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Observation of Penning electron detachment from H^- induced by metastable H^*/Ng^* atoms (Ng = He, Ne, Ar, Kr, Xe)

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ABSTRACT

In Penning detachment, the excess electron of an anion is detached during the anion's collision with an electronically excited neutral species ($A^- + N^* \rightarrow A + N + e^-$). Penning detachment of H^- has special relevance to the dynamics of stellar atmospheres and to possible technological uses. Penning detachment by excited (metastable) hydrogen and helium atoms may be the most important H^- loss-step in the solar atmosphere. Here, the Penning detachment of H^-/D^- by collisions with $H^*(2^2S)$ and $He^*(2^3S/2^1S)$ excited atoms, i.e., $H^-/D^- + H^*/He^* \rightarrow H/D + H/He + e^-$, was observed for the first time via direct H^-/D^- anion depletion experiments. Penning detachment of H^- by metastable noble gases (Ng^* = He^*, Ne^*, Ar^*, Kr^*, Xe^*) was observed as well, with potential applications in tokamak fusion devices being proposed.

I. INTRODUCTION

Penning ionization is a collisional process in which the energy of an electronically excited neutral species, N^*, is transferred to another neutral species, resulting in its ionization ($A + N^* \rightarrow A^+ + N + e^-$). By analogy, Penning *detachment* is a related fundamental process in which an electron is detached from an anion, A^-, by collision with an electronically excited neutral species ($A^- + N^* \rightarrow A + N + e^-$). Blaney and Berry, who coined the term, Penning detachment, carried out its theoretical investigation in 1971[1] and developed it further in the 1990s.[2–6] While Penning ionization utilizes van der Waals attraction between the two neutral species, Penning detachment relies on the ion-induced dipole attraction between an anion and an excited neutral species. Thus, Penning detachment was predicted to have a larger cross section than Penning ionization due to the Coulombic interaction between the colliding species.[1,6]

The kinetic rate constant for the ionospheric reaction, $O_2^- + O_2(a^1\Delta_g) \rightarrow 2\ O_2 + e^-$, was measured experimentally by Fehsenfeld *et al.* using the flowing afterglow technique in 1969.[7] This rate constant was then refined by Upschulte *et al.*[8] Later, Viggiano and coworkers studied this reaction, determining its rate constant to be ~7×10^{-10} $cm^3\ s^{-1}$, the presently accepted value.[9,10] Midey *et al.* also expanded their measurements to other atmospherically relevant Penning detachment reactions, such as $SO_2^- + O_2(a^1\Delta_g)$ and $HO_2^- + O_2(a^1\Delta_g)$.[11] The relatively large cross sections of these reactions, i.e., 10^{-11}–10^{-10} $cm^3\ s^{-1}$, were attributed to long-range, ion-induced dipole interactions as postulated by Berry *et al.*[1,3,4]

Penning detachment of H^- is a topic of special interest. Berry *et al.* simulated the Penning detachment cross sections of H^- via its collision with He^*, Li^*, and Ca^* in various excited states and at several collision energies.[1–4] The Penning detachment of H^- may be especially pertinent to the dynamics of stellar atmospheres. H^- itself is responsible for the opacity of the sun due to its interaction with >0.75 eV (<1.6 μm) photons and, thus, to the photodetachment of its excess electron ($H^- + h\nu \rightarrow H + e^-$).[12–14] In other words, H^- in the solar photosphere plays the sacrificial role of attenuating radiation that had originated from deep inside the sun before it can reach the Earth. Since both theoretically predicted[1,3,4] and experimentally estimated[15] Penning detachment cross sections of H^- (10^{-15}–10^{-12} cm^2) are orders of magnitude greater than the photodetachment cross section of H^- (~10^{-17} cm^2[16,17]), Penning detachment may be an important (if not the dominant) H^- loss-step in the "reaction mechanism" of the solar atmosphere. Thus, while the photodetachment of H^- protects the Earth from

dangerous rays, Penning detachment of H^- diminishes the density of that shield. Since the sun's photosphere consists of ~75% hydrogen and ~25% helium,[18] Penning detachment of H^- can be initiated by collisions with electronically excited neutral hydrogen, H^*, and/or helium, He^*, atoms. The required H^- Penning detachment energy is the electron binding energy of H^-, i.e., the electron affinity (EA) of the H atom (0.75 eV).[19] Since the first excitation energies of both H and He atoms, i.e., 10.2 and 19.8 eV, respectively,[20] are significantly larger than the EA of H, both H^* and He^* have more than enough energy to initiate the Penning detachment of H^-. The Penning detachment of H^- may also have significant technological applications. For example, the injection of fast neutral beams of H or D atoms into tokamak-like nuclear fusion devices is envisioned as a means of heating their plasmas.[21] In that case, the inherently high cross section of Penning detachment would be advantageous for producing fast neutral H/D atomic beams, when accelerated H^-/D^- beams collide with electronically excited atoms along their paths, viz., $\overrightarrow{D}^- + N* \rightarrow \overrightarrow{D} + N + e^-$.[2] In effect, this is a specialized form of charge stripping.

