even clearer in the $T$ dependence of $(T/I)$ (main panel of Fig. 2c).

**Superconductivity in H$_x$TiSe$_2$.** The evolution of the SC phase in H$_x$TiSe$_2$ appears completely unaffected by the presence of CDW order, as summarized by the values of $T_c$ as a function of gating time (blue circles in Fig. 2b). Notably, a complete SC transition with a sizeable $T_c^{on} \sim 3.7$ K is observed not only in the fully-doped H$_2$TiSe$_2$, where no Fermi-surface reconstruction occurs, but also in the partially-doped H$_x$TiSe$_2$, where the Fermi surface becomes again partially gapped (see inset in Fig. 1f). In a magnetic field $\mu_B H$ perpendicular to the $ab$ plane of the H$_x$TiSe$_2$ crystal (Fig. 3a and
Supplementary Section IV; see Methods) the SC transition broadens and shifts to lower $T$. At 2 K, a well-defined zero-resistance state (ZRS) is observed at least up to $\mu_0 H = 30 \text{ mT}$ and the intermediate dissipative regime exhibits the typical behaviour of a thermally-activated flux flow (TAFF), $\rho(T, H) = \rho_0 \exp[-U(H)/k_B T]$, at any $T$ and $H$. This is clear from Fig. 3b, where $\rho/\rho_0$ is plotted in logarithmic scale against $T^{-1}$. The activation barrier for vortex motion, obtained from these curves, scales logarithmically with increasing magnetic field, $U(H) = U_0 \ln(B_0/\mu_0 H)$ (right panel in Fig. 3b), indicating a collective flux creeping [48]. A fit to the $U(H)$ data gives $U_0 \approx 8.9 \text{ meV}$ and $B_0 \approx 0.39 T$, comparable to the values found in ion-gated TiSe$_2$ [30]. Notably, this direct transition from ZRS to TAFF is analogous to that found in overdoped Li$_x$TiSe$_2$ [32] and Cu$_x$TiSe$_2$ [25], and provides no evidence of the anomalous quantum metallic behavior that was claimed to destroy the ZRS at arbitrarily small magnetic fields in ion-gated TiSe$_2$ [30] and in under- and optimally-doped Li$_x$TiSe$_2$ [32].

Fig. 3c shows the $T$-dependence of the zero-field cooled (ZFC) magnetic moment $m(T)$ measured below $\sim 5 \text{ K}$ at $\mu_0 H = 1 \text{ mT}$ (Methods). A rather sharp transition is observed at $T_c = 3.6 \pm 0.1 \text{ K}$, in reasonable agreement with the $T_c$ value determined by transport measurements. As expected for the Meissner state, the isothermal $m(H)$, measured at $T = 2 \text{ K}$ following a ZFC procedure, decreases linearly with increasing $H$, up to $1.3 \pm 0.3 \text{ mT}$ (Fig. 3d). Above this field, $m(H)$ starts deviating from a linear dependence, thus defining the lower critical field $H_{c1}(2 \text{ K})$. Upon further increasing $H$, $m(H)$ first reaches a minimum at $\approx 5.8 \text{ mT}$ and then it decreases in modulus, returning to zero at the upper critical field, in good agreement with the $H_{c2}(T)$ value determined from transport measurements (where we use the criterion of 95% normal-state resistivity).

By combining the resistivity- and magnetization measurements, we can construct the SC $T-H$ phase diagram of H$_x$TiSe$_2$ shown in Fig. 3e. The Meissner state exists for magnetic fields $H \leq H_{c1}$, above which SC vortices penetrate the sample volume and move in the TAFF regime until $H = H_{c2}$, here defined as the field where $\rho$ reaches 95% of its normal-state value. Interestingly, $H_{c2}(T)$ shows a prominent kink around $\approx 0.85 T_c$, where its slope changes abruptly.

![Graphs and plots](image-url)
FIG. 4. Muon spin rotation in superconducting H$_2$TiSe$_2$. a,b, Zero-field cooling transverse-field muon-spin polarization $P_{\perp}(t)$ in a 14-mT magnetic field applied parallel to the $ab$ planes, a, or in a 10-mT field applied parallel to the c-axis, b. Solid lines are fits to the model described by Eq. (4). c, Temperature dependence of the depolarization rate (red circles) in a magnetic field $\mu_0 H = 10$ mT, applied parallel to the c-axis. Note the lack of saturation at low temperatures. The dark-blue square represents the depolarization rate recorded after field cooling in the same applied magnetic field. The grey dashed line represents the average nuclear dipolar contribution, here, $\sigma_n = 0.32 \pm 0.02 \mu$s$^{-1}$.

from $\approx -0.23$ to $\approx -0.13$ T/K. These two slopes correspond to an in-plane coherence length $\xi_{ab}(0)$ of 26 and 20 nm, respectively (Methods). This feature is invariably observed across all the measured H$_2$TiSe$_2$ samples and it deviates considerably from the single-band mean-field behaviour exhibited by both the 3D Cu$_2$TiSe$_3$ and the ion-gated 2D TiSe$_2$, hence suggesting that H$_2$TiSe$_2$ may be a multi-band superconductor.

Further insight into the superconducting properties of the H$_2$TiSe$_2$ is obtained by transverse-field (TF) $\mu$SR measurements [49, 50] (Methods). Figs. 4a,b show the zero-field cooling (ZFC) TF-polarization curves recorded either in an applied field parallel to the $ab$-planes, $\mu_0 H = 14$ mT, or parallel to the c-axis, $\mu_0 H = 10$ mT. As to the former (panel a), no significant differences were detected between datasets taken at $T = 0.28$ K and $T > T_c$. For fields applied parallel to the c-axis, instead, clearly distinct datasets are observed in the SC- and normal state. The volume fraction of those muons probing the vortex state, $f_{SC}$, was determined by fitting the time-dependent TF-polarization data by using a two-step calibration procedure [see details in Methods and Eq. (4)]. We find a lower limit for the SC volume fraction $f_{SC} = 44 \pm 1\%$, thus confirming the bulk nature of H$_2$TiSe$_2$ superconductivity, leaving however open the possibility that some sample regions may still be normal, as expected in case of an inhomogeneous distribution of H dopants.

