

Rydberg Molecules for Ion-Atom Scattering in the Ultracold Regime

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We propose a novel experimental method to extend the investigation of ion-atom collisions from the so far studied cold, essentially classical regime to the ultracold, quantum regime. The key aspect of this method is the use of Rydberg molecules to initialize the ultracold ion-atom scattering event. We exemplify the proposed method with the lithium ion-atom system, for which we present simulations of how the initial Rydberg molecule wave function, freed by photoionization, evolves in the presence of the ion-atom scattering potential. We predict bounds for the ion-atom scattering length from *ab initio* calculations of the interaction potential. We demonstrate that, in the predicted bounds, the scattering length can be experimentally determined from the velocity of the scattered wave packet in the case of ${}^6\text{Li}^+ - {}^6\text{Li}$ and from the molecular ion fraction in the case of ${}^7\text{Li}^+ - {}^7\text{Li}$. The proposed method to utilize Rydberg molecules for ultracold ion-atom scattering, here particularized for the lithium ion-atom system, is readily applicable to other ion-atom systems as well.

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The considerable achievements made in the field of degenerate quantum gases over the past decades rely on the exact understanding and control of interactions between neutral atoms in the ultracold regime [1,2]. Considering the interactions between ions and atoms, substantial work has been done in the cold, but essentially classical regime, deploying hybrid ion-atom traps. These hybrid traps combine a Paul trap for the ion with an optical and/or a magnetic trap for the atoms. Both elastic and inelastic collisions have been studied in these traps for various ion-atom combinations [3–5]. However, the ultracold, quantum regime, i.e., the *S*-wave collision regime, could not be reached with any of these systems (see Fig. 1). Cetina, Grier, and Vuletić showed [17] that by the use of a Paul trap there arises a micromotion-induced limit on the minimum collision energy which can be reached. Only for a combination of a heavy ion with a light atom, e.g., the $\text{Ca}^+ - \text{Li}$ or the $\text{Yb}^+ - \text{Li}$ system, might the *S*-wave collision regime be entered. For both of these ion-atom combinations, collision measurements have recently been carried out in the millikelvin energy range [8,10] which is, however, still in the classical regime. Schaetz and co-workers [18] follow a different path to enter the ultracold regime. To avoid the spurious heating of the ion by the Paul trap, they optically trap the ion, and they are currently working on the simultaneous optical trapping of the ion and the atoms [19].

The generation and characterization of many different types of Rydberg molecules has been an active area of research in the past few years. These molecules consist of a

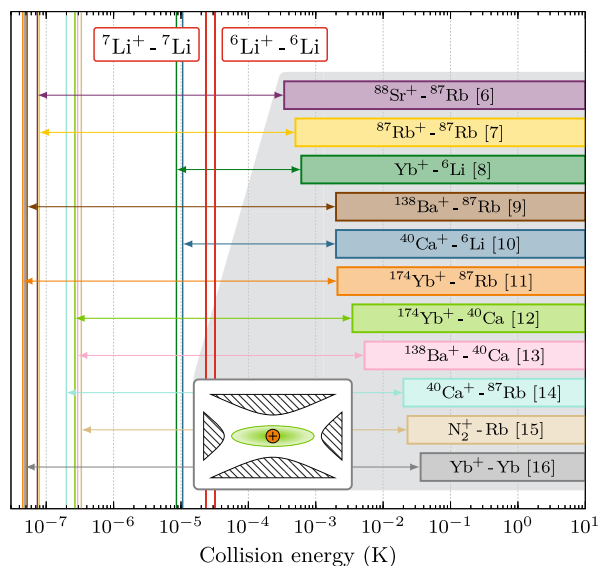


FIG. 1. In the past few years, the ion-atom interaction could be studied down to the millikelvin regime for various ion-atom combinations by the use of hybrid traps, with the ion held in a Paul trap (inset). However, the ultracold, quantum scattering regime could not be reached yet (see color-coded lines for the respective *S*-wave scattering limits E_0). We propose an experimental method to enter the ultracold ion-atom scattering regime using Rydberg molecules. We demonstrate this method with the lithium ion-atom system which features an early onset of the *S*-wave scattering regime due to its small reduced mass.