Nevertheless, despite the importance of H^- Penning detachment, its experimental investigation has been limited. In 1991, in a pioneering study, Dowek *et al.* accelerated H^- anions to 0.5–1.5 keV and collided them with excited $Na^*(3p)$ atoms, measuring the energy loss spectra of the neutralized H atoms.[15] From their data, they estimated the cross section for the Penning detachment of H^- to be 10^{-15}–10^{-14} cm^2, consistent with the magnitude predicted by Berry *et al.*[1–6]

Recently, we developed the capability to *directly* observe Penning detachment using time-of-flight mass spectrometry (TOF-MS) and specialized pulsed timing sequences that enabled the detection of a subtle ion depletion. With this, we showed that Penning detachment for SF_5^- + K^{**} collisions occurred when the total available energy (the excitation energy of the neutral atom plus the anion-neutral collision energy) exceeded the EA value of SF_5.[22] Combining that methodology with a discharge source for forming metastable H^* and Ng^* (Ng = He, Ne, Ar, Kr, Xe), we herein demonstrate, through *direct* mass spectrometric observations of anion depletion, the occurrence of H^-/D^- Penning detachment. Below, we begin by reporting on the Penning detachment of H^- + He^* and then of H^- + H^*, in Secs. III A and III B, respectively, because those are the anion-excited neutral combinations with explicit relevance to the solar atmosphere. After demonstrating H^- Penning detachment in these systems, we next expand the list of metastable noble gases (Ng^*) used to induce Penning detachment to include Ne^*, Ar^*, Kr^*, and Xe^* and then speculate on their possible technological applications in fast neutral beam injectors for nuclear fusion reactors in Sec. III C.

II. METHODS

These experiments were conducted using our pulsed laser photoemission ion source/time-of-flight mass spectrometric apparatus described in previous publications,[22–25] with the addition of a discharge source for producing metastable H^* and Ng^* (Ng = He, Ne, Ar, Kr, Xe) species for the crossed-beam experiments. Figure 1 shows a schematic of the experimental setup. The H^- ion beam was produced via dissociative electron attachment of H_2 by

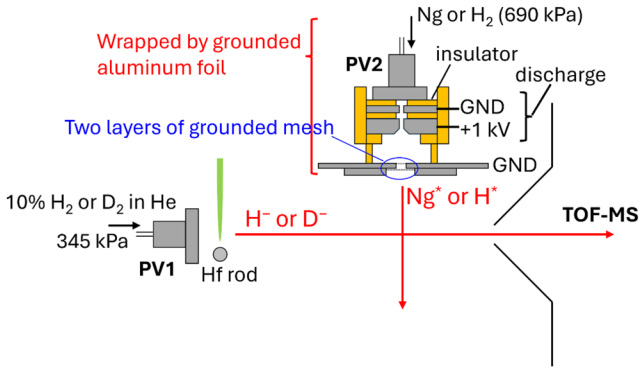

FIG. 1. Crossed-beam experimental arrangement with a pulsed laser photoemission ion source and a pulsed DC discharge source. PV = pulse valve, TOF-MS = time-of-flight mass spectrometer. The H^-/D^- ion beam, formed from H_2/D_2 by laser photoemission of electrons from a hafnium rod, was crossed with a beam of excited noble gas atoms, Ng* (Ng = He, Ne, Ar, Kr, Xe) or excited hydrogen atoms, H^*, formed by the discharge, and subsequently extracted into the TOF-MS.

pulsing an H_2/He (10%/90%) gas mixture (345 kPa) from pulse valve 1, labeled as PV1 in Fig. 1 (Parker–Hannifin, 10 Hz, pulse duration ~160 μs) over a translating, rotating hafnium rod that was simultaneously being irradiated by the second harmonic output of a Nd:YAG laser (532 nm, Continuum, Surelite II-10, 10 Hz). This H^- ion beam was then crossed with H^* or Ng^* (Ng = He, Ne, Ar, Kr, Xe) electronically metastable atoms that were produced by a pulsed DC discharge. The discharge setup, designed after that of Lu *et al.*,[26] consists of pulse valve 2, labeled as PV2 in Fig. 1 (Parker–Hannifin, 5 Hz, pulse duration ~225 μs) and two stainless-steel plates spaced apart by ~1 mm, with a high voltage potential (+1 kV, supplied from a high voltage power supply through a 180 Ω current-limiting resistor) being applied between them. Pulsing H_2 or Ng gases (690 kPa) through this high-voltage region caused a discharge (5–10 mA) and formed a plasma jet. In order to prevent the electric fields of the high voltage components of the discharge arrangement from affecting the trajectories of the anions (especially of the lightest mass anion, H^-), the entire discharge setup and its high voltage cable were confined to a "Faraday cage," composed of grounded stainless-steel plates and aluminum foil. The H^* or Ng^* beam exited the Faraday cage through two layers of grounded stainless-steel mesh. The visible plasma decayed before it reached these meshes, which meant that only unexcited atoms and metastable H^* or Ng^* atoms exited the cage. More information about this beam from the discharge source is provided later in this section. After the H^- ion beam was crossed with the H^* or Ng^* beam, it was extracted into a Wiley–McLaren type, time-of-flight mass spectrometer (TOF-MS). To mitigate the shot-to-shot fluctuation of the ion intensity in the pulsed ion source, the H^- ion intensities with/without H^* or Ng^* were recorded simultaneously by the timing scheme used in our previous Penning detachment study,[22] and as shown in Fig. 2. The H^- ion beam, which originated from PV1 and the laser photoemission ion source, was pulsed at 10 Hz, while the H^* or Ng^* beam, which originated from PV2 and the discharge source, was pulsed at 5 Hz.