In the ZFC case, the temperature dependence of the in-plane Gaussian depolarization rate of the implanted muons $\sigma(T)$, resulting from fits to Eq. (4), is shown in Fig. 4c. It includes the contributions of $\sigma_n$ and $\sigma_{\perp}$, the depolarization rates in the normal and SC state, respectively, and is given by $\sigma = \sqrt{\sigma_n^2 + \sigma_{\perp}^2}$. $\sigma_n$ is due to the contribution of the randomly-oriented nuclear dipole moments, here fully dominated by the intercalated H nuclei, whose moments are only partially quenched by the applied magnetic field. Therefore, the observation of a finite $\sigma_n = 0.32 \pm 0.02 \mu$s$^{-1}$ in the normal state (dashed line in Fig. 4c) provides an independent confirmation of the sizeable H intake in the H$_2$TiSe$_2$ samples.

The effective magnetic penetration depth was estimated by measuring also a TF spectrum at base $T$ (dark-blue square in Fig. 4c), now using a standard field-cooling (FC) procedure, which provides a SC-depolarization rate $\sigma_{\perp} = 0.14 \pm 0.03 \mu$s$^{-1}$ at $T = 0.28$ K. This, in turn, implies a rather large value for the in-plane magnetic penetration depth, $\lambda_{ab} = 900 \pm 100$ nm (Methods), indicative of a low superfluid density.

Most notably, the $T$ dependence of $\sigma$ does not show any signs of saturation down to the lowest temperature (0.28 K). At the same time, auxiliary zero-field (ZF) measurements confirm that time-reversal symmetry is preserved in H$_2$TiSe$_2$ (see Supplementary Section V). This result suggests that H$_2$TiSe$_2$ hosts a gapless-like SC state, thus making future spectroscopic investigations of the symmetry of SC gap(s) of this material highly desirable.

**Density functional theory of H$_2$TiSe$_2$.** The effects of H intercalation on the structural, electronic and possibly SC phase of 1T-H$_2$TiSe$_2$ were investigated from a theoretical standpoint by means of *ab initio* density functional theory (DFT) calculations (Methods and Supplementary Section VI). The simulations reveal the existence of several metastable intercalation sites for H in the 1T-TiSe$_2$ lattice, indicating that it can easily be “trapped” (at $T = 0$) in different local energy minima. Nevertheless, at low concentrations ($x \lesssim 0.1$) H preferentially sits in the van der Waals (vdW) gap at the “bridge” position between two Se-atoms belonging to different planes (Fig. 5a) and acts as an electron donor, rigidly shifting the Fermi level in the conduction band of TiSe$_2$ (Fig. 5b). This simple rigid-band-shift picture breaks down at intermediate concentrations ($x \approx 1$). Although here H populates preferentially the same intercalation sites, it strongly distorts the intrinsic bandstructure of 1T-TiSe$_2$, lowering the first conduction band, which results in a partially-filled Ti-$d_{z^2}$ band in the intrinsic energy gap (Fig. 5c). A further increase in doping level, to the concentration determined in fully-doped H$_2$TiSe$_2$ samples by NMR ($x \approx 2$), leads to the emergence of two possible phases. One is characterized by the formation of H$_2$ molecules in the vdW gap and a band structure akin to that of intrinsic 1T-TiSe$_2$ (Supplementary Fig. 8). The other is an insulating phase, achieved when the stoichiometry is exactly 2 H atoms per unit cell (Fig. 5d). Real H$_2$TiSe$_2$ samples are likely characterized by a strong disorder in the distribution of H atoms and they will thus exhibit a mixture of different phases. Disorder effects at high H concentrations also hinder the construction of a reliable structural model (indeed, all structural models were found to be dynamically unstable, indicating the formation of long-range structural distortions involving both H atoms and the TiSe$_2$ matrix).
FIG. 5. Density functional theory of $\text{H}_2\text{TiSe}_2$. a Ball-and-stick model of the protonated $1T:\text{TiSe}_2$ structure. In the first column we report the lateral and top view of the ground-state adsorption site for $1T-\text{H}_2\text{TiSe}_2$ (also shown in Fig. 1a). In the second column we report the adsorption sites for $1T-\text{H}_2\text{TiSe}_2$ (metastable with respect to the $\text{H}_2$ molecule formation inside the van der Waals gap). The Brillouin zone with high symmetry points is also shown. b The unfolded electronic band structure of $1T-\text{H}_0.125\text{TiSe}_2$ is shown as orange scale, the intensity following the spectral weight of the band. It is compared with the $0.1e^-$ doped $1T-\text{TiSe}_2$ dispersion obtained in the jellium approximation (green line). c Electronic bandstructure and density of states of $1T-\text{H}_1\text{TiSe}_2$ with one H atom placed in the vDW gap at the Se-Se bridge position (red) compared with the pristine $1T-\text{TiSe}_2$ dispersion (gray). d Electronic bandstructure and density of states of $1T-\text{H}_2\text{TiSe}_2$ in the adsorption configuration reported in panel a (red) compared with the pristine $1T-\text{TiSe}_2$ dispersion (gray).