Rydberg atom and at least one ground state atom which is bound to the Rydberg ionic core at a very large internuclear distance via its attractive interaction with the Rydberg electron [20]. Triplet s -state Rydberg dimers, trimers, tetramers, and pentamers have been observed [21–23], and molecular lifetimes have been measured [24,25]. Furthermore, triplet d -state dimers have been studied [26,27] as well as mixed singlet-triplet dimers [28,29]. Finally, trilobite [30–33] and butterfly [34] molecules have been investigated.

State-of-the-art *ab initio* calculations could determine the interaction potential of light few-electron systems to such a precision that reliable predictions of the scattering length could be made, e.g., for the scattering of two helium atoms, either in their ground state [35] or in the metastable 2^3S_1 state [36]. Accurate estimations of the scattering length could also be given for weakly interacting many-electron systems with a very small reduced mass, e.g., for metastable helium scattering off alkali-metal atoms [37,38]. Precisely predicting the scattering length for heavier systems is very challenging, though.

In this Letter, we propose a novel experimental method to extend the investigation of ion-atom interactions from the hitherto studied cold regime to the unexplored ultracold regime. The key aspect of this method is the unprecedented use of a Rydberg molecule as a tool to initialize an ultracold ion-atom scattering event. This makes a separate trap for the ion, be it a Paul trap or an optical trap, expendable. The proposed method allows for the experimental determination of the ion-atom scattering length and thus provides a very valuable benchmark for its *ab initio* calculation.

The starting point of the proposed procedure is the photoassociation of a single Rydberg molecule in an ultracold, dilute atomic cloud. The Rydberg molecule is then photoionized to start the ultracold ion-atom scattering event between the Rydberg ionic core and the ground state atom; i.e., the initial Rydberg molecule wave function, freed by photoionization, evolves in the presence of the ion-atom scattering potential. Depending on the scattering length, either the entire scattered wave packet is free and dispersively expanding, or it splits into a free part and a bound part, indicating the formation of a molecular ion. The detection of the free ion and/or the molecular ion with a time- and position-sensitive single-ion detector concludes the single ultracold ion-atom scattering event. The frequent repetition of this single scattering event eventually allows for the determination of the ion-atom scattering length.

We exemplify the proposed method to enter the ultracold ion-atom scattering regime with the lithium ion-atom system. It features an early onset of the S -wave scattering regime due to its small reduced mass μ . Its S -wave scattering limit $E_0 = (2\mu^2 C_4)^{-1}$ [16] ($C_4 = 164.2$ a.u. [39]) is approximately 2 orders of magnitude larger than the respective limits for the ion-atom systems so far studied in the millikelvin range, except for the $^{40}\text{Ca}^+-^6\text{Li}$ and the Yb^+-^6Li system (see Fig. 1).

We present an *ab initio* calculation for the interaction potential of the strongly interacting five-electron Li^+-Li system, which is for the first time precise enough to yield usable bounds for the ion-atom scattering length.

Rydberg molecules are key to the proposed method in order to initialize the ultracold ion-atom scattering event. The binding in these molecules is established by the repeated elastic low-energy scattering between the quasi-free Rydberg electron at position \mathbf{r} and the neutral but polarizable ground state atom at position \mathbf{R} relative to the ionic core. Fermi's pseudopotential [40], extended to include p -wave scattering [41], adequately describes this low-energy scattering:

$$\hat{V}_{eA}^T(\mathbf{r}-\mathbf{R}) = 2\pi a_0^T \delta^3(\mathbf{r}-\mathbf{R}) + 6\pi a_1^T \delta^3(\mathbf{r}-\mathbf{R}) \hat{\mathbf{V}} \cdot \hat{\mathbf{V}}, \quad (1)$$

