High-resolution optical spectroscopy of Os\textsuperscript{−} with a view to laser cooling of atomic anions

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Abstract. Atomic anions are generally not amenable to optical spectroscopy because they are loosely bound systems and rarely have bound excited states. Until recently, there was only one known negative ion with a strong bound–bound electronic transition, the osmium anion Os\textsuperscript{−}. The electric-dipole transition between the \(^4\)F\(_{9/2}\) ground and \(^6\)D\(_{5/2}\) excited state of this ion provides unique insight into the structure of atomic anions. In addition, it may enable the preparation of ultracold ensembles of negative ions. Laser excitation of the electric-dipole transition in Os\textsuperscript{−} ions could be used to laser-cool them to microkelvin temperatures. If demonstrated to be successful, the technique would allow the cooling of any species of negatively charged ions – from subatomic particles to molecular anions – to ultracold temperatures by sympathetic cooling. We have been investigating the bound–bound electric-dipole transition in Os\textsuperscript{−} by high-resolution laser spectroscopy with a view to using it for the first laser cooling of negative ions. The principle of the method, its potential applications, as well as experimental results are presented.

1. Introduction

Laser cooling is a well-established technique [1] which employs light to cool atoms or ions to very low temperatures. Its simplest form is the so-called optical molasses or Doppler cooling. The principle is based on the directional absorption of a photon by excitation of an atomic or ionic system, followed by spontaneous emission of a photon in a random direction at some later time. The laser light is red-detuned with respect to the natural transition frequency, such that resonant absorption can only occur when the atom/ion momentum and the photon momentum are opposed. After a large number of scattering processes, the sample reaches an equilibrium between laser cooling by directed absorption and heating by random emission. The corresponding temperature is called the Doppler temperature \(T_D = \hbar \Gamma / (2k_B)\), where \(\hbar\) is the reduced Planck constant, \(k_B\) is Boltzmann’s constant and \(\Gamma\) is the linewidth of the transition. The laser cooling technique was envisaged in 1975 [2] and demonstrated shortly after in positive ions [3, 4]. Several years later, the cooling of neutral atoms confined in a magnetic trap was achieved [5].

Since its inception more than thirty years ago, this new technique has paved the way for such spectacular developments as high-precision laser spectroscopy [6], Bose–Einstein condensation [7, 8], ion crystals in storage rings [9], ultracold molecules (cooled indirectly [10] and directly [11]) and ultra-precise atomic clocks [12]. The preparation of ultracold ensembles is also of the utmost
importance for the field of antimatter research. At CERN’s Antiproton Decelerator, antihydrogen atoms are being produced with a view to studying the CPT symmetry between matter and antimatter [13], as well as the effect of gravity on an antimatter beam [14]. Antihydrogen is the bound system of an antiproton and a positron. Whether its formation occurs by spontaneous recombination [15] or by resonant charge exchange [16], it is enhanced at lower temperatures, when excited bound states can also withstand ionization and contribute to the recombination rate. Furthermore, due to the large antiproton–positron mass ratio, the temperature of the antiproton prior to recombination essentially determines that of the formed antihydrogen. Therefore, the pre-cooling of antiprotons, for example by sympathetic cooling with a laser-cooled anion, constitutes a very promising route towards ultracold antihydrogen [17]. However, to this day, the laser cooling of negative ions has not yet been achieved.

This is due to the fact that the structure of atomic anions is fundamentally different from that of neutral atoms or positive ions because of the nature of the potential experienced by the valence electron [18]. Classically, negative ions should not exist, as it is not energetically favorable for a negatively charged electron to attach itself to a neutral core. Most elements, however, nevertheless form negative ions. They are created by polarization of the neutral atom and are stable due to quantum-mechanical correlation effects. The so-called correlation energy, the energy gained when all $Z + 1$ electrons adjust their wavefunctions in accordance with the Pauli exclusion principle and electrostatic repulsion, is typically about an order of magnitude smaller than the binding energies in atoms or positive ions. The potential is both shallow and short-ranged; therefore, only a limited number of bound states (if any) exist. Bound excited states are known to exist in only a small fraction of elements that form negative ions [19]. Most of these states have the same parity as the ground state, such that no strong optical transitions can be observed. Electric-dipole transitions, which can only occur between states of opposite parity, are of particular interest because in addition to being accessible to investigations with spectroscopic techniques, they could in principle be used to laser-cool the negative ion.

