Candidate for Laser Cooling of a Negative Ion: Observations of Bound-Bound Transitions in La^-

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Despite the tremendous advances in laser cooling of neutral atoms and positive ions, no negatively charged ion has been directly laser cooled. The negative ion of lanthanum, La^-, has been proposed as the best candidate for laser cooling of any atomic anion [S. M. O'Malley and D. R. Beck, Phys. Rev. A 81, 032503 (2010)]. Tunable infrared laser photodetachment spectroscopy is used to measure the bound-state structure of La^-, revealing a spectrum of unprecedented richness with multiple bound-bound electric dipole transitions. The potential laser-cooling transition ($^3F_2^e \rightarrow {}^3D_1^o$) is identified and its excitation energy is measured. The results confirm that La^- is a very promising negative ion for laser-cooling applications.

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Laser cooling of neutral atoms and positive ions has revolutionized the ability to control and manipulate matter on the atomic scale, enabling important advances in Bose-Einstein condensation, precision spectroscopy, atom interferometry, and tests of fundamental symmetries [1–3]. However, laser cooling has not yet been achieved for *negative* ions. The challenge for negative ions is fundamental to their nature. In sharp contrast to neutral atoms and positive ions, which have an infinite number of bound states, atomic negative ions typically have only a single bound-state configuration [4,5]. Therefore, the cycling transition between two bound states required for laser cooling is not available for most negative ions. Finding even one negative ion with a structure favorable for efficient laser cooling could open the previously inaccessible ultracold regime for effectively *all* negatively charged species through collisional sympathetic cooling [6,7]. A particularly important proposed application is to use laser-cooled negative ions to sympathetically cool antiprotons in the production of ultracold antihydrogen for gravitational tests of antimatter [6,8].

While laser cooling of positive ions has become a widespread technique [9], laser cooling of negative ions presents additional challenges [6,10]. First, and foremost, negative ions that possess bound states of opposite parity are exceedingly rare. Electric dipole transitions between bound states have been previously observed for only two atomic negative ions: Os^- [11–13] and Ce^- [14,15]. However, neither of these ions is ideal for laser cooling, because the transitions are spin forbidden (thus weak) and the upper states decay to multiple metastable lower states, requiring repumping out of dark states. In contrast, unique properties of the negative ion of lanthanum (La^-) make it perhaps the best candidate among all negative ions for efficient laser cooling [7,16].

La^- was predicted to have multiple bound states of opposite parity by early theoretical studies [17–19]. More recently, detailed relativistic configuration-interaction calculations by O'Malley and Beck [20] indicated that La^- has 7 even-parity bound states ($[Xe]5d^26s^2$) and 8 odd-parity bound states ($[Xe]5d6s^26p$), with ground state ($5d^26s^2\,{}^3F_2^e$) bound by 545 meV. La^- has been experimentally investigated with laser photoelectron energy spectroscopy by Covington *et al.* [21], who reported that the ground state is bound by 470(20) meV with at least one excited state bound by 170(20) meV.

Many electric dipole transitions are theoretically predicted between bound states of La^- via $5d \rightarrow 6p$ or $6p \rightarrow 5d$ excitations [7]. The transition from the ($5d^26s^2\,{}^3F_2^e$) ground state to the ($5d6s^26p\,{}^3D_1^o$) excited state at a calculated excitation energy of 337 meV has been proposed by O'Malley and Beck as the best candidate for laser cooling based on its favorable transition strength and decay branching relative to the best previously identified option of Os^- [7]. The calculated Einstein A coefficient for the spin-allowed La^- $^3F_2^e \rightarrow {}^3D_1^o$ transition (2.9×10^4 s^{-1} [7]) is almost 2 orders of magnitude larger than that measured for the spin-forbidden Os^- $^4F_{9/2}^e \rightarrow {}^6D_{9/2}^o$ transition ($\sim$330 s^{-1} [12]), which would make laser cooling faster. Furthermore, the calculated photodetachment cross sections from the upper states of Os^- and La^- are comparable [16], therefore, the stronger transition in La^- should also lead to reduced loss of ions due to photodetachment. In addition, the upper state in the La^- transition is calculated to decay almost completely back to the initial lower state (99.98% [7]), possibly eliminating the need for repumping out of dark states.