where $a_l^T(k) = -\tan[\delta_l^T(k)]/k^{2l+1}$ is the energy-dependent triplet (T) s -wave ($l=0$) and p -wave ($l=1$) scattering length, respectively, as a function of the respective phase shifts $\delta_l^T(k)$ [42]. The wave number k of the Rydberg electron (the wave number of the ultracold ground state atom is negligible) at position \mathbf{R} is given by the semiclassical approximation $k(R)^2/2 = 1/R - 1/[2(\tilde{n}^*)^2]$, where \tilde{n}^* is the effective principal quantum number of the Rydberg level of interest [20]. The Rydberg molecule Hamiltonian, combining all three binary interactions between the Rydberg electron e , the Rydberg ionic core I , and the ground state atom A , then reads

$$\hat{H}_{AA}(\mathbf{r}, \mathbf{R}) = \hat{H}_{eI}(\mathbf{r}) + \hat{H}_{IA}^{\gg}(\mathbf{R}) + \hat{V}_{eA}^T(\mathbf{r}-\mathbf{R}) \hat{P}^T, \quad (2)$$

where \hat{H}_{eI} includes the spin-orbit coupling [42] and $\hat{H}_{IA}^{\gg}(\mathbf{R}) = \hat{\mathbf{P}}^2/(2\mu_{IA}) - C_4/(2R^4)$ describes the IA interaction at large internuclear distances, with $\hat{\mathbf{P}}$ and μ_{IA} being the momentum and the reduced mass, respectively. $\hat{P}^T = \hat{\mathbf{s}} \cdot \hat{\mathbf{s}} + 3/4$ is the triplet projection operator, with $\hat{\mathbf{s}}$ and $\hat{\mathbf{s}}$ the electronic spin of the Rydberg and the ground state electron, respectively. Applying the Born-Oppenheimer approximation then yields the nuclear Schrödinger equation $[\hat{\mathbf{P}}^2/(2\mu_{IA}) + V_{AA}(R)]\Psi_{AA}(\mathbf{R}) = E_{AA}\Psi_{AA}(\mathbf{R})$ with the spherically symmetric Rydberg molecule potentials V_{AA} , the Rydberg molecule wave functions Ψ_{AA} , and the corresponding binding energies E_{AA} calculated numerically [42]. The Rydberg molecule wave function of interest, $\tilde{\Psi}_{AA}$, is displayed in Fig. 2(a) for both lithium isotopes. It is bound in the $\text{Li}(30s_{1/2})-\text{Li}(2s_{1/2})^3\Sigma$ Rydberg molecule potential \tilde{V}_{AA} , and it is in its rovibrational ground state ($\tilde{v} = \tilde{J} = 0$) [70], thus being spherically symmetric.

For the chosen Rydberg electron principal quantum number $\tilde{n} = 30$, the first excited vibrational state ($v = 1$) is approximately 5 MHz above the ground state, and the first excited rotational state ($J = 1$) is approximately $2\tilde{B} \approx 300$ kHz above the ground state [see Fig. 2(b)], where

