

Dielectronic Recombination of Ground-State and Metastable Li^+ Ions

A. A. Saghir,¹ J. Linkemann,¹ M. Schmitt,¹ D. Schwalm,¹ A. Wolf,¹ T. Bartsch,² A. Hoffknecht,² A. Müller,²
W. G. Graham,³ A. D. Price,⁴ N. R. Badnell,⁴ T. W. Gorczyca,⁵ J. A. Tanis⁵

¹*Max-Planck-Institut für Kernphysik, Heidelberg, and Physikalisches Institut der Universität, D-69029 Heidelberg, Germany*

²*Institut für Kernphysik, Strahlencentrum der Justus-Liebig-Universität, D-35392 Giessen, Germany*

³*Department of Pure and Applied Physics, Queen's University, Belfast BT7 1NN, Northern Ireland*

⁴*Department of Physics and Applied Physics, University of Strathclyde, Glasgow G4 0NG, United Kingdom*

⁵*Department of Physics, Western Michigan University, Kalamazoo, Michigan 49008, USA*

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Dielectronic recombination has been investigated for $\Delta n = 1$ resonances of ground-state $\text{Li}^+(1s^2)$ and for $\Delta n = 0$ resonances of metastable $\text{Li}^+(1s2s^3S)$. The ground-state spectrum shows three prominent transitions between 53 and 64 eV, while the metastable spectrum exhibits many transitions with energies < 3.2 eV. Reasonably good agreement of R-matrix, LS coupling calculations with the measured recombination rate coefficient is obtained. The time dependence of the recombination rate yields a radiative lifetime of 52.2 ± 5.0 s for the 2^3S level of Li^+ .

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In collisions between ions and electrons, recombination [1] can occur either by radiative recombination (RR) (inverse of the photoelectric effect), or by dielectronic recombination (DR). This process starts by the resonant capture of a free electron, mediated by its interaction with a bound electron (inverse of an Auger transition), and then proceeds by a radiative transition to a stable recombined system. Dielectronic recombination is of fundamental interest because it gives insight into electron correlation, and of applied interest for the understanding of astrophysical and laboratory plasmas. Extensive experimental studies providing significant tests of the theory [1] have been conducted for H-like, He-like, and Li-like ions heavier than about carbon. For such systems, perturbative techniques can be successfully used in theoretical calculations because the electron–electron interaction is relatively weak compared to the electron–nucleus interaction. In contrast, for lighter ions perturbative techniques cease to produce results at the same level of accuracy. Hence, high quality data for light systems are required to test the reliability of theoretical predictions.

For the lightest H-like ion, He^+ , DR was studied previously by three groups [2–4] with successively higher energy resolution, and through a consequent feedback between experiment and theory good mutual agreement could be obtained. For the lightest He-like ion, Li^+ , the two-electron configuration places additional constraints on the theory of RR and DR. Moreover, the existence of relatively long-lived metastable $1s2s^1S$ and $1s2s^3S$ states with natural lifetimes of about 0.5 ms and 50 s, respectively, requires recombination for both the ground state and the metastable state (especially the long-lived

triplet state) to be understood. To date, only low-resolution DR measurements for Li^+ have been carried out [5]; the integrated ground-state and metastable recombination rates could be extracted, but more detailed comparisons between experiment and theory for specific excited-state configurations were not possible.

Here we report a high-resolution investigation of DR in Li^+ . Individual intermediate-excited state configurations contributing to DR could be resolved for ground-state $\text{Li}^+(1s^2^1S)$ ions, where DR occurs via $\Delta n = 1$ resonances ($1s^2 + e \rightarrow 1s2ln'l'$) at relative electron–ion energies of 53–64 eV, as well as for metastable $\text{Li}^+(1s2s^3S)$ ions which give rise to $\Delta n = 0$ resonances ($1s2s + e \rightarrow 1s2ln'l'$) below 3.2 eV. The metastable spectrum is found to be particularly rich with many closely-spaced transitions. The time dependence of DR from metastable ions was also used to determine the radiative lifetime of the 2^3S level. Moreover, RR has been observed for relative electron–ion energies close to zero.

