

Efficient associative ionization of ultracold lithium and the long-lived Li_2^+

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We report on the efficient production of Li_2^+ ions in a magneto-optical trap (MOT) of Li atoms prepared in an ensemble of $2S$, $2P$, and $3S$ states. A linear Paul trap surrounding the MOT is used to trap and investigate the time evolution of the ion populations. Associative ionization of $\text{Li}(2P_{3/2})$ and $\text{Li}(3S_{1/2})$ atoms, with a giant cross section of $\sim 2.2 \times 10^6 a_0^2$, is the dominant Li_2^+ production channel. Li_2^+ decays to Li^+ via photodissociation and also in the absence of light, which are investigated experimentally and theoretically. A fraction of the Li_2^+ ions are long-lived in the presence of the MOT light, implying that they are deeply bound and hence immune to dissociation, which opens up the possibility for studying Li_2^+ molecular ion interactions with alkali atoms.

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Introduction. Hybrid ion-atom trapping platforms [1–15] are well suited for exploring interaction of molecular ions with cotrapped atomic or ionic species. Choosing to work with simple molecular ions is desirable as they are theoretically tractable [16,17]. To enable long interrogation times of molecular ions, it is essential to investigate their dominant loss channels [18–20] and analyze whether certain rovibrational levels might be protected against dissociation. Additionally, it is useful to understand and explore molecular ion formation pathways that are both efficient and experimentally simple to implement, preferably from cotrapped cold atoms. Starting from an ultracold dilute atomic lithium (Li) gas, with average interatomic separation of $\sim 10 \mu\text{m}$, we report very high rates for the formation of Li_2^+ simply via the $2P_{3/2} \rightarrow 3S_{1/2}$ excitation of ^7Li atoms in a magneto-optical trap (MOT). We determine associative ionization (AI) of $\text{Li}(2P_{3/2})$ and $\text{Li}(3S_{1/2})$ atoms to be the mechanism for the formation of Li_2^+ . Moreover, the measured AI cross section is comparable to the giant values reported for AI in a dense ultracold rubidium (Rb) Rydberg gas [21]. Our hybrid ion-atom apparatus [22] confines the Li_2^+ ions for further study, in contrast to previous AI experiments [21,23–35]. We find that the Li_2^+ ions decay to Li^+ and the possible photodissociative [18], collisional [36], and field dissociative channels [37,38] are investigated. Furthermore, we find that a fraction of the formed Li_2^+ ions are long-lived in the presence of MOT light. They are expected to be in deeply bound vibrational levels. We discuss their

immunity against dissociation, enabling possibilities for their extended cotrapping with alkali MOT atoms.

Experimental details and ion formation during $2P_{3/2} \rightarrow 3S_{1/2}$ excitation of MOT atoms. The experiment [Fig. 1(a)] consists of a ^7Li MOT created at the center of a linear Paul trap with four linear and two dc end-cap electrodes. The MOT typically contains $\sim 1.7 \times 10^6$ atoms at a temperature of $\sim 500 \mu\text{K}$, with a peak density of $\sim 1.8 \times 10^{15}$ atoms/ m^3 . More details on the MOT operation and laser settings are provided in Supplemental material [39]. The Paul trap is operated with a frequency and amplitude of rf (Ω_{rf} , V_{rf}) applied to one diagonal pair of electrodes while the other pair is grounded [41,42]. The end caps are at constant potential V_{ec} . The ions, once created, are trapped in the ion trap and extracted onto a microchannel plate (MCP) by switching off the rf voltage at zero phase [22], while simultaneously applying a brief, negative high-voltage pulse to the grid electrode [see Fig. 1(a)]. Ions hitting the MCP build a time-of-flight (ToF) mass spectrum and can be counted (Fig. 2).

The experiment is conducted as follows. The ^7Li MOT is loaded under standard conditions while the ion trap is kept on with operating parameters $V_{\text{rf}} = 70 \text{ V}$, $\Omega_{\text{rf}} = 1 \text{ MHz}$, and $V_{\text{ec}} = 4 \text{ V}$ (Configuration A, Table I in Supplemental Material [39]). When an 813 nm narrow-linewidth laser with peak intensity $\sim 1 \text{ mW}/\text{cm}^2$ and driving the $2P_{3/2} \rightarrow 3S_{1/2}$ ($F = 1$ or $F = 2$) transition of ^7Li MOT atoms is turned on [Fig. 1(b); see Supplemental Material [39]], and the above extraction sequence is followed, a mass spectrum exhibiting two peaks is observed (Fig. 2, black curve). When only the MOT is operational, no ions are produced or detected upon extraction. The narrow peak at $\approx 4 \mu\text{s}$ is assigned to the Li^+ signal, as it coincides with the peak (green curve in Fig. 2) recorded when a sole UV light emitting diode (LED) (M340L4, Thorlabs) is employed to directly photoionize the $\text{Li}(2P_{3/2})$ atoms in the MOT. The broad distribution around $12 \mu\text{s}$ could be induced by any ion with a mass larger than that of the Li^+ monomer, including Li_m^+ ions with $m > 1$. Due