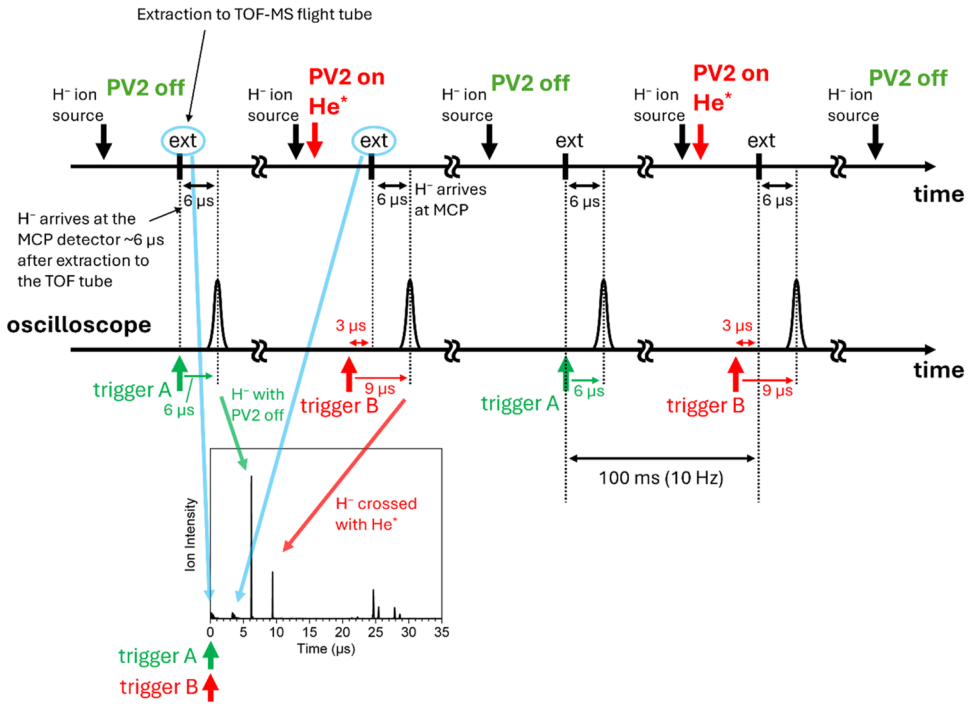

FIG. 2. Timing scheme for the pulsed apparatus' operation and the correspondences between the recorded times of the H^- ion signals. The inset shows the mass spectrum in Fig. 4(a). The collisions between H^- + He^* are shown here as an example. The H^- that was not crossed with He^* was recorded at ~6 μs, while the H^- crossed with He^* was recorded at ~9 μs. The electrical noise at ~0 and ~3 μs is from the TOF-MS extraction plates during the PV2 off/on pulses, respectively.

In this way, alternate pulses/shots of H^- were crossed with pulses of H^* or Ng^*. The mass spectra with the PV2 on/off were recorded on one oscilloscope (GaGe, Compuscope 82G) by combining the two 5 Hz triggering signals, time-shifted by a few microseconds. In the Penning detachment experiment's pulse sequence, here illustrated in Fig. 2 with H^- + He^* collisions *as an example*, He was not pulsed from PV2 in the first cycle. In our setup, the flight time of the H^- through the TOF-MS flight tube was ~6 μs. The oscilloscope was triggered simultaneously with the TOF-MS extraction plates, so that the H^- ion signal that was not crossed with He^* was recorded at ~6 μs in the mass spectrum. In the second cycle, He was pulsed from PV2 through the discharge source and crossed with H^-. The oscilloscope was triggered ~3 μs earlier than the TOF-MS extraction plates. Thus, the H^- ion signal that was crossed with He^* was recorded by the oscilloscope at 3 + 6 μs = 9 μs. These two cycles were repeated 500 times to accumulate the H^- ion signal when it was crossed with He^*, as well as the H^- signal when it was not crossed with He^*. This same procedure was used in studying both H^* and Ng^* metastable atom collisions with H^-.

The same measurements were performed by pulsing a D_2/He (10%/90%) gas mixture from PV1 instead of the H_2/He gas mixture, to observe the Penning detachment of D^- + He^*. We also pulsed H_2 from PV2 to produce H^* by discharge and observed the Penning detachment of H^-/D^- + H^*.

The formation of metastable He^* beam by our discharge source was confirmed by allowing it to cross a beam of neutral potassium atoms and detecting the K^+ ion formed by Penning ionization ($K + He^* \rightarrow K^+ + He + e^-$). We also found that the intensities of the $He^+/H^+/H_2^+$ cations formed by discharge were very much lower than those of the H^-/D^- anions formed by our laser photoemission ion source. Thus, any effects due to anion–cation neutralization would have been negligible. See the supplementary material for these cation-mode mass spectrometric results.