DISCUSSION

In summary, our results show that ionic liquid gating-induced protonation allows for a robust and non-volatile tuning of the electronic ground state of $1T-\text{TiSe}_2$, an archetypal correlated layered semimetal. We demonstrate that this tuning is qualitatively different from what is obtained by other doping methods, such as electrostatic gating and Cu- or Li-intercalation. An increased level of hydrogen doping suppresses the intensity of the charge-density wave phase of undoped TiSe$_2$ and triggers the onset of superconductivity. Still, vestigial traces of the charge-density wave ordering, observed even in $\text{H}_2\text{TiSe}_2$ – a stoichiometry unattainable via Li or Cu intercalation – hint at the coexistence of both phases in a wide doping range. The observed gapless-like and possibly multi-band character of the superconducting phase together with the absence of an anomalous metallic phase are also at odds with what is reported in other superconducting TiSe$_2$ compounds. Our experimental results are consistent with ab initio calculations showing how the effect of H intercalation is not limited to a rigid-band doping, but can lead to a full band-structure engineering of the undoped TiSe$_2$ compound.

Ionic liquid gating-induced protonation makes it possible to explore the chemical richness of the transition-metal dichalcogenides across the periodic table within a single material. Indeed, $1T-\text{TiSe}_2$ features the undoped semi-metallic (and non-superconducting) phase of the $1T-\text{TiX}_2$ family, which hosts unoccupied $d_{xz}$ bands originating from transition-metal ions, as deduced from the analysis of the band structure. Upon H doping up to $\text{H}_1\text{TiSe}_2$, the ground state of TiSe$_2$ moves towards the metallic (superconducting) phase, obtained by partially lowering and occupying the $d_{xz}$ bands, mimicking the exact band population found in Nb-based transition-metal dichalcogenides of the $2H$ polytype, such as $2H-\text{NbSe}_2$ and $2H-\text{NbS}_2$, which are superconductors even without doping. By adding one more H atom per unit cell, the series ends with the insulating phase when the $d_{xz}$ band is fully occupied, as in semiconducting $2H-\text{MoS}_2$ or $2H-\text{WS}_2$. This clearly indicates that the superconducting phases realized in $\text{H}_x\text{TiSe}_2$ should be of a different nature with respect to those observed in Cu$_x\text{TiSe}_2$ or in electron-doped MoS$_2$, reflecting the different orbitals involved in the electron-electron pairing and the capability of H doping to significantly alter the phonon bands as well, by injecting high-frequency spectral contributions arising from light H atoms.
Our findings establish protonation as a unique doping technique, distinct from the more ubiquitous chemical substitution and alkali intercalation, and open the way for further discoveries in the field of superconductivity, in particular looking at the recent astonishing results on hydrogen-based superconductors with “near-to-room-temperature” critical temperatures [51]. Gate-driven protonation will enable accessing new electronic phases of the host compounds at ambient pressure, where hydrogen can play a dual role as charge dopant and affecting the phonon frequencies and electron-phonon coupling. Theoretical proposals along this route are recently appearing, all confirming that superconductivity can be induced in different materials by hydrogen incorporation. Among others, we cite the hydrogen-induced superconducting phases in PdCu [52], diborides like MgB$_2$ [53] and TiB$_2$ [54], chromium [55], Mo$_2$C [56], hBN [57], and in carbon nanostructures [58]. The experimental realization of these theoretical proposals, made possible by the simple and reliable technique shown in this work, can reverse the accepted paradigm to access high-temperature superconducting phases of hydrides from the high-pressure side. Here we propose an alternative route for stabilizing new hydrogen-rich compounds, starting from promising materials at ambient pressure, driving them to the predicted superconducting state and then, eventually, further enhancing their superconducting properties by applying low or moderate pressures.

**METHODS**

**Ionic liquid gating-induced protonation.** Freshly-cleaved 1T-TiSe$_2$ crystals (HQ Graphene) were electrically contacted by drop-casting small droplets of silver paste (RS Components) to thin gold wires and crystals (HQ Graphene) were electrically contacted by drop-casting small droplets of silver paste (RS Components) to thin gold wires and cold-spraying a constant current source. The four-wire resistance $R = V_{xx}/I_{DS}$ was monitored in situ by sourcing a constant current $I_{DS} \approx 100 \mu A$ between the outer drain (D) and source (S) contacts with a Keithley 220 current source, and measuring the longitudinal voltage drop $V_{xx}$ between the inner voltage contacts with an HP3457 multimeter. The resistivity was then determined as $\rho = Rtw^{-1}$, where $t$ and $w$ are the sample thickness and width, and $l$ is the distance between the inner voltage contacts. Common-mode offsets were removed using the current-reversal method. The protonated TiSe$_2$ samples were then extracted from the cell and rinsed with acetone and ethanol to remove ionic-liquid residues before further ex-situ characterizations. In between measurements, samples were stored in standard desiccators either under low vacuum or in argon atmosphere to avoid moisture contamination.

**Electric transport measurements.** All protonated TiSe$_2$ crystals discussed in this work were characterized via temperature-dependent resistivity measurements carried out in the high-vacuum chamber of a Cryomech pulse-tube cryocooler with a base temperature of $\approx 2.8$ K. The magnetotransport properties of selected crystals were measured either at $\approx 4.2$ K in the variable-temperature inser of a $^3$He Oxford cryostat, or up to $\approx 300$ K in a Quantum Design physical properties measurement system (PPMS), both equipped with 9 T superconducting magnets. The resistivity was determined as in the room-temperature gating runs, except that the source-drain current was sourced via an Agilent B2912 source-measure unit (Oxford cryostat) or using a standard 4-probe technique with the Resistivity option for the PPMS. The user bridge board of the PPMS has a digital-to-analog converter (DAC) which adjusts the excitation current and a delta-sigma A/D converter which reads the voltage output. In AC mode, the user bridge board applies a DC excitation to the sample and at each measurement it reverses the current averaging the absolute value of the positive and negative voltage readings. This operation eliminates errors from DC offset voltages and produces the most accurate readings. Both the longitudinal ($V_{xx}$) and transverse ($V_{xy}$) voltage drops were measured via an Agilent 34420 nanovoltmeter (Oxford cryostat) or by means of a standard 6-terminal method with the Resistivity option for the PPMS. The magnetic field $H$ was always applied orthogonal to the samples’ ab plane. The Hall coefficient was determined from the antisymmetric $R_H = V_{xy}/I_{DS}$ data as:

$$R_H = \frac{t}{\mu_0} \times \frac{dR_{xx}(T)}{dH}$$  

and the Hall density was calculated as $n_H = (eR_H)^{-1}$ where $e$ is the elementary charge.