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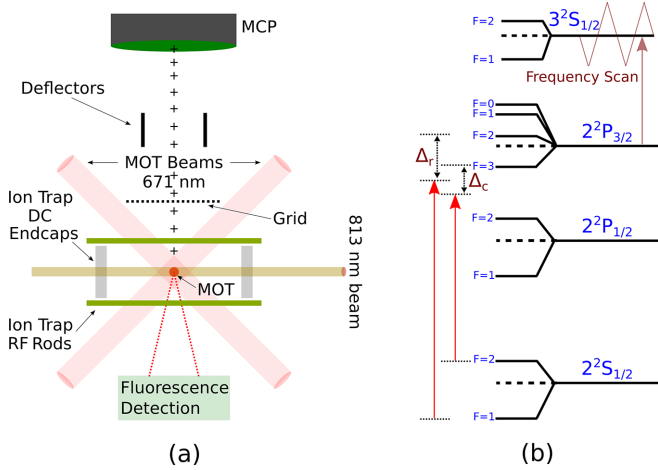


FIG. 1. (a) Schematic representation of the experimental setup. The MOT is positioned at the ion trap center. (b) Energy level diagram of ^7Li for the MOT operation and for the excitation of the MOT atoms to the $3S_{1/2}$ state. The $3S_{1/2} \rightarrow 2P_{3/2}$ fluorescence is monitored by scanning the 813 nm laser across the $2P_{3/2} \rightarrow 3S_{1/2}$ transition frequency [39,40]. See Supplemental Material [39] for details of the fluorescence detection optical setup.

to the pulsed grid extraction, the ToF of the detected ions does not scale as the square root of ion masses. We, therefore, use the parametric excitation (PE) technique [43,44] to characterize the broad distribution. A small perturbation with a frequency f_p is applied to the trapped ions. By tuning f_p , the trapped ions for various Q/M can be selectively emptied (see the Supplemental Material [39]). We first load the trap from MOT atoms by pulsing the UV LED for a short time interval and determine the PE resonance, $f_p(\text{Li}^+)$, for Li^+ by tuning f_p in configuration A [39]. To determine PE resonance frequency for Li_m^+ ions created when applying the 813 nm laser, we eliminate Li^+ by tuning the extraction pulse on the grid electrode such that the trapped Li^+ ions do not reach the detector while Li_m^+ ions do (configuration B, Table I in Supplemental Material [39]). Then, f_p is tuned to locate the PE resonance, $f_p(\text{Li}_m^+)$, for Li_m^+ . The ratio $f_p(\text{Li}^+)/f_p(\text{Li}_m^+)$ is

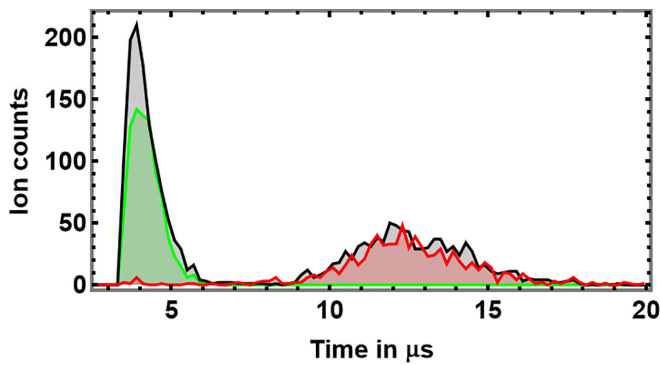


FIG. 2. ToF spectrum, recorded in configuration A [39], of the ions created by the 813 nm laser (black curve) and the UV LED (green curve). The red curve shows a loss of the 813 nm generated ions, which appear at the same ToF as the UV LED generated ions, in the presence of a parametric frequency $f_p(\text{Li}^+) = 149$ kHz (Table I).

TABLE I. Comparison of the most prominent resonant frequency for Li^+ and Li_m^+ measured by varying the frequency of the parametric drive (f_p), in steps of 1 kHz, and recording the number of ions reaching the MCP at each frequency value. The peak-to-peak parametric drive amplitude, in units of millivolts (mV_{pp}), is kept to be 180 and 67.5 mV_{pp} , respectively, for Li^+ and Li_m^+ .

V_{ec} (V)	$f_p(\text{Li}^+)$ (kHz)	$f_p(\text{Li}_m^+)$ (kHz)	$f_p(\text{Li}^+)/f_p(\text{Li}_m^+)$
4	149 ± 0.5	65 ± 0.5	2.29 ± 0.03
2	155 ± 0.5	72 ± 0.5	2.15 ± 0.02
1	158 ± 0.5	76 ± 0.5	2.08 ± 0.02

determined for different values of V_{ec} and converges to 2 when $V_{\text{ec}} \rightarrow 0$ (see Table I and Refs. [39,45]). This establishes that the broad distribution peaked at 12 μs in Fig. 2 contains Li_2^+ ions.