Opposite-parity bound states have been predicted for the anions of some lanthanides and actinides [20, 21, 22, 23] and for cesium [24, 25, 26] on the basis of theoretical calculations. However, experimental investigations of cesium and lanthanum have so far not substantiated these predictions [27, 28]. Recently, a strong resonant transition just below the photodetachment threshold was fortuitously discovered in the negative osmium ion and investigated by infrared laser photodetachment spectroscopy [29]. Figure 1 shows the energy level diagram for Os$^-$ which results from these measurements and from calculations on the ground state configuration [30]. In the experimental study of Os$^-$, the transition frequency between the $5d^76s^2\, ^4P^o_{9/2}$ ground and $5d^66s^26p\, ^6D^o_J$ excited state (in the near infrared, wavelength $\lambda \approx 1162.7$ nm) was determined with an uncertainty of $\approx 5$ GHz. It was found that the bound excited state is very weakly.

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**Figure 1.** (Color online.) Energy level diagram of the negative osmium ion. The red arrow indicates the transition between the $5d^76s^2\, ^4F^o_{9/2}$ ground state and the $5d^66s^26p\, ^6D^o_J$ excited state, which is relevant for laser cooling.
bound (binding energy $\approx 11.5$ meV) and that its Einstein coefficient is $A \approx 10^4$ s$^{-1}$. The narrow linewidth of only 10 kHz means that the Doppler temperature achievable by laser cooling is $T_D \approx 240$ nK, more than seven orders of magnitude below the temperature of liquid helium.

On the basis of this experimental evidence, a theoretical investigation into the suitability of Os$^-$ for laser cooling was conducted [17]. Quantitative estimates were derived for standard operating parameters as used in Penning traps for antimatter research [31]. The extremely small binding energy of the valence electron in the excited state means that the excited ion is fragile and may easily be neutralized when it is exposed to strong electric fields. While the trapping field is too small to cause breakup, the ions encounter high electric fields in Coulomb collisions with each other. The probability per unit time $W$ for the breakup of atoms in static electric fields [32] exhibits a sharp cutoff for fields below $\approx 2$ kV cm$^{-1}$, corresponding to ion collisions at a temperature of $\approx 100$ K. Therefore, the osmium ions must be pre-cooled at least to liquid-nitrogen temperature before laser excitation can begin.

The branching ratio for the neutralization of anions by absorption of a second laser photon was estimated to be $\approx 10^{-6}$ in resonance and at the saturation intensity, translating to negligible losses during the scattering of some $10^5$ photons required to cool ions from 80 K to the Doppler temperature. An estimate of the branching ratios towards the intermediate states was also performed, based on theoretical calculations of their energies and lifetimes [30] in the absence of experimental data for these parameters. It was concluded that the repumping of those states which can be populated by allowed transitions from the $J_e$ state would likely be necessary. In summary, it was established that the laser cooling of Os$^-$ should be technically feasible. However, many aspects of the technique, ranging from the scattering rate (and hence, the cooling time) to the fraction of ions lost by two-photon absorption, depend heavily on the cross-section of the cooling transition, the cross-section towards photodetachment, as well as the configuration of the bound excited state. Therefore, a beam of Os$^-$ was investigated by high-resolution collinear laser spectroscopy in order to determine these properties of the bound–bound transition.

2. Experimental setup
The experimental apparatus, at the Max Planck Institute for Nuclear Physics (MPIK) in Heidelberg, consists of a negative ion source, a mass separator, and a collinear laser spectroscopy setup. A cylindrical Penning trap placed in the magnetic field of a superconducting magnet is being prepared for future trapping and cooling of anions. Negative Os ions are produced in a Middleton-type sputter ion source [33]. They are extracted from the source and accelerated to $E = 2.5\ldots6.5$ keV by electrostatic potentials. The primary ion beam consists mainly of the most abundant isotope $^{192}$Os$^-$, but contains other atomic and molecular contaminant ions, including the other naturally occurring Os isotopes. The beam is therefore passed through a large dipole magnet for mass separation, which has a resolving power of $R \approx 180$. The ion beam is then electrostatically deflected into the spectroscopy arm of the apparatus, shown in Figure 2, which consists of entrance and exit diaphragms (diameter 7.5 mm, length of interaction region 520 mm), an ionizer, a deflector, a micro-channel-plate (MCP) detector and a Faraday cup.