In superconducting samples, the onset transition temperature $T_{c}^{on}$ was determined as the threshold where $\rho(T)$ reaches 95% of its normal-state value $\rho_0$, and the zero-temperature in-plane coherence length as

$$\xi(0) = \frac{\Phi_0/2\pi}{\mu_0(\partial H_{c2}/\partial T)_{T=0}}$$

where $H_{c2}$ is the magnetic field at which $\rho(H)$ reaches 95% of its normal-state value, $\mu_0$ is the vacuum permeability, $\partial H_{c2}/\partial T$ is the slope of the $H_{c2} - T$ curve, and $\Phi_0$ is the magnetic flux quantum.

**X-ray diffraction.** X-ray powder diffraction patterns of the TiSe$_2$ samples were collected using a 114.6 mm Gandolfi camera, with Ni-filtered Cu K-$\alpha$ radiation source and an exposure time of 48 hours. Diffraction was impressed on a photographic film and reduced using the software X-RAY [59] to obtain the intensity profiles as a function of the diffraction angle.

**Raman spectroscopy.** Raman spectra were acquired on freshly-cleaved surfaces in ambient conditions using a Renishaw InVia H43662 micro-Raman spectrometer. All spectra were acquired using an excitation wavelength of 514 nm, a laser power $< 1$ mW focused through a 100X objective, an exposure time of 20 s, and 50 accumulations.

**Nuclear magnetic resonance.** $^1$H-NMR measurements at $\mu_0 H \approx 3.5$ T (magnetic field parallel to the crystallographic ab plane) were performed using a TecMag Apollo spectrometer coupled to a resonant circuit made of an in-series combination of a 470 pF capacitor and of a seven-loop solenoidal coil. The coil was deformed in order to mimic the flake-like shape of the crystals and to maximize the geometrical filling factor, in turn. The spin-lattice relaxation time $T_1$ was quantified via a conventional inversion-recovery pulsed sequence. In particular, $T_1^{-1}$ was extracted based on a best-fitting of the experimental recovery curves based on a stretched-exponential function

$$M(\tau) = M(\infty) \left[1 - 2f \exp \left(-\frac{\tau}{\tau_0}\right)^\beta\right].$$

Here, $M(\tau)$ is the component of the nuclear magnetization along the quantization axis at time $\tau$ after the first inversion radio-frequency pulse, $M(\infty)$ is the equilibrium magnetization, $f \leq 1$ allows for non-ideal inversion conditions and $\beta$ is the stretching exponent. $\beta \approx 0.9$ was quantified independently on temperature, in good agreement with the purely-exponential behaviour expected for spin-1/2 nuclei.

**Magnetization measurements.** Systematic measurements of the magnetic moment as a function of temperature and magnetic field were carried out on a small H$_3$TiSe$_2$ single crystal by means of a superconducting quantum interference device (SQUID) magnetometer. Since the sample mass was less than 0.1 mg (i.e., below the sensibility threshold of a standard laboratory balance), the magnetic field had to be applied perpendicular to the sample surface (i.e., to ab planes). Such setup maximizes the effects of the demagnetizing factor, thus enhancing the diamagnetic signal in the superconducting state. The unavailability of a reliable value for the sample mass (or volume) prevents us from providing...
an accurate estimate of the shielding fraction in the superconducting state.

**Muon-spin rotation measurements.** Muon-spin rotation (μSR) is an extremely sensitive probe of the local (i.e., microscopic) electronic properties, which uses spin-polarized positive muons implanted in the sample under test [49, 50]. Depending on the material density, muons typically penetrate over a depth of several hundreds of microns and, thus, are implanted homogeneously over the whole sample volume. Because of this, muons are considered as a bulk probe of matter. All the μSR measurements were carried out at the Dolly spectrometer (τE1 beaml ine) of the Swiss Muon Source at the Paul Scherrer Institute, Villigen, Switzerland. A \(^3\)He cryostat was used to reach temperatures down to 0.28 K. A mosaic of H\(_2\)TiSe\(_2\) single crystals was glued using GE-varnish on a 25-μm thick copper foil, here acting as a thermal link. A 100-μm-thick high-purity silver degrader was fixed in front of the sample. All measurements were performed using an active veto scheme, thus removing the background signal due to muons which miss the sample. μSR measurements were performed following both standard field-cooling (FC) and nonstandard zero-field cooling (ZFC) protocols. In the former case, a regular lattice of vortex lines is established over the sample volume. This is a key requirement in order to accurately determine the magnetic penetration depth and the superfluid density. In the ZFC case, instead, we induce an artificially disordered vortex lattice in the SC state that, in turn, causes highly inhomogeneous local magnetic fields at the implanted muon sites and, hence, a much higher muon-spin depolarization rate than that observed in a conventional FC- (or normal-state) experiment. This procedure is particularly suited for evaluating the superconducting volume fraction of superconductors with a weak magnetic-flux expulsion, as the H-doped TiSe\(_2\) in the present case.

**Muon spin rotation fits.** In all cases, the time-dependent TF polarization was fitted using the following function:

\[
P_{TF}(t) = f_{sc} \cos(\gamma_\mu B_{sc} t + \phi) e^{-\tau^2 t^2/2} + f_{tail} \cos(\gamma_\mu B_{tail} t + \phi) e^{-\tau^2 t^2/2} (4)
\]

Here, \(f_{tail} = 1 - f_{sc}\) is the fraction of muons implanted in the silver degrader (see also Supplementary Section V) and in the non-superconducting parts of the sample, \(\gamma_\mu/2\pi = 135.53\) MHz/T is the muon gyromagnetic ratio, \(B_{sc}\) and \(B_{tail}\) are the magnetic fields probed by the muons implanted in the sample and in the silver degrader, and \(\phi\) is a common initial phase. Finally, \(\Lambda\) is the relaxation rate originating from the muons implanted in the silver degrader.