Although we could not characterize the excited state composition of the metastable He^* and H^* beams at their intersections with the H^- anion beam, we presume that He^* consisted mostly of its first excited state, 2^3S, and to some lesser extent of its second excited state, 2^1S, and that H^* consisted mostly of its first excited state, 2^2S. More detailed explanations of the He^* and H^* states are provided in Secs. III A and III B, respectively.

III. RESULTS AND DISCUSSION

A. Penning detachment of H^-/D^- caused by He^*

Based on their known lifetimes, we first consider the composition of the metastable He^* beam that was crossed with H^-. The visible light emission of the discharge plasma within the Faraday cage region originated from He^* at its principal quantum numbers, n = 3 and 4, these decaying to the 2^1P, 2^3P, 2^1S, and 2^3S states.[27,28] $He^*(2^1P)$ decays to the ground state, 1^1S with a lifetime of 0.58 ns,[29] while $He^*(2^3P)$ decays to the 2^3S state with a lifetime of 99.0 ns.[30] On the timescale of our experiments (10–100 μs), these states decay before the He^* beam reaches its intersection with the H^- anion beam. $He^*(2^3S)$ is a metastable state with an unusually long lifetime of 7870 s,[31] because its relaxation to the ground state, 1^1S, is doubly forbidden by the selection rules of spin multiplicity and orbital angular momentum. $He^*(2^1S)$ is also metastable due to its forbidden

relaxation; thus, its lifetime of 19.7 ms[32] is long enough for it to be effective in our experiments. Note that in the pulsed valve helium discharge measured by Halfmann *et al.*, the He^* beam consisted of 90% 2^3S and 10% 2^1S.[33] In addition to $He^*(2^3S)$ and $He^*(2^1S)$, discharge of helium gas could form excimers (excited dimers), He_2^* ($a\ ^3\Sigma_u^+$), that has a long lifetime (13[34]–18 s[35]) and high electronic excitation energy (17.9 eV[36]) enough to detach an electron from H^-. However, the effect of He_2^* will be much smaller than that of He^*, because excimer formation is favored at high pressure that promotes three-body collisions,[37,38] that is different from our experimental conditions of the discharging supersonic expansion beam in a vacuum chamber with the base pressure of ~2×10^{-6} Torr.

A typical time-of-flight mass spectrum obtained by pulsing a H_2/He gas mixture through the laser photoemission ion source is shown in Fig. 3(a). In addition to the intense H^- signal, weak intensities of O^- and OH^- also appeared in the mass spectrum due to the residual oxygen in the gas line and/or an oxide layer on the surface of the hafnium rod.

The top panel of Fig. 4(a) shows two time-of-flight mass spectra overlaid with a ~3 μs time shift, one with PV2 off (no He^*) and the other with PV2 on (with He^*). The time shift was arbitrarily chosen so that the $H^-/O^-/OH^-$ anion signals with PV2 on/off do not overlap. The intensity of H^- ions crossed with He^*, recorded at ~9 μs, was significantly lower than that of H^- ions not crossed with He^*, recorded at ~6 μs. The bottom panel of Fig. 4(a) shows the mass spectra when the discharge voltage was off, i.e., it shows the H^- ion intensity with/without the ground state He beam. The depletion of H^- was not observed there. The same phenomena were observed for

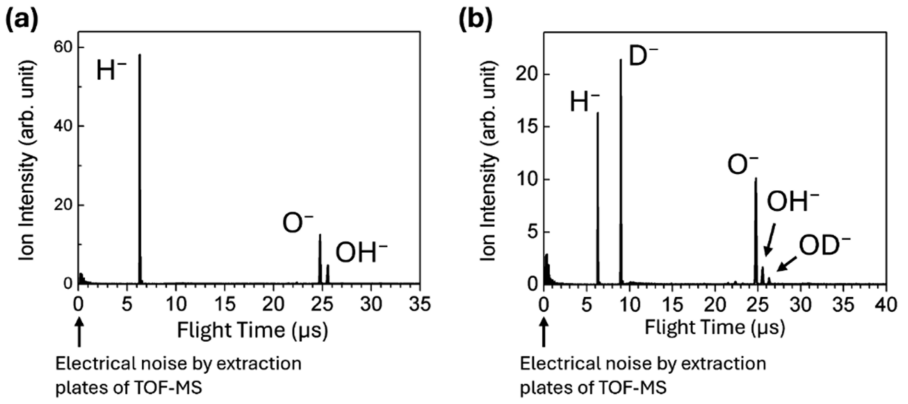

FIG. 3. Time-of-flight mass spectra obtained by pulsing (a) a H_2/He (10%/90%) gas mixture and (b) a D_2/He (10%/90%) gas mixture from pulse valve 1 (PV1) through the laser photoemission ion source in Fig. 1. Pulse valve 2 (PV2) was off.