At the Heidelberg ion-storage ring and electron cooler facility (TSR) a beam of 13.3 MeV $^7\text{Li}^+$ ions was produced in a tandem accelerator and injected into the ring. Using multiturn stacking injection, which lasted about 0.1 ms, a typical circulating ion current of 5 μA was obtained. While stored, the ions passed through the collinear electron beam of the electron cooler. First, by matching the electron and ion velocities at a laboratory electron energy of 1.04 keV (‘cooling energy’) the ion beam was phase-space cooled to low (~ 0.3 mrad) divergence and $\sim 10^{-4}$ relative longitudinal momentum spread within about 10 s. Recombination of the Li^+ ions was then measured as a function of the energy E corresponding to the average relative velocity between the electrons and the ions (referred to as relative energy) by detuning the laboratory electron energy from the cooling energy by a variable amount. In the measurements, the relative energy was alternately set (on a time scale of milliseconds) first to $E \approx 140$ eV to determine the background recombination rate, then to a desired value in the energy ranges of ground- or metastable-state recombination, and then back to the cooling energy.

Those ions which recombined to form neutral Li are no longer deflected by the storage ring dipole magnet following the electron cooler, and can thus be counted with a surface-barrier detector behind this magnet. Field ion-

ization in the motional electric field experienced by the fast Li atoms in the dipole magnet introduces a principal quantum number cutoff [6] of $n_c = 7$ so that atoms reaching the magnet in states with $n > n_c$ are not detected.

The energy resolution was determined by the electron temperatures of $kT_{\perp} = 18$ meV and $kT_{\parallel} = 0.2$ meV [7], which resulted in a FWHM energy spread of ~ 0.02 eV in the electron-ion center-of-mass (c.m.) frame at $E \lesssim 0.2$ eV, increasing to ~ 0.4 eV at $E = 60$ eV. The electron current was 35 mA in the lower and 60 mA in the upper energy range, respectively, corresponding to electron densities n_e of 5 and 8×10^6 cm $^{-3}$.

Recombination was measured in a time interval of 12–70 s after each injection, the total cycle time being close to the $1/e$ storage lifetime of ~ 60 s determined by the ground-state stripping rate in the rest gas, λ_g^s . Measurements were repeated for successive injections over several hours. From earlier experiments [8] employing laser cooling of ${}^7\text{Li}^+$ ions on the 2^3S - 2^3P transition, a substantial initial fraction $f_m^0 \approx 0.1$ – 0.3 of metastable 2^3S ions is known to exist in the TSR under these running conditions. The unknown initial fraction of metastable singlet (2^1S) ions is expected to have decayed by the time the data were recorded. The decay constant of the triplet (2^3S) metastable Li^+ ions stored in the ring was $\sim (19\text{ s})^{-1}$, given mainly by the sum of the rest-gas stripping rate λ_m^s and the radiative decay rate λ_{mg}^{γ} of the metastable ions. Stripping of 2^3S ions is expected [9] to occur faster than that of 1^1S ions because of the lower ionization potential of the triplet state. The energy region of metastable DR ($E = 0$ – 3.5 eV) was scanned in the two time intervals of 12–42 and 54–70 s after injection, while the ground-state DR spectrum ($E = 52$ – 64 eV) was measured between 42–54 s. Details concerning the determination of the relative energy and the c.m. electron energy distribution can be found in Ref. [10]. The accuracy of the relative-energy scale is estimated to be ± 0.02 eV at 1 eV and ± 0.09 at 60 eV.

With the recombination rate coefficients $\alpha_g(E)$ and $\alpha_m(E)$ for ground and metastable ions, respectively, and the metastable ion fraction $f_m(t)$, the measured, background subtracted recombination rate is given by

$$R(E, t) = \eta\gamma^{-2} \cdot N_i(t) \cdot n_e \times \left[(1 - f_m(t))\alpha_g(E) + f_m(t)\alpha_m(E) \right], \quad (1)$$

where $\gamma = 1.002$ is the Lorentz factor due to the relativistic transformation between the ion rest frame and the laboratory frame, and η the ratio between the interaction length (1.5 m) and the ring circumference (55.4 m). The number of stored ions $N_i(t)$ was determined from the circulating beam current measured by a non-destructive current probe as well as by counting events at a beam profile monitor [11].