Both \(\Lambda\) and \(f_{tail}\) parameters were obtained in a two-step calibration via a ZFC TF experiment at 0.28 K (see Fig. 4). First, the long-time tail (\(t > 5\) μs) was fitted with a single oscillating component (\(f_{osc} = 0\)), determining \(\Lambda = 30 \pm 6\) ns\(^{-1}\). In this case, due to the fast signal decay in the SC phase, the long-time tail reflects only those muons implanted in the silver degrader (and in non-superconducting parts of the sample). Secondly, by fixing \(\Lambda\) to the previously determined value, the data were fitted over the whole time range to obtain \(f_{tail} = 0.56 \pm 0.02\). These two parameters were then kept fixed during all the subsequent TF-fits.

From the SC depolarization rate \(\sigma_{\nu}\) under the assumption of an ideal triangular vortex lattice, and by considering that the applied field is negligibly small with respect to the upper critical field determined from resistivity and magnetization measurements (\(H_{c2} > 0.1\) T), the magnetic penetration depth is determined as \(\Lambda = (0.00371 \times \phi_0 B_{sc}^2 / \sigma_{\nu}^2)^{1/4}\) [60, 61].

**Density functional theory calculations.** First-principles calculations were performed using the QUANTUM ESpresso package [62, 63]. The experimental lattice parameters were adopted for all the calculations and the Generalized Gradient Approximation (GGA) for the exchange and correlation energy, since in 1T-TiSe\(_2\) the GGA functional, on top of the previously determined value, the data were fitted over the whole time range to obtain \(f_{tail} = 0.56 \pm 0.02\). These two parameters were then kept fixed during all the subsequent TF-fits.

From the SC depolarization rate \(\sigma_{\nu}\) under the assumption of an ideal triangular vortex lattice, and by considering that the applied field is negligibly small with respect to the upper critical field determined from resistivity and magnetization measurements (\(H_{c2} > 0.1\) T), the magnetic penetration depth is determined as \(\Lambda = (0.00371 \times \phi_0 B_{sc}^2 / \sigma_{\nu}^2)^{1/4}\) [60, 61].

**DATA AVAILABILITY**

The data that support the findings of this study are available from the authors upon reasonable request.

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**AUTHOR CONTRIBUTIONS**

E.P., G.Profeta and R.S.G. conceived the idea. R.S.G. directed the project. E.P., D.D., and R.S.G. designed and performed the protonation and the electric transport measurements. G.Prando and R.C. performed the NMR characterization. M.M. and M.P. contributed to the electric transport measurements. C.T. and G.Profeta performed the ab initio calculations. S.R. provided the pristine samples and performed the XRD characterization. G.L. performed the magnetization measurements. G.Prando, G.L., and T.S. performed the μSR measurements. All authors contributed to the discussion and interpretation of the results. E.P., G.Prando, G.L., T.S., G.Profeta, D.D., and R.S.G. wrote the manuscript with input from all authors.

**COMPETING INTERESTS**

The authors declare no competing interests.

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Supplementary Information for
Coexisting superconductivity and charge-density wave in hydrogen-doped
titanium diselenide via ionic liquid gating-induced protonation

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CONTENTS

I. X-ray photoelectron spectroscopy of the titanium diselenide crystals 2
II. Quantification of intercalated protons in the titanium diselenide crystals 3
III. Temperature-dependent transverse resistivity measurements 6
IV. Additional temperature-dependent magnetotransport measurements in the SC phase of H_xTiSe_2 6
V. Zero-field muon spin rotation measurements 7
VI. Additional details on the density functional theory calculations 9
   A. Dynamical properties: Raman spectra 9
   B. Dynamical properties: dynamical and superconducting properties in doped TiSe_2 10

References 10

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I. X-RAY PHOTOELECTRON SPECTROSCOPY OF THE TITANIUM DISELENIDE CRYSTALS

We employed X-ray photoelectron spectroscopy (XPS) to confirm that the ionic liquid gating induced protonation did not result in the intercalation of undesired species in the TiSe$_2$ lattice, such as the cations of the ionic liquid itself [1]. XPS spectra were acquired with a PHI Model 5000 electron spectrometer equipped with an aluminum anode (1486 eV) monochromatic source, with a power of 25 W, at pressures below $5 \times 10^{-8}$ mbar. All crystals were cleaved immediately before loading them in the XPS load-lock, preliminarily degassed overnight at room temperature, and a surface cleaning step was performed by etching the first few atomic layers via sputtering with the built-in Ar-ion gun. The binding energies of the acquired spectra were corrected for specimen charging by referencing the C 1s line (acquired in dedicated survey scans before the Ar cleaning procedure) to 284.8 eV. Peak assignments were obtained using the Multi Pak Software 9.7 for peak recognition.