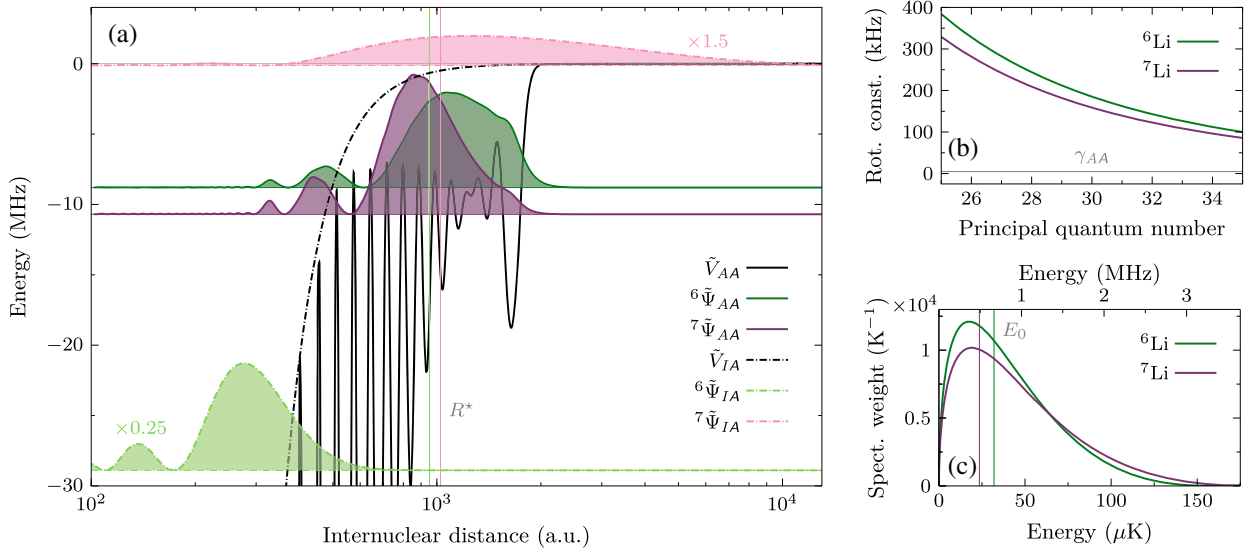


FIG. 2. Using Rydberg molecules to initialize an ultracold ion-atom scattering event, exemplified with lithium. The Rydberg molecule wave function of interest, more precisely, $R^2|\tilde{\Psi}_{AA}(R)|^2$, is shown in (a) for both isotopes. It is bound in the homonuclear $\text{Li}(30s)\text{-Li}(2s)$ potential $\tilde{V}_{AA}(R)$. It is in its spherically symmetric rovibrational ground state ($\tilde{\nu} = \tilde{J} = 0$), which can be experimentally addressed, evident from (b), as the rotational constant is larger than the Rydberg molecule decay linewidth γ_{AA} . Freed by photoionization, the initial Rydberg molecule wave function evolves in the spherically symmetric ion-atom interaction potential $\tilde{V}_{IA}(R)$, with R^* denoting its characteristic radius. Because of angular momentum conservation, only S -wave scattering occurs ($\tilde{J} = 0$) despite the components above E_0 in the Rydberg molecule energy spectrum; see (c). The overlap between $\tilde{\Psi}_{AA}$ and the last bound molecular ion wave function $\tilde{\Psi}_{IA}$ [see (a)] determines the bound fraction in the scattered wave packet.

$B = (2\mu_{IA}r_{cl}^2)^{-1}$ is the rotational constant of the Rydberg molecule with the internuclear distance being approximated by the classical turning point $r_{cl} = 2(n^*)^2$ of the Rydberg electron. Hence, $2\tilde{B}$ is approximately 60 times larger than the typical Rydberg molecule decay linewidth γ_{AA} in a dilute atomic cloud [24,25]. Besides, broadening mechanisms associated with the photoassociation of the Rydberg molecule (Doppler broadening, power broadening, laser linewidth, and finite laser pulse duration) can be made much smaller than $2\tilde{B}$ in an ultracold atomic cloud and with suitable laser parameters. Thus, the rovibrational ground state of the Rydberg molecule of interest can be experimentally addressed. Working with a spin-polarized atomic cloud and appropriate photoassociation laser polarization(s) also justifies neglecting singlet scattering between the Rydberg electron and the ground state atom [42]. Furthermore, focusing down the photoassociation laser(s) allows for the formation of a single Rydberg molecule per atomic cloud by means of the Rydberg blockade [71]. In combination with a dilute atomic cloud, this ensures that after photoionization there is only a single ion-atom scattering event happening at a time.