In addition to the energy scans, the time dependence of the recombination rate on selected DR peaks was measured, performing a sequence of fast scans

over resonances at $E = 0.14$ and 1.2 eV (representing mainly metastable-ion DR) and 54 eV (representing only ground-state DR); simultaneously the beam current signals from the current probe and the beam profile monitor as well as the count rates at $E = 0$ and at $E = 140$ eV were recorded. The scan sequence was repeated 25 times after each injection, covering storage times of 12–75 s. The integrated count rates were fitted jointly as functions of time by two-component exponential decay curves, varying the two decay constants common to all curves and appropriate separate amplitudes. Under the assumption (justified below) that collisional re-feeding of the metastable state by rest gas collisions can be neglected, the two resulting time constants are $\lambda_1 = \lambda_g^s$ and $\lambda_2 = \lambda_m^s + \lambda_{mg}^q + \lambda_{mg}^{\gamma} + \lambda_m^e$, where λ_{mg}^q denotes the collisional quenching rate and λ_m^e is the electron impact ionization rate [12] of metastable ions in the electron cooler occurring while the relative energy is above the 2^3S ionization threshold (the same effect for ground-state ions is negligible). Measurements of the time variation at five residual gas pressures differing by factors of up to ~ 3 yielded for $\lambda_{1,2}$ the results shown in Fig. 1. As λ_g^s , λ_m^s , and λ_{mg}^q all vary proportional to the rest gas pressure, $(\lambda_m^s + \lambda_{mg}^q)/\lambda_g^s$ can be deduced from the slope of the straight line through these data, while the rest-gas independent decay rate $\lambda_{mg}^{\gamma} + \lambda_m^e$ of the metastable state follows from linear extrapolation to $\lambda_1 = 0$. After subtraction of the estimated [12] electron impact ionization rate of $\lambda_m^e = 0.003 \pm 0.001$ s $^{-1}$ the radiative decay rate of $\lambda_{mg}^{\gamma} = 0.0191 \pm 0.0018$ s $^{-1}$ is obtained, which corresponds to a natural lifetime of $\tau_{M1} = 52.2 \pm 5.0$ s (1σ error) for the 2^3S level. This result matches well the existing theoretical predictions [13,14] of 49.04–49.14 s as well as the only previous experimental result of $\tau_{M1} = 58.6 \pm 12.9$ s (2σ error) [15]. The fact that the slope of λ_2 vs. λ_1 lies close to the expected ratio of the metastable and ground-state rest-gas stripping rates (~ 2) [9] indicates that the collisional quenching rate was small.

After normalization to the ion number $N_i(t)$ the time-dependent rate in the 54-eV peak is proportional to $1 - f_m(t)$ [see Eq. (1)], while the rates in the 0.14- and 1.2-eV peaks dominantly vary as $f_m(t)$ with a small additional contribution from ground-state RR that could be estimated. Fits to the normalized rates in the 54-eV peak yielded only rather inaccurate results for the initial metastable fraction $f_m(0) = f_m^0$, scattering between 0.1 and 0.4, because the change of the ground-state fraction $1 - f_m(t)$ during the measuring time was only slightly larger than the statistical counting errors. Corresponding fits to the low- E peaks (focusing on the signal decay at longer storage times) allowed the rate of collisional re-feeding of the 2^3S state to be estimated to be < 0.02 of the ground-state stripping rate λ_g^s , justifying the assumption made above within the statistical error limits.

The rates $R(E, t)$ were converted to the experimental rate coefficients $\alpha_g(E)$ and $\alpha_m(E)$ using Eq. (1); appropriate rate equations together with the measured time constants $\lambda_{1,2}$ yielded the functional dependence $f_m(t)$.