We go on to investigate the formation mechanism of these ions. The ionization energy of the $2P_{3/2}$ and $3S_{1/2}$ levels does not allow the creation of Li^+ by single-photon ionization of lithium atoms from these levels by the 670 or 813 nm lasers. In addition, multiphoton ionization is unlikely as there is no resonant intermediate state to enhance ionization [46,47]. This raises the issue of the origin of the Li^+ ions. First, in configuration A [39], we observe that in the presence of a parametric drive at 149 kHz (Table I), there is a loss of the 813 nm generated ions that have the same ToF as the UV LED generated Li^+ ions (red curve in Fig. 2), reconfirming that this fraction of the ions is indeed Li^+ . We further test whether the 813 nm excitation generates only Li_2^+ to begin with. In configuration A, while shining the 813 nm laser, the application of $f_p(\text{Li}_m^+) = 65$ kHz eliminates both the Li^+ and Li_2^+ peaks in the ToF spectrum of Fig. 2, except for rare counts at the ToF of Li^+ . In contrast, the Li^+ ions created with the UV LED are unaffected by the 65 kHz excitation, as determined in a separate experiment. This strongly indicates that the Li^+ ions are created from Li_2^+ and the ions in the broad peak are exclusively Li_2^+ ions. For this experiment, the PE amplitude of Li_2^+ was increased by ≈ 9.3 times the typical value (Table I) so that the Li_2^+ ions are rapidly ejected out from the trap before a sizable fraction of Li^+ forms.

Investigating Li_2^+ formation mechanisms. To identify the process leading to Li_2^+ production, we calculate the potential energy curves (PECs) for Li_2 and Li_2^+ (Fig. 3), using the same methodology as reported earlier [48,49]. A colliding pair of $2P_{3/2}$ and $3S_{1/2}$ atoms have enough energy to reach the Li_2 ionization threshold undergoing associative ionization [23–30,50–52], which occurs due to autoionization of the two interacting excited atoms scattering along several PECs that asymptotically correlate to the $2P_{3/2} + 3S_{1/2}$ dissociation limit. A fraction of these colliding pairs generate Li_2^+ and the rest radiatively decay back to ground atomic states. By tuning the 813 nm laser over a range of frequencies > 100 GHz across the $2P_{3/2} \rightarrow 3S_{1/2}$ resonance, the Li_2^+ signal manifests only when the sum of the photon energies of the 670 and 813 nm laser equals the energy difference between the $2S_{1/2}$ and $3S_{1/2}$ atomic levels. This weighs against other processes that involve, as an intermediate step, the photoassociation (PA) of neutral Li_2 in a specific bound rovibrational level that can be

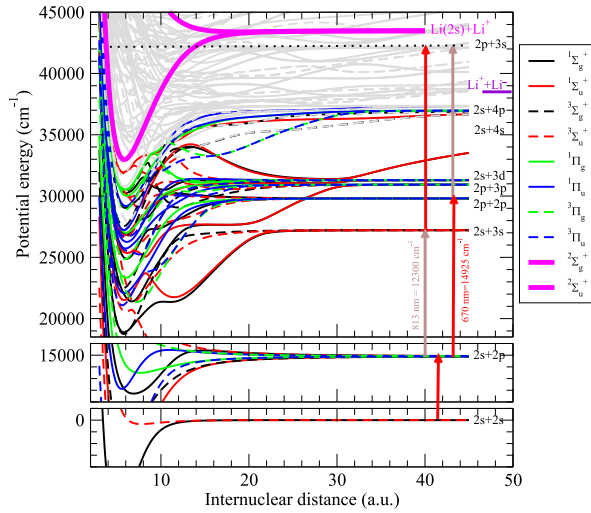


FIG. 3. PECs of Li_2 ground and excited electronic states up to the energy range of the lowest Li_2^+ PECs (thick magenta lines), computed according to Refs. [48,49]. The energy of $\text{Li}^+ + \text{Li}^-$, representing polar dissociation, is indicated for completeness. The gray curves illustrate the complexity of the PECs of highly excited states, which are irrelevant at short distances when they enter the ionization continuum. The arrows picture the possible excitation pathways of the Li atoms.

either photoionized (PI) directly (PA-PI [32]) at short range or further excited to an autoionizing state, commonly referred to as photoassociative ionization [33].