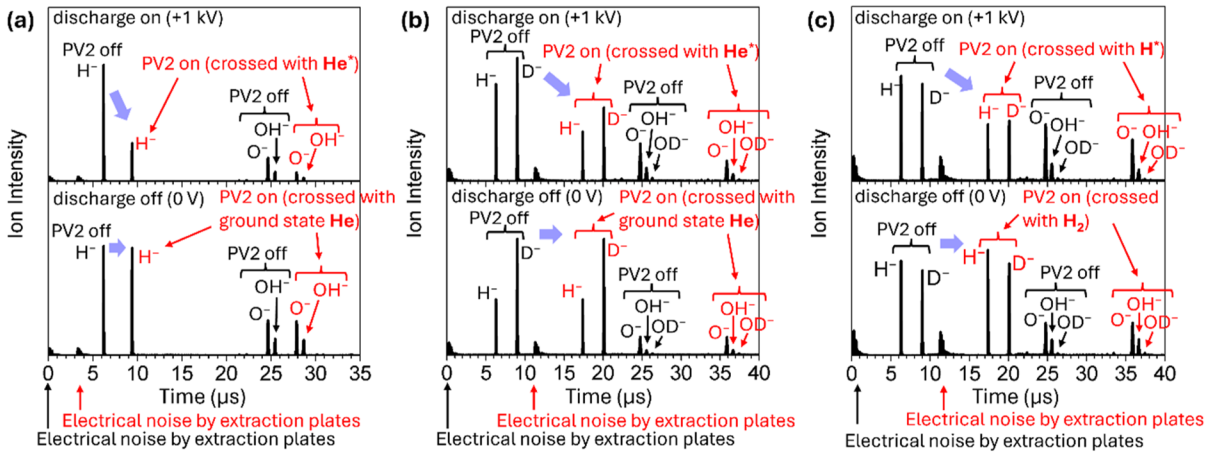

FIG. 4. (a) Mass spectra recorded by pulsing the H_2/He gas mixture from pulse valve 1 (PV1) and pulsing He from pulse valve 2 (PV2) using the crossed-beam/discharge setup in Fig. 1 and the timing scheme in Fig. 2. In the top panel (discharge on), the mass spectra of the anions with and without He^* present were overlaid with a ~3 μs time shift. In the bottom panel (discharge off), the mass spectra with and without ground state He present were overlaid. (b) The corresponding mass spectra by pulsing the D_2/He gas mixture from PV1 and He from PV2. In the top panel, the mass spectra of the anions with/without the He^* beam were overlaid with ~11 μs time shift. In the bottom panel, the mass spectra of the anions with/without ground state He beam were overlaid. (c) Corresponding mass spectra by pulsing the D_2/He gas mixture from PV1 and H_2 from PV2. In the top panel, the mass spectra of the anions with/without the H^* beam were overlaid with ~11 μs time shift. In the bottom panel, the mass spectra of the anions with/without ground state H_2 beam were overlaid. The blue arrows show that the H^-/D^- ion intensities decreased by crossing with the metastable He^*/H^* due to Penning detachment, while they did not decrease by crossing with the ground state He/H_2.

the accompanying O^- and OH^- ion intensities as well. The depletion ratio of each anion was calculated by the following formula: (Depletion Ratio) = [(I with PV2 off) − (I with PV2 on)]/(I with PV2 off), where I is the anion intensity based on the peak area in the mass spectra. The averages and standard deviations of the depletion ratios by five repeated measurements are plotted in Fig. 5(a). As high as 55%–60% of the $H^-/O^-/OH^-$ anions were depleted by the excited helium atoms, while almost no anions were depleted by the ground state helium. The occurrence of anion depletions only when the helium was electronically excited means that it was caused by Penning detachment ($A^- + He^* \rightarrow A + He + e^-$, where A = H, O, and OH). This is consistent with our previous observations of SF_5^- + K** Penning detachment, where it occurred when the total available energy (the anion-neutral collision energy and the excitation energy of the neutral) exceeded the EA of SF_5.[22] The collision energy can be estimated using the approximate velocity of a beam formed by supersonic expansion: $v = (5k_BT/m)^{1/2}$, where k_B is the Boltzmann constant, T is the temperature of the gas before expansion, and m is the effective mass of the atoms and molecules in the gas.[39] Using this velocity, the collision energies of the molecules meeting at a right angle[22] would be ~0.027 eV for $H^- + He^{(*)}$ and ~0.11 eV for $O^-/OH^- + He^{(*)}$. The energies required to detach an electron from H^-, O^-, and OH^- are EA(H) = 0.75 eV,[19] EA(O) = 1.46 eV,[40] and EA(OH) = 1.83 eV,[41] respectively. Therefore, the collision energy alone is not enough to cause electron detachment. Once the He atom is excited to its lowest excited state (2^3S_1, 19.8 eV), however, there is plenty energy available for causing the Penning detachment of all three anions. This explains why the three anions in question exhibited the same depletion ratios in Fig. 5(a).

Next, we performed the same experiment for $D^- + He^*$ by pulsing D_2 instead of H_2 from PV1. A typical mass spectrum is shown in Fig. 3(b). H^- and OH^- were observed in the mass spectrum in addition to D^-, O^-, and OD^-, due to the residual H_2 in the gas line and/or hydrogen atoms adsorbed on the hafnium rod surface. The top panel of Fig. 4(b) shows the two mass spectra of anions with/without the He^* beam (PV2 on/off) overlaid with a time shift of ~11 μs. As plotted in Fig. 5(b), all of these anions were depleted by 35%–50% by He^*. These depletions were not observed when they were crossed with ground state He atoms [see the bottom panel of Fig. 4(b)].