Figure 1 shows the full survey scans up to 1200 eV acquired on a pristine TiSe$_2$ crystal (solid black line) and a H$_2$TiSe$_2$ crystal (solid red line) after the surface cleaning by Ar-ion sputtering, together with the corresponding peak assignments. Only peaks arising from Ti, Se, and O atomic species are observed in both scans. The Ti and Se signals obviously arise from the TiSe$_2$ lattice, whereas the presence of an O signal indicates a small degree of oxidation even in the pristine crystal, which is nearly unavoidable when any TiSe$_2$ surface is exposed to ambient air [2]. The intensity of the O signal is found to increase in the H$_2$TiSe$_2$ crystal: we ascribe this to an enhanced level of oxidation in the exposed TiSe$_2$ surfaces triggered by the harsh electrochemical environment of the protonation cell, which cannot be fully removed by the Ar cleaning treatment across the whole area probed by the X-ray beam. Most importantly, no additional peaks ascribable to the atomic species building up the EMIM-BF$_4$ ionic liquid molecular structure (C, N, B or F) are detected in the H$_2$TiSe$_2$ crystal, thereby confirming a negligible incorporation (if any) of either the EMIM$^+$ cation or the BF$_4^−$ anion in the TiSe$_2$ lattice structure, in full agreement with the minute unit cell expansion detected by x-ray diffraction as discussed in the Main Text.
II. QUANTIFICATION OF INTERCALATED PROTONS IN THE TITANIUM DISELENIDE CRYSTALS

We quantified the number of protons in the investigated collection of TiSe$_2$H$_x$ crystals, with overall mass ($2.90 \pm 0.06$) mg and volume $\sim 3 \times 3 \times 0.5$ mm$^3$, by means of $^1$H nuclear magnetic resonance (NMR). We prepared a resonant circuit using an in-series combination of a 470 pF capacitor and of a seven-loop solenoidal coil which was deformed in order to mimic the flake-like shape of the crystals and to maximize the geometrical filling factor in turn. We also prepared a flake-like reference sample of hexamethylbenzene ($\text{C}_{12}\text{H}_{18}$), with similar mass ($3.16 \pm 0.05$) mg and dimensions if compared to the TiSe$_2$H$_x$ crystals, aiming at a comparable geometrical filling factor of the solenoidal coil.

The proton quantification was performed at constant temperature ($T = 292.5$ K) and magnetic field $\mu_0H \approx 3.46$ T, corresponding to a Larmor frequency $\nu_L \approx 147.83$ MHz for the $^1$H nuclear magnetic moments. The procedure relied on the two-pulse solid-echo sequence shown in the diagram above. The first radiofrequency (RF) pulse generates a free-induction decay signal which is refocused into a spin-echo signal by the second pulse. Both pulses have the same duration $\tau_{\text{pulse}}$. The spin-echo is centred at a time $2\tau_e$ after the first pulse, $\tau_e$ being the time separation between the two pulses. After the acquisition time $\tau_a$, the idle time $\tau_r$ is such that $\tau_r \gg 5T_1$, where $T_1$ is the spin-lattice relaxation time of the considered sample. This latter calibration guarantees that the system reaches conditions of thermodynamical equilibrium before the sequence is started over again and repeated until a satisfactory signal/noise ratio is reached.

The acquisition window is adjusted so that only the second half of the spin-echo signal is detected (see the diagram above). The resulting signal undergoes fast Fourier transform and the transformed signal is numerically integrated, resulting in the value $I$. The whole process is repeated for different $\tau_e$ values and, eventually, the value of $I$ is plotted as a function of $2\tau_e$. Representative curves for both TiSe$_2$H$_x$ and C$_{12}$H$_{18}$ are reported in the left-hand and right-hand panels of Fig. 2, respectively. The experimental data are best-fitted based on exponential-decay (TiSe$_2$H$_x$) and Gaussian-decay (C$_{12}$H$_{18}$) curves, making it possible to extrapolate the integrated signal amplitude back to the limit $2\tau_e = 0$. This extrapolated

![Image](image_url)
value is independent on any signal suppression due to sample-specific $T_2$ processes and is directly related to the number of resonating $^1$H nuclear magnetic moments – as such, this is the relevant quantity for the proton quantification procedure. Incidentally, we stress that both the TiSe$_2$H$_x$ crystals and the reference C$_{12}$H$_{18}$ sample were wrapped in teflon tape and we ensured that both the empty coil and the teflon tape did contribute with negligible signal amplitude. We repeated the procedure described above for different RF pulse durations, aiming at the maximization of the extrapolated $I$ value at $2\tau_x = 0$ (achieved for a $\pi/2$ pulse, with duration $\tau_{\pi/2}$).

The results for TiSe$_2$H$_x$ and C$_{12}$H$_{18}$ are reported in the left-hand and right-hand panels of Fig. 3, respectively. The ratio between the maximum $I$ values for TiSe$_2$H$_x$ and C$_{12}$H$_{18}$ should be equal to the number of protons in the two samples. However, we notice that the maxima for the two samples correspond to two different calibrated pulse durations ($\tau_{\pi/2} = 1.18 \pm 0.05$ $\mu$s for TiSe$_2$H$_x$ and $\tau_{\pi/2} = 1.74 \pm 0.04$ $\mu$s for C$_{12}$H$_{18}$), suggesting different quality factors for the circuit when the different samples are inserted in the coil. In particular, a higher quality factor is associated to the circuit transferring power more effectively, i.e., with a shorter $\tau_{\pi/2}$. At the same time, based on the reciprocity principle, a higher quality factor also corresponds to a higher coil sensitivity for the signal detection. Overall, neglecting the small discrepancies in the geometrical filling factor in the two measurements, we have that [3, 4]

$$\frac{(N_p)_{\text{TiSe}_2H_x}}{(N_p)_{\text{C}_{12}H_{18}}} = \frac{(I_{\text{max}} \times \tau_{\pi/2})_{\text{TiSe}_2H_x}}{(I_{\text{max}} \times \tau_{\pi/2})_{\text{C}_{12}H_{18}}}$$