The ion beam and the laser beam ($\approx 1$ mm diameter) are passed collinearly through the entire interaction region. In this way, the effect of velocity bunching [34] reduces the Doppler width of the resonance by up to a factor of 10 (ion temperature $\approx 1500$ K, beam energy 5 keV). In the ionizer, the beam passes through three parallel meshes placed in a plane perpendicular to the beam, at which a voltage of up to 6.5 kV can be applied, corresponding to a longitudinal electric field of up to $2 \times 10^6$ V m$^{-1}$. A deflector leads the ions into a Faraday cup, whereas the MCP counts neutralized particles which are not deflected. Ions which have been excited to the $J_e$ state in the interaction region are neutralized in one of two ways: Either the ion absorbs a second photon leading to photodetachment of its excess electron, or the electron is field-detached by the electric field in the ionizer. In both cases, the neutral atoms are detected by the MCP.
Figure 2. (Color online.) Sketch of the spectroscopy section of the experimental apparatus showing ion beam diaphragms, ionizer, deflector, MCP detector and Faraday cup. The laser beam is shown as a red arrow, the ion/atom beams as blue arrows. The inset depicts a typical resonance of the electric-dipole transition with (dark blue) and without (light blue) electric-field detachment, at an ion beam energy of 5 keV.

placed in the forward direction. An increase in the number of neutralized ions is therefore a signal for resonant excitation of the electric-dipole transition.

The laser is a commercial optical parametric oscillator system custom-built for this application [35]. It is based on a periodically poled lithium niobate (PPLN) crystal placed in a bow-tie cavity, pumped by a frequency-doubled Nd:YAG laser. The non-linear crystal produces signal and idler waves at 980 nm and 1163 nm, respectively, the latter being sustained by the resonator mode. When pumped at a power of 2 W, the OPO produces close to 200 mW; its frequency can be swept continuously over a range of 1.5 GHz. The laser bandwidth was measured to be smaller than 5 MHz with a Fabry–Pérot interferometer. The wavelength is recorded and regulated with a wavemeter, which in turn is calibrated by a stabilized diode laser.

3. Experimental results

3.1. Transition frequency and cross-section

A typical resonance of the bound–bound transition in $^{192}$Os$^{-}$ is shown as the inset in Figure 2. The corresponding signal obtained without the ionizing potential is also indicated, illustrating the dramatic enhancement due to the field detachment. The width of the (mainly Gaussian) resonance, $\Gamma_{\text{res}} \approx 45$ MHz, is dominated by the Doppler width due to the thermal motion of individual ions in the beam; its slight asymmetry is due to a corresponding asymmetry in the velocity distribution of the ions. In collinear laser spectroscopy, the measured transition frequency must be corrected for the Doppler effect. In order to also take into account a possible slight offset in the beam energy, a number of measurements at different beam energies were performed and the data points were fitted to the well-known Doppler shift function. The result of these measurements and the fit are shown in Figure 3 [36]. From the fit, a transition frequency of 257.831190(30) THz was obtained [corresponding to a wavelength of 1162.74706(14) nm], in good agreement with the prior measurement [29], but more than two orders of magnitude more precise, making this the most precise measurement of any feature in an atomic anion to date.

The resonant cross-section for photoexcitation of the $^6D_{3/2}$ state can be determined by considering the time evolution of the ground and excited state populations in the beam, as well as the number of neutralized atoms. Neglecting decay to intermediate levels, a set of differential rate equations [37] can be analytically solved to yield the number of excited and detached ions.
Figure 3. (Color online.) Blue-shifted resonance frequencies as a function of the ion beam energy. The solid line is the fit of the Doppler shift function to the data; its extrapolation to zero beam energy is shown in the inset. The lower pane shows the residuals of the fit.

Figure 4. (Color online.) Number of detected atoms as a function of the laser power, recorded in resonance and for a fixed beam energy. The solid line is a fit to the data according to the rate equation model.

$N_e(t)$ and $N_d(t)$ as a function of the time of flight $t$ in the interaction region. The total number of neutralized particles $N_{\text{neut}}$ is obtained by numerical integration of $N_e(t) + N_d(t)$ over time and the radial extent of the overlapping beams. It is a function of the average laser power and has four independent parameters: The resonant and non-resonant cross-sections $\sigma_0$ and $\sigma_d$, the number of ions within the overlap region $N_0$ and the lifetime $\tau$ of the excited state. The latter is related to the observed cross-section by $\tau = c^2/(4\pi^2\sigma_0\nu_0^2\Gamma_{\text{res}})$, but was nevertheless treated as an independent parameter in this analysis.