B. Penning detachment of H^-/D^- caused by H^*

We studied the Penning detachment of H^-/D^- by H^* using the same experimental arrangement descripted above. For the H^* beam formed by the discharge of H_2, we presume that it consists mostly of the metastable, first excited state, 2^2S, formed by dissociative excitation ($H_2 + e^- \rightarrow H + H^* + e^-$).[42,43] The visible light emission of the H_2 plasma in the Faraday cage region came from the Balmer series of H^* and also the Fulcher-α band of H_2^*.[44] The Balmer series originates from the relaxation of H^* in the principal quantum numbers, $n \geq 3$ down to the 2^2P and 2^2S final states. $H^*(2^2P)$ decays essentially instantly to the ground state, 1^2S, with a lifetime of 1.6 ns.[45] $H^*(2^2S)$ is a metastable state with a lifetime of 0.12 s,[46] due to its forbidden relaxation to the ground state, 1^2S. The Fulcher-α transition of H_2 is $d^3\Pi_u^- \rightarrow a^3\Sigma_g^+$ with an emission wavelength prominently at 590–650 nm.[44,47] The lifetime of $H_2^*(a^3\Sigma_g^+)$ is of the order of 10 ns[48] and much shorter than our experimental timescale. Therefore, at its crossing point with the H^- anion beam, the excited H^* species from the H_2 discharge is mostly the metastable, $H^*(2^2S)$. It lives long enough to reach the interaction/crossing point.

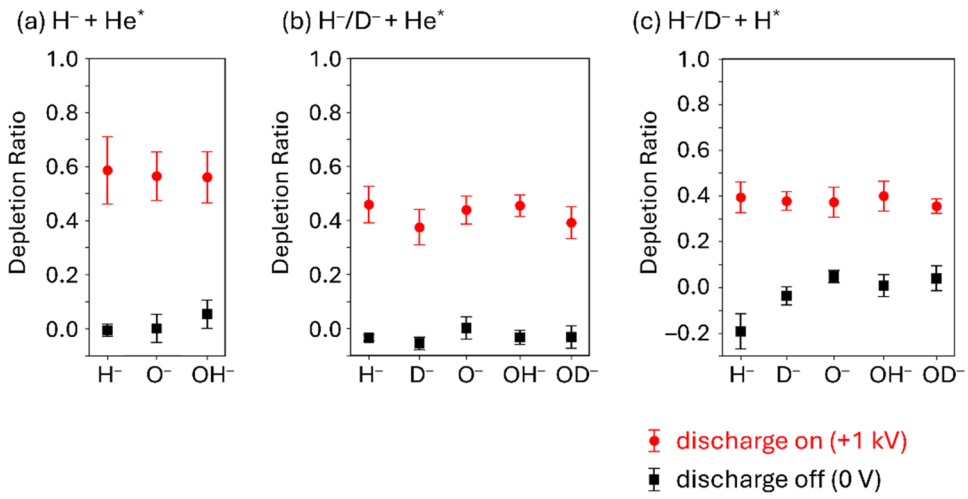

FIG. 5. Depletion ratios of the anions by crossing them with He^*/He and H^*/H_2. (a) $H^-/O^-/OH^-$ crossed with He^* (red) and ground state He (black); these data correspond to those in Fig. 4(a). (b) $H^-/D^-/O^-/OH^-/OD^-$ crossed with He^* (red) and ground state He (black); these data correspond to those in Fig. 4(b). (c) $H^-/D^-/O^-/OH^-/OD^-$ crossed with H^* (red) and ground state H_2 (black); these data correspond to those in Fig. 4(c). The depletion ratio of H^- when crossed with the ground state H_2 (discharge off) was recorded negative, which corresponds to the H^- signal crossed with H_2 ("PV2 on") was slightly more intense than that not crossed with H_2 ("PV2 off") in the bottom panel of Fig. 4(c) due to the fluctuation of the H^- ion intensity. Each measurement was repeated five times, and the error bars represent the standard deviations.

The D_2/He gas mixture was pulsed from PV1 through the laser photoemission ion source to form $H^-/D^-/O^-/OH^-/OD^-$ [the typical mass spectrum shown in Fig. 3(b)], while H_2 was pulsed from PV2 through the discharge source to form H^*. As shown in Figs. 4(c) and 5(c), the anions crossed with H^* showed depletion of 35%–40% by Penning detachment, while those crossed with the ground state H_2 showed almost no depletion. As with He^*, the metastable H^* in its first excited state (2^2S, 10.2 eV) has sufficient energy to cause Penning detachment of all observed anions.