Photoionization frees the initial Rydberg molecule wave function by removing the Rydberg electron. Choosing a suitable photoionization scheme ensures, first, that the energy imparted onto the ion-atom system in the photoionization process is negligible in comparison with the S -wave scattering limit and, second, that the ionization

process is fast compared to the effective trapping frequency of the Rydberg molecule potential [42]. This makes the photoionization diabatic; i.e., the shape of the initial Rydberg molecule wave function is preserved during ionization. The initial shape $\Psi_{IA}(\mathbf{R}, t = 0)$ of the ion-atom wave packet is thus set for the subsequent ultracold scattering.

The scattering of the initial ion-atom wave packet is then described by the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi_{IA}(\mathbf{R}, t) = \hat{H}_{IA}(\mathbf{R})\Psi_{IA}(\mathbf{R}, t), \quad (3)$$

where \hat{H}_{IA} is the nuclear Hamiltonian of the molecular ion [42], containing the spherically symmetric ground state molecular ion potential $\tilde{V}_{IA}(R)$. We carried out *ab initio* calculations to determine \tilde{V}_{IA} [42] which yielded a potential depth $D_e = 10468 \text{ cm}^{-1}$ with a conservatively estimated error of $\pm 10 \text{ cm}^{-1}$, thus in excellent agreement with the measured value of $(10464 \pm 6) \text{ cm}^{-1}$ [72]. For our molecular ion potential with $D_e = 10468 \text{ cm}^{-1}$, we calculate a ${}^6\text{Li}^+{}^6\text{Li}$ ion-atom doublet S -wave scattering length of $\mathcal{A}_6 = -1014 \text{ a.u.}$, with bounds $(\mathcal{A}_6^-; \mathcal{A}_6^+) = (-778; -1294) \text{ a.u.}$ corresponding to potentials scaled by (0.999; 1.001), respectively, reflecting our accuracy of 0.1% in D_e . For ${}^7\text{Li}^+{}^7\text{Li}$ we determine the scattering length \mathcal{A}_7 to be 7162 a.u. , with bounds of (107825; 3664) a.u. Hence, the

scattering lengths differ considerably for the two lithium isotopes, with the magnitude of \mathcal{A}_6 being comparable to the characteristic radius of ion-atom interaction $R_6^* = \sqrt{\mu_{IA}C_4} = 949$ a.u. [11], whereas \mathcal{A}_7 is approximately 7 times $R_7^* = 1025$ a.u. This reflects also in the markedly dissimilar bounds we predict for the two scattering lengths, with tight bounds on \mathcal{A}_6 , while \mathcal{A}_7 is extremely sensitive to changes of the molecular ion potential. Correspondingly, the last bound molecular ion wave function $\tilde{\Psi}_{IA}$ has a large extension and accordingly a small binding energy, whereas $\tilde{\Psi}_{IA}$ is deeply bound at comparatively small internuclear distances, as can be seen in Fig. 2(a) (note the logarithmic scale for the internuclear distance). The vibrational molecular ion wave functions $\Psi_{IA}^v(\mathbf{R})$ and corresponding eigenenergies E_{IA}^v , with $\hat{H}_{IA}(\mathbf{R})\Psi_{IA}^v(\mathbf{R}) = E_{IA}^v\Psi_{IA}^v(\mathbf{R})$, are then used to express the scattered ion-atom wave packet in the form

$$\Psi_{IA}(\mathbf{R}, t) = \sum_v \pi_v e^{-iE_{IA}^v t} \Psi_{IA}^v(\mathbf{R}), \quad (4)$$