In the low energy range (0–3.5 eV) the measured rates contain contributions to DR and to RR from metastable ions [$\alpha_m(E)$] and to RR from ground-state ions [$\alpha_g(E)$]. They were extracted separately combining the data from the two storage time intervals in which this energy region was scanned. The experimental recombination rate coefficient $\alpha_m(E)$ for metastable Li^+ ions is shown in Fig. 2. Also shown is the theoretical rate coefficient (see below) for both DR and RR convoluted with the experimental electron velocity distribution. The intrinsic determination of the metastable fraction being too inaccurate, it was set to $f_m^0 = 0.19$, which yields the best agreement of the data between 0.25 and 0.35 eV (see bottom part of figure) with the theoretical prediction. Thus, f_m^0 is adjusted to fit the calculated *non-resonant* (RR) rate of metastable Li^+ . Different values of f_m^0 would essentially scale the experimental result for $\alpha_m(E)$ as $\propto 1/f_m^0$. The value of $f_m^0 = 0.19$ is compatible with the observed time dependences, as well as with the values estimated from earlier laser cooling experiments [8]. The systematic error in the normalization to the ion and electron beam intensity is estimated to $\pm 20\%$; however, in view of the uncertainty in f_m^0 we attribute an overall systematic error of $\pm 50\%$ to $\alpha_m(E)$. The resulting smooth ground-state RR rate coefficient α_g reaches a value of $(2 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at near-zero relative energy and drops to $(2 \pm 1) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at $E = 0.3 \text{ eV}$.

In the high energy range (52–65 eV) only $\Delta n = 1$ DR of ground-state ions occurs, the contribution from the RR of metastable and ground-state ions being negligible. ($\Delta n = 1$ DR of metastable Li^+ ions, leading to triply excited Li, lies in different energy regions not scanned in this experiment.) The DR rate coefficient $\alpha_g(E)$ for ground-state Li^+ ions is shown in Fig. 3. The uncertainty in f_m^0 here yields only a small contribution to the systematic error since the metastable fraction at the time of measurement is already down to $\lesssim 0.04$. Hence, a systematic error of $\pm 20\%$ is estimated for $\alpha_g(E)$.

To obtain the theoretical rate coefficients shown in Figs. 2 and 3 unified photorecombination cross sections representing both DR and RR were computed in LS coupling using a radiation damped R-matrix approach [16,17]. In fact, this case is one of the few where damping is negligible [18], and we obtained the same results by applying detailed balance to undamped R-matrix photoionization cross sections. To compare the calculations with experiment, contributions to DR where one of the electrons occupies a configuration with $n' > n_c = 7$ were excluded from the calculations. The $\Delta n = 0$ DR spectrum of metastable Li^+ ions (Fig. 2) is dominated by n' -manifolds converging to the $2^3S\text{-}2^1P$ excitation threshold at 3.2 eV [configurations $1s2p(^1P)n'l'$]. At low energies terms of the configuration $1s2p(^3P)3l'$ also appear. There is good agreement between theory and experiment up to 0.6 eV, although the theoretical line energies seem to be too high by $\sim 0.03 \text{ eV}$ and the double structure of the peak at 0.14 eV is not reproduced. At higher energies the theory appears to overestimate the DR cross section

significantly, but still yields a reasonable representation of the general spectral shape.

It appears that with $n_c = 7$ we do not account for the recombination rate observed above 3 eV. This is probably due to Li atoms formed with $n > n_c$, cascading to lower n states during the time-of-flight (0.3 μs) prior to the dipole magnets. Furthermore, the sharp cutoff n_c represents only an approximate description of the field ionization process [6]. Particularly large discrepancies between theory and experiment occur above the $2^3S\text{-}2^3P$ excitation threshold (2.28 eV). Here, states with high angular momentum $l' \geq 3$ strongly contribute to the calculated DR rate, as demonstrated by eliminating these states from the calculation (lower, dashed curve in Fig. 2). Using this l cutoff brings the calculated DR rate much closer in magnitude to the experiment. The possibility that Li atoms in high l states (formed by radiative stabilization of high- l resonances) suffer field ionization even below the cutoff n_c can probably be ruled out. A possible experimental explanation for these discrepancies could arise from stray electric fields in the interaction region, estimated to be $\lesssim 3 \text{ V/cm}$; the DR rate above $\sim 1.9 \text{ eV}$ is reduced by autoionization into additional open continua ($1s2s^1S$, $1s2p^3P$) and, as remains to be verified in detail, high- l resonances may assume larger autoionization rates than calculated through l -mixing in the stray electric fields.

Regarding the ground-state DR (Fig. 3) experiment and theory are in good agreement for the $1s2l2l'$ configurations near 54 and 56 eV. These terms are well known from ion–atom collision [19,20] and photoionization studies [21,22]. Along the $1s2p(^1P)n'l'$ series one higher resonance, probably from $1s2p(^1P)3l'$, is observed near 60 eV, but higher series members apparently are reduced by autoionization into the $1s2l$ continua. Near 60 eV the energy-integrated theoretical rate coefficient, representing several unresolved DR resonances, exceeds the experimental value (apparently a single resonance) by about a factor of 3. Also, the calculations predict a higher peak near 62 eV due to Rydberg states with $n = 4\text{--}7$.