The present study was designed to map out the bound-state structure of La^-, providing the first experimental information on its complex optical spectrum and initial evaluation of its suitability for laser cooling. Tunable infrared laser spectroscopy was used to measure the photodetachment spectrum of La^- revealing a number of

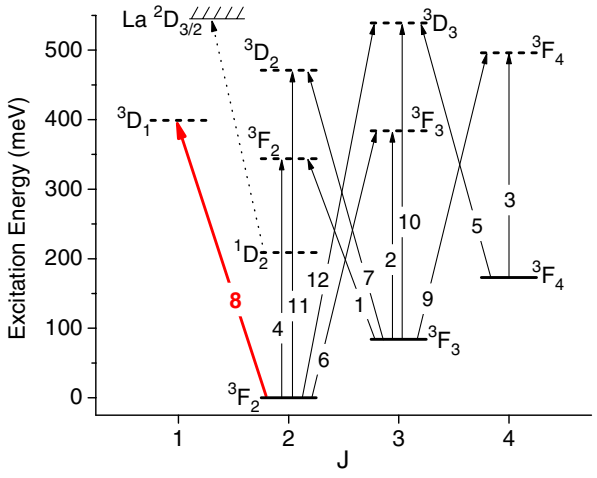

FIG. 1 (color online). La^- partial energy level diagram. Solid arrows indicate observed transitions between states of even parity $5d^26s^2$ (solid lines) and odd parity $5d6s^26p$ (dashed lines); the potential laser-cooling transition 8 is in bold red. The dotted arrow indicates the measured threshold for photodetachment from La^- $^1D_2^o$ to La ground state ($5d6s^2$ $^2D_{3/2}$); the excitation energies shown for these two states are based on the calculated La electron affinity (545 meV [20]).

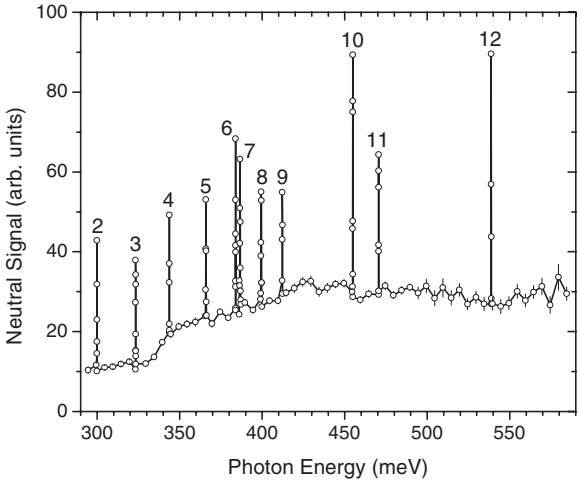

FIG. 2. La^- neutral atom photodetachment signal showing 11 of 12 observed resonance peaks. Broadly binned (5 meV) data over the entire range with finely binned data over the numbered peaks; bin widths: 0.1 meV for peaks 5, 7, and 8, and 0.01 meV for all other peaks.

resonance peaks due to electric dipole transitions between bound states of opposite parity, which are observed through a two-step process of one-photon excitation followed by absorption of a second photon to detach an electron. Patterns in the spectrum facilitate unique identification of all of the observed transitions, including the potential laser-cooling transition $^3F_2^e \rightarrow {}^3D_1^o$ (see Fig. 1). La^- is shown to have the richest bound-state spectrum ever observed for an atomic negative ion, and the results corroborate its potential for laser-cooling applications.

Photodetachment from La^- was measured as a function of photon energy using a crossed ion-beam–laser-beam system described previously [15,22]. Negative ions produced by a cesium sputter source [23] using a cathode packed with powdered lanthanum oxide covered by a tungsten layer [24] were accelerated to 12 keV and magnetically mass selected producing ~30 pA of $^{139}La^-$. The ion beam was intersected perpendicularly by a pulsed laser beam, following which residual negative ions were electrostatically deflected into a Faraday cup, while neutral atoms produced by photodetachment continued undeflected to a detector. The neutral atom signal was normalized to the ion-beam current and the laser photon flux measured for each laser pulse. The spectra were obtained by repeatedly scanning the laser wavelength over a range and then sorting the data into photon energy bins of selectable width.

The ions were photodetached by the "idler" output of an optical parametric oscillator-amplifier (OPO-OPA) pumped by a Nd:YAG laser, giving an operating range of 5000–2120 nm (248–585 meV) with continuous scanning over 4200–2120 nm (295–585 meV). Survey scans were performed with the pump laser operating broadband, giving an OPA bandwidth of ~30 GHz (~0.1 meV). Narrow scans near peaks used injection seeding of the pump laser to reduce the OPA bandwidth to ~3 GHz (~0.01 meV). The laser pulses were typically ~50 μJ with duration ~5 ns.