In the equation above, we have defined $I_{\text{max}}$ as the maximum value $I_{\text{max}}$ (see Fig. 3) normalized by the number of repetitions of the sequence. We can calculate $(N_p)_{\text{C}_{12}H_{18}}$ based on the sample mass $(3.16 \pm 0.05$ mg) and the associated molar mass $(162.27$ g/mol$_{\text{C}_{12}H_{18}}$) and, specifically, we have

$$(N_p)_{\text{C}_{12}H_{18}} = 18 \times \left( \frac{(3.16 \pm 0.05) \times 10^{-3} \text{g}}{162.27 \text{g/mol}_{\text{C}_{12}H_{18}}} \times N_A \right) = (2.11 \pm 0.03) \times 10^{20}$$

with $N_A$ the Avogadro constant. Now, $(N_p)_{\text{TiSe}_2H_x}$ – i.e., the total number of resonating $^1$H nuclear magnetic moments inside the TiSe$_2$H$_x$ sample – is the only unknown quantity in Eq. 1. Based on the experimental values extracted from Fig. 3, we have a direct quantification of $(N_p)_{\text{TiSe}_2H_x}$ as

$$(N_p)_{\text{TiSe}_2H_x} = (1.7 \pm 0.2) \times 10^{19}.$$  

(3)

This is more easily expressed as $x$, i.e., the number of $^1$H nuclear magnetic moments per crystallographic cell of TiSe$_2$H$_x$. The number of crystallographic cells in the TiSe$_2$H$_x$ crystals $(N_c)_{\text{TiSe}_2H_x}$ can be approximated based on the sample mass $(2.90 \pm 0.06$ mg) and the molar mass of pristine TiSe$_2$ $(205.81$ g/mol$_{\text{TiSe}_2}$) as

$$(N_c)_{\text{TiSe}_2H_x} \simeq \frac{(2.90 \pm 0.06) \times 10^{-3} \text{g}}{205.81 \text{g/mol}_{\text{TiSe}_2}} \times N_A = (8.5 \pm 0.2) \times 10^{18}.$$  

(4)
Overall, our final result is

\[ x = \frac{(N_p)_{\text{TiSe}_2H_x}}{(N_c)_{\text{TiSe}_2H_x}} = 2.0 \pm 0.3. \]  

(5)
Magnetic field \( (B = \mu_0 H) \)-dependent transverse resistivity \( (\rho_{xy}) \) measurements were carried out at temperatures ranging between 5 K and 300 K on three representative TiSe\(_2\) crystals as discussed in the Main Text and in the Methods. Figure 4 reports the full sets of temperature-dependent antisymmetrized \( B - \rho_{xy} \) curves. The corresponding values of \( R_H \) reported in the Main Text are obtained by linearly fitting the experimental data at a given temperature in the entire \( B \) range.

FIG. 4. Antisymmetrized transverse resistivity \( \rho_{xy} \) as a function of the out-of-plane magnetic field \( B \) measured at different temperatures \( T \) between 5 and 300 K in three TiSe\(_2\) samples with different CDW intensities. a, a pristine TiSe\(_2\) sample with \( I_{CDW} = 0.9 \). b, an intermediately-doped H\(_x\)TiSe\(_2\) sample with \( I_{CDW} = 0.13 \). c, a fully-doped H\(_2\)TiSe\(_2\) sample with \( I_{CDW} = 0.016 \). The resulting \( T \)-dependence of the Hall coefficient is plotted in Fig. 2e of the Main Text.

IV. ADDITIONAL TEMPERATURE-DEPENDENT MAGNETOTRANSPORT MEASUREMENTS IN THE SC PHASE OF H\(_x\)TiSe\(_2\)

Figure 5 shows the temperature-dependent resistivity of two additional H\(_x\)TiSe\(_2\) crystals across the superconducting transition, at different values of the magnetic field applied perpendicular to the \( ab \) planes. The resistivity is normalized to its value in the normal state immediately above the SC transition.

FIG. 5. Resistivity \( \rho \) of two fully-doped H\(_2\)TiSe\(_2\) crystals as a function of temperature \( T \) in the superconducting transition, normalized by its normal-state value \( \rho_0 \), for increasing magnetic field \( H \) applied orthogonal to the crystal \( ab \) plane.
Figure 6 shows a selected set of zero-field muon spin rotation (ZF-$\mu$SR) measurements whose aim was twofold: to detect a possible time-reversal symmetry breaking (TRSB), usually associated with unconventional pairing, and to evaluate the amount of hydrogen atoms effectively intercalated in the layered TiSe$_2$ structure. As to the former, by measuring the time-dependent polarization in a strictly zero field (the background magnetic fields being actively compensated) one can detect the tiny magnetic fields associated with the electrons paired in a spin-triplet state. The TRSB has been observed in Sr$_2$RuO$_4$ [5] and related compounds [6], as well as in some topological superconductors, such as Sr$_{0.1}$Bi$_2$Se$_3$ [7]. In Figure 6c, we show the time-dependent ZF polarization above and below the superconducting transition. Clearly, the two datasets fully overlap, thus excluding a possible increase of depolarization rate in the superconducting state due to spontaneous magnetic fields and ruling out any TRSB.

All the ZF-$\mu$SR datasets were fitted by means of the model below:

$$P_{ZF}(t) = f_{\text{tail}} \cdot \exp(-\Lambda t) + (1 - f_{\text{tail}}) \cdot G_{KT}(t) \cdot \exp(-\nu t).$$ (6)

Here, the long-time relaxing tail is due to the muons implanted in the silver degrader. Both $f_{\text{tail}}$ and $\Lambda$ were fixed to the values determined by TF-$\mu$SR measurements. Under some broad assumptions, the second term can be referred to the sample: $G_{KT}(t)$ is the static Gaussian Kubo-Toyabe function reflecting the contribution of randomly-oriented nuclear magnetic moments. Such term is multiplied by a simple exponential decay which accounts for possible dynamic processes, such as muon- and/or hydrogen hopping (expected to occur at high temperatures [8, 9]), with $\nu$ being the hopping rate.