In summary, Li^+ ions with a strong population of the long-lived 2^3S state were stored for times on the order of the natural lifetime of the metastable level. This lifetime was determined with an error of $\pm 10\%$, confirming the theoretical predictions. Experimental DR rate coefficients were obtained separately for the metastable and the ground state. DR from the 2^3S ions shows a rich spectrum of lines from doubly excited, higher angular momenta configurations of Li that cannot be reached by photoionization from the Li ground state and have not been observed before; their description presents a significant and important challenge to the theory of this fundamental two-electron system. An R-matrix calculation reproduces the spectral shape reasonably well. The ground-state DR spectrum shows three prominent and several weaker lines at energies of 54–62 eV, and there is reasonable agreement with theoretical calculations except for lines near the $1s2l$ excitation thresholds

(> 60 eV).

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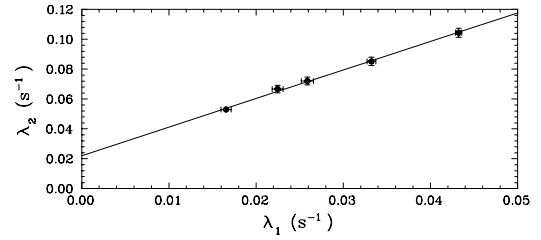


FIG. 1. Decay constants representing the total decay rates λ_1 of ground-state and λ_2 of metastable Li^+ ions, as measured for five residual gas pressures. Extrapolation to $\lambda_1 = 0$ (corresponding to vanishing pressure) yields $\lambda_{mg}^g + \lambda_m^e = 0.0221 \pm 0.0015 \text{ s}^{-1}$.

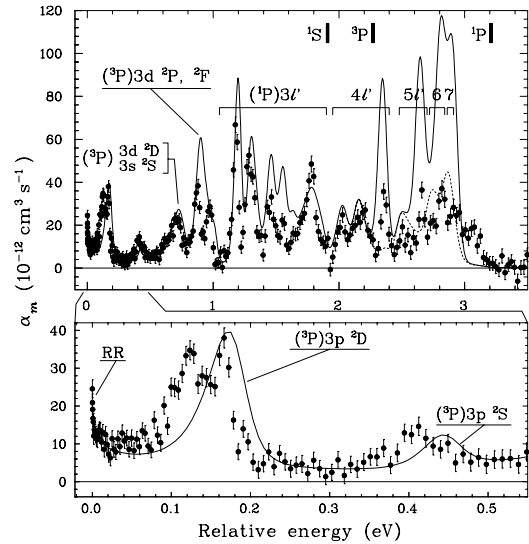


FIG. 2. Recombination rate coefficient $\alpha_m(E)$ for metastable Li^+ ($1s2s^3S$) ions. Dots: experimental data, obtained assuming an initial metastable fraction of $f_m^0 = 0.19$. Full line: theory for $n_c = 7$; labels refer to configurations $1s2p(^{1,3}P)n'l'$ and to excitation thresholds from the 2^3S state. Dashed line: theory omitting all states with $l' \geq 3$.

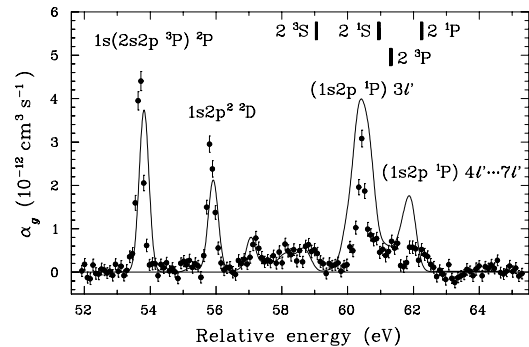


FIG. 3. Dielectronic recombination rate coefficient $\alpha_g(E)$ for ground-state Li^+ ($1s^2$) ions. Dots: experimental data; line: theory for $n_c = 7$. Excitation thresholds from the 1^1S state are indicated.