The measured spectrum of neutral atom production from La^- (Fig. 2) consists of a smoothly changing cross section due to nonresonant photodetachment together with a number of sharp resonance peaks. The energetic sputtering process in the ion source populates many excited states of La^-, most of which should survive the ~25 μs flight time from source to interaction region based on their calculated lifetimes of tens of μs to ms [7]. Therefore, the spectrum contains contributions due to photodetachment from a range of ground and excited state ions.

The only distinctive nonresonant feature in the spectrum over the measured energy range is an abrupt increase in the signal above 335 meV (expanded view in Fig. 3), indicating the opening of a new channel for photodetachment. For a limited range above a photodetachment threshold, the partial cross section follows the Wigner law: $\sigma \propto (E - E_t)^{\ell+1/2}$ where E is the photon energy, E_t is the threshold energy, and ℓ is the orbital angular momentum of the photoelectron [25]. The rapid rise of the cross section above 335 meV is characteristic of s-wave ($\ell = 0$) photodetachment, indicating the threshold is due to detachment of an initial p electron. An s-wave Wigner law fit to the data (Fig. 3) determines the threshold energy to be 335.6(8) meV. Because no additional s-wave thresholds are observed at higher energies in our spectrum, this threshold is interpreted as the opening of detachment from the most strongly bound odd state ($5d6s^26p$ $^1D_2^o$) of La^- to the neutral atom ground state $5d6s^2$ $^2D_{3/2}$. The measured

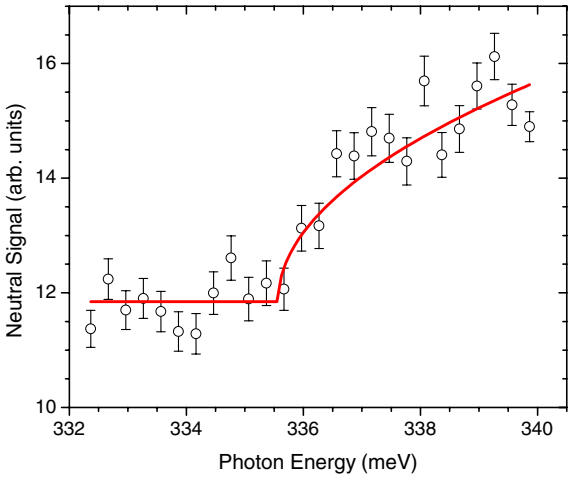

FIG. 3 (color online). Photodetachment threshold from the $(5d6s^2 6p\ {}^1D_2^o)$ excited state, data (circles), s-wave Wigner Law fit (line).

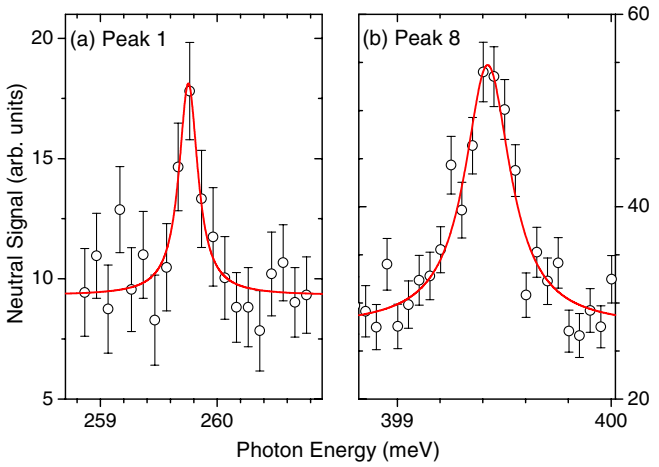

FIG. 4 (color online). La^- photodetachment signal for (a) peak 1 and (b) peak 8 (the potential laser-cooling transition ${}^3F_2^e \rightarrow {}^3D_1^o$), data (circles), Lorentzian fit (line).

threshold energy is 98 meV less than the calculated binding energy for ${}^1D_2^o$ (434 meV [20]).

Photodetachment from the low-lying even states of La^- ($5d^2 6s^2\ {}^3F_2^e$, ${}^3F_3^e$, and ${}^3F_4^e$) would produce p-wave ($\ell = 1$) detachment thresholds, for which the cross section increases slowly. The spectrum does not show any pronounced p-wave thresholds up to 585 meV, although there is a slight increase in the signal at the highest photon energies. The measured range extends above the experimental value for the electron affinity of La [470(20) meV [21]] and the calculated value (545 meV [20]). However, p-wave thresholds would be difficult to discern with the present data because of the slow rise in the cross section on top of the substantial background from loosely bound ions.