From the calculations shown in Fig. 3, it is impossible to identify the molecular states responsible for AI, as the relevant energy zone close to the $2P_{3/2} + 3S_{1/2}$ dissociation limit corresponds to highly excited states with adiabatic PECs that have a poor accuracy at short distances, as they cross the ionization threshold (gray curves in Fig. 3). Based on the calculated PECs, we infer that the Li_2^+ ions are created in the $X^2\Sigma_g^+$ ground electronic state with a vibrational level not higher than $v_g = 47$, with a binding energy of about 1378 cm^{-1} or more. We measured the total number of created Li_2^+ and Li^+ ions for constant MOT density, which is linear with the intensity of the 813 nm laser, indicating that a single photon is involved [39,53]. For a constant 813 nm laser intensity, the number of detected ions varies quadratically with the MOT density, which is the signature of a two-atom process [31,39]. The large ion formation rates ($\approx 1000 \text{ ions/s}$ [39]) observed, for our dilute MOT exposed to a weak 813 nm pulse, reveal a large AI cross section. We experimentally measure the collision rate coefficient to be $7.5 (\pm 1.3) \times 10^{-15} \text{ m}^3/\text{s}$. For our MOT at $\approx 500 \mu\text{K}$, the AI cross section is $\sim 2.2 (\pm 0.4) \times 10^6 a_0^2$ (see Appendix A for details). This is comparable to the giant values reported for AI in a dense ultracold rubidium Rydberg gas [21], where the enhancement of the cross section was attributed to the role of Fermi's contact interaction between the ground-state Rb atom and the Rydberg electron [54,55].

Investigating Li^+ formation and Li_2^+ stability. As shown above, the Li^+ must originate from the Li_2^+ ions. Three options are plausible: (1) photodissociation (PD) of Li_2^+ by the MOT

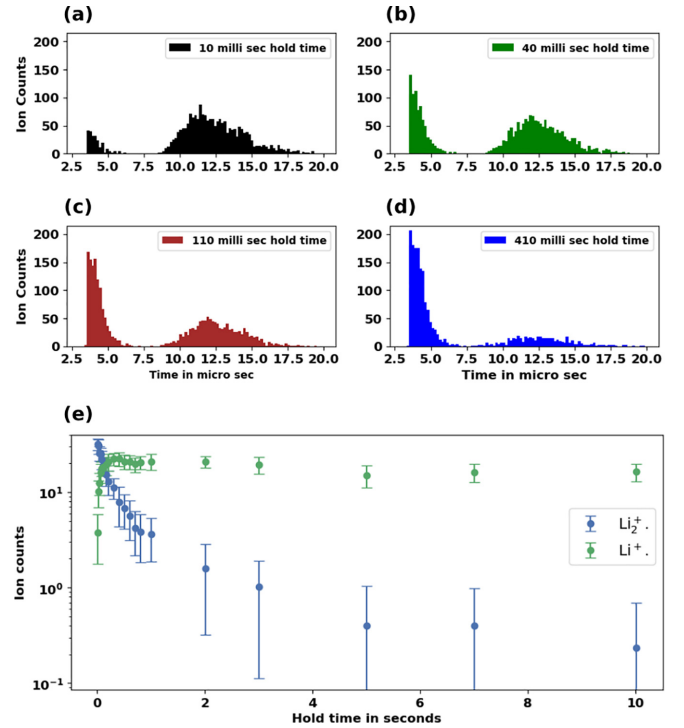


FIG. 4. (a)–(d) ToF spectra of the ions generated by the 813 nm laser pulse, for increasing holding times in the presence of the MOT. Hold time is measured with respect to the rising edge of the 813 nm pulse. In the ToF spectra, we identify the signal below and above $7 \mu\text{s}$ as Li^+ and Li_2^+ , respectively [39]. For each holding time, 60 measurements are performed and used to construct the histograms. (e) Variation of the mean number of Li^+ and Li_2^+ ions per shot with the holding time. The error bars represent one standard deviation.

lasers [18] or by the 813 nm laser; (2) charge exchange (CE) with neutral Li atoms [36]; and (3) direct autoionization of colliding $3S_{1/2} + 3S_{1/2}$ atoms along the lowest $A^2\Sigma_u^+$ dissociative Li_2^+ PEC. In an earlier work with a similar excitation scheme for Rb MOT atoms, the direct autoionization pathway, referred to as photoassociative dissociative ionization (PADI), was dominant [53].

We study the ion population dynamics in configuration A [39], which is suitable for trapping and detecting both Li^+ and Li_2^+ . Atoms are irradiated by a 10 ms pulse of the 813 nm ($5 \text{ mW}/\text{cm}^2$) laser. The created ions are held in the ion trap, in the presence of atoms, for varying holding times of duration 10 ms and longer, and extracted toward the MCP (Fig. 4). In panels (a)–(d), we see that the population of Li^+ increases with increasing holding times, while the Li_2^+ population decreases. Panel (e) shows that after a fast decrease (increase) of the Li_2^+ (Li^+) signal, the mean number of each ion species stabilizes over long holding times (see Supplemental Material [39] for the counting methodology). This experiment confirms that as time progresses, the Li_2^+ ions are converted into Li^+ ions. The small number of Li^+ seen for the 10 ms holding time measurement [Fig. 4(a)] could be due to the $3S_{1/2} + 3S_{1/2}$ scattering channel, which would directly produce Li^+ via PADI or the other channels discussed below.