C. A possible role for H^- Penning detachment in nuclear fusion reactors

Here, we present our studies of H^- Penning detachment with additional metastable noble gas atoms, Ng^* (Ng = He, Ne, Ar, Kr, Xe), along with our speculation that these, including H^*, may find applications in tokamak nuclear fusion devices. In a tokamak, the plasma, which is confined by magnetic fields, can be heated by injection of ultra-fast neutral D atoms, these having been prepared by collisionally, charge-stripping highly accelerated (~1 MeV) D^- negative ions. The components of the resulting neutral beam injector (NBI), thus, consist of a D^- ion source, an accelerator, a collisional neutralizer stage, and a residual ion dump.[49,50] Neutralization (charge stripping) is often carried out via collisional electron detachment of D^- with D_2 gas ($\vec{D}^- + D_2 \rightarrow \vec{D} + D_2 + e^-$).[49,50] The energy of the resulting fast neutral D beam is then monitored by a calorimeter.[49,50] For a tokamak to perform well as a fusion device, however, the global power efficiency of its NBI needs to be ≥60%.[51] Since NBIs with current D_2 gas neutralizers cannot achieve this efficiency, there is ongoing interest in developing NBIs using alternative neutralization methods.[50,52–55] There are two broad choices: neutralize fast cations with electrons or charge-strip electrons from fast anions. Neither the former cation approach, nor the latter collisional electron detachment method, nor even photodetachment of anions, are efficient enough. *Here, we suggest that Penning detachment of D^- should also be considered as an efficient mechanism for neutralizing fast D^- anions.* Importantly, the inherently high cross section of Penning detachment can be expected to be advantageous in enhancing the D^- neutralization efficiency, viz., $\vec{D}^- + Ng^* \left(\text{or } H^*\right) \rightarrow \vec{D} + Ng \ (\text{or } H) + e^-$. The question remains as to which Ng^* to use.

Below, we present our results on H^- Penning detachment using Ng^* (and H^*) and speculate on their potential applications in NBIs. These experiments were done under essentially the same H^- source and gas discharge conditions as were shown in Fig. 1. The discharging voltage was set at +700 V and was provided through a current-limiting resistor of 14 kΩ, to achieve relatively stable discharges for all of the gases used. Note that since our vacuum chamber was evacuated by a diffusion pump, the heavier gases were evacuated at a lower pumping speed. The repetition rate of the H^- source (pulse valve 1 backed by 200 kPa hydrogen and the photoemission laser) was set to 5 Hz, while that of the discharge gas source (pulse valve 2 backed by 200 kPa hydrogen or noble gas) was set to 2.5 Hz, so that the heavier gases during the "PV2 on" shot (especially Kr and Xe) were able to be pumped away before the next "PV2 off" shot. Pulse valve 2 was pulsed at an earlier time for the heavier gases, because the supersonic beam of heavier gas is slower. As summarized in Table S1 in the supplementary material, the metastable states of all the noble gases used in these experiments have relatively long lifetimes and high excitation energies, the latter being easily enough to detach an electron from H^-. In contrast to the long-lived excimer of helium elaborated in Sec. III A, the lifetimes of neon, argon, krypton, and xenon excimers are much shorter than the time it takes for them to reach the crossing point with the H^- beam, as detailed in the supplementary material. Therefore, the effect of excimers is negligible for these noble gases. Figure 6 shows typical mass spectra, both with the H^- signal not crossed with the metastable discharge gas (PV2 off) recorded at ~6.3 μs, and with the H^- crossed with the metastable discharge gas (PV2 on) recorded at ~7.1 μs. Signal was accumulated for 250 cycles, and these spectra were measured ten times. The resultant H^- Penning detachment depletion ratios are presented in Fig. 7. While there were intensity

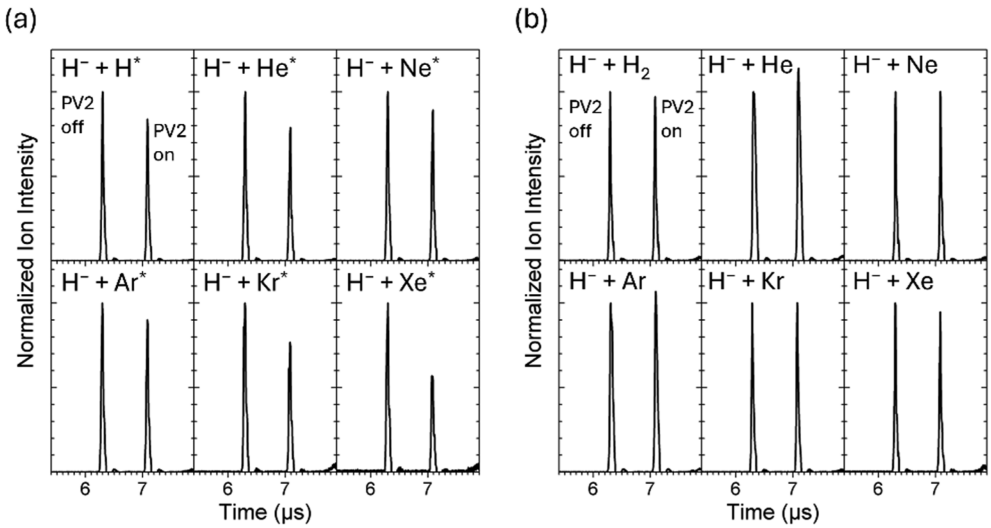

FIG. 6. Mass spectra of H^- recorded by pulsing H_2 from pulse valve 1 (PV1) at 5 Hz and pulsing H_2/He/Ne/Ar/Kr/Xe from pulse valve 2 (PV2) at 2.5 Hz, with the discharging voltage to excite the collision partners of H^- being (a) on (+700 v) and (b) off. The mass spectra of H^- crossed with and without the neutral collision partners from PV2 were overlaid with ~0.8 μs time offset. Figure S3 in the supplementary material shows pictures of the discharges during these measurements.