More importantly than the nonresonant structure, the photodetachment spectrum (Fig. 2) reveals eleven narrow resonance peaks (peaks 2–12) over the energy range 295–585 meV, with an additional peak near 260 meV (peak 1). Expanded views of peaks 1 and 8 are shown in Fig. 4. The peaks are fit with Lorentzians to obtain their center energies and widths (Table I). The measured peak widths should be considered upper limits and may be considerably broader than the natural widths, because of the OPA laser linewidth (~0.01 meV), unresolved hyperfine structure, and power broadening effects [26]. The peak amplitudes depend on several factors, including the relative population of the initial target state ions, the transition strengths, and the continuum photodetachment cross sections. Also, there may be additional weak peaks that are not discerned due to signal-to-noise limitations.

Peaks in the neutral atom spectrum can be caused either by one-photon detachment via a quasibound resonance in the continuum which subsequently autodetaches, or by resonance enhanced $(1 + 1)$ photon detachment in which

TABLE I. Transition assignments and measured peak energies and widths (one-sigma uncertainties in parentheses) compared to calculated energies and electric dipole Einstein A coefficients from O'Malley and Beck [7]. Peak widths are upper limits.

Peak	Measured energy (meV)	Width (meV)	Transition	Calculated energy (meV)	Calculated A coeff. (s^{-1})
1	259.76(4)	[a]	${}^3F_3^e \rightarrow {}^3F_2^o$	192	260
2	299.94(3)	0.016(6)	${}^3F_3^e \rightarrow {}^3F_3^o$	238	900
3	323.33(3)	0.025(6)	${}^3F_4^e \rightarrow {}^3F_4^o$	271	1700
4	343.69(3)	0.014(6)	${}^3F_2^e \rightarrow {}^3F_2^o$	259	530
5	365.94(3)	0.19(4)	${}^3F_4^e \rightarrow {}^3D_3^o$	326	31 000
6	383.87(3)	0.021(6)	${}^3F_2^e \rightarrow {}^3F_3^o$	305	160
7	386.59(4)	0.24(7)	${}^3F_3^e \rightarrow {}^3D_2^o$	329	26 000
8	**399.42(3)**	**0.28(3)**	${}^3F_2^e \rightarrow {}^3D_1^o$	**337**	**29 000**
9	412.24(3)	0.020(4)	${}^3F_3^e \rightarrow {}^3F_4^o$	339	150
10	454.86(3)	0.021(6)	${}^3F_3^e \rightarrow {}^3D_3^o$	394	1800
11	470.55(3)	0.032(8)	${}^3F_2^e \rightarrow {}^3D_2^o$	396	3600
12	538.80(3)	0.016(6)	${}^3F_2^e \rightarrow {}^3D_3^o$	461	21

[a]Measured with unseeded laser; width information not available.

one photon excites the ion from a lower bound state to an upper bound state which then absorbs a second photon to detach an electron. In principle, these two processes can be differentiated by the dependence of the signal on laser pulse energy: Single-photon processes should depend linearly on pulse energy, while two-photon processes depend quadratically in the nonsaturated regime. It has not been possible to make conclusive measurements of the pulse energy dependence for the peaks because of the substantial background signal due to nonresonant photodetachment of loosely bound ions in the beam. However, interpretation of the spectrum indicates that at least five of the peaks are due to the $(1+1)$ detachment process via bound-bound transitions, as discussed below.

Our measurements are consistent with the theoretical calculations by O'Malley and Beck of bound-bound electric dipole transitions in this energy range [7]. Many electric dipole transitions between the low-lying even states ($^3F^e_{2,3,4}$) and the excited odd states ($^3D^o_{1,2,3}$ and $^3F^o_{2,3,4}$) are allowed by the selection rules ΔL and $\Delta J = 0, \pm 1$. Identification of the transitions responsible for the observed peaks requires more than just comparison to the theoretically calculated energies, because the uncertainties in the calculations may be 50 meV or more [27]. Patterns in the separations of the peaks provide the key additional information. If two lower states make transitions to the same two upper states, the resulting spectrum shows pairs of peaks that are separated by identical energy intervals. For example, the separation of peaks 2 and 6 [88.93(3) meV] is the same as peaks 10 and 12 [88.94(3) meV]. Seven such equal separation pairs are found among the eleven peaks in the range 295–585 meV: peaks 2–6, 7–11, and 10–12; 2–7 and 6–11; 2–10 and 6–12; 3–5 and 9–10; 3–9 and 5–10; 7–10 and 11–12. Careful analysis using these distinctive patterns led to the unique identification of the transitions responsible for all of the peaks; see Fig. 1 and Table I. The energy separations noted above for peaks 2–6 and 10–12 correspond to the fine structure interval of the ground state $^3F^e(J = 2\text{–}3)$.