We next investigate PD of Li_2^+ by the MOT lasers. This study is additionally aimed toward investigating whether

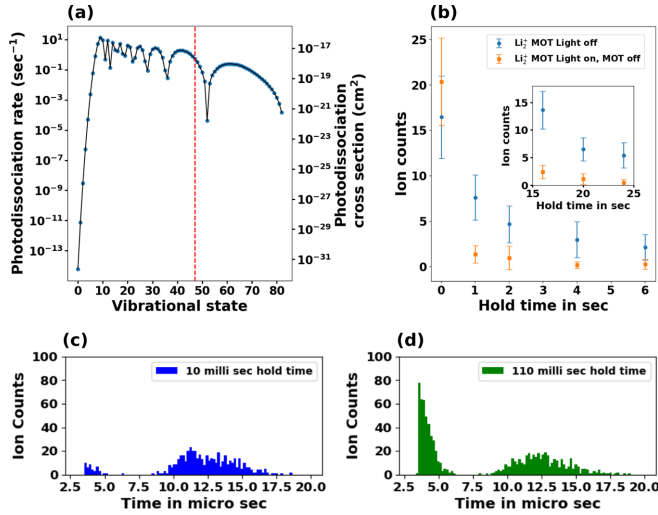


FIG. 5. (a) Calculated Li_2^+ PD cross section and nonthermalized rate at 670 nm ($\approx 77 \text{ mW/cm}^2$ [39]) for the vibrational levels of the $X^2\Sigma_g^+$ ground state toward the dissociation continuum of the lowest $A^2\Sigma_u^+$ state. The red dashed line marks the $v_g = 47$ vibrational level, which is the highest level that can be populated when entering by the $2P_{3/2} + 3S_{1/2}$ scattering channel. (b) Lifetime measurements of Li_2^+ made in configuration C [39] in the presence and absence of the MOT laser. The inset shows the existence of long-lived Li_2^+ ions in the presence of MOT light. Panels (c) and (d) show the change in ToF spectra indicating conversion of Li_2^+ to Li^+ even in the absence of MOT light. The MOT level was not ensured to be the same in panels (c) and (d) as we just wanted to depict change in the ToF.

certain vibrational levels of Li_2^+ are immune to PD as this makes them ideal to be simultaneously trapped for extended durations with ultracold atoms, unlike many other molecular ion species [18,19,56,57]. In Fig. 5(a), we display the computed PD cross section and rate [18,58] at 670 nm of the Li_2^+ ground electronic state ($X^2\Sigma_g^+$) vibrational levels toward the dissociation continuum of the $A^2\Sigma_u^+$ state, using the PECs of Fig. 3. We see that the deeply bound vibrational levels cannot be photodissociated by the 670 nm light due to unfavorable dipole matrix element. This holds for wavelengths $>670 \text{ nm}$ as well. Interestingly, we find that these levels are also energetically protected against CE with Li atoms and cannot be dissociated by the ion trap electric field (see Figs. 6 and 8 and related discussion in Appendix B). Ions populating such levels are thus expected to exhibit a long lifetime in the ion trap even in the presence of MOT light. Signatures of this can be seen in the large holding time data of Fig. 4(e).

To further probe the PD of Li_2^+ , we perform measurements similar to those of Fig. 4, operating the ion trap in configuration C (Table I in Supplemental Material [39]), which traps only Li_2^+ . The MOT is loaded for 20 s, and the 813 nm laser with 5 mW/cm^2 intensity is switched on for 10 ms just before switching off the repumper and emptying the MOT. In 10 ms, more than 70% of the MOT atoms leave the volume of the overlapping MOT beams as determined experimentally using the release and recapture method [59]. The ions created by the 813 nm laser are held in the ion trap for various durations either in the presence or in the absence of the MOT cooling light, and are extracted toward the MCP. The results clearly

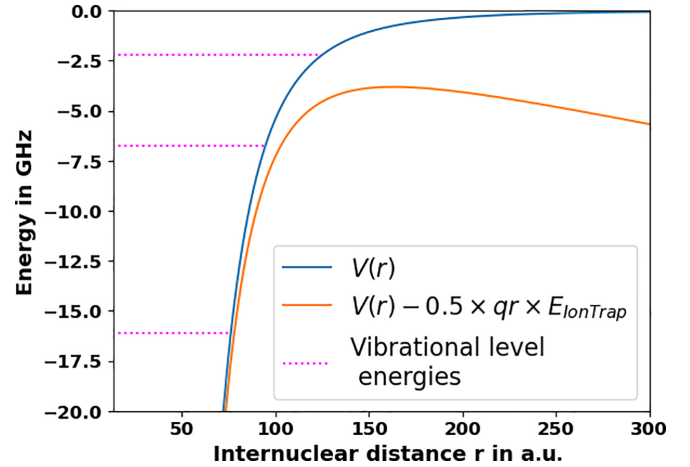


FIG. 6. Modification [20,38] of the $X^2\Sigma_g^+$ PEC[$V(r)$] of the Li_2^+ ion (charge $q = 1$) due to the maximal electric field ($E_{\text{ionTrap}} \sim 30 \text{ V/cm}$) that the molecular ion can be subjected to inside the ion trap, during ion trap operation, when operating the trap in configuration A (see Table I in Supplemental Material [39]). From the figure, we see that only the weakly bound vibrational levels may dissociate via electric field of the trap.