Figure 7 presents the temperature evolution of the ZF depolarization and the hopping rates, as resulting from fitting $P_{ZF}(t)$ data to Eq. (6). First, we observe that our results agree closely (at least qualitatively) with those related to ZrV$_2$H$_x$, a Laves-phase material [10], where one can distinguish two different regimes. At low temperatures (below 50 K), muons are static and show a relatively large depolarization rate, $\sigma_{ZF} = 0.346(6) \mu$s$^{-1}$. For $T > 50$ K, $\sigma_{ZF}$ decreases progressively because motional narrowing sets in. The latter is fully effective for $T > 180$ K, where both a sharp decrease of $\sigma_{ZF}$ and a corresponding increase of $\nu$ take place. As observed already in ZrV$_2$H$_x$, also in our case, muon motions seem to be highly correlated with those of the intercalated hydrogen atoms: most of the interstitial sites available for muon hopping being occupied by the hydrogen. When, at high temperatures, hydrogen too starts diffusing, “new” interstitial sites become available for the muon diffusion, thus explaining the sharp decrease in depolarization rate observed for $T > 180$ K. Experimental data on ZrV$_2$H$_x$ suggest also that, in such system, muon hopping is slower than hydrogen hopping [10, 11], a counter-intuitive result considering the ninefold lower mass of muon compared to that of proton. To date, there are no clear explanations for this apparently contradictory result.
Interestingly, it was also shown that, at low temperatures, the $\sigma_{ZF}$ value increases with increasing H content [11], reaching $0.37 \mu s^{-1}$ for $x = 4.8$. Since this decay rate agrees with that observed in our case, it suggests a high degree of H intercalation in TiSe$_2$ too, thereby confirming – at least qualitatively – the results of the proton quantification by NMR discussed above.
VI. ADDITIONAL DETAILS ON THE DENSITY FUNCTIONAL THEORY CALCULATIONS

The random-search algorithm analysis highlighted the existence of several different metastable intercalation sites, indicating that hydrogen can easily be “trapped” (at $T = 0$) in different local minima. The lowest-energy phase discovered features the H-atom located in the van der Waals gap, at the “bridge” position between two Se-atoms belonging to different planes. Interestingly, a metastable phase where the H atom is located inside the TiSe$_2$ trilayer is found very close in energy to the lowest-energy one ($\Delta E \sim 0.06$ eV). The band structure of 1T-H$_{0.125}$TiSe$_2$, unfolded in the $(1 \times 1 \times 1)$ Brillouin Zone (Main Fig. 5b) strongly resembles that of ideal TiSe$_2$, but with the Fermi level now shifted in the conduction band populating the electron valley at the $L$-point of the Brillouin zone, with an estimated electron doping is of about $0.1e^-$ with respect to the pristine 1T-TiSe$_2$. Thus at low-doping regime, H acts as an electron-donor, without appreciable changes of the band structure.

Following the experimental indications for large H doping, the hydrogen concentration was then increased to $x = 1$ and $x = 2$. At $x = 1$, the obtained intercalation sites are in line with the dilute case, but the band structure becomes strongly modified (Main Fig. 5c). At this higher doping level hydrogen still acts as an electron donor, but it now induces a strong band reconstruction lowering the Ti-$d_{z^2}$ which becomes half-filled. A nominal doping of $x = 2$ (i.e. considering two inequivalent H atoms per unit cell, in line with the H content determined in fully-doped TiSe$_2$ crystals via NMR) results in the formation of the H$_2$ molecule (laying in the VdW gap with the H-H bond parallel to the TiSe$_2$ plane) and with a negligible effect on the band structure of the pristine TiSe$_2$ (see Fig. 8). However, the random search provides other (metastable) phases where H atoms remain in the atomic form and are bonded to the Se or Ti atoms, thus avoiding the formation of the molecule. The electronic structure of one of this metastable phases, in which one H atom is intercalated in the vdW gap and the other within the trilayer, shows a transition to an insulating phase as the Ti-$d_{z^2}$ becomes completely filled (Main Fig. 5d).

**FIG. 8.** Electronic band structure of 1T-H$_2$TiSe$_2$ where the H dopants are intercalated as H$_2$ molecules (red) compared with the pristine 1T-TiSe$_2$ dispersion (gray).

**A. Dynamical properties: Raman spectra**

As mentioned in the main text, the inclusion of H dopants removes the symmetries of the systems making all modes Raman active. Although formally all modes are Raman active, it is not certain that their intensity is actually detectable. Since after the inclusion of H atoms the systems are metallic (at least the system with only one H), it is not possible to calculate the theoretical intensity of the peaks. It is however possible to analyse the phononic eigenvectors against the Raman-active ones in the pristine system searching for a possible relation in atomic displacements. From this analysis we can justify the appearance of peaks at $\sim 156$ and $\sim 260$ cm$^{-1}$ in the experimental Raman spectra of H$_2$TiSe$_2$ (Main Fig. 1g). The first one is related to the configuration involving a single H atom in the “bridge position” modifying the Se vibrational properties. The second peak is compatible with the inclusion of two H atoms, one in the VdW gap and the other one in the TiSe$_2$ plane. The presence of both signals is a further indication of the disorder and the different amount of hydrogen in the samples.
B. Dynamical properties: dynamical and superconducting properties in doped TiSe₂

We verified that 1T-TiSe₂ can support an electron-phonon coupling able to justify the measured $T_c$. Since our modelling of the hydrogenated system prevents us from making a true and completely ab-initio calculation, the behaviour of the system with a single H atom per unit cell was mimicked by doping the pristine 1T-TiSe₂ in the jellium approximation. This choice of doping is such that it brings the $d_{xz}$ band close to half-filling, trying to reproduce the behaviour of H inclusion as closely as possible. The electron-phonon coupling was converged using a $48 \times 48 \times 28$ k-point grid for the electronic momenta. The superconducting critical temperature was estimated using the Allen-Dynes modified Mc-Millan equation [12, 13] with $\mu^* = 0.1$ [14, 15]. As known for the 1T-TiSe₂ single layer [15, 16], doping is responsible for the dynamical stabilization of the system. In turn, the re-entry of the phononic instability is responsible for the large electron-phonon coupling able to support sizable $\omega_{\text{log}}$ factor [17].

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