The number of neutralized atoms detected on the MCP was recorded as a function of the laser power, which was varied via a polarizing beam splitter, leaving all other beam characteristics unchanged. A typical measurement with its corresponding fit according to the rate equation model is shown in Figure 4 [36]. Taking into account the simulated ion beam divergence in the interaction region, effectively reducing the interaction volume by about 30%, a resonant cross-section of $\sigma_0 = 2.5(7) \times 10^{-15}$ cm$^2$ was obtained from 10 such measurements. The fit function is not sufficiently sensitive to the parameter $\tau$ to extract a definite value for the lifetime of the excited state; however, it can also be determined from the cross-section. In this way a value of $\tau = 3(1)$ ms was found, corresponding to an Einstein coefficient of $A = 330$ s$^{-1}$, confirming that the resonance is due to a weak electric-dipole transition. The photodetachment cross-section was found to be $\sigma_d \approx 10^{-17}$ cm$^2$.

3.2. Hyperfine structure

Two of the seven naturally occurring Os isotopes, $^{187}$Os and $^{189}$Os, have a non-vanishing nuclear spin. In these systems, the interaction between the nuclear spin $I$ and the total electronic angular momentum $J$ leads to a hyperfine splitting (HFS) of the transition lines. Due to its nuclear spin
of \( I = 1/2 \), only a magnetic-dipole (M1) hyperfine interaction is present in \(^{187}\text{Os}\), described by the HFS constant \( A \). In \(^{189}\text{Os}\), with a nuclear spin of \( I = 3/2 \), both a magnetic-dipole and an electric-quadrupole (E2) hyperfine interaction are observed. These are parametrized by the HFS constants \( A \) and \( B \). The quantum number of the total angular momentum \( F \) can take on the values \(|J - I| \leq F \leq J + I\). Due to the selection rules applicable to an electric-dipole transition (total angular momentum \( \Delta F = 0, \pm 1 \)), the number of observed lines conveys information on the total electronic angular momentum.

Figure 5 shows the observed hyperfine structure in \(^{187}\text{Os}^-\) (left) and \(^{189}\text{Os}^-\) (right) [38]. Each of the spectra exhibits a number of strong resonances for \( F = F' \) and weak resonances for \( F = F' \pm 1 \). The solid red lines in the graphs represent a superposition of Gaussian curves using calculated relative intensities [39] and leaving the peak center frequencies as free parameters. Since the total electronic angular momentum of the ground state is known to be \( J_g = 9/2 \), it follows unambiguously that the total electronic angular momentum of the excited state must also be \( J_e = 9/2 \), because for \( J_e = 7/2 \) or \( J_e = 11/2 \) the number of possible transitions would be smaller for both isotopes (two for \(^{187}\text{Os}^-\) and nine for \(^{189}\text{Os}^-\)).

The measured peak frequencies were also used to obtain the HFS constants using the Casimir formulas [40]. Since for this quantitative analysis only relative frequency shifts are considered, the uncertainty of the peak positions was reduced from 35 MHz to 3 MHz. The Casimir formulas result in an overdetermined system of linear equations for the HFS constants, with one equation for each observed transition, where the transition frequencies are assigned to the corresponding equations by means of the characteristic intensities. In this process, an ambiguity arises because the transition \( F \rightarrow F' \) has the same intensity as \( F' \rightarrow F \). The two possible assignments result in two different sets of solutions for the HFS constants. Therefore, the HFS constants cannot be obtained from the experimental data alone.

In order to resolve the ambiguity, extensive multi-configuration Dirac–Fock (MCDF) calculations [41, 42] were carried out for the electric-dipole transition and its HFS in \(^{189}\text{Os}^-\). In these computations, which are particularly suitable for atomic systems with complex shell structures, the wavefunction expansions were systematically increased up to \( \approx 50,000 \) configuration state functions in order to incorporate the major correlations in the electronic structure. From the “best” calculations of the low-lying \( J = 9/2 \) levels of Os\(^-\) (cf. Figure 1), the HFS constants \( A = 299 \text{ MHz} \) for the \( ^{4}\text{P}_{9/2} \) ground state and \( A = 233 \text{ MHz} \) for the \( ^{6}\text{D}_{9/2} \) excited state were obtained [43]. These values agree well with one of the solutions for the experimental
hyperfine parameters, with $A = 216(2)$ MHz and $A = 184(2)$ MHz, respectively. The correct solution set for $^{189}\text{Os}^-$ was identified by considering that $A \propto \mu I$, where $\mu I$ is the nuclear magnetic moment. All HFS constants for the two isotopes are summarized in Table 1.