indicate that the molecular ions have a much shorter lifetime in the presence of MOT light, which then contributes to the loss of Li_2^+ [Fig. 5(b)]. We further investigated the presence of long-lived molecular ions in the presence of the MOT light. The pulse width of the 813 nm laser was increased to 500 ms to produce a large number of ions so that, statistically, a sizable fraction of the ions may be generated in low vibrational levels and thus with a low PD rate. The result of the measurements, showing the presence of long-lived Li_2^+ , is illustrated in the inset of Fig. 5(b). We present data only at large holding times because the counting of ions at small holding times is not possible due to MCP saturation. We also observed a similar formation mechanism of Li_2^+ in ^6Li MOT. Signatures of $^6\text{Li}_2^+$ formation were reported earlier in a ^6Li MOT illuminated with a femtosecond laser [60].

From Fig. 5(b), we also observe a rapid decrease in the number of Li_2^+ in going from 10 ms to 1 s holding time even in the absence of MOT light. Since this loss is not due to the trap lifetime, we probe the short timescale dynamics in the absence of MOT light. The measurements, similar to the ones in Fig. 5(b), were made in configuration A that traps both Li^+ and Li_2^+ . We present two measurements, shown in Figs. 5(c) and 5(d): they indicate a change in the ToF histograms at different hold times and signals toward the nonoptical rapid conversion of Li_2^+ to Li^+ . This was further investigated by checking, experimentally and theoretically, for electric field dissociation, ion-ion collisions, and CE with the background Li atoms (see Appendix B). By a process of elimination, we infer that the CE of Li_2^+ with the background Li atoms is the most likely cause for Li^+ formation, in the absence of light. An explicit proof, however, needs to be deferred to future experiments.

Conclusion and outlook. In conclusion, we employed the hybrid trap to probe the AI of colliding $\text{Li}(2P)$ and $\text{Li}(3S)$ atoms and the evolution of the formed molecular ions. We measure large AI cross sections. This motivates further AI

studies with highly excited lithium Rydberg atoms, similar to the case for rubidium [21], and suggests AI to be an active channel in studies employing a resonant excitation. Additionally, a fraction of the Li_2^+ ions are long-lived and expected to be deeply bound. They exhibit immunity to photodissociation at 670 nm. This stability allows for investigations into the interactions of such Li_2^+ ions with MOTs of other atomic species such as K, Cs, and Rb, which operate at wavelengths above 670 nm and at similar intensities. For the purpose of exclusively creating stable, deeply bound Li_2^+ , in the future it will be interesting to search for Li_2 molecular Rydberg states that autoionize only to the deeply bound vibrational levels of Li_2^+ . Finally, our method could be extended for loading ion traps with heteronuclear molecular ions.

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Data availability. There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

Appendix A: Associative ionization rate coefficient. We model the AI as a two-body collision with a cross section defined as σ_{AI} . The AI rate per unit volume V is defined as [27]

$$\begin{aligned} \frac{dZ}{dV} &= n_{2P}(r) \times n_{3S}(r) \times \sigma_{\text{AI}} \times \vartheta \\ &= K_{\text{AI}} \times n_{2P}(r) \times n_{3S}(r). \end{aligned} \quad (1)$$

Here, Z is the AI rate, ϑ is the relative average speed of the reactants, $n_{2P}(r)$ and $n_{3S}(r)$ are, respectively, the $\text{Li}(2P)$ and $\text{Li}(3S)$ atomic densities at a radial distance r from the MOT center, and $K_{\text{AI}} = \langle \sigma_{\text{AI}} \times \vartheta \rangle$ is the rate coefficient for AI. The atomic densities $n_{2P}(r)$ and $n_{3S}(r)$ that share the Gaussian density profile of the MOT are given by the expression

$$n_j(r) = n_j(0) e^{-r^2/2\sigma_{\text{MOT}}^2}, \quad \text{where } j \equiv 2P, 3S. \quad (2)$$

Here, $n_j(0)$ ($j \equiv 2P, 3S$) are the corresponding peak atomic densities and σ_{MOT} is the MOT standard deviation. By measuring σ_{MOT} and the number of atoms, N_{2P} and N_{3S} , in the $\text{Li}(2P)$ and $\text{Li}(3S)$ atomic states, respectively, one can determine the corresponding atomic densities using Eq. (2) and the relation

$$\int_0^\infty n_j(r) dV = n_j(0) \int_0^\infty e^{-r^2/2\sigma_{\text{MOT}}^2} dV = N_j. \quad (3)$$