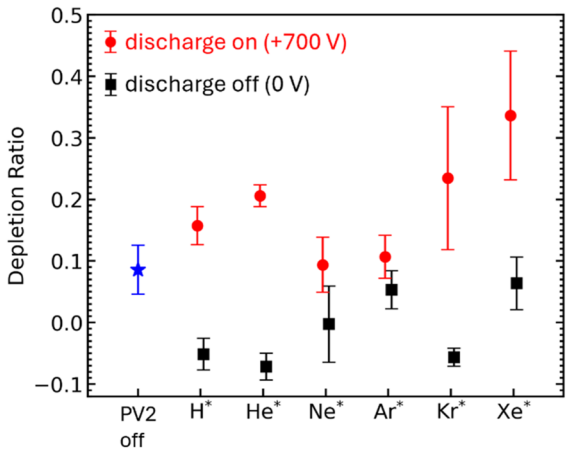

FIG. 7. Penning detachment depletion ratios for H^- due to crossing it with $H^*/He^*/Ne^*/Ar^*/Kr^*/Xe^*$ [red, corresponding to Fig. 6(a)] and those of H^- by crossing it with ground state $H_2/He/Ne/Ar/Kr/Xe$ [black, corresponding to Fig. 6(b)]. The blue star marks the depletion ratio of H^- when pulse valve 2 was kept off, i.e., H^- was not crossed with anything. Each measurement was repeated ten times, and the error bars represent the standard deviations.

fluctuations during data acquisition, as a general trend the heavier gases, i.e., krypton and xenon, showed significantly higher H^- depletion rates. The wider error bars for Kr^* and Xe^* data in Fig. 7 reflect intensity fluctuations due to discharge instabilities in those gases, these occurring because Kr and Xe can easily ionize compared to the lighter noble gases.[56] In any case, their larger depletion ratios can likely be attributed to their larger Penning detachment cross sections. According to Berry *et al.*, the high cross sections of Penning detachment originate from the Coulombic attractions between the anions and the polarized excited neutrals.[1,6] Thus, Kr^* and Xe^* might be expected to yield larger Penning detachment cross sections due to the higher polarizabilities of krypton and xenon atoms (see Table S1 in the supplementary material for polarizability values). As another explanation for their larger depletion ratios, it might be that larger densities of Kr^* and Xe^* metastable atoms were present, these being due to their discharges having been more efficient, or simply because krypton and xenon atoms are heavier and move slower.

Thus, if Kr^* or Xe^* were chosen as the collision partners in the D^- charge-stripping reaction, viz., $\vec{D}^- + Kr^*/Xe^* \rightarrow \vec{D} + Kr/Xe + e^-$, one would benefit from their high cross sections of both collisional electron detachment[57] and Penning electron detachment. We suggest that the role of Penning detachment in this application is worth considering.

Although xenon plasma neutralization was considered in the 1980s–1990s,[58–60] it was not pursued, and in any case, it did not consider Penning detachment as a pertinent mechanism. Furthermore, there are various practical/engineering implications to the use of krypton or xenon in this application. Some of these are considered in the supplementary material.

IV. CONCLUSIONS

Penning detachment of H^- and D^- as well as of O^-, OH^-, and OD^- by metastable $He^*(2^3S$ and $2^1S)$ and $H^*(2^2S)$ was demonstrated for the first time by *direct* mass-spectrometric observation of anion depletion. Although numerical Penning detachment cross sections were not determined from these results due to a lack of quantitative values for anion and excited neutral beam densities, these results, nevertheless, implied that Penning detachment will have a significant effect on kinetic processes occurring under circumstances where H^- and He^*/H^* coexist, e.g., in stellar atmospheres. Penning detachment of H^- by metastable noble gases (He^*, Ne^*, Ar^*, Kr^*, and Xe^*) was also demonstrated, with potential applications involving fast neutral beam injection into tokamaks being proposed.

SUPPLEMENTARY MATERIAL

See the supplementary material for confirmation of He^* formation by the discharge source (Fig. S1); mass spectrometric results of cations formed by discharge (Fig. S2); properties of $H/H_2/D_2/He/Ne/Ar/Kr/Xe$ (Table S1); excimers of noble gas (Table S2); pictures of the pulsed DC discharges of $H_2/He/Ne/Ar/Kr/Xe$ (Fig. S3); and comments on the application of heavy noble gas Penning detachment to the neutral beam injectors of tokamaks.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

T.C., S.W., K.F., and M.B. performed the experimental investigations. K.H.B. supervised the work.

Tatsuya Chiba: Investigation (equal); Writing – original draft (equal). **Shiying Wang**: Investigation (equal). **Kathryn Foreman**: Investigation (equal). **Moritz Blankenhorn**: Investigation (equal). **Kit H. Bowen**: Investigation (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

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

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