4. Discussion and conclusion

The presence of a bound–bound electric-dipole transition in the osmium anion has been confirmed by high-resolution collinear laser spectroscopy. The resonant transition frequency in $^{192}\text{Os}^-$ was measured with a precision of $10^{-7}$. The observed resonant photoexcitation cross-section indicates that the natural linewidth is even narrower than suggested by the prior experimental result [29]. Given the very small Einstein $A$ coefficient $A \approx 330$ s$^{-1}$, the Doppler temperature achievable by laser cooling will likely be limited by the laser bandwidth. At a cooling rate of $\Gamma_c \approx 50$ Hz, it will be necessary to pre-cool the ions to liquid-helium temperature by electron cooling. Laser cooling from 4 K to the Doppler temperature will then take roughly 5 min. While in the excited state, the ion may absorb a second laser photon, leading to neutralization and loss of the particle from the trap. The branching ratio towards this process strongly depends on the laser bandwidth and intensity, but should not be a significant source of ion loss.

An analysis of the hyperfine structure in $^{187}\text{Os}^-$ and $^{189}\text{Os}^-$ revealed the yet unknown total electronic angular momentum of the $^6D^o_J$ excited state to be $J_e = 9/2$. With this information the expected Zeeman splitting of the energy levels in the external field $B_{\text{ext}}$ of a Penning trap can be calculated. The corresponding energy shift is $\Delta E_{\text{magn}} = g_J \mu_B M_J B_{\text{ext}}$, where $g_J$ is the Landé factor, $\mu_B$ is the Bohr magneton and $M_J$ is the projection of the total electronic angular momentum. Under the assumption that the Russell-Saunders regime applies and setting the electron $g$ factor to its Dirac value $g = 2$, the Landé factors $g_J(^4F_{9/2}) = 1.33$ and $g_J(^6D_{9/2}) = 1.56$ are obtained, resulting in the energy level diagram shown in Figure 6 [38].

The transition is split into 28 components, comprised of ten $\pi$ transitions, nine $\sigma^-$ and nine $\sigma^+$ transitions, symbolized by straight arrows in the figure. Their strengths are given by the squares of the corresponding Clebsch-Gordan coefficients. The red wiggly arrow indicates the $^4F_{9/2} \rightarrow ^6D_{9/2}$, $M_J = -9/2 \rightarrow -9/2$ transition, which is one of the two strongest Zeeman lines and hence a possible laser cooling transition. The excited state will then decay back to the original sublevel of the ground state with the spontaneous decay rate $\Gamma_c$. The $M_J = -7/2$ sublevel of the ground state may also be populated with a rate $2\Gamma_c/9$. Furthermore, the selection rules also allow the decay to the $M_J = -7/2$ sublevel of the intermediate $^4F_{7/2}$ state (not shown in the figure). The decay rate to that level is unknown, but can be estimated to be $\Gamma_c/33$ by considering that the rates scale approximately with the third power of the transition frequency. Both of these ‘dark’ states are not addressed by the cooling laser and will therefore have to be repumped with additional lasers.

In conclusion, the study of the bound–bound electric-dipole transition in the osmium anion by high-resolution laser spectroscopy suggests that the first laser cooling of atomic anions is more challenging than initially anticipated. The cooling transition rate is very low, necessitating a precycling of the ions to keep the cooling times reasonable and minimize ion losses. Furthermore, the most suitable cooling transition between Zeeman sublevels is not closed, requiring two additional

| Nuclide | $^4F^o_{9/2}$ HFS const. | $^6D^o_{9/2}$ HFS const. |
|---------|--------------------------|--------------------------|
|         | $A$ ($\text{MHz}$) | $B$ ($\text{MHz}$) | $A$ ($\text{MHz}$) | $B$ ($\text{MHz}$) |
| $^{187}\text{Os}^-$ | 64(2) | — | 54(2) | — |
| $^{189}\text{Os}^-$ | 216(2) | 396(4) | 184(2) | 479(4) |

Table 1. Experimental $M1$ and $E2$ hyperfine structure constants for $^{187}\text{Os}^-$ and $^{189}\text{Os}^-$.
Figure 6. (Color online.) Expected energy level diagram of $^{192}$Os$^-$ in an external magnetic field, based on calculated Landé factors. The cooling transition is indicated by a green wiggly arrow, the decay to a dark state by a red wiggly arrow. The straight arrows indicate $\pi$, $\sigma^-$ and $\sigma^+$ transitions.

narrow-bandwidth lasers for repumping. However, these are merely technical difficulties which can surely be overcome. Nevertheless, other anions candidates with bound–bound electric dipole transitions [23] should also be studied by laser spectroscopy to identify an ion system which is potentially more suitable for laser cooling.

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