The AI rate, obtained by integrating Eq. (1), can be expressed as

$$Z = K_{\text{AI}} \int_0^\infty n_{2P}(r) n_{3S}(r) dV. \quad (4)$$

By measuring Z , $n_{2P}(r)$, and $n_{3S}(r)$ and using Eq. (4), K_{AI} can be determined experimentally. For these measurements, the MOT is illuminated by a 813 nm pulse of 10 ms duration. The ions are not trapped but are continuously extracted, by biasing

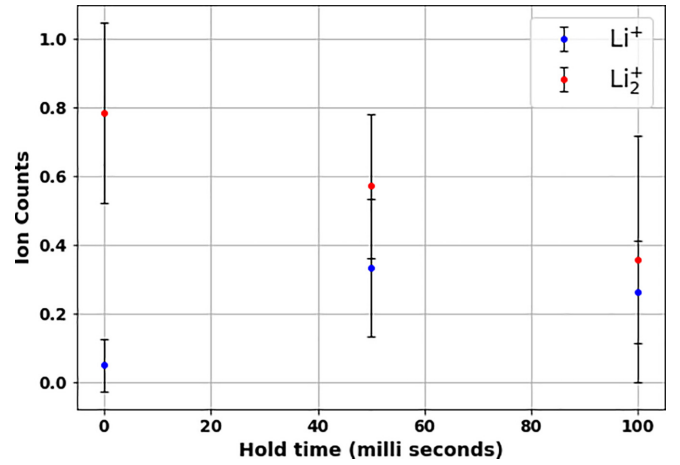


FIG. 7. Evolution of Li_2^+ and Li^+ populations for low number of ions and in the absence of MOT light.

ion trap electrodes appropriately, onto the MCP over the 10 ms time window and are counted. Measurements over 500 such cycles result in an AI rate of $Z = 9.2 (\pm 0.7)$ per 10 ms for steady-state atomic populations of $N_{2P} = 14.9 (\pm 0.3) \times 10^4$ and $N_{3S} = 2.3 (\pm 0.2) \times 10^3$. From this measurement, the value of the AI rate coefficient can be determined to be $K_{\text{AI}} \approx 7.5 (\pm 1.3) \times 10^{-15} \text{ m}^3/\text{s}$. Note that $\sigma_{\text{MOT}} \approx 0.4 \text{ mm}$. The various uncertainties associated with estimating the MOT size are not included in calculating the errors in K_{AI} . However, a 10% error in estimation of σ_{MOT} gives a factor of 2 error in the estimate of K_{AI} . The average speed of atoms for our 500 μK MOT is about 1.23 m/s. This results in an associative ionization cross section of $\sigma_{\text{AI}} \sim 2.2 (\pm 0.4) \times 10^6 a_0^2$. This value is also of similar order of magnitude to the cross section of colliding lithium ion and atom in their ground states [61].

Appendix B: Discussion on the nonoptical fast decay of Li_2^+ ions. From Figs. 4(e) and 5(b)–5(d), there is clear evidence of fast decay of Li_2^+ . This decay channel persists even in the absence of MOT atoms and all laser light. A few mechanisms for the determination of this nonoptical decay channel are discussed below.

The action of the electric field on Li_2^+ . Here, we examine the possibility of the dissociation of Li_2^+ ions in the $X^2\Sigma_g^+$ state either because of the electric field due to the ion trap or because of the high voltage on the grid electrode applied during ion extraction. We present our analysis for configuration A that is suitable for trapping both Li_2^+ and Li^+ ions. The maximum electric field of the ion trap, in configuration A, during ion trap operation is $E_{\text{IonTrap}} \approx 30 \text{ V/cm}$ (details about the ion trap geometry, etc. will be reported in a future publication [22]). As depicted in Fig. 6, in the presence of this electric field, the $X^2\Sigma_g^+$ electronic state of Li_2^+ gets modified [see Eq. (1) in Refs. [20,38]]. As is evident from Fig. 6, all except the least bound vibrational level of Li_2^+ , in the $X^2\Sigma_g^+$ electronic state, are protected against dissociation by the ion trap electric field. Hence, dissociation of Li_2^+ by the ion trap electric field is unlikely to be the reason for the nonoptical fast conversion of Li_2^+ to Li^+ .