Stringent tests of the assignments are provided by comparisons of transitions reaching the same upper state from different lower states; the self-consistency of the measurements is excellent, as all transition energies agree within experimental uncertainty. Furthermore, the interpretation of the data indicated there was one additional transition below the previously measured range that was within the operating range of the laser: the $^3F^e_3 \rightarrow {}^3F^o_2$ transition at a predicted energy of 259.75(3) meV. A subsequent scan near this energy indeed revealed this additional peak, peak 1 (see Fig. 4), at a measured energy of 259.76(4) meV, matching the prediction.

The measured transitions can be used to determine the energies of the relevant excited states of La^- relative to the $^3F^e_2$ ground state (see Table II). The calculations [20] indicate that all of the excited states are bound and the excitation energies of the $^3F^e_{2,3,4}$, $^3F^o_{2,3}$, and $^3D^o_1$ states are much less than the measured binding energy of the ground state of La^- [470(20) meV [21]], therefore transitions involving these states are definitely bound-bound transitions (peaks 1, 2, 4, 6, and 8). The remaining excited states ($^3F^o_4$ and $^3D^o_{2,3}$) are near or above the measured ground state binding energy, so whether transitions involving these states are bound-bound or bound-quasibound is not settled at present. However, the narrow widths measured for the peaks suggest that all of the upper states may be bound, since quasibound states above the neutral atom ground state would likely be subject to rapid autodetachment, resulting in shorter lifetimes and larger peak widths.

TABLE II. Measured excitation energies of La^- states relative to the $^3F^e_2$ ground state compared with calculations from O'Malley and Beck [20]. The measurement uncertainty is 0.03 meV.

State	Measured (mev)	Calculated (meV)	Deviation (meV)
$^3F^e_3$	83.94	67	17
$^3F^e_4$	172.86	135	38
$^3F^o_2$	343.69	259	85
$^3F^o_3$	383.87	305	79
$^3D^o_1$	399.42	337	62
$^3D^o_2$	470.55	396	75
$^3F^o_4$	496.18	406	90
$^3D^o_3$	538.80	461	78

The measured and calculated state energies [20] closely agree for all of the fine structure intervals (deviations of less than 21 meV), but the calculated energies of the odd states are consistently ~80 meV smaller than measured. The calculations would be brought in to complete agreement with the measurements by a global shift of the odd states up in energy relative to the even states; such a shift is reasonable given the very different core-valence correlations between the odd and even states [27]. Decreased binding of the odd states is also indicated by our measured photodetachment threshold energy for $(5d6s^2 6p\ ^1D^o_2)$, which is 98 meV less than the calculated binding energy of this state [20].

Of primary importance, the potential laser-cooling transition between bound states $^3F^e_2 \rightarrow {}^3D^o_1$ is identified as peak 8 at energy 399.42(3) meV. Furthermore, the measurements confirm two key aspects of this transition that make it a promising candidate for laser cooling: decay branching and transition strength [7]. Whereas transitions are observed to all of the other excited states from at least two different lower states, the $^3D^o_1$ state is reached only from the $^3F^e_2$ ground state. Thus, the upper state is shown to connect almost exclusively with the initial lower state in accord with the electric dipole selection rules, which could possibly eliminate the need for repumping out of dark states in the laser-cooling process. In addition, the measured width of peak 8 indicates that it is due to a relatively strong

transition. Three of the peaks (5, 7, and 8) show widths of ~0.2 meV, roughly 10 times larger than the other peaks. The large measured widths of these three peaks, much greater than the calculated natural widths [7], are likely caused by power broadening [26], indicating that these transitions are much stronger than the others. This observation agrees well with the calculated Einstein A coefficients [7], which are an order of magnitude larger for these three transitions than any of the others. Thus, the $^3F_2^e \rightarrow {}^3D_1^o$ transition is shown to be strong for a negative ion, which would make laser cooling faster.

In summary, La^- has the richest bound-state structure of any atomic negative ion observed to date and 12 electric dipole transitions have been assigned. The energy of the $^3F_2^e \rightarrow {}^3D_1^o$ transition has been measured, and the observations demonstrate the favorable properties of this transition for efficient laser cooling. Further experimental investigations are needed, such as measurements of the transition strengths and higher resolution spectroscopy, as well as additional theoretical analysis. The present results confirm that La^- is a very promising negative ion for laser-cooling applications and provide a map for further exploration of its unique properties.

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