where the sum runs over bound ($E_{IA}^v < 0$) and scattering states ($E_{IA}^v > 0$) and $\pi_v = \langle \Psi_{IA}(\mathbf{R}, t=0) | \Psi_{IA}^v(\mathbf{R}) \rangle$ is the projection of the initial ion-atom wave packet on the vibrational state Ψ_{IA}^v . With the ion-atom interaction potential $\tilde{V}_{IA}(R)$ being spherically symmetric, and without an electric field \mathcal{E} present, the initial orbital angular momentum J of the ion-atom wave packet, given by the Rydberg molecule wave function, is conserved during scattering; i.e., scattering channels for different partial waves do not couple. Consequently, the molecular ion wave functions used to express the scattered wave packet in Eq. (4) have this very orbital angular momentum J . For the case studied in this Letter, where the initial Rydberg molecule wave function is in its spherically symmetric rotational ground state ($\tilde{J} = 0$), the orbital angular momentum conservation implies that only S -wave ion-atom scattering can occur despite the fact that $\tilde{\Psi}_{AA}$ has an energy spectrum with components above the S -wave scattering limit, as is illustrated in Fig. 2(c). The effect of electric stray fields $\mathcal{E}_{\text{stray}}$ is discussed in Supplemental Material [42].

We conducted ion-atom scattering calculations for both lithium isotopes, with $\Psi_{IA}(\mathbf{R}, t=0)$ given by the respective Rydberg molecule wave function $\tilde{\Psi}_{AA}$ displayed in Fig. 2(a), and for the respective ion-atom scattering length tuned over a wide range [42]. These calculations revealed two different scattering regimes depending on the scattering length \mathcal{A} . For positive scattering lengths, exemplarily illustrated in Fig. 3(a) for ${}^6\text{Li}^+ - {}^6\text{Li}$ scattering with a scattering length of $+R_6^*$, the scattered wave packet splits into a free, dispersively expanding shell and a bound shell, the position and shape of which reveal that the last bound molecular ion state has been formed. Both shells are spherically symmetric and thus demonstrate that only