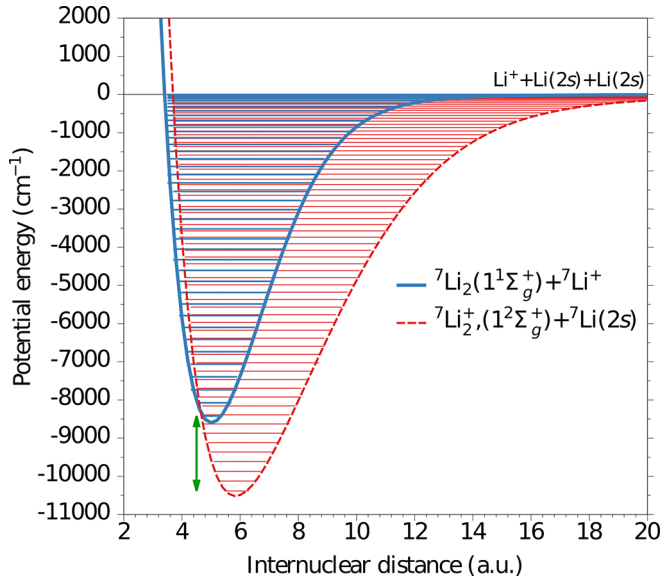


FIG. 8. The ground-state PEC's for the ${}^7\text{Li}_2^+ + {}^7\text{Li}$ system with ${}^7\text{Li}$ placed at infinity (incoming collision channel) and the ${}^7\text{Li}_2 + {}^7\text{Li}^+$ system with ${}^7\text{Li}^+$ placed at infinity (outgoing collision channel) are shown along with the vibrational levels of the respective molecular system (${}^7\text{Li}_2$ in blue and ${}^7\text{Li}_2^+$ in red) [36]. Here, the internuclear distance on the horizontal axis is the bond length of respective molecular systems. At the ion-atom-atom asymptotic limit, these PEC's correlate to ${}^7\text{Li}(2s) + {}^7\text{Li}(2s) + {}^7\text{Li}^+$ [36]. The green vertical line near the minima of the curves highlights the energy difference between the ground vibrational levels of ${}^7\text{Li}_2$ and ${}^7\text{Li}_2^+$, i.e., $\sim -1960\text{cm}^{-1}$, illustrating that the low-lying levels of ${}^7\text{Li}_2^+$ ($v_g < 7$) are well protected against charge exchange.

Likewise, it can be experimentally argued that the electric field of the high voltage on the grid electrode, applied during extraction, is not the cause of the nonoptical conversion of Li_2^+ to Li^+ . This is because the 813 nm generated Li^+ ions respond to the ion trap parametric resonance for Li^+ suggesting that the conversion of Li_2^+ to Li^+ is happening within the ion trap.

Molecular, ion-ion collision-led dissociation. To test this experimentally, we operate the experiment in a regime where less than one Li_2^+ ion is produced in the trap, in each experimental cycle. In this case, the lifetime of trapped Li_2^+ follows the same trend as when a number of ions are created in the trap, during regular operation. These results are

shown in Fig. 7. This eliminates the possibility of molecular ion-ion collisions as the mechanism for the nonoptical decay.

Collision with background atoms emitted by the atomic dispenser. In Fig. 8, the ground-state PEC's for the incoming (${}^7\text{Li}_2^+ + {}^7\text{Li}$) and the outgoing (${}^7\text{Li}_2 + {}^7\text{Li}^+$) collision channels are shown along with the vibrational levels of the respective molecular systems. From the figure, we can infer the possibility of charge exchange (direct [62] and/or Jahn-Teller-induced [36]) between Li_2^+ and a Li atom for that class of Li_2^+ ions whose vibrational levels lie within the overlapping region. Since the initial fast conversion of Li_2^+ to Li^+ happens even in the absence of MOT atoms and MOT light, we consider whether this is due to CE of Li_2^+ with background or dispenser Li atoms.

As a preliminary check, we find that the theoretical Langevin rate for CE is small to explain the initial nonoptical fast conversion of Li_2^+ to $\text{Li}^+ + \text{Li}$. As the pressure in our chamber is measured far away from the ion trap, and we load the MOT by firing a dispenser of Li, it is entirely possible that the local density of the background gas in the vicinity of the ion trap is significantly higher. During CE, if we assume just a swap of charge between Li_2^+ and dispenser-emitted Li atoms (at ≈ 400 K, with a most probable velocity of ≈ 972 m/s), then this will produce Li^+ ions with an energy of about 0.035 eV. Such Li^+ ions will be trapped, and will not lead to a broadening of the ToF signal, because of its low energy. This is consistent with our observations.

The vibrational levels ($v_g < 7$) in the lower-energy range of the Li_2^+ curve are immune to this mechanism because here the charge-exchange process is energetically forbidden. This implies that the lower vibrational states of Li_2^+ ion are protected against charge exchange. They are also immune to photodissociation and electric field dissociation, as argued before, and hence will be long-lived in the trap. This is consistent with the experimental observations in the inset of Fig. 5(b) and the large hold time data of Fig. 4(e), even though we cannot determine the vibrational states of the molecular ion experimentally. Thus, by elimination, CE seems to be the most likely process for the rapid molecular ion loss, which is consistent with experimental observations. That said, an explicit proof of this proposed mechanism needs to be deferred to future experiments. One experimental test could be to create Li_2^+ in the ground vibrational level of the ${}^2\Sigma_g^+$ electronic state and see if these Li_2^+ molecular ions exhibit a nonoptical conversion to Li^+ as observed in our study.

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