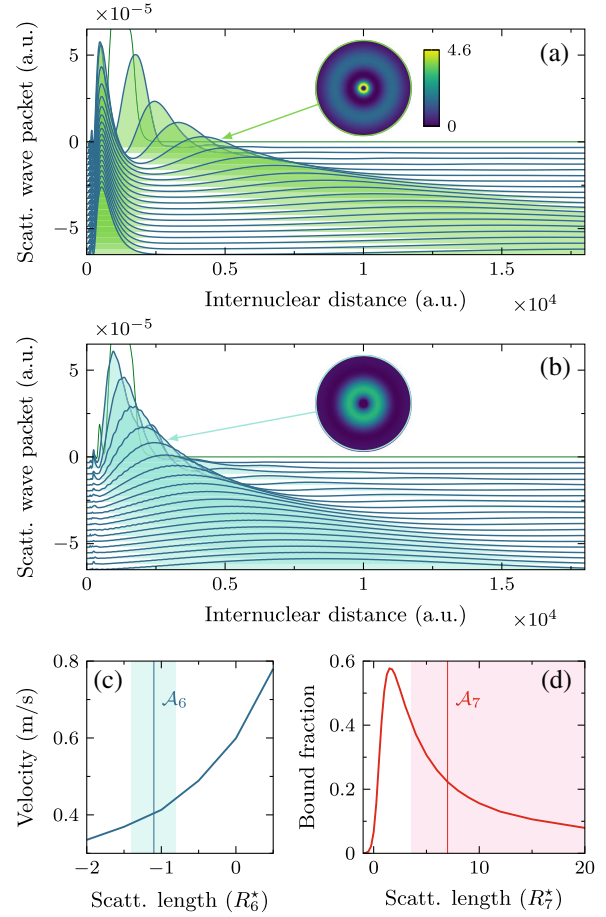


FIG. 3. Ultracold lithium ion-atom scattering processes, initialized with Rydberg molecules, for different scattering lengths \mathcal{A} . For $\mathcal{A} > 0$ [demonstrated in (a) for ${}^6\text{Li}^+ - {}^6\text{Li}$ scattering with $\mathcal{A} = +R_6^*$], the scattered wave packet splits into a free, expanding shell and a bound shell, indicating molecular ion formation. For $\mathcal{A} < 0$ [exemplified in (b) for $\mathcal{A} = -R_6^*$], the entire scattered wave packet is free. In (a) and (b), the time evolution of the scattered wave packet $R^2|\Psi_{IA}(R, t)|^2$ is shown from $t = 0$ [$\Psi_{IA}(t=0) = \tilde{\Psi}_{AA}$, unfilled curve, vertical axis applies] to $1 \mu\text{s}$ in steps of 50 ns (top to bottom, curves shifted by -3.25×10^{-6} a.u. each). The insets demonstrate the S -wave character of the scattered wave packet [R extension of 7×10^3 a.u., same color scale in (a) and (b)]. For $\mathcal{A} < 0$ ($\mathcal{A} > 0$), the shell expansion velocity ζ (the bound fraction b) is a sensitive quantity to determine the scattering length; see (c) and (d), where also the scattering lengths $\mathcal{A}_{6,7}$ from our *ab initio* calculations are indicated (vertical lines with the shaded areas marking the bounds).

S -wave scattering occurs. For negative scattering lengths, the entire scattered wave packet is free as is exemplarily shown in Fig. 3(b) for ${}^6\text{Li}^+ - {}^6\text{Li}$ scattering with a scattering length of $-R_6^*$. This is due to the negligible overlap between the initial Rydberg molecule wave function and the last bound molecular ion wave function, as can be seen in Fig. 2(a) for the example of $\tilde{\Psi}_{AA}$ and $\tilde{\Psi}_{IA}$ with $\mathcal{A}_6 = -1.1R_6^*$. In the regime of negative scattering lengths, the velocity ζ with

which the maximum of the expanding shell moves is a sensitive quantity to determine the scattering length, as can be seen from Fig. 3(c). With our predicted bounds on \mathcal{A}_6 , the ${}^6\text{Li}^+{}^6\text{Li}$ scattering falls into this regime. For positive scattering lengths, the bound fraction b of the total scattered ion-atom wave packet can be used to precisely determine the scattering length, as is demonstrated in Fig. 3(d) for ${}^7\text{Li}^+{}^7\text{Li}$ scattering, falling in this regime according to our scattering length calculations.

To experimentally measure the expansion velocity ζ , the freely moving scattered ion of a single ultracold scattering event is imaged onto a time- and position-sensitive single-ion detector. After many repetitions of this single scattering event, the scattered ion-atom wave packet can eventually be reconstructed, either in momentum space when, e.g., using a MOTRIMS [73] or VMI [74] apparatus or in real space when employing an ion microscope for imaging. Given the submicron resolution of these ion microscopes [75,76], an evolution time in the microsecond range is sufficient to resolve the shape of the scattered wave packet. The bound fraction b can be measured in time of flight where the molecular ions Li_2^+ separate from the lighter free Li^+ ions. For guiding the ions onto the detector, a suitably small extraction electric field has to be used not to dissociate the weakly bound molecular ions.

The presented experimental method to use Rydberg molecules for the investigation of ultracold ion-atom scattering, particularized for the lithium ion-atom system in this Letter, is readily applicable to other ion-atom systems, e.g., to homo- or heteronuclear alkali or alkaline earth ion-atom systems for which Rydberg molecules can be formed [50,77,78]. In such a manner, the *ab initio* calculations of ion-atom scattering lengths could be benchmarked for increasingly complicated systems. Furthermore, having the ion-atom scattering lengths precisely determined with the proposed two-body scattering experiment would immediately allow for a more faithful and accurate description of the many-body, polaronic properties of an ion impurity immersed in an atomic quantum gas [79–83]. Finally, keeping the Rydberg electron as a spectator and Faraday cage for the ion-atom collision [84–88] might be possible also in the ultracold regime using circular Rydberg